1.16 *N*-Heterocyclic Carbene Adducts of Main Group Compounds

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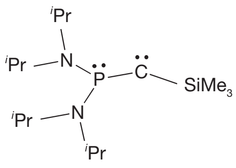
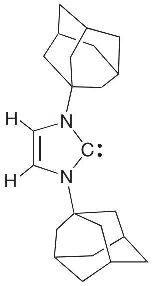
1.16.1 Introduction

Carbenes represent a general molecular class which features carbon in the less common divalent state (:CR_2). The isolation of the first examples of carbenes that were stable at room temperature was accomplished ~20 years ago by the groups of Bertrand[1,2] and Arduengo[3–8] (**1** and **2**). These discoveries paved the way for a dramatic growth in the exploration of carbene chemistry, in particular that of stable *N*-heterocyclic carbenes (NHCs) such as **2**; as a result, carbenes are now used in many chemical applications throughout the periodic table.[9–13] Part of the success of NHCs lies in their ease of synthesis and high degree of electronic and steric tunability, with the groups of Arduengo, Nolan, Kuhn, and Bertrand, each playing a vital role in the development of new NHC ligand frameworks.[2,14–21]



1

Bertrand 1988



2

Arduengo 1991

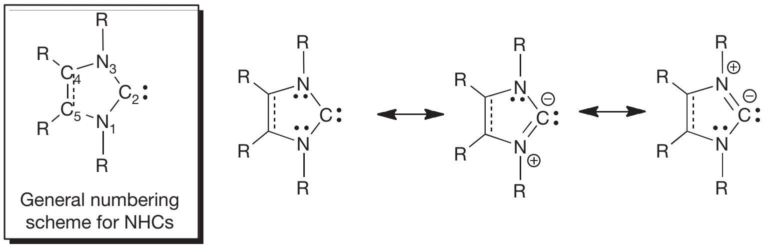
The presence of π-donating nitrogen atoms adjacent to the carbenic carbon (C2, Scheme 1) in NHCs leads to the stabilization of a singlet ground state, and a bonding arrangement wherein the carbene carbon is nucleophilic. In general, NHCs are considered to be strong σ-donors (akin to phosphanes) and poor π-acceptors.[22] Like many phosphanes, NHCs are quite chemically resistant when bound to transition metals, and consequently highly active metal catalysts based upon NHC ligands are now commonplace.[23]

In parallel with the expanding role of NHCs in transition metal chemistry, there has been a recent surge in activity in the main group (groups 1–2 and 13–17) due to the application of NHCs as donors to stabilize highly reactive, and unusual, bonding arrangements.[24,25] Kuhn and Al-Sheikh nicely reviewed the coordination chemistry of carbenes with main group elements in 2005[26]; however with the numerous recent advances in this field, an updated survey of the main group chemistry of NHCs is still warranted. As a result, this chapter deals with recent (primarily years 2000–2010) chemistry of NHCs with elements from groups 1–2 and 13–17, respectively; in addition, there is a final section devoted to the synthesis of NHCs that feature inorganic elements either as noninnocent pendant groups or as key structural components of the carbene ring framework. In general, the NHC complexes will be shown diagrammatically as having dative $C_{NHC}\!:\rightarrow E$ (E = main group element) bonding; however, it should be mentioned that cases with substantial $E{=}C_{NHC}$ π-bonding do exist. Due to space restraints, the chemistry of acyclic aminocarbenes will not be covered.[27,28] The stable NHCs that are discussed most often in the literature and also throughout this chapter are listed on the following page.

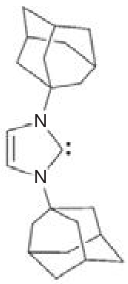
1.16.2 NHC Adducts with Main Group Elements

1.16.2.1 Adducts with Elements from Groups 1 and 2

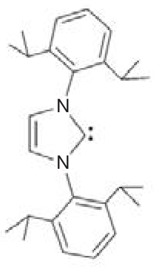
Donor–acceptor (or Lewis base–acid) adducts between NHCs and alkali metals were among the first examples of main group complexes to be prepared directly from free NHCs. In this regard, Arduengo and coworkers synthesized a series of complexes involving the carbene derivatives, I^{t}Bu, IAd, and IMes, and the organolithium reagent, $Li[1,2,4\text{-}(Me_3Si)_3C_5H_2]$ (eqn [1]).[29] Complexes **3–5** were isolated as thermally stable colorless solids (mp > 170 °C). X-ray crystallography was performed on the I^{t}Bu analog, **3**, and revealed the presence of a slightly tilted C_{NHC}–Li–Cp^{Centroid} angle of 167.5° in the solid state, along with a C_{NHC}–Li bond distance (2.115(4) Å) that was in the range expected for σ-linked aryl-Li moieties.[29] In a related study, the potassium bis(trimethylsilyl)amide adduct $\{[H_2C(CH_2N^iPr)_2C{:}]{\bullet}K[N(SiMe_2)_2]\}_2$ **7** was isolated from the reaction of the six-membered NHC, $[CH_2(CH_2N^iPr)_2C{:}]$ **6**, with an equivalent of $K[N(SiMe_3)_2]_2$ in toluene (eqn [2]).[30]



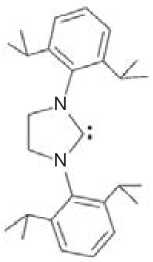
Scheme 1 General numbering scheme and important canonical forms for *N*-heterocyclic carbenes.



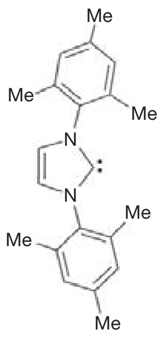
IAd



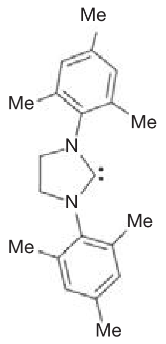
IPr



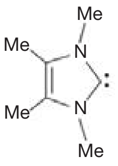
SIPr



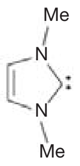
IMes



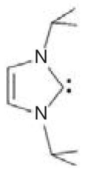
SIMes



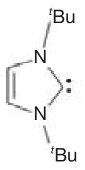
ImMe$_4$



ImMe$_2$



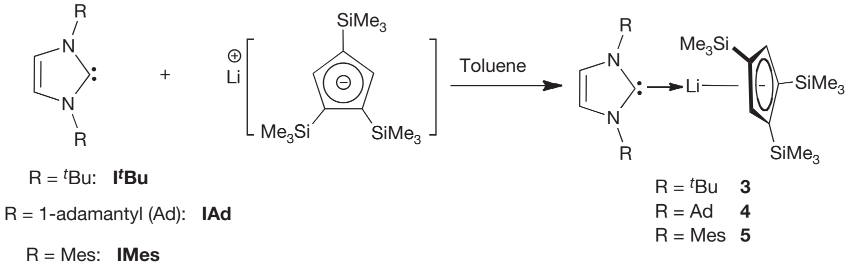
Im^{i}Pr$_2$



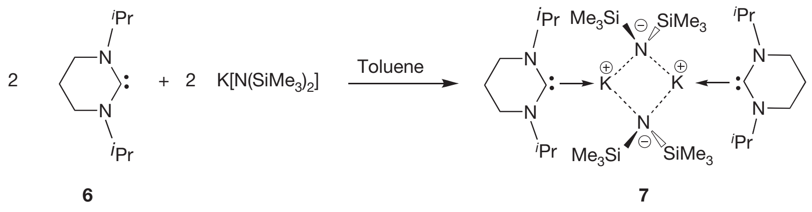
Im^{t}Bu$_2$

Complex **7** forms a diamond core K_2N_2 motif that is supported by flanking K–C contacts (ca. 3.00 Å) that were considered to be largely electrostatic in nature. The interaction of the carbenes, ImMe$_2{}^i$Pr$_2$ and **6**, with various alkali metal salts was also studied by $^{13}C\{^1H\}$ NMR spectroscopy, and a progressive upfield shift of the carbenic resonances (C2 in Scheme 1) was observed upon the addition of alkali metal salt; therefore, the NHC–M interactions (M = Li, Na, and K) appear to undergo rapid dissociation/association on a timescale that is faster than the nuclear magnetic resonance (NMR) measurement.[30]

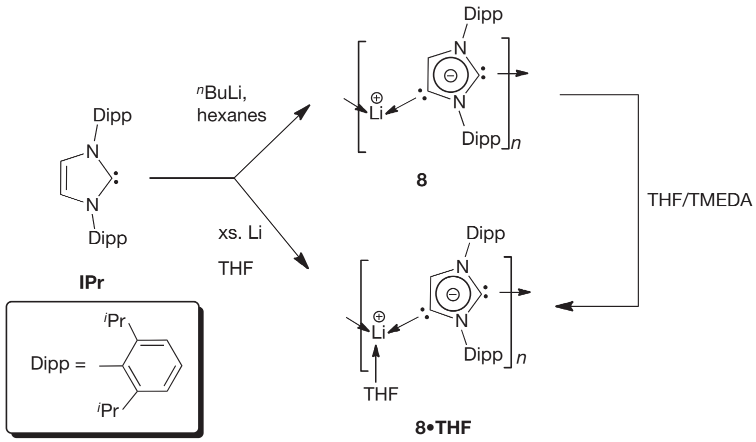
Robinson and coworkers recently described the synthesis of a synthetically versatile anionic NHC **8** from the direct lithiation of IPr with either ^{n}BuLi or Li metal (Scheme 2).[31] Both routes led to the formation of structurally authenticated coordination polymers with the anionic NHC units bridged by Li or Li(THF) moieties (**8** and **8**·THF, respectively). Due to



[1]



[2]



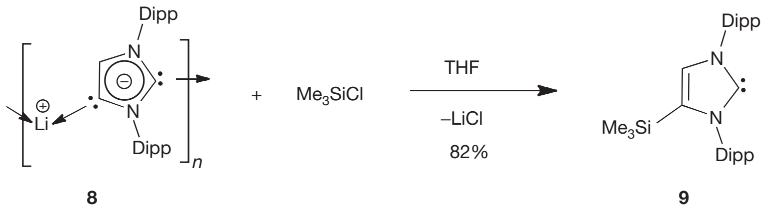
Scheme 2 Preparation of lithiated *N*-heterocyclic carbenes.

the stronger electron-donating properties at the C_5 position of the NHC, **8** can undergo selective electrophilic addition at this position to yield backbone-substituted NHCs such as **9** (eqn [3]); this strategy should be applicable in the preparation of a wide range of new NHC analogs of differing electronic and steric parameters, and thus this work represents an important addition to the synthetic NHC toolkit.[31]

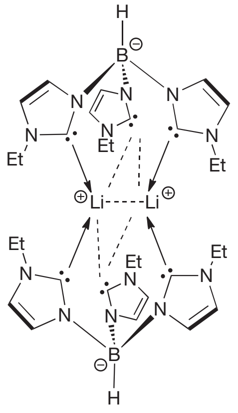
Lithium adducts featuring bis- and tris(3-alkylimidazol-2-ylidene)borates were prepared by Fehlhammer and coworkers.[32,33] Depending on the steric bulk of the flanking alkyl groups, a wide range of structural archetypes can be obtained with the novel homoleptic Li_2 adduct **10** being particularly noteworthy. Furthermore, the *tert*-butyl-substituted bis(3-alkylimidazol-2-ylidene)borates **11** and **12** were shown to exhibit significantly divergent structures in the solid state, each induced by altering the steric bulk at the endocyclic borate center.[34,35]

The novel anionic cyclic amino P-ylidic carbene **13** was recently synthesized; although direct C–Li coupling could not be observed by two-dimensional NMR spectroscopy, the presence of Li was substantiated by the detection of ^{6}Li and ^{7}Li NMR resonances, and through illustrative ligand transfer chemistry with various metal complexes such as $[Pd(allyl)Cl]_2$ (eqn [4]).[36]

The incorporation of anionic amido or alkoxide groups within NHC ligand frameworks is an active field of research. As a result, a few selected highlights from this area are presented in this section. The Arnold group has made significant headway in developing alkoxide- and amide-linked NHC ligand architectures (and their alkali metal adducts) in order to support the coordination of lanthanide and actinide elements.[37–40] Notably, salts of these anionic NHCs are often more air stable than ‘traditional’ NHCs, and not surprisingly given the above-mentioned chemistry, a high degree of structural versatility exists within their alkali metal salts. Representative ligand scaffolds developed by this group include: the NHC–amine·LiBr dimer **15**,[37] and the hemilabile NHC–alkoxide ligands **16**, wherein impressive synthetic control at three positions (R^1, R^2, and R^3) can lead to the formation of chiral complexes.[39] Moreover, the aryloxide–NHC potassium salts **17** and **18** were generated *in situ* and shown to be effect chelators for palladium, with potential future applications in catalysis envisioned.[41] More recently, dianionic bis(amido)–NHC ligand systems such as **19** were developed by Fryzuk and coworkers, and transmetallation chemistry with Ta was



[3]



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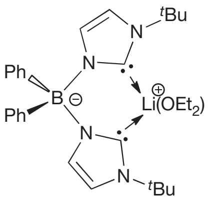

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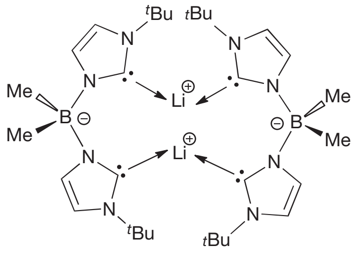

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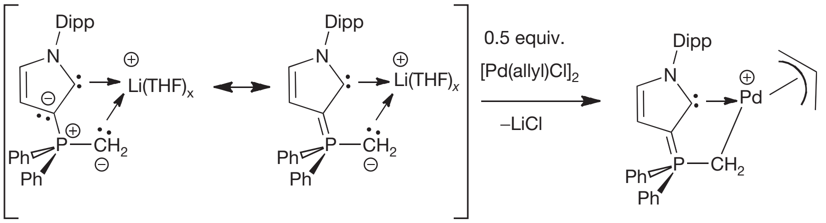
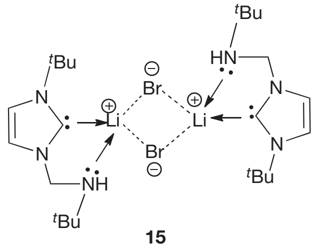


13 **14**

[4]

demonstrated; often coordination was accompanied by novel endocyclic C—H bond activation processes, and the pathway of bond activation was studied in detail via density functional theory.[42] Due to the insolubility of **19**, direct structural interrogation by x-ray crystallography was not possible; however, a chelate structure with a diamond-core Li_2N_2 arrangement was postulated, as this structural motif is often encountered within the related bis(amido)phosphane–lithium adducts.

The coordination chemistry of NHCs with the lightest group 2 element, beryllium, has only been studied by a few research groups, with widespread exploration limited by the challenges associated with working with highly toxic Be compounds. The first report of an NHC–beryllium adduct arose from the reaction of $ImMe_2$ with $BeCl_2$, whereby the interesting tetracoordinate Be(II) salt $[(ImMe_2)_3{\cdot}BeCl]Cl$ **20** was produced in high yield (eqn [5]).[43] Compound **20** was characterized by x-ray crystallography, and this study revealed the presence of Be–C_{NHC} bonds (2.076(6) to 2.091(7) Å) that were significantly elongated with respect to typical Be–C single bonds observed previously (ca. 1.81–1.85 Å).[43] Just over a decade later, the first NHC–diorganoberyllium adduct, $Ph_2Be{\cdot}ImMe_2{}^iPr_2$ **21**, was prepared as a thermally stable, yet moisture sensitive, colorless solid.[44] This complex was shown to be monomeric in the solid state with a planar Be



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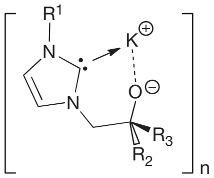
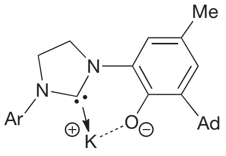
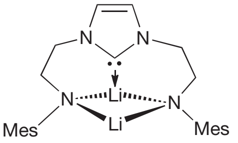


16

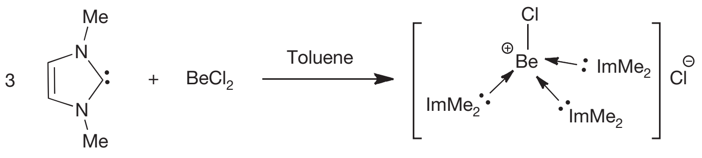
R^1	R^2	R^3	Ref
Me	Me	Me	39
^{i}Pr	Me	Me	39
^{t}Bu	H	Me	39



Ar = Dipp **17**
Ar = Mes **18**



19

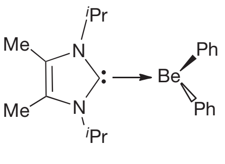


ImMe$_2$ **20** [5]

coordination environment, and a short Be–C$_{NHC}$ bond length of 1.807(4) Å (Be–C$_{Ph}$ = 1.751(5) Å avg.), suggesting that a stronger Be–NHC interaction was present in **21** relative to that found in the cationic NHC adduct **20**.[44]

Adduct formation between NHCs, IMes and IAd, and diethylmagnesium was reported by Arduengo and coworkers.[45] The thermally stable adduct IMes·MgEt$_2$ **22** (mp = 169–170 °C) adopts a dimeric arrangement in the solid state that is supported by bridging Mg–C(Et)–Mg interactions.[45] Similar NHC–M coordination chemistry was later uncovered when 1,3,4,5-tetramethylimidazol-2-ylidene, ImMe$_4$, was reacted with the hindered metallocenes Cp*$_2$M (M = Mg, Ca, Sr and Ba) in benzene.[46,47] Each of the products, ImMe$_4$·MCp*$_2$ **23–26,** was obtained as 1:1 adducts with rigorously η^5 Cp*–M coordination in the case of the heavier alkaline earths Ca, Sr, and Ba, while in the Mg adduct **23**, steric strain between the coordinated ligands causes one of the Cp* groups to adopt a ring-slipped η^3-binding mode. Moreover, when the heaviest group 2 metallocenes of the series (Cp*$_2$Sr and Cp*$_2$Ba) were reacted with 2 equiv. of ImMe$_4$, the stable bis-adducts [(ImMe$_4$)$_2$·MCp*$_2$] (M = Sr and Ba; **27**) were obtained.[46] The Hill group has also made important advances in the domain of group 2 element-carbene chemistry. For example, this research group reported the synthesis of the monomeric bis(trimethylsilyl)amide element adducts NHC·M[N(SiMe$_3$)$_2$]$_2$ **28** (NHC = IPr and IMes; M = Ca, Sr and Ba).[48,49] In each adduct, coordination of the NHC to the alkaline earth metal resulted in a detectable upfield shift of the carbene ^{13}C{^{1}H} NMR resonance by 20–26 ppm relative to that of the free, uncoordinated, carbene; in addition, the overall trend in chemical shift change mirrored the degree of Lewis acidity of the group 2 element (e.g., Ca > Sr > Ba).[48] Soon after, the same group reported the preparation of the novel magnesium hydride cluster [Mg$_4$H$_6$(IPr)$_2${N(SiMe$_3$)$_2$}$_2$] **30** via a amido/hydride exchange reaction between IPr·Mg[N(SiMe$_3$)$_2$] **29** and PhSiH$_3$ (eqn [6]).[50] The mixed amido/hydride cluster **30** is stable up to 158 °C and does not undergo further amide/hydride metathesis in the presence of excess silane, while NMR spectroscopic data suggest that the cage structure of **30** remains intact in solution.[50] By changing the nature of the amide and NHC bound to Mg, it is anticipated that further interesting cluster motifs could be accessed.

The bis(imidazolin-2-ylidene-1-yl)borate complexes **31** and **32** were shown to be efficient catalysts for the intramolecular hydroamination of terminal aminoalkenes.[51,52] This method holds promise due to the mild catalytic conditions employed and the inexpensive nature of the metals used. The Mg–NHC(alkoxide) complexes **33** and **34** both catalyzed the



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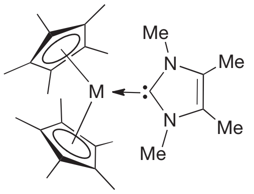
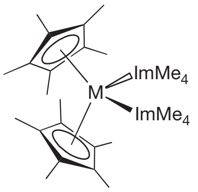
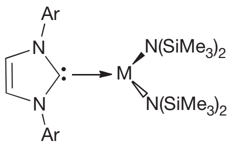


M	
M = Mg	**23**
M = Ca	**24**
M = Sr	**25**
M = Ba	**26**

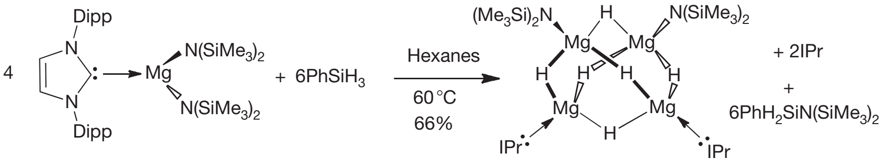


M = Sr or Ba
27

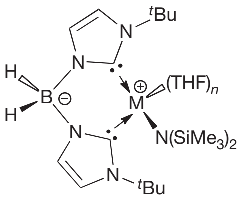


28

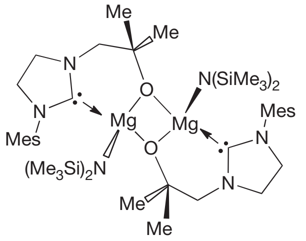
Ar	M	Ref
Mes	Ca	48
Mes	Sr	48
Mes	Ba	48
Dipp	Ca	48



29 **30** [6]



M = Ca; n = 1 **31**
M = Sr; n = 2 **32**



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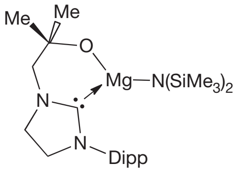


34

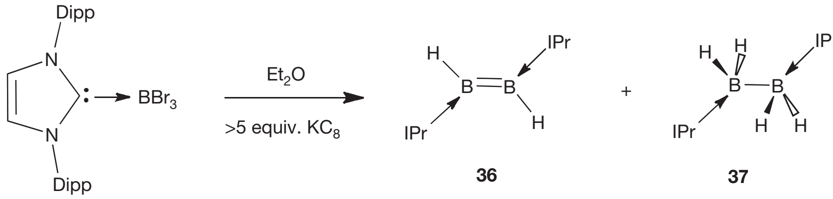
ring-opening polymerization (ROP) of *rac*-lactide under ambient conditions to give polylactides of moderate molecular weight ($1.8–2.6 \times 10^4$ g mol^{-1}) in under 1 h.[53,54] The nature of the steric bulk of the NHC had a profound impact on the degree of monomer conversion during the ROP of lactide. Specifically, only a 27% conversion of monomer was detected in the presence of the Dipp analog **34**, whereas a nearly quantitative conversion of *rac*-lactide was seen when the Mes derivative **33** was employed as a catalyst.[53]

1.16.2.2 Group 13 Complexes (B, Al, Ga, In, and Tl)

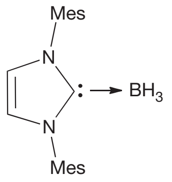
Interest in the use of NHCs as Lewis bases within the main group increased considerably with the successful preparation of the stable diboronene adduct IPr·HB═BH·IPr **36** by Robinson and coworkers in 2007 (eqn [7]).[55] Compound **36** was obtained in low yield (12%) from the reduction of the bromoborane adduct IPr·BBr_3 **35** with an excess of KC_8 in diethyl ether. The crystallographically determined B—B bond length in **36** was consistent with the presence of a B═B double bond [1.560(18) Å], and notably, this bond length was considerably shorter than the distance found in the previously known B═B bonded dianion $[Ph(NMe_2)BB(NMe_2)Ph]^{2-}$ **38** [1.636(11) Å].[56] The formation of IPr·HB═BH·IPr **36** likely proceeds via hydrogen atom abstraction from the diethyl ether solvent, and when IPr·BBr_3 **35** was combined with a large excess of KC_8 (>10 equiv.), the singly bonded diborane adduct IPr·H_2BBH_2·IPr **37** was obtained as the sole isolable product. Detailed experimental and theoretical studies involving the less hindered diboronene analog, IMes·HB═BH·IMes **39**, have shown that three distinct structural motifs of **39** can exist in the solid state (planar, *cis* bent and *trans* bent forms), suggesting that a high degree of geometrical flexibility is inherent to these carbene–diboronene adducts.[57]

Significant progress has been made in the synthesis and reactivity of NHC–borane adducts, with representative examples such as IMes·BH_3 **40**,[58] Cl_2IMes·BF_3 **41**,[59] $ImMe_2{}^iPr_2$·BH_3 **42**,[60] and IPr·BEt_3 **43**[61] appearing in the literature as early as 1993. The triethylborane adduct, **43**, has found use as an easy-to-handle carbene transfer agent in the preparation of various NHC–metal complexes.[61,62]

The NHC–boryl radical $[IPr·BH_2]^•$ **45** was generated via a hydrogen abstraction reaction between IPr·BH_3 **44** and photogenerated $^tBuO^•$ radicals (eqn [8]), and identification of **45** in solution was accomplished by EPR spectroscopy.[63] This synthetic method was later applied in the preparation of a family of NHC–boryl radicals each with varying steric and electronic environments.[64] In addition, IPr·BH_3 **44** and the 1,2,4-triazol-3-ylidene borane adduct **46** were shown to be efficient reagents for the Barton–McCombie reduction of xanthates.[63,65] Moreover, the boryl radical $[IPr·BH_2]^•$ **45** has been used as an initiator for the radical polymerization of trimethylolpropane triacrylate.[66]



35 **36** **37** [7]



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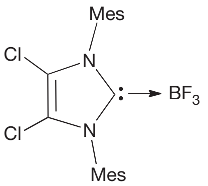

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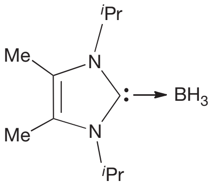

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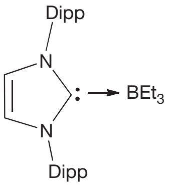

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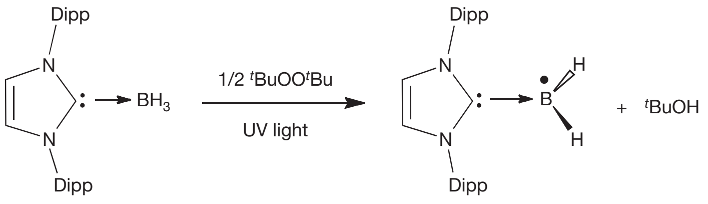
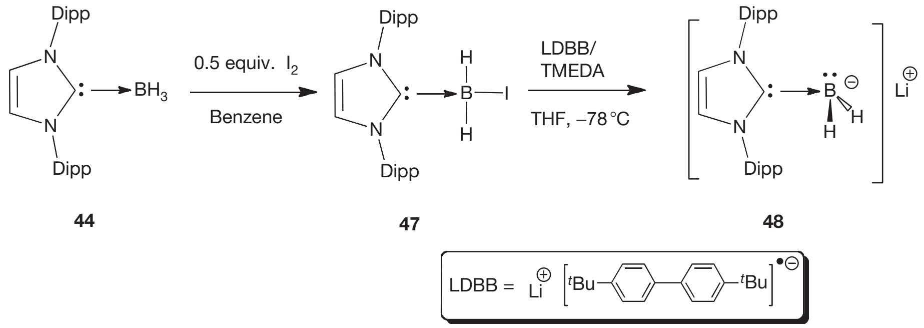


44 **45** [8]



44 **47** **48**

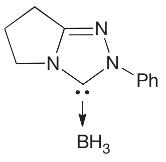
Scheme 3 Synthesis of the nucleophilic NHC-borane adduct **48**.

In another recent development, the anionic nucleophilic NHC–boryl adduct, $[\mathrm{IPr{\cdot}BH_2}]^-$ **48**, has been cleanly generated *in situ* following the protocol outlined in Scheme 3.[67] This rare source of nucleophilic boron was shown to undergo substitution chemistry with various organic electrophiles.[67]

The haloborane adducts $\mathrm{IPr{\cdot}BH_2X}$ (X=Cl, Br, and I; **49**, **50**, and **47**) could be generated in high yield from the reaction of $\mathrm{IPr{\cdot}BH_3}$ **44** with either alkylhalides (RX) or haloacids (HX).[68] In the same study, nucleophilic displacement chemistry involving the reactive B–X bonds in **47**, **49**, and **50** was demonstrated to occur with a wide range of anionic reagents to give various monosubstituted $\mathrm{NHC{-}BH_2{-}Nu}$ adducts (Nu=F, Cl, Ph, SCN, OCN, N_3, NO_2, and CN).[68] The asymmetric reduction of ketones involving the chiral borane adduct **51** was described.[69] The novel carbene-stabilized borenium salt, $[\mathrm{ImMe_2{\cdot}BMes_2}]\mathrm{OTf}$ ($\mathrm{Mes{=}2{,}4{,}6\text{-}Me_3C_6H_2}$; $\mathrm{OTf{=}OSO_2CF_3}$) **52**, was prepared by Gabbaï et al. and shown to undergo reversible one-electron reduction to yield the boryl radical $\mathrm{ImMe_2{\cdot}BMes_2}$ **53**.[70]

In 2000, Zheng and Herberich isolated the stable borabenzene–carbene adduct $\mathrm{ImMe_4{\cdot}[1{,}3\text{-}Me_2BC_5H_3]}$ **54**.[71] A decade later, the Piers group used the donating ability of the saturated NHC, SIMes, to isolate the first stable 9-boraanthracene adducts, **55** and **56**.[72] These species were obtained as highly air- and moisture-sensitive bright orange solids, and exposure of solutions of **55** to dioxygen led to a rapid decolorization and the formation of the novel endoperoxide **57**.[72] Braunschweig and coworkers synthesized a carbene adduct featuring an anionic borole heterocycle **60** (Scheme 4).[73] Compound **60** was isolated as a deep red-purple solid, and x-ray crystallography revealed the presence of a planar $\mathrm{BC_4}$ ring and intraring C–C and C–B bond lengths that were consistent with electron delocalization throughout the entire borole manifold. An accompanying theoretical study was used to probe the bonding in **60**. Namely, the highest occupied molecular orbital (HOMO) of **60** contained significant electron density within a p_z orbital on boron, while the NHC ligand was shown to donate electron density into an empty sp^2 orbital at the same boron site. Interestingly, the NHC ligand in **60** acts as both an electron donor and an acceptor, and thus significant $\mathrm{B{-}C_{NHC}}$ π-backbonding was detected.[73]

The reactivity of $\mathrm{ImMe_4{\cdot}BH_3}$ **61** with various phosphane adducts of $\mathrm{B(C_6F_5)_3}$ and $\mathrm{Ga(C_6F_5)_3}$ has been reported



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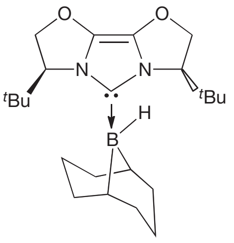

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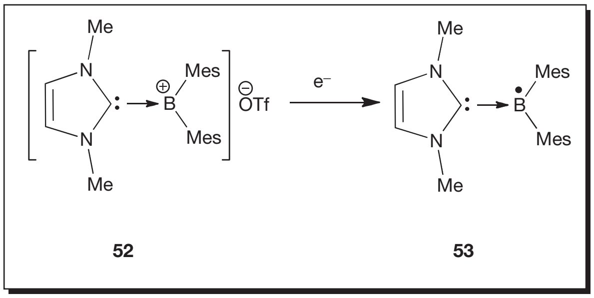
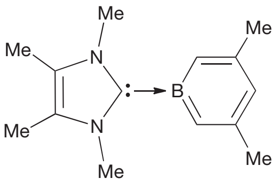


52 **53**



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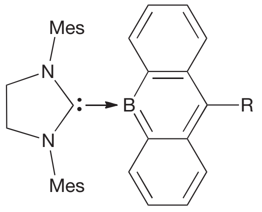
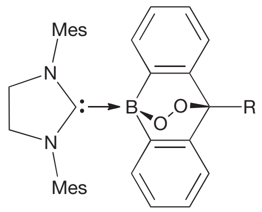


R = H **55**
R = C_6F_5 **56**



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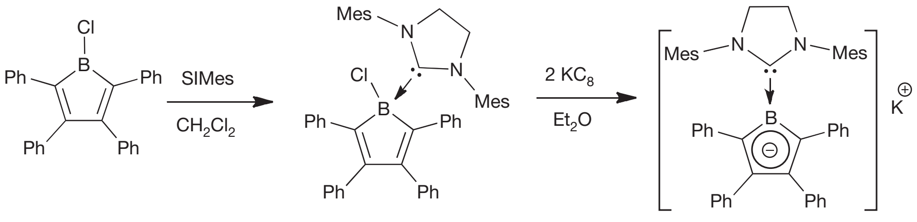
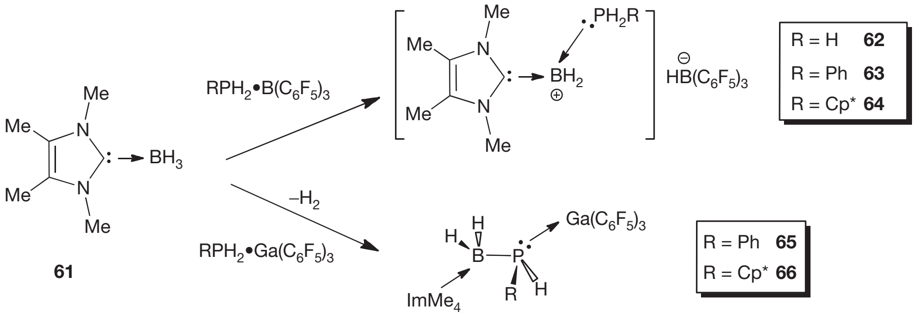


58 **59** **60**

Scheme 4 Preparation of the anionic heterocyclic borole adduct **60**.

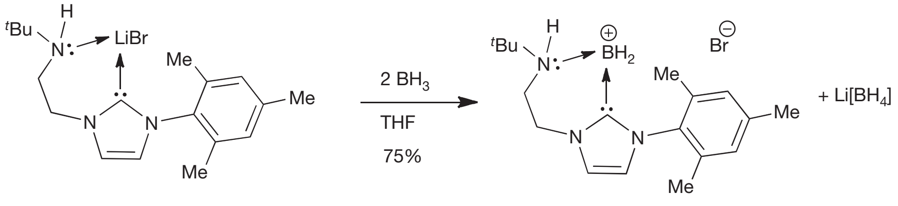
(Scheme 5)[74]; among the products obtained were the borate salts $[(C_6F_5)_3BH][RPH_2{\cdot}BH_2{\cdot}ImMe_4]$ (R = H, Ph, and Cp*; **62–64**; Cp* = η^5-C_5Me_5) and the dehydrogenated phosphanyl-boranes $(F_5C_6)_3Ga{\cdot}PR(H)$-$BH_2{\cdot}ImMe_4$ (R = Ph, and Cp*; **65** and **66**).[74] Malacria et al. showed that NHC–BH_3 adducts (e.g., IPr·BH_3 **44**) could be readily synthesized via phosphane and amine exchange involving both phosphane–borane (R_3P–BH_3) and amine–borane (R_3N–BH_3) adducts and NHCs.[75] Recently, the NHC–borane adduct, $ImMe_2{\cdot}BH_3$ **67**, has been shown to bind electron-deficient group 6 metal carbonyls fragments $M(CO)_5$ (M = Cr, Mo, and W) via agostic B–H···M interactions.[76] Lastly, an interesting Li/B exchange reaction was used to prepare the stable borenium NHC complex **69** in high yield (eqn [9]).[77]

The use of frustrated Lewis acid/base pairs (FLPs) to induce the heterocyclic cleavage of H_2 under mild conditions was first reported in 2006 by Stephan and coworkers.[78,79] In line with this concept, FLP combinations involving NHCs as Lewis bases and $B(C_6F_5)_3$ as the Lewis acid have been developed (e.g., $Im^tBu_2/B(C_6F_5)_3$). These systems have been shown to cooperatively activate H_2,[80–83] the N–H bonds of amines,[81] and facilitate the dehydrogenation of alkanes[83] and germanes[84,85]; this



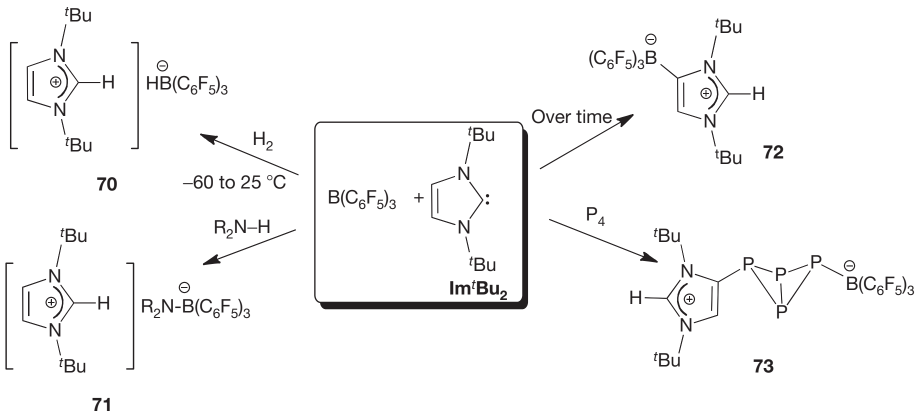
61

Scheme 5 Dehydrocoupling of $ImMe_4{\cdot}BH_3$ with phosphane borane and gallane adducts.



[9]

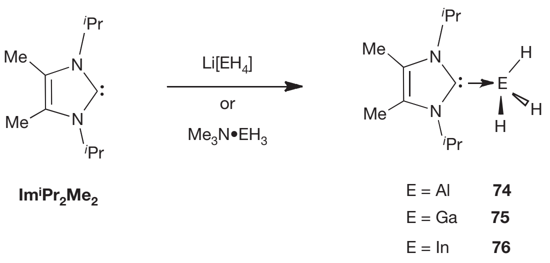
68 **69**



Scheme 6 Small molecule activation with a carbene–borane frustrated Lewis pair (FLP).

strategy has been recently extended to include the activation of P_4 (Scheme 6).[86]

The chemistry of the heavier group 13 triel elements (Al–Tl) with NHCs remains a highly active domain of study. In this regard, the Jones group have developed elegant synthetic methods to access carbene-group 13 trihydrides of the general form NHC–EH_3 (E = Al, Ga, and In; eqn [10]).[87–89] The presence of the strong carbene donors adds an impressive degree of thermal stability to the respective hydride. For example, the NHC complex IMes·InH_3 **77** is stable to 115 °C in the solid state while the related phosphane adduct, Cy_3P·InH_3, decomposes slowly at room temperature.[90]

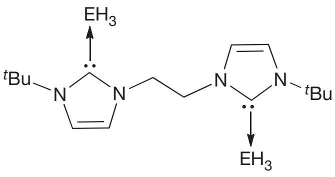


[10]

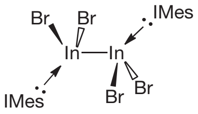
In addition, the hindered stable indane adduct, IMes·InH_3 **77**, has been shown to be an effective reagent for the reduction of ketones[91]; however, this reagent needs to be handled in nonchlorinated solvents as when **77** is dissolved in dichloromethane, quantitative H/Cl exchange transpired to give the indium(III) chloride IMes·$InCl_3$ **78**.[92] The thermally stable bis-alane, -gallane, and -indane adducts **79–81** were prepared using a similar strategy as outlined in eqn [10].[92] The structurally novel In(II) dihalide adduct, IMes·Br_2In–$InBr_2$·IMes **82**, was isolated as a product from the disproportionation reaction between InBr and IMes.[93] In an attempt to form a Ga(I) halide NHC adduct, IPr was reacted with 'GaI'; in place of isolating a well-defined Ga(I) adduct, the unusual pentaiododigallane adduct **83** was obtained in moderate yield.[94] A number of group 13 trihalide complexes of the general form (NHC-EX_3 **84**; E = Al–Tl; X = Cl–I) have been synthesized.[95–99] For example, the group of Cole has reported a series of studies involving the generation of mixed halohydride adducts (e.g., IMes·$AlBr_2H$ **85**) via efficient H/X exchange chemistry.[100–103]

The successful stabilization of the parent dialane H_2Al–AlH_2 in the form of the bis-carbene adduct IPr·H_2Al–AlH_2·IPr **88** was recently reported.[104] Complex **88** was prepared from a novel hydrogen atom transfer reaction involving the Al(III) precursor, IPr·AlH_3 **86**, and the Mg(I) dimer, $[HC(MeCNMes)_2\ Mg]_2$ (Mes = 2,4,6-$Me_3C_6H_2$) **87**,[105] with concomitant formation of the known Mg(II) hydride $[HC(MeCNMes)_2Mg(\mu\text{-}H)]_2$ **89** as a byproduct (eqn [11]). The dialane adduct IPr·H_2Al–AlH_2·IPr **88** was characterized by x-ray crystallography and shown to possess an Al–Al bond length of 2.6375(8) Å; this distance is consistent with the presence of an Al–Al single bond. Theoretical calculations place the bond dissociation energy in the model complex $ImMe_2$·H_2Al–AlH_2·$ImMe_2$ **90** at 46 kcal mol^{-1} (11 kcal mol^{-1} weaker than predicted for donor-free dialane, H_2Al–AlH_2).[104]

Roesky et al. have described NHC adducts of *N*-heterocyclic Al(III) hydrides, [{HC[C(CH_2)NAr](MeCNAr)}AlH·NHC] (Ar = Dipp = 2,6-$^iPr_2C_6H_3$; NHC = $ImMe_4$ and $ImMe_2{}^iPr_2$; **91** and **92**).[106] The formation of **91** and **92** likely



E = Al **79**
E = Ga **80**
E = In **81**



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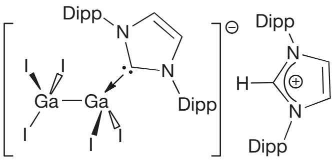

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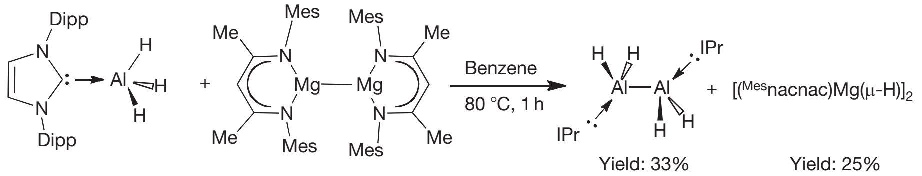


[11]

86

[(Mesnacnac)Mg]$_2$

87

88

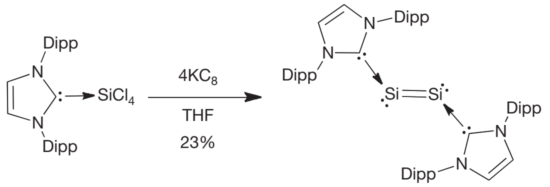
89

involves a carbene-assisted deprotonation of the nacnac ligand backbone, followed by H atom transfer to Al.[106] In a related study, Cp*$_3$Ga was shown to react with ImMe$_4$ to give the novel gallium hydride adduct, Cp*$_2$GaH·ImMe$_4$ **93**, and tetramethylfulvene as a byproduct.[107]

The group of Robinson reported the reduction of the hindered arylgallium(III) dichloride NHC adduct, ImMe$_2$^{i}Pr$_2$·GaCl$_2$Mes **94**. When the reductions were conducted in hexane solvent with excess KC$_8$ as a reducing agent, the predominant product obtained was the Ga(II) complex, ImMe$_2$^{i}Pr$_2$·Cl(Mes)Ga–Ga(Mes)Cl·ImMe$_2$^{i}Pr$_2$ **95**. However when potassium metal was used as the reducing agent in toluene, the neutral carbene-capped Mes$_4$Ga$_6$ cluster, **96**, was obtained.[108] The synthesis of a tris(imidazolin-2-ylidene-1-yl)arene complex with Tl(I) triflate **97** has been reported; the goal of this study was to develop a less redox-active ligand delivery agent for transition metal coordination chemistry.[109]

1.16.2.3 Group 14 Complexes (Si, Ge, Sn, and Pb)

A major breakthrough in main group chemistry transpired in 2008 when Robinson and coworkers stabilized a formally neutral disilene Si$_2$ unit in the form of the NHC bis-adduct IPr·Si═Si·IPr, **99** (eqn [12]).[110] This species was obtained via the reduction of IPr·SiCl$_4$ **98** with KC$_8$ in THF, and when hexane was used as the solvent, the chlorosilane IPr·ClSi–SiCl·IPr **100** was isolated. The disilene adduct IPr·SiSi·IPr **99** is an orange-red solid with a crystallographically determined Si–Si distance of 2.2294(11) Å; this distance is in the range commonly observed within disilenes R$_2$Si═SiR$_2$ (2.14–2.29 Å).[111] Moreover, theoretical calculations support the bonding scheme shown in eqn [12] as a Wiberg bond index of 1.73 was calculated for the model complex ImPh$_2$·Si═Si·ImPh$_2$ (ImPh$_2$ = [(HCNPh)$_2$C:]) **101**.[110] A more recent addition to this field appeared in 2009 with the synthesis of the related digermene adduct, IPr·Ge═Ge·IPr **102**, by Jones and coworkers.[112] The digermene adduct **102** was obtained as a deep red solid from the reduction of the Ge(II) precursor IPr·GeCl$_2$ **103** with the Mg(I) reagents [HC(MeCNAr)$_2$Mg]$_2$ (Ar = Mes or Dipp; **87** or **104**); of note, all attempts to reduce IPr·GeCl$_2$ **103** with the stronger reducing agent Na or KC$_8$ in diethyl ether led to the exclusive formation of germanium metal and free IPr. As with the disilene analog **99**, the germanium centers in IPr·Ge═Ge·IPr **102** are linked by double bonds and a Ge–Ge distance of 2.3490 (8) Å was determined by x-ray crystallography.[112]

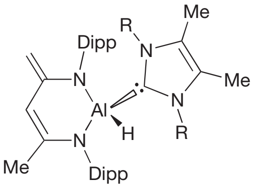


[12]

98

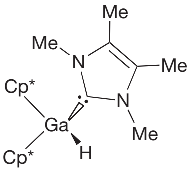
99

The stable dihalosilylene adducts IPr·SiX$_2$ (X = Cl and Br; **105** and **107**, respectively) were reported simultaneously by two independent research groups in 2009 (eqn [13] and **Scheme 7**).[113,114] The presence of electron-donating NHCs imparted dramatic stability to the silicon dihalides; for



R = Me **91**

R = ^{i}Pr **92**



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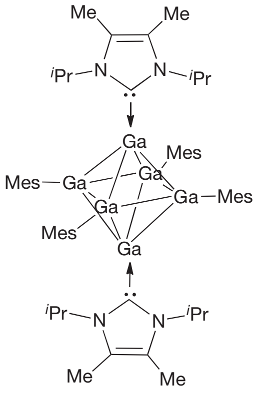

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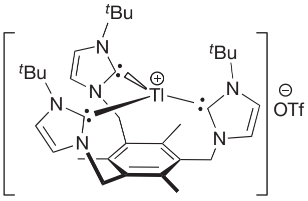

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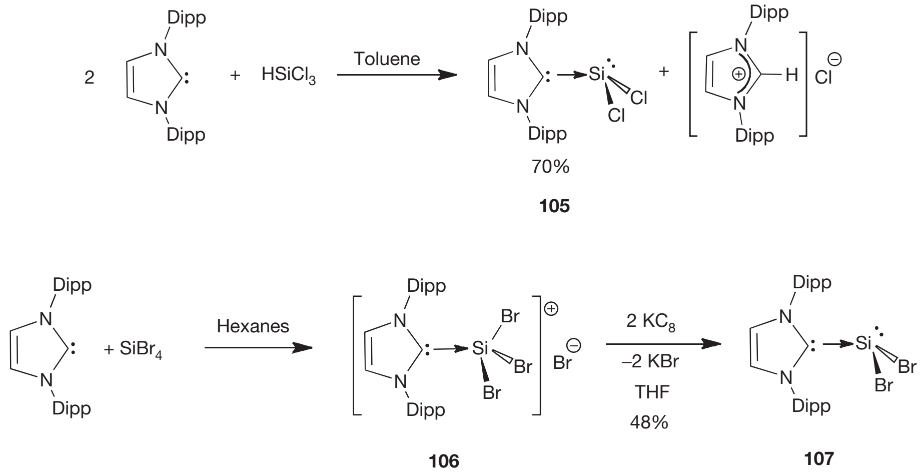
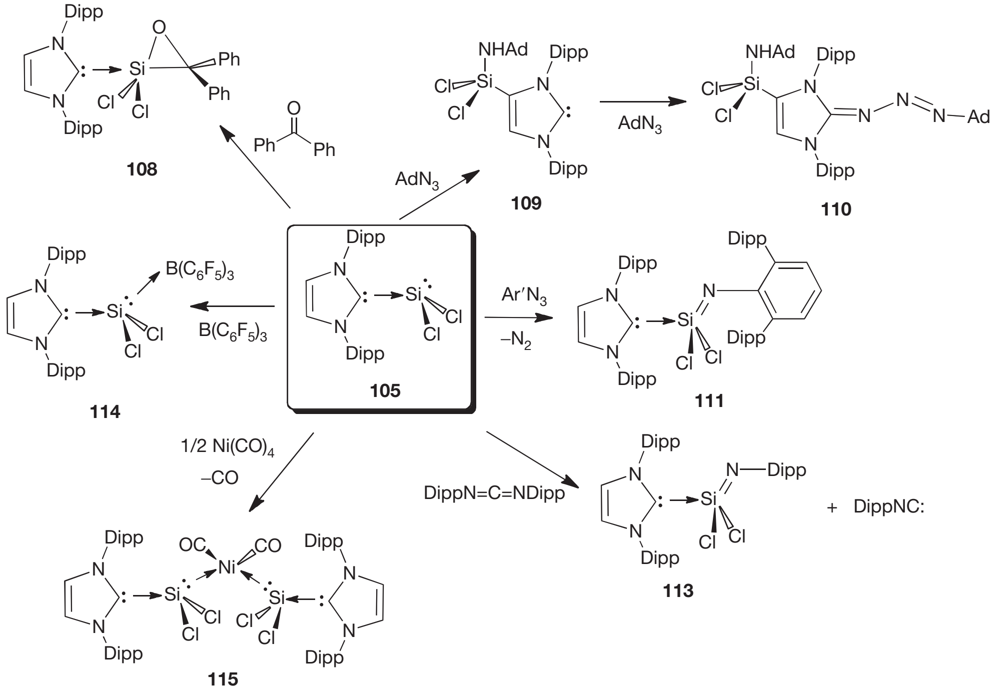


[13]

Scheme 7 Synthesis of the dihalosilylene adducts IPr·SiX$_2$ (X = Cl and Br; **105** and **107**).

comparison, the free silylenes, such as SiF_2 and $SiCl_2$, are only stable as free entities under cryogenic conditions.[115] Notably, complexes **105** and **107** are both stable in solution for extended periods of time, and the IPr·SiCl$_2$ adduct **105** is stable in the solid state (under N_2 atmosphere) up to a temperature of 210 °C. The bonding in these Si(II) adducts was analyzed by theoretical methods and the C_{IPr}–Si interactions were largely dative in nature with minimal π-bonding present.[113,114]

The chemistry of IPr·SiCl$_2$ **105** has been recently explored in depth. Some of these studies are summarized in Scheme 8, and the reactions listed serve to highlight the diverse chemistry available to Si(II) carbene adducts. For example, the novel silaoxirane adduct **108** was formed by the cycloaddition reaction of IPr·SiCl$_2$ **105** with benzophenone.[116] Treatment of **105** with the hindered alkyl azide, AdN_3 (Ad = adamantyl), resulted in a product formally derived from a H-atom abstraction from a backbone C–H bond in IPr (by a putative Si=N group) followed by SiCl$_2$ group migration to give the Si(IV) amide, **109**; addition of an extra equivalent of AdN_3 to **109** resulted in the oxidation of the carbenic center to yield the triazine complex **110**.[117] When the extremely bulky terphenyl azides, Ar′N$_3$ and Ar*N$_3$ (Ar′ = 2,6-Dipp$_2$C$_6$H$_3$; Ar* = 2,6-Trip$_2$C$_6$H$_3$; Trip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$), were reacted with IPr·SiCl$_2$ **105**, clean oxidation of the silylene occurred to yield the stable silazene adducts IPr·Cl$_2$Si=NAr′ **111** and IPr·Cl$_2$Si=NAr* **112**, respectively.[118] Roesky and coworkers also observed N=C bond cleavage when the carbodiimide DippN=C=NDipp was reacted with **105**; in this reaction, imide transfer to the Si



Scheme 8 Representative chemistry of IPr·SiCl$_2$ **105**.

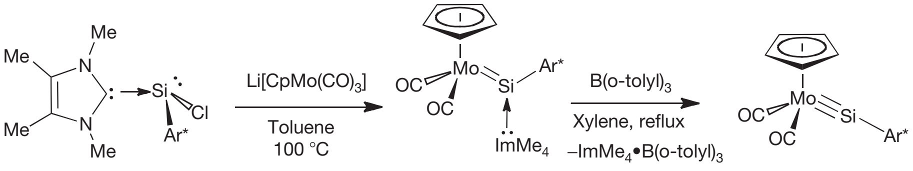
center transpired to yield IPr·$Cl_2Si{=}NDipp$ **113** and the isonitrile, DippNC as products.[118] As depicted in eqn [13], the silicon center in IPr·$SiCl_2$ **105** possesses a stereochemically active lone pair and thus is anticipated to display Lewis basic (electron-donating) behavior. Congruently, the interaction of **105** with the Lewis acid $B(C_6F_5)_3$ gave the stable adduct IPr·$SiCl_2$·$B(C_6F_5)_3$ **114**, a rare example of a main group compound wherein a Si center participates as both an electron donor and acceptor.[119] Similarly, **105** was shown to act as an electron-donating ligand with late transition metal centers, and in one instance, the Ni carbonyl complex, $[(IPr{\cdot}SiCl_2)_2Ni(CO)_2]$ **115**, was prepared in high yield from the reaction of 2 equiv. of **105** with $Ni(CO)_4$.[120,121]

Filippou et al. reported an elegant carbene-mediated synthesis of a stable molybdenum silylidyne complex, $Cp(CO)_2Mo{\equiv}SiAr^*$ **118**, featuring a structurally authenticated Mo≡Si triple bond (**Scheme 9**).[122] The synthetic procedure involved the use of the carbene, $ImMe_4$, to stabilize the required Si(II) intermediates (**116** and **117**), and treatment of the arylmetallosilylene adduct, $Cp(CO)_2Mo{-}Si(Ar^*){\cdot}ImMe_4$ **117**, with B(*o*-tolyl)$_3$ effected the removal of $ImMe_4$ from the Si center and induced the formation of a stable Mo≡Si triple bond [Mo–Si distance = 2.2241(7) Å; Mo–Si–C(Ar*) = 173.49 (8)°][123]; this work complements prior work in the synthesis of Mo–E multiple bonds (E = Si, Ge, Sn, and Pb).[124–128]

Driess and coworkers developed a general synthetic route to carbene-stabilized silanones ($R_2Si{=}O$) and their heavier congeners.[129–131] Starting from the silylene adduct [DippNC(CH$_2$)CHC(Me)NDippSi]·$ImMe_4$ **119**, oxidation of the Si(II) center with either N_2O, S_8, Se, or Te cleanly afforded the silane–chalcone derivatives **120–123** (eqn [14]).[129,130] The Si–O distance in the silanone complex **120** (1.541(2) Å) is quite short; however, the presence of a significantly nonplanar Si center indicates that the bonding in **120** is best described by the ylidic canonical form $Si^{\delta+}{-}O^{\delta-}$.[129] The strategy depicted in eqn [14] could also be used to prepare the germone adduct [DippNC(CH$_2$)CHC(Me)NDippGe(O)]·$ImMe_4$ **124**; this NHC–germone adduct adopts similar overall structural features and bonding arrangement as its lighter silicon congener **120**.[131] In a recent study by the same group, the stepwise oxidation of the $ImMe_2{}^iPr_2$-stabilized silylene **125** with dioxygen as a chemical oxidant afforded the structurally exotic dioxosilirane intermediate **126** which underwent a scission of the dioxo linkage when allowed to stand in toluene to give the silanone–ketone adduct **126** (**Scheme 10**).[132]

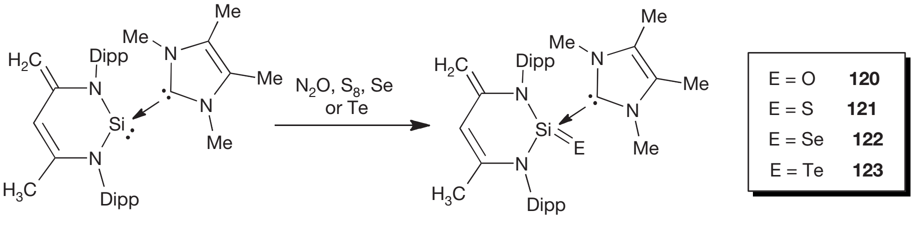
Given the role that complexes of the general form NHC·SiX_4 (X = F, Cl, and Br; **128**) have had in advancing some of the chemistry presented above,[133] a recent theoretical study featuring these complexes has appeared in the literature.[134] Moreover, detailed theoretical investigations involving both the known adducts NHC·Si=Si·NHC[135] and the currently unknown atomic tetrel (group 14) bis-adduct NHC·Si·NHC[136] were published.

Two important developments in the domain of NHC-silylene and -silylyne chemistry appeared in 2010. In the first report, stable silacyclopentadiene adducts $[Ph_4C_4Si]{\cdot}NHC$ **130** and **131** were prepared via a carbene-mediated dehy-



116 **117** **118**

Scheme 9 Carbene-assisted synthesis of a molybdenum-silylidyne complex.



[14]

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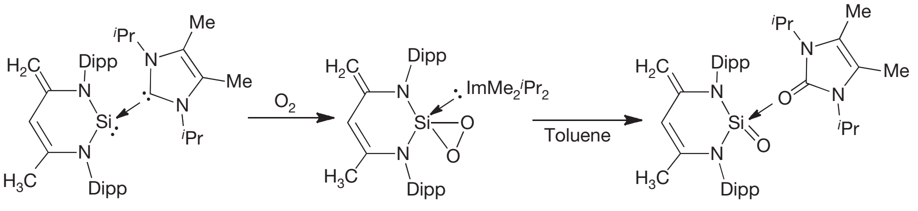


125 **126** **127**

Scheme 10 Silane–chalcone chemistry supported by *N*-heterocyclic carbenes.

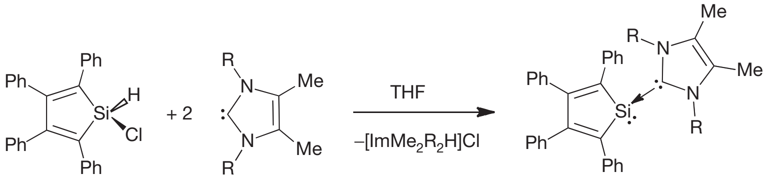
drohalogenation reaction involving the hydrochlorosilane [Ph_4C_4SiHCl] **129** (eqn [15]).[137] In a second study, treatment of Sekiguchi's disilyne, ${}^{i}Pr(Dsi)_2Si{-}Si{\equiv}Si{-}Si(Dsi)_2{}^{i}Pr$ **132,** with $ImMe_4$ led to the formation of the stable silylyne monoadduct **133** wherein donation of the carbene lone pair into a Si–Si π* orbital had transpired (**Scheme 11**).[138] This additional C_{NHC}–Si interaction resulted in a significant elongation of the Si–Si multiple bond length from a value of 2.0622(9) Å originally found in the precursor disilyne **132**, to the observed Si=-Si length of 2.1989(6) Å in **133**; for comparison, Robinson's disilene adduct IPr·Si=Si·IPr **99** has a similar Si–Si distance of 2.2294(11) Å.[110] Moreover, upon carbene complexation, the adjacent silicon center of the central Si_2 unit in **133** was rendered sufficiently nucleophilic to coordinate a molecule of $ZnCl_2$, leading to the *cis*-disilyne adduct **134** (**Scheme 11**); this observation represents an experimental demonstration of the dual Lewis acidic/basic nature of disilynes (RSiSiR).

Lappert and coworkers published a series of studies concerning the synthesis of stable NHC-silylene, -germylene, and -stannylene adducts.[139–141] Specifically, the stable carbene {[1,2-(${}^{t}BuCH_2N)_2C_6H_4$]C:} **135** cleanly reacted with its heavier congeners to give the low valent group 14 donor–acceptor adducts **136–138** (eqn [16]).[139,140] The silylene-carbene adduct **136** has a C–Si bond length of 2.162(5) Å and pyramidal geometry at Si, consistent with a lack of significant C_{NHC}–Si π-bonding.[139]

As alluded to in **Section 1.16.1**, NHCs are extensively used as ligands in various catalytic applications, and in some instances uncomplexed NHCs have been used directly in catalysis.[23] In line with this field, the NHC-catalyzed ROP of cyclic siloxanes (e.g., $[Me_2SiO]_4$; D_4) in the presence of alcohols was reported to yield high-molecular-weight polydimethylsiloxane, $[Me_2SiO]_n$.[142] In addition, a review article detailing advances in the NHC-mediated activation of silanes and the application of this chemistry in catalysis appeared in 2010.[143]

The coordination chemistry involving the heaviest group 14 elements (Ge, Sn, and Pb) was established soon after the initial discovery of stable, free NHCs by Arduengo and coworkers.[2] For example, the same group reported the synthesis of the GeI_2 adduct, IMes·GeI_2 **139**, in 1993.[144] Low valent group 14 adducts involving tin (e.g., $ImMe_4{\cdot}SnCl_2$ **140** and $ImMe_2{}^{i}Pr_2{\cdot}SnAr_2$ ($Ar = 2,4,6\text{-}(F_3C)_3C_6H_2$) **141**)[145,146] and lead followed suit, with the lead adduct, $ImMe_2{}^{i}Pr_2{\cdot}Pb(Trip)_2$ **142** ($Trip = 2,4,6\text{-}{}^{i}Pr_3C_6H_2$) being only marginally stable in the solid state with decomposition in solution observed at temperatures above −70 °C.[147]

Much of the collective knowledge with respect to the chemistry of Ge(II) adducts of the general form NHC–GeR_2 is due to studies from Baines et al. In an initial report, the tetramesityldigermene $Mes_2Ge{=}GeMes_2$ **143** was reacted with $ImMe_2{}^{i}Pr_2$ which resulted in the complete scission of the Ge–Ge linkages in **143** to give the stable diarylgermylene adduct, $ImMe_2{}^{i}Pr_2{\cdot}GeMes_2$ **144** (eqn [17]).[148] Soon after, the interesting



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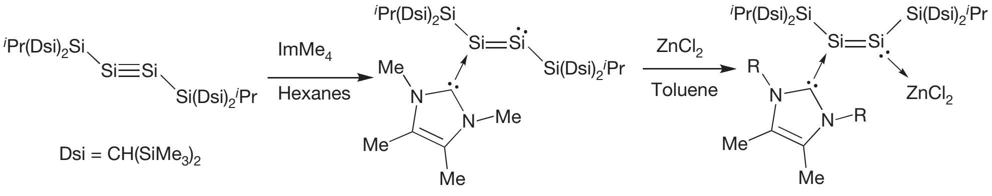
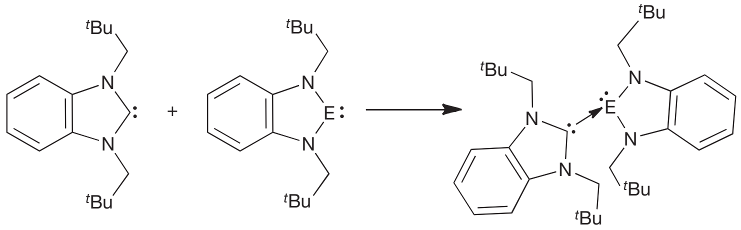
R = Me **130**
R = ^{i}Pr **131**

[15]



132 **133** **134**

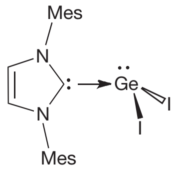
Scheme 11 Preparation of a donor–acceptor complex of a disilylyne.



E = Si **136**
E = Ge **137**
E = Sn **138**

135

[16]



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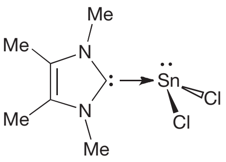

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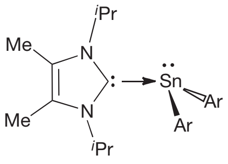
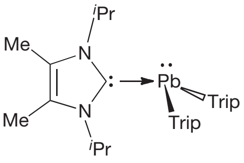


Ar = 2,4,6-$(F_3C)_3C_6H_2$

141

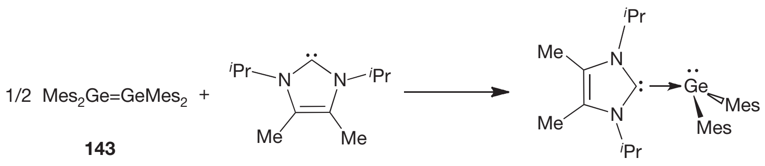


142

dicationic Ge(II) adduct, $[(ImMe_2{}^iPr_2)_3Ge]I_2$ **146**, was prepared (eqn [18]).[149,150] The interaction of $ImMe_2{}^iPr_2{\cdot}GeCl(OTf)$ $(OTf{=}OSO_2CF_3{}^-)$ **147** with cryptand [2.2.2] in tetrahydrofuran (THF) gave a mixture of products including the surprisingly stable Ge(II) cryptand adduct **148** (eqn [19]).[151] Detailed studies by x-ray absorption near edge structure (XANES) revealed that the bonding between the cryptand ligand and the Ge^{2+} center in **148** was largely ionic, while a stronger donor–acceptor (carbene–germylene) interaction was present in $ImMe_2{}^iPr_2{\cdot}GeCl$ (OTf) **147**.[152] More recently, detailed theoretical and experimental investigations concerning the stability and reactivity of germylene adducts of the general form NHC–GeR_2 (R=Mes, F, Cl, Br, I, NCS, and O^tBu; **151**) were published.[153,154]

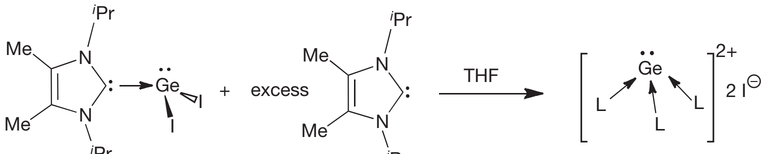
The highly reactive germanium hydride GeH_2, a postulated intermediate in the synthesis of semiconducting germanium, was isolated within the donor–acceptor complex, $IPr{\cdot}GeH_2{\cdot}BH_3$ **152**, by Rivard et al.[155] The synthetic route involved the reaction of $IPr{\cdot}GeCl_2$ **103** with 2 equiv. of $Li[BH_4]$ in ether. Upon thermolysis at 100 °C in toluene, $IPr{\cdot}GeH_2{\cdot}BH_3$ **152** extrudes 'GeH_2' to give the known adduct $IPr{\cdot}BH_3$ **44** (**Scheme 12**). Soon after, Roesky et al. applied the above-mentioned strategy in the attempted isolation of the carbene dihydrosilane adduct $IPr{\cdot}SiH_2{\cdot}BH_3$; however, when $IPr{\cdot}SiCl_2$ **105** was combined with excess $Li[BH_4]$, the stable silicon dichloride adduct $IPr{\cdot}SiCl_2{\cdot}BH_3$ **153** was isolated with no evidence for the formation of the target SiH_2 moeity.[156] Recently, the first examples of stable transition metal complexes bearing the heavy methylene analogs, GeH_2 and SnH_2, as ligands were prepared. By using a combination of the strong NHC donor, IPr, with the Lewis acidic unit $W(CO)_5$, the thermally stable group 14 element dihydride complexes $IPr{\cdot}EH_2{\cdot}W(CO)_5$ (E=Ge and Sn; **156** and **157**; **Scheme 13**) could be isolated.[157] The identity of the EH_2 adducts was confirmed by x-ray crystallography, and a combination of IR and NMR spectroscopic (via deuterium labeling), and theoretical studies. The SnH_2 adduct **157** was shown to be up to 141 °C in the solid state, and preliminary reactivity studies showed that the Sn(II) dihydride unit could undergo clean hydrostannylation chemistry with benzaldehyde at room temperature (**Scheme 13**).[157]

Hahn reported the formation of an NHC–stannylene adduct **161** via the cleavage of the electron-rich dibenzotetrazafulvalene **158** (eqn [20]).[158] In another interesting study, $IMes{\cdot}SnCl_2$ **162** has been shown to be an effective catalyst for the synthesis of polyurethanes.[159]



143 **144**

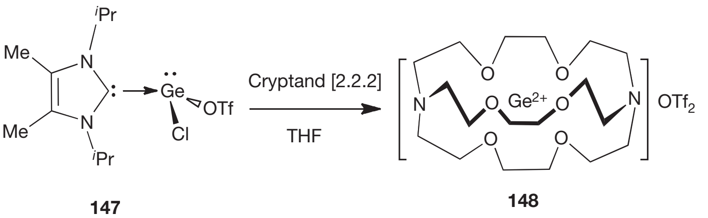
[17]



L = $ImMe_2{}^iPr_2$

145 **146**

[18]



+ $ImMe_2{}^iPr_2{\bullet}GeCl_2$

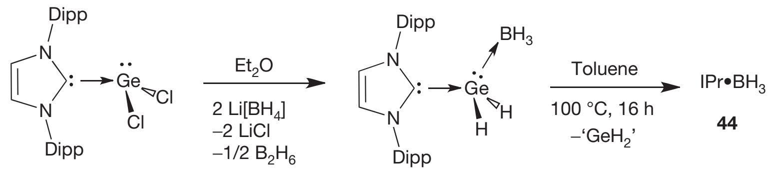
149

\+

$[(ImMe_2{}^iPr_2)_2GeCl]OTf$

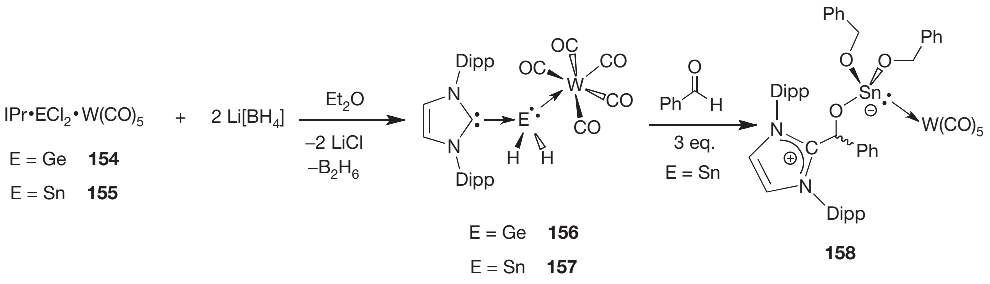
147 **148** **150**

[19]

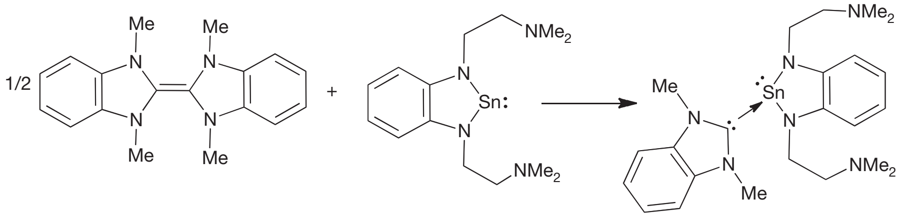


103 **152**

Scheme 12 Synthesis of the Ge(II) dihydride adduct **152** and subsequent thermolysis chemistry.



Scheme 13 Aldehyde insertion chemistry involving the Sn(II) dihydride adduct $IPr•SnH_2•W(CO)_5$ **157**.



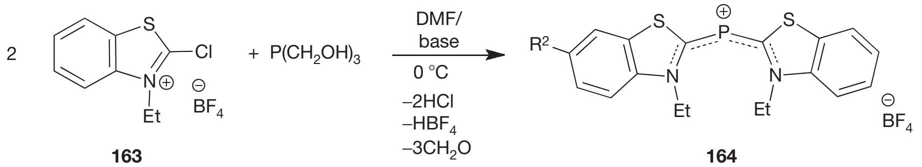
159 **160** **161** [20]

1.16.2.4 Group 15 Complexes (N, P, As, and Sb)

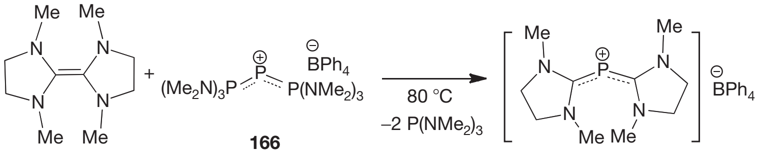
The interaction of NHC units with main group elements has some its earliest roots in pnicogen (group 15) chemistry. In 1964, Dimroth and Hoffmann prepared the low valent phosphorus complex **164**, a formal bis(NHC) adduct of a P(I) cation, from the reaction of the chlorobenzothiazolium salt **163** with $P(CH_2OH)_3$ (eqn [21]).[160]

Schmidpeter later reacted the dihydroimidiazol-2-ylidine dimer **165** with the electrophilic phosphenium salt **166** to give the carbene adduct $\{[(H_2CNMe)_2C]_2P\}BF_4$ **167** (eqn [22]). Overall this transformation can be regarded as an NHC/$P(NMe_2)_3$ ligand displacement reaction.[161] More recently, the group of Macdonald uncovered similar reactivity when various NHCs were shown to displace dppe from the phosphenium precursors **168** and **169** to give stable P(I) adducts of the general form $[NHC{\cdot}P{\cdot}NHC]^+X^-$ (**170**) (eqn [23]).[162] An alternative route to a phosphenium carbene adduct was reported in the same study, and involved the dehalogenation of PCl_3 with excess $ImMe_4$ to give the intercepted P(I) adduct $[(ImMe_4)_2P]Cl$ **171** along with a halocarbenium salt **172** as a byproduct (eqn [24]).[162] The bonding in the phosphenium adducts (**170**) was investigated using theoretical calculations, and these studies indicated that the dominant C_{NHC}–P interactions are dative ($C_{NHC}\rightarrow P$) in nature with additional P–C π-bonding detected; therefore, the true bonding motif in these adducts lies in between the canonical forms presented in eqn [23].[162]

The stable fluorophosphane adduct, $IMes{\cdot}PF_4Ph$, **173** was prepared by Arduengo and coworkers,[163] while the interaction of $ImMe_4$ with the cyclopentaphosphane, $(PhP)_5$, led to the formation of the phenylphosphinidene adduct, $ImMe_4{\cdot}PPh$, **174**.[164] The presence of two stereochemically active lone pairs at phosphorus in phosphinidene–NHC adducts such as **174** was experimentally verified when the stable bis(borane) adduct $IMes{\cdot}PPh(BH_3)_2$ **175** was later prepared.[165] Soon after, Kuhn et al. reported a series of NHC adducts involving

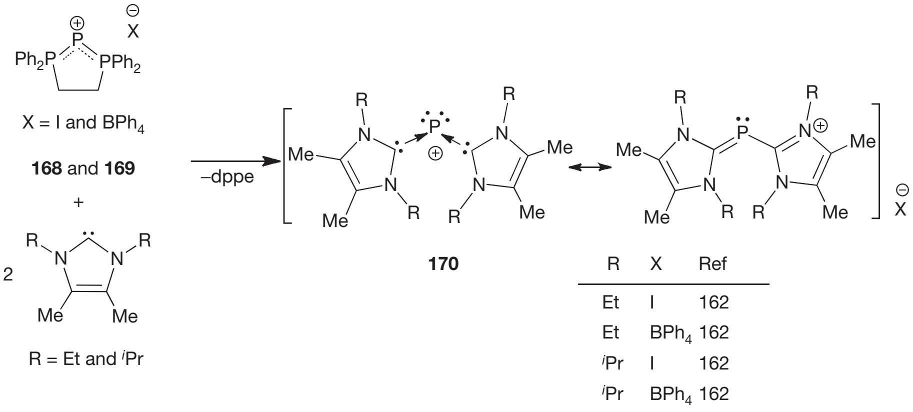


163 **164** [21]



165 **166** **167**

[22]



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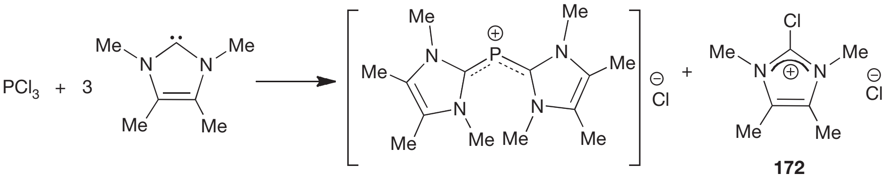
R	X	Ref
Et	I	162
Et	BPh$_4$	162
^{i}Pr	I	162
^{i}Pr	BPh$_4$	162

[23]



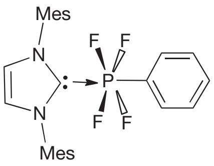
171 **172**

[24]

$POCl_2^+$,[166] PPh_2^+,[167] PO_3H,[168] and $Ph_2P–ECl_3$ (E = Al and Ga)[168,169] units. Stable adducts between the strong donor, $ImMe_2{}^iPr_2$, and the iminophosphanes X–P═N–Mes* (X = Cl and OTf; Mes* = 2,4,6-$^tBu_3C_6H_2$) were reported by the Burford group;[170] the P–N distances in $ImMe_2{}^iPr_2$·[XPNMes*] (X = Cl and OTf; **176** and **177**) were 1.585(5) and 1.574(4) Å, respectively, and are slightly elongated in comparison to the distances in the base-free iminophosphanes, indicating the retention of considerable P═N double bond character within these carbene adducts.[171] More recently, Weigand and coworkers reported the isolation of the novel carbene-stabilized phosphorus halide cations, $[L{\cdot}PCl_2]^+$ and $[(L)_2{\cdot}PCl]^{2+}$.[172]

In 2007, Bertrand and coworkers reported the activation of P_4 by the stable cyclic (alkyl)-(amino)carbene (CAAC) **178**,[18] to give linear P_4 arrays with either all *trans* (**179**) or *cis–trans* cores sandwiched by CAAC ligands.[173] As represented in Scheme 14, the central P–P distances in the *trans*-isomer, **179**, were in the range expected for P–P double bonds (ca. 2.08 Å), while the elongated terminal P–P distances of 2.19–2.20 Å suggested that single bonds were present.[174] The dark blue adduct **179** showed a high degree of thermal stability under inert atmosphere (up to 130 °C), and in the presence of 2,3-dimethylbutadiene, the cycloaddition product **180** was obtained (Scheme 14).[173] A related linear P_4 adduct SIMes·P_4·SIMes **181** was formed by the reaction of the hindered saturated NHC, SIMes, with P_4; when the P_4 adduct **181** was heated to 70 °C for 16 h, phosphorus cluster growth transpired to yield the novel P_{12} NHC bis-adduct **182** as a thermally stable yellow solid. This transformation is promising within the context of accessing new phosphorus allotropes and nanoparticles in a controlled manner.[175] By altering the steric bulk about the CAAC donor, the smaller P_2 and branched P_4 adducts **183** and **184** were obtained directly from white phosphorus.[176]

Robinson et al. also reported a reductive pathway toward the diphosphidine adducts IPr·P_2·IPr **187** and IMes·P_2·IMes **188**.[177] The synthetic strategy employed followed an analogous route



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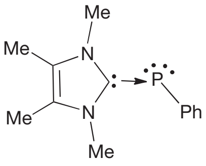

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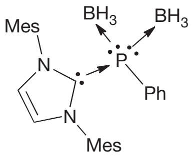

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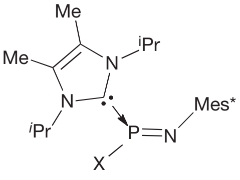

X = Cl **176**
X = OTf **177**

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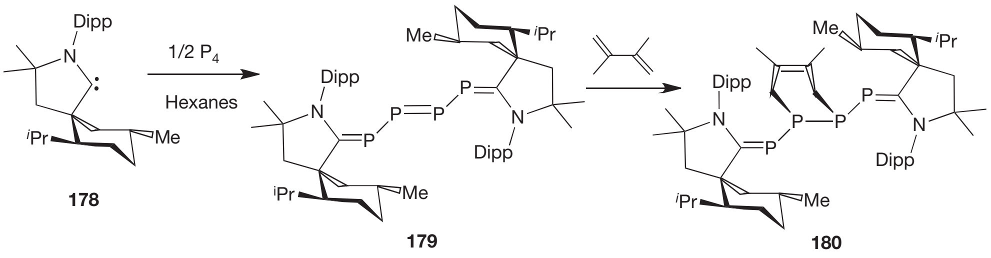
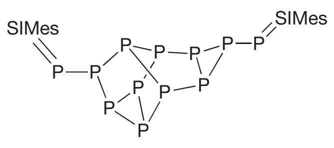


Scheme 14 Activation of white phosphorus by the CAAC donor **178** and associated cycloaddition chemistry.



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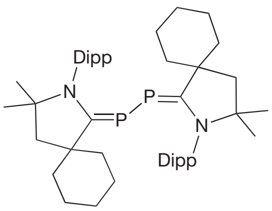

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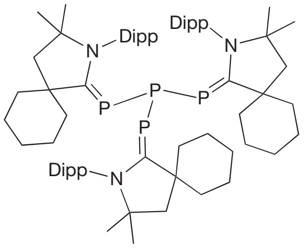
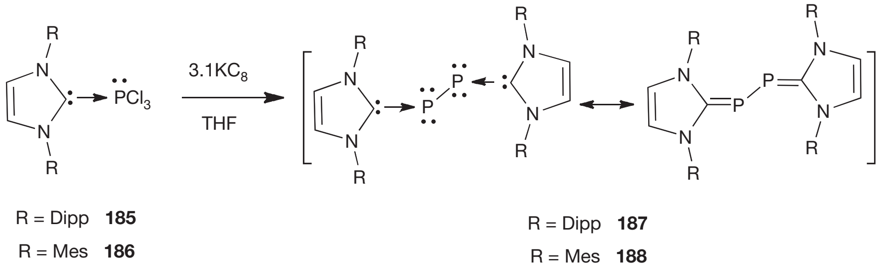


184

used to prepare the diboronene adduct IPr·HB═BH·IPr **36**. Namely, the chlorophosphane precursors NHC·PCl_3 (NHC = IPr and IMes; **185** and **186**) were reacted with 3.1 equiv. of KC_8 in THF to give the diphosphorus adducts **187** and **188** as air- and moisture-sensitive red solids in low to modest yields (eqn [25]).[177] The P–P distances within these diphosphorus adducts were found to be 2.2052(10) and 2.1897(11) Å, respectively, and are in the range expected for P–P single bonds; however, some P → C π-backbonding was noted between the C_{NHC} donors and the phosphorus centers of the P_2 unit.[177] More recently, the isolation of the stable, neutral diarsenic congener IPr·As–As·IPr **190** was achieved from the reduction of the arsenic(III) chloride adduct, IPr·$AsCl_3$ **189**, with KC_8 in THF.[178] The Robinson group also reported the attempted reduction of the P_2 unit in IPr·P_2·IPr **187** with Li metal; in place of isolating an anionic P_2 carbene adduct, reductive cleavage of the diphosphinidene unit was observed, followed by a formal H migration process, to yield an anionic NHC complex of the parent phosphinidene, PH, **191** (eqn [26]).[179]

A phosphinyl radical cation with significant spin density on phosphorus (0.67 e^-) has been isolated as a stable crystalline brown solid (mp = 96–99 °C) **195** using the protocol outlined in Scheme 15.[180] The P_2 adducts IPr·P_2·IPr **187** and CAAC·P_2·CAAC **183** can each undergo one-electron oxidation in the presence of $[Ph_3C][B(C_6F_5)_4]$ to give the radical cations **196** and **197** (Scheme 16).[181] In addition, the monocation **196** can be oxidized to yield the stable diphosphorus dication adduct $[IPr·P_2·IPr]OTf_2$ **198**. This chemistry highlights the comparatively stronger electron-donating ability of the IPr ligand relative to the CAAC system.[182] With the aid of detailed experimental and theoretical studies, it was determined that upon oxidation of the NHC–P_2–NHC arrays, electron density is progressively removed from an orbital that is a mixture of P–P π*- and P–C π-bonding character.[181] Therefore upon oxidation, weakening of the P–C(carbene) bonds, and strengthening of the core P–P bonding interaction were observed to eventually give a dication that is best represented as a donor–acceptor adduct of a P_2^{2+} unit (Scheme 16); moreover, the



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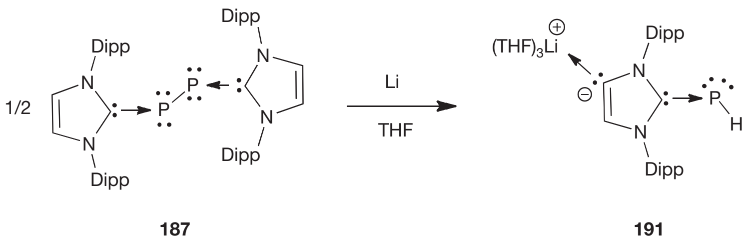

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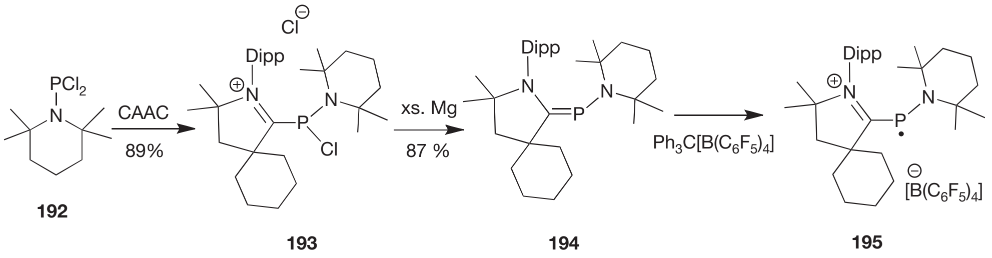
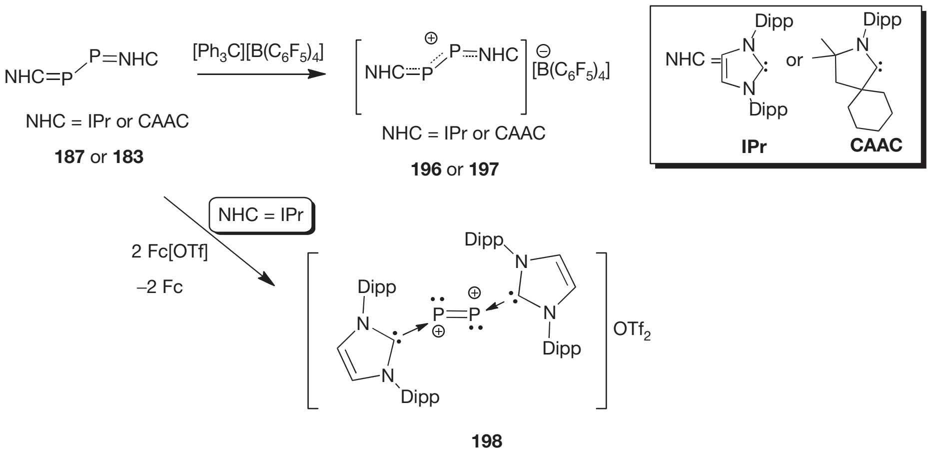


Scheme 15 Preparation and oxidation of the phosphinidene–carbene complex **194**.

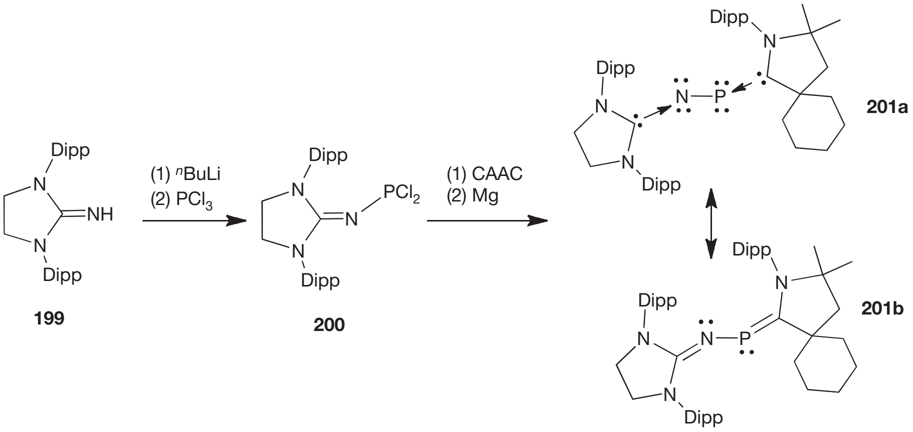


Scheme 16 Redox chemistry involving the P_2 adducts **183** and **187**.

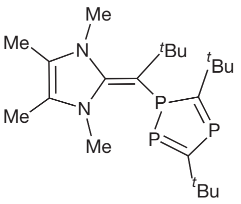
bonding parameters in **198** (P–C_{NHC}: 1.840(2) Å and P–P = 2.0826(12) Å) are in line with the bonding arrangement depicted in Scheme 16.

Phosphorus mononitride (PN) has attracted interest from a fundamental standpoint as a heavier congener of dinitrogen, and due to its presence in the planetary atmospheres of both Saturn and Jupiter. An important step toward isolating this reactive species at room temperature was uncovered by Bertrand and coworkers. Starting from the imino-carbene [$(H_2CNDipp)_2C{=}NH$] **199**, a formal bis(carbene) adduct of PN, **201** was prepared in two steps (Scheme 17).[182] Unlike molecular PN, which features a P–N triple bond, the P–N bonding in **201** is in line with that of a single bond (P–N = 1.7085(16) Å), and as a result, two possible canonical forms (**201a** and **201b**) can be used to illustrate the bonding in **201**; the shortened P–C and P–N distances indicate that form **201a** is likely a better representation of the bonding in this PN complex. Interestingly, **201** can undergo a reversible one-electron oxidation to yield the stable cationic PN adduct [CAAC·PN·SIPr]$^{\bullet+}$ **202**, and EPR measurements detected strong radical coupling to phosphorus ($g = 2.0048$; $a(^{31}P) = 44$ G) with negligible coupling to nitrogen, indicating that the radical is localized mainly on the heavier P atom of the PN unit.[182]

The trimerization of $^tBuC{\equiv}P$ in the presence of $ImMe_4$ was reported by Hahn and coworkers to yield the stable



Scheme 17 Isolation of a formal bis(carbene) adduct of PN.



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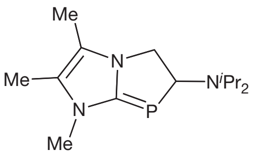

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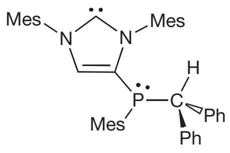


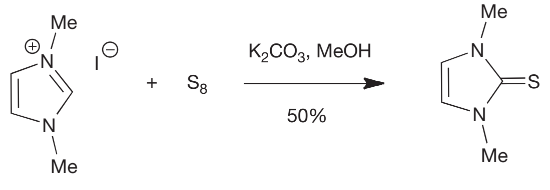
205

triphosphole heterocycle **203**.[183–186] When the aminophosphaalkyne ${}^{i}Pr_2N{-}C{\equiv}P$ was combined with $ImMe_4$, C–H activation of a flanking N–Me group of the carbene transpired to give the insertion product **204**.[183] More recently, Gates et al. studied the reaction of the NHC, IMes, with the phosphaalkene $Ph_2C{=}PMes$.[187] Surprisingly, the novel 4-phosphino carbene **205** was obtained as the sole product with no evidence for the formation of the intended adduct $IMes{\cdot}(Mes)P{=}CPh_2$.[187]

The chemistry of NHCs with the heavier pnicogens, arsenic and antimony, has been explored to a lesser extent when compared to phosphorus; however, some interesting chemistry has been uncovered. In addition to the above-mentioned synthesis of the diarsenic(0) adduct IPr·As–As·IPr **190**,[178] the arsinidene adducts IMes·AsR (R = Ph and C_6F_5; **206** and **207**) were reported by Cowley and coworkers,[188] while the thermally stable stibane–chlorocarbene adduct $Cl_2IMes{\cdot}Sb(CF_3)_3$ **208** was described by Arduengo et al.[189]

1.16.2.5 Group 16 Complexes (O, S, Se, and Te)

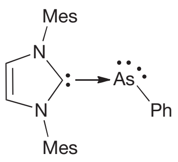
Initial chemistry with NHCs and chalcogen elements began in 1986 when Arduengo and coworkers demonstrated that the *in situ* generated carbene, $ImMe_2$, could be trapped as a stable thione adduct $ImMe_2{=}S$ **210** (eqn [27])[190]; this strategy was later extended to include the preparation of the imidazoleselone **211**.[191] After the discovery of stable NHCs (e.g., IAd and IMes) in 1991, various NHC chalcogen adducts (NHC=E; E = S, Se, and Te) were prepared directly from the reactions with S_8, Se, and Te. For example, the NHC–tellurium adducts IMes=Te and $Cl_2IMes{=}Te$ (**212** and **213**) were reported by Arduengo et al.,[192] while the less hindered $ImMe_2R_2$ adducts (**214–216**) were synthesized in the laboratories of Kuhn.[193] In addition, smooth chalcogen adduct formation was observed with Enders triazolium NHC to give the stable adduct **217**.[194,195] The thermodynamic parameters associated with the binding of sulfur to both stable NHCs and phosphane derivatives were measured, and the following increasing trend in exothermic reaction enthalpies was noted: $PPh_3 < PMe_2Ph < IAd < PCy_3 < IMes$.[196]



209 **210** [27]

Kuhn and coworkers have published a series of reports concerning the complexation of Lewis acidic sulfur halides of variable oxidation states (+2 to +6).[197,198] Scheme 18 outlines a significant portion of this work and serves to illustrate the versatility of NHCs as Lewis basic donors. For example, the thermally stable T-shaped SCl_2 adduct **218** (C_{NHC}–S–Cl angles: 86.6(1) and 89.5(1)°) was prepared via the direct reaction of SCl_2 with $ImMe_2{}^{i}Pr_2$.[197] The sulfur difluoride analog $ImMe_2{}^{i}Pr_2{\cdot}SF_2$ **219** could be readily obtained from the chloro analog **218** by halide metathesis with AgF. Similarly, thionyl chloride, $SOCl_2$,[197] and SO_3,[198] each form stable NHC adducts (**220** and **221**) with $ImMe_2{}^{i}Pr_2$. The sulfur center in $ImMe_2{}^{i}Pr_2{\cdot}S(O)Cl_2$ **220** is rendered sufficiently nucleophilic to allow for its alkylation with MeI to give the novel salt $[ImMe_2{}^{i}Pr_2{\cdot}S(O)MeCl_2]I$ **222**.[197] In the case of the dihalosulfones SO_2XF (X = Cl and F) and SF_4, the haloimidiazolium salts **223–225** were the sole products isolated.[197] Moreover, stable adducts between NHCs and SO_2 were reported both by Skrypnik and Lyashchuk ($IAd{\cdot}SO_2$ **226**)[199] and by the group of Denk ($SI^tBu{\cdot}SO_2$ **227**).[200] Of note, the unsaturated carbene I^tBu showed no sign of interaction with sulfur dioxide, indicating that subtle electronic effects can be quite important in dictating the reactivity in this system; this observation was supported by theoretical calculations which predict only a marginal stability for the $I^tBu{\cdot}SO_2$ adduct **228**.[200]

In 2001, the formal biscarbene–SeBrI adduct **229** was prepared; as with the SCl_2 adduct **218** reported previously by Kuhn, the SeBrI units in **229** adopt T-shaped coordination geometries with each Br–Se–I unit orthogonally disposed to the planar NHC rings.[201] Upon closer inspection of the x-ray data, close intramolecular contacts between each Br atom and an adjacent iodine center were noted. The TeI_2 adduct $ImMe_2{}^{i}Pr_2{\cdot}TeI_2$ **230** was the sole product obtained (66% yield) from the reaction of $ImMe_2{}^{i}Pr_2$ with TeI_4 in refluxing tetrahydrofuran (Scheme 19).[202] The reaction has been postulated to proceed via an unstable the Te(IV) adduct $ImMe_2{}^{i}Pr_2{\cdot}TeI_4$ which undergoes reductive elimination of an



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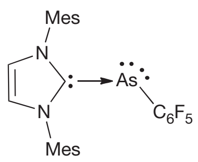

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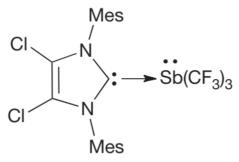

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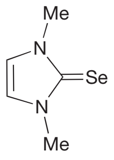

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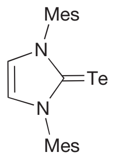

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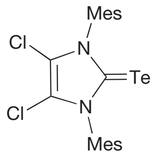

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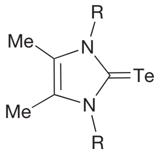
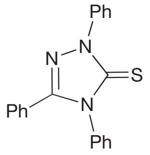


R = Me **214**
R = Et **215**
R = ^{i}Pr **216**



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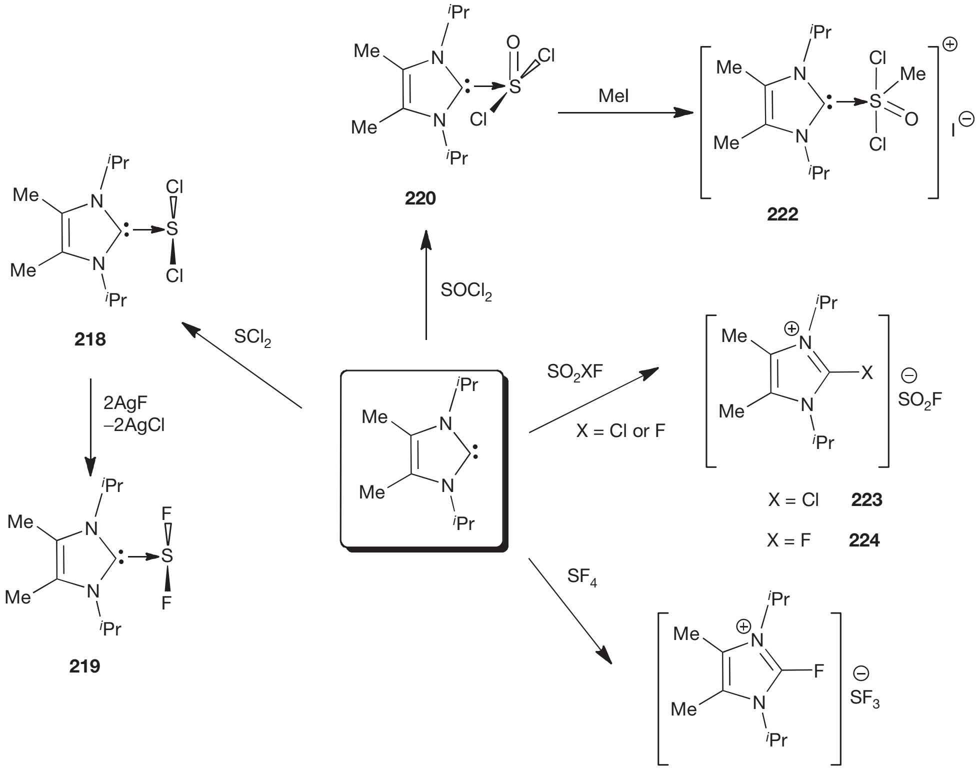
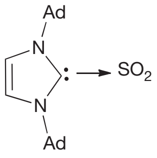


Scheme 18 Reactivity of ImMe$_2$^{i}Pr$_2$ with sulfur halides.



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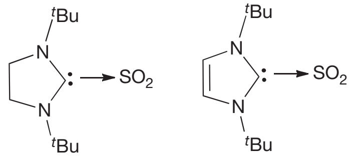
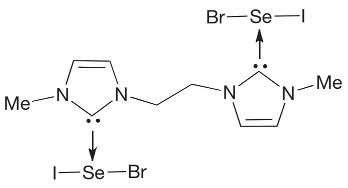


Stable **227**

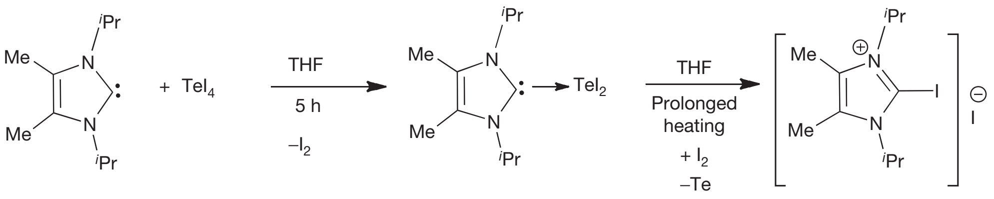
Unstable **228**



229

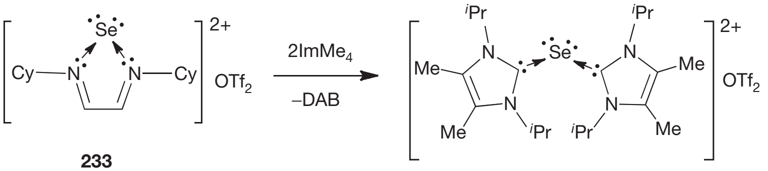
equivalent of iodine at elevated temperature to give **230**; prolonged heating of the reaction mixtures led to quantitative demetallation of **230** via the reaction of the I_2 co-product to give the iodide salt **231** as the final product (Scheme 19).[202] A series of cationic adducts **232** bearing Lewis acidic $[Ar''Te]^+$ units ($Ar'' = 2,6\text{-}Mes_2C_6H_2$) were recently synthesized by the reaction of ImMe$_4$ with the aryltellurium iodide Ar″TeI; theoretical studies revealed that the dissociation energies in these adducts were significantly greater than found in the respective phosphane adducts $[ArTe{\cdot}PR_3]^+$, thus illustrating the strong electron donating ability of NHCs.[203]

Ragogna et al. have successfully stabilized dicationic heterocyclic carbene analogs featuring Se^{2+} and Te^{2+} centers chelated by bidentate nitrogen donor ligands.[204] Moreover, this group showed that Se^{2+} group transfer from the cationic diazabutadiene precursor **233** transpired in the presence of NHC

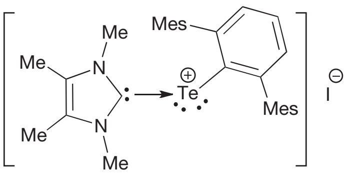


$ImMe_2{}^iPr_2$ **230** **231**

Scheme 19 Tellurium iodide complexation by an NHC.



233 **234** [28]



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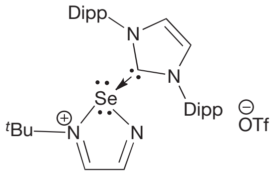

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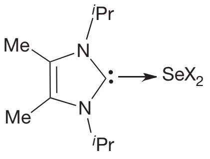
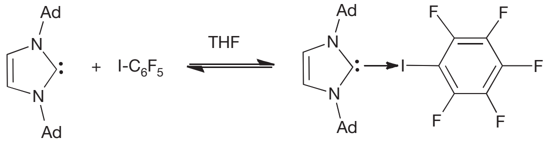


X = Cl **236**
X = I **237**

donors to yield the novel bis-NHC Se^{2+} adduct $[(ImMe_4)_2{\cdot}Se]$ OTf_2 **234** (eqn [28]).[205] The same group reported the heterocyclic diazaselenolium adduct **235**, and the $SeCl_2$ and SeI_2 adducts (**236** and **237**).[206,207]



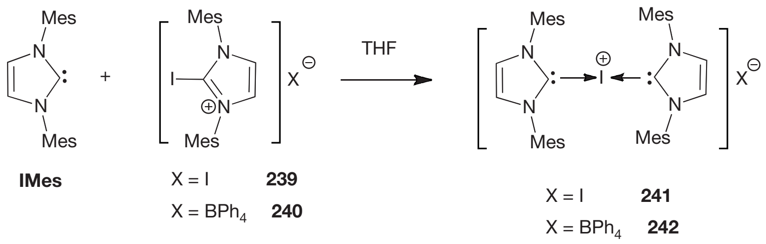
238 [29]

1.16.2.6 Group 17 Complexes (F, Cl, I, and Br)

As seen in the previous sections, the formation of the NHC halonium salts [NHC–X]X often results from redox-mediated reactions such as the reduction of PCl_3 to P(+1) adducts in the presence of excess $ImMe_4$ (eqn [24]).[162] Moreover, these salts can be prepared in high yield starting from the free carbene, and halogen sources such as Cl_2, Br_2, I_2, C_2Cl_6, and dichloroethane.[208–211] The NHC, IAd, is sufficiently nucleophilic to interact with $I–C_6F_5$ to form the novel iodide-bridged complex $IAd{\cdot}IC_6F_5$ **238**.[212] As indicated in eqn [29], **238** exists in equilibrium with free IAd and IC_6F_5 in solution, and x-ray crystallography identified the presence of a nearly linear $C_{NHC}–I–C_{Aryl}$ linkage with a $C_{NHC}–I$ distance that is considerably elongated (2.754(3) Å) with respect to the C–I distance within the IC_6F_5 moiety (2.159(3) Å); these data support the weak nature of the $C_{NHC}–I$ bonding interaction in **238**.[212]

Arduengo and coworkers reported the formation of bis-NHC adducts of the iodine (+1) cation $[(IMes)_2{\cdot}I]X$ ($X = I^-$ and BPh_4^-; **241** and **242**; eqn [30]).[213] These salts were stable in acetonitrile solution and exhibited a high degree of thermal stability (mp = 255–258 °C and 218–221 °C for **241** and **242**, respectively); moreover, the $[(IMes)_2{\cdot}I]$ cation could be detected by mass spectrometry. Compound **242** was further analyzed by single-crystal x-ray crystallography, and was shown to contain a quasi-linear $C_{NHC}–I–C_{NHC}$ geometry with C–I distances that ranged from 2.286 to 2.363 Å.[213]

Surprisingly divergent reaction profiles are obtained when NHCs are reacted with various haloalkanes. In addition to direct halogen transfer to yield the halogenato salts [NHCX] X, nucleophilic substitution processes and elimination chemistry can also occur. For example, the anthracenylmethylene-substituted NHC **243** participates in nucleophilic substitution chemistry with dichloromethane to yield the imidiazolium salt **244** (Scheme 20).[214] The hydrogen atom of the CH_2Cl unit in **244** is sufficiently acidic to engage in a dehydrohalogenation reaction with further equivalents of the basic carbene **243** to form the stable halogenated olefin **245**.[214] Of note, NHC salts of similar structure to **244** (e.g., $[ImMe_4–CH_2–X]X$; X = Cl and Br; **248** and **249**) were prepared via the halogenation of $ImMe_4{=}CH_2$ **247** with C_2Cl_6 and Br_2 (eqn [31]).[215] Interaction of $BrCF_2CF_2I$ with $ImMe_2{}^iPr_2$ gave the bis-NHC adduct **250** wherein a molecule of $BrCF_2CF_2I$ is sandwiched between



IMes

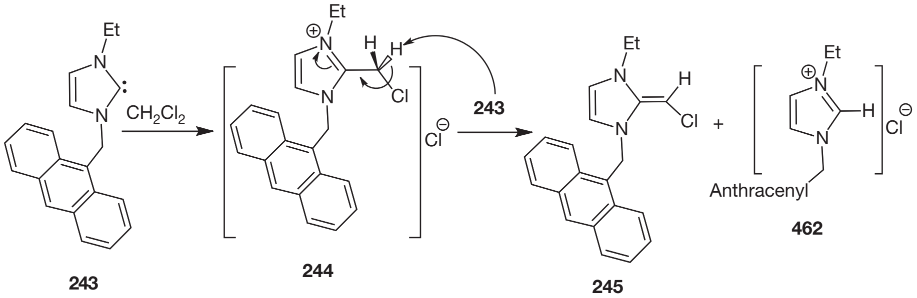
X = I 239

X = BPh_4 240

X = I 241

X = BPh_4 242

[30]



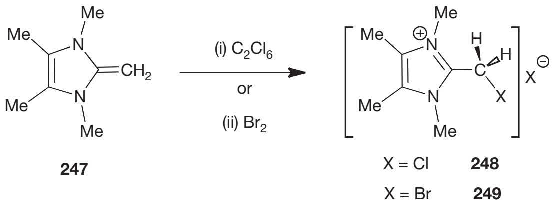
243

244

245

462

Scheme 20 Formation of the *N*-heterocyclic olefin **245**.



247

X = Cl 248

X = Br 249

[31

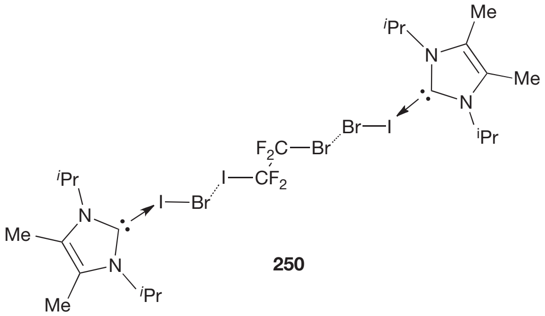
two IBr·NHC units (presumably derived from the carbene-induced elimination of IBr from $BrCF_2CF_2I$).[216] The air-stable NHC **251** can be cleanly prepared in a 85% yield by the efficient reaction of IMes with 2 equiv. of CCl_4 in THF; this carbene has been used as a ligand for metal-mediated olefin polymerization and olefin metathesis chemistry.[217,218]

1.16.3 Stable NHCs Featuring Inorganic Elements

The ability to tune the electronic and steric parameters of NHCs has become a hallmark of this ligand class. In order to add even more versatility to this ligand system, researchers have sought to incorporate inorganic elements directly within the NHC backbone or as pendant groups.

In 2010, Bertrand et al. communicated a strategy for incorporating functional groups at the 4- and 5-positions of an NHC ring (Scheme 21).[209] The hindered NHC, IPr, was reacted with various electrophiles (E–X) to yield the C_{NHC}-substituted imidiazolium salts **252**. Treatment of these salts with the strong base, $K[N(SiMe_3)_2]$ (KHMDS), afforded NHCs wherein the electrophilic groups (E) migrated to the backbone **253**. This general protocol can be used to install electron-withdrawing (F_3CSO_2 and PhC(O)) or electron-donating groups (Me_3Si and Ph_2P) onto the carbene backbone; moreover, the preparation of difunctional NHCs such as the mixed phosphido-ketone NHC **255** was demonstrated.[209]

Organic five-membered *N*,*N*-heterocyclic carbene platforms such as those found in IMes and IPr are by far the most dominant structural motifs observed in NHC chemistry. A new avenue of research in this field appeared in 2004 with the preparation of a hybrid inorganic–organic NHC bearing a noncarbon linker in the NHC backbone. Specifically, Despagnet-Ayoub and Grubbs reported the synthesis of a four-membered carbene featuring an CNPN ring motif **261** in a two-step procedure starting from the diarylsilylamidine **256** (Scheme 22).[219] The synthesis of the carbenes required an initial ring-closing reaction between the diarylsilylamidines **256** and **257**, and the dichlorophosphorus amide $^iPr_2N–PCl_2$. When less hindered Mes groups were present at nitrogen, the carbene formed



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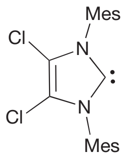
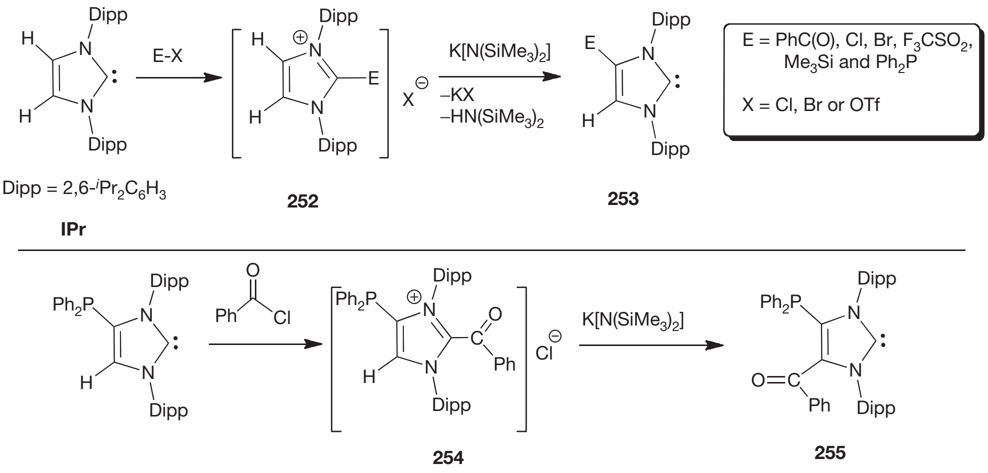
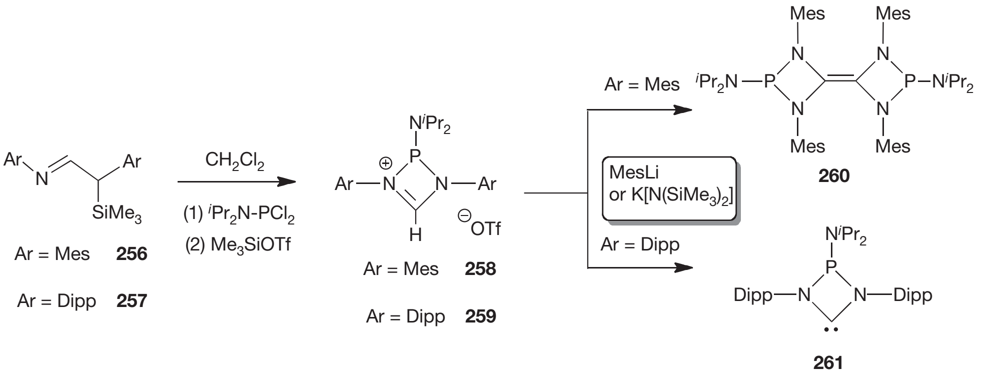


251



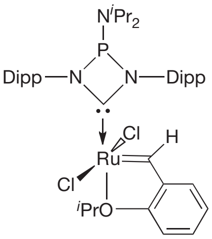
Scheme 21 Synthesis of backbone-substituted *N*-heterocyclic carbenes.



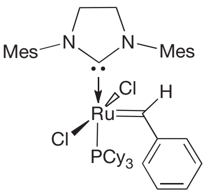
Scheme 22 Preparation of the phosphorus-containing NHC **261** and the dimeric analogue **260**.

upon deprotonation of the heterocyclic precursor **258** rapidly dimerized to give the olefinic product **260**. Incorporation of flanking Dipp groups at nitrogen led to the formation of the NHC **261** that was stable at −50 °C; however, this carbene underwent decomposition at room temperature after 2 h.[219] The same group reported the use of **261** as a ligand for Ru-alkylidene-mediated olefin metathesis; while complex **262** displayed catalytic activity, its performance lagged in comparison to the commonly used systems (**263** and **264**) bearing SIMes ligands.[220]

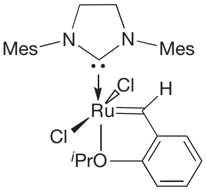
Soon after this work appeared, the groups of Roesler and Bertrand independently reported the synthesis of five- and six-membered NHCs with boron atoms as part of the NHC framework (**265–267**); these novel carbenes were prepared in high yield following a similar condensation route as highlighted in Scheme 22.[221,222] The diborane analog {[(Me$_2$NBN(Dipp))]$_2$C:} **265** was isolated as a thermally stable solid (stable for weeks in solution) that exhibited an unusually downfield-shifted ^{13}C{^{1}H} NMR resonance for the carbene carbon (304 ppm in C$_6$D$_6$). Moreover, NHC **265** was shown to be more electron releasing than the 'standard' NHCs IPr and IMes.[221] The six-membered borazine-carbenes [MesN(RBNCy)$_2$C:] (R = NMe$_2$ and Ph; **266** and **267**) were quite thermally stable (mp = 176 °C for **267**), and the clean formation of the rhodium(I) carbonyl complexes **268** and **269** was accomplished; the average value of the ν(CO) stretching frequencies in **268** and **269** (2029–2038 cm^{-1}) was slightly lower than carbonyl stretches found in the related Rh(CO)$_2$Cl adducts of SIMes and IPr, indicating that the boron-based NHCs **266** and **267** were marginally stronger σ-donors. The power of



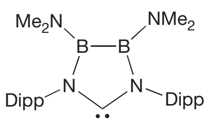
262



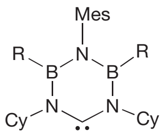
263



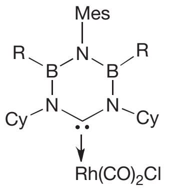
264



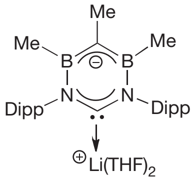
265



R = NMe₂ **266**
R = Ph **267**



R = NMe₂ **268**
R = Ph **269**

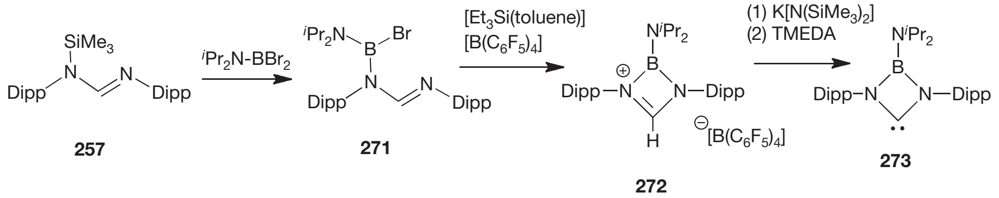


270

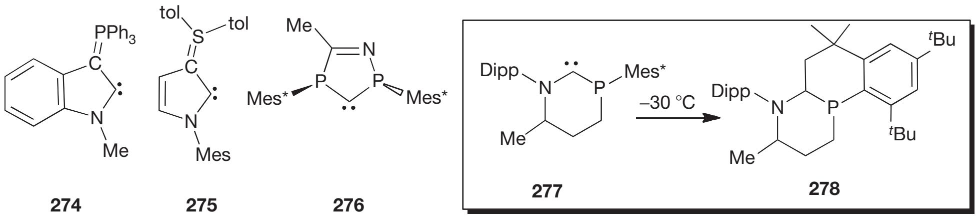
each of the above-mentioned synthesis is the ease with which new chemical groups with varying steric and electronic parameters can be installed at the inorganic element (B or P) of the NHC backbone. Roesler et al. also prepared the anionic NHC **270** which is structurally related to **267** via a formal replacement of a backbone NMes group with an organic moiety (CMe).[223–225] The anionic carbene heterocycle in **270** exhibits metrical parameters consistent with a planar 6π arrangement, and thus could be regarded as an isoelectronic analog of the widely used anionic terphenyl ligand class (e.g., $\mathrm{Ar'} = 2,6\text{-}\mathrm{Dipp_2C_6H_2}$).[226]

An elegant route to the four-membered *N*-heterocyclic carbene [$^i\mathrm{Pr_2NB(NDipp)_2C}$:] **273** was disclosed in 2006 (Scheme 23).[227] The key synthetic breakthrough was the use of the strong Lewis acid $[\mathrm{Et_3Si(toluene)}][\mathrm{B(C_6F_5)_4}]$ to abstract a halide from the boron center in **271** to give the ring-closed boraformamidinium salt **272**; deprotonation of **272** with $\mathrm{K[N(SiMe_3)_2]}$, followed by treatment with tetramethylethylenediamine (TMEDA), gave the target carbene heterocycle [$^i\mathrm{Pr_2NB(NDipp)_2C}$:] **273** in moderate yield (54%) as a yellow solid (mp = 98 °C). As with the related boron-containing NHC **265**, a strongly deshielded resonance at 312.6 ppm for the carbenic carbon was detected by $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectroscopy in $\mathrm{C_6D_6}$, while x-ray crystallography revealed the presence of a planar NBNC heterocyclic core with a narrow $\mathrm{N{-}C_{NHC}{-}N}$ angle of 94.02(16)°.[227]

Ylidic NHCs bearing either sulfur or phosphorus atoms at the 3-position of the NHC were recently prepared by the group of Kawashima (Scheme 24).[228,229] Both carbenes **274**[228] and **275**[229] were stable at low temperature (−40 °C) and diagnostic downfield $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR resonances were observed for the carbenic carbon centers. Structural authentication of these species was achieved via complexation of sulfur (to form the thioketones $\mathrm{R_2C{=}S}$) or $\mathrm{Rh(CO)_2Cl}$.[11,12] The first example of a stable P-heterocyclic carbene bearing two phosphorus centers adjacent to a carbene carbon **276** was synthesized in 2005 by Bertrand et al.[230,231] Compound **276** contains slightly pyramidalized phosphorus centers in the solid state (angle sum 348° and 353°) indicating a reduction in P–C π-bonding involving the carbenic carbon. Despite the chiral nature of the P centers in **276** in the solid state, NMR studies in solution reveal that the *ortho*-^{t}Bu groups of the flanking Mes* substituents are equivalent down to −100 °C, suggesting that rapid inversion is taking place at phosphorus, consistent with low inversion barriers at these sites.[230] Interestingly, the degree of planarity at P increases with the steric bulk of the substituents and a corresponding singlet–triplet gap of 41.4 kcal mol^{-1} was calculated for **276**; similar calculations performed on the P-heterocyclic carbene (PHC) derivative with H atoms at P show a significant decrease in $\Delta E_{\mathrm{S\text{-}T}}$ (22.6 kcal mol^{-1}) and pronounced pyramidalization at P (angle sum = 328°).[230] The saturated P,N-heterocyclic carbene **277** was also reported by the same group; however, this carbene was only stable at −78 °C; upon warming to −30 °C for 2 days, carbene-induced C–H activation of an adjacent ^{t}Bu group transpired to give the fused polyheterocycle **278** (Scheme 24).[19] Direct evidence for the formation of **277** was obtained via $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectroscopy wherein a diagnostic resonance for the carbene center was located at 314.5 ppm with clearly resolved coupling to phosphorus (doublet, $^1J_{\mathrm{PC}} = 122$ Hz).[19]



Scheme 23 Synthesis of the boramine carbene **273**.



Scheme 24 Ylidic and phosphorus-containing *N*-heterocyclic carbenes.

1.16.4 Conclusion

Judging by the dramatic increase in the number and variety of publications concerning NHC-based chemistry in the main group, the future of this domain of research is, as expected, quite promising.[232] Most of this work was motivated by the discovery of new bonding arrangements, including the isolation of new examples of inorganic multiple bonds.[233,234] Potential targets which might conceivably be accessed with NHC donors include: BN and the carbonyl analogs SiO, GeO, and SnO. Moreover, due to the dative (coordinately labile) nature of many NHC-main group element adducts, the use of these compounds as precursors to novel nanoparticle, polymeric, or cluster motifs via thermolysis chemistry should prove to be a fertile area of study;[235–237] especially exciting would be the synthesis of new nanomaterials of previously unknown composition and properties. Moreover, the use of NHCs to activate inorganic bonds for the subsequent synthesis of value-added compounds (e.g., to prepare phosphanes from P_4), and the isolation of increasingly exotic main group radical species, should lead to further exciting advances in main group chemistry in the upcoming years.[238,239] Lastly, the development of new NHC frameworks, and the corresponding development of main group element-based catalytic processes (as well as metal-like behavior) are certainly promising avenues for future study.[240,241]

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1.17 Low-Coordinate Main Group Compounds – Group 13

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Abbreviations

Ac	Acetate
acac	Acetylacetonate
Ar	Aryl
Ar*	General terphenyl substituent
Ar^f	3,5-Bis(trifluoromethyl)phenyl
BIAN	Bis(imino)acenaphthene
Bp	Bis(pyrazolyl)borate
Bu	Butyl
CDT	Cyclododecatriene
CGMT theory	Carter–Goddard–Malrieu–Trinquier theory
Ch	Chalcogen (group 16 element)
COD	Cyclooctadiene
COE	Cyclooctene
COT	Cyclooctatriene
bipy	2,2′-Bipyridine
Cp	Cyclopentadienide
Cp′	Variously substituted cyclopentadienide
Cp*	Pentamethylcyclopentadienide
Ct	Centroid of Cp
Cy	Cyclohexyl
DAB	1,4-Diazabutadiene
DCC	*N*,*N*′-Dicyclohexylcarbodiimine
DCPE	1,2-Bis(dicyclohexylphosphino)ethane
DDP	$CH(CMeNC_6H_3\text{–}2,6\text{-}^iPr_2)_2$
DFT	Density functional theory
DIMPY	Diaryliminopyridine
Dipp	2,6-Diisopropylphenyl
DMAP	4-Dimethylaminopyridine
DME	1,2-Dimethoxyethane
DMP	2,6-Dimethylphenyl
DMPE	1,2-Bis(dimethylphosphino)ethane
dppe	1,2-Bis(diphenylphosphino)ethane
DVDS	Divinyl disiloxane
Et	Ethyl
Fl	Fluorenyl
^{i}Pr	Isopropyl
HOMO	Highest occupied molecular orbital
L	Ligand
LUMO	Lowest unoccupied molecular orbital
Me	Methyl
Mes	Mesityl

http://dx.doi.org/10.1016/B978-0-08-097774-4.00121-2

MO	Molecular orbital	**pz**	Pyrazolyl
NBD	Norbornadiene	**quin**	Quinoline
NCA	Noncoordinating anion	**[red]**	Reduction process
NHB	N-heterocyclic boryl anion	**^{t}Bu**	Tertiary butyl
NHC	N-heterocyclic carbene	**TCIB**	Tris(chalcogenolatoimidazolyl)borate
NHGa	N-heterocyclic gallyl anion	**THF**	Tetrahydrofuran
o	Ortho	**TMP**	2,2,6,6-Tetramethylpiperidine
OTf	Trifluoromethane sulfonate, ‘triflate’	**Tol**	Toluene
p	Para	**Tp**	Tris(pyrazolyl)borate
Ph	Phenyl	**Tripp**	Triisopropylphenyl
phen	Phenanthroline	**TTIB**	Tris(thioimidazolyl)borate
Pn	Pnictogen (group 15 element)	**X**	Halogen (group 17 element)
Pr	Propyl	**XRD**	x-Ray diffraction
pyr	Pyridine	**Xyl**	3,5-Dimethylphenyl

The structural drawings in this work were created using ChemDraw – in schemes presenting the general synthetic approach to a class of compound, please note that not all of the reported substitution patterns are necessarily illustrated. Atomic distances presented herein are given in angstrom units (Å) and bond angles are reported in degrees (°). Solid-state structural pictures presented in this chapter have been generated using the SHELX programs suite.[1] In most of the illustrations, hydrogen atoms are not included for the sake of clarity. These data were collected from structures reported in the Cambridge Structural Database (CSD).[2] Atomic patterns for the group 13 metal(loid)s used in crystal structure figures are as illustrated below:

1.17.1 Introduction

This chapter focuses on the chemistry of group 13 compounds in which the metal(loid) center exhibits a lower-than-usual coordination number. Most simply defined, the coordination number of an atom is simply the sum of the number of other atoms to which it is bonded in anyway. Compounds in which an element has a lower-than-usual coordination number often exhibit chemical and physical properties that are considerably different from those in which the element has a higher coordination number. These differences often render such low-coordinate compounds suitable for uses ranging from synthons and reagents, to catalysts and materials precursors. For uncomplexed neutral compounds of the lighter group 13 elements, the anticipated coordination number for the trivalent state elements is 3; however, the electron-deficient nature of such elements means that coordination numbers of 4, 5, 6, and higher are often observed for both neutral and anionic species. In light of the foregoing, this chapter concentrates on the description of compounds in which the group 13 element (sometimes called ‘triel’) exhibits a coordination environment of 2 or less. It should be emphasized that because of periodic trends (e.g., ‘inert s-pair’,[3] weaker bond energies,[4,5] and relativistic effects[6,7]), thallium is usually more stable in a univalent state and may be anticipated to exist as monocoordinate or zero-coordinate (completely ionic) species. Although this fact indicates that low-coordinate environments should be considered ‘normal’ for thallium, we have included a variety of di- and monocoordinate thallium compounds in this chapter in order to compare or contrast such compounds to those of the lighter analogs. For the lighter triel elements, there are three principal manners in which a lower coordination number can be achieved: the compound can contain a group 13 element in a lower-than-usual valence state; the group 13 element can be multiply bonded to an adjacent element; or the compound can contain a cationic fragment based on the group 13 center. A compound that contains an element in a valence state lower than 3 will often feature a low-coordinate environment because the presence of the nonbonding electrons on the metal(loid) can occupy a potential coordination site – such compounds can include both univalent species that are generally diamagnetic and can also include divalent species that are typically paramagnetic. Many examples of these categories of compounds, in particular the group 13 radicals,[8] are presented in **Chapter 1.11** and although pertinent examples are presented, a detailed discussion of such compounds is not presented here. An alternative way of achieving a low coordination number is for the metal (loid) center to be multiply bonded to a ligand,[9–11] thus decreasing the number of atoms bound to the triel. As with the aforementioned radicals, multiply bonded compounds are examined in detail in **Chapter 1.09**; such compounds are not examined in detail in this chapter.

Prior to the examination of the different types of low-coordinate species, it is worth emphasizing a few points regarding the scope of this chapter and the kinds of compounds that have been included or not included. This edition of *Comprehensive Inorganic Chemistry* is intended to cover compounds that have been reported since the year 2000 and most of the coverage conforms to that goal; however, given the many discoveries in this area in the late 1990s, many important compounds and reviews from just prior to 2000 are also included. Because the defining concept of this chapter is coordination number, the majority of the compounds presented in this chapter are restricted to those that have been characterized structurally (particularly through the use of single-crystal x-ray diffraction and reported in the CSD[2]); this restriction generally requires the compound to be sufficiently stable and long-lived so as to have been isolated under typical inert-atmosphere laboratory conditions – most of the compounds reported herein are very moisture and air sensitive. In light of this caveat, it should be emphasized that there are numerous relevant compounds that have been identified spectroscopically, usually either in the gas phase or through the use of matrix-isolation techniques – most of which also predate the 2000 time frame – that are not described in this chapter but that have certainly provided a depth of understanding about some of the more reactive low-coordinate triel species.[12] The sections describing the two principal classes of compounds covered in this chapter are divided into subsections that are classified on the basis of the classes of ligand or substituent that is bonded to the low-coordinate group 13 center (e.g., ligands featuring nitrogen donors). It should also be noted that the coordination numbers assigned to some types of ligands are not always unambiguous and the rationale for the authors' chosen assignments will be described in the appropriate sections. For example, a cyclopentadienyl substituent (C_5H_5, Cp) can exhibit bonding to an element including purely sigma-bonding (σ-Cp) to types of π-bonding featuring hapticities ranging from 1 to 5 (η^x-Cp, $x = 1$–5). While the coordination number of a σ-Cp substituent is clearly '1' (as may also be the situation for an η^1-Cp substituent), the coordination numbers of η^2-Cp to η^5-Cp substituents are somewhat more ambiguous. For the sake of clarity, the authors have chosen to treat all Cp substituents as having coordination numbers of '1', called '*pseudo*-monodentate', for the purposes of the discussion in this chapter. Similar arguments can be made for complexes featuring ligands that are isolobal to Cp groups such as arene ligands and for ligands such as tris(pyrazolyl)borates.

1.17.2 Part 1 – Low-Coordinate Compounds Attributable to Valence State

As a preface to the discussion of compounds that exhibit lower-than-usual coordination numbers on the basis of lower-than-usual valence states, it is important to define some of the types of models employed to describe coordination chemistry, namely, oxidation state, valence state, and coordination number. In its most simple formulation, an oxidation state is a model used to describe the number of electrons associated with a particular atom and often to infer the chemical behavior of the compound in which the element is found.[13] Formal oxidation states are typically assigned to an element on the basis of simple counting rules and axioms. Although oxidation states are used extensively (and successfully) to rationalize the redox chemistry of transition-metal complexes, there are significant deficiencies with such formal oxidation state models that become particularly apparent when such rules are applied to main group, p-block elements. For example, the following carbon-based compounds all feature a carbon atom with a formal 0 oxidation state: diamond, graphite, graphene, fullerenes, chlorocarbene ($\mathbf{C}$HCl), formaldehyde ($H_2\mathbf{C}O$), 2-butyne ($H_3C{-}\mathbf{C}{\equiv}\mathbf{C}{-}CH_3$), and dichloromethane ($\mathbf{C}H_2Cl_2$). In spite of the identical formal oxidation state, the structures, stabilities, and reactivities exhibited by each of these compounds differ fantastically.

The valence state of an atom is a related, but distinct, model to assess the number of electrons associated with a particular element; it may be summarized succinctly as the number of electrons used for chemistry (either in the formation of bonds to other elements or as charges). In contrast to a formal oxidation state, which can often be assigned on the basis of an empirical molecular formula, the valence state assigned to a particular atom usually requires knowledge of the actual distribution of the electrons within the molecule. As outlined by Parkin and others, oxidation states and valence states are often assumed incorrectly to be synonymous: there are certain instances in which the two numbers (or at least their magnitudes) coincide; however, such cases are fortuitous.[14] While the identification of an unusual oxidation state may suggest that there is something unconventional about the chemistry of a given compound, because the valence state is more dependent on the electron distribution, it often provides significantly more insight into the structure, bonding, and reactivity of the compound in which the element is found. In the context of this chapter, the presence of a group 13 element in a lower-than-usual valence state implies the presence of one or two nonbonding electrons and thus often gives rise to a lower-than-usual coordination number.

To aid in the differentiation between these different models, several examples of compounds containing group 13 in low formal oxidation states are illustrated in **Figure 1**.

A final general note prior to the examination of compounds that feature low-coordinate low-valent group 13 centers concerns the preparation of such materials. In theory, many low-valent compounds could be prepared through the metathesis reaction of the metal salt of the desired substituent with a low-valent element halide. However, in practice, halide salts of the monovalent elements are only commercially available for thallium and indium, and indium monohalides are notoriously insoluble or unstable in organic solvents. While metastable univalent halides for aluminum and gallium have been generated, they are not conveniently available to most researchers.[15] Furthermore, the material known as 'GaI', prepared by the sonication of gallium metal with one half equivalent of iodine, does not have the composition suggested by the common formula.[16] Given the foregoing, in many instances the preparation of low-valent compounds is accomplished by the preparation and subsequent reduction of precursor molecules containing the elements in higher oxidation states and coordination numbers.[17–19]

1.17.2.1 Nitrogen-Based Ligands

One of the richest and most well-investigated classes of compounds containing low-coordinate, low-valent groups 13 compounds are those based on ligands that coordinate to the metal (loid) element through at least one nitrogen atom.[20] In this section, ligands containing imido-type ligands are presented first (subdivided into compounds that typically form six-membered rings, then five- and four-membered rings) followed by a compilation of relevant compounds featuring amido donors.

1.17.2.1.1 β-Diketimine ligands

β-Diketiminate ligands are monoanionic bidentate nitrogen-based analogs of β-diketonate ligands; the most common β-diketonate ligand is acetylacetonate ('acac'); its β-diketiminate derivatives are often referred to as 'NacNac' ligands. One advantageous feature of β-diketiminate ligands, in comparison to their oxygen-based analogs, is the presence of substituents (see R-groups in **Figure 2**) on the nitrogen atoms. These substituents impart an aspect of 'tuneability' to the ligand in that the steric bulk and the electronic properties can be modified easily through the judicious selection of the R-groups on the nitrogen atoms.

1.17.2.1.1.1 Synthesis

The preparation of most group 13 compounds described in this section begins with the appropriately substituted parent β-diketimine such as H^{R}NacNac (where R is the substituent on each nitrogen atom). Deprotonation of the β-diketiminate affords a salt of the anionic bidentate ligand and, of course, depending on which base is employed, salts of different cations can be obtained. Most commonly, potassium bases are chosen and thus the potassium salts of the β-diketiminate ligands are generated. Such potassium salts can also be prepared from the related lithium or sodium salts by way of alkali metal exchange with potassium metal. To generate the desired univalent group 13 complex, either the metallated ligand may be treated with the appropriate low-valent metal halide to give the dicoordinate complex or, in situations where the low-valent halides are not available, salt metathesis may be used to generate a higher-valent complex such as a metal dichloride which can be subsequently reduced to the low-valent compound.[21]

For the gallium, indium, and thallium analogs, salt metathesis of the potassium diketiminate salt with 'GaI', InI, and TlI, respectively, can be used to generate the chelated univalent triel complex with the concomitant elimination of KI. In the case of aluminum, the lack of available Al(I) halides necessitates a different synthetic approach. Thus, the dimethyl aluminum (III) β-diketiminate complex is generated first, followed by treatment with I_2 to produce the diiodo congener. Reduction

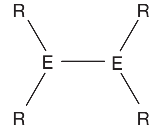
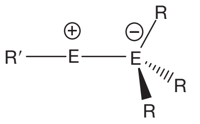
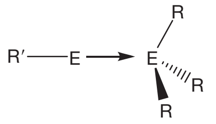
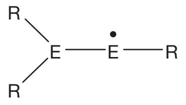
									
Formal oxidation state	E (+2)	E(+2)	E(+2)	E(+2)	E(+1)	E(+3)	E(+1)	E(+2)	E(+1)
Valence state	E^{III}	E^{III}	E^{III}	E^{III}	E^{III}	E^{III}	E^{I}	E^{III}	E^{II}
Coordination number	3	3	2	4	2	4	1	3	2

Figure 1 Diagram illustrating the differences between oxidation states, valence states, and coordination numbers for a series of group 13 compounds.

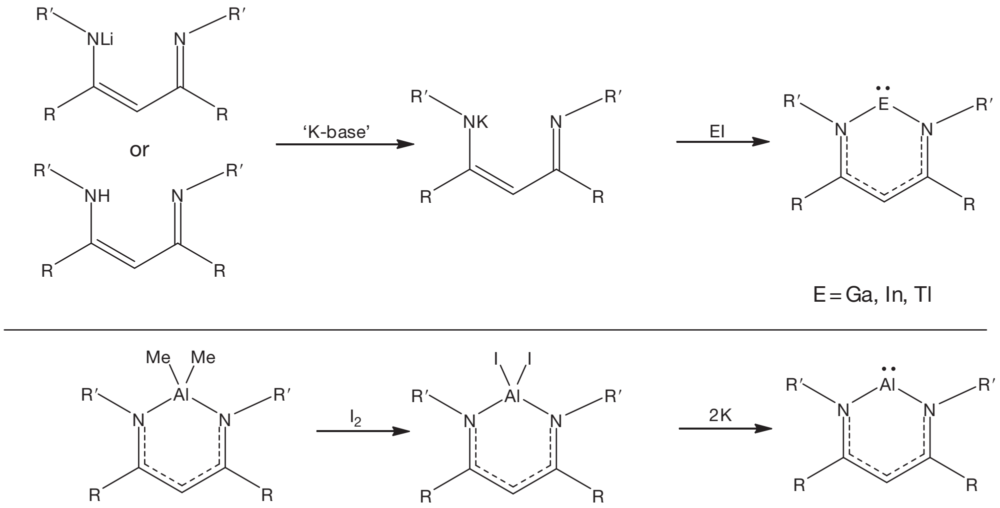


Figure 2 Representative synthesis for monovalent group 13 β-diketiminate complexes.

of the diiodo aluminum(III) complex with 2 equiv. of potassium metal results in the formation of the target Al(I) species.

1.17.2.1.1.2 Structural features

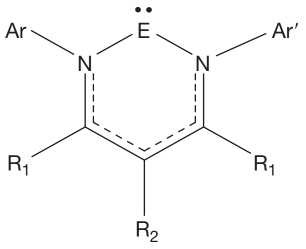
A summary of some of the important structural features exhibited by reported β-diketiminate complexes of monovalent group 13 elements is presented in **Table 1**.

As illustrated in **Table 1**, the nitrogen—metal bond length increases as ones goes from Al to Tl in the manner that one would anticipate on the basis of the relative sizes of the metal atoms. Although most of the complexes that have been characterized crystallographically have 2,6-diisopropylphenyl (Dipp) substituents on each nitrogen atom, changes in the properties of the aryl substituents on the nitrogen atoms can have a dramatic effect on the N—E bond distance for complexes of a given metal. For example, the introduction of an electron-donating anisole group in compound **1.7** yields two very distinct nitrogen—indium bonds. Elongation of the nitrogen—indium bond is observed at both nitrogen centers; however, a more drastic elongation is seen at the nitrogen-bearing the electron-rich arene ring. Likewise, when the aryl isopropyl groups on compound **1.4** are replaced with smaller methyl groups (**1.10**), a shorter thallium—nitrogen bond is observed.

Substitutions of the R-groups on the carbon backbone of the β-diketiminate ligand can also lead to significant changes in the metrical parameters observed for analogs complexes of a single metal. Introduction of bulkier groups appears to have little to no effect as illustrated for compound **1.6**, which contains ^{t}Bu groups in the backbone and which has a slightly longer Al—N bond compared to its methyl-backbone analog, **1.1** (**Figure 3**). A more substantial difference is observed, however, when the backbone substituents are replaced with fragments that possess different electronic properties. For example, the backbone of compound **1.5** contains electron-withdrawing CF_3 groups, which remove electron density from the ligand and thus result in an elongated N—In bond.

Perhaps more importantly, Hill and coworkers found that when the N-aryl groups used in such compounds are significantly less bulky, dimerization of the metal β-diketiminate complex can occur.[27] As illustrated by the structure of compound **1.7**, when only one of the 2,6-Dipp substituents is replaced, the ligand still provides significant bulk to prevent dimerization. However, when less sterically demanding aryl substituents such as mesityl (2,4,6-trimethylphenyl) or even 2,6-dimethylphenyl groups, enough room is created to allow for dimerization, as shown in **Figure 4**.

Table 1 Complexed β-diketiminate species with N—E bond distances

	E	*R₁*	*R₂*	*Ar*	*Ar′*	*N—E*
						
1.1[22]	Al	Me	H	Dipp		1.958
						1.957
1.2[23]	Ga	Me	H	Dipp		2.0528
						2.0560
1.3[24]	In	Me	H	Dipp		2.268
						2.276
1.4[25]	Tl	Me	H	Dipp		2.428
						2.403
1.5[25]	In	CF_3	H	Dipp		2.357
						2.364
1.6[26]	Al	^{t}Bu	H	Dipp		1.9637
1.7[27]	In	Me	H	Dipp	*o*-OMePh[a]	2.277
						2.557[a]
1.8[28]	Tl+	Ph	H	$SiMe_3$		2.456
						2.449
1.9[28]	Tl	H	Ph	Dipp		2.471
						2.423
1.10[29]	Tl	Me	H	DMP		2.402

[a] Indicates which aryl group is attached to the nitrogen for the corresponding bond length.

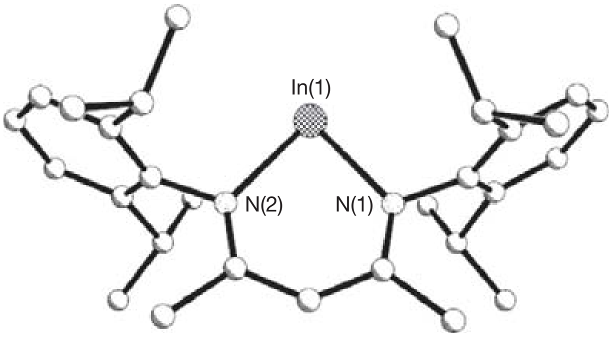


Figure 3 Solid-state structure of In[((Dipp)NCMe)$_2$CH], **1.1**.

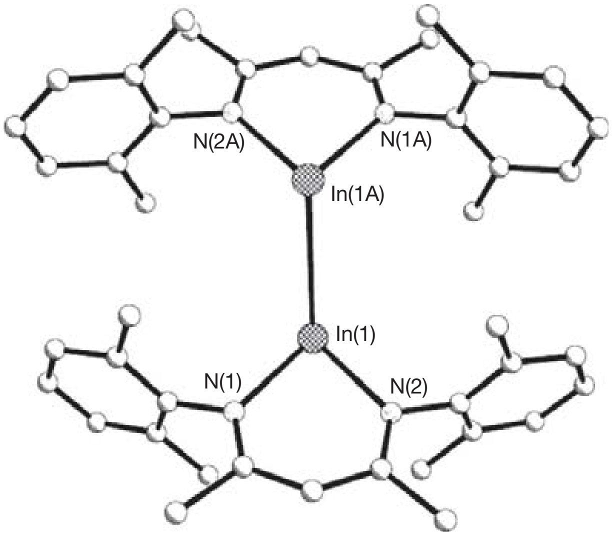


Figure 4 Crystal structure of dimerized In[((DMP)NCMe)$_2$CH]. Selected bond distances: N(1)—In = 2.262 Å, N(2)—In = 2.256 Å, and In(1)—In(1A) = 3.1967 Å.

This dimerized complex has shorter N—In bond lengths than the mononuclear complex, **1.3**. This can be attributed to less steric hindrance around the metal center allowing for closer contact to the nitrogen fragments.

Even more impressive is the result obtained for the isomeric complex featuring the N-xylyl group in which the methyl substituents on the arenes are in the 3- and 5-position. Attempts to prepare the univalent indium diketiminate complex through the reaction of $H[((Xyl)NCMe)_2CH]$ (HL^1) with $K(N(SiMe_3)_2)$ and InI instead result in the formation of the catenated hexaindium compound $I(InL^1)_6I$.[30] This compound features five unsupported In—In bonds ranging from 2.8122 to 2.8535 Å with pseudo-tetrahedral geometries at each indium center and remains intact in solution. In addition to any potential closed-shell contributions to the bonding within the compound, there are formally two electrons provided by the terminal iodide anions that may be delocalized throughout the sigma system.

1.17.2.1.1.3 Reactivity

There have been numerous investigations in which group 13 β-diketiminate complexes have been employed as reagents and they exhibit a rich and interesting chemistry. As one would perhaps anticipate given the low-coordinate and low-valent nature of these species, much of the chemistry displayed by such compounds involves the formation of compounds in which the coordination number and/or valence state of the group 13 center is increased. As illustrated in the following schemes for Al, Ga, and In, respectively, common classes of reactions include: insertion into element—halogen bonds and other reactive element—element bonds; the formation of coordination complexes with main group and transition-metal acceptors; and the coordination of unsaturated compounds and small molecule activation, among others. Prior to the examination of observed chemistry, it should be noted that the univalent aluminum β-diketiminates tend to be considerably more reducing and more reactive overall than the heavier congeners, as one would anticipate on the basis of periodic trends. At the other end of the spectrum, the stability of the 'lone pair' on thallium in its monovalent β-diketiminates appears to preclude donor or oxidation chemistry and such species have only been used as metathesis reagents to introduce the β-diketiminate ligand onto other elements.

The aluminum β-diketiminate complex **1.1** has demonstrated a variety of interesting reactivity as illustrated in Figure 5.

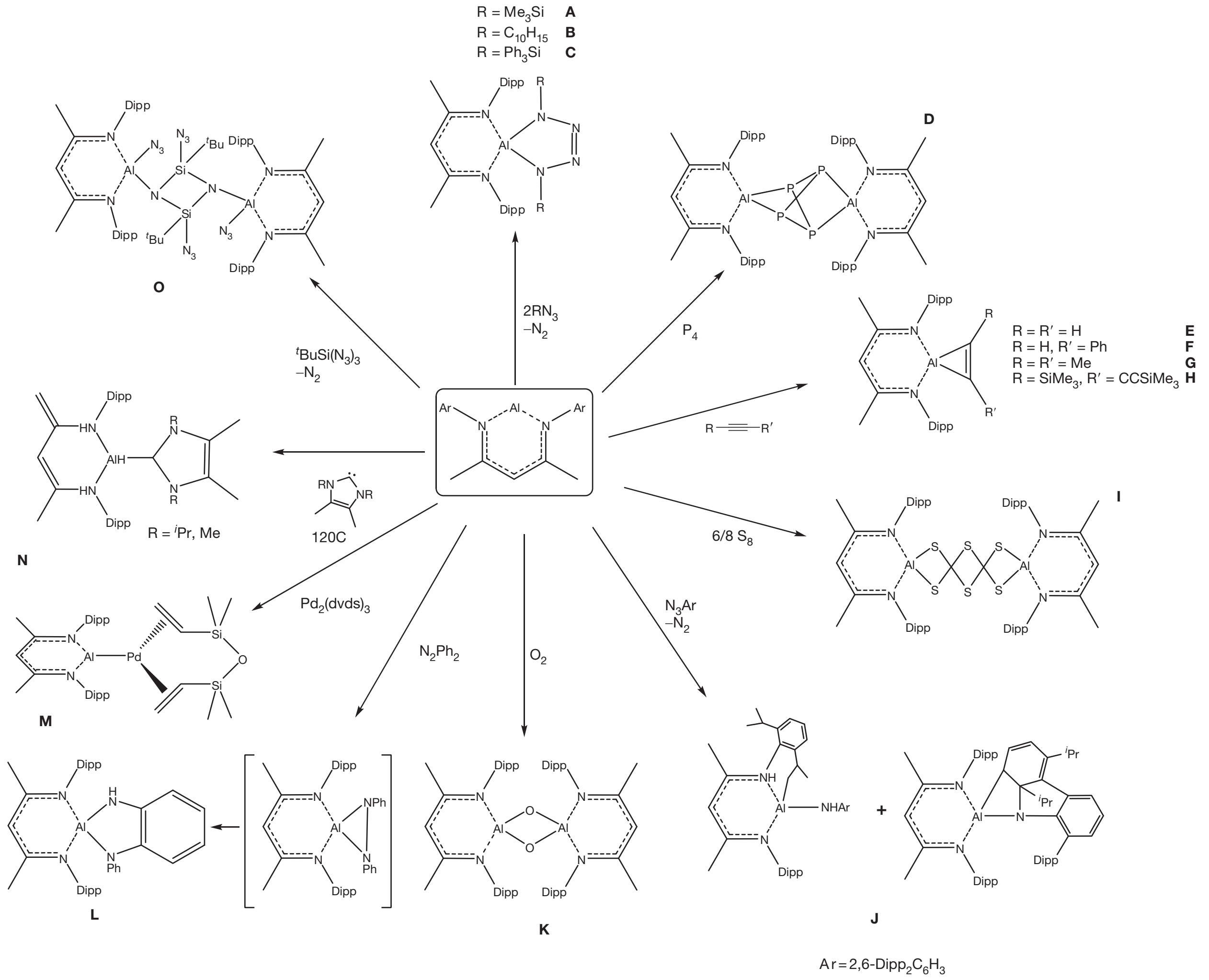


Figure 5 Summary of reported reactivity for Al β-diketiminate compounds. Data taken from the following work: **A**,[22] **B–C**,[31] **D**,[32] **E**,[33,34] **F–H**,[34] **I**,[35] **J**,[36] **K**,[37] **L**,[38] **M**,[34] **N**,[39] and **O**.[31]

In addition to the predictable ligand chemistry as depicted by product **M**, the aluminum β-diketiminate also exhibits a large variety of chemistry in which the aluminum center becomes oxidized. Simple oxidations with chalcogens such as O_2 and S_8 or the pnictogen P_4 generate products such as **J**, **I**, and **D** derived from the formal insertion of the low-valent aluminum center into the element—element bonds. Furthermore, the reaction of the low-valent aluminum complex with alkynes generates aluminum(III) cycloaddition products such as **E–H** that feature three-membered AlC_2 rings. Complex **1.1** is oxidized by aliphatic and silyl azides of the general form N_3R as shown in **A–C** to produce intermediate LAl—NR species (L = H[CMeNDipp]$_2$). These highly reactive Al—N compounds further react with another equivalent of azide in a [2+3]-cycloaddition resulting in the planar AlN_4 five-membered ring products. Similarly, the reaction of **1.1** with *tert*-butylsilyltriazide is postulated to generate an unsaturated aluminum imide which undergoes the transfer of an azide group from Si to Al and a [2+2]-dimerization to generate **O**. The analogs reaction with bulky terphenylazides is proposed to generate a similar LAl—NAr intermediate that promotes C–H activation of the aryl substituent and results in the formation of the formal insertion product **K** and another isomer that is derived formally from the cycloaddition of the Al—N fragment with one of the Dipp ligands from the azide. Related behavior is observed when **1.1** reacts with azobenzene to produce **L**, presumably after the formation of a three-membered ring intermediate akin to the products obtained in the oxidation/cycloaddition reaction of **1.1** with alkynes. The reaction of **1.1** with N-heterocyclic carbenes (NHCs) also promotes a tautomerization; however, in this instance, one of the hydrogen atoms from the methyl substituents on the ligand backbone is transferred to the Al center resulting in an increase in its valence and coordination number.

As illustrated in Figure 6, the Ga^{Dipp}NacNac complex **1.2** can function as neutral, two-electron donors to transition-metal

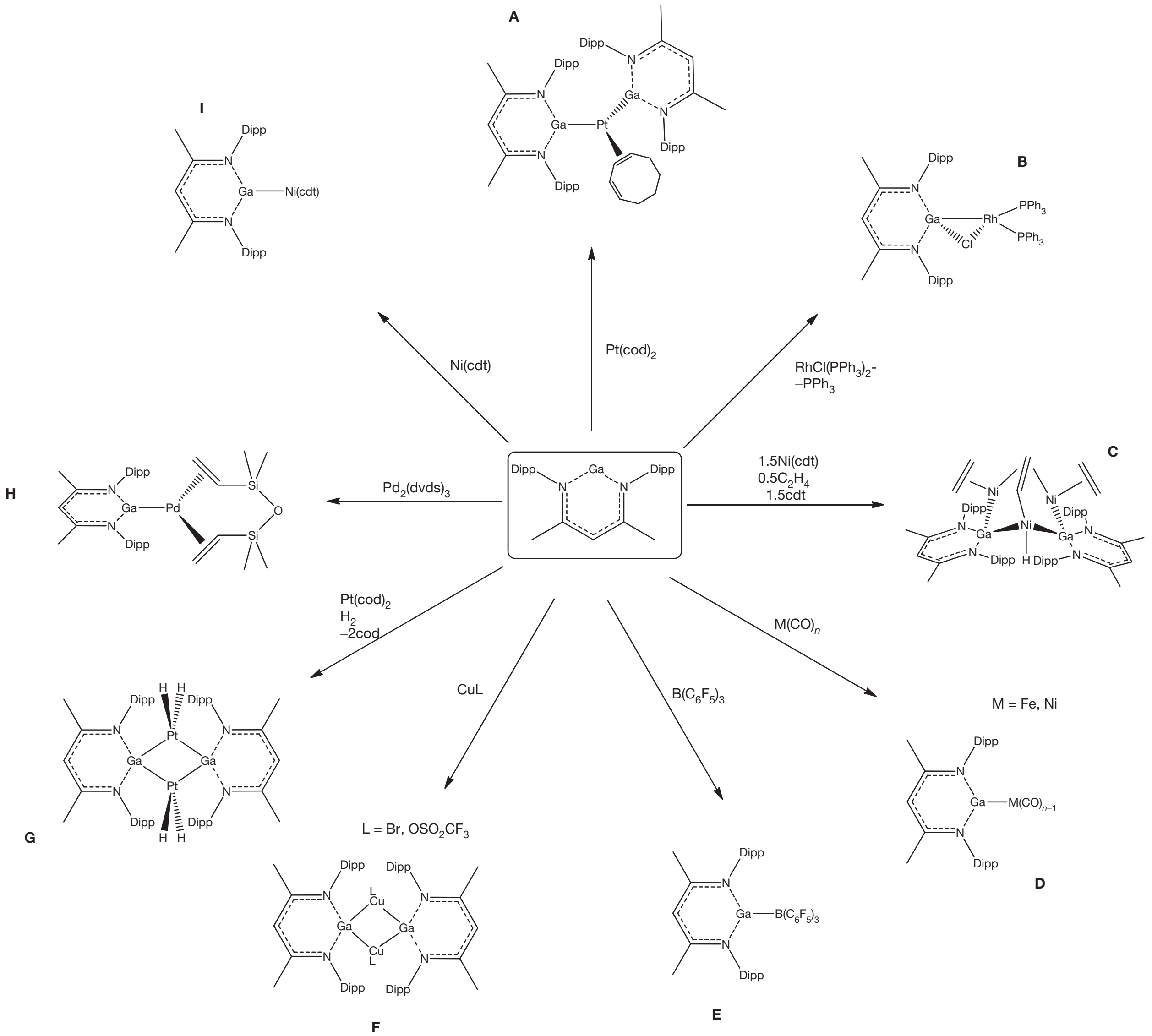


Figure 6 Coordination chemistry reported for Ga β-diketiminate compounds. Data taken from the following work: **A**,[40] **B**,[41] **C**,[42] **D**,[43,44] **E**,[45] **F**,[46] **G**,[40] **H**,[40] and **I**.[42]

and main group acceptors either as a terminal ligand or in a bridging fashion. While most of the resultant complexes exhibit structures that are, as one would anticipate, for a bulky donor, the rhodium complex **B** features a structure in which the chlorine atom ligand on the rhodium center is clearly interacting with the formally vacant orbital on the gallium atom to yield a three-membered metallacycle. This product may be considered as a partial insertion of the low-valent gallium species into the rhodium—chlorine bond. The use of a more electron-rich rhodium(I) source results in the complete insertion of the univalent gallium reagent into the Rh—Cl bond, as illustrated in Figure 7. In fact, formal oxidative addition or insertion chemistry, in which the valence state and coordination number of the group 13 center are increased, is a very common mode of reactivity for most group 13 β-diketiminate complexes, as illustrated in Figures 7 and 8.

Somewhat in contrast to the lighter analogs described above, the reactivity of the indium β-diketiminate complexes is limited exclusively to formal oxidative addition reactions that result in the insertion of the indium atom into the element—halogen bond, as illustrated in Figure 8.

1.17.2.1.2 *Pyrazolyl-based ligands*

As free fragments, pyrazoles are aromatic heterocyclic diazoles, in which the five-membered ring contains two nitrogen atoms in adjacent positions. In contrast to the superficially similar cyclopentadienide ligands, pyrazoles and the corresponding pyrazolate anions tend to function as σ-type ligands via the nitrogen atoms rather than as π-donors using the π-system of the heterocycle, as will be illustrated below.

In the context of low-valent group 13 chemistry, the two major classes of pyrazolyl-based ligands that have been used to prepare compounds containing low-coordinate triel centers are the monoanionic bis(pyrazolyl)borates (Bp) of the general form $[H_2B(pz)_2]^{1-}$, sometimes called 'scorpionate' ligands, and the tris(pyrazolyl)borates (Tp) of the general form $[HB(pz)_3]^{1-}$; the tetrakis(pyrazolyl)borates $[B(pz)_4]^{1-}$ often behave similarly to the Tp ligands but are not used as frequently.[58–60] Although it is obvious that the bis(pyrazolyl)borate ligands, which are analogs to the β-diketiminate described above, can support a di-coordinate metal fragment the case for including complexes featuring tris(pyrazolyl)borate ligands perhaps requires some further clarification. As noted by Trofimenko, tris(pyrazolyl)

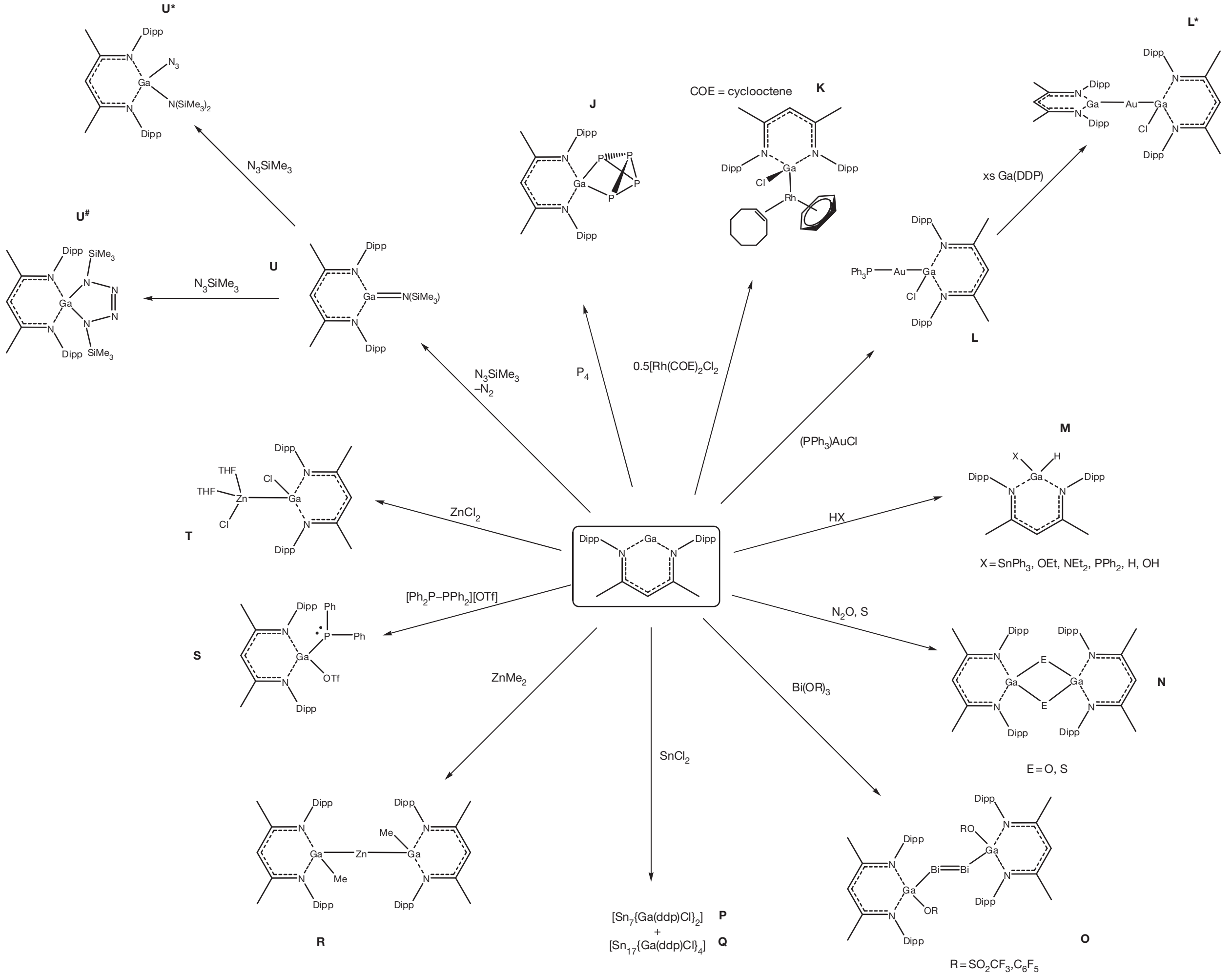


Figure 7 Examples of oxidative addition and insertion chemistry reported reactivity of Ga β-diketiminate compounds. Data taken from the following work: **J**,[47] **K**,[41] **L**,[48] **M**,[49] **N**,[50] **O**,[51] **P**,[52] **Q**,[52] **R**,[53] **S**,[54] **T**,[53] and **U**.[55]

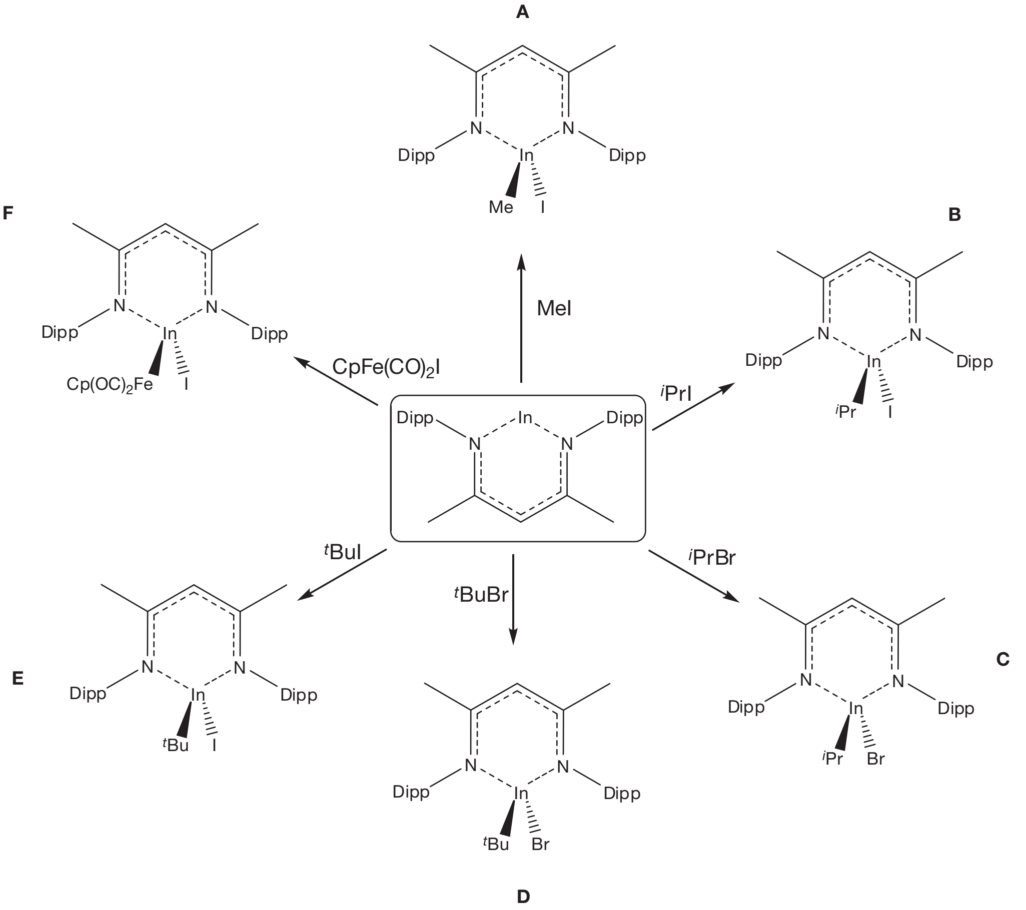


Figure 8 Oxidative addition reactions of In β-diketiminate compounds into element halide bonds. Data taken from the following work: **A–E**,[56] **F**.[57]

borate ligands are isolobal with cyclopentadienyl ligands and can function as six-electron ligands that can donate to both σ- and π-type orbitals. In light of this analogy, in this section, such ligands will be treated as pseudo-monocoordinating ligands. One final note regarding the various pyrazolyl-based ligands is that the steric properties of these ligands are readily modified by changing the substituents on the carbon atoms of the heterocycle, typically those at the 3- and 5-position, and the resultant ligands – particularly the roughly cylindrical Tp variants – have sufficient bulk to allow for the isolation of some types of reactive species that remain elusive for the related Cp-type substituents.

Many of the compounds presented in this subsection, particularly the compounds of gallium and indium, were published prior to 2000. Although these results predate the target time frame, they provide important supplementary information regarding the compounds that have been synthesized after year 2000 and pertinent examples are included in discussion.

1.17.2.1.2.1 Synthesis

Most of the pyrazolate complexes in this subsection are thallium(I) salts and thus the general preparative approach is illustrated for that element in Figure 9. The ligand preparation is accomplished by treating the desired substituted pyrazole with reacting 2 or 3 equiv. of the appropriate alkali-borohydride. The resulting alkali metal salt is subsequently treated with a suitable Tl^+ source, such as thallium acetate, and the desired thallium(I) pyrazolate is isolated in what may be considered either a ion-metathesis or a transmetallation reaction.[61]

1.17.2.1.2.2 Structural features

In contrast to the numerous examples described above for the group 13 β-diketiminate complexes, low-coordinate bis(pyrazolyl)borate complexes are only known for thallium(I). Important structural features of the bis(pyrazolyl)borates complexes of thallium are presented in Table 2.

As one would anticipate, the steric bulk of the R-groups on the pyrazolyl fragments has a great influence on the geometries observed for the resultant complexes. In general, the six-membered ring formed by the thallium, boron, and four nitrogen atoms in each BpTl complex exhibits a 'boat' conformation. Larger substituents give rise to a more bent structure, which is measured by the angle between the two planes generated from thallium and its neighboring nitrogens, and from boron and its neighboring nitrogens. There does not appear to be any obvious correlation between the Tl—N distances in a given complex and the size of the substituents on the pyrazolyl fragments; however, the Tl—N distance does tend to be shorter for complexes featuring more electron-rich Bp ligands in comparison to those that are less electron-rich (Figure 10).

Compound **2.10** is the most planar of all the aforementioned BpTl compounds which is most likely attributed to the

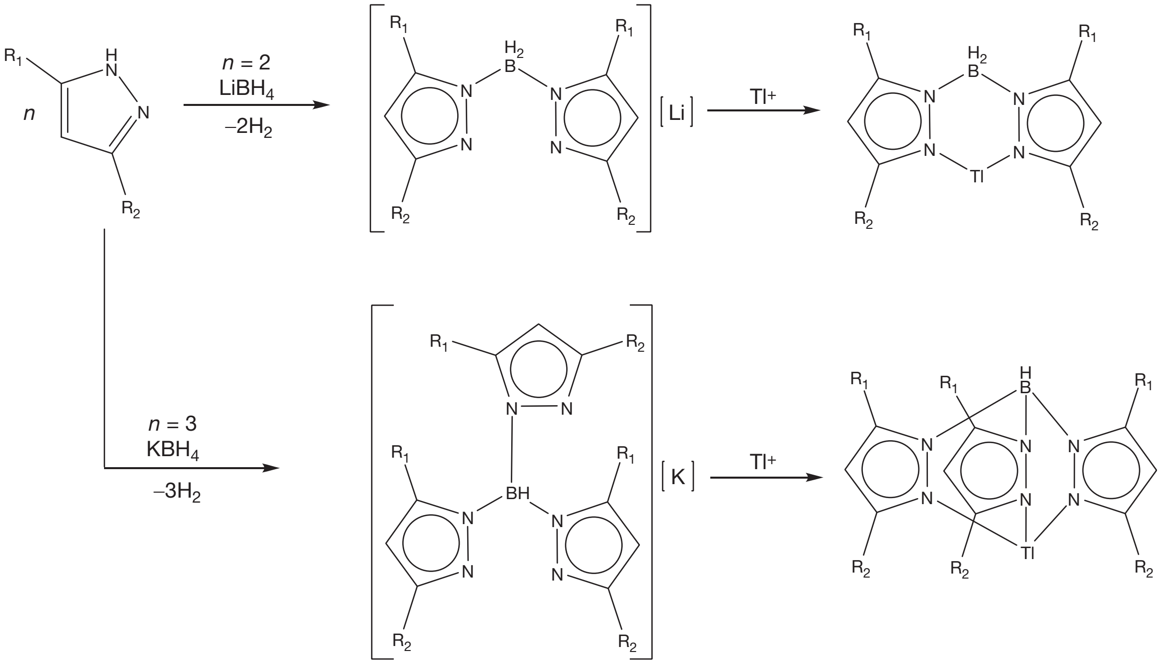


Figure 9 General synthesis of bis- and tris(pyrazolyl)hydroborato thallium. The Tl^+ source is derived from various Tl(I) salts, for example, TlOCHO, TlOEt, TlAc, etc.

steric effects of the substituents on the boron. Compound **2.5** has one of the largest interplanar angles and is due to the effect of the 2-pyrazine substituents on the pyrazolyl heterocycles. The nitrogen centers on these pyrazine groups are also capable of interacting with the Tl^I ion and effectively allow the Bp ligand to function as a tetradentate ligand. It should be noted, however, that the N—Tl bond distances from the pyrazine ligands range from 2.940 to 3.143 Å and are thus considerably longer than the Tl–N contacts from the pyrazolyl nitrogen atoms.

Surprisingly, compound **2.6** contains the largest, bulkiest R-groups but features a modest $(NTlN)^p \bullet (NBN)^p$ angle. While this may seem contradictory to previous statements regarding the correlation between this angle and the size of R-groups, this anomaly can be explained in terms of the angle between the pyrazolyls and the thallium center. Compound **2.6** has the largest N—Tl—N angle (~78°) and the largest dihedral angle (~16°), signifying that the two pyrazolyl ligands are parting and twisting from each other to allow room for the extremely large R-groups (Figure 11).

Although the scorpionate-type ligands provide for interesting structures of thallium(I), it is only with the more sterically demanding and electron-donating tris(pyrazolyl)borate ligand system that low-valent complexes of the lighter group 13 elements have proved to be amenable to isolation. Regardless, it should be noted that, because of their synthetic utility, the vast majority of such univalent group 13 complexes of Tp ligands also feature thallium(I). Thus, structural details of relevant pseudo-monocoordinate thallium(I) complexes of tris(pyrazolyl)borate ligands are presented in Table 3, and those of the much rarer lighter analogs are listed separately in Table 4.

The structures typically feature Tl—N distances ranging from 2.5 to 2.8 Å with small, electron-donating substituents providing values at the shorter end of the scale and polydentate or electron-withdrawing substituents producing complexes with longer distances. One example of a complex featuring such a polydentate substitution pattern is illustrated in Figure 12.

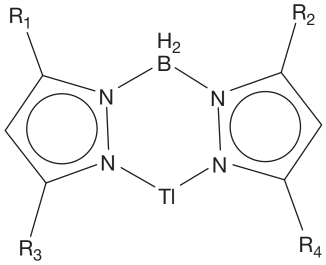
An interesting compound related to these tris(pyrazolyl) borates is White's tris(pyrazolyl) trithallate compound, $[Tl]_3[N_2C_3HPh_2]_3$ (Figure 13).[97] In this complex, the three pyrazolate heterocycles are linked to three Tl metal centers, each with an oxidation state of +1. The Tl—N bond distance is on the higher end of the scale with 2.609–2.712 Å and a N—Tl—N bond angle of 78.98–81.49°.

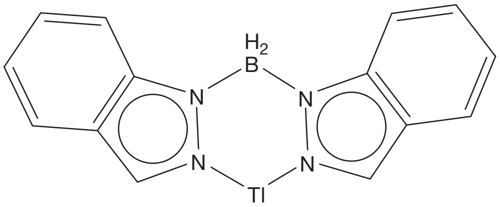
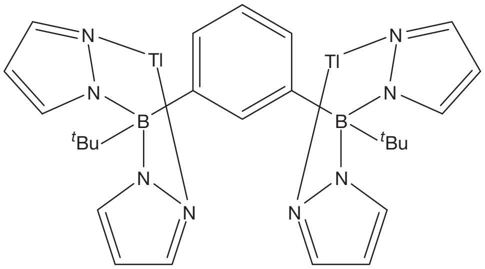
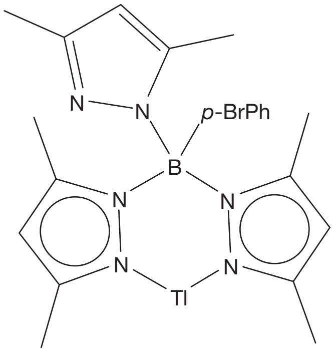
Examination of Table 4 reveals that there are only a handful of pseudo-monocoordinate complexes of the lighter group 13 elements and, as one would anticipate on the basis of periodic trends, that most of these are complexes of indium. Predictably, the E—N bond distances are significantly shorter than those of the analogs Tl complexes and, in the case of indium, the metrical parameters appear to follow the same general trends as observed for considerably more numerous thallium congeners.

1.17.2.1.2.3 Reactivity

The large number of thallium(I) Bp and Tp complexes highlights the importance of compounds such as metathesis reagents that are soluble in many organic solvents. Thus, in many cases, such thallium compounds are employed to introduce the pyrazole-based ligands to other metals, including some of the lighter group 13 metals described above. By contrast, the chemistry demonstrated by the monovalent gallium and indium Tp complexes is considerably more varied. While some of the reactions exhibited by these TpE complexes are similar to those described previously for the low-valent β-diketiminates, such as functioning as two-electron ligands to transition-metal complexes[102,103] and main group Lewis acids[98,104–106]

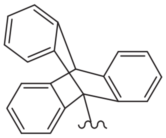
Table 2 Selected metrical parameters for bis(pyrazolyl)borate complexes of thallium(I)



	R1	*R2*	*R3*	*R4*	*N—Tl*	$(NTlN)^p\bullet(NBN)^p$	*N—Tl—N*
2.1[61]	Me	Me	^{t}Bu	^{t}Bu	2.591–2.597	71.11	73.62
2.2[61]	^{i}Pr	^{i}Pr	^{t}Bu	^{t}Bu	2.628–2.664	66.50	72.13
2.3[61]	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	2.632–2.645	64.70	67.44
2.4[62]	H	H	H	H	2.799–2.814	69.58	71.94
2.5[63]	H	H	2-Pyrazine	2-Pyrazine	2.644–2.752	80.20	71.28
2.6[64]	H	H	L	L	2.696–2.705	75.95	78.23
2.7[65]	^{t}Bu	H	^{t}Bu	H	2.634–2.681	70.61	72.89–75.20
2.8[66]					2.565–2.652	86.76	75.58
2.9[67]					2.470–2.634	82.98	70.39–72.08
2.10[68]					2.559–2.607	136.07	69.64

$(NTlN)^p\bullet(NBN)^p$ is the angle between the plane generated from thallium and its neighboring nitrogens and the plane generated from boron and its neighboring nitrogens

L =



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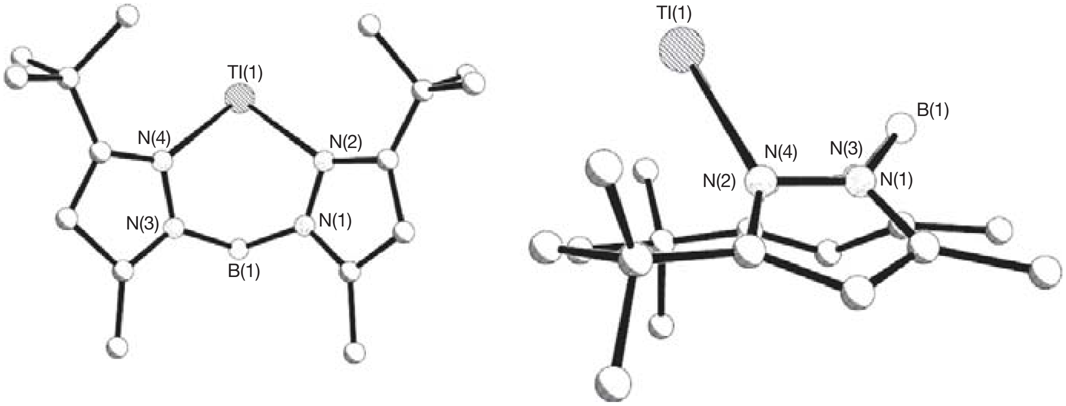


Figure 10 Depiction of the solid-state structure of **2.1**. Left: Overhead view. Right: Side view profiling the 'boat' conformation and the constrained pyrazolyl fragments.

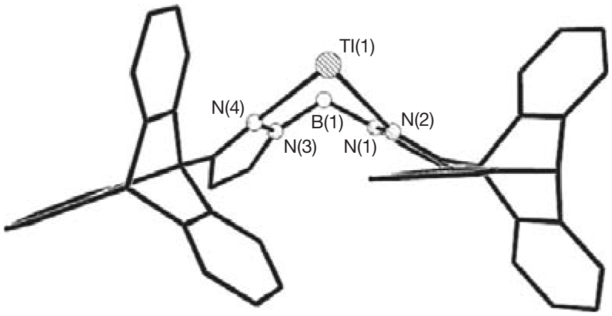


Figure 11 Crystal structure of compound **2.6**, viewed from the side to display orientation of R-groups in solid state.

or undergoing oxidative addition/insertion reactions,[107] the steric bulk of substituted Tp groups also allows for some unique chemistry. For example, the oxidation of some TpE species (Figure 14) with chalcogens results in the formation of complexes of the general form TpE—Ch (Ch = S, Se, and Te)[108–110]; in contrast to the β-diketiminate analogs, these tris(pyrazolyl) borate complexes do not dimerize and thus feature multiple bonds between the group 13 element and the chalcogen. Such multiple-bonded compounds are discussed in detail in Chapter 1.09 of this work and will not be examined further.

The oxidized complexes depicted in Figure 14 each feature pseudo-dicoordinate environments at the triel centers. The average of the Ga—N bond distances in the gallium(+3) complexes **2.54**–**2.56** increases modestly as the size of the chalcogen increases from S to Te; however, the overall range of values is relatively small (2.042–2.072 Å). More notably, all of the Ga—N bonds in the oxidized complexes are considerably shorter than those (2.240 Å) in the starting gallium(+1) compound **2.49**. The reasons for these changes in the metrical parameters are the same as those outlined for the analogs donor–acceptor complexes, namely, depopulation of a 'lone pair' orbital with triel-ligand antibonding character and the increased charge density of the metal upon loss of the valence electrons. In addition to the three gallium analogs, an indium selenide congener **2.57** was also prepared and the structure of the compound is illustrated in Figure 15 and it is worth noting that a decrease in the In—N bond distance of ca. 0.2 Å in comparison to **2.50** is observed.

1.17.2.1.3 α-Diimine-type ligands: NHB and NHGa anions

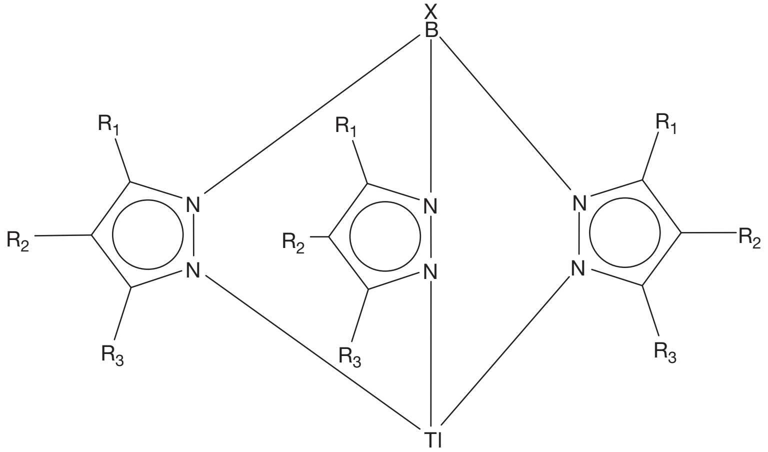
The chemistry of p-block analogs of NHCs, in which the main group element is dicoordinate and formally has a total of six valence electrons, has been a focus of investigation in inorganic chemistry for several decades.[20,111,112] It is only relatively recently, however, that examples featuring group 13 have been prepared and studied. A computational study by Schoeller et al. provided insight into the electronic structure of group 13 NHC analogs and suggested that such compounds should be amenable to isolation.[111] More recently, an investigation by Tuononen et al. examined the electronic properties of all of the p-block NHC analogs from groups 13–16.[112] One of the most important observations they reported is that there is significant covalent bonding and π-delocalization between the diamido ligand and the lighter group 13 atom, particularly for B. For heavier elements such as indium, the nature of the ligand–metal interaction appears to be best described as primarily ionic with no significant π-delocalization (Figure 16). Interestingly, to date the only examples of salts containing such anions that have been isolated (see below) contain either boron (N-heterocyclic boryl anion, NHB, salts) or gallium (N-heterocyclic gallyl anion, NHGa, salts), which are the two most electronegative of the group 13 elements.

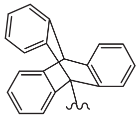
1.17.2.1.3.1 Synthesis

As illustrated in Figure 17, in general, the synthesis of salts containing NHB begins with the reduction of the desired α-diimine (also often called 1,4-diazabutadiene or DAB) ligand using alkali or alkaline earth metals. The metathesis reaction of the resulting diamido ligand with the appropriate group 13 trihalide usually yields the heterocyclic diamido group 13 halide precursor. Next, reduction of the trivalent halide precursor, typically using alkali or alkaline earth metals, provides the corresponding metal salt of the target group 13 anion.

Although the synthetic approach described above accurately describes the products and intermediate observed for most α-diimine ligands, it must be noted that the first isolated example of any group 13 NHC analogs, namely the salt [K([18] crown-6)•2THF][Ga(N^{t}BuCH)$_2$] (THF, tetrahydrofuran), was isolated from a slightly different precursor. Instead of the anticipated diamidochlorogallane heterocycle, the treatment of the dilithiated α-diimine with $GaCl_3$ resulted in the formation of a

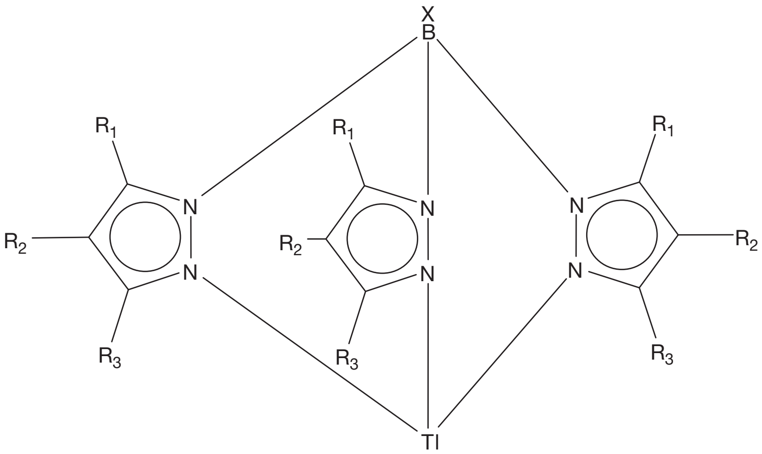
Table 3 Tris(pyrazolyl) thallium compounds with selected bond distances and angles given

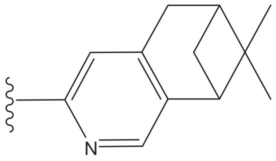
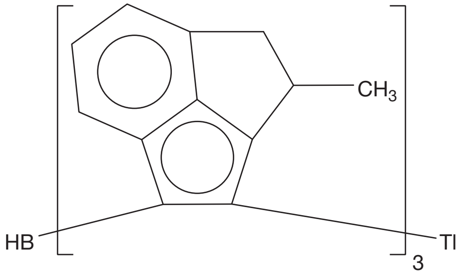


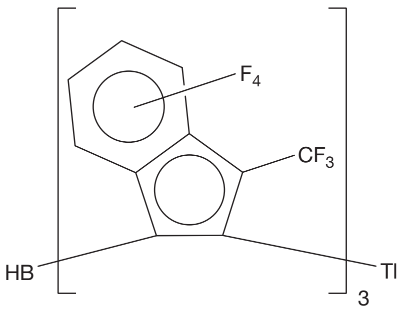
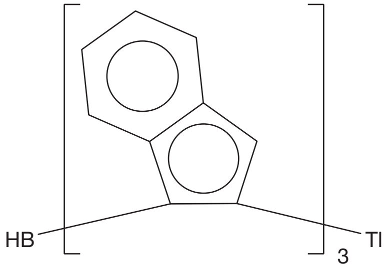
	R_1	*R_2*	*R_3*	*X*	*N—Tl*	*N—Tl—N*
2.11[69]	H	H	^{t}Bu	Ph	2.528–2.584	71.60
2.12[70]	CH_3	H	Ph	H	2.513–2.608	75.22–78.20
	CH_3[a]	H[a]	CH_3[a]			
2.13[70]	H	H	Ph	H	2.598–2.633	69.40–89.12
2.14[71]	CH_3	H	CH_3	H	2.499–2.534	73.85–75.68
2.15[72]	CH_3	H	CH_2Ph	H	2.579–2.598	72.44–77.06
2.16[72]	H	Ph	CH_2Ph	H	2.574–2.711	69.58–78.29
2.17[73]	H	^{t}Bu	*p*-Tol	H	2.550–2.580	73.54–74.15
2.18[74]	H	H	$CHPh_2$	H	2.588–2.728	71.03–76.08
2.19[75]	H	H	Mes	H	2.522–2.585	71.64–75.72
2.20[75][b]	H	H	Mes	H	2.508–2.588	72.79–77.09
2.21[76]	H	H	H	H	2.527–2.745	71.00–77.68
	^{t}Bu[a]	H[a]	^{t}Bu[a]			
2.22[77]	H	H	$CO(NC_4H_8)$	H	2.704–2.713	67.26–72.38
2.23[78]	H	H	2,4-OMe–C_6H_3	H	2.583	74.86
2.24[79]	H	H	*o*-MeOPh	H	2.540–2.696	72.61–75.34
2.25[80]	H	H	C_3H_5	H	2.532	76.57
2.26[64]	H	H		H	2.670–2.798	66.40–83.24
2.27[81]	2-SC_4H_4	N	CF_3	H	2.603–2.635	70.98–72.60
2.28[66,82,83]	H	H	H	H	2.548–2.730	69.57–73.61
2.29[84]	H	H	*p*-Pyr	H	2.577–2.791	67.30–77.91
2.30[83]	H	H	Ph	η^1 Cp–Fe–Cp	2.519–2.602	70.57–75.18

(*Continued*)

Table 3 (Continued)



	R_1	R_2	R_3	X	$N—Tl$	$N—Tl—N$
2.31[85]	H	H		H	2.720–2.721	69.77–69.86
2.32[86]	H	H	^{t}Bu	CH_3	2.531–2.550	74.16–78.81
2.33[86]	H	H	Mes	CH_3	2.530–2.564	71.54–73.62
2.34[87]	H	H	CF_3	CH_3	2.601–2.623	70.17–73.38
2.35[88]	H	H	CMe_2CH_2OMe	H	2.597–2.703	73.61–77.80
2.36[89]	*p*-Tol	Br	Br	H	2.603–2.604	72.05–72.06
2.37[89]	*p*-ClPh	Br	Br	H	2.601–2.668	69.65–72.82
2.38[89]	H	Br	*p*-ClPh	H	2.630–2.675	71.73–75.42
2.39[89]	CH_3	Br	Ph	H	2.598–2.600	74.22–74.24
2.40[89]	Ph	Br	Br	H	2.596–2.597	71.99–72.00
2.41[90]	CH_3	H	$CF_2CF_2CF_3$	H	2.657	72.64–72.66
2.42[91]	H	CN	^{t}Bu	H	2.713	76.30
2.43[92]	H	H	C_4H_7	H	2.562	75.20
2.44[92]	H	H	C_5H_9	H	2.483–2.607	72.53–77.94
2.45[93]	H	CN	Ph	H	2.803–2.804	72.80–72.79
2.46[94]				H	2.455–2.597	74.46–78.53

2.47[95]		H	2.583–2.747	68.41–74.58
2.48[96]		H	2.583–2.747	68.41–74.58

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[a] Only one ligand has these substitutions.

[b] One ligand has reverse connectivity.

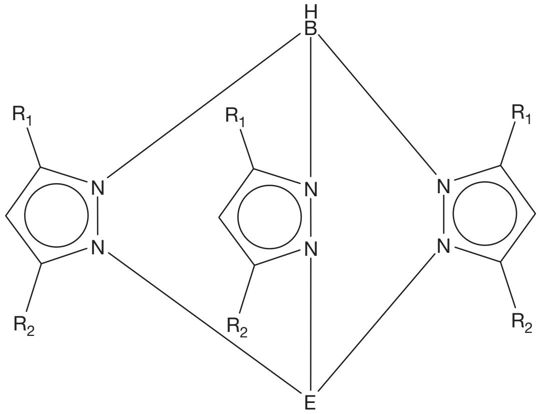
dimeric tricyclic structural isomer, as illustrated in Figure 17. However, reduction of this trivalent halogallane with potassium did indeed produce the target NHGa salt.[113]

The noninnocence of DAB ligands in regard to redox chemistry is well known and some univalent gallyl anions have been generated from paramagnetic precursors in which the unpaired electron resides primarily on the organic ligand. For example, salts containing NHGa anions have been prepared by the reduction of paramagnetic gallium(III) precursors of the type DAB-GaI$_2$ and gallium(II) dimers of the general form (DABGaI)$_2$.[114] An alternative but similar method that has been demonstrated to generate salts of monovalent gallium anions of the related delocalized bis(imino)acenaphthene (BIAN) system begins with the direct treatment of the diimine with gallium metal. This produces the digallane BIANGa–GaBIAN, which can be reduced with alkali or alkaline earth metals to yield the desired salts.[115]

1.17.2.1.3.2 Structural features

Important metrical parameters for structurally characterized salts of NHB and NHGa ions are presented in Table 5. In the absence of donors, such as crown ethers, that completely encapsulate the counter-cation, there is close association between the monovalent group 13 anions and alkali or alkaline earth cations.

Table 4 Tris(pyrazolyl) compounds of both gallium and indium



	E	*R$_1$*	*R$_2$*	*N—E*	*E—B*	*N—E—N*
2.49[98]	Ga	^{t}Bu	^{t}Bu	2.240	3.214	84.25
2.50[99]	In	^{t}Bu	^{t}Bu	2.459–2.475	3.365	77.23–81.92
2.51[99]	In	H	^{t}Bu	2.485–2.495	3.496	77.08–80.43
2.52[100]	In	H	Ph	2.430	3.500	78.22–78.24
2.53[101]	In	CF$_3$	CF$_3$	2.533–2.600	3.754	71.39–71.79

Selected bond distances and angles shown.

Although the three-coordinate nature of most the compounds depicted in Table 5 appears to violate the low-coordinate criteria of this chapter, it must be emphasized that one of the contacts is attributable to the counter-cation. The electron-rich nature of the univalent group 13 element allows the resultant anionic diimine complexes to function as donors and, in the absence of superior ligands, these associate with the cations in the solid state, as illustrated for an NHB salt in Figure 18. Where comparable examples of 'free' and coordinated salts exist, such as for the BIAN[122] salts **3.8** and **3.9**, it appears as if the absence of cation–anion contacts results in longer N—E bonds.[115,121] This is as one would anticipate on the basis of the formal reduction of electron density at the triel center upon coordination to an acceptor. In any event, the perturbations of the nominally dicoordinate group 13 anions are relatively minor and, as noted below, regardless of the solid-state structures, the reactivity exhibited by these salts is consistent with the ions being adequately separated in solution.

1.17.2.1.3.3 Reactivity

As one would anticipate on the basis of their isovalent relationship with NHCs in addition to the negative charge they possess, these anionic group 13 complexes are potent electron donors and nucleophiles. As illustrated in Figure 19, NHB anions can attack aldehydes, esters, ketones, and other unsaturated compounds. Furthermore, the presence of the s-block metal counter-cations renders such salts particularly effective for reactions with halogenated reagents; the products derived from such reactions are typically those that one would anticipate for a salt metathesis process. Given the importance of cross-coupling reactions using boryl reagents in organic synthesis, the convenient preparation of organoboryl demonstrated by this class of ligands has the potential to be of great practical importance.

Although the products derived from NHGa salts may not appear to be as immediately useful as those of the corresponding boryl anions, the investigation of the reactivity of such species, in particular salts of the anion **3.6**, has revealed a phenomenal amount of interesting chemistry, as illustrated in Figure 20. As one would anticipate, NHGa anions have proved to be excellent donors to metals and acceptors from the s-, p-, d-, and f-blocks.[20,126] One notable observation is that the NHGa anion proves to be a stronger donor than analogs heavier group 14 carbenoids and thus it functions as a donor in the adducts that are formed.[127] Furthermore, the NHGa anions

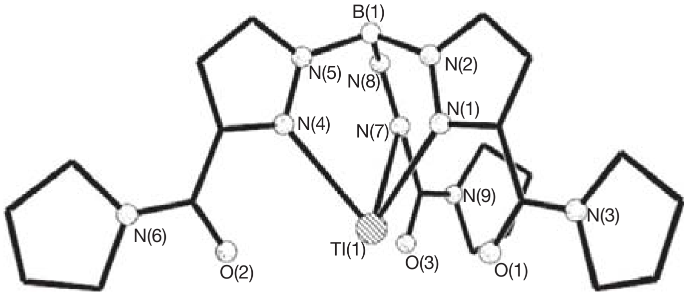


Figure 12 Solid-state structure of **2.22**. The R′ groups (OCNC$_4$H$_4$) is rotated so that the oxygen atoms point toward the empty p-orbitals on thallium.

are observed to insert in a formal manner into element hydrogen bonds such as those of imidazolium ions and those of water.[128] It has also proved possible to oxidize NHGa anions to generate species with Ga—Ga bonds, in effect accomplishing the reverse of the reductive process that may be used to prepare NHGa salts – the products of such reactions are catenated compounds (either diamagnetic or paramagnetic) that are described in other chapters of this work. As seen previously for the similar β-diketiminate species, oxidation of the Ga center with chalcogens or azides results in the formation of σ-bonded dimers rather than multiply bonded compounds.

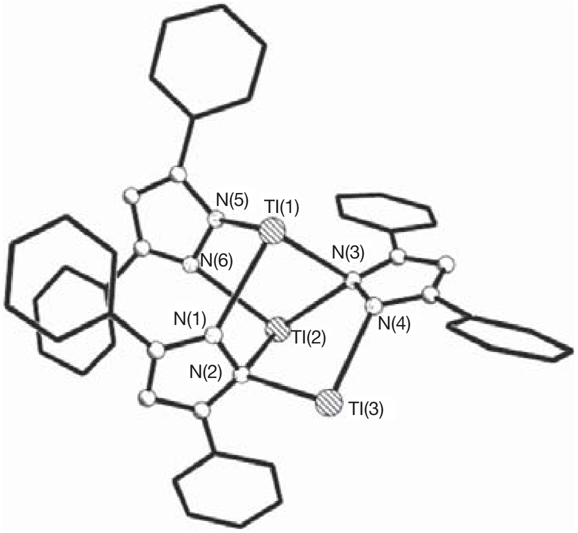


Figure 13 Solid-state structure of $[Tl]_3[N_2C_3HPh_2]_3$.

Finally, it is worth noting that in spite of their apparent similarity, salts of NHB and NHGa anions sometimes exhibit different reactivity. For example, whereas the treatment of Cp*(^{t}BuN)TiCl(pyr) (pyr, pyridine) with **3.6D** results in the formation of the anticipated complex of the form Cp*(^{t}BuN)Ti(NHGa)(pyr), the corresponding reaction with **3.1D** produces instead an amido complex of the form Cp*(^{t}BuN)Ti(pyr)(2-NHB–C_5H_5N), which is derived from the attack of the NHB ligand at the 2-position of a pyridyl group.[123]

1.17.2.1.4 NCN ligands: amidinates and guanidinates

Amidinate and guanidinate ligands, collectively termed 'NCN ligands' in this section, are similar in nature to the β-diketiminate family of ligands presented above in that they each contain two nitrogen donor atoms, bear a single negative charge, and feature a delocalized organic backbone. Furthermore, both classes of ligand employ bulky aryl groups that allow for

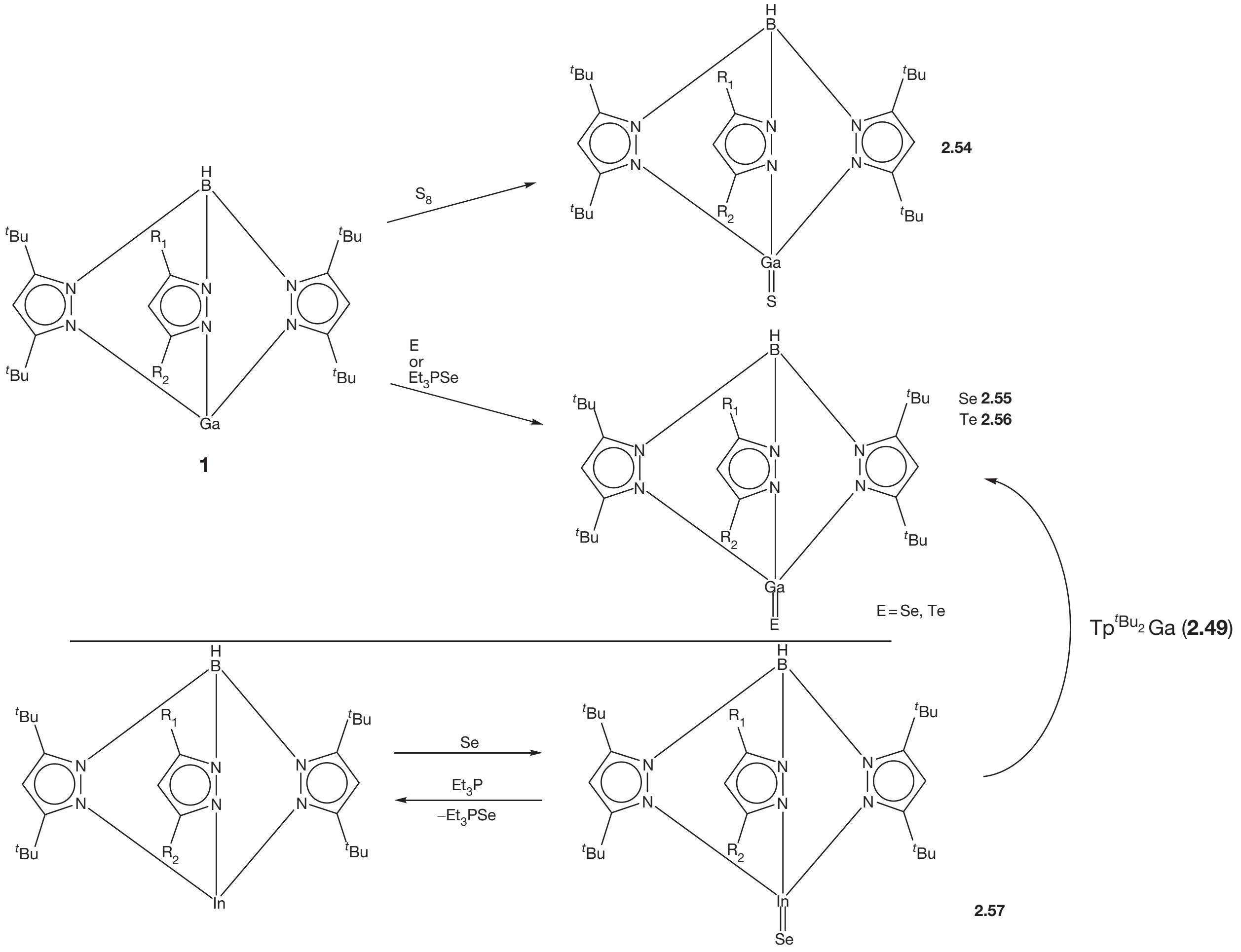


Figure 14 Oxidation reaction of gallium and indium tris(pyrazolyl)borate complexes with chalcogens.

kinetic stabilization of the dicoordinate triel site and provide tuneability to the ligand properties. The most obvious differences between the classes of ligands is that NCN ligands only have a single bridging carbon between the two nitrogen donor sites and thus produce four-membered ring when the ligand functions as an N,N-chelate. In the guanidinates, the presence of an amino substituent on backbone carbon atom renders the ligands more electron rich than the corresponding amidinates. A perhaps less obvious, but very important, consequence of the smaller bite angle of these types of ligands is the effect on their steric properties: the geometrical constraints of the four-membered ring orient the substituents on the nitrogen atoms further away from the dicoordinate center (in comparison to the six- and five-membered ring systems described above); thus, the effectiveness of their kinetic shielding is diminished. These properties do have a significant effect on the complexes that such ligands can stabilize and, in contrast to the six-membered ring complexes described above, no examples of stable complexes for boron or aluminum have been reported for these classes of chelating nitrogen ligands.[144]

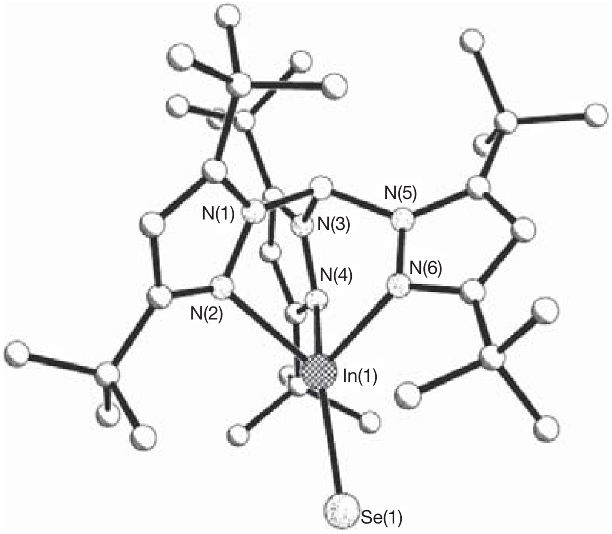


Figure 15 Solid-state structure of $\text{Tp}^{t\text{-Bu}}\text{In}{=}\text{Se}$. Selected metrical parameters: In—N: 2.238–2.246 Å.

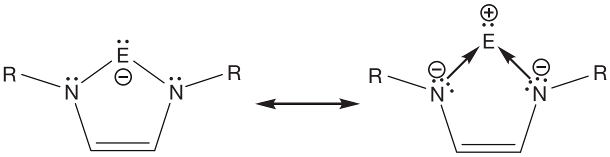


Figure 16 Lewis structures for N-heterocyclic group 13 anions. The resonance structure on the left is a depiction of how the boron and gallium analogs bind. The canonical structure on the right is perhaps most representative of indium.

1.17.2.1.4.1 Synthesis

The preparation of most NCN complexes typically begins with the deprotonation of the desired HNCN ligand, usually with an alkyllithium reagent, to generate the desired lithium salt. Addition of this metallated precursor to appropriate univalent group 13 halide results in the metathetical formation of the target E(NCN) complex as outlined below (**Figure 21**).[145,146]

1.17.2.1.4.2 Structural features

Interestingly, only bulky guanidinate ligands have allowed for the isolation of univalent group 13 complexes that contain dicoordinate metal centers in the four-membered ring that one would anticipate; the important structural features for the Ga and In complexes that have been reported are presented in **Table 6**. However, bulky amidinate and guanidinate ligands have proved to be able to stabilize pseudo-dicoordinate univalent group 13 complexes by way of an alternative mode of coordination. Rather than functioning as an N,N′-chelate, the ligands are observed to bind the metal as an N,π-arene-chelate. Because of their considerably different structural features, the data for the relevant Tl guanidinates as well as In and Tl amidinates are presented separately in **Table 7**.

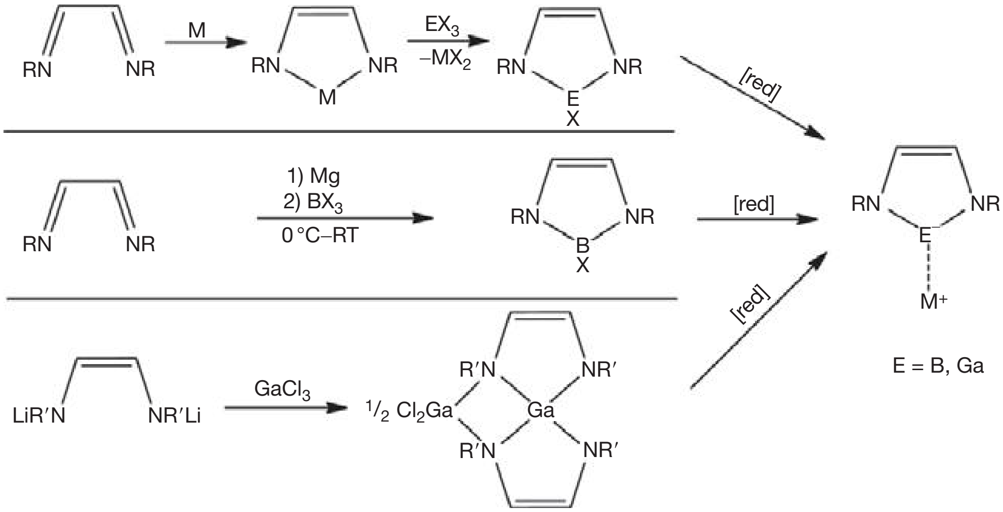
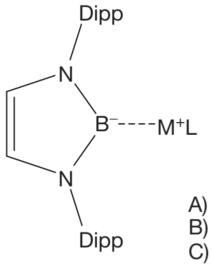
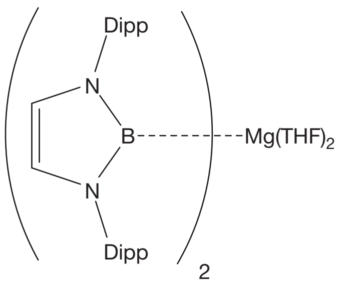
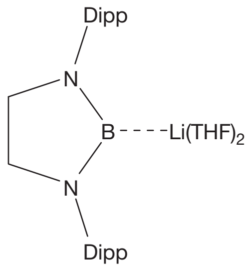
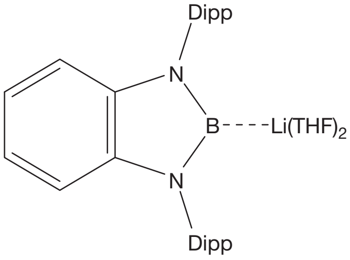
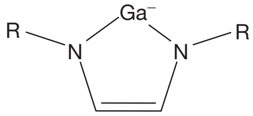


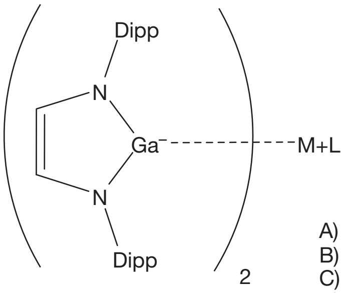
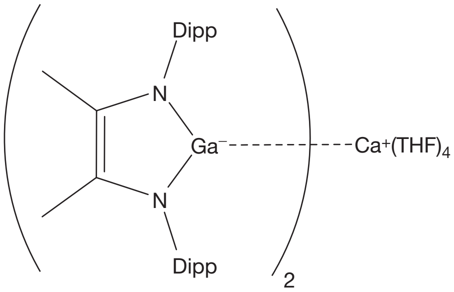
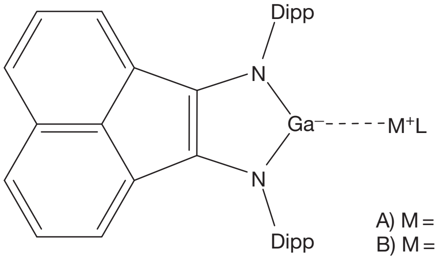
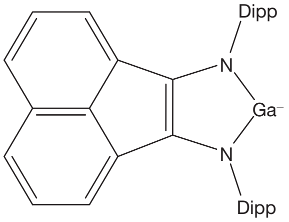
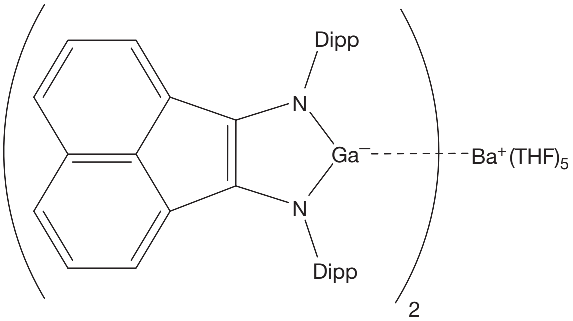
Figure 17 General synthesis for salt of N-heterocyclic boryl and gallyl anions. R = various alkyl and aryl substituents; $\text{R}'={}^t\text{Bu}$.

Table 5 Structural diagrams and metrical parameters for NHB and NHGa salts that have been characterized by XRD

	Structure	*N—E*	*N—E—N*	*E—M*
3.1A[116,117]	 A) M = Li; L = DME B) M = Mg; L = $(THF)_2Br$ C) M = Mg; L = $(THF)(Br_2Li(THF)_2)$ D) M = Li; L = $(THF)_2$	1.465–1.467	99.23	2.291
3.1B[118]		1.453–1.465	100.77	2.282
3.1C[118]		1.452–1.468	100.48–100.49	2.283–2.303
3.1D[117,119]		1.474–1.481	98.64	2.276
3.2[118]		1.471–1.487	99.21	2.377
3.3[117]		1.455	101.89	2.272
3.4[117]		1.475	99.97	2.217
3.5A[113]	 A) [18-crown-6][K]$^+$$(THF)_2$; R = ^{t}Bu B) $^1/_2$[18-crown-6]$_3$[K]$_2^{2+}$; R = Dipp	1.757–2.023	79.96–86.59	
3.5B[114]		1.844–1.983	83.02–87.21	

(*Continued*)

Table 5 (Continued)

	Structure	*N—E*	*N—E—N*	*E—M*
3.6A[120]	 A) M = Ca; L = $(THF)_4$ B) M = Mg; L = $(THF)_3$ C) M = K, L = OEt_2 D) M = K, L = TMEDA	1.919–1.954	83.67	3.159
3.6B[120]		1.916–1.923	84.11	2.717–2.727
3.6C[114]		2.005–2.009	81.88	3.378–3.422
3.6D[114]		2.011–2.014	82.04	3.532
3.7[120]		1.926–1.941	82.47	3.199
3.8A[121]	 A) M = Li; L = $(OEt_2)_3$ B) M = Na; L = $(OEt)_2$ C) M = Na; L = $(DME)_2$ D) M = Na; L = $(THF)_3OEt_2$ E) M = K; L = $(THF)_5$	1.959–1.995	83.67–83.80	2.718–2.833
3.8B[121]		1.969–1.978	83.29	3.049
3.8C[115]		1.964–1.971	82.97	2.984
3.8D[115]		1.949–1.997	83.02	3.111
3.8E[115]		1.986–2.004	82.98	3.440
3.9A[115]	 A) [18-crown-6][Na]$^+$ $(THF)_2$ B) Na$^+$ $(OPPh_3)_3(THF)$	2.011–2.015	81.81	
3.9B[115]		1.999	81.91	
3.10[115]		1.962–2.102	83.30–84.75	3.643–3.654

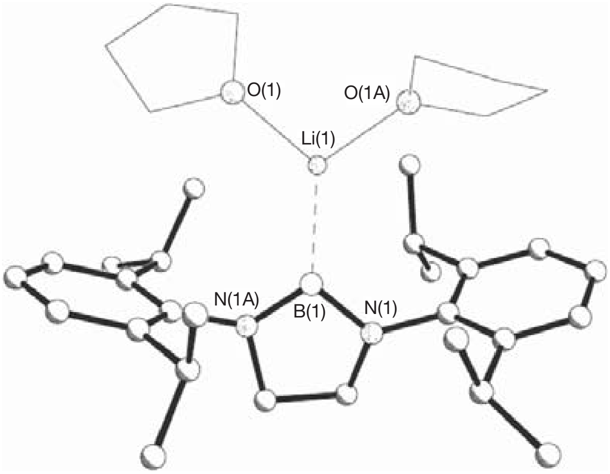


Figure 18 Solid-state structure of **3.4**, [Li(THF)$_2$][B((Dipp)NCH$_2$)$_2$]. B(1)—Li(1): 2.272 Å.

As one would anticipate, the N—E bond distances increase from Ga to In due to the increased atomic radii of the triel atom. Although the sample size of two is clearly too small to draw any firm conclusions, changing the amino substituent on the backbone from N(Cy)$_2$ to 2,6-dimethylpiperidine yields no change in E—N bond length. As expected for such four-membered rings, N—E—N angles are all very acute and are less than 60° for both of the indium(I) complexes.

It should be noted that computational investigations suggest that such univalent complexes should be excellent σ-donors but relatively poor π-acceptors and that bonding between the ligand and metal is highly ionic in nature.[145] The experimental examination of the charge density of the gallium analog is consistent with the computational predictions and proves that the π-delocalization occurs only within the organic framework and does not extend to the metal center.[147]

As indicated above, the thallium derivative (compound 4.4, Table 7) of the same ligand that produces four-membered ring N,N′-chelates for gallium and indium exhibits a considerably different structure.[145] Instead, the metal is bound by only one of

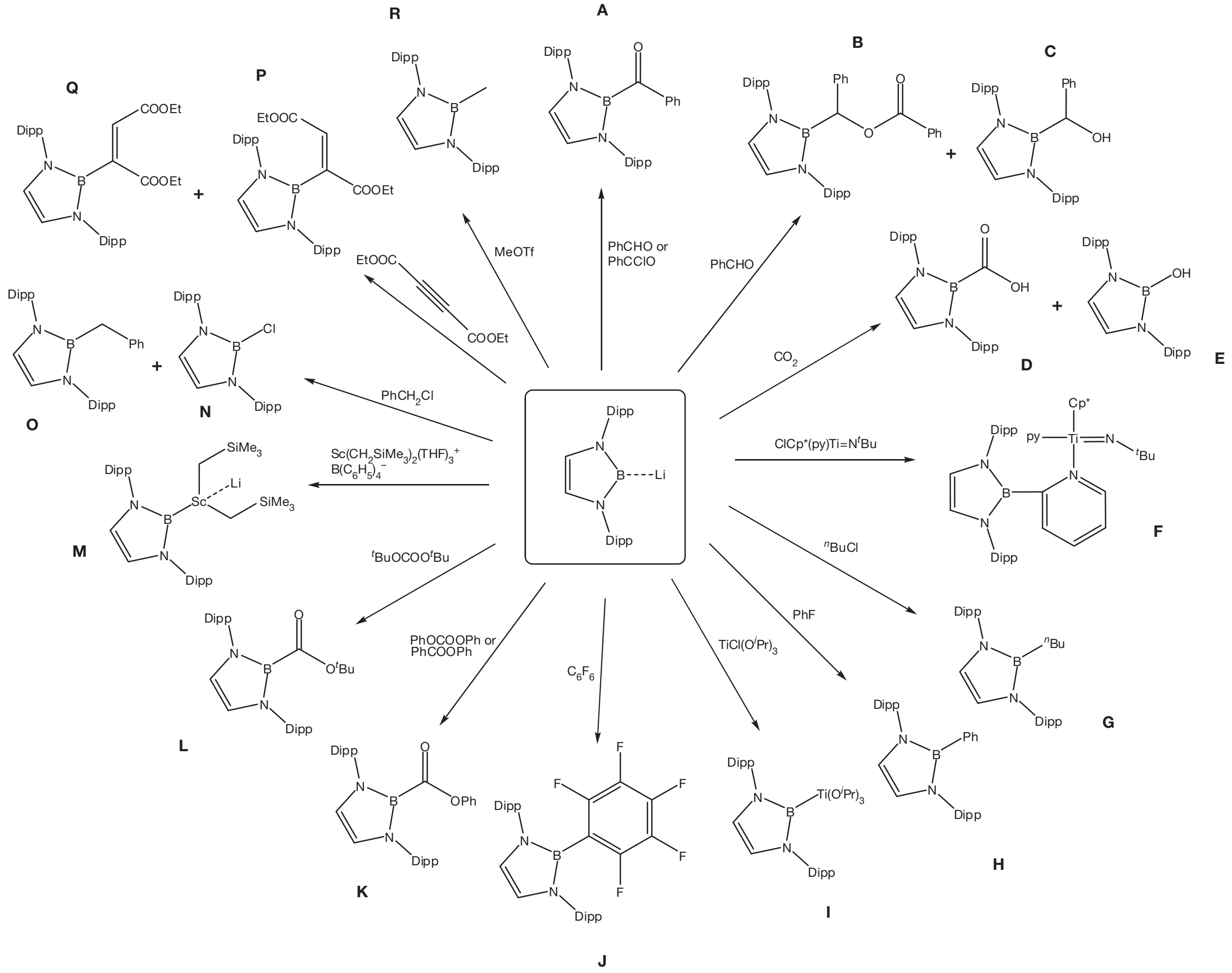


Figure 19 Summary of reported reactivity for anionic NHB salts. **A**,[117,118] **B**,[117,118] **C**,[116–118] **D–E**,[117] **F**,[123] **G**,[116] **H**,[117] **I**,[123] **J–L**,[117] **M**,[124] **N–O**,[117] **P–Q**,[125] and **R**.[116]

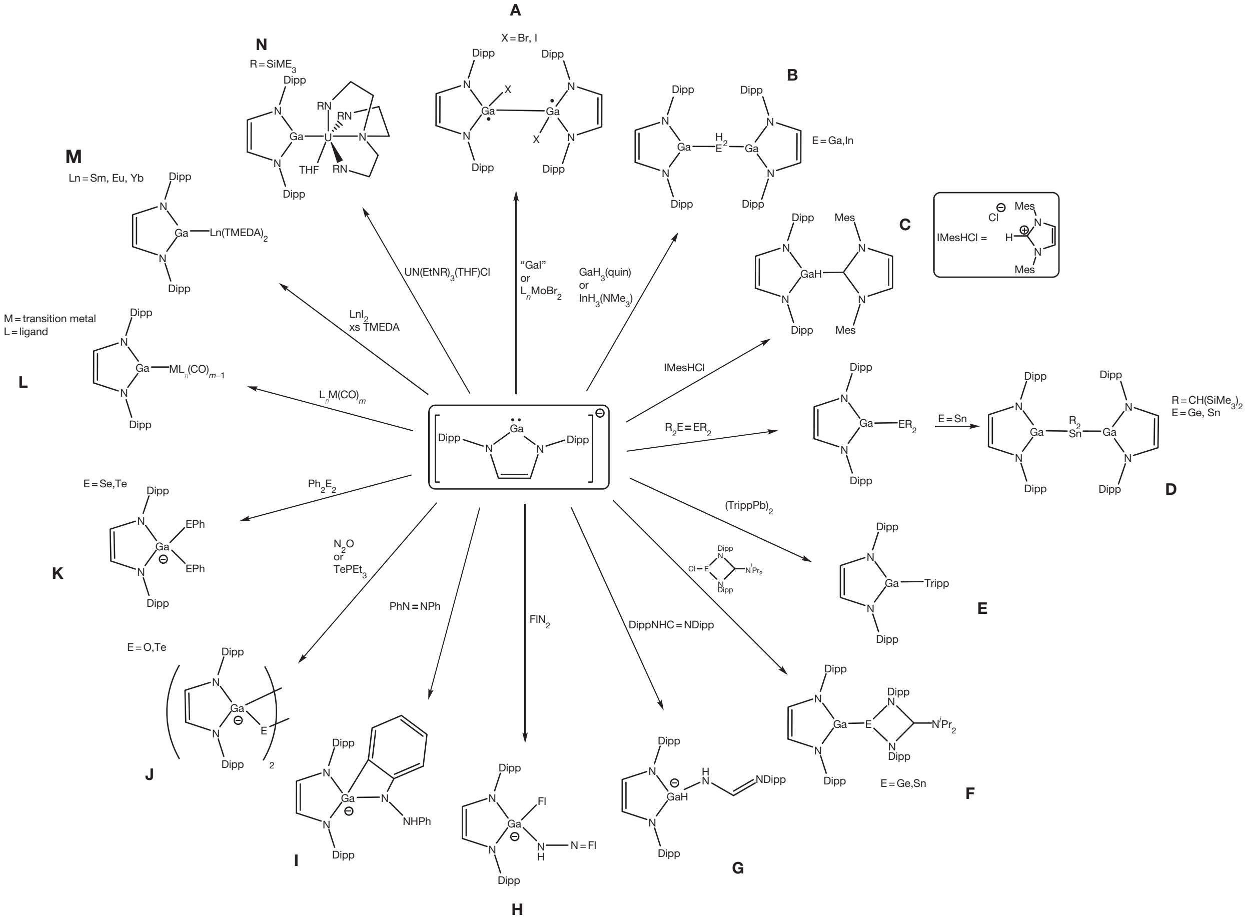
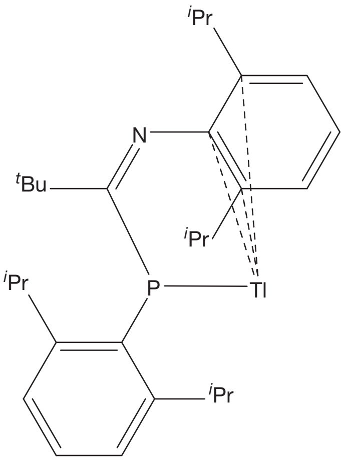


Figure 20 Summary of reported reactivity for anionic NHGa salts. Data taken from the following work: **A**,[129] **B**,[130] **C**,[128] **D–F**,[127] **G**,[131] **H–I**,[132] **J–K**,[133] **L**,[134–141] **M**,[142] and **N**.[143]

the nitrogen atoms and forms an η^3-arene complex with one of the Dipp groups. The adoption of such a 'coordination isomer' structure is attributable to the larger size of the thallium(I) cation: the adoption of a pseudo-five-membered ring allows for a considerably less strained complex, and the greater electron density and geometric properties of the arene ring allow the ligand to more effectively satisfy the coordination requirements of the larger cation. Furthermore, it must be noted that similar behavior is also observed for the univalent complexes of indium when the NCN ligand employed is less electron rich or less sterically demanding than the guanidinate used in complexes **4.2** and **4.3**. In particular, when the ligand features substituents such as ^{t}Bu (in amidinate complex **4.6**) or P(Cy)$_2$ (in the phosphaguanidinate complex **4.8**) on the carbon atom of the backbone, the arene-bound isomer is obtained in lieu of the four-membered ring.

Finally, it should be noted that an analogs compound was isolated in which one of the nitrogen atoms is replaced by a phosphorus atom. This phosphaguanidinate ligand binds univalent thallium cation in an analogs fashion as a P,π-aryl-chelate; the complex was described as the first thallium(I) phosphanide.[149] The observation that the thallium center in **4.11** is bound by the phosphalkene fragment rather than the imine fragment is consistent with both the superior donor ability of the phosphorus fragment and the expectations on the basis of ligand hardness arguments.



1.17.2.1.4.3 Reactivity

In contrast to the six- and five-membered ring analogs, relatively few studies of the reactivity of these NCN ligand complexes of univalent group 13 species have been reported. As anticipated on the basis of the computational investigations, and the behavior

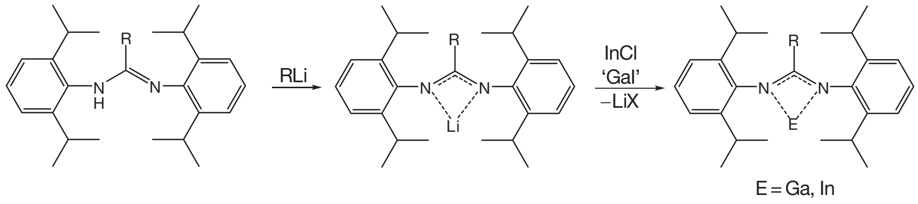
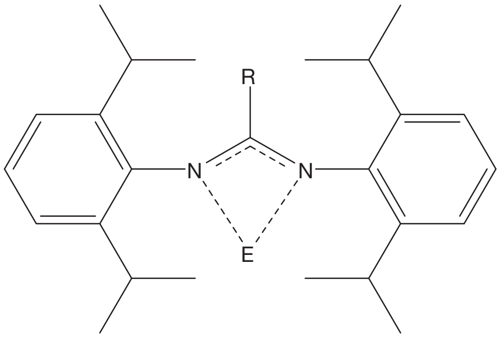


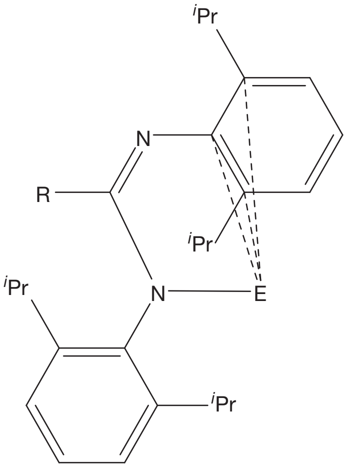
Figure 21 Representative general synthetic approach employed for amidinate (R = hydrocarbyl) and guanidinate (R = amino) complexes of gallium(I) and indium(I).

Table 6 Selected metrical parameters for four-membered ring chelate univalent group 13 complexes of guanidinates



	E	*R*	*N—E*	*N—E—N*
4.1[145]	Ga	$N(Cy)_2$	2.087–2.095	63.8
4.2[145]	In	$N(Cy)_2$	2.298	58.1
4.3[146]	In	2,6-Dimethylpiperidine	2.298	57.9

Table 7 Selected metrical parameters for the η^3 arene-stabilized 'coordination isomer' complexes of NCN ligands with univalent group 13 metals



	E	*R*	*N—E*	*Average E—C*
4.4[145]	Tl	$N(Cy)_2$	2.460	3.054
4.5[148]	Tl	^{t}Bu	2.445	2.994
4.6[148]	In	^{t}Bu	2.329	2.943
4.7[146]	Tl	$P(Cy)_2$	2.416	2.967
4.8[146]	In	$P(Cy)_2$	2.283	2.904
4.9[146]	Tl	$N(^i Pr)_2$	2.429	3.010
4.10[146]	Tl	2,6-Dimethylpiperidine	2.432	3.044

of the related complexes described earlier in this work, the principal mode of reactivity demonstrated by these complexes is the ability to act as ligands for transition metals through the replacement of labile ligands (Figure 22). It should also be noted that the gallium analog has been shown to undergo oxidative insertion chemistry with iodine and Me_3SiI.[146]

1.17.2.1.5 Triazenide ligands

Triazenide ligands are similar in structure to the aforementioned NCN ligands with the principal difference being that the two donating nitrogen centers are linked by a dicoordinate nitrogen center rather than by a substituted methine fragment. This significant alteration removes the possibility of functionalizing the backbone to tailor the properties of the ligand; thus, only the substituents on the chelating nitrogen centers, which are typically aryl groups, are available to be modified. Furthermore, the triazenide ligands are less electron rich than even the corresponding amidinates,[153] which might also constrain the ability of such ligands to stabilize more reactive group 13 elements. The limitations of this type of ligand are such that it has only proved to be possible to prepare thallium(I) triazenide complexes at present.

1.17.2.1.5.1 Synthesis

The preparation of thallium triazenide complexes can be performed easily in a single step. The treatment of the protonated triazene with thalliumethoxide liberates ethanol and produces the target thallium salt.[154] It is likely that ion-metathesis routes might also be suitable to generate such salts but ethanolysis reaction is particularly clean and effective for the triphenyl derivatives described herein (Figure 23).

1.17.2.1.5.2 Structural features

In light of the previous discussion concerning the thallium complexes formed by amidinate and guanidinate ligands, one might not have expected triazenide ligands to support low-coordinate complexes featuring N,N′-chelation. In fact, the use of triazenide ligands with simple arene ligands does not provide monomeric low-coordinate complexes for thallium but rather affords dimeric structures bridged by additional Tl—N bonds.[155,156] Monomeric low-coordinate complexes of thallium(I) have only proved to be isolable through the use of triazenide ligands with arene groups at the ortho-position of the N-aryl substituent, as presented in Table 8.

As with the thallium complexes of the NCN ligands presented above, the metal center is indeed stabilized by the arene groups in the ligand. As illustrated in Table 8, this stabilization is not from the aryl fragment directly attached to the nitrogen center, but rather from an additional aryl group at the 2-position of the N-aryl substituent. The orientation of the ortho-aryl group is

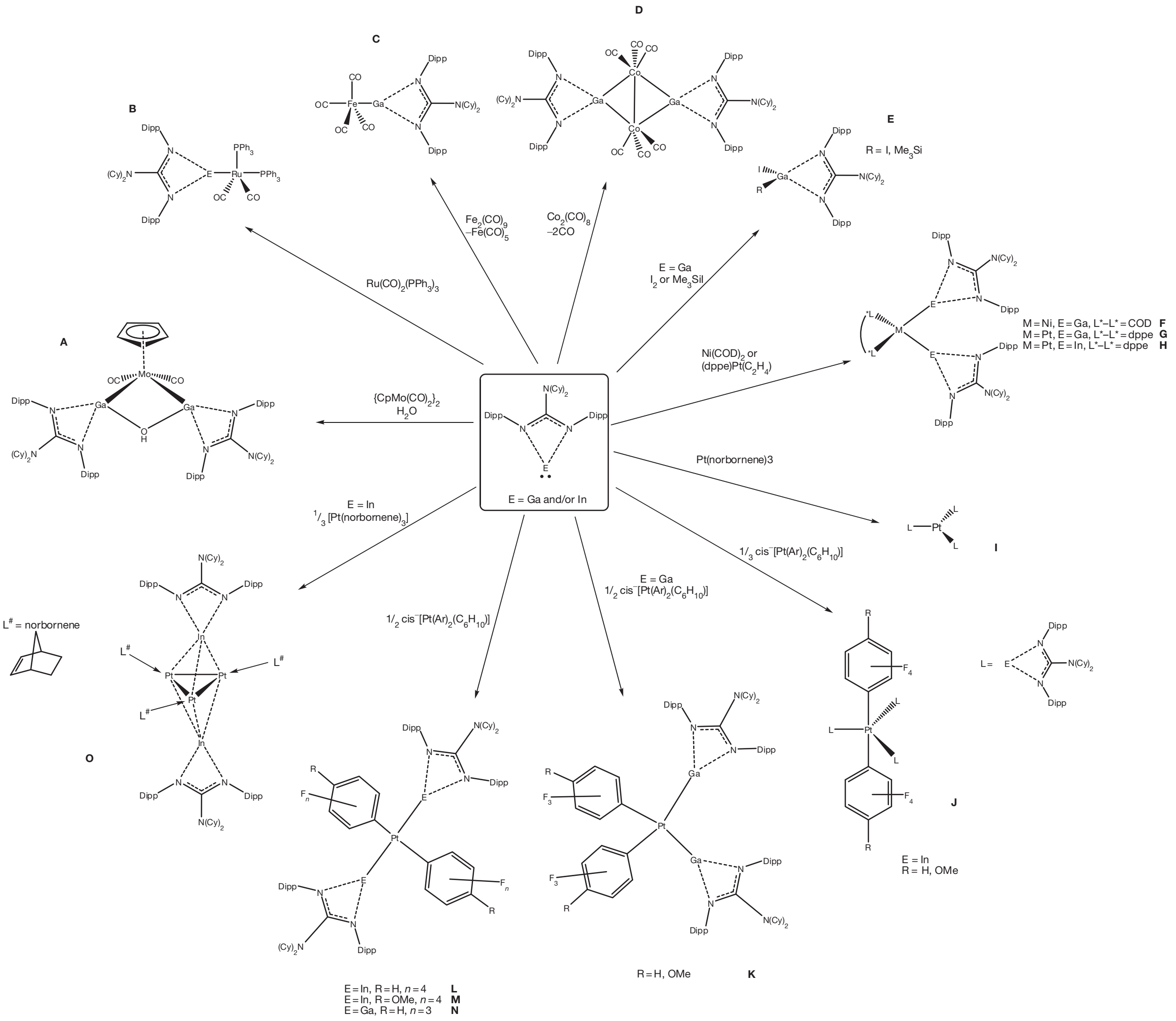


Figure 22 Reactivity observed for four-membered ring guanidinate complexes of univalent gallium and indium. Data taken from the following work: **A–D**,[150] **E**,[146] **F–I**,[151] and **J–O**.[152] No reactivity studies have been reported yet for the arene-bound analogs.

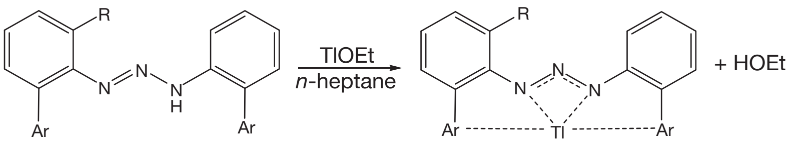
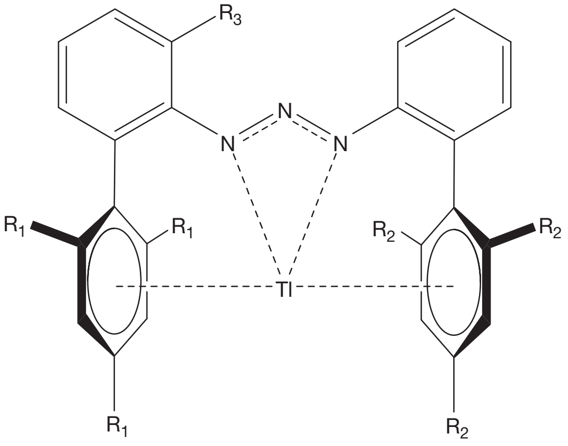


Figure 23 General synthesis for thallium triazines.

such that its π-system can readily interact with the thallium center while the nitrogen donor remains in close proximity to the metal. When both nitrogen centers bear suitable biphenyl or terphenyl substituents, the ligands are able to form a four-membered N_3Tl ring with the metal. A key feature to point out is that in compounds **5.2** and **5.3** the N—Tl bond to the nitrogen atom bearing the substituent containing the additional mesityl groups is over 0.1 Å longer than the other N—Tl distance. This difference is attributed to the steric bulk of the mesityl groups, which inhibit the interaction with the associated nitrogen and the metal center.

Another noteworthy feature is that the substitution pattern on the ortho-aryl fragments of the N-bound biphenyl or terphenyl substituents appears to determine whether the resultant complex will exist as a monomer or as a dimer. For example, the presence of a 3,5-dimethyl substitution pattern versus the 2,4,5-substitution pattern for the complexes above results in the formation of a dimeric complex, as illustrated for complex **5.4** in Figure 24. It has been noted that the ligands in compound **5.4** act like an organic cage and effectively encapsulate the Tl_2 fragment.

Table 8 Selected metrical parameters for thallium(I) triazenide complexes



	R_1	*R_2*	*R_3*	*N—Tl*	*$\eta^{\#}$-C*	*C—Tl*	*Average C—Tl*
5.1[154]	^{i}Pr	^{i}Pr	H	2.607	5	3.372–3.564	3.461
				2.578		3.300–3.493	3.399
5.2[154]	CH_3	CH_3	Mes	2.668[a]	5	3.372–3.526[a]	3.433[a]
				2.546		3.273–3.527	3.378
5.3[154]	CH_3	^{i}Pr	Mes	2.637[a]	5[a] and 4	3.390–3.492[a]	3.442[a]
				2.525		3.293–3.479	3.380

[a] Denotes values given on the same side as the R_1- and R_3-group.

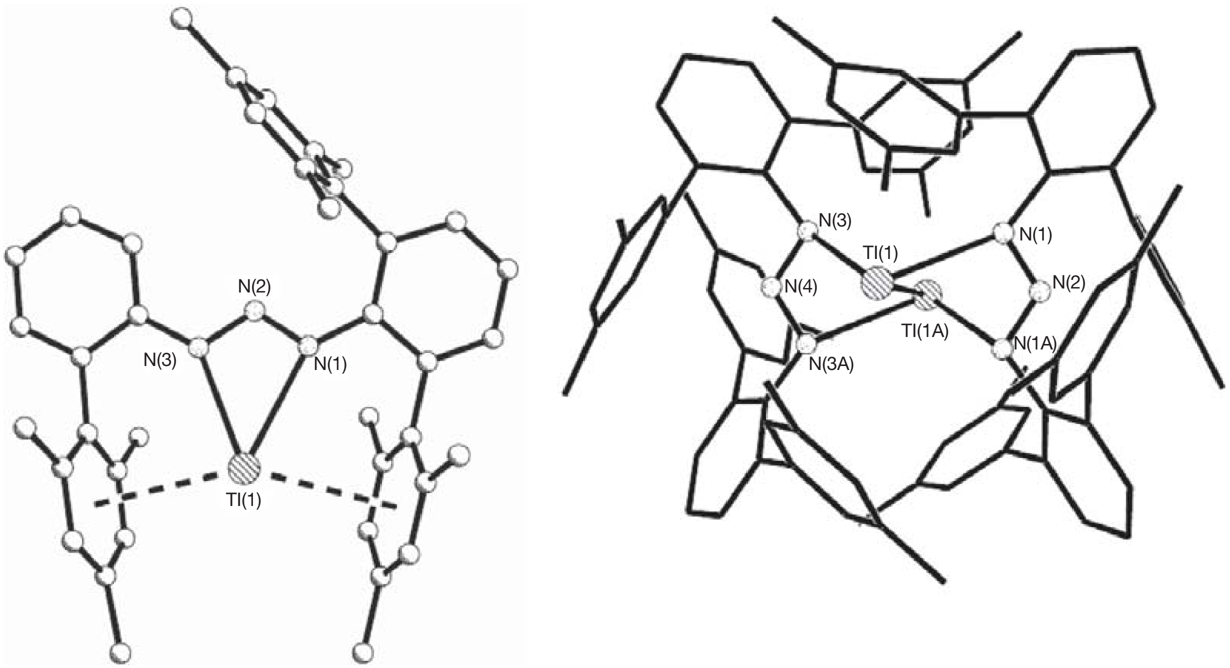


Figure 24 Left: Monomeric structure of compound **5.1**.[154] Right: Solid-state structure of **5.4**, shown as the dimeric species.

1.17.2.1.5.3 Reactivity

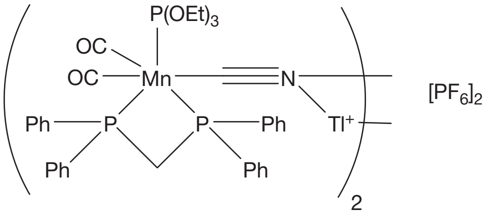
Although the reactivity of thallium triazenide complexes has not been pursued as yet, one may anticipate that such complexes will likely find use as metathesis reagents for the introduction of triazenides to other metals.

Compounds related to these triazenide and amidinate complexes that deserve mention in this section are Cundari's thallium triazapentadienyl complexes.[157] These amido complexes adopt similar geometries in the solid state and feature arene-stabilization (Mes **5.5** or Dipp **5.6**) of the metal center. Instead of an NNN moiety, the trinitrogen ligands feature an NCNCN backbone, with each carbon bearing a $CF_2CF_2CF_3$ group. As such, the ligands may be considered as N-fused bis-amidinates in which the central nitrogen atom and the terminal arenes function as donors to the thallium center, as shown in Figure 25.

1.17.2.1.6 Amido-based ligand

In almost every instance, stable, simple amido-based complexes featuring dicoordinate group 13 centers have only been reported for thallium. There are a few instances in which indium is present in the system and coordinated to amido groups. In most cases, these are trivalent indium centers and are not low coordinate but there is a unique example featuring a dicoordinate indium(I) center. The presence of relatively bulky silyl groups (the majority being Me_3Si–) on the nitrogen centers in each of the compounds that have been successfully isolated is noteworthy.

All of the amide ligand complexes described in Table 9 consist of polydentate amido donors (sometimes also bearing pyridyl fragments) that function as chelates to the thallium(I) ions. Most of the neutral bidentate complexes feature Tl_2N_2 rings that feature dicoordinate thallium(I) moieties with Tl—N distances of around 2.4–2.5 Å that are typical of the class as seen in complexes **6.1–6.3**. The tridentate ligands provide thallium(I) complexes that can be described as monomeric (**6.4**) or dimeric structures featuring bridging Tl_2N_2 rings with longer Tl—N distances in excess of 2.7 Å (e.g., **6.5**) or linked by other metal–nitrogen contacts (**6.6**). Some mixed valent[166] thallium amides, such as compounds **6.7**, **6.8**, and **6.10**, not only feature such Tl_2N_2 rings but also feature direct Tl—Tl bonds; the unique mixed-valent indium compound **6.9** is directly analogs to **6.10**. Finally, mixed-valent Tl^{I}–E^{III} complexes such as **6.11–6.13** are best understood as contact ion pairs between a Tl^{+} cation and an $E^{III}N_4$ anion; the Tl^{I}—N distances all exceed 2.5 Å in these complexes.



One further compound that should perhaps be noted in this subsection is the hexafluoridophosphate salt of the cyanomanganese complex **6.15**, which was obtained by the treatment of Tl[PF_6] with the cyanomanganese precursor. The structure of **6.15** consists of a centro-symmetric dimeric structure linked by two dicoordinate thallium(I) centers in a N_2Tl_2 ring.[167] The compound features N—Tl bond distances of 2.636 and 2.772 Å, an N—Tl—N angle of 76.34° and a Tl—Tl distance of 4.253 Å. The structure is a very rare example of a monodentate nitrogen donor binding to a thallium(I) center albeit with very long Tl—N distances that make it appear more like a contact ion pair.

Finally, it must be emphasized that the use of extremely bulky amido ligands has actually allowed for the isolation of monocoordinate compounds of gallium and thallium. Whereas the reactions of salts of most amido substituents with low-valent group 13 synthons typically yield oligomeric group 13 amides or related cluster compounds,[15,168] the treatment of the very bulky lithium amide Li[(2,6-$Mes_2C_6H_3$)(Me_3Si)N] with 'GaI' results in the formation of the monomeric univalent gallium amide (2,6-$Mes_2C_6H_3$)(Me_3Si)NGa, **6.16**.[169] The structure of **6.16**, illustrated in Figure 26, features a monocoordinate gallium atom with a Ga—N distance of 1.980 Å; not surprisingly, there appears to be a relatively close contact between the most proximate aryl group and the gallium center with a C_{ipso}—Ga distance of 2.65 Å. The treatment of the gallium amide **6.16** with the bulky aryl azide 2,6-$Mes_2C_6H_3N_3$ results in the elimination of N_2 and the formation of the amidoimidogallium compound (2,6-$Mes_2C_6H_3$)(Me_3Si)NGa—N(2,6-$Mes_2C_6H_3$). This gallium(III) compound features a dicoordinate gallium center with Ga—N distances of

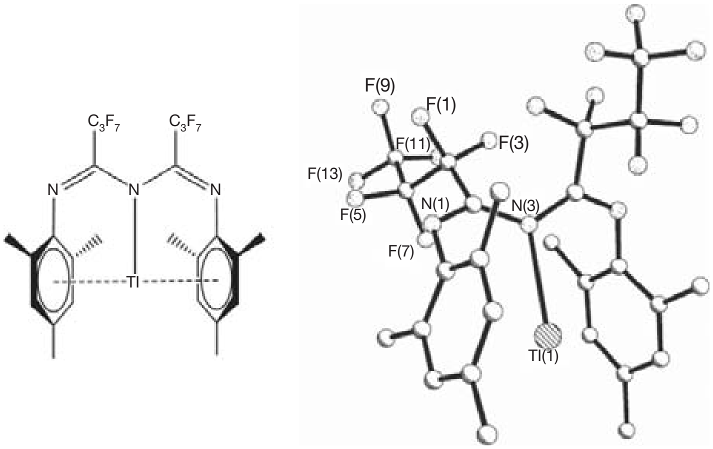
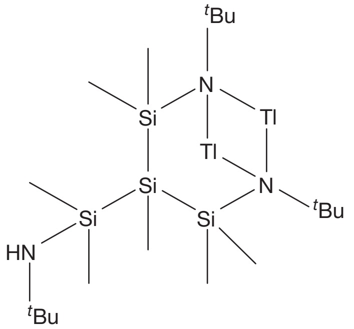
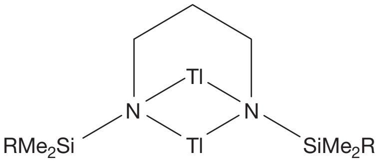
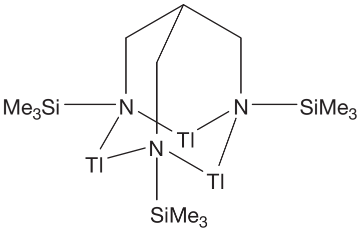
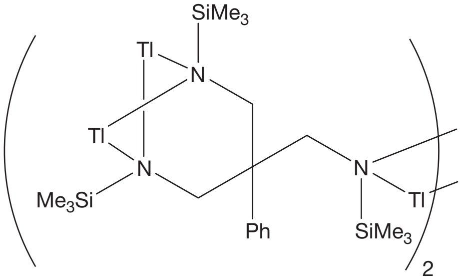
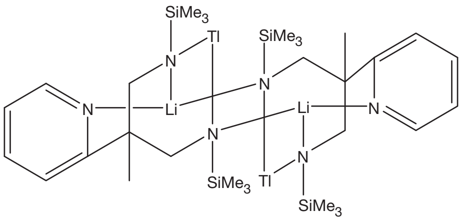
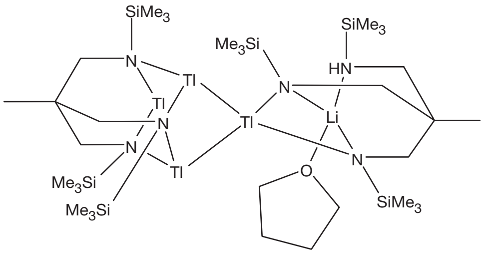


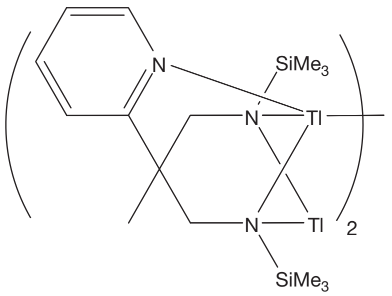
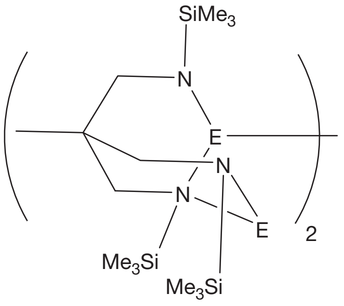
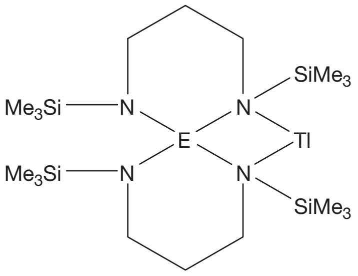
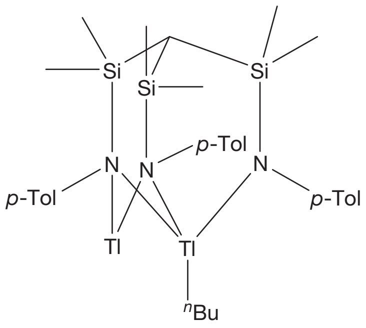
Figure 25 Left: Structural drawing of $(MesNCC_3F_7)_2NTl$ **5.5**. Right: Solid-state structure of $(MesNCC_3F_7)_2NTl$. Selected bond distances: **5.5**: N(3)—Tl(1): 2.608–2.675 Å. **5.6**: N—Tl: 2.666–2.732 Å.

Table 9 Selected metrical parameters for thallium(I) triazenide complexes

Structure	*#*	*E—N*	*N—E—N*	*E—E*
	**6.1**[158]	2.522–2.548	83.45–83.97	3.582
	R = Me **6.2**[159]	2.408–2.471	73.88–74.78	3.489
	R = ^{t}Bu **6.3**[159] **6.4**[160]	2.405–4.481 2.341–2.551	74.71 80.81–89.73	3.480 3.411–4.731
	**6.5**[161]	2.416–2.765	72.47–89.30	3.452–3.692
	**6.6**[162]	2.455–2.483	83.29	N/A
	**6.7**[160]	2.324–2.464	75.83–86.83	3.315–3.904

(*Continued*)

Table 9 (Continued)

Structure	*#*	*E—N*	*N—E—N*	*E—E*
	**6.8**[162]	2.406–2.470 2.467–2.573* *From pyr	72.32–74.61	3.433–3.489
 * = from bridging E	E = In **6.9**[163] E = Tl **6.10**[163]	2.418–2.440 2.081–2.983* 2.504–2.539 2.140–2.289*	71.62 26.51–96.26* 70.35 53.57–93.50	3.421 2.807* 3.540 2.734*
	E = In **6.11**[164] E = Tl **6.12**[164]	E: 2.599–2.601 E: 2.531–2.539	78.60 78.21	3.481 3.514
	**6.13**[165]	2.694–2.721	69.64	3.362

1.743 and 1.862 Å, an N—Ga—N angle of 144.0°, and a C—N$_{\text{imido}}$—Ga angle of 133.9°; these metrical parameters are thus consistent with the presence of multiple bonding, especially between the gallium center and the dicoordinate nitrogen atom of the imido group.

Not surprisingly, bulky amides have also proved to be suitable for the isolation of monomeric univalent thallium compounds, of which one, (Dipp)(Me$_3$Si)NTl, **6.17**, was isolated as early as 1994.[170] This compound features a N—Tl distance of 2.305–2.307 Å and long intermolecular interactions between the arene group on one molecule and the thallium center of an adjacent molecule. The other crystallographically characterized example of such a monomeric thallium amide, (2,6-Mes$_2$C$_6$H$_3$)(Me)NTl, **6.18**, was reported more recently by

Power and coworkers.[171] This metal amide was prepared through the reaction of TlCl with the aryllithium reagent described above and has N—Tl distances ranging from 2.348 to 2.379 Å for the two crystallographically independent molecules. Perhaps surprisingly, the TlN(Me)C$_{ipso}$ moiety is roughly coplanar with the central arene of the terphenyl group – this unusual orientation allows each thallium center to engage in an intramolecular contact with an *ortho*-arene from the ligand.

It should also be noted that attempts to generate univalent aluminum amides analogs to **6.16** or **6.17** have yielded only oligomeric (usually tetrameric) clusters.[172,173] Similarly, the use of smaller amide ligands also results in the formation of tetrameric gallium(I) amides rather than monomeric species.[174]

One final class of nitrogen-based complexes that should be mentioned are the cationic indium(I) 2,6-di(arylimino)pyridyl (DIMPY) complexes of Richeson and coworkers. Whereas the reaction of indium(I) halides with DIMPY ligands results in disproportionation and the generation of indium(III) products, the treatment of InOTf (OTf, trifluoromethane sulfonate, 'triflate') with the same ligands provides salts of the coordination complexes of the general form [(DIMPY)In][OTf].[175] The structure of one such salt **6.18** is illustrated in Figure 27 and exhibits an In—N$_{pyr}$ distance of 2.495 Å and considerably longer contacts of 2.689 and 2.747 Å to the nitrogen atoms of the imino groups. On the basis of structural, computational, and solid-state NMR investigations, the authors conclude that the cations in these salts are best considered as weakly interacting coordination complexes.[176,177] Attempts to prepare similar complexes of univalent gallium using 'GaI' were unsuccessful and resulted primarily in the formation of radical species.[178]

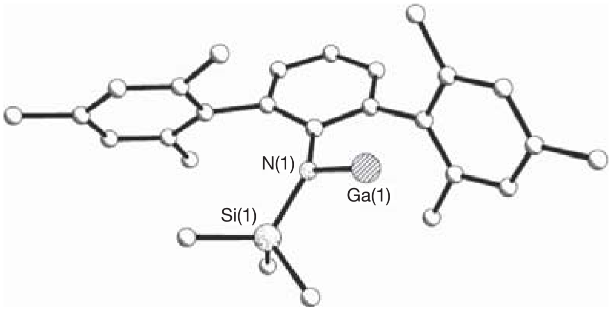


Figure 26 Solid-state structure of (2,6-Mes$_2$C$_6$H$_3$)(Me$_3$Si)NGa, **6.16**.

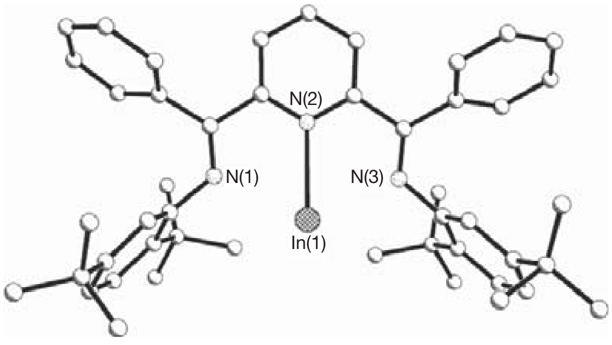


Figure 27 Solid-state structure of [(2,6-[(2,5-^{t}Bu$_2$C$_6$H$_3$)NC(Ph)]C$_5$H$_3$N)In][OTf] **6.18**. Counterion OTf$^-$ is not shown for clarity.

Finally, it should be noted that the treatment of bulky carbazolyl ligands with ECl (E = In, Tl) results in the formation of π-complexed arene species **6.19** and **6.20**, as illustrated in Figure 28, rather than compounds containing N—E σ-bonds.[179] As with many of the analogs carbocyclic univalent group 13 compounds described in subsequent sections, these species exist as infinite one-dimensional (1D)-coordination polymers in the solid state. The use of somewhat less-bulky carbazolyl ligands in such reactions generated mixed-valent group 13 compounds[166] featuring pseudo-dicoordinate In(+1) centers that are ligated by two of the arene rings from the carbazole ligands on the In(+2) fragments (**6.21**) or tricoordinate thallium(+1) salts (**6.22**).

1.17.2.2 Carbon-Based Ligands

Although there are fewer distinct classes of carbon-based ligands in comparison to nitrogen-based ligands that have been employed to prepare and isolate compounds containing low-coordinate group 13 centers, some of the families of ligands that have proved to be successful have yielded many individual examples. In the following subsections, complexes derived from σ-bonded carbon-based ligands are presented first followed by those featuring π-bonded carbocyclic ligands.

1.17.2.2.1 σ-Arenes and σ-alkyls

Large, sterically demanding substituents have proved to be absolutely essential for the isolation of low-coordinate group 13 compounds because of the inherently high reactivity of such species and their propensity for oligomerization. The most effective class of σ-bonded substituents are the bulky terphenyl ligands (Ar*)[180] that have even allowed for the isolation of monocoordinate group 13 centers.

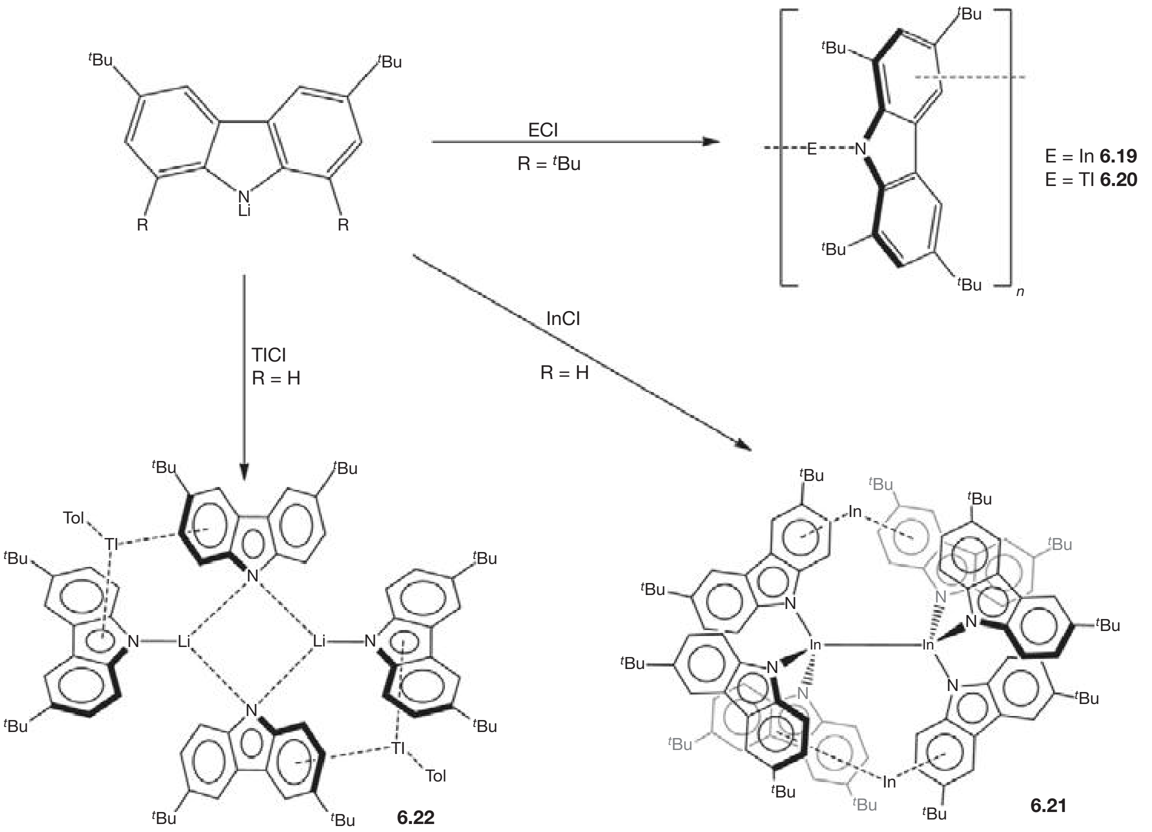
1.17.2.2.1.1 Synthesis

The preparative approach used to generate monovalent group 13 compounds with bulky terphenyl substituents is relatively straightforward. The reaction of metallated form of the chosen terphenyl ligand with the appropriate group 13 monohalide produces the target E(I) compound with the concomitant loss of the metal halide salt, as illustrated in Figure 29. In many instances, byproducts are observed that result from the formal disproportionation of the monovalent group 13 reagent – in some cases, further reduction of disproportionation products such as Ar*Ga(I)–Ga(I)Ar* is necessary to generate the target monovalent terphenyl compound.

1.17.2.2.1.2 Structural features

The particularly bulky terphenyl substituents bearing ^{i}Pr groups at the 2- and 6-position of the *ortho*-arene fragments have proved to be capable of supporting monocoordinate univalent group 13 centers for gallium, indium, and thallium; depictions of the known complexes and the C—E bond distances are presented **7.1** (Table 10).

The metrical parameters and other features of the univalent complexes are perhaps predictable, with E^I—C$_{arene}$ bonds that tend to be somewhat longer than those of comparable E^{III}—C$_{arene}$ bonds because of the differences in ionic radii. The most



6.22

6.21

Figure 28 Products from the reaction of bulky carbazole ligands with ECl.

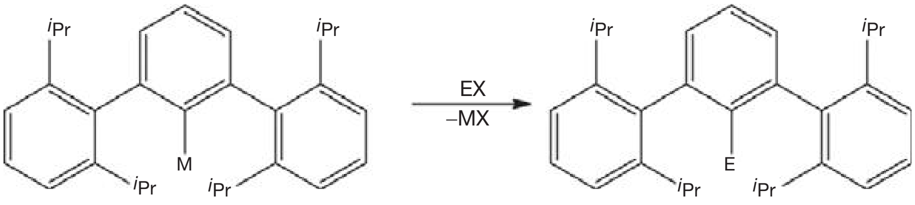


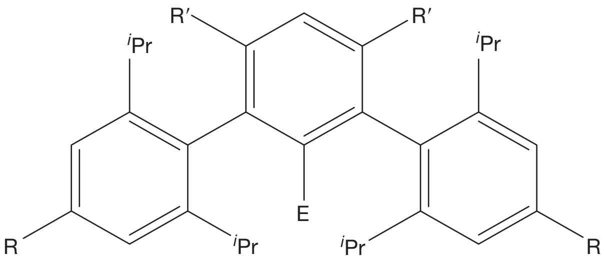
Figure 29 Representative synthetic approach employed for the preparation of for monovalent group 13 terphenyl compounds.

notable aspect of the structures, an example of which is illustrated in Figure 30, is that they are unambiguously monomeric even in the solid state. This is in contrast with even the bulkiest of alkyl substituents (see below), which produce oligomeric complexes in the solid state.

It must be noted that the reaction illustrated in Figure 29 does not always yield monomeric products: some bulky terphenyl groups do not preclude the formation of possible metal—metal bonds and dimeric structures are observed in the solid state for the compounds listed in Table 11.

Each of the compounds presented in Table 11 features very long element—element bonds and distinctly bent environments about the dicoordinate group 13 metal centers. In fact, the strength of the bonding in these 'dimers' is very weak ($<$9 kcal mol^{-1} for the strongest), and computational studies suggest that it is comparable in strength to those of closed-shell interactions.[181] Consequently, these compounds readily dissociate in solution and serve as effective sources of Ar*E species.

Table 10 Structurally characterized monocoordinate group 13 terphenyl compounds



	E	*R*	*R′*	*E—C*
7.1[181]	Ga	^{i}Pr	^{i}Pr	2.035–2.045
7.2[181]	Ga	H	^{i}Pr	2.033
7.3[182,183]	In	^{i}Pr	H	2.256–2.260
7.4[184]	Tl	^{i}Pr	H	2.337

1.17.2.2.1.3 Reactivity

Univalent group 13 terphenyl compounds have demonstrated a considerable range of reactivity and, as one would anticipate for a unicoordinate metal compound, the coordination number of the metal is increased in every instance. The thallium terphenyl compounds, as usual, are typically used as agents to transfer the organic ligand to other elements, as illustrated in Figure 31. However, the products observed in the reaction of Ar*Tl with P_4 are interesting multiply bonded polyphosphorus species. As summarized in Figure 31, most of the lighter Ar*E compounds have been observed to undergo a variety of oxidation and oxidative addition/insertion reactions and they have been used extensively as two-electron donors. In spite of their considerable steric bulk, the oxidation of Ar*E complexes with chalcogen sources produces σ-bonded dimeric Ar*E(μ^2-Ch)$_2$EAr* heterocycles rather than multiply bonded species. By contrast, the related oxidation reaction with bulky organo-azides yields monomeric multiply bonded compounds that are described below. Oxidative cycloaddition reactions produce dimetallic heterocycles when the monovalent gallium terphenyl compounds react with olefin or acetylene derivatives; some of the products derived from the latter can be further reduced to generate anionic digallabenzenes. Reduction of Ar*Ga species generates dimetallic dianions that feature metal—metal multiple bonds and that are discussed in detail elsewhere in this series. Low-valent gallium terphenyl compounds are found to insert into a variety of bonds including the N—H bond in ammonia and the H—H bond in molecular hydrogen!

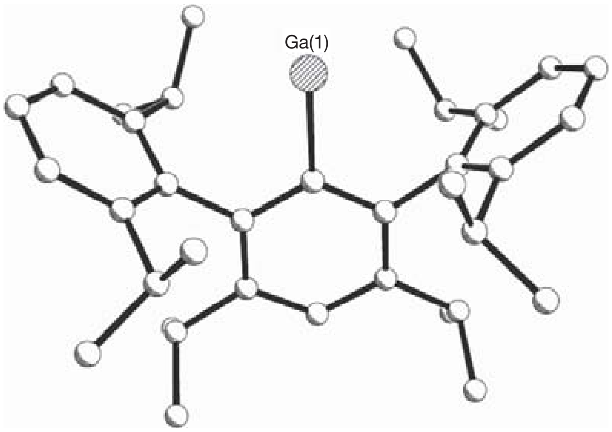
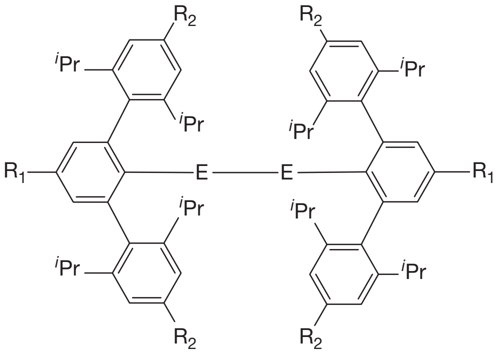


Figure 30 Solid-state structure of **7.2**, gallium terphenyl.

In spite of the steric bulk of the terphenyl substituents, compounds such as **7.1**–**7.3** have proved to be useful as two-electron donors for transition metals and Lewis acids, as shown in Tables 12 and 13 and in Figure 31. Thus, the treatment of the univalent group 13 terphenyl compound with either transition-metal complexes featuring a labile ligand or the strong Lewis acid B(C_6F_5)$_3$ results in the formation of the anticipated complexes. Because the resultant complexes feature the group 13 metal in a dicoordinate bonding environment, some pertinent structural details are presented in Tables 13 and 14 and discussed below.

The composition and selected metrical parameters for reported complexes of univalent group 13 terphenyl donors are presented in Table 12. All of the donor–acceptor adducts feature essentially linear geometries at the dicoordinate group 13 site with bond distances that are consistent with the different sizes of the group 13 elements. It is worth noting that the E—C distance decreases markedly upon complexation – this behavior is somewhat counter intuitive given that bond distances are often correlated with coordination number – however, the observation is as one would anticipate given that the formation of the donor–acceptor complex effectively removes electron density from the group 13 center. Furthermore, as discussed below for related systems, the molecular orbital (MO) associated with the lone pair of electrons on the group 13 element in the (putative) monovalent donor often has a considerable σ-antibonding C–E component; the

Table 11 Selected structural features of dimeric Ar*E compounds



	E	*R₁*	*R₂*	*E—C*	*C—E—E*	*E—E*
7.5[181]	Ga	^{t}Bu	^{i}Pr	2.007–2.053	118.74–136.97	2.431–2.718
7.6[181]	Ga	CF_3	^{i}Pr	1.827–2.044	121.68–159.11	2.603
7.7[185]	In	H	^{i}Pr	2.256	121.23	2.979
7.8[186]	Tl	H	^{i}Pr	2.314	119.73	3.093
7.9[187]	Ga	H	H	2.026	123.15	2.627

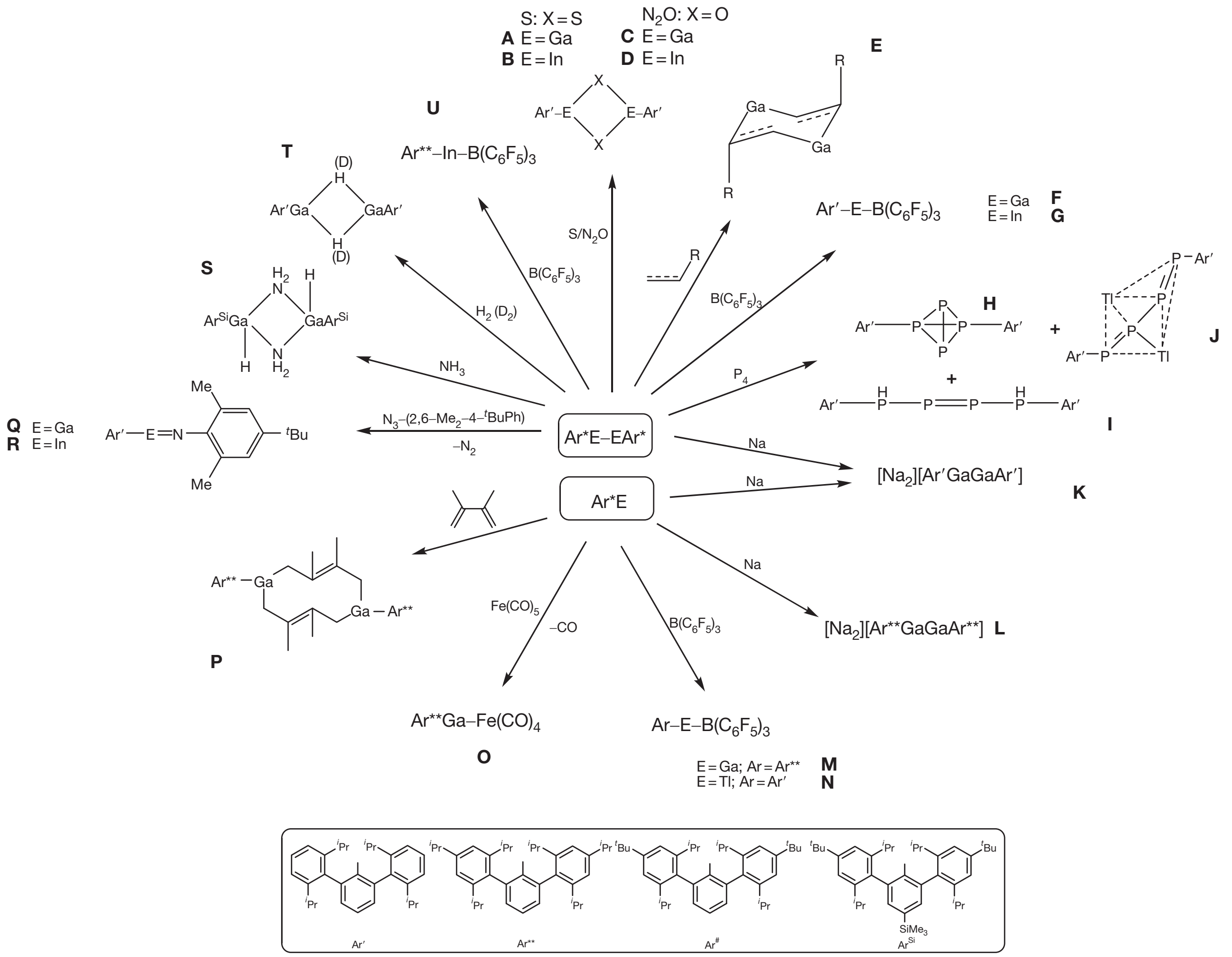


Figure 31 Summary of reported reactivity for Ar*E and Ar*E–EAr* compounds. The various Ar groups (Ar′, Ar*, Ar#, and Ar^{Si}) are given. Data taken from the following work: **A–D**,[188] **E**,[189,190] **F**,[43] **G**,[185] **H–J**,[191] **K**, [43,187] **L**,[43] **M**,[43] **N**,[186] **O**,[43] P,[43] **Q–R**,[192] **S–T**,[193] and **U**.[185]

depopulation of this MO via electron donation to an acceptor results in the shortening of the C—E bond.[181] Although the nature of such a correlation is not necessarily direct because of differences in the steric interactions between the donors and the acceptors, the sum of the C—B—C angles in the $B(C_6F_5)_3$ complexes suggests that the univalent group 13 terphenyl compounds are comparable donors to trialkyl (~337–338°) and triaryl phosphanes (~340°), with the gallium compounds being better donors than the indium or thallium congeners.

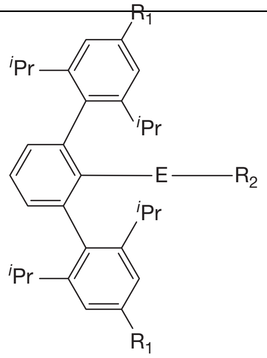
Also included in Table 12 are the imino compounds **7.18** and **7.19** derived from the treatment of univalent gallium or indium terphenyl sources with a bulky terphenyl azide. The resultant compounds still feature low-coordinate group 13 centers with short E—N bonds, distinctly bent geometries at the E and N atoms, and formal multiple bonding between the nitrogen and the metal center. The bent arrangement is in stark contrast to the linear arrangement in corresponding Ar–BN–R compounds[195]; however, such multiple-bonded compounds are examined in detail in Chapter 1.09 and will not be examined in further detail herein.

Although they were not prepared from isolated Ar*E reagents, the metallocene complexes presented in Table 13 are worthy of mention in this section. The one-pot simultaneous reduction of Ar^*ECl_2 and Cp_2MCl_2 (E = Ga, In; M = Ti, Zr, Hf) using either sodium or magnesium as the reductant provides the metallocene complexes **7.20–7.25**.

The metrical parameters for each of the metallocene complexes collected in Table 13 are as one would anticipate. Each of the group 13 centers features an almost linear geometry with C—E distances that are comparable to those of the corresponding 'free' ligand. The examination of MOs generated by computational investigations suggests that the bonding between the Ar*E fragment and the transition-metal features components of both ligand–metal σ-bonding and metal–ligand π-backbonding; such arguments will be examined in more detail below.

A related compound that features terphenyl ligands and dicoordinate gallium centers is the so-called 'metalloaromatic'[199] compound, $[K_2][Ga_4(Ar^*)_2]$, **7.26** (illustrated in Figure 32), obtained by Twamley and Power from the potassium reduction of Ar^*GaCl_2.[200] The compound consists of a planar Ga_4 core and two potassium counter-cations, all of which are encapsulated by the two terphenyl ligands. The interaction between the π-clouds on the ortho-aryl rings of the terphenyl ligands and the potassium cations provides additional stabilization to the

Table 12 Selected metrical parameters for complexes derived from univalent group 13 terphenyl compounds



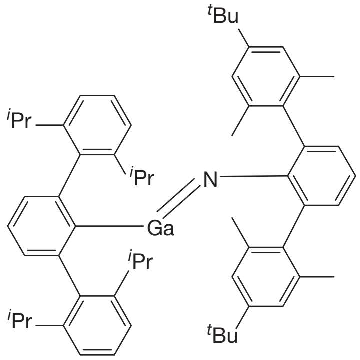
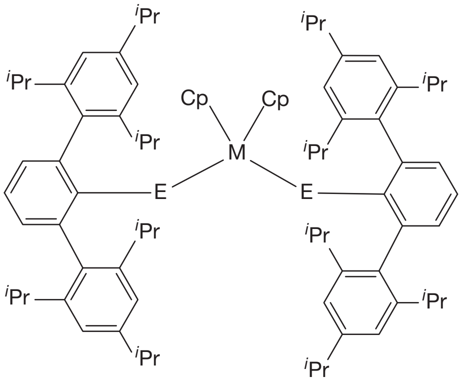
	E	*R_1*	*R_2*	*E–C*	*E–R_2*	*C–E–R_2*	*Σ(CBC)*
7.10[182]	In	^{i}Pr	$Mn(CO)_2Cp$	2.155	2.411	175.38	
7.11[185]	In	H	$B(C_6F_5)_3$	2.138	2.296–2.299	176.22–176.50	338.9–339.8
7.12[185]	In	^{i}Pr	$B(C_6F_5)_3$	2.152	2.322	176.28	337.8
7.13[186]	Tl	H	$B(C_6F_5)_3$	2.165	2.311	173.58	341.0
7.14[194]	Ga	^{i}Pr	$Fe(CO)_4$	1.943	2.225	179.24	
7.15[43]	Ga	^{i}Pr	$B(C_6F_5)_3$	1.943	2.110	173.29	337.2
7.16[43]	Ga	^{t}Bu	$B(C_6F_5)_3$	1.939	2.108	172.97	340.0
7.17[43]	Ga	H	$B(C_6F_5)_3$	1.947–1.949	2.118–2.129	175.51–176.45	337.4–337.6
7.18[169,192]				1.940	1.701	148.24	
7.19[192]				2.127	1.928	142.22	

Table 13 Selected metrical parameters for metallocene complexes of univalent group 13 terphenyl ligands

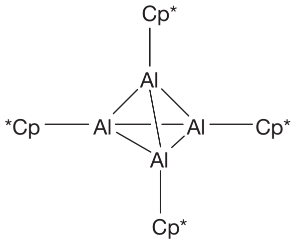
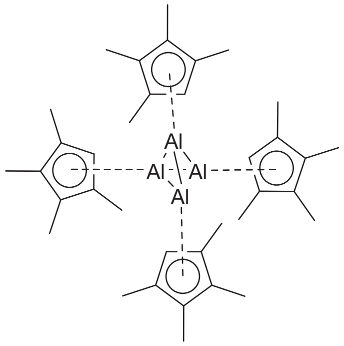
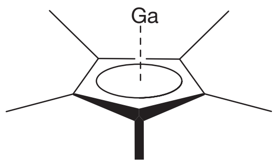
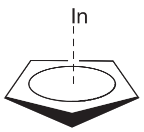
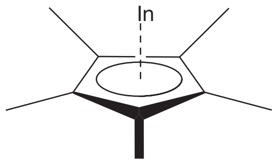


	E	*M*	*E–C*	*E–M*	*E–M–E*
7.20[196]	Ga	Hf	2.021	2.620	171.66
7.21[197,198]	Ga	Zr	2.003	2.635	172.42
7.22[198]	Ga	Ti	2.025	2.492	171.02
7.23[196]	In	Hf	2.192	2.766	171.17
7.24[198]	In	Ti	2.208	2.669	169.97
7.25[198]	In	Zr	2.204	2.792	171.32

complex. Although this compound features dicoordinate gallium centers, it is also a compound that features multiple bonding and catenation; more detailed descriptions of this and other related species are provided in other relevant chapters of this series.

Whereas the bulky terphenyl aromatic groups are sufficiently bulky to stabilize unambiguously monomeric compounds that feature a σ-bond to a carbon atom, the situation for bulky aliphatic is somewhat more complicated. It is clear that large, bulky protecting groups are required for kinetic and thermodynamic stabilization to prevent oligomerization for these types of compounds; however, at least in the solid state, sterically demanding aliphatic substituents have not yet proved to be able to provide monomeric species. However, there are several examples of σ-bound complexes that effectively behave as if they are monomeric R–E species in solution. For example, Uhl's tetrameric compound $[TlC(SiMe_3)_3]_4$ **7.27**, illustrated in **Figure 33**, which features bulky $C(SiMe_3)_3$ ('trisyl') ligands exhibits a very distorted tetrahedral geometry in the solid state. Although this compound is clearly not low coordinate in the solid state, the reactivity observed by the reagent suggests that it dissociates from this tetrahedral arrangement in solution and serves as a source of R–Tl.[201]

Table 14 Structural parameters for some important cyclopentadienyl compounds of monovalent group 13 elements

#	*Structure*	*E—C*	*E—Ct*	*E—E*
8.1[219,220]		2.297–2.378	1.998–2.032	2.767–2.773
8.2[221]		2.300–2.383	1.976–1.997	2.686–2.741
8.3[222]		2.380–2.421	2.081	4.173
8.4[223–225]		2.862–2.983	2.687	
8.5[226,227]		2.581–2.613	2.302	3.943
8.6[228]	CpTl	2.928–3.076	2.753	

Note that although most of these were reported prior to the year 2000, the metrical parameters have been included for comparative purposes.

The other examples of lighter group 13 compounds with $C(SiMe_3)_3$ and related trisilyl ligands are also observed as tetramers with E—E bonds in the solid state and thus the chemistry of such species is detailed in **Chapter 1.01** of this series.[201–207] However, although such clusters are more strongly bound than those of thallium, these lighter congeners also have been used as sources of neutral, two-electron donors of the general form R–E for transition-metal complexes. The transition-metal complexes that result from the ligation of these putative monocoordinate univalent ligands contain dicoordinate group 13 centers; the structural details of such compounds are examined below and many related metal complexes are discussed in **Sections 1.17.2.3.1, 1.17.2.3.4**, and **1.17.2.3.5**. For the trisyl group 13 ligands, prominent examples include Uhl's homoleptic nickel complexes, $Ni(EC(SiMe_3)_3)_4$ (E=Ga, **7.28**;[208] In, **7.29**[209]), each of which features four ER fragments around the metal center. The complexes, which were generated through the reaction of $Ni(COD)_2$ with $[EC(SiMe_3)_3]_4$, each exhibit the anticipated undistorted tetrahedral structure, as illustrated for the gallium analog in **Figure 34**. The Ni—E bond distances (Ni—Ga: 2.170 Å; Ni—In: 2.304 Å) are considerably shorter than other comparable bonds (*vide infra*) and are consistent with the presence of metal—ligand π-backbonding in each case. Uhl and coworkers also synthesized a platinum analog, $Pt(InC(SiMe_3)_3)_4$, **7.30**. The In—Pt distance in the complex of 2.441 Å is, again, much shorter than those observed for other In—Pt bonds.[210] It is also worth noting that the E—C bonds in complexes **7.28** (2.014 Å), **7.29** (2.221 Å), and **7.30** (2.25 Å) are all comparable to or longer than those in the starting tetrameric precursors, as one would anticipate for a situation

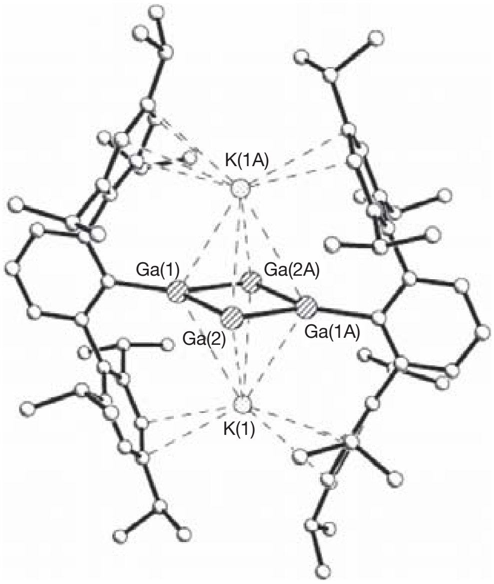


Figure 32 Solid-state structure of $[K_2][Ga_4Ar^*_2]$ **7.26**. Selected bond parameters: Ga—Ga: 2.462 and 2.468 Å; Ga—C: 2.006 Å; Ga(1)—Ga(2A)—Ga(1A): 92.77°; and Ga(2A)—Ga(1A)—Ga(2): 87.23°.

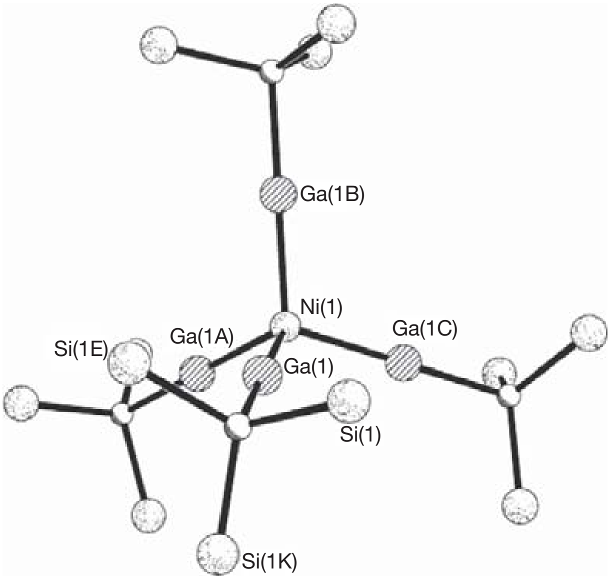


Figure 34 Solid-state structure of $Ni[GaC(SiMe_3)_3]_4$. Methyl groups on Si have been omitted for clarity. Si—Ga—Ni: 180.00°.

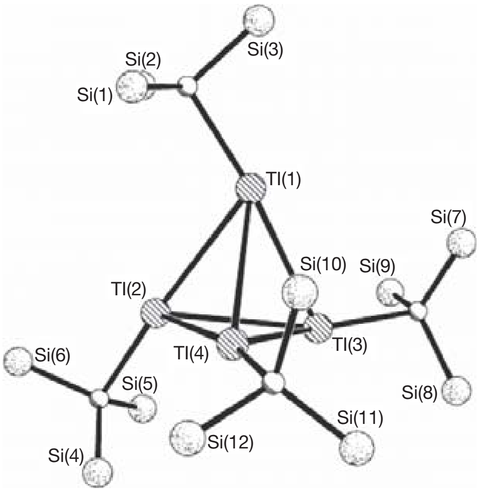


Figure 33 Solid-state structure of $[TlC(SiMe_3)_3]_4$. Select bond distances Tl—C: 2.333–2.383 Å; Tl—Tl: 3.322–3.638 Å. Methyl groups have been omitted for clarity.

in which the E–C σ*-orbital is populated by metal—ligand π-backbonding.

A related tetrahedral platinum–gallium complex prepared by the reaction of the Pt(0) source $(DCPE)Pt(H)(CH_2{}^tBu)$ with $[GaC(SiMe_3)_3]_4$ (DCPE, 1,2-bis(dicyclohexylphosphino)ethane) was reported by Fischer and coworkers and incorporates two $GaC(SiMe_3)_3$ fragments on the metal in addition to a DCPE ligand which occupies the other two binding sites in an κ^2 fashion.[211] The $(\kappa^2\text{-DCPE})Pt(GaC(SiMe_3)_3)_2$ complex **7.31** has Pt—Ga bonds of 2.315 and 2.318 Å and Ga—C bonds of 2.058 and 2.060 Å.

An interesting ruthenium complex bearing a dicoordinate group 13 trisyl ligand was also synthesized by the same group through the reaction of $[Cp^*RuCl]_4$ with 3 equiv. of $[GaC(SiMe_3)_3]_4$ and structurally characterized. The resultant complex has the formula $[RuCp^*(InC(SiMe_3)_3)_3Cl]$, **7.32**, but it actually contains only one dicoordinate indium center.[212] The chloride anion interacts strongly with the formally empty orbitals on two of the indium ligands to produce a bridged (trisyl)In–μ^2-Cl–In(trisyl) 'chelate' with tricoordinate indium centers that have In—Ru distances of 2.588 and 2.589 Å, and In—C distances of 2.258 and 2.261 Å. By contrast, the ligand that features the dicoordinate indium has an In—Ru distance of 2.510 Å and an In—C distance of 2.210 Å.

One final interesting and unique compound that should be noted in this section is Lappert's $[Li]_2[Tl(CHSiMe_3SiMe(OMe)_2)]_2$, **7.33**, which is a lithium salt of a univalent thallate anion in which each thallium center is σ-bonded to two carbon fragments that bear silyl groups.[213] The salt was prepared as a redistribution product obtained by the treatment of the lithiated disilyl anion with TlCl. The relative stability of thallium(I) is sufficient to allow for the formation of such an electron-rich anion, for which there are no analogs lighter congeners. As illustrated in Figure 35, the structure of the salt, which occurs in two different polymorphic forms, consists of a bent dicoordinate thallium center with Tl—C distances ranging from 2.512 to 2.580 Å, and C—Tl—C angles ranging from 89.6° to 91.1°. The lithium counter-cation is situated in close proximity to the methoxy groups on the silane moieties and, as a result, the compound dimerizes in the solid state, bridging through the cations.

1.17.2.2.2 Cyclopentadienyl and arene ligand: sandwich, inverse-sandwich, and open-face sandwich cyclopentadienyl compounds

Cyclopentadienyl ligands (Cp′, $C_5R^1R^2R^3R^4R^5$) have the ability to function as ligands ranging from two-electron σ-donors to six-electron donors that provide both σ- and π-electron densities. Furthermore, the substituents about the C_5 ring may be

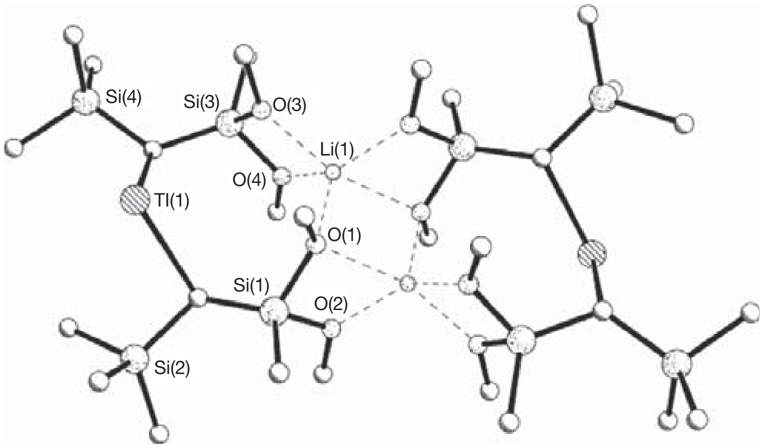


Figure 35 Solid-state structure of $[Li]_2[Tl(CHSiMe_3SiMe(OMe)_2)]_2$ **7.33**. Selected metrical parameters: Tl—C: 2.512–2.580 Å; C—Tl—C: 89.6–91.1°.

chosen to modify the steric and electronic properties of the ligands; such steric and electronic flexibility has been exploited to prepare complexes of Cp′ groups with elements from all blocks of the periodic table. Main group cyclopentadienyl complexes have been investigated for many decades and, because of their ability to act as steric shields and to function as σ- and π-donors, such ligands have proved particularly suitable for the stabilization of E(I) species. Major reviews by Jutzi in 1999 and 2000 described the preparation and chemistry of such main group Cp′ compounds, including synthesis, reactivity, and MO treatments of the bonding for a variety of ECp compounds that predate the time frame for this chapter.[214,215]

Given the considerable number of low-valent cyclopentadienyl compounds that have been prepared, this category is further divided into different sections on the basis of the nature of the bonding environment about the group 13 center that is observed. Finally, it should be reemphasized that although most of the cyclopentadienyl ligands in the following sections are bonded in an η^5-manner, all of the Cp′ ligands in this work are treated as occupying a one-coordination site regardless of the nature of their interaction with the group 13 element and, similarly, we define η^6-arene complexes to be pseudo-monocoordinate.

This section focuses on: (1) compounds in which one metal center is bound to two Cp′ ligands, also known as a 'sandwich' complex; (2) compounds in which two metal centers are bound to opposite sides of a single Cp′ ring creating an 'inverse-sandwich' complex; and (3) 'open-face sandwich' compounds in which one Cp′ ligand is attached to the metal center. Because arenes are isolobal with Cp′ ligands, a selection of related arene complexes of monovalent group 13 ions is also included in this section. It should be noted that there is a very extensive history of group 13 arene complexes[216] and the chemistry of such complexes has been reviewed recently.[217,218]

1.17.2.2.2.1 Synthesis

The preparation of monovalent group 13 cyclopentadienyl compounds has generally been accomplished in one of two ways. In most cases, the compounds were first prepared through the ion-metathesis reaction of a low-valent group 13 halide with a metallated cyclopentadienide salt (e.g., Cp′Li or Cp'_2Mg). However, because the low-valent group 13 halides for aluminum and gallium are not generally available, the more generally used preparative route entails the reduction of a trivalent precursor of the general form $Cp'EX_2$. It should be noted that the polymethylcyclopentadienyl aluminum examples exist as tetramers in the solid state while those of gallium and indium exist as distorted-octahedral hexamers in the solid state; these oligomers appear to dissociate in solution and the reactivity of the compounds is consistent with the presence of monomeric Cp*E fragments. All of the simple univalent group 13 cyclopentadienyl complexes listed in Table 14 feature η^5-bonded Cp′ rings and, in spite of their larger steric bulk, the presence of more electron-rich substituted Cp′ groups results in shorter Cp′—E distances.

It should be noted that during the revision of this chapter, a convenient preparation of CpGa (**8.7**) from 'GaI' and NaCp at low temperature was reported; the compound is only stable at low temperature and can form donor–acceptor complexes similar to those of Cp*Ga.[229]

Macdonald and Cowley presented a detailed computational examination of the bonding and electronic structures of model complexes for several univalent group 13 compounds, including the half-sandwich compounds CpE, Cp*E (E=B, Al, Ga, In).[230] More recently, Frenking and Rayón have published an in-depth study, including comprehensive energy decomposition analyses, of several classes of main group cyclopentadienyl complexes, including those of the general form ECp′ (E=B, Al, Ga, In, Tl) which provide details regarding the structures, bonding energies, orbital contributions, and other fundamental aspects of these complexes.[231] Overall, these calculations confirm that although much of the interaction between the Cp groups and the metal in such complexes is electrostatic, there is a sizeable covalent component. Furthermore, the highest occupied molecular orbital (HOMO) in most cases is the orbital attributable to the 'lone pair' on the metal and corroborates the use of such compounds as ligands; examples of the complexes formed from such ligands are treated in Sections 1.17.2.2.4 and 1.17.2.3.5 (*vide infra*).

In addition to the ligand chemistry displayed by Cp′E molecules, there is also a vast amount of oxidation, oxidative addition, and cycloaddition chemistry similar to that described above for the analogs β-diketeniminate univalent group 13 compounds. Furthermore, because of their volatility, many of these cyclopentadienides have also proved to be useful precursors for the formation of materials containing group 13 elements. Essentially all of this reactivity was reported prior to the year 2000 and has already been reviewed.[18,19,214,215]

A large variety of related sandwich and half-sandwich compounds of formally low-coordinate univalent group 13 elements bonded to cyclopentadienyl and/or arenes have also been isolated. The preparative routes to many of these compounds are similar and often involve the protonolytic cleavage of a small volatile molecule – for example, Cp′H from Cp′E precursors – to afford the desired products. Arene-complexed group 13 cations are often observed when such reactions are performed in aromatic solvents. The syntheses of these compounds are presented in **Table 15** and important metrical parameters are given in **Table 16**.

Although most of the syntheses listed above are accomplished through protonolysis, the synthesis of compounds **8.11**–**8.13** takes advantage of the redox reaction of the silver salt of the bulky fluoridoaluminate anion with gallium metal in order to generate the Ga(I) products. This approach was required because synthetic attempts that employed 'GaI' as the starting material were found to lead to undesired products.[234] The preparation of **8.14** also involved a redox reaction; however, in this case, the ferrocene reagent effected the reduction of $GaCl_3$ formally to Ga_2Cl_4, which adopts the mixed-valent ionic form $[Ga][GaCl_4]$ in the presence of aromatic donors such as ferrocene. This reaction can also be accomplished directly by the treatment of ferrocene with Ga_2Cl_4.[235]

It is also noteworthy that multidecker sandwich thallium(I) complexes are readily formed either through the addition of Cp anions (for **8.20**) or using the tripodal titanium amide ligand illustrated for complex **8.23**.

1.17.2.2.2.2 Structural features

Again, all of the complexes feature η^5-bonded cyclopentadienyl groups and/or η^6-bonded arenes to the univalent group 13 element. Almost all of the sandwich complexes also feature 'bent' arrangements of the π-donors rather than parallel arrangements. Such geometries are often attributed to the presence of a stereochemically active pair of electrons on the metal center; however, the presence of relatively close contacts between the cations and corresponding anions also contributes to the observed structures.[216,217] The distances between a given metal and the corresponding π-donor ligand follow the anticipated trends: inverse-sandwich compounds in which one ligand interacts with two metals exhibit longer distances than those of the corresponding Cp′E[244]; anionic cyclopentadienyl ligands form shorter bonds than do neutral arene donors; more electron-rich donors tend to form shorter bonds than less electron-rich ligands.

It is noteworthy that only for thallium(I) has it proved to be possible to generate anionic bent-metallocene complexes such as **8.19** through the reaction of a neutral Cp′Tl compound with a source of cyclopentadienyl anions. Salts of the simplest such pseudo-dicoordinate complexes were first obtained by Wright and coworkers in the early 1990s.[240,245] Attempts to generate the lighter analogs often results in disproportionation or decomposition of the group 13 precursor.

While the reactivity of most of the sandwich compounds listed in **Table 15** has not been examined in great detail, compounds such as **8.8** and **8.11**–**8.13** have proved to be rarely useful sources of Ga^+ ions, in particular for transition-metal complexes.[232,234,246] Furthermore, the complexes with the extremely noncoordinating fluorinated aluminate anions such as **8.11**–**8.13** and **8.18** have allowed for the isolation of some unprecedented stable phosphane complexes of univalent gallium and indium.[234,239]

1.17.2.2.3 Phospholyl ligands

Phospholyl ligands are a class of monoanionic ligands closely related to cyclopentadienyl ligands in which C–R fragments have been formally replaced by an isovalent P center – in fact, such groups are also often called 'phospha-cyclopentadienyl' ligands.[247–249] In light of this close relationship, phospholyl complexes of univalent group 13 ions are included in this subsection about carbon-based ligands.

1.17.2.2.3.1 Synthesis

The preparation of all reported group 13 phospholyl compounds is generally very similar to each other. The treatment of an alkali metal phospholyl salt with the appropriate group 13 monohalide results in the formation of the target group 13 phospholyl complex with the elimination of the corresponding alkali metal halide salt. A representative reaction scheme is presented below for the P_3-phospholyls (**Figure 36**).

It should also be noted that in some cases the phospholyl group is in effect generated during complex formation. For example, the treatment of $[Li][(MeP)P_2(C^tBu)_3]$ with EX results in the spontaneous extrusion of $(PMe)_n$ and generates phospholyl complexes of the general form $[P_2(C^tBu)_3]E$.[250]

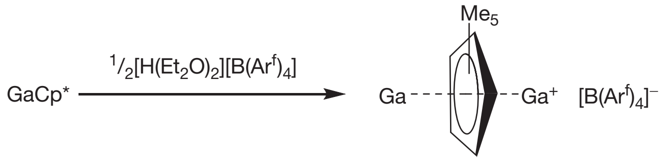
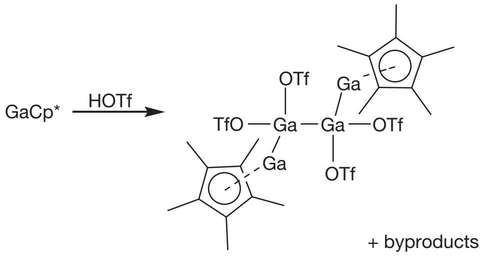
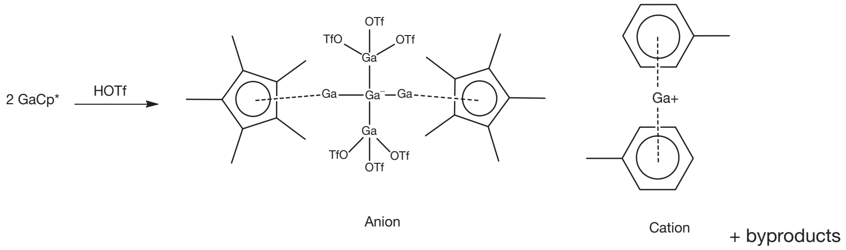
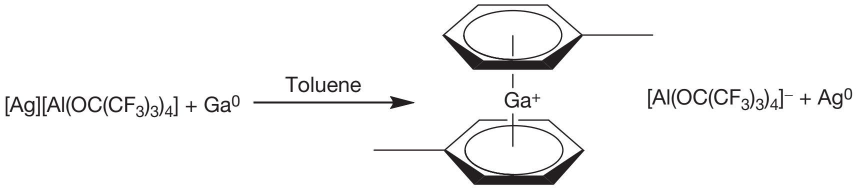
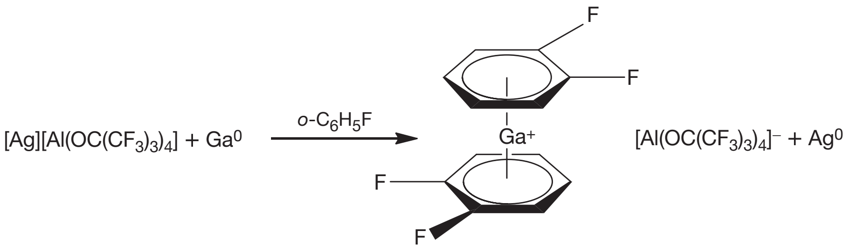
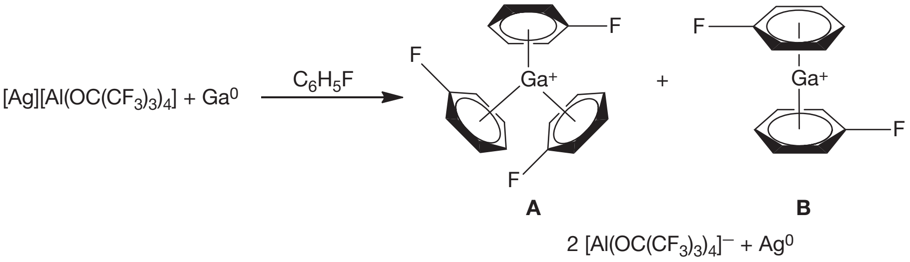
1.17.2.2.3.2 Structural features

As with the analogs Cp′E complexes, the complexes of phospholyl ligands with univalent group 13 all exhibit η^5-bonded phospholyl groups. Important metrical parameters for structurally characterized complexes are presented in **Table 17**.

The bulky ^{t}Bu groups adjacent to the phosphorus centers are typically employed to protect the lone pair and promote η^5-coordination rather than σ-coordination.[258] Although the presence of the multiple ^{t}Bu groups about the ligands also appears to decrease the degree of oligomerization of the group 13 complexes in the solid state, long-range dimers and 1D-coordination-polymer assemblies are observed. In spite of the foregoing, it should be noted that the thallium derivative **9.2**, which contains an unsubstituted phospholyl ligand, binds in an η^5-fashion. Perhaps expectedly, the complex forms a 1D-coordination polymer in the solid state with alternating Tl cations and phospholyl ligands as illustrated in **Figure 37**.

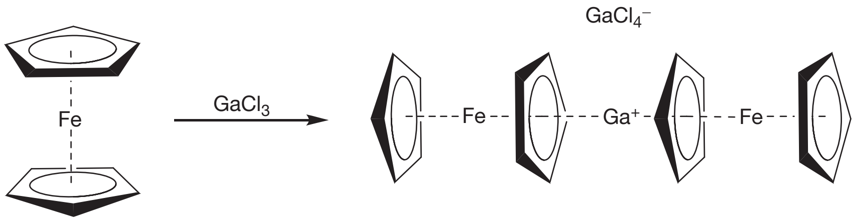
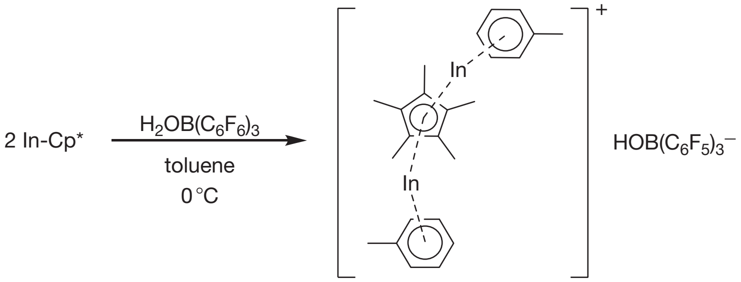
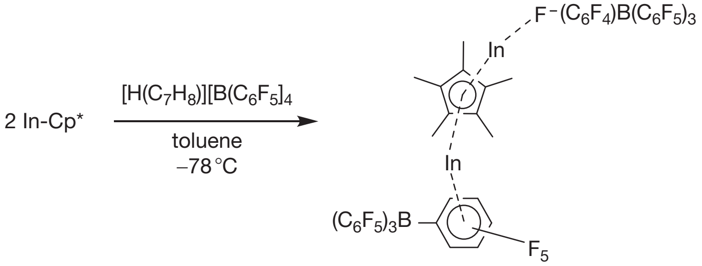
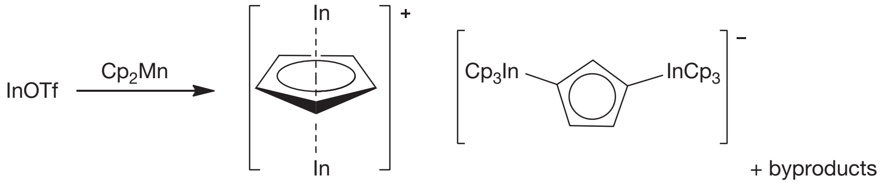
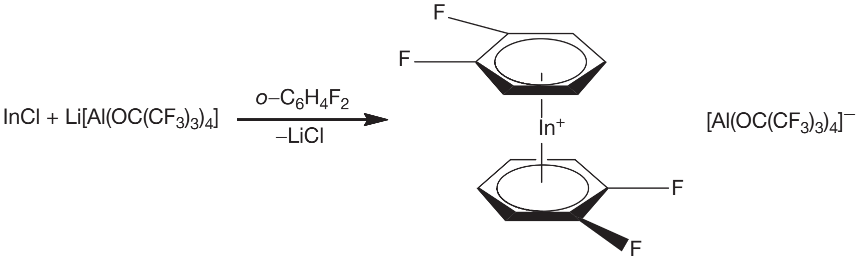
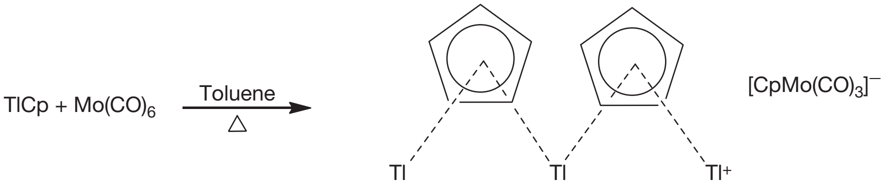
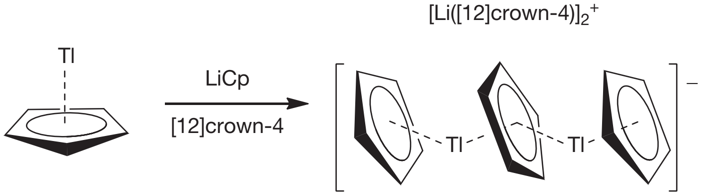
As presented in **Table 18**, the number of phosphorus atoms in the five-membered ring ligand has a drastic effect on the distance between the centroid and the metal center. For example, compounds **9.1** and **9.6** only differ in that there are two additional phosphorus atoms in the ring; however, an increase in the ring centroid to gallium distance of over 0.12 Å is observed because of the alteration. Such elongations are attributed to the observation that the presence of the phosphorus atom has an overall electron-withdrawing effect in comparison to the CR fragments.[248]

Table 15 Synthetic approaches to sandwich and inverse-sandwich complexes of univalent group 13 ions

	Syntheses
8.8[232]	
8.9[233]	
8.10[233]	
8.11[234]	
8.12[234]	
8.13[234]	

(*Continued*)

Table 15 (Continued)

	Syntheses
8.14[235]	
8.15[236]	
8.16[237]	
8.17[238]	
8.18[239]	
8.19[225]	
8.20[240]	

(*Continued*)

Table 15 (Continued)

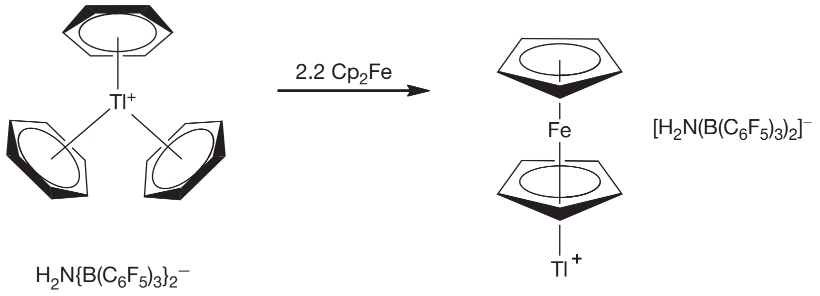
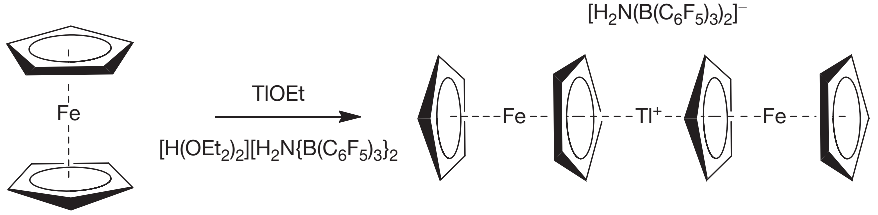
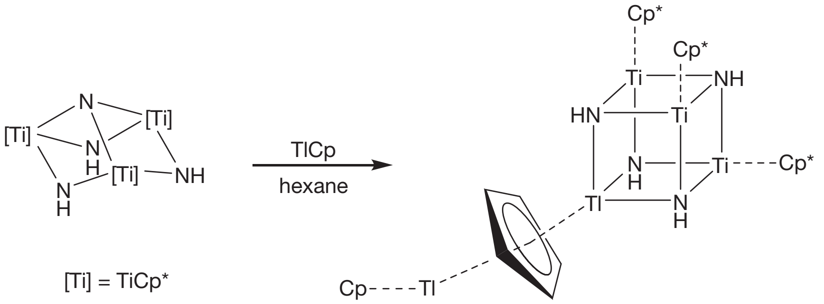
	Syntheses
8.21[241]	
8.22[242]	
8.23[243]	

Table 16 Selected metrical parameters for sandwich-like univalent group 13 complexes

	E—C	*E—Ct*	*E—E*	*E—Ct—E*	*Ct—E—Ct*
8.8	2.505–2.563	2.228–2.237		178.21	
8.9	2.092–2.247	1.826–1.839	2.435		
8.10 anion	2.202–2.247	1.861–1.874	2.441–2.458		
8.10 cation	3.033–3.181	2.775–2.790			126.80
8.11	2.864–3.094	2.627–2.642			137.70–139.89
8.12	2.873–3.139	2.658–2.724			125.48–158.98
8.13A	3.029–3.491	2.741–3.048			112.41–117.36
8.13B	2.913–3.084	2.668–2.669			141.66
8.14	2.998–3.346	2.825–2.999			110.31
8.15	2.680–2.839	2.435–2.528		175.95	
8.16	2.676–2.773	2.435–2.461		175.30	
8.17	2.866–2.986	2.659		180.00	
8.18		2.878–2.894			154.86
8.19	2.819–3.499	2.581–3.199		110.25–119.00	
8.20	2.830–3.152	2.631–2.831		175.06	133.35–134.97
8.21	2.967–3.134	2.794		174.79* *with Fe	
8.22	3.053–3.285	2.931			180.00
8.23	2.707–3.226	2.582–2.874			171.51

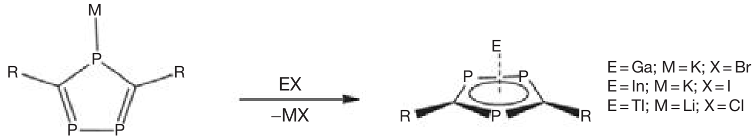


Figure 36 Synthetic approach for group 13 phospholyl open-face sandwich complexes.

1.17.2.2.3.3 Reactivity

Although one may anticipate that the chemistry of such univalent group 13 phospholyl complexes will be similar to that of the analogs cyclopentadienyl complexes, there have been almost no reactivity studies reported for such species. In fact, the only reported reactivity is the formation of the transition-metal complex (η^5-2,5-^{t}Bu$_2$C$_4$P)Ga–Cr(CO)$_5$ through the treatment of **9.1** with Cr(CO)$_5$COE[251] This complex features a Ga—Cr bond distance of 2.390 Å, which is comparable to the distance of 2.405 Å observed for the corresponding Cp*Ga–Cr (CO)$_5$, as described in **Section 1.17.2.3.5**.

1.17.2.2.4 Donor–acceptor complexes of Cp′E ligands

As with many of the low-valent group 13 complexes described above, the presence of a 'lone pair' on the triel center in Cp′E complexes allows them to function as Lewis bases. In fact, the relative stability and convenient (and early) preparation of Cp′E compounds rendered them suitable to be used as donors in the first examples of such donor–acceptor complexes. Furthermore, because compounds of trivalent group 13 elements are the classic examples of Lewis acids, the development of group 13 donors allowed for the ready preparation of mixed-valent group 13 donor–acceptor complexes. This class of complexes that feature elongated 'piano stool' arrangements has recently been reviewed by Cowley[259] and the bonding in such donor–acceptor complexes has been elucidated and reviewed by Frenking.[260]

1.17.2.2.4.1 Synthesis

The preparation for many of the triel–triel donor–acceptor complexes is straightforward. Treatment of the appropriate Cp′E donor with the chosen E′R$_3$ acceptor produces the target Cp′E–E′R$_3$ complex rapidly and in quantitative yield.[261–265] As suggested above, the Cp′E species need not be monomeric in the solid state and examples with several different substitution patterns on the Cp′ ligand have been obtained. However, it must be noted that not all group 13 Lewis acids are suitable for use. While tris(fluoroaryl)-substituted acceptors generally appear to work, the attempted use of group 13 trihalides usually results in decomposition or redox reactions.

It should be noted that main group Lewis acids featuring group 2 metals have also proved to be suitable acceptors for such complexes; these are also prepared by the reaction of equimolar quantities of the donor and acceptor fragments.[266]

1.17.2.2.4.2 Structural features

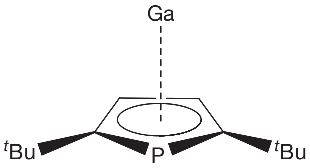
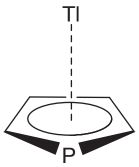
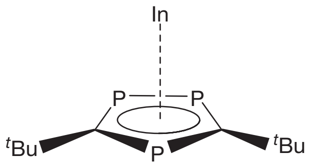
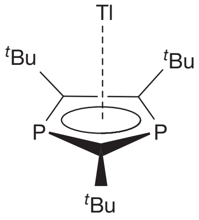
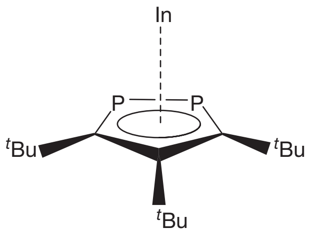
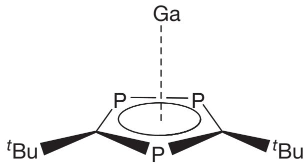
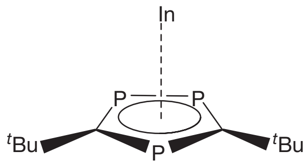
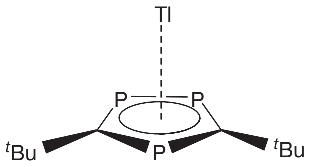
Almost all of the reported donor–acceptor complexes containing univalent cyclopentadienyl donors contain Cp*E fragments and important metrical parameters for such compounds are presented in **Table 18**.

Each of the MR$_3$ fragment goes from being formally trigonal planar in the starting material to a tetrahedral geometry upon the formation of the dative bond from the Cp′E compound. As indicated previously, the magnitude of the deviation from planarity (as measured by the sum of the C—E—C angles in the acid fragment) has been used to assess the relative strength of the donor. Such analyses suggest that Cp*E donors are comparable to Ph$_3$P for E = Al and Ga and weaker donors than trialkylphosphanes. The formation of the dative bond also has a pronounced effect on the other metrical parameters within the resultant complex. Compared to their respective starting materials, a considerable decrease in the average E—Cp* distance is observed in the univalent donor fragments. This change is attributable to the depopulation of the 'lone pair' orbital, which has some Cp*—E antibonding character, and to the increased partial positive charge on the group 13 center in the donor, which would also produce a closer contact to the Cp*-ring as the effective size of the element effectively decreases.[230] It is also worth emphasizing that although most of the donor–acceptor complexes listed in **Table 18** feature nearly linear Ct–E$_1$–E$_2$ fragments, very significant deviations are observed for complexes such as **10.10**–**10.12**, in which the η^1-Cp* on the acceptor fragment appears to interact with the donor group 13 element. Similar interactions of the donor triel with, for example, F atoms from the acceptor fragment also result in nonlinear arrangements in complexes such as **10.13**.

It is noteworthy that the complexes prepared by Piers and coworkers featuring 9-borafluorene fragments (**10.13**–**10.15**) were made in order to determine if a formal metal-to-ligand two-electron charge transfer would occur. Such a process would formally produce an aluminum(III) center and a dianionic 9-borafluorene fragment that is isoelectronic with a Cp′ ligand. The resultant product would be a neutral analog of the aluminocenium cations [Cp′$_2$Al]$^+$ described in **Section 1.17.3.3** (*vide infra*). However, the structural parameters and electronic structures of **10.13**–**10.15** indicate that the donor–acceptor description of the complexes is the most appropriate and that there is no indication of such a charge transfer having occurred.[268]

Finally, it should be noted that although there are no stable univalent boron cyclopentadienyl compounds of the type Cp′B, coordination complexes analogs to those described above have indeed been isolated. The compound Cp*B–BCl$_3$ (**10.18**) is best prepared through the treatment of Cl$_2$BBCl$_2$ with 1 equiv. of Cp*–SiMe$_3$[269]; the rearrangement of the presumed intermediate Cp*ClBBCl$_2$ to the donor–acceptor isomeric form has been computed to be favorable.[270] The related complex Cp*B–BCl$_2$SiCl$_3$ (**10.19**) was obtained through the reaction of Cp*$_2$Si with Cl$_2$BBCl$_2$ (**10.18** was first observed as a byproduct in this reaction) again after ligand redistribution and structural rearrangement. Complexes **10.18** and **10.19** feature B—B bonds of 1.681 and 1.687 Å, respectively, Ct—B distances of 1.260 and 1.289 Å, respectively, and exhibit Ct—B—B angles of 179.35° and 176.55°. Thus, in spite of the alternative synthetic route, the metrical parameters and

Table 17 Selected metrical parameters for univalent group 13 phospholyl complexes

	Structure	*C—E*	*E—P*	*E—Ct*
9.1[251,252]		2.464–2.531	2.652	2.147
9.2[253]		2.973–3.267	3.163–3.299	2.810–2.847
9.3[254]		2.812–2.839	2.904–2.912	2.472
9.4[250]		3.093	3.170–3.325	2.815–2.894
9.5[255]		2.811–2.839	2.904–2.912	2.501
9.6[256]		2.680	2.782–2.796	2.261
9.7[257]		2.982	3.036–3.109	2.598
9.8[256]		3.216	3.212–3.349	2.845

structural features of these complexes are exactly as one would anticipate on the basis of the structures of the heavier analogs.

1.17.2.3 Transition-Metal Complexes

In light of the electron-rich nature of the univalent group 13 compounds described in many of the previous sections in this chapter, it will come as no surprise that such compounds have been used extensively as ligands for transition metals. For some classes of group 13 donors, such as the monocoordinate terphenyl complexes, the resultant transition-metal complexes still contain dicoordinate triel centers and were described within that section. There are, however, dozens of transition-metal complexes synthesized from Cp′E donors that are described below. Furthermore, there are many complexes that contain low-coordinate group 13 fragments that have been formed in the process of complex formation rather than from a stable monomeric E^I source. Such complexes are presented in the following sections; the first sections examine complexes of borylene ligands (which must be generated *in situ*) and the following sections are subdivided on the basis of the overall composition of the complexes. The nature of the bonding between low-coordinate species of many types, including that of univalent group 13 donors, and transition-metal fragments has been reviewed in detail.[271,260]

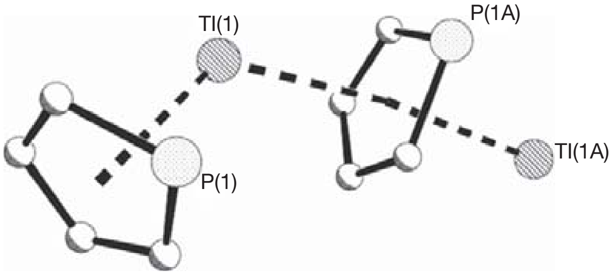
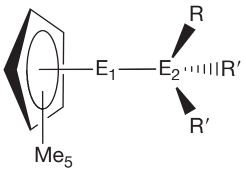


Figure 37 Solid-state structure of **9.2**, $[PC_4H_4][Tl]$, showing the polymeric chains of alternating phospholyls and thalliums.

1.17.2.3.1 Borylene ligands on transition-metal complexes

Because of their high reactivity, borylenes (also called boranediyls) of the general form RB have not yet been isolated as stable, monomeric species. In fact, such fragments have only proved isolable in compounds in which they are coordinated to some sort of acceptor molecule, which is typically a transition-metal complex, and nearly all examples of borylene fragments have actually been generated in a metal-coordinated form. For example, the first structurally authenticated terminal borylene complexes reported were $Cp^*B–Fe(CO)_4$[272] and

Table 18 Selected metrical parameters for donor–acceptor complexes of Cp*E ligands with main group acceptors



	E_1, E_2	R, R'	E_1—Ct	C—E_1	E_1—E_2	Ct—E_1—E_2	ΣC—E_2—C
10.1[261]	Al, B	$R,R' = C_6F_5$	1.802	1.633–1.637	2.168	172.89	339.7
10.2[262]	Al, Al	$R,R' = C_6F_5$	1.810	2.161–2.201	2.591	170.10	333.0
10.3[45,263]	Ga, B	$R,R' = C_6F_5$	1.865	2.217–2.238	2.161	176.65	342.1–342.2
10.4[264]	Ga, Al	$R,R' = C_6F_5$	1.865	2.172–2.269	2.523	170.55	338.3–344.6
			1.860		2.508	160.68	
10.5[265]	Al, Al	$R,R' = {}^tBu$	1.858	2.209–2.224	2.689	175.02	348.2
10.6[265]	Ga, Al	$R,R' = {}^tBu$	1.914	2.236–2.268	2.629	174.30	351.3
10.7[265]	In, Al	$R,R' = {}^tBu$	2.173	2.451–2.499	2.843	170.00	353.1
10.8[265]	In, Ga	$R,R' = {}^tBu$	2.187	2.462–2.505	2.845	170.25	353.9
10.9[265]	Al, Ga	$R,R' = {}^tBu$	1.863	2.198–2.221	2.620	175.49	348.5
10.10[263]	Ga, Ga	$R = \eta^1\text{-}C_5Me_5$ $R' = Cl$	1.939	2.174–2.414	2.425	133.86	
10.11[263]	Ga, Ga	$R = \eta^1\text{-}C_5Me_5$ $R' = I$	1.916	2.184–2.376	2.438	137.27	
10.12[267]	Al, Al	$R = AlCp^*$ $R' = I$	1.828–1.838	2.144–2.245	2.522–2.530	147.35–152.45	
10.13[268]	Al, B	$R = C_6F_5$ $(R')_2 = 2,2'\text{-}C_{12}F_8$	1.782	2.146–2.165	2.115	160.96	333.0
10.14[268]	Al, B	$R = Me$ $(R')_2 = 2,2'\text{-}C_{12}F_8$	1.814–1.817	2.167–2.202	2.149–2.152	160.87–162.76	333.1
10.15[268]	Al, B	$R = Ph$ $(R')_2 = 2,2'\text{-}C_{12}H_8$	1.809	2.176–2.181	2.135	164.12	343.5
10.16[266]	Ga, Ca	$R = Cp^*$ $R' = N/A$	1.990	2.316–2.338	3.183	173.31	
10.17[266]	Ga, Sr	$R = Cp^*$ $R' = \eta^1\text{-}THF$	2.003	2.319–2.357	3.435	175.15	

$(Me_3Si)_2NB–W(CO)_5$[273]; each of these complexes was generated by the *in situ* reduction of the corresponding boron(III) dihalide (RBX_2) with the alkali metal salts of the appropriate dianionic transition-metal carbonyl (i.e., $[K]_2[Fe(CO)_4]$ or $[Na]_2[W(CO)_4]$). As such, the authors have chosen to treat transition-metal borylene complexes in their own subsection. Furthermore, it must be noted that the majority of the borylene complexes discussed in this chapter feature a coordinated boron atom that is also multiple bonded to a nitrogen or oxygen atom; the lone pair(s) of electrons on the nitrogen/oxygen atom is able to populate one (or both) of the formally vacant 2p π-type orbitals on the boron, alleviating electron deficiency. In this context, many of these compounds noted herein may also be described in **Chapter 1.09** so a detailed discussion of the compounds is not warranted. Furthermore, because the boron center is also directly attached to a transition metal, π-backbonding from the metal to the ligand is also a potential source of electrons for the electron-deficient boron center.[274,275]

The large and expanding field of transition-metal borylene complexes has been repeatedly and comprehensively reviewed by Braunschweig; therefore, this section aims to provide general structural information regarding these complexes. More in-depth information about these types of complexes and other related boron–transition-metal complexes, including bridged borylenes,[276] borane to borylene transformations,[277] fluoroborylenes,[278] and general bonding and chemistry,[279–284] is available in the reviews and the literature cited therein.

1.17.2.3.1.1 Synthesis

As indicated above, the unavailability of stable borylene sources requires that the initial preparation of borylene ligands be accomplished in the coordination sphere of a transition metal – these are sometimes called ‘first-generation’ borylene complexes.[283] Typically, the double salt elimination reaction of a suitably substituted dihaloborane with an alkali metal salt of a dianionic transition-metal complex results in the formation of the terminal borylene complex, as illustrated in **Figure 38**. This reaction involves the formal reduction of the boron to the +1 oxidation state and during the generation of the coordinated neutral BR ligand. The analogs dimetalloboride complexes, featuring boron atoms bound only to metals, have been prepared in a similar manner using a $Cp^*Fe(CO)_2BCl_2$ precursor (i.e., the R group is a transition-metal complex). Alternatively, such complexes have been prepared by either halide abstraction or alkali metal reductions of dimetallo-haloborane precursors. The related anionic iminoboryl and oxoboryl ligands are also prepared *in situ* in the coordination sphere of a late transition metal. Again, an appropriately substituted dihaloborane is employed as the source of the boron fragment. The production of the anionic ligands results from an initial oxidative addition of the metal into a boron—halogen bond, followed by the elimination of 1 equiv. of halosilane to generate the boron—element triple bond.

It is noteworthy that many other transition-metal borylene complexes have subsequently been prepared using the ‘first-generation’ complexes, particularly those group 6 pentacarbonyl fragments which are used as borylene transfer agents under photolytic conditions.[282]

1.17.2.3.1.2 Structural features

Important metrical parameters for transition-metal complexes of iminoboryl and oxoboryl ligands are presented in **Table 19**. Those for complexes of boride ligands are collected in **Table 20**, and the values for borylene complexes are presented in **Tables 19–21**.

There are two major factors that affect the B—M bond distance: the nature of the substituent directly attached to the boron center as well as the nature of the other substituents on the transition metal (in certain cases, the ligand that sits *trans* to boron may be particularly important). Numerous computational studies have demonstrated that although the nature of the bonding between the transition metal and the boron center is considerably ionic in character, the amount of metal—ligand π-backbonding is strongly influenced by the substituent on boron.[230,290–293] In effect, π-donor substituents can populate the formally vacant orbitals on B and decrease the amount of backbonding and thus produce a longer M—B bond. For example, complex **11.11** has by far the smallest B—Pt distance at ca. 1.859 Å of any of the compounds in **Table 19** and features an aromatic mesityl group on the boron atom. Because the mesityl group is not an effective π-donor, backbonding from P to B provides for a short B—M bond. In contrast, compounds such as **11.1–11.7**, which feature very effective π-donor substituents (imido and oxo groups), all exhibit much longer Pt—B distances. As illustrated in **Figure 39**, the linear arrangement of the imido fragment in **11.1** is consistent with its being characterized as a π-electron donor to both formally vacant orbitals on the B atom. The coordination of the Lewis acid at the oxo site in complexes **11.8** and **11.9** results in a decrease in O—B bonding, as evidenced by the increased distance, and thus allows for more metal-to-ligand backbonding which provides a shorter Pt—B bond. The presence of more effective π-acceptor ligands, such as CO, on the transition-metal fragment also reduces the amount of metal-to-ligand backbonding, as will be illustrated for the complexes in **Table 21**.

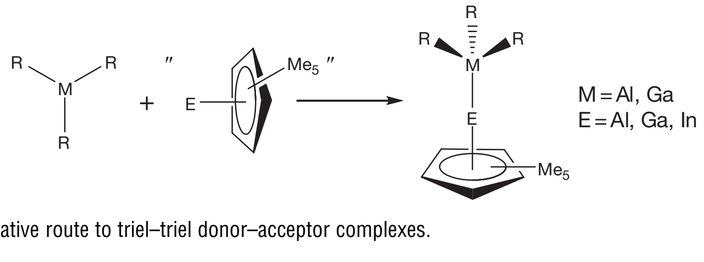
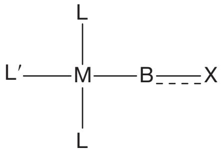
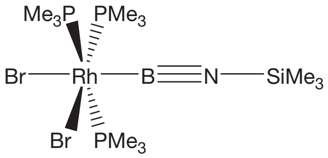


Figure 38 Most general preparative route to triel–triel donor–acceptor complexes.

Table 19 Structural characteristics of iminoboryl, oxoboryl, and arylborylene complexes



	L	*L′*	*M*	*X*	*B—M*	*B—X*	*M—B—X*
11.1[285]	PCy_3	Br	Pt	$NSiMe_3$	1.960	1.260	178.77
11.2[285]	PCy_3	Br	Pd	$NSiMe_3$	1.958–1.967	1.251–1.562	176.08–178.25
11.3[286]	$P(^iPr)_3$	Br	Pt	$NSiMe_3$	1.959	1.226–1.228	176.84–177.99
11.4[286]	PCy_3	CCPh	Pt	$NSiMe_3$	2.016	1.265	179.31
11.5[134]	PCy_3	Br	Pt	O	N/A	N/A	N/A
11.6[134]	PCy_3	SPh	Pt	O	1.982	1.210	177.26
11.7[136]	PCy_3	$NCCh_3$	Pt	O	1.971	1.197	179.15
11.8[136]	PCy_3	Br	Pt	$OBAr^f_3$	1.928	1.233	177.84
11.9[136]	PCy_3	Br	Pt	$OB(C_6F_5)_3$	1.935	1.245	176.66
11.10[286]					1.955	1.255	177.06
11.11[287]	PCy_3	Br	$^aPt^+$	Mes	1.859	1.494	176.52
11.12[288,289]	CO	Cp^a	$^bFe^+$	Mes	1.785–1.792	1.491–1.504	177.43–178.26

[a] Counterion: $[B(C_6F_5)_4]^-$.

[b] Counterion: $[B(Ar^F)_4]^-$.

Compound **11.5** is too disordered to provide reliable metrical parameters.

1.17.2.3.1.3 Reactivity

Much of the chemistry that has been reported for iminoboryl and oxoboryl transition-metal complexes may be readily understood in terms of the presence of multiple bonding between the boron atom and the nitrogen or oxygen atoms of the ligand, as illustrated in Figure 40. As such, the chemistry of such species will be examined elsewhere in this work.

1.17.2.3.2 Structural features of boride complexes

The majority of the following complexes presented in Tables 20 and 21 contain carbonyl ligands attached to the transition-metal center. Because of their propensity to function as π-acceptors, carbonyl ligands in transition-metal fragments attached to boron ligands can provide excellent insight into the nature of the metal—boron bond as the vibrational frequencies and C—O distances can indicate how much electron density is provided to the carbonyl groups rather than to the boron ligand. In practice, the longer the CO bond (*cf.* the distance of 1.128 Å in free $C{\equiv}O_{(g)}$)[299], the higher the degree of backbonding to the CO groups and, consequently, the smaller the backbonding to the BR ligands. Of course, changes in the electron density at the metal center, as a result of either different number of valence d-electrons or different ligands present in its coordination sphere, must always be taken into account in such analyses.

The boride complexes depicted in Table 20 include examples of cationic, neutral, and anionic species but each of them features an essentially linear M–B–M′ fragment about the dicoordinate boron center and B—M distances that may be consistent with multiple bonding. For a given metal, however, the observed B—M distance is clearly influenced by the types of ligands present in the coordination sphere of the metal; these distances can be rationalized as described above. For example, the B—Mo bond distance in the cationic complex **11.13** of 1.910 Å is considerably longer than the average distance of 1.872 Å found for the anionic complex **11.17**. This observation is consistent with the presence of more carbonyl substituents in the former and electron-rich Cp′ groups in the latter resulting in more Mo—B backbonding in **11.17** (Figure 41).

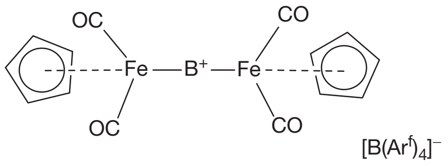
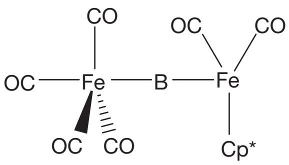
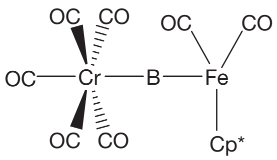
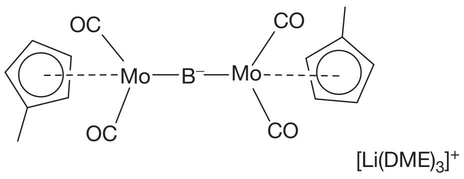
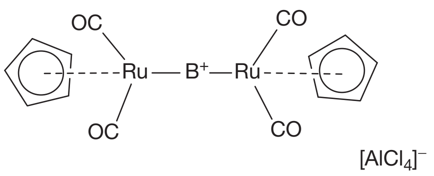
The reactivity of dimetallo-boride complexes has not yet been investigated extensively; however, photolysis of **11.16** in the presence of the alkyne $Me_3SiC{\equiv}CSiMe_3$ results in the loss of the $Cr(CO)_5$ fragment and produces the first example of a transition-metal borirene complex, as illustrated in Figure 42.[304] Furthermore, the treatment of the salt **11.17** with MeI results in the elimination of LiI and the formation of the neutral complex $MeB(MnCp'(CO)_2)_2$, in which the boron center has been alkylated.[302]

1.17.2.3.3 Structural features of aminoborylene complexes

The most extensively investigated class of low-coordinate boron ligand complexes are those containing amido substituents on the boron center. Important metrical parameters for these complexes are presented in Table 21.

The large variety of examples featured in Table 21 include neutral and cationic aminoborylene complexes. Essentially all of the complexes contain linear M—B—N fragments with B—N distances that are consistent with the presence of a

Table 20 Selected structural features of dimetallo-boride complexes

	Structure	*M—B*	*M—B—M*	*C—O*
11.13[300]	$(OC)_3Mo—B^+—Mo(CO)_3$ $[B(Ar^f)_4]^-$	1.910	180.00	1.122–1.126
11.14[300]		1.829	174.55	1.125–1.143
11.15[301]		1.863–1.867	175.38	1.142–1.147
11.16[301]		1.862 1.975	177.75	1.134–1.145
11.17[302]		1.863–1.881	176.11–180.00	1.164–1.172
11.18[303]		1.931–1.962	175.52	1.130–1.142

double bond; an example of a dinuclear borylene complex is depicted in Figure 43. For a given metal, the longest M—B distances are, as anticipated, found for complexes bearing the largest proportion of carbonyl ligands on the transition metal. For example, the B—W distance of 2.151 Å in the pentacarbonyl complex **11.23** is markedly longer than the distance of 2.058 Å in the phosphane tetracarbonyl complex **11.25**.

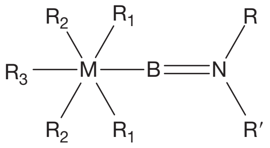
It is also worth reemphasizing that while the presence of amido groups on the boron center can provide electron density to one of the formally vacant 2p-orbitals on B, the other orbital remains vacant and is amenable to π-backbonding. In this context, it is not surprising that all of the B—Fe distances for the iron complexes in Table 21 are considerably shorter than the 2.010 Å distance in $Cp^*B–Fe(CO)_4$, in which the Cp* ligand can effectively populate both vacant orbitals and diminish the amount of π-backbonding.[230,272]

1.17.2.3.3.1 Reactivity

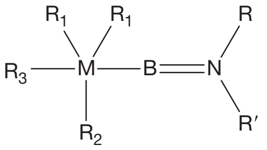
An extensive range of chemistry has been observed for borylene complexes of transition metals as illustrated in Figure 44. Important examples of the reactivity include borylene transfers to other transition metals or main group fragments, several reactions of nucleophiles at the boron center, insertion reactions, and a variety of reactions attributable to the B—N double bond.

Finally, it is worth noting that although no complexes containing terminal B–F ligands that are stable under ambient conditions have yet been reported, such compounds have been identified recently using matrix-isolation methods[322] and the preparation of compounds containing bridging BF ligands has also been accomplished.[323] A mini review by Vidovic and Aldridge outlines the coordinative ability of group 13 monohalides to transition metals, specifically a comparative analysis to CO, N_2, and other common ligands.[324] Boron(I) fluoride, for example, is a significantly better ligand than CO or N_2 due to its higher HOMO energy as well as more localized electrons for binding. In a comparison with other B(I) and related compounds, the halide series was found to be better π-acceptors than other B(I) compounds (e.g., BNH_2 and BO) due to a lower lowest unoccupied molecular orbital (LUMO) energy. The quest for stable examples of such complexes is ongoing.

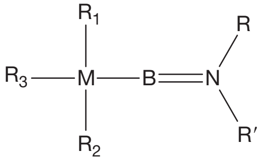
Table 21 Structural features of $MBNR_2$ compounds



	R₁	*R₂*	*R₃*	*R*	*R′*	*M*	*Counterion*	*B—M*	*B—N*	*M—B—N*	*C—O*
11.19[295]	$P(Cy)_3$		Br	$SiMe_3$	$AlCl_3$	Pt		1.904	1.331	170.37	N/A
11.20[305]	CO	CO	CO	$SiMe_3$		Cr		1.995	1.353	177.42	1.142–1.163
11.21[306]	CO		Cp	Cy		Fe	$[B(Ar^f)_4]^-$	1.858	1.325	178.79	1.116–1.146
11.22[307]	CO		Cp	Cy		Ru	$[B(Ar^f)_4]^-$	1.960	1.320	175.38	1.140–1.146
11.23[273]	CO	CO	CO	$SiMe_3$		W		2.151	1.338	177.87	1.140–1.146
11.24[308]	CO	CO	CO	$SiMe_3$		Mo		2.152	1.355	177.81	1.139–1.148
11.25[308]	CO	CO	PCy_3	$SiMe_3$		W		2.058	1.378	175.77	1.146–1.162
11.26[308]	CO	CO	PCy_3	$SiMe_3$		Mo		2.059	1.366	175.32	1.141–1.147
11.27[305,308,309]	CO	CO	PCy_3	$SiMe_3$		Cr		1.915	1.364	175.92	1.143–1.151



	R₁	*R₂*	*R₃*	*R*	*R′*	*M*	*Counterion*	*B—M*	*B—N*	*M—B—N*	*C—O*
11.28[310]	CO	CO	Cp	$SiMe_3$		V		1.960	1.378	177.91	1.154–1.177
11.29[311]		CO	Cp*	$SiMe_3$		Ir		1.892	1.365	175.91	1.169
11.30[311]		$B{=}NR_2$	Cp*	$SiMe_3$		Ir		1.892	1.365	175.91	1.169



	R₁	*R₂*	*R₃*	*R*	*R′*	*M*	*Counterion*	*B—M*	*B—N*	*M—B—N*	*C—O*
11.31[307]	CO	Me_3P	Cp	Cy		Fe	$[B(Ar^f)_4]^-$	1.820	1.347	177.69	1.140
11.32[307]	CO	Me_3P	Cp	Cy		Ru	$[B(Ar^f)_4]^-$	1.927	1.346	170.81	1.134
11.33[307]	CO	κ^1-DMPE	Cp	Cy		Fe	$[B(Ar^f)_4]^-$	1.828–1.829	1.343–1.350	171.19–175.54	1.143–1.153
11.34A[312]	Cp	κ^2-DMPE		Me		Fe	A: $[BPh_4]^-$	1.804–1.811	1.351–1.361	175.01–175.97	N/A
11.34B[312]							B: $[B(Ar^f)_4]^-$				

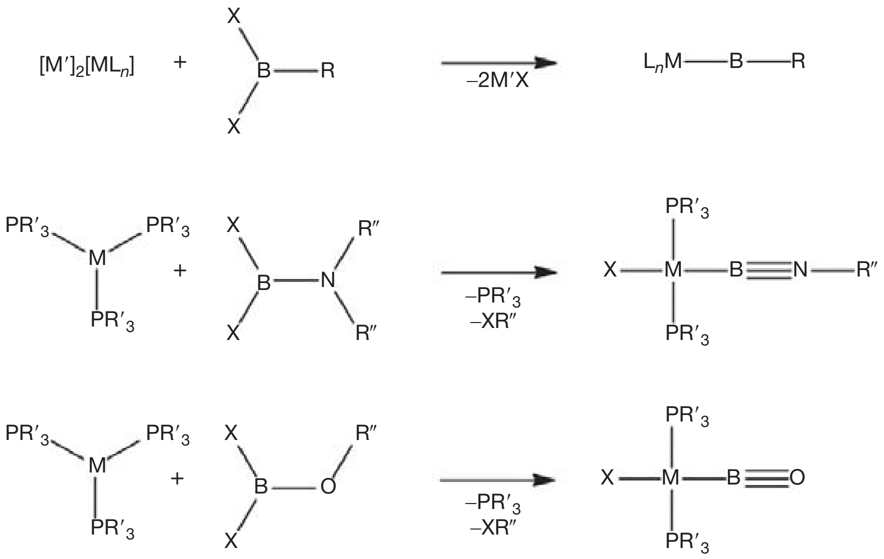


Figure 39 ‘First-generation’ syntheses for borylene, iminoboryl and oxoboryl complexes. R = Cp*, dialkylamino, disilylamino, mesityl, ^{t}Bu, Si(SiMe$_3$)$_3$; R′ = alkyl, aryl; and R″ = trialkylsilyl.

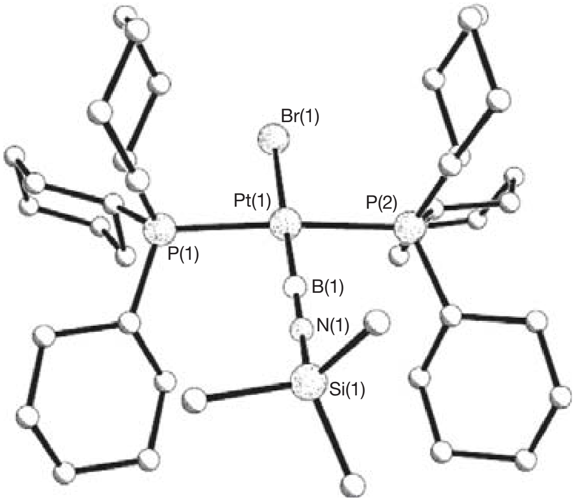


Figure 40 Crystal structure of **11.1** showing the square planarity at the metal center and the linear boron fragment.

1.17.2.3.4 Transition-metal complexes of heavier monovalent group 13 ligands

As indicated in earlier sections, the ability of univalent group 13 compounds to function as two-electron donors allows such species to be used as ligands for a variety of transition-metal complexes. In contrast to the analogs boron species described in the previous section, the availability of stable univalent compounds and monomeric species that effectively function as sources of ER ligands allows for much more flexibility in the design of synthetic approaches to such complexes. The preparative and reaction chemistry of transition-metal complexes of monovalent ligands of heavier group 13 elements has been reviewed in significant detail.[325,326]

1.17.2.3.4.1 Synthesis

Given the considerable variety of transition-metal complexes containing univalent group 13 fragments, an overall reaction scheme is not feasible for all the compounds presented. Some of the methods described above for the related boron analogs have certainly been applied to the preparation of such complexes, such as double salt elimination and other metathesis reactions; halide abstraction for the formation of cationic fragments; and reduction of halogen precursors. However, given the availability of many stable sources of ER fragments (or Tl$^+$ ions), most of the transition-metal complexes described below have been generated by the displacement of labile ligands from a target transition-metal complex by the ER source. Important structural features of various different classes of complexes are presented in Tables 22–25; because of the vast number of Cp* complexes, these are discussed separately in Section 1.17.2.3.5.

1.17.2.3.4.2 Structural features

A series of ‘metallocryptand’ complexes have been reported by Catalano and coworkers as part of their investigation of closed-shell interactions.[327] These complexes, listed in Table 22, are generally prepared by the *in situ* reaction of the Tl$^+$ source, the bridging polydentate ligands, and the group 10 or 11 transition metals that form the bridgeheads of the metallocryptand ligands.

All of the complexes in Table 22 feature nearly linear M–Tl–M′ arrangements about the thallium cation, and the constraints of the ligands result in M—Tl distances that typically fall within the sum of the van der Waals radii of the two elements. The nature of the bonding present between the metals remains poorly understood but the formation of well-defined complexes has allowed for the detailed examination of the spectroscopic and physical properties of complexes of closed-shell species.[327]

In addition to the metallocryptands, there are a considerable number of complexes containing dicoordinate group 13 elements bound only to two transition-metal fragments, as illustrated by the entries in Table 23. These complexes have been prepared using a variety of different methods including *in situ* hydrogenation of a ruthenium precursor and several

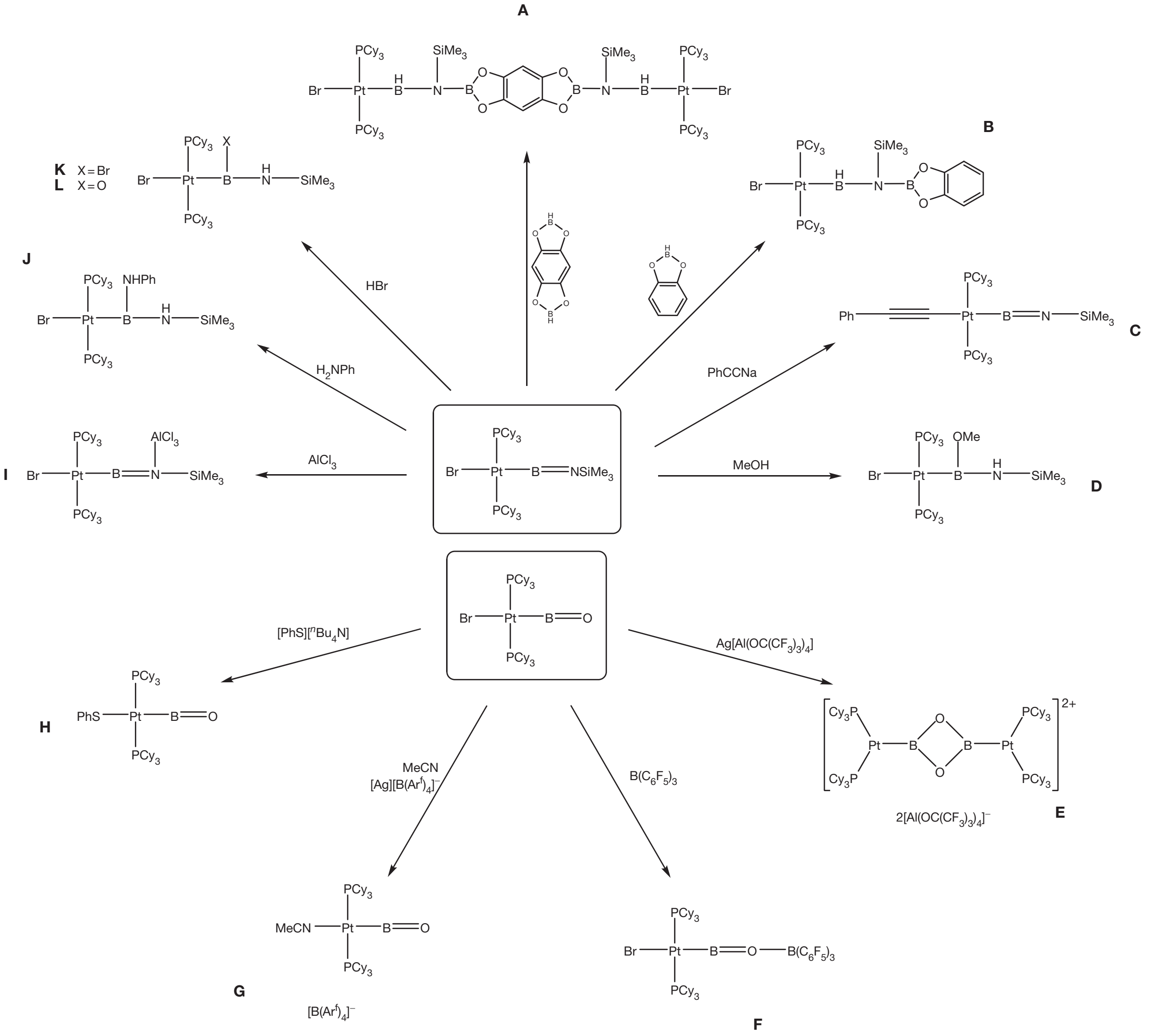


Figure 41 Summary of reported reactivity for platinum iminoboryl and oxoboryl complexes. Data taken from the following work: **A–B**,[294] **C**[286] **D**,[295] **E**,[296] **F–G**,[297] **H**,[298] **I**,[295] **J**,[286] **K**,[294] and **L**.[286]

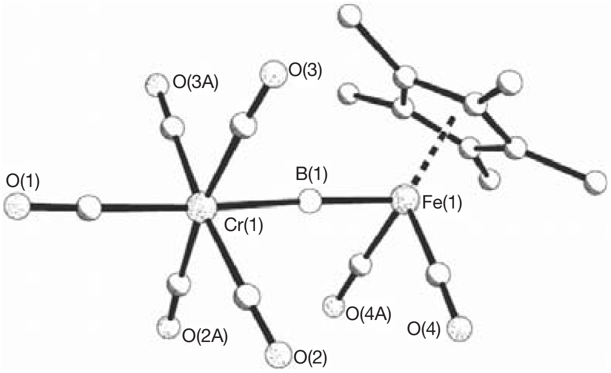


Figure 42 Solid-state structure of $(OC)_5CrBFeCp^*(CO)_2$, **11.15**.

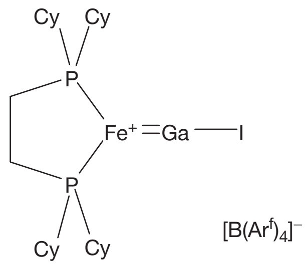
ligand displacement reactions; however, the majority have been generated by halide abstraction or metathesis reactions.

Apart from the thallium complexes **12.21**–**12.22**, which are conceptually similar to the metallocryptand species described above, and **12.23**, in which is the thallium center sits in a bridging position, the M–E–M′ fragments are almost linear for each of the complexes. Furthermore, the bond distances for many of the complexes are short enough to be consistent with the presence of metal–group 13 multiple bonding. For example, the shortest Ga—Ru bond in **12.10** of 2.322 Å is significantly shorter than the average distance of ca. 2.401 Å observed for the Cp*Ga ligands attached to the same metal center.

As with the borylene complexes described previously, there are, of course, also several complexes for which the univalent group 13 ligand is not a stable entity. In such cases, the ligand must be formed in the coordination sphere of the metal. For example, a series of remarkable complexes containing MeGa ligands were prepared by Fischer and coworkers through the ligand redistribution reactions that occur following the treatment of homoleptic Cp*Ga of rhodium and molybdenum with dimethyl zinc.[342–344]

Each of the MeGa ligands adopts a linear arrangement, as anticipated, and the lengths of the Ga—M bonds are considerably shorter than those observed for similar Cp*Ga–M linkages (*vide infra*).

Another complex that features a univalent gallium ligand that is not stable outside the coordination sphere of a transition metal is the salt, $[(DCPE)Fe{-}GaI][B(Ar^f)_4]$, **12.27**, reported by Aldridge and coworkers, which contains a terminal gallium(I) iodide ligand.[345,346] This complex was prepared by halide abstraction from $(DCPE)FeGaI_2$ and was the first isolated example of a terminal group 13 halide ligand. Complex **12.27** features a Ga—Fe distance of 2.222 Å, a Ga—I distance of 2.444 Å, and an Fe—Ga—I angle of 171.37°; again, these metrical parameters are consistent with the presence of Fe—Ga multiple bonding.



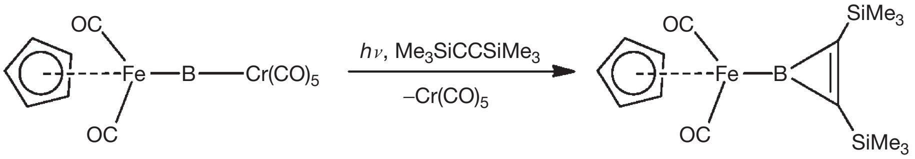


Figure 43 Reaction of metal boride complex **11.16** to produce a transition-metal borirene.

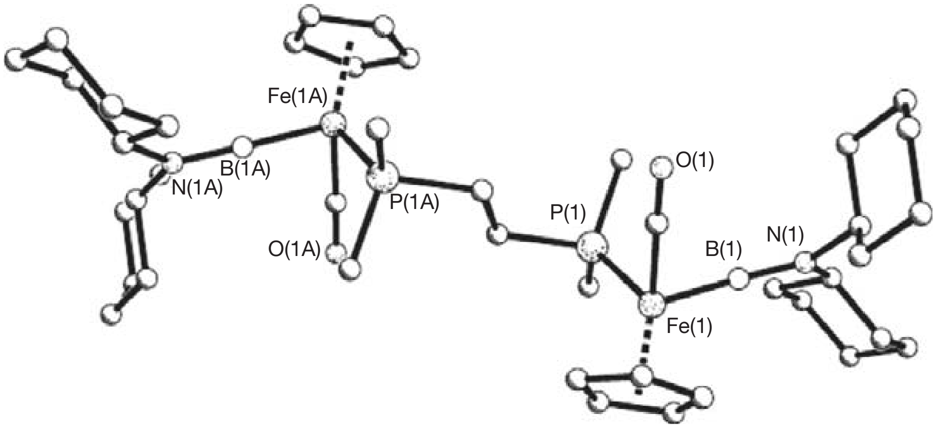
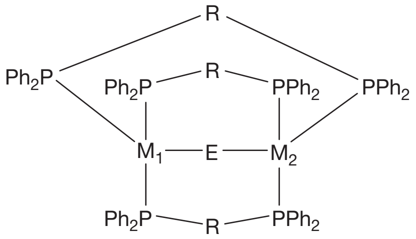


Figure 44 Solid-state structure of **11.32** showing the bridging nature of the DMPE ligand to two different iron centers, each of which is bound by a $BNCy_2$ ligand.

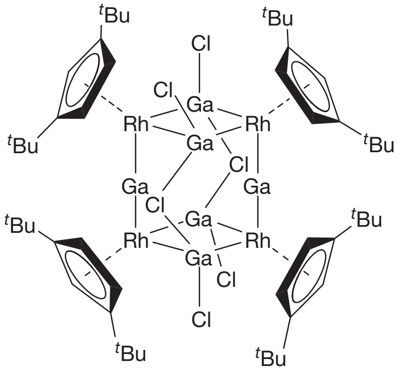
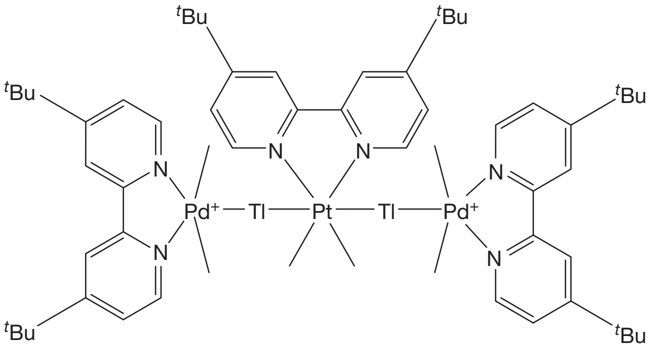
Table 22 Metallocryptand complexes of Tl(+1)



	E	*M₁*	*M₂*	*R*	*Counterion*	*E—M₁*	*E—M₂*	*M₁—E—M₂*
12.1[328]	Tl	Au	Au	2,9-Phen	ClO_4^-	2.911–2.917		174.46
12.2[329]	Tl	Pd	Au	2,9-Phen	PF_6^-	2.748	2.861	174.54
12.3[329]	Tl	Pd	Au	2,9-Phen	BF_4^-	2.779	2.793	169.57
12.4[329]	Tl	Pd	Au	2,9-Phen	Cl^-	2.672	2.887	174.44
12.5[329]	Tl	Pt	Au	2,9-Phen	PF_6^-	2.771	2.900	172.30
12.6[330]	Tl	Pt	Pt	2,9-Phen	NO_3^-	2.791–2.792		175.27
12.7[330]	Tl	Pt	Pt	6,6′-Bipy	NO_3^-	2.795		180.00
12.8[330]	Tl	Pd	Pd	2,9-Phen	NO_3^-	2.791		160.62
12.9[330]	Tl	Pd	Pd	6,6′-Bipy	NO_3^-	2.760		180.00

Table 23 Complexes featuring dicoordinate group 13 elements bonded to two transition-metal fragments

$$(L_1)(L_2)_nM_1 = E = M_2(L_3)(L_4)_m$$

	E	*M₁*	*M₂*	*L₁*	*L₂*	*L₃*	*L₄*	n	m	*Counterion*	*E—M₁*	*E—M₂*	*M—E—M*
12.10[331]	Ga^+	RuH	RuH_2		GaCp*		GaCp*	4	3	$[NO_3]^-$	2.387	2.322	178.03
12.11[332]	Ga	Fe	Fe	Cp*	κ^2-Dppe		CO	1	4		2.248	2.293	176.01
12.12[333,334]	Ga^+	Fe	Fe	Cp*	CO	Cp*	CO	2	2	$[B(Ar^f)_4]^-$	2.266–2.272		178.99
12.13[334]	In^+	Fe	Fe	Cp*	CO	Cp*	CO	2	2	$[B(Ar^f)_4]^-$	2.459–2.469		175.32
12.14[335]	Ga	Fe	W	Cp*	κ^2-Dppe		CO	1	5		2.269	2.586	173.78
12.15[336]	Tl^+	Pt^{2-}			C_6F_5		C_6F_5	4	4	NBu_4^+	2.978–3.043		174.01
12.16[337]	Ga	Fe	Fe	Cp*	κ^2-Dmpe		CO	1	4		2.241	2.320	178.64
12.18[338]	Ga	Fe	Fe	Cp*	κ^2-Dppe	$P(OPh)_3$	CO	1	3		2.269	2.284	176.43
12.19[338]	Ga	Fe	Fe	Cp	κ^2-Dppe	PMe_3	CO	1	3		2.277	2.268	177.39
12.20											2.340–2.346		174.40–174.60
12.21[339]										PF_6^-	2.796–2.994		131.39–132.93

(*Continued*)

Table 23 (Continued)

$(L_1)(L_2)_nM_1 =\!=\!= E =\!=\!= M_2(L_3)(L_4)_m$

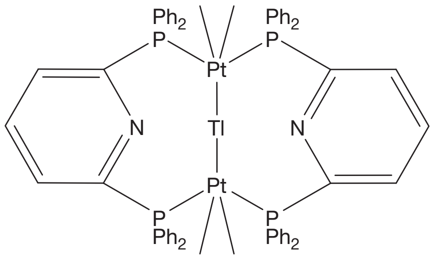
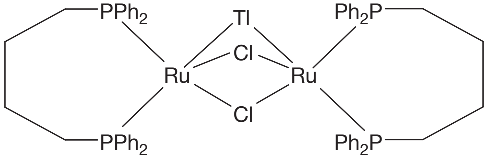
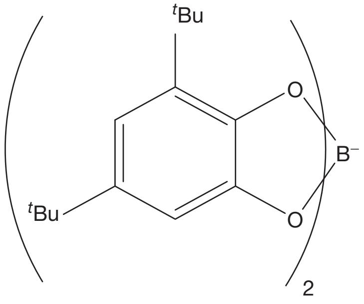
	E	M_1	M_2	L_1	L_2	L_3	L_4	n	m	Counterion	E—M_1	E—M_2	M—E—M
12.22[340]										ClO_4^-	2.796–2.809		157.87
12.23[341]											2.805–3.123		68.04

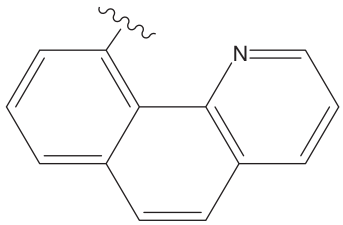
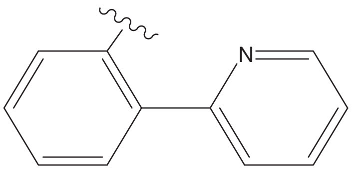
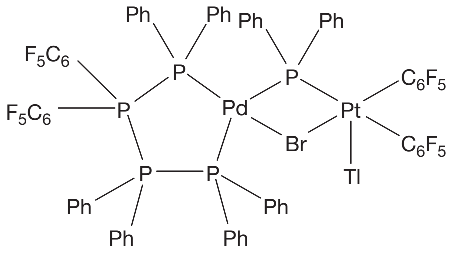
Table 24 Complexes containing MeGa ligands

$(Me\text{–}Ga)_k\text{–}M(L_1)_n(L_2)_m$

	M	k	*L₁*	n	*L₂*	m	*Anion*	*Ga—C*	*Ga—M*	*C—Ga—M*
12.24[342]	Rh	1	GaCp*	4			$[B(Ar^f)_4]^-$	1.957	2.471	176.10
12.25[343]	Rh	1	ZnCp*	4	ZnMe	3		1.953	2.383	179.73
12.26[343,344]	Mo	2	ZnCp*	4				1.885–1.942	2.385–2.406	176.12–179.12
12.27[343,344]	Mo	2	ZnCp*	4	ZnMe	4		1.961–1.975	2.488–2.579	175.49–179.24

Table 25 Complexes featuring terminal thallium ligands

$Tl_kM(L_1)_n(L_2)_m$

	k	*M*	*L₁*	n	*L₂*	m	*Counterion*	*Tl—M*
12.29[347]	1	Pt		1	CN	2		2.991
12.30[347]	1	Pt		1	CN	2		3.008
12.31A[348]	1	Pt	PPh_2-2-pyr	3			$[NO_3]^-$	2.911
12.31B[348]							$[AcO]^-$	2.866
12.32A[349]	1	Ni	COD	1	NC-2,6-Mes_2–C_6H_3	2	$[TfO]^-$	3.023
12.32B[349]							$[B(Ar^f)_4]^-$	2.853
12.33[349]	1	Ni	NC-2,6-Mes_2–C_6H_3	3			$[TfO]^-$	2.610
12.34[350]	1	Pd	NC-2,6-$Dipp_2$–C_6H_3	2			$[TfO]^-$	2.855
12.35[351]	2	Pt	C_6F_5	2	C≡CPh	2		2.992–3.027
12.36[352]								2.939

There are a handful of examples of complexes in which a group 13 metal is terminally bound to a transition metal; such ligands are sometimes described as being 'naked'. Because of the ready availability of Tl(+1) sources, it should come at no surprise that most of these compounds are complexes of thallium(I); these complexes are listed in Table 25.

In many instances, such complexes might perhaps be considered as contact ion pairs of anionic metal ligands and the Tl^+ cation, and, in fact, Figueroa and coworkers describe the thallium ligand as a 'coordination site protecting agent' in complexes **12.31** and **12.32**. It is also worth indicating that pyridyl fragments in complexes **12.30A** and **12.30B** are oriented in a manner such that they can bind the Tl^+ cation; as with the metallocryptands presented above, these have been used to probe closed-shell bonding interactions. Other investigations of complexes such as **12.33**–**12.35** have concentrated on the luminescent properties of the Pt–Tl complexes.[347,351,353]

There are also a number of complexes containing 'naked' gallium ligands, as both terminal and bridging ligands, and even a complex with a 'naked' indium ligand that has been isolated, as presented in Table 26. Because there are very few well-defined sources of Ga$^+$ cations,[234,354] such complexes have sometimes also been prepared by the protonolytic or oxidative cleavage of Cp* groups from precursor complexes containing Cp*Ga ligands.

The complexes containing 'naked' terminal gallium ligands, such as **12.39** (Figure 45), all feature M—Ga distances that are considerably shorter than those observed for analogs Cp*Ga—M distances (*vide infra*). This behavior has been attributed to such ions being superior π-backbond acceptors than the corresponding gallanediyl ligands and, in fact, the complexes are best described as consisting of an anionic transition-metal fragment donating to a Ga$^+$ acceptor! In this context, the Ga$^+$ ion was described as a main group analog of a proton.[354]

The metrical parameters for the bridging Ga$^+$ ligands in complexes **12.40** and **12.41** indicate an asymmetric bridging interaction for these cluster compounds; however, disorder in the structures reduces the reliability of these values. Although the chemistry of such compounds has not been investigated extensively, they are considered as models for intermediates involved in the formation of intermetallic phases from Cp*Ga–ML$_n$ precursors.[325]

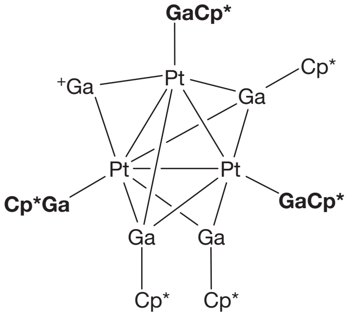
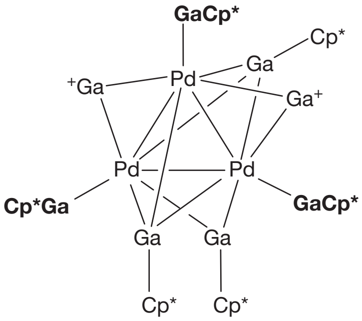
1.17.2.3.5 Transition-metal complexes of Cp′E ligands

In contrast to the analogs borylene complexes, the vast majority of transition-metal complexes of RE ligands for the heavier group 13 elements involve univalent group 13 cyclopentadienyl compounds of the type described in Section 1.17.2.2.2. The properties of the Cp′ substituents (steric, electronic, physical, and chemical)[215] that are present in these heavier Cp′E ligands render the complexes suitable for use as sources for the chemical vapor deposition formation of materials such as group 13 intermetallics, and the preparation of such complexes has been investigated extensively.[325,326] It should be noted that almost all of the transition-metal structures of the group 13 cyclopentadienyl complexes have featured the pentamethylcyclopentadienyl ligand. Apart from the pair of complexes featuring Cp*B ligands, which must be prepared *in situ* for the reasons described previously, transition-metal complexes of Cp*E ligands have most often been prepared by the treatment of a metal complex with a labile ligand with the desired Cp*E reagent and important metrical parameters for such complexes are collected in Tables 27–30.

All of the complexes in Table 27 feature ligands with approximately linear Cp*(centroid)–E–M arrangements with E—M bond distances that vary depending on elements involved. As

Table 26 Complexes featuring 'naked' Ga$^+$ and In$^+$ ligands

$E_kM(L_1)_n(L_2)_m$

	E	*M*	*L$_1$*	n	*L$_2$*	m	*Anion*	*E—M*	*M—E—M*
12.36(13.22)[354]	Ga	Pt	GaCp*	4			$[B(Ar^f)_4]^-$	2.459	
12.37[354]	In	Pt	PPh$_3$	3			$[B(Ar^f)_4]^-$	2.580	
12.38(13.38)[355]	Ga	Ru	GaCp*	2	PCy$_3$	2	$[B(Ar^f)_4]^-$	2.300	
12.39(13.24)[356]	Ga	Ni	GaCp*	4			$[B(Ar^f)_4]^-$	2.361	
Bridging complexes									
12.40(13.75)[356]							$[B(Ar^f)_4]^-$	2.378–2.595	65.34
12.41(13.76)[356]							$[B(Ar^f)_4]^-$	2.455–2.504	67.40

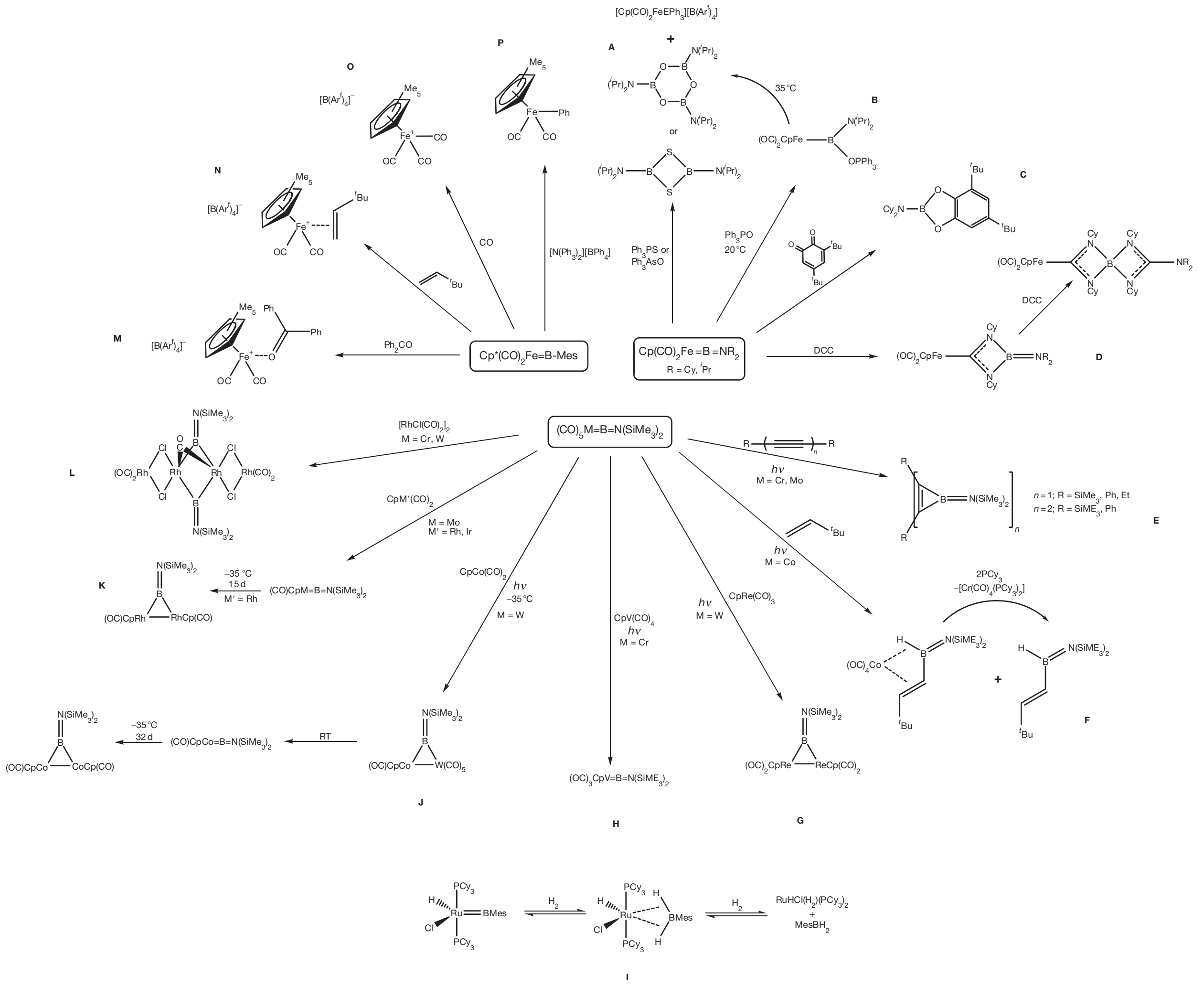


Figure 45 Reported reactivity for transition-metal borylene complexes. **A–C**,[313,314] **D**,[315,316] **E**,[317] **F**,[318] **G–H**,[310] **I**,[319] **J**,[320] **K**,[311] **L**, and [321] **M–P**.[289]

Table 27 Complexes of Cp*E ligands with transition-metal carbonyl fragments

$(Cp^*E)_kM(CO)_n$

	E	k	*M*	n	*C—O (Å)*	*E—Ct (Å)*	*E—C (Å)*	*E—M (Å)*	*Ct—E—M (°)*
13.1[272]	B	1	Fe	4	1.140–1.157	1.347	1.811–1.818	2.010	178.61
13.2[357]	Al	1	Fe	4	1.131–1.144	1.775	2.139–2.152	2.233	176.77
13.3[358]	Ga	1	Fe	4	1.142–1.147	1.864	2.194–2.258	2.273	168.35
13.4[220]	Al	1	Cr	5	1.142–1.144	1.819	2.176–2.187	2.376	171.67
13.5[359]	Ga	3	Mo	3	1.154–1.169	1.941–1.948	2.245–2.317	2.519–2.523	161.87–166.23
13.6[359]	Ga	3	W	3	1.158–1.171	1.936–1.952	2.229–2.323	2.520–2.525	161.78–166.30
13.7[358]	Ga	1	Cr	5	1.140–1.152	1.910	2.237–2.282	2.405	167.52
13.8[360]	Ga	1	W	5	1.111–1.143	1.915	2.243–2.280	2.566	168.17
13.9[361]	Ga	2	Mo	4	1.145–1.158	1.922–1.928	2.223–2.435	2.537–2.554	160.82–167.85
13.10[a362]	B	1	Fe^+	3	1.145–1.149	1.326	1.792–1.802	1.978	177.86
13.11[363]	In	1	Cr	5	1.143–1.149	2.167	2.405–2.561	2.586	157.73

[a] Exists as the $[AlCl_4]^-$ salt.

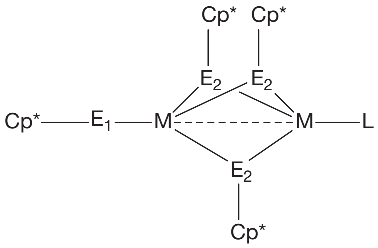
indicated previously, the nature of the metal–ligand bonding in such complexes (and related species) has been the subject of numerous computational investigations.[211,230,364–368] It should be noted that the metal–triel bonds are usually considered to be very ionic in nature and, because of the good p-donating abilities of Cp′-type substituents, the amount of metal-to-ligand π-backbonding is often considerably less than the amount predicted for other substituents. Furthermore, the amount of backbonding also appears to be diminished by the presence of superior π-acceptor ligands, such as carbonyls, in the

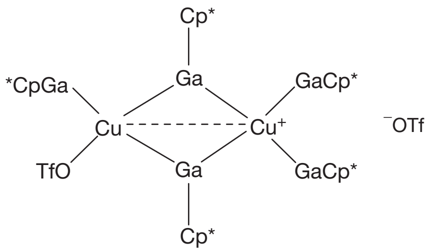
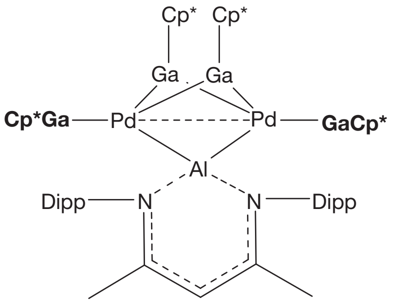
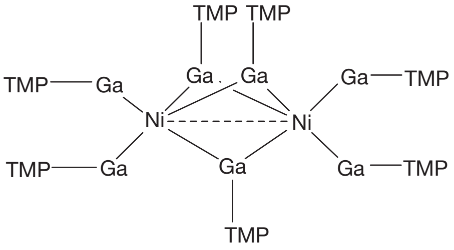
Table 28 Selected metrical parameters for noncarbonyl transition-metal complexes of Cp*E ligands

$(\mathrm{Cp^*E})_k\mathrm{M}(\mathrm{L_1})_n(\mathrm{L_2})_m$

	E	k	*M*	L_1	n	L_2	m	*Counterion*	*E—Ct (Å)*	*E—C*	*E—M*	*Ct—E—M*
13.12[369]	Ga	3	Ru	η^4-COD	1				1.987–2.026	2.254–2.387	2.364–2.394	159.89–165.06
13.13[369]	Ga	3	$\mathrm{Rh^+}$	η^4-COD	1			$[\mathrm{B(Ar^f)_4}]^-$	1.912–1.960	2.214–2.314	2.359–2.405	161.15–168.30
13.14[369]	Al	3	$\mathrm{Rh^+}$	η^4-COD	1			$[\mathrm{B(Ar^f)_4}]^-$	1.853–1.884	2.192–2.246	2.309–2.319	162.30–169.41
13.15[370]	Al	3	Ni	$\mathrm{SiEt_3}$	1	H	1		1.917–1.945	2.257–2.314	2.180–2.208	166.40–174.46
13.16[212]	Ga	3	$\mathrm{Ru^+}$	Cp*	1			$\mathrm{BPh_4}^-$	1.959–1.962	2.263–2.351	2.377–2.394	171.17–173.00
13.17[212]	Ga	3	$\mathrm{Ru^+}$	Cp*	1			$\mathrm{Cl_3Ga}$–η^1-$\mathrm{Cp^{*-}}$	1.964–1.986	2.257–2.367	2.380–2.396	168.34–170.52
13.18[371]	Ga	4	Pt						1.995	2.313–2.347	2.333	160.68
13.19[371]	Ga	4	Pd	GaCp*					2.019	2.331–2.372	2.367	155.55
13.20[372]	Ga	3	$\mathrm{Ru^+}$	η^4-COD	1	H	1	$[\mathrm{B(Ar^f)_4}]^-$	1.924–1.946	2.240–2.322	2.404–2.422	157.72–168.71
13.21[361]	Ga	4	Ni						2.004	2.329–2.351	2.218	164.71
13.22[373]	Al	4	Pd						1.929	2.257–2.284	2.295	169.21
13.23[373]	Al	4	Ni						1.932	2.271–2.286	2.173	173.48
13.24[374]	Ga	3	$\mathrm{Fe^+}$	Cp*	1		0	$[\mathrm{B(Ar^f)_4}]^-$	1.969–1.981	2.261–2.377	2.309–2.322	17 100–173.85
13.25[374]	Ga	3	$\mathrm{Co^{2+}}$	Cp*	1		0	$[\mathrm{B(Ar^f)_4}]^-$	1.872–1.907	2.206–2.279	2.280–2.317	172.50–176.43
13.26[374]	Ga	4	$\mathrm{Cu^+}$				0	$[\mathrm{B(Ar^f)_4}]^-$	1.931–1.946	2.263–2.308	2.350–2.352	153.16–158.10
13.27[374]	Ga	4	$\mathrm{Ag^+}$				0	$\mathrm{BPh_4}^-$	1.942–1.956	2.248–2.328	2.511–2.528	148.39–159.63
13.28[53]	Ga	4	$\mathrm{Zn^{2+}}$				0	$[\mathrm{B(Ar^f)_4}]^-$	1.850–1.861	2.197–2.236	2.404–2.411	165.20–70.21
13.29[355]	Ga	3	Ru	η^4-$\mathrm{C(CH_2)_3}$			0		1.970–2.009	2.281–2.379	2.342–2.358	168.32–168.58
13.30[342]	Ga	4	Rh	GaMe–η^1-Cp*	1		0		2.007–2.053	2.312–2.427	2.347–2.394	165.77–174.24
13.31(**12.24**)[342]	Ga	4	$\mathrm{Rh^+}$	GaMe	1		0	$[\mathrm{B(Ar^f)_4}]^-$	1.956–1.997	2.141–2.404	2.282–2.310	163.15–172.80
13.32[342]	Ga	4	$\mathrm{Rh^+}$	GaMePy	1		0	$[\mathrm{B(Ar^f)_4}]^-$	1.953–2.025	2.250–2.401	2.333–2.362	157.39–175.74
13.33(**12.37**)[354]	Ga	4	Pt	$\mathrm{Ga^+}$	1		0	$[\mathrm{B(Ar^f)_4}]^-$	1.908–1.948	2.207–2.306	2.358–2.444	163.81–171.51
13.34[355]	Ga	4	$\mathrm{Ru^+}$	η^3-$\mathrm{C(CH_2)_3}$	1		0	$[\mathrm{B(Ar^f)_4}]^-$	1.960–1.995	2.240–2.444	2.385–2.443	150.72–172.38
13.35(**12.40**)[356]	Ga	4	Ni	$\mathrm{Ga^+}$	1		0	$[\mathrm{B(Ar^f)_4}]^-$	1.923–1.957	2.218–2.354	2.253–2.320	165.32–172.43
13.36[211]	In	2	Pt	κ^2-DCPE	1		0		2.280–2.281	2.554–2.604	2.556–2.569	169.52–170.43
13.37[368]	Ga	2	Pt	κ^2-DCPE	1		0		2.018–2.067	2.321–2.429	2.355–2.382	172.34–176.34
13.38[368]	Al	2	Pt	κ^2-DCPE	1		0		1.952–1.982	2.278–2.356	2.317–2.335	173.24–177.60
13.39[344]	Ga	5	Mo	η^1-Cp*Ga	1		0		2.024–2.127	2.261–2.606	2.458–2.493	166.04–175.21
13.40[369]	Ga	1	Ru	η^4-1,2-Butadiene	1	$\mathrm{PPh_3}$	2		2.001	2.295–2.380	2.401	160.61
13.41[369]	Ga	2	$\mathrm{Rh^+}$	η^4-NBD	1	$\mathrm{PCy_3}$	1	$[\mathrm{B(Ar^f)_4}]^-$	1.916–1.983	2.242–2.338	2.375–2.441	165.78–166.27
13.42[375]	Ga	1	Rh	Cp*	1	$\mathrm{CH_3}$	2		1.943	2.251–2.337	2.329	167.22
13.43[376]	Ga	2	Rh	Cp*	1	$\mathrm{GaCl_3}$	1		1.927–1.960	2.220–2.385	2.344–2.345	167.26–169.20
13.44[376]	Ga	2	Rh	Cp*	1	$\mathrm{GaCl_2}$-η^1-Cp*	1		1.977–2.116	2.159–2.680	2.358–2.389	151.93–157.17
13.45 FEBXIU[376]	In	1	$\mathrm{Rh^-}$	1,3-$\mathrm{(Cl_2In)_2C_5Me_5}$	1			$[\mathrm{Cp^*_2Rh}]^+$	N/A (η^1-Cp*)	2.259	2.535	163.87
13.46 FEBYOB[212]	In	1	Ru	Cp*	1	κ^2-$\mathrm{(Cp^*In)_2Cl}$	1		2.206	2.494–2.526	2.557	169.77
13.47 HACWEO[377]	In	1	Rh	Cp*	1	InCp*Cl	2		2.193	2,380–2.574	2.522	151.47
13.48[212]	Ga	2	Ru	η^6-*p*-^{i}PrTol	1	$\mathrm{GaCl_3}$	1		1.913–1.933	2.190–2.338	2.368–2.372	162.99–166.73
13.49[212]	Ga	2	Ru	Cp*	1	GaCl–η^1-Cp*	1		1.985–1.992	2.199–2.427	2.359–2.368	163.42–166.93
13.50[355]	Ga	2	Ru	H	2	$\mathrm{PCy_3}$	2		2.046–2.053	2.343–2.414	2.401–2.402	175.34–176.37
13.51[378]	Ga	2	Fe	Cp*	1	$\mathrm{GaCl_2}$–η^1-THF	1		1.986–2.007	2.251–2.398	2.277–2.280	167.89–170.29
13.52(**12.39**)[355]	Ga	2	Ru	$\mathrm{Ga^+}$	1	$\mathrm{PCy_3}$	2	$[\mathrm{B(Ar^f)_4}]^-$	1.978–1.987	2.260–2.376	2.421–2.425	164.94–165.08
13.53[379]	Ga	4	Ru	η^1-Cp*Ga	1	GaCl–η^1-Cp*	2		1.992–2.015	2.308–2.392	2.399–2.408	165.98–173.63

Table 29 Bond distances and angles given are based on terminal, nonbridging ER fragments

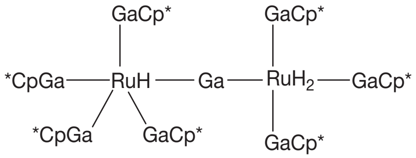
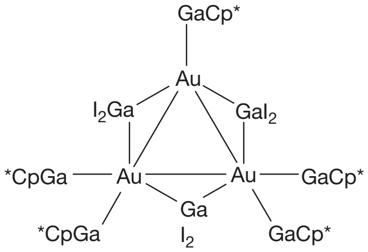
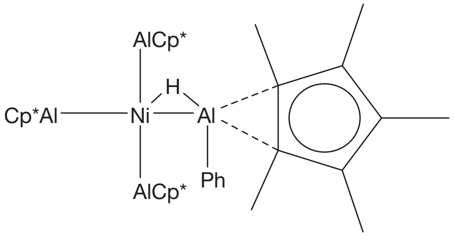
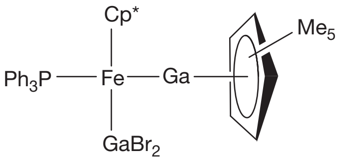
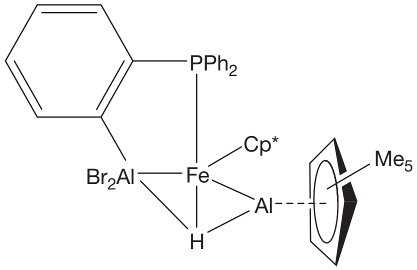


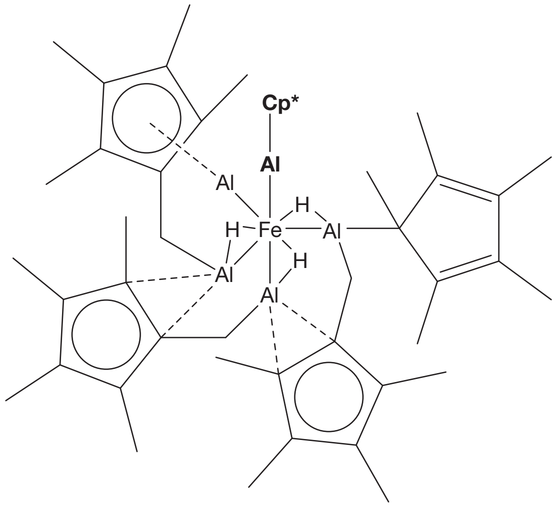
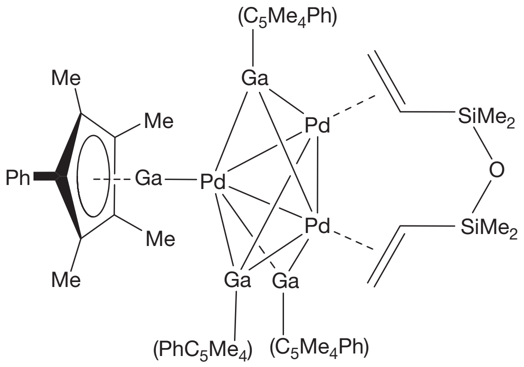
	E₁	*E₂*	*M*	*L*	*E—Ct*	*E—C*	*E—M*	*Ct—E—M*
13.54[a] [380]	Ga	Ga	Pd	η^5-C_5Me_4Ph	1.987–1.988	2.302–2.348	2.336–2.338	173.24–173.69
13.55[381]	Ga	Ga	Pt	GaCp*	1.967–1.970	2.282–2.338	2.326–2.331	177.50–179.05
13.56[382]	Ga	Ga	Pd	GaCp*	1.999–2.019	2.293–2.403	2.355–2.362	176.50–178.62
13.57[382]	Al	Al	Pd	GaCp*	1.974–1.994	2.291–2.477	2.323	176.69–179.11
13.58[382]	Ga	P	Pt	PPh_3	1.974	2.306–2.324	2.351	178.73
13.59[382]	Ga	P	Pt	PPh_3	1.976	2.299–2.320	2.338	179.31
			Pd					
13.60[46]	Ga	Ga	Cu	$(OTf)_3$	1.965	2.212–2.435	2.327	176.30
13.61[382]	Al	Ga	Pt	Cp*	1.976–1.988	2.299–2.350	2.331–2.333	177.38–177.75
13.62[46]					1.982–2.002	2.256–2.422	2.388–2.401	165.97–172.89
13.63[383]					2.067–2.081	2.290–2.479	2.376–2.417	176.06–176.12
13.64[384]					Ga–N: 1.850–1.874	N/A	2.191–2.210	165.02–173.11

[a] The cyclopentadienyl substituent in this complex is η^5-C_5Me_4Ph rather than Cp*.

coordination sphere of the transition metal. Thus, in complexes such as **13.2** (illustrated in Figure 46), the Al—Fe bond is most reasonably considered as a single bond. While the relatively small steric demand of carbonyl ligands may affect the bond distances observed in some complexes, it appears as if the electronic consequences of formally replacing CO ligands with Cp* ligands have a greater effect. For example, examination of the Ga—W distances in complexes Cp*GaW(CO)$_5$ (**13.6**) and (Cp*Ga)$_3$W(CO)$_3$ (**13.8**) reveals that there are shorter distances in the complex with more Cp*Ga ligands in spite of the larger

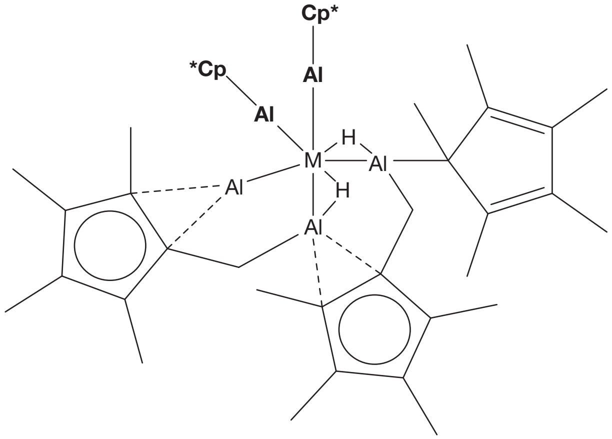
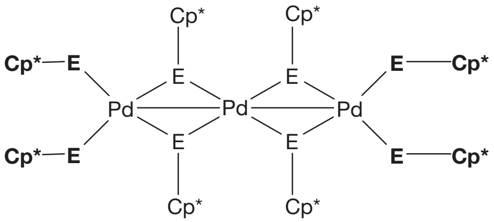
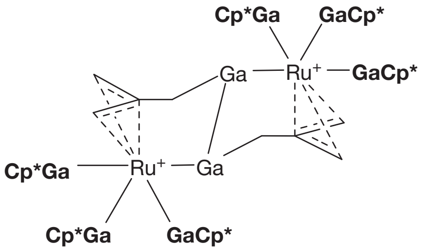
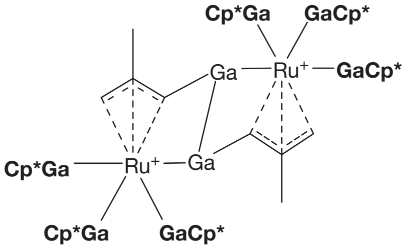
Table 30 Miscellaneous transition metal complexes containing pentamethylcyclopentadienyl group 13 ligands

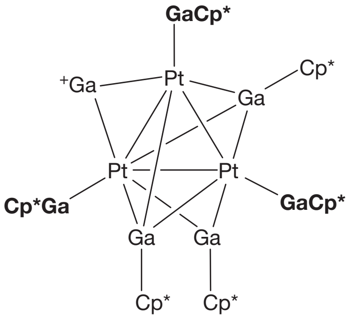
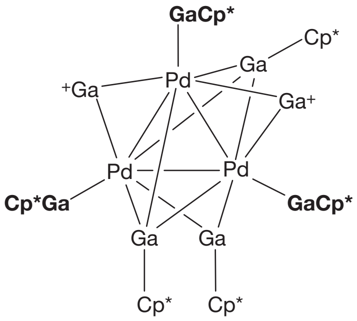
	Structure	*E—Ct*	*E—C*	*E—M*	*Ct—E—M*
13.65[331]		1.962–2.039	2.289–2.442	2.334–2.440	162.03–177.64
13.66[385]		1.880–2.006	2.169–2.375	2.377–2.620	154.02–180.00
13.67[370]		1.909–1.917	2.211–2.293	2.210–2.169	162.44–169.05
13.68[379]		1.971–1.974	2.276–2.345	2.296–2.301	176.49–178.55
13.69[379]		1.847	2.194–2.218	2.270	170.82

13.70[386]		1.889	2.215–2.265	2.210	162.11
13.71[380]		2.008	2.327–2.364	2.367	171.59

(*Continued*)

Table 30 (Continued)

	Structure		*E—Ct*	*E—C*	*E—M*	*Ct—E—M*
13.72[386]		M = Fe	1.909–1.915	2.227–2.295	2.212–2.242	161.00–172.22
13.73[386]		M = Ru	1.892–1.902	2.227–2.276	2.294–2.332	162.53–166.58
13.74[387]		E = In	2.267–2.331	2.526–2.658	2.540–2.565	147.23–174.26
13.75[382]		E = Ga	2.046–2.068	2.340–2.399	2.398–2.418	168.86–175.28
13.76[355]		Anion: $[B(Ar^f)_4]^-$	1.916–1.961	2.223–2.383	2.371–2.427	154.26–176.63
13.77[355]		Anion: $[B(Ar^f)_4]^-$	1.921–1.994	2.203–2.433	2.361–2.413	154.85–169.63

13.78[356] 	Anion: $[B(Ar^f)_4]^-$	1.900–1.903	2.127–2.359	2.283–2.345	164.05–178.23
13.79[356] 	Anion: $[B(Ar^f)_4]^-$	1.923–1.951	2.221–2.341	2.382–2.394	164.08–174.35

steric requirements of the ligand. This behavior is consistent with Cp*Ga ligands providing more (or, perhaps more accurately, removing less) electron density from the metal center than CO and thus results in more extensive π-backbonding for each of the Cp*Ga units.

There are numerous complexes of Cp*E ligands that have also been made with transition-metal fragments that do not bear carbonyl substituents. Such complexes include homoleptic complexes of Cp*E ligands, structures containing bridging Cp*E ligands (which are formally tricoordinate and are thus not examined explicitly in this chapter), ionic complexes, and cluster-like complexes. Selected metrical parameters for the terminal Cp*E fragments in such complexes are presented in Tables 28–30. It is to be noted that some of the complexes containing terminal Cp*E ligands that were described in other contexts in previous tables have been included here also for completeness.

The trends in metal—triel bond distances are consistent with the factors described above; however, there are some interesting observations from the group of complexes presented in Table 28. Of particular note is the observation of η^1-Cp*E ligands in complexes such as **13.39**, **13.45**, and **13.53**. The hapticity of Cp′ rings is conveniently assessed by examination of the metrical parameters within a Cp′ ring and between the Cp′ ring and the metal in the solid state; however, at least for the heavier group 13 elements, rapid 'ring whizzing' within a single Cp* fragment usually prevents the unambiguous identification of such arrangements in solution by techniques such as ^{1}H or ^{13}C NMR. The adoption of the η^1-Cp*E arrangement in these complexes is likely a consequence of both the steric interactions within the coordination sphere and an increase in the magnitude of metal—ligand π-backbonding, which would be anticipated to favor σ-Cp*E arrangements at the extreme. Support for such assessment is illustrated by the metrical parameters in complex **13.39**, in which the Ga—Mo bond to the η^1-Cp*Ga ligand (2.384 Å) is markedly shorter than the shortest distance to an η^5-Cp*Ga ligand (2.458 Å).

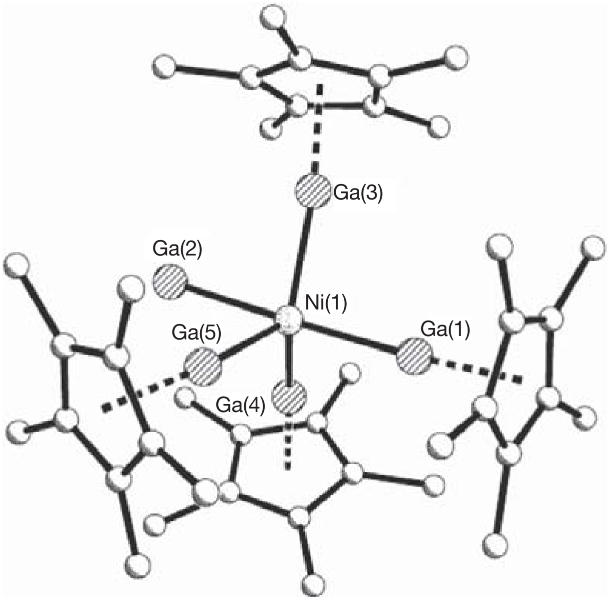


Figure 46 Solid-state structure of the complex **12.39** illustrating a terminal 'naked' gallium.

As one would perhaps anticipate on the basis of the reactivity of 'free' RE species, there are also a considerable number of complexes featuring ligands derived from the insertion of Cp*E into metal—element (mostly metal—halogen) bonds, some of which involve subsequent rearrangements or substituent redistribution. The resultant ligands, such as the Cp*InCl ligands in **13.47**, often feature halide bridges between adjacent group 13 elements.

There are also a large number of complexes that have been reported that contain bridging and terminal Cp′E fragments, as illustrated in Table 29. Given the scope of this chapter, only the metrical parameters for the pseudo-dicoordinate terminal ligands are presented; however, it should be noted that the bridging ligands typically exhibit longer Cp*—E distances because of their increased suitability to accept electron density from the two metal centers.

Although it is not a complex of a univalent gallium cyclopentadienyl ligand, compound **13.64** has been included in Table 29 illustrate that related dinuclear complexes are also able to be generated with other univalent ligands. As with the Cp′E ligands, it is noted that the N—Ga distances in the bridging fragments are substantially longer than those in the terminal ligands. Furthermore, the N—Ga distances to the terminal ligands in **13.64** are slightly longer than that in the only comparable mononuclear complex, TMP–Ga–Cr(CO)$_6$ (TMP, 2,2,6,6-tetramethylpiperidine), as one would anticipate on the basis of the carbonyl ligands in the latter complex.[384]

Polynuclear clusters, complexes containing bridging ligands, and a few miscellaneous transition-metal complexes of Cp*E ligands are presented in Table 30.

Several of the complexes in Table 30 contain hydride or organic-bridged fragments that are again derived from the formal insertion of Cp′E ligands into metal—element and C—H bonds. These complexes emphasize the propensity of univalent group 13 species to undergo reactions that increase the oxidation state and coordination number of the group 13 element.

Perhaps not surprisingly, it should also be noted that Cp*E ligands (E=Al, Ga) have also proved to be useful for the coordination of lanthanides and actinides, as presented in Table 31.

The complexes presented in Table 31 all feature η^5-Cp*E ligands and Cp′ groups in the coordination sphere of the metal. Experimental and computational investigations on these species suggest that the bonding is best described as being covalent donor–acceptor in nature with the donation occurring primarily to the metal d-orbitals.[392] Due to the steric bulk of the Cp* ligands, the M—E—Ct angle is not linear, generating a 'bent' ECp* ligand (as illustrated in Figure 47).

1.17.2.3.6 Chalcogen-based ligands

Substituents based on chalcogen ligands are a mainstay in inorganic coordination chemistry and organometallic chemistry. There are, as one would anticipate, a considerable number of simple thallium(+1) salts of chalcogenide ligands that contain dicoordinate thallium centers and recent examples are described later in this section.[393] For thallium, it has even proved to be possible to isolate salts of the form [K(2,2,2-cryptand)]$_2$[Tl$_2$Ch$_2$]

(Ch = Se **14.1**, Te **14.2**), the anions of which contain dicoordinate thallium(+1) centers in a ring with a puckered conformation. The Tl—Se distances in **14.1** are almost equal to each other (2.781–2.782 Å), whereas the Tl—Te distances have a larger range (2.957–3.031 Å).[394,395] There are also a handful of stable ionic indium(+1) salts of oxyanions that are known; however, the corresponding compounds of heavier group 16 ligands tend to form oligomeric or polymeric materials in which the coordination number for the indium atom is 3 or more.[396] For indium and the lighter group 13 elements, many chalcogen-based ligands produce compounds that undergo spontaneous disproportionation. There are, however, a few examples of stable chalcogenolato complexes featuring the lighter group 13 elements in low-coordinate environments that are stable. Although it was reported considerably prior to the target time frame for this chapter, Roesky and coworkers' 1989 compounds, $[E_2(\mu\text{-}O(2,4,6\text{-}(CF_3)_3C_6H_2))_2]$ (E = In **14.3**, Tl **14.4**), deserve special mention in that each exhibits a discrete dimeric structure in the solid state, consisting of a four-membered ring with alternating triel and O atoms; the triel atoms are dicoordinate and feature In—O distances of 2.303–2.323 Å (Tl—O distances of 2.460–2.469 Å) and an O—In—O angle of 70.61° (O—Tl—O angle of 70.85°).[397,398] In fact, such a cyclic dimeric structure is even adopted by the parent indium(+1) compound InH, which was examined experimentally more than 10 years later by Pullumbi and coworkers using matrix-isolation methods.[399] Interestingly, an analogs Tl_2O_2 motif is observed for the thallium(+1) complex of the tris(pyrazolyl)methanesulfonate anion $[(Pz^{t\text{-}Bu})_3CSO_3]^-$. Rather than binding the thallium cation via the nitrogen atoms in the manner described in Section 1.17.2.1.2, the anion binds instead through one of the oxygen atoms on each sulfonate group to produce a dimeric structure of the form $Tl_2(\mu\text{-}OSO_2C(Pz^{t\text{-}Bu})_3)_2$ **14.5**, featuring Tl—O distances of 2.708–2.748 Å and an O—Tl—O angle of 80.85°.[400]

Macdonald and coworkers reported the structure of the relatively stable and soluble trifluoromethanesulfonate salt of indium(+1) **14.6** that features a similar arrangement, as illustrated in Figure 48. Although the compound is probably best considered as an ionic species, two adjacent [In][OTf] fragments adopt a dimeric arrangement in the solid-state reminiscent of the E_2O_2 moieties described above in a similar fashion.[401] The triflate group is, however, considerably more electron withdrawing than the 2,4,6-tris(trifluoromethyl)phenyl group and the In—O bond distances within the $In_2(\mu\text{-}OTf)_2$ fragment are considerably longer (2.578–2.646 Å) and are at best consistent with being contact ion pairs. Such an assessment is corroborated by the metrical parameters within the triflate anion, which are consistent with those of a 'free' anion. Furthermore, it should be noted that the treatment of [In][OTf] with [18]crown-6 results in a monomeric contact ion pair of the form [In([18]crown-6)][OTf] in which the closest In—O distance is 2.370 Å; thus, the distances within '$In_2(\mu\text{-}OTf)_2$' are clearly exceptionally long.[402]

As discussed in Section 1.17.2.1.1, β-diketiminate anions have proved to be suitable ligands for the isolation of many univalent group 13 compounds, including even examples for Al and Ga. By contrast, the corresponding acac ligands (and other related β-diketonate ligands), which have been employed extensively in the classical coordination chemistry of many metals, are not effective for the stabilization of univalent group 13 elements other than thallium. However, even for thallium, the absence of steric bulk around the metal center allows for the dimerization or oligomerization of these β-diketonate complexes. Although the solid-state structures do not feature the low-coordinate environments, these species often dissociate in solution and behave as monomers (as identified by NMR spectroscopy). As such, they have been included in this chapter. Even for thallium, there are only a handful of examples of

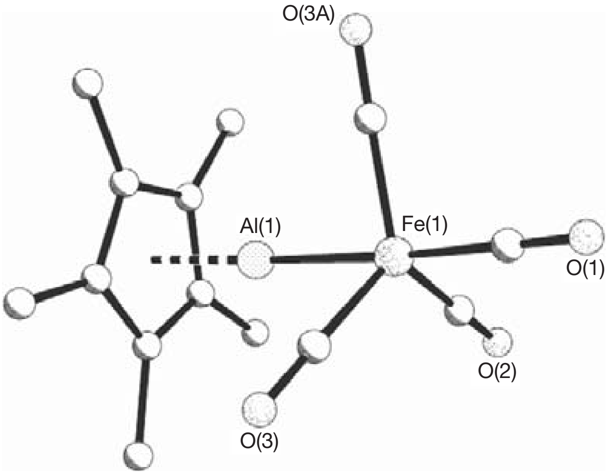


Figure 47 Solid-state structure of **13.2**, η^5-Cp*AlFe(CO)$_4$.

Table 31 Lanthanide and actinide complexes of Cp*M ligands

$(Cp^*E)_mML_n$

	M	E	m	L	n	M—E	E—Ct	M—E—Ct
13.80[388]	Eu	Al	1	Cp*	2	3.365	1.899	161.82
13.81[388]	Yb	Al	1	Cp*	2	3.198	1.905	171.97
13.82[389]	Yb[a]	Ga	1	Cp*	2	3.287	2.012	176.10
13.83[389]	Eu	Ga	2	Cp*	2	3.250–3.391	1.990[b]	164.28[b]
13.84[390]	U	Al	1	$C_5H_4SiMe_3$	3	3.117–3.124	1.886–1.904	164.15–165.96
13.85[391]	U	Ga	1	$C_5H_4SiMe_3$	3	3.065–3.080	1.976	161.28–163.95
13.86[391]	Nd	Ga	1	$C_5H_4SiMe_3$	3	3.153	1.982[b]	160.54[b]

[a] One molecule of THF is coordinating to the metal center.

[b] Centroid generated from disordered Cp* ligands.

β-diketonate ligands coordinated to thallium. In the solid state, the parent acac complex [Tl][$(OCMe)_2CH$] (**14.7**) forms polymeric chains in which one of the oxygen atoms in the acac ligand also binds to a neighboring chelated thallium center. The intramolecular Tl—O bond distances are 2.512 and 2.527 Å, whereas the intermolecular Tl—O distances are 2.825 Å.[403] Laguna and coworkers reported that the treatment of **14.7** with [Tl][$AuAr_2$] (Ar = C_6F_5, C_6Cl_5) produces aurate salts of dimeric trinuclear or tetranuclear thallium acac cations, $[Tl]_n[(OCMe)_2CH]_2$ ($n = 3$ or 4), respectively.[403] Interestingly, in spite of the different number of thallium atoms bonded to each acac fragment in $[(Tl)_3[(OCMe)_2CH]_2]^+$ **14.8** and $[(Tl)_4[(OCMe)_2CH]_2]^{2+}$ **14.9** (**Figure 49**), the average Tl—O bond distances for the tetracoordinate thallium ions remain relatively the same at ca. 2.71 Å. There is, however, a larger range of Tl—O distances for the dicoordinate thallium centers between the trinuclear (2.577 Å) and the tetranuclear (2.676–2.685 Å) complexes, as one would anticipate. It should be noted that there are close contacts and strong interactions between the dicoordinate thallium centers and the gold atoms which give rise to materials with interesting luminescent properties.[404]

Although it predates the target time frame somewhat, perhaps the nearest example of a monomeric dicoordinate thallium(+1) β-diketonate complex that has been structurally characterized is [Tl][$(OC(p\text{-}MeO\text{-}C_6H_4))_2CH$] **14.10**. This complex exhibits an envelope conformation with Tl—O distances of 2.456 and 2.501 Å and an O—Tl—O angle of 71.4°; however, the complex also features relatively close Tl···Tl interactions of 3.747 Å and packs in a manner that also allows for close Tl···O contacts on adjacent molecules.[405] In fact, it should be noted that the propensity for such complexes to engage in intermolecular interactions renders them useful as supramolecular synthons.

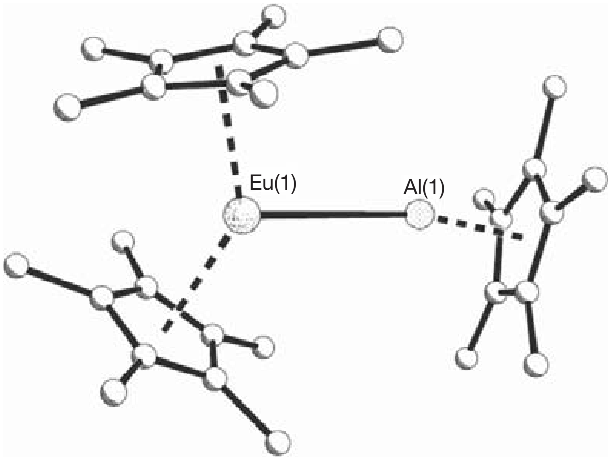


Figure 48 Solid-state structure of $Cp^*_2Eu\text{–}AlCp^*$, **13.80**.

There are two examples of low-coordinate group 13 compounds derived from sterically demanding terphenyl thiolate and selenate ligands that mandate discussion. In spite of the considerable bulk of the ligands, Niemeyer's thio- and selenophenolates, TlSAr* **14.11** and TlSeAr* **14.12**, also dimerize in a manner to that of the phenolate **14.4** to produce nearly planar four-membered rings of alternating thallium and sulfur/selenium atoms. The Tl—S distances in **14.11** range from 2.851 to 2.902 Å and the S—Tl—S angles are 66.7–66.9° while the Tl—Se distances in **14.12** range from 2.960 to 3.016 Å and the Se—Tl—Se angles range from 66.5 to 67.9°. As seen in previous sections, the triisopropylphenyl (Tripp) fragments on the terphenyl groups are oriented in a manner to form π-complexes with the Tl center (**Figure 50**).

A class of chalcogen-based ligands that are similar to the tris(pyrazolyl)borates mentioned earlier are the tris(thioimidazolyl)borates (TTIBs) that have been investigated extensively by Parkin and coworkers. These ligands resemble the Tp ligands in that they are monoanionic donors comprised of three heterocycles bound to a borate center; however, the ligands bind via the sulfur atom on the thioimidazole rings, rather than via the heterocyclic nitrogen atom. As with the bis- and tris(pyrazolyl)borate compounds presented in **Section 1.17.2.1.2**, the thioimidazoles can be considered to behave as pseudo-monocoordinate donors, at least in the context of the univalent group 13 complexes they provide. Metrical parameters for structurally characterized triel complexes that have been reported are presented in **Table 32**.

The 'free' univalent group 13 complexes of TTIB ligands were prepared by metathesis reactions using available indium (+1) and thallium(+1) reagents. These have only been characterized for indium (**14.13**) and thallium (**14.14**), although the latter adopts a dimeric structure in the solid state. However, the donor–acceptor complexes for gallium (**14.15–14.17**) have been amenable to isolation (from reactions of the metallated ligand with a gallium 'mono'-, 'di'-, and trihalides). The related indium complex of $B(C_6F_5)_3$ was generated by the treatment of

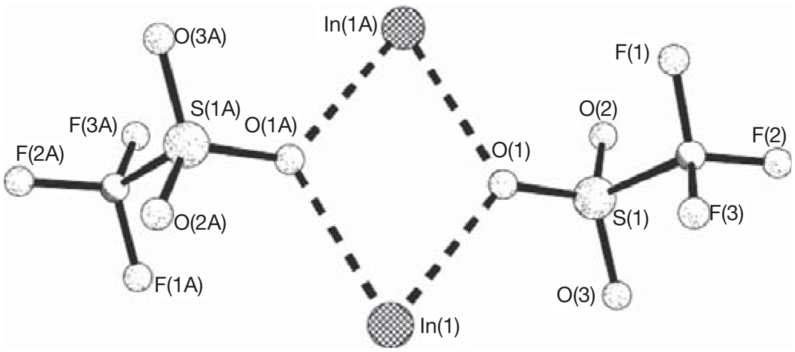


Figure 49 Solid-state structure of [In][OTf], **14.6**, as a dimeric species.

14.13 with the perfluoroarylborane, and a large decrease in the In—S distances is observed upon complexation.

The salt [([TTIB$^{t\text{-Bu}}$]Ga)$_2$GaI$_2$][I] **14.20** (Figure 51) was one of the products isolated from the treatment of [K][TTIB$^{t\text{-Bu}}$] with 'GaI'. The cation in this compound can be understood as a complex of two gallium tris(thioimidazole)borate donors to a single GaI$_2$$^+$.

Kuchta and Parkin have synthesized several gallium-based compounds that bear a striking resemblance to the tris(pyrazolyl)borates. The main difference is that instead of the gallium possessing a lone pair of electrons or donating them as a donor–acceptor complex, the metal is oxidized and bears a double bond to a chalocogen (S,[109] Se,[108] or Te[108]). The chalcogen bound to the triel has little effect on the electronics of the system. Although on average the Ga—N bond increases going from S to Te, the range is quite small (2.042–2.072 Å). Compared to the unchalcogenated compound (**2.21**), the Ga—N bonds are considerably shorter (2.240 Å for Tp$^{t\text{-Bu}}$Ga). This effect was also observed for the donor–acceptor complexes of the tris(pyrazolyl)borates. The metals in these chalcogenated compounds have an oxidation state of +3 and are more electron deficient and thus move closer to the

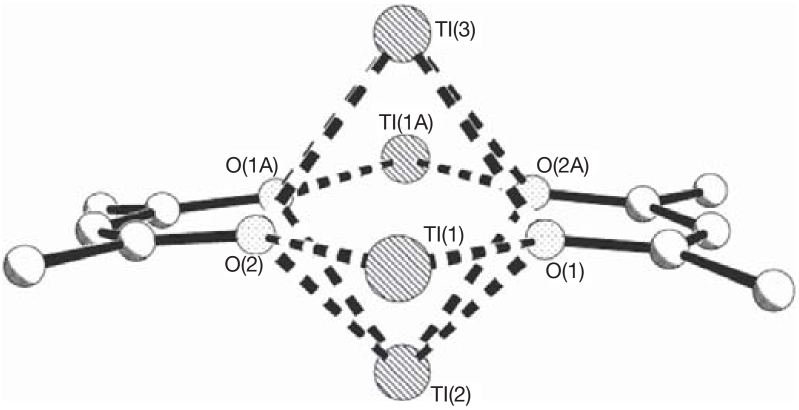
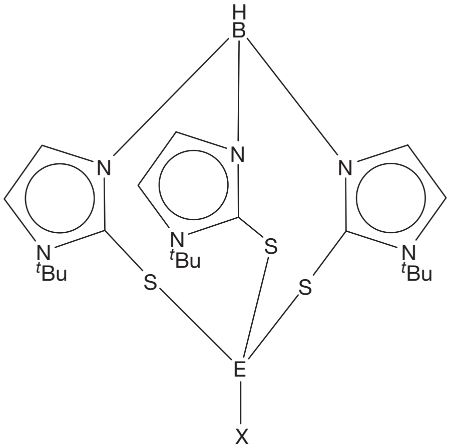


Figure 50 Solid-state structure of [Tl]$_4$[(OCMe)$_2$CH]$_2$, **14.9**. [Au(C$_6$Cl$_5$)$_2$]$^-$ counter anions are not shown.

Table 32 Structural features for tris(thioimidazolyl)borate ligands for Ga, In, and Tl



#	E	X	E—S	E—X	S—E—S
14.13[406]	In		2.749		87.89
14.14[a406]	Tl		2.997–3.239		99.73
14.15[407]	Ga	GaCl$_3$	2.327	2.405	102.46
14.16[407]	Ga	GaI$_3$	2.321–2.342	2.425	102.44–105.81
14.17[407]	Ga	B(C$_6$F$_5$)$_3$	2.359–2.361	2.177	100.83–100.87
14.18[407]	Ga	SGaCl$_3$	2.297–2.311	2.202	103.06–107.60
14.19[406]	In	B(C$_6$F$_5$)$_3$	2.549–2.586	2.374	94.80–97.29

[a] Dimeric structure.

electron-rich nitrogen centers. In addition to these three gallium analogs, an indium congener was also synthesized that is doubly bound to selenium (Figure 52).

Finally, as discussed previously, the favorable properties of thallium(+1) salts, including stability in many systems and often solubility in organic solvents, render such species excellent reagents in spite of their high toxicity. In this light, thallium(+1) salts have been prepared for many classes of anion and ligands, some of which contain chalcogen donors. Some recent examples of salts in which the thallium(+1) centers could potentially exist in dicoordinate environments are presented in Table 33. In many instances, these complexes are probably best considered as contact ion pairs and require no extensive discussion. Furthermore, the large coordination sphere of thallium(+1) and its propensity to engage in intermolecular interactions actually mean that most of the complexes depicted as 'monomers' in Table 33 are, in fact, parts of dimeric, oligomeric, or polymeric structures in the solid state.

Whereas the thallium dithiophosphonate **14.22** truly exists as a dimer in the solid state with bridging Tl—S distances of 3.242 Å, the imidophosphonate derivatives **14.21** feature much longer intramolecular Tl–S contacts of 3.599 Å and are thus much closer to being monomeric. Consequently, **14.21** is considerably more soluble in organic solvents and is postulated to be a monomer upon dissolution.

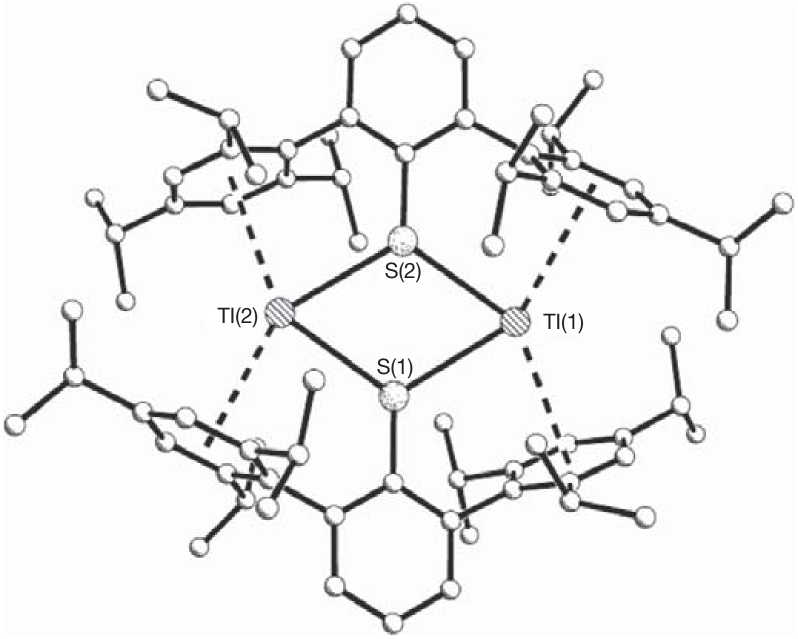


Figure 51 Solid-state structure of dimerized TlS–2,6-(Tripp)$_2$C$_6$H$_3$ illustrating the interaction of the π-system on the Tripp ligands with the Tl centers.

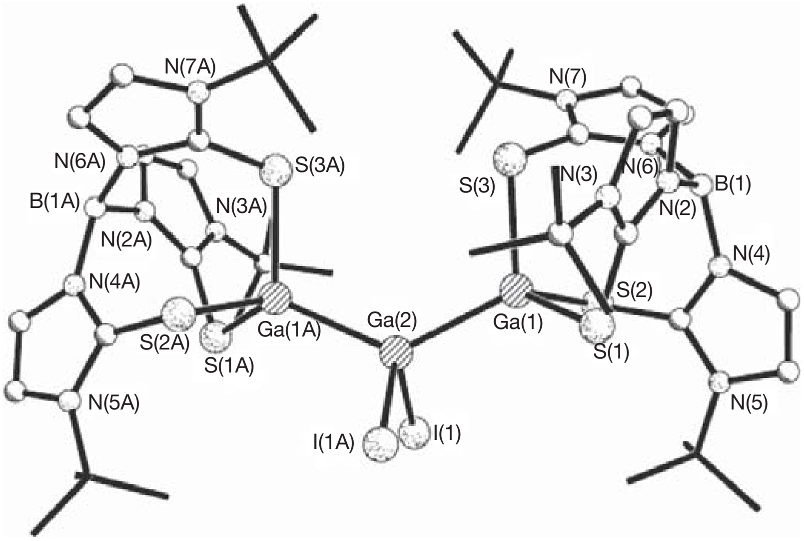
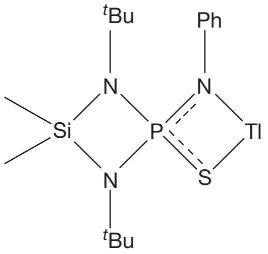
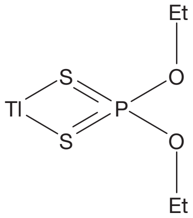
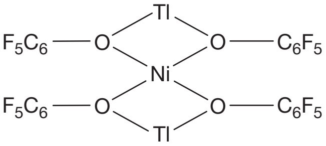
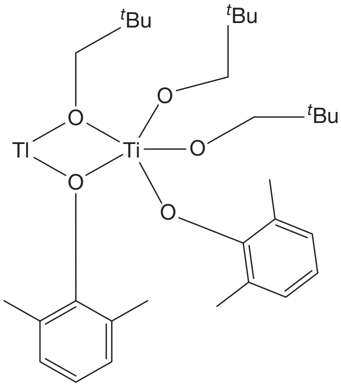
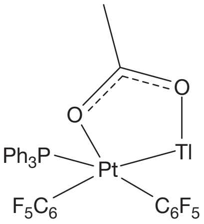
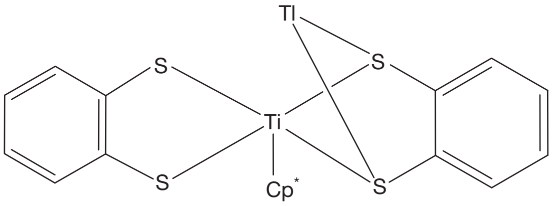


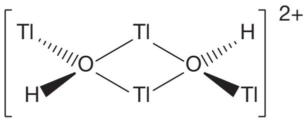
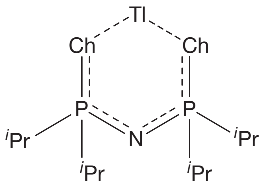
Figure 52 Solid-state structure of ([TTIB^{Bu}]Ga)$_2$GaI$_2$, **14.20**. Counterion I$^-$ is not shown. Selected metrical parameters: Ga—S: 2.348–2.353 Å; Ga—Ga: 2.177 Å; S—Ga—S: 100.83–100.87°.

Table 33 Structural features of miscellaneous thallium salts of chalcogen-containing ligands

	Structure	*Bond distances*	*Bond angles*
14.21[408]		Tl—S: 2.886 Tl—N: 2.535	N—Tl—S: 63.44
14.22[409]		Tl—S: 3.164 and 3.118	S—Tl—S: 63.15
14.23[410]		Tl—O: 2.547–2.650	O—Tl—O: 61.50 and 63.19
14.24[411]		Tl—OAr: 2.545 Tl—OnPn: 2.600	O—Tl—O: 59.59
14.25[412]		Tl—O: 2.489 Tl—Pt: 2.994	Pt—Tl—O: 74.61
14.26[413]		Tl—S: 3.148 and 3.167	S—Tl—S: 59.66

(*Continued*)

Table 33 (Continued)

	Structure	*Bond distances*	*Bond angles*
14.27[242]	 $2\ [H_2N(B(C_6F_5)_3)_2]^-$	Tl_μ—O: 2.483–2.526 $Tl_{terminal}$—O: 2.398	O—Tl—O: 77.77
14.28[414] (Ch = S) **14.29**[414] (Ch = Se) **14.30**[414] (Ch = Te)		Tl—Ch: 2.920–2.922 3.051–3.060 3.223–3.233	Ch—Tl—Ch: 90.35 77.82–87.63 79.98–88.97

Most of the transition-metallate complexes (**14.23–14.25**) also feature relatively short intramolecular Tl—Ch bonds; however, the titanate complex **14.24** is exceptional in that its closest intramolecular interactions are with the π-systems on a mesitylene fragments from an adjacent molecule. The dithallium nickel complex **14.23** also features close contacts with the π-system of a toluene solvent molecule in the structure, in addition to intramolecular O–Tl contacts (3.110–3.214 Å) and even F–Tl contacts. Overall, the titanate salt **14.24** appears to be the most 'monomeric' of the transition-metallate complexes listed.

Perhaps the most unique compound listed in Table 33 is the tetrathallium dication in salt **14.27**, which was obtained from the partial hydrolysis of the salt $[Tl(OEt_2)_2][H_2N(B(C_6F_5)_3)_2]$. This dication features nominally dicoordinate and monocoordinate thallium(+1) centers although each of these is engaged in numerous close contacts with atoms from adjacent anions and dichloromethane solvent molecules. Regardless, the lengths of the Tl—O bonds, both for the bridging and terminal thallium atoms, are particularly short.

Finally, the series of chalcogenolates **14.28–14.30** reported by Ritch and Chivers exhibit coordination polymeric structures with extensive Tl—Ch contacts that are only slightly longer than the intermolecular distances. The thiolate complex **14.28** features a ladder-like arrangement, whereas the heavier chalcogenolate analogs adopt a more complex coordination polymeric arrangement in which each of the Tl centers effectively has a distorted trigonal prismatic six-coordinate environment. Thus, as with most of the other compounds listed in Table 33, the actual coordination number of thallium is not consistent with the simple structural drawing and the compounds are not truly low coordinate.

1.17.2.3.7 Radicals and related species – supersilyl ligands

There are hundreds of group 13 compounds in which silyl groups are directly bound to the triel but only a handful of these feature low-coordinate environments at the group 13 center. The silyl groups found in these low-coordinate species often bear particularly large substituents such as ^{t}Bu or Ph groups. Overall, such bulky silyl ligands are often sufficiently sterically demanding to prevent oligomerization of low-coordinate species. In addition, the ability of silyl substituents to engage in negative hyperconjugation with electron-rich centers has also allowed for the isolation of some truly remarkable low-coordinate compounds.[415,416] For example, Wiberg and coworkers reported the radical $^tBu_3SiGa–Ga(Si^tBu_3)_2$ **15.1**, which features three tris(*tert*-butyl)silyl ligands which are sufficiently bulky to prevent dimerization of the paramagnetic molecule.[417] It is synthesized from the disproportionation of $GaCl_3$ with excess $NaSi^tBu_3$ and contains a rare divalent, dicoordinate gallium center. The Ga—Ga distances of 2.420–2.426 Å are comparable to the other Ga—Ga bonds such as those in the donor–acceptor complexes described in previous sections and the Si—Ga—Ga angle of 169.72–170.34° illustrates that the single unpaired electron engenders only a slight deviation from linearity. Reduction of the radical **15.1** with sodium metal leads to the sodium salt of the corresponding anion $[Na(THF)_3][^tBu_3SiGa–Ga(Si^tBu_3)_2]$.[417] The sodium counter-cation is in close contact with the dicoordinate anionic gallium center as shown in Figure 53.

The average Ga—Si distance remains more or less unaffected when going from the radical to the reduced species; however, a significant decrease in the Ga—Ga bond is observed and the anion in **15.2** has a Ga—Ga bond distance of 2.380 Å. This decrease in bond length is indicative of a partial π-bonding between the gallium atoms as the 'lone pair' on the univalent dicoordinate gallium center (Ga(1)) can donate in the vacant p-orbital of the trivalent tricoordinate gallium center (Ga(2)).

Sekiguchi and coworkers reported similar anionic complexes of the type, $[Li(THF)_4][E(Si(Si^tBu_2Me)_2)_2]$ (E = Ga **15.3**, In **15.4**), as illustrated in Figure 54, that exhibit structures that are perhaps best described as being main group allene-like compounds.[418] These compounds are synthesized by salt elimination from the reaction of $(^tBu_2MeSi)_2SiLi_2$ and ECl_3 to afford the desired product. The structures deviate from linearity, as evidenced by the Si—E—Si angles of 161.61° for the gallium compound and 161.36° for the indium and feature pyramidal rather than planar environments at the silicon atoms bound to the triel. Both of these structural features are, as one would predict, on the basis of the theory regarding multiple bonds between main group elements espoused by Carter–Goddard–Malrieu–Trinquier (CGMT) theory.[419] Again, although these anions feature low-coordinate triel atoms, they also contain multiple bonding and are thus considered in more detail in another chapter of this work.

Finally, it should be noted that the salt $[Li(THF)_4][In(Ge(Si^tBu_2Me)_2)]$ **15.5**, which is analogs to **15.4**, has been prepared using bulky germyl ligands.[420] As one would anticipate on the basis of CGMT theory, the structure is considerably more bent than the silicon complex with a Ge—In—Ge bond angle of 158.45 and it features an average Ge—In bond length of 2.542 Å.

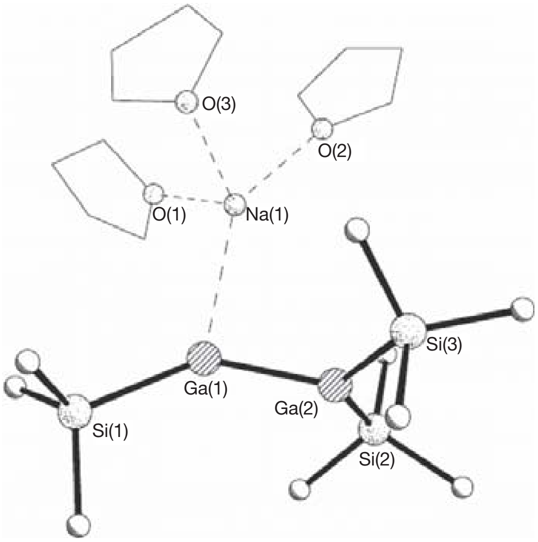


Figure 53 Solid-state structure of $[^tBu_3SiGa–Ga(Si^tBu_3)_2][Na(THF)_3]$. Select bond distances: Ga(1)—Na: 3.205 Å; Ga(1)—Ga(2): 2.380 Å Ga(1)—Si(1): 2.500 Å. Methyl substituents on the ^{t}Bu groups have been omitted for clarity.

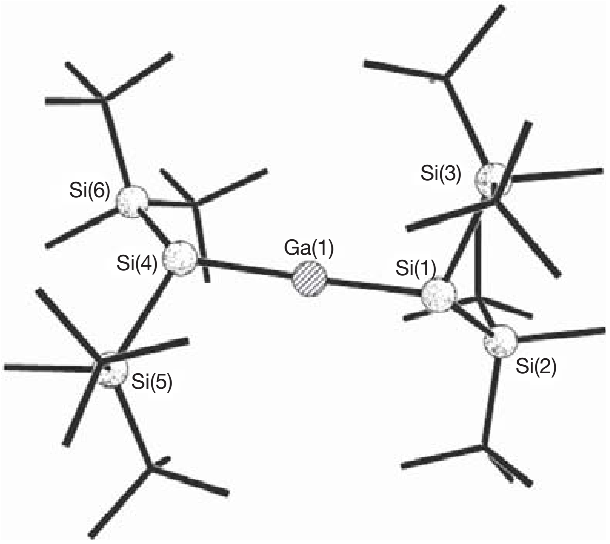


Figure 54 Solid-state structure of $[Li(THF)_4][Ga(Si(Si^tBu_2Me)_2)_2]$, **15.3**. The $[Li(THF)_4]^+$ counter-cation is not shown. Selected bond lengths: Ga–Si: 2.281 (avg.) Indium analog: In–Si: 2.482 (avg.).

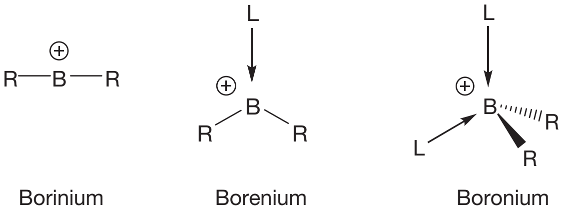
1.17.3 Part 2 – Low-Coordinate Compounds Attributable to Cationic Charge

Although it is perhaps an obvious statement, the removal of a ligand or substituent from a tricoordinate group 13 element should necessarily result in a compound featuring a low-coordinate triel center, at least in the absence of subsequent coordination of the vacant site by an available electron donor. In most instances, the highly electrophilic nature of cationic group 13 molecules (at least for the lighter analogs) results in those fragments being ligated in either an inter- or an intramolecular manner by donors that may include solvent molecules to produce compounds that exhibit higher coordination numbers. There are, however, a limited number of compounds in which the cationic group 13 center remains low coordinate, at least formally, and these are described in the following sections.

1.17.3.1 Borinium Cations

Borinium cations of the general form $[R_2B]^+$ are of interest as potent electrophiles and as reactive intermediates.[421,422] Because of their electron-deficient nature – in the absence of electron-donating substituents the boron center formally bears only four valence electrons – and their coordinative unsaturation, most putative borinium cations are rapidly coordinated by solvent or other donor molecules to produce tricoordinate borenium cations or tetracoordinate boronium cations, as illustrated in Figure 55. In that context, it should be noted that the identification and investigation of most free $[R_2B]^+$ species (R = e.g., alkyl, halo or alkoxyl) had been conducted in the gas phase prior to 2000.[422] In fact, even the highly reactive parent cation $[H_2B]^+$ has proved to be susceptible to generation and reactivity studies in the confines of mass spectrometers.[423] As one would anticipate, such cations – $[Me_2B]^+$ and $[MeO_2B]^+$ investigated most extensively – behave as electrophiles and Lewis acids and $[F_2B]^+$ has demonstrated the ability to function as an initiator for the oligomerization of ethylene.[424–426]

The vast majority of isolable salts containing borinium cations that actually exhibit a coordination number of 2 feature nitrogen atoms coordinated to the boron center to produce alkene-like, allene-like, or alkyne-like cations. Thus, like many of the complexes presented in Section 1.17.3.1, such species are best described as containing boron—nitrogen multiple bonds and are covered in other chapters of this book. The two major classes of ligands that have proved to be suitable for the isolation of essentially dicoordinate boron cations in the condensed phase are the phosphinimides and the cyclopentadienide derivatives.



Borinium Borenium Boronium

Figure 55 The three different classes of cationic boron compounds.

It should however be noted that, regardless of the substituents on boron, such cationic borinium species are typically generated in one of two ways (as illustrated in **Figure 56**): (1) the treatment of a suitable tricoordinate borane with an appropriate anion (e.g., halide, hydride, and methanide) abstracting agent and (2) the silylation of an imine-substituted borene.

Phosphinimide ligands of the form $[R_3PN]^-$ are monodentate ligands formally derived from phosphinimines of the general type R_3PNH; the deployment of large organic substituents on the phosphorus center can make such ligands very sterically demanding and thus render them suitable for the stabilization of very reactive species. Disubstituted tricoordinate boron phosphinimine derivatives may be readily prepared by different routes including the treatment of 2 equiv. of R_3PNH with an appropriate boron hydride precursor (e.g., $H_3B{\bullet}SMe_2$) to generate $(R_3PN)_2BH$ or the treatment of 2 equiv. of the lithiated phosphinimide reagent with boron trichloride to yield $(R_3PN)_2BCl$.[427] Related neutral phosphinimide derivatives of the heavier group 13 species have also been prepared by the treatment of R_3PNH with group 13 alkyls or through the reaction of the silylated reagent $R_3PNSiMe_3$ with corresponding group 13 halides.

The subsequent reaction of the bis(phosphinimato)borane (when $R = {}^{t}Bu$) with hydride abstracting agents such as salts of the triphenylmethyl (trityl) cation or anion metathesis reagents such as lithium salts then produces the corresponding salts of containing the dicoordinate borinium cations depicted in **Figure 57**.[427,428] These salts have been structurally characterized and feature linear N—B—N fragments with bond angles of 180° that exhibit N—B distance ranging from 1.236 to 1.258 Å. These N—B distances are considerably shorter than those observed for $(Ph_3PN)_3B$ (1.433–1.457 Å)[429] and are also suggestive of B—N multiple bonding. In that context, it is also worth noting that the P—N—B angles in the borinium cations (162.1° and 180.0°) are also considerably larger than those in the neutral borane (130.8–133.6°) and are also consistent with a degree of phosphinimine—boron multiple bonding, although the larger ${}^{t}Bu$ groups in the cations versus the phenyl substituents in the neutral borane undoubtedly affect these metrical parameters too. Regardless, and in spite of the conventional Lewis-type drawing, there is a distinct possibility that some donation of the lone pair on the nitrogen atom stabilizes the borinium cation in these examples as it does for the imido and amido borinium cations mentioned above.

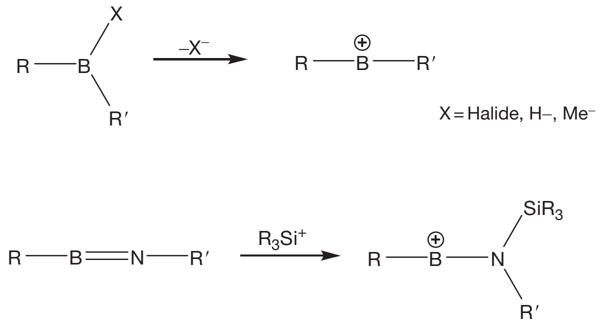


Figure 56 Synthetic routes to dicoordinate cationic borinium species.

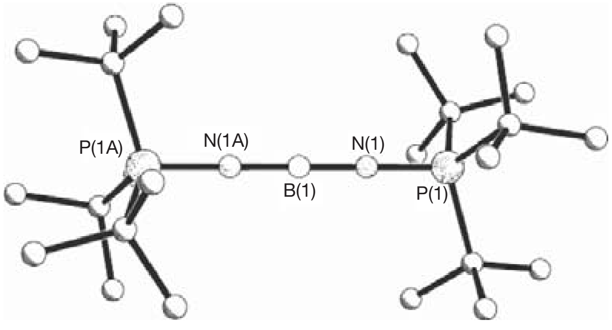


Figure 57 Solid-state structure of $[B(NP(CMe_3)_3)_2]^+$, **16.1**. Counterion Cl^- not shown.

Because of their particular steric properties, their flexible binding modes, and their electron-donating abilities, it is perhaps not surprising that the cyclopentadienyl ligands,[214] in particular the Cp* ligand,[215] have also allowed for the isolation of a number of pseudo-dicoordinate boron cations. As indicated above, although the Cp′-type ligands are considered as singly coordinating ligands, it should be reemphasized that such ligands can function as donors of anywhere between two electrons (e.g., σ- or η^1-Cp) and six electrons (e.g., η^5-Cp); however, Cp–E linkages are not typically considered as multiple bonds in the same manner as they often are for the isolobal imido and phosphinimido ligands.

Salts of the form $[Cp^*B{-}X][EX_4]$ were first prepared and investigated by Jutzi and coworkers through the reaction of Cp^*BX_2 with EX_3 (E = B, Al)[430] in the late 1970s; however, the structure of the salt $[Cp^*B{-}Br][AlBr_4]$[430,431] was not reported until 1987. The structurally characterized salt was obtained as a product from the redox/ligand redistribution reaction of Cp*Al with BBr_3. Each borinium cation features an η^5-Cp* substituent with an essentially linear centroid–B–Br fragment (176.3° and 180.0° for the two independent cations) and with centroid—B distances of 1.147 and 1.016 Å and B—Br distances of 1.925 and 1.870 Å. In a somewhat simplistic manner, the relative stability of this borinium cation can be understood as follows: if the η^5-Cp* group is acting as a six-electron donor in this system, then the boron center in the cation actually has an eight-valence-electron configuration and is thus not as electronically unsaturated as in the simpler gas-phase borinium cations described above. It is also worth noting that the bonding in such cyclopentadienyl-substituted borinium species has also been rationalized in the context of carborane clusters – cations such as $[Cp^*B{-}Br]^+$ (**16.2**) can be considered a *nido*-carborane[432]; however, the treatment of such cations with pyr bases produces the distinctly un-carborane-like four-coordinate boronium cations bearing σ-Cp* substituents.

The related bis-pentamethylcyclopentadienyl sandwich cation $[Cp^*_2B]^+$ was first characterized spectroscopically in the salt $[Cp^*_2B][BCl_4]$ (**16.3**), prepared by the treatment of Cp^*_2BCl with BCl_3, by Jutzi and coworkers in the late 1970s.[433] NMR investigations revealed that the cation contains one η^5-Cp* ligand and one σ-Cp* group; several salts of this 'borocenium' cation were subsequently generated by Cowley and coworkers again using halide abstraction from Cp^*_2BCl or methanide abstraction from Cp^*_2BMe, and the structure of the cation was finally confirmed for the salt $[Cp^*_2B][AlCl_4]$ (**16.4**) by x-ray crystallography and solid-state NMR spectroscopy.[433–436] As illustrated in **Figure 57**, each cation does indeed feature an η^5-Cp* ligand with centroid—B distances of 1.282–1.290 Å and one σ-Cp* group with C_{ipso}—B distances of 1.583–1.586 Å. The rings are not parallel to each other, as observed for the isoelectronic species $Cp^*{}_2Be$[437–440] and the structure was described as being the most 'tightly-squeezed' metallocene possible. As with the halogenated analogs described above, the relative stability of this class of borinium cation may be conveniently rationalized in terms of there being a potential eight-valence-electron count on the boron center in conjunction with the steric properties of the Cp* ligand. Considerably more in-depth computational investigations reveal that the nonplanar arrangement of the cyclopentadienyl ligands is considerably more favorable (50 kcal mol^{-1}) than the putative D_{5h} or D_{5d} symmetry structures typical of many metallocenes of heavier elements (including those of Al and Mg) because of the small size of the B(+3) ion and its constituent orbitals (**Figure 58**).[434,441]

A related borinium cation is observed in the salt [Cp*B–$SiCl_2$Cp*][Cp*BCl_3] (**16.5**) which was generated by the non-stoichiometric ligand redistribution and redox reaction of $Cp^*{}_2Si$ with Cp*BCl_2.[442] As one may anticipate, the cation contains an η^5-Cp* ligand; however, the centroid—B—Si angle of 170.8° is somewhat distorted from linearity for reasons that were attributed to crystal packing effects. The related salts [Cp*B–SiX_2Cp*][BX_4] (X = Cl (**16.6A**) and Br (**16.6B**)) were obtained through the similar reaction of $Cp^*{}_2Si$ with BX_3; however, analogs neutral compounds of the form Cp*SiX_2–Cp*B–SiX_2Cp* were also obtained as byproducts. The brominated analog was structurally characterized and features a very distorted η^4-Cp* ligand to the pseudo-dicoordinate boron center and, in contrast to most of the other pentamethylcyclopentadienyl described herein, the overall boron fragment in this compound truly appears to be much more appropriately described in the context of an *arachno*-carborane cluster. In particular, the distorted bridging ring in the neutral structure contrasts with those of the 'donor–acceptor' complex Cp*B–BCl_3 and the related compound Cp*B–$SiCl_2BCl_3$[269] described above.

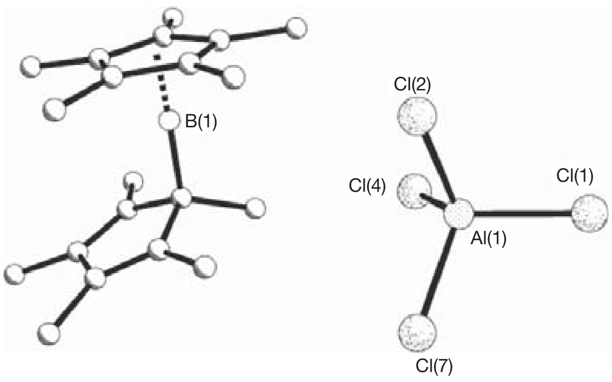


Figure 58 Solid-state structure of [(η^5-Cp*)B(σ-Cp*)][$AlCl_4$], (**16.4**). Asymmetric unit contains two cations and anions; only one of each is depicted here.

1.17.3.2 Cations of the Heavier Group 13 Elements

In contrast to the borinium salts, there are considerably more classes of substituents that have allowed for the isolation of well-characterized stable compounds containing heavier trivalent group 13 elements in low-coordinate environments as a consequence of a positive charge.[443] In fact, it has long been apparent that for In and Tl even seemingly simple compounds of the type ER_2X sometimes auto-ionize and exist in the solid state as salts of the form [ER_2][X], featuring linear dicoordinate metal centers, even for R = Me.[444,445] This behavior is presumably a consequence of the relatively weak E–X bonds for the heavier elements and may be assisted by the favorability of the lattice energy associated with a salt structure.

For the lighter elements Al and Ga, simple dialkyl or diaryl cations are invariably ligated by electron donors and feature coordination numbers higher than 2; however, the use of sterically demanding alkyl (or related silyl and germyl) substituents or the use of very noncoordinating anions (NCAs), or a combination of both strategies, has allowed for the isolation of dicoordinate cations of the lighter elements.

For example, Reed and coworkers' use of the extremely noncoordinating carborane anions $[B_{11}CH_6X_6]^-$ (X = Cl (**17.1**), Br (**17.2**)) allowed for the isolation of the carborane 'salts' of $[Et_2Al]^+$ through the reaction of the trityl carborane reagents with triethylaluminum.[446] The structure of the product, illustrated in **Figure 59**, reveals that there is considerable interaction between the putative $[Et_2Al]^+$ cation and the anion such that the C—Al—C angle is less than 140° in each case (138.5° for **17.1** and 130.0° for **17.2**). Thus, the very electrophilic aluminum cation is even clearly able to draw electron density even from such exceedingly NCAs to form a tight ion pair. It should be noted, however, that these compounds do indeed behave as potent electrophiles and are effective initiators of ethene oligomerization.

By contrast, the presence of considerably larger substituents on the aluminum or gallium centers can indeed allow for the isolation of true dicoordinate species. Although there are no structurally characterized alkyl derivatives, Sekiguchi and coworkers were able to isolate salts of the form [^{t}Bu_2MeSi–E–Si(^{t}Bu)$_2$Si^tBu_2Me][$B(C_6F_5)_4$] (E = Al, (**17.3**) Ga (**17.4**)) which feature dicoordinate cations of Al and Ga with bulky silyl substituents.[447] The salts were generated by the abstraction of a methanide equivalent from the alane (or gallane) E(Si^t-Bu_2Me)$_3$ using the silylium reagent [$SiEt_3$][$B(C_6F_5)_4$], followed by a 1,2-silyl group migration. The cations, as illustrated in **Figure 60**, feature linear Si–E–Si fragments and the authors posit that the cations might be stabilized by a hyperconiugative interaction with the adjacent Si—Si bond.

Whereas linear dialkyl aluminum and gallium cations have not yet been structurally characterized, there are examples of almost linear diaryl analogs. In particular, the treatment of the bulky bis-terphenylalane $(2,6\text{-}Mes_2C_6H_3)_2AlH$ with the hydride abstracting agent [CPh_3][$B(C_6F_5)_4$] generated the perfluorinated tetraphenylborate salt [$(2,6\text{-}Mes_2C_6H_3)_2Al$][$B(C_6F_5)_4$] (**17.5**), which crystallizes either as a free salt or as a benzene solvate.[448] In the free salt, illustrated in **Figure 61**, the $[(2,6\text{-}Mes_2C_6H_3)_2Al]^+$ cation features a C—Al—C angle of 156.54° and a value of 159.17° is observed in the benzene solvate structure. In each case, the C—Al distances, which

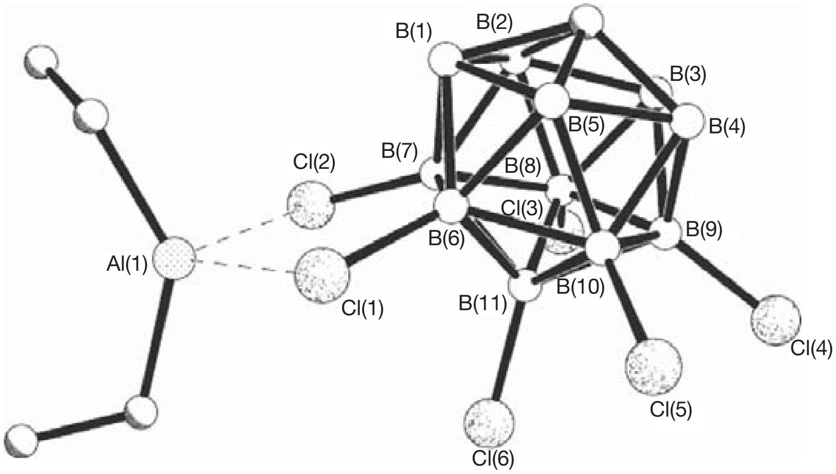


Figure 59 Solid-state structure of $[CB_{11}Cl_6][AlEt_2]$, **17.1**.

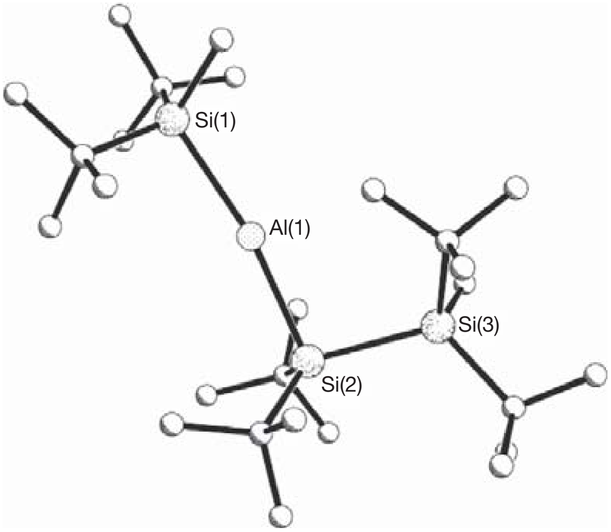


Figure 60 Solid-state structure of $[Al(SiMe(CMe_3)_2)(Si(CMe_3)_2(SiMe(CMe_3)_2))]^+$, **17.3**. Counterion $[B(C_6F_5)_4]^-$ not shown.

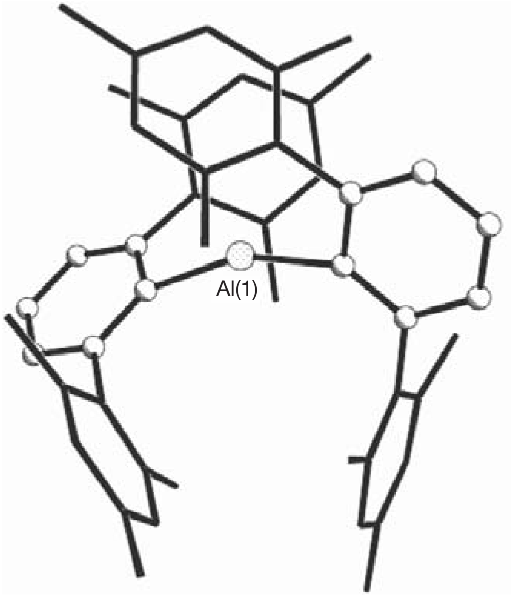


Figure 61 Solid-state structure of $[Al(2,6\text{-}Mes_2C_6H_3)_2]^+$, **17.5**. Counterion $[B(C_6F_5)_4]^-$ not shown.

range from 1.9379 to 1.9428 Å, are somewhat shorter than the corresponding C—Al distances of the alane precursor, as one would perhaps anticipate on the basis of the higher charge and lower coordination number at the Al center. It should be noted that both the free and solvate structures feature distortions that suggest that the highly electrophilic Al cation interacts with the π-system of the flanking mesityl substituents in either an η^1-fashion with the *ipso*-carbon atoms alone or an η^2-fashion with the *ipso*- and *ortho*-carbon atoms. It appears as if the favorability of these interactions is likely the cause of the distortion of the C–Al–C moiety from linearity.

In a similar vein, it should be noted that Linti and coworkers were able to isolate related salts containing anions that feature formally cationic dicoordinate gallium or indium centers. The salt $[Li(THF)_4][(Ph_3Ge)_3Ga–Ga–Ga(GePh_3)_3]$ (**17.6**) was obtained as one of several products generated by the treatment of 'GaI' with $(THF)_3LiGePh_3$ in toluene.[449] The trigallium anion may be rationalized as consisting of a linear cationic Ga^{III} center bound to two tetracoordinate anionic Ga^{III} centers with Ga—Ga bonds of 2.536 and 2.548 Å and a Ga—Ga—Ga angle of 178.8°. The same research group later isolated an analogs indium salt with the composition $[Na(THF)_6][(Ph_3Si)_3In–In–In(SiPh_3)_3]$ (**17.7**) as one of several compounds generated in the reaction of Cp*In with $(THF)_3NaSiPh_3$ in toluene at low temperature.[450] The structure of the anion features a crystallographically imposed perfectly linear In_3 fragment with In—In bonds of 2.8269 Å. In both cases, the experimentally observed metrical parameters were in reasonable agreement with those found from density functional theory (DFT) optimizations of less-bulky model complexes and the authors suggest that the compound provides insight into the formation of polyhedral gallium or indium clusters, which are among the other products obtained in conjunction with these salts.

It is worth noting that a salt featuring the analogs gallium cation was prepared by the same research group prior to the aluminum variant by a slightly different route. The treatment of the chloro bis-terphenylgallane $(2,6\text{-}Mes_2C_6H_3)_2GaCl$ with 2 equiv. of the salt $[Li][Al(OCH(CF_3)_2)_4]$ produced the salt $[(2,6\text{-}Mes_2C_6H_3)_2Ga][Li][(Al(OCH(CF_3)_2)_4)_2]$ (**17.8**, Figure 62) with the concomitant elimination of LiCl.[451] In contrast to the aluminum cations described above, the C—Ga—C angle of 175.69° in the $[(2,6\text{-}Mes_2C_6H_3)_2Ga]^+$ cation is essentially linear and the gallium center does not appear to engage in π-bonding with the mesityl groups of the terphenyl ligands. The authors noted that, in spite of the encapsulating arrangement of the two terphenyl substituents, the gallium cation is able to react with bases such as DMAP and pyr to form three-coordinate adducts.

Given the relative stability of even simple dialkyl-indium and -thallium cations, it is not surprising that even moderately bulky diaryl cations of each of these elements have also proved to be amenable to isolation and structural characterization. Thus, the treatment of Mes_2InF with BF_3 produces $[Mes_2In][BF_4]$ (**17.9**).[452] Although the structure is disordered, as one would anticipate, the cation contains an essentially linear C—In—C arrangement with an angle of 173.59° and there are long-range In···F contacts to the anions that provide each indium atom with a roughly octahedral coordination environment in the solid state. It is noteworthy that the same product was also isolated from the ligand redistribution reaction of Mes_3In and $BF_3{\bullet}Et_2O$, and the heavier thallium congener of the tetrafluoridoborate salt, namely $[Mes_2Tl][BF_4]$ (**17.20**), was generated analogsly.[453] Interestingly, while the dimesitylthallium cation features a crystallographically constrained linear C–Tl–C fragment with C_{ipso}—Tl bonds of 2.153(8) Å, the coplanar arrangement of the two aryl substituents is in contrast with those of the aluminum (**17.5**) and gallium (**17.8**) cations described above. The strongly interacting $[BF_4]^-$ anions produce a coordination-polymer-like crystalline structure in which the nearest cations are each rotated by 90° from each other. The related salt $[Mes_2Tl][MesTlCl_3]$ (**17.21**) was prepared by the reaction of $TlCl_3$ with AgMes[454] or through the ligand redistribution reaction of 2 equiv. of $TlMes_3$ with $TlCl_3$. Again, the structure of the dimesitylthallium cation, illustrated in Figure 63, exhibits a nearly linear C–Tl–C moiety (171.8°) and nearly coplanar aromatic substituents; this observation suggests that the coplanar arrangement of the aryl groups is not simply a packing artifact and is perhaps indicative that the large size of thallium decreases the potential steric repulsion of the *ortho*-methyl groups on the mesityl ligands.

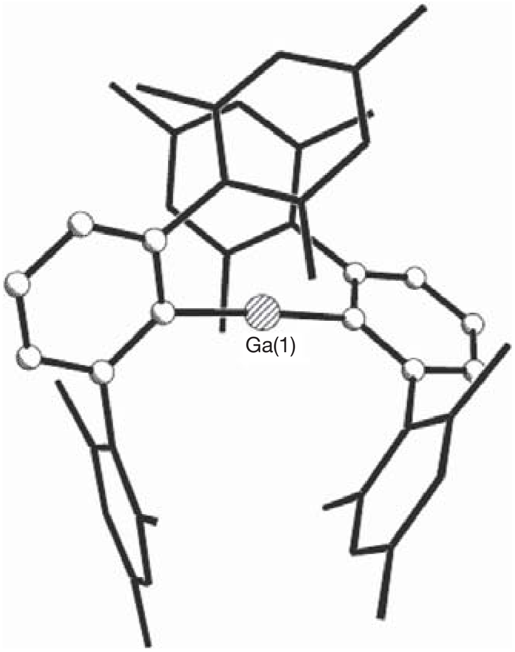


Figure 62 Solid-state structure of $[Ga(2,6\text{-}Mes_2C_6H_3)_2]^+$, **17.8**. Counterion $Li[Al(OCH(CF_3)_2)_4]^-$ not shown.

Finally, it should be noted that similar halide abstraction and ligand redistribution reactions are also reported to be viable routes to salts of the cation $[Bn_2In]^+$; however, these materials were not structurally characterized.[452,454]

1.17.3.3 Cyclopentadienyl Compounds

The vast majority of the cyclopentadienyl cations of trivalent heavier group 13 elements are known for aluminum.

1.17.3.3.1 Structural features

Whereas dialkyl and diaryl cations of aluminum are rare, reactive, and require significant steric bulk for isolation, the corresponding pseudo-linear bis-pentamethylcyclopentadienyl aluminum cations, called 'aluminocenium' cations because they are cationic aluminum metallocenes, have been obtained from numerous reactions. For example, the first reported salt of the decamethylaluminocenium cation, $[Cp^*{}_2Al][Cp^*AlCl_3]$ (**18.11**), was obtained by Schnökel and coworkers as a disproportionation product from the reaction of Cp*Al with $AlCl_3$ (which contrasts sharply with the products observed for the corresponding reaction of Cp*Al with $Al(C_6F_5)_3$ described above (**10.2**)).[462] As indicated in Table 34 and illustrated in Figure 64, the cation features an almost ideal D_{5d} geometry with a linear $ring_{centroid}$–Al–$ring_{centroid}$ arrangement that is reminiscent of the 3d-metal analogs such as ferrocene. The adoption of the bis (η^5-Cp*) structure rather than the asymmetric structure exhibited by the boron analog is likely a consequence of the larger size of Al versus B in addition to the highly ionic nature of the bonding afforded by the very electropositive nature of Al, which allows for the formally 12-valence-electron arrangement.[435]

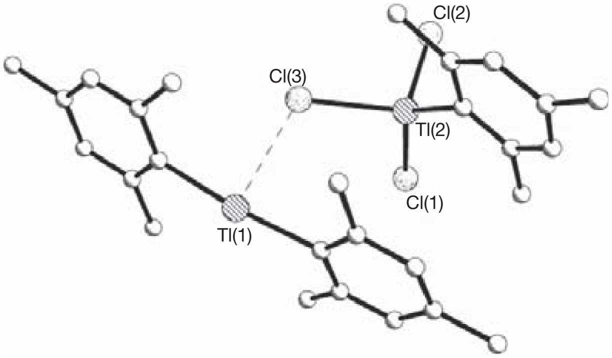
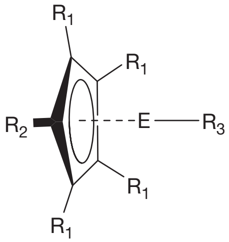
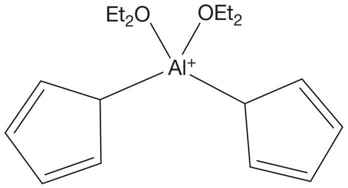
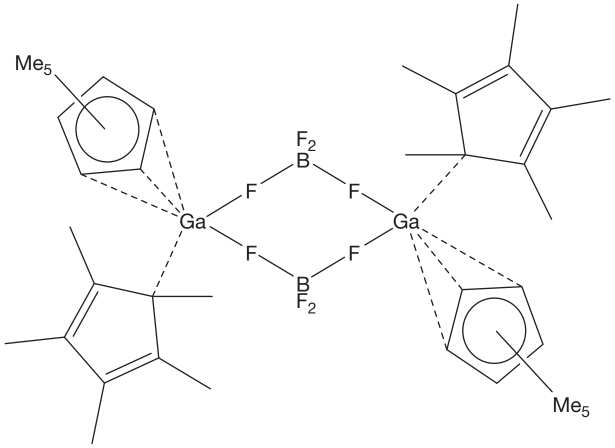


Figure 63 Solid-state structure of $[TlMes_2][TlCl_3Mes]$, **17.21**.

Table 34 Structural features of Cp′ECp′ cations



	E	*R$_1$*	*R$_2$*	*R$_3$*	*Counterion*	*E—C*	*E—Ct*	*E—R$_3$*	*Ct—E—R*
18.1[455]	Al$^+$	Me	H	η^5-C$_5$Me$_4$H	B(C$_6$F$_5$)$_4^-$	2.105–2.169	1.765		179.97
18.2[435]	Ga$^+$	Me	Me	η^1-C$_5$Me$_5$	AlCl$_4^-$	2.097–2.395	1.904	1.996	140.52
18.3[435,456]	Al$^+$	Me	Me	η^5-C$_5$Me$_5$	AlCl$_4^-$	2.141–2.158	1.767–1.774		179.48–179.85
18.4[457]	Al$^+$	Me	Me	η^5-C$_5$Me$_5$	Cp*(Cp*$_2$Cl$_3$Mg$_3$)$_2^-$	2.099–2.166	1.727		179.36
18.5[458]	Al$^+$	Me	Me	η^5-C$_5$Me$_5$	PhMeB (σ-Cp)$_2$ ZrCl$_2^-$	2.145–2.162	1.778–1.779		178.88
18.6[459]	Al$^+$	Me	Me	η^5-C$_5$Me$_5$	Al(OCCF$_3$)$_4^-$	2.129–2.165	1.788–1.789		179.51
18.7[460]	Al$^+$	Me	Me	η^5-C$_5$Me$_5$	CH$_3$B(C$_6$F$_5$)$_3^-$	2.148–2.179	1.780–1.784		180.00
18.8[434,435] (**16.4**)	B$^+$	Me	Me	η^1-C$_5$Me$_5$	AlCl$_4^-$	1.757–1.781	1.290	1.583	177.09
18.9[459]					Al(OCCF$_3$)$_4^-$	Al–Cp 1.986–1.996	Cp–Al–Cp 116.29		
18.10[435,461]					BF$_4^-$	Ga–Ct 2.134	Ga–C 2.001–2.741	Ga–η^1-Cp* 1.971	

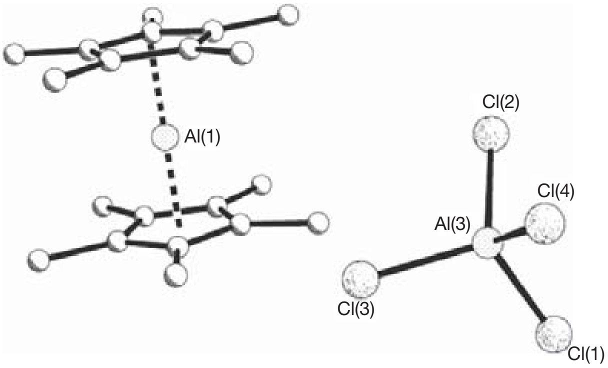


Figure 64 Solid-state structure of $[Al(\eta^5\text{-}Cp^*)_2][AlCl_4]$(**18.3**). Two cations and anions are present in the asymmetric unit. Only one of each is depicted here.

The same group subsequently isolated several other decamethylaluminocenium salts from the redox reactions of Cp*Al with a variety of main group reagents; these salts include: $[Cp^*_2Al][(C_5Bz_5)_2Li]$ (**18.12**),[463] $[Cp^*_2Al][Cp^*BiAl_3I_{12}]$ (**18.13**),[464] and $[Cp^*_2Al][Cp^*_5Mg_6Cl_8]$ (**18.4**).[457] Somewhat similarly, Jutzi and coworkers obtained the salts $[Cp^*_2Al][AlX_4]$ (X = Cl (**18.3**), Br (**18.14**)) through the ligand-exchange reaction of Cp^*_2Si with AlX_3.[442] More conventional preparative routes that have been used to obtain decamethylaluminocenium salts include: chloride abstraction from 'Cp^*_2AlCl' using $AlCl_3$ to give $[Cp^*_2Al][AlCl_4]$ (**18.3**)[456] and methanide abstraction from Cp^*_2AlMe to produce $[Cp^*_2Al][B(C_6F_5)_3Me]$ (**18.7**)[460] (using $B(C_6F_5)_3$) or $[Cp^*_2Al][ZrCl_2(C_5H_4)_2BPhMe]$ (**18.5**)[458] (using $ZrCl_2(C_5H_4)_2BPh{\bullet}SMe_2$). It is important to note that, regardless of the route used to obtain any of these decamethylaluminocenium salts or the nature of the counter-anion present in the salt, the metrical parameters for the cation are almost always the same: each features an almost ideal D_{5d} arrangement with centroid—Al distances of around 1.76–1.78 Å. Overall, because the $[Cp^*_2Al]^+$ cation is obtained so readily in systems containing Al and pentamethylcyclopentadienyl precursors, it appears as if salts of the cation are somewhat of a thermodynamic sink for such systems; however, some salts of the decamethylaluminocenium cation are reported to decompose over time in halocarbon solutions.[465]

In contrast to the apparent favorability of the permethylated cations, less substituted aluminocenium cations have proved to be much less amenable to isolation. For example, Shapiro and coworkers found that although salts of the tetramethylcyclopentadienyl analogs $[Cp'_2Al]^+$ ($Cp' = C_5Me_4H$) could be prepared and isolated, they are considerably less stable than their more highly substituted relatives.[455] In fact, the salt $[Cp'_2Al][AlCl_4]$ (**18.15**) is found to be in equilibrium with Cp'_2AlCl and Cp'_3Al in solution and attempts to generate $[Cp'_2Al][B(C_6F_5)_3Me]$ by methanide abstraction from Cp'_2AlMe using $B(C_6F_5)_3$ resulted only in ligand redistribution. The authors were able to generate a more stable product through the reaction of Cp'_3Al with $[CPh_3][B(C_6F_5)_4]$ that generates $[Cp'_2Al][B(C_6F_5)_4]$ (**18.1**) with the concomitant elimination of $Cp'CPh_3$. In the crystalline state, two independent cations were present and each features two η^5-Cp′ substituents. One of the cations has a linear centroid–Al–centroid structure with centroid—Al distances of 1.765 Å and the other, which is disordered, features a slightly bent arrangement with a centroid—Al—centroid angle of around 174.7°. This salt was found to be a more effective initiator of isobutene polymerization than $[Cp^*_2Al][B(C_6F_5)_3Me]$ (**18.16**); however, both are less effective initiators than is the parent aluminocenium salt described below.

It must be noted, of course, that the first salt containing the parent $[Cp_2Al]^+$ ion $[Cp_2Al][B(C_6F_5)_3Me]$ was prepared by methanide abstraction from Cp_2AlMe using $B(C_6F_5)_3$ and reported by Bochmann and coworkers in 1996. The salt is not stable in dichloromethane solution above −20 °C and it proved to be a potent initiator of isobutene polymerization even at −78 °C.[466] This suggests that the larger steric bulk, perhaps in conjunction with the more electron-rich nature, of the Cp* is crucial to render the aluminocenium ions stable enough for isolation at room temperature under most conditions. However, it must be emphasized that the use of the particular NCA $[Al(OR^f)_4]^-$ ($R^f = C(CF_3)_3$) allowed for the isolation and crystallization at −28 °C of a salt of the parent cation, $[Cp_2Al][Al(OR^f)_4]$ (**18.6**) in 2009.[459] The salt was prepared by the protonolytic cleavage of CpH from $AlCp_3$ by $[H(OEt_2)_2][Al(OR_F)_4]$ and was always isolated as a mixture of the free salt and an ether solvate. The free salt contains the cation $[(\eta^5\text{-}Cp)_2Al]^+$ that features a staggered almost D_{5d} symmetry cation with a centroid—Al distance of 1.789 Å, which is longer than in the methylated analogs described above – this is as one would anticipate given that Cp ligands are less electron rich than their alkylated derivatives. In the ether solvate structure, the arrangement of the cation is markedly different: the aluminum center is coordinated by the two ether ligands to produce a tetrahedral four-coordinate cation of the type $[(\sigma\text{-}Cp)_2Al{\bullet}(OEt_2)_2]^+$ (**18.9**) containing clearly σ-bonded cyclopentadienyl groups with Al—C_{ipso} distances of 1.986–1.996 Å. The authors determined that $[Cp_2Al][Al(OR^f)_4]$ is a superior initiator of isobutene polymerization than $[Cp_2Al][B(C_6F_5)_3Me]$, presumably because of the reduced cation–anion interactions in the former, and both of the parent salts are much more effective initiators that are either of the methylated analogs described above. The relative Lewis acidities of the cations were assessed by the authors on the basis of computational investigations of fluoride ion affinities and correlate well with the observed reactivity pattern. Perhaps not surprisingly, given the smaller number of π-electrons and considerably reduced steric bulk, attempts to generate the related bis-allyl Al cations result in the formation of four- and five-coordinate base/solvent-stabilized cations.[467]

Although it is usually considered in the context of clusters rather than metallocenes, the salt $[Li(OEt_2)_3][[(([Me_3Si]_2N)Al)_3]_2Al]$ (**18.17**), illustrated in Figure 65, obtained by Schnöckel and coworkers during their investigations of the reactivity of metastable univalent aluminum halides, may be considered analogs to the aluminocenium cations described above.[468] If each $[(([Me_3Si]_2N)Al)_3]^{2-}$ ring is considered formally as an aromatic π-donor ligand, the sandwich-like structure of the observed anion is clearly related to the aluminocenium ions described above.

The first example of a salt containing a gallocenium cation, $[Cp^*{}_2Ga][BF_4]$ (**18.10**), was reported in 2000 by Cowley and coworkers.[461] In contrast to the related salts of B and Al described above, attempted generation of decamethylgallocenium salts using halide and methanide abstraction protocols from precursors of the type $Cp^*{}_2GaX$ and $Cp^*{}_2GaMe$ typically resulted in the isolation of decomposition products, and the most reliable route to decamethylgallocenium salts was found to be the acidolysis of a Cp* substituent from $GaCp^*{}_3$. Thus, $[Cp^*{}_2Ga][BF_4]$ was obtained by the treatment of $GaCp^*{}_3$ with HBF_4 in dichloromethane and the structure of the salt is illustrated in Figure 66 (top). The solid-state structure reveals that, in contrast to either of the lighter congeners, the decamethylgallocenium cations interact quite noticeably with the tetrafluoridoborate counter-anions. The relatively short Ga···F contacts range from 2.176 to 2.184 Å, and the B—F bond distances for the bridging fluorine atoms (1.422 Å) are significantly longer than are those of the nonbridging atoms (1.358–1.361 Å). More importantly, the strength of the interaction is such that the cation features one η^3-Cp* group and one σ-Cp* group; this structure is markedly different from the $[(\eta^5\text{-}Cp^*)(\sigma\text{-}Cp^*)Ga]^+$ arrangement that is predicted by DFT geometry optimizations. It must be emphasized that these calculations also reveal that the putative $[(\eta^5\text{-}Cp^*)_2Ga]^+$ analogs to that observed for aluminum is not a minimum on the potential energy hypersurface.

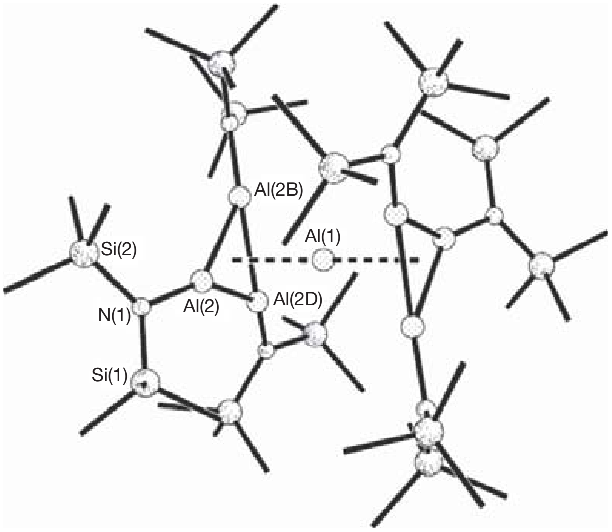


Figure 65 Solid-state structure of $[Al((AlN(SiMe_3)_2)_3)_2]^-$, **18.17**. Counterion $[Li(OEt_2)_3]^+$ not shown.

Treatment of $Cp^*{}_3Ga$ with $AlCl_3$ in dichloromethane yielded the related salt $[Cp^*{}_2Ga][AlCl_4]$ in which the anion is produced by a ligand-exchange symmetrization process that is typical of group 13 species.[435] In the crystalline state, as illustrated in Figure 66 (bottom), the tetrachloridoaluminate anion, does not interact nearly as strongly with the

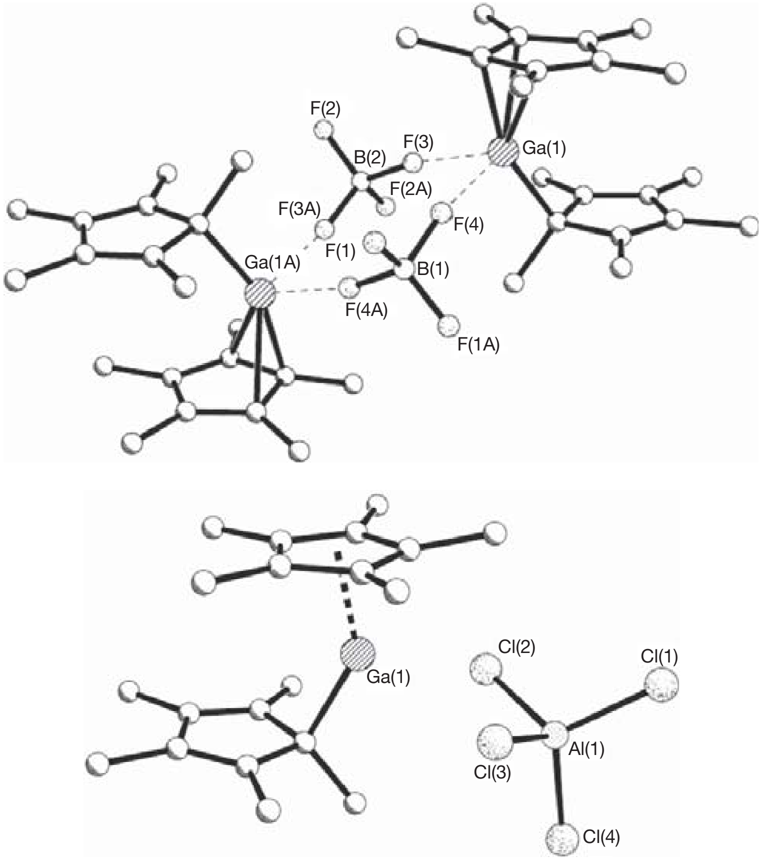


Figure 66 Top: Solid-state structure of $[(\eta^3\text{-}Cp^*)\text{–}Ga\text{–}(\sigma\text{-}Cp^*)]_2[BF_4]_2$ (**18.10**). Bottom: Solid-state structure of $[(\eta^5\text{-}Cp^*)\text{–}Ga\text{–}(\sigma\text{-}Cp^*)][AlCl_4]$ (**18.2**).

gallocenium ion and thus the observed arrangement is best described as $[(\eta^5\text{-Cp*})(\sigma\text{-Cp*})\text{Ga}]^+$ and is only marginally distorted from the predicted gas-phase structure. Overall, it is apparent that the decamethylgallocenium cation exhibits features that are markedly different from its lighter congeners: (1) it has an idealized structure that is more similar to that of the eight-valence-electron boron analog rather than the 12-valence-electron aluminum derivative – this is likely a consequence of the greater electronegativity of gallium than aluminum and (2) the decamethylgallocenium cation interacts much more strongly with counter-anions than do either of the lighter analogs and the consequences of these interactions result in very significant distortions from the ideal geometry. Finally, it should be noted that the DFT calculations on models of $[\text{Cp*}_2\text{E}]^+$ reveal that, in spite of its geometrical structure, the gallocenium cation has an electronic structure that is much more similar to that of the aluminum analog but with a considerably lower LUMO energy and smaller HOMO–LUMO energy; these are consistent with the acceptor behavior and higher reactivity of the decamethylgallocenium ion.

Analogs bis-cyclopentadienyl metallocenium cations for indium(+3) and thallium(+3) are not known; however, several inverse-sandwich compounds featuring univalent indium and thallium have been characterized as described above (**Section 1.17.2.2.2**).

Finally, it is perhaps worth noting that salts of the analogs bis–tris(pyrazolyl)borate cations of the form $[\text{Tp}_2\text{E}]^+$ (E=Al,[109] Ga,[149,279,280] In[260,364]) and the related bis–tris (chalcogenolatoimidazolyl)borate cations of the form $[\text{TCIB}_2\text{E}]^+$ (Ch=S, E=Ga,[407] In[406]; Ch=Se, E=Ga, In[469]) have been isolated and structurally characterized. In contrast to the metallocenes described above, the cations in each of these trivalent group 13 salts all feature essentially undistorted octahedral arrangements with no metal–anion interactions. Furthermore, salts containing the corresponding dications, namely $[\text{LGa–GaL}]^{2+}$, have been structurally characterized and feature Ga—Ga bonds of 2.366 Å (L=Tp) and 2.396–2.411 (L=TTIB); no analogs Cp′ analogs have been reported but the ion is clearly related to remarkable group 12 complexes such as Cp*Zn–ZnCp*.[470]

1.17.4 Conclusion

There are a tremendous number of group 13 compounds in which the triel centers feature a coordination environment with fewer than three ligands. Such species feature many different types of substituents that provide the necessary steric and/or electronic stabilization that is required to prevent the triel center from adopting a higher coordination number.

Predictably, the reactivity exhibited by all classes of low-coordinate group 13 compounds almost universally results in an increase in the coordination number at that metal. For the electron-rich low-valent species described at the start of this chapter, the increase in coordination number is achieved either through oxidative addition into suitable bonds or through the formation of coordination complexes with suitable acceptors. Conversely, the low-coordinate electron-deficient species described in the second part of the chapter increase their coordination numbers principally by behaving as acceptors. The great diversity of structural types and chemical properties engendered by the substituents employed to prepare low-coordinate group 13 compounds provides for reagents with a vast number of applications, ranging from chemical synthesis and catalysis, to materials precursors. Given the rapid development of ligands and triel sources suitable for the preparation of low-coordinate group 13 compounds since the late 1990s, the future bodes well for the generation of new compounds and new applications for such species.

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1.18 Low-Coordinate Main Group Compounds – Group 14 (Si, Ge)

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1.18.1 Introduction

Low-coordinated species of carbon, such as olefins, carbonyl compounds, imines, and carbenes, play very important roles in organic chemistry. On the other hand, their homologs of heavier group 14 elements (Si, Ge, Sn, and Pb) have not been deeply explored so far most probably due to their extremely high reactivity and inherent instability under ambient conditions, while these low-coordinated species have been postulated in many reactions only as reactive intermediates.[1] Especially, much attention has been paid to the heavier analogs of carbenes, that is, silylenes (R_2Si:), germylenes (R_2Ge:), stannylenes (R_2Sn:), and plumbylenes (R_2Pb:), as monomeric species of the polymetallanes (especially, a silylene is thought to be a monomer of a polysilane, which should be of great importance in fundamental and applied chemistry) from the viewpoints of the differences and similarities of their properties compared with those of carbenes.[2] For the stabilization of highly reactive compounds such as low-coordinated species of heavier group 14 elements, there are two conceivable methodologies, that is, thermodynamic and kinetic stabilization. The former is defined as stabilization of the ground state by the mesomeric effect of neighboring heteroatoms, that is, introduction of electron-donating or -withdrawing substituents, and/or complexation with transition metals. The latter is stabilization resulting from raising the transition state by taking advantage of steric protection using bulky groups, which suppress self-oligomerization and side-reactions with other reagents such as oxygen and water. Nowadays, several examples of stable metallylenes have been synthesized and reported by utilizing these two stabilization methodologies, and therefore, chemical and physical properties of metallylenes are well disclosed based on the experimental results and theoretical calculations until now. Since some review articles are now available on the history of the synthesis of low-coordinated heavier main group elements,[1–3] the contents in this chapter will be restricted to deal with the recent examples of stable metallylenes with +II oxidation states of heavier group 14 elements without any other 'extra' coordination, that is, σ^2, λ^2-metallylenes (>E:).

1.18.2 Nature of Low-Coordinated Species of Heavier Group 14 Elements

The valence *n*s and *n*p electrons play important roles in the chemistry of main group elements, in contrast to the $(n-1)$d electrons in the chemistry of transition metals. Figure 1 shows the radii of atomic orbitals (maximal electron density), which are calculated for group 14 elements. The valence *n*s and *n*p orbitals show great difference in their sizes for the heavier atoms (Si, Ge, Sn, and Pb), though the size of the 2s atomic orbital of carbon is almost equal to that of the 2p atomic orbitals.[4] Accordingly, *n*s–*n*p-hybridized orbitals exhibit negligible change in their shape as compared with *n*p orbitals, suggesting similar integrals in the cases of making chemical bonding with using *n*p orbitals and using hybridized orbitals (Figure 2). Thus, it is unfavorable to mix stable *n*s orbital with unstable (higher-energy level) *n*p orbital. Therefore, the heavier atoms have a lower tendency to form s–p hybrid orbitals with high p character and they prefer to retain the $(ns)^2(np)^2$ valence electronic configuration, in contrast to the case of carbon. Indeed, the intrinsic thermodynamic stability of low-coordinated species of 'metallylenes,' that is, silylenes (R_2Si:), germylenes (R_2Ge:), stannylenes (R_2Sn:), and plumbylenes (R_2Pb:), increases on descending the group. For example, $PbCl_2$ and $SnCl_2$ are very stable ionic compounds, while these compounds may be called as dichloroplumbylene and dichlorostannylene. However, these dihalides exist as polymer or ion pair in solution and in the solid state. On the other hand, dihalosilylenes are known to be hardly isolable compounds, though $GeCl_2\cdot$(1,4-dioxane) is known to be a stable and isolable compound as a dichlorogermylene complex. In addition, it may be expected that the sizes of the *n*s and *n*p orbitals increase monotonously going down the periodic table from C to Pb, since the principal quantum number (n) increases. Unexpectedly, however, one can see that the sizes of orbitals change irregularly. The irregularity in Si → Ge and Sn → Pb is most likely interpreted in terms of so-called 'd-block contraction' and 'relativistic effect.' Anyway, one can see obviously two boundary lines drawn between carbon and silicon, and between germanium and tin. The first boundary line indicates the preference of heavier atoms for $(ns)^2(np)^2$ valence electronic configuration to the hybridization of s and p orbitals as described above. Taking into consideration the second boundary line, that is, the large difference of the orbital sizes between Ge and Sn, it should be expected that the properties of silicon and/or germanium compounds may differ from those of tin and/or lead compounds. Accordingly, this chapter describes the chemistry of low-coordinated species of silicon and germanium; then the next chapter does that of tin and lead.

As described above, heavier group 14 elements are reluctant to form hybridized orbitals, and prefer $(ns)^2(np)^3$ valence

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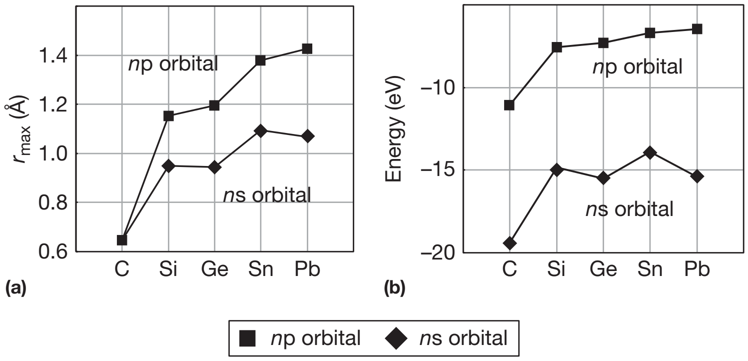


Figure 1 (a) Size and (b) orbital energy of valence *n*s and *n*p orbitals of group 14 elements.

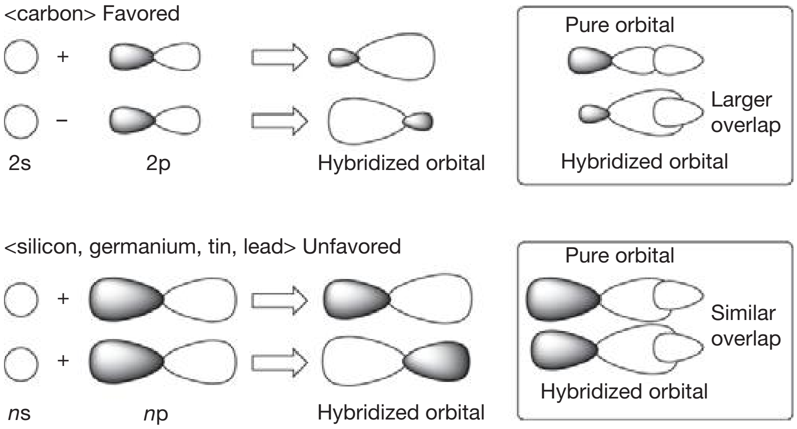


Figure 2 Hybridization of *n*s- and *n*p- orbitals in group 14 elements.

electronic configuration in their divalent species (metallylenes). Therefore, metallylenes (R_2M:) have the singlet ground state with making two R–M chemical bonds as high *n*p character, a lone pair as valence *n*s orbital, and a vacant *n*p orbital (Figure 3). The extremely high reactivity of metallylenes should be due to their vacant p orbitals, since the six valence electrons are less than eight electrons from the viewpoint of octet rule and the lone pair of the metallylenes should be inert due to its high s character. In order to stabilize such metallylenes enough to be isolated as stable compounds, thermodynamic and/or kinetic stabilization should be afforded toward the reactive vacant p orbital. Thus, several numbers of 'isolable' metallylenes have been synthesized by using the thermodynamic stabilization of coordinating Cp* ligands, heteroatoms, such as N, O, and P, and/or the kinetic stabilization utilizing bulky substituents (Figure 4).[2] Especially, donor-coordinated stable metallylenes, that is, $\sigma^{m(>3)}$, λ^2-metallylenes, have been widely researched recently due to its stability enough to handle at room temperature (Scheme 1).[5,6] However, the characteristic reactivity of a metallylene due to a vacant p orbital is not observed in the case of such donor-stabilized metallylenes, because the vacant p orbital of the metallylenes is occupied by the donor molecules. When the vacant p orbital of a metallylene is not well stabilized and the steric protection is not enough to keep the metallylene center as monomeric state, the metallylene would undergo self-dimerization to give the corresponding double-bond compound. If the steric protection would be much less effective, it would undergo self-oligomerization to give cyclic or linear oligomeric species. Thus, the balance of the steric protection and the thermodynamic stabilization to the vacant p orbital of a metallylene should decide its fate to exist as a monomer, dimerize to give the double bond, or undergo oligomerization.

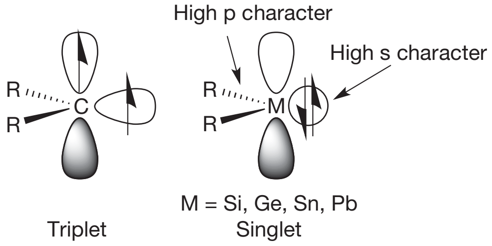


Figure 3 Difference of electronic structures between a carbene and a metallylene.

1.18.3 Synthesis of Stable Silylenes and Germylenes

Since metallylenes have lower oxidation state, for example, they are M^{II} (M=Si, Ge, Sn, Pb) species, the proper synthetic methods for the synthesis of metallylenes should be two ways as follows: (i) reduction of M^{IV} species as a precursor and

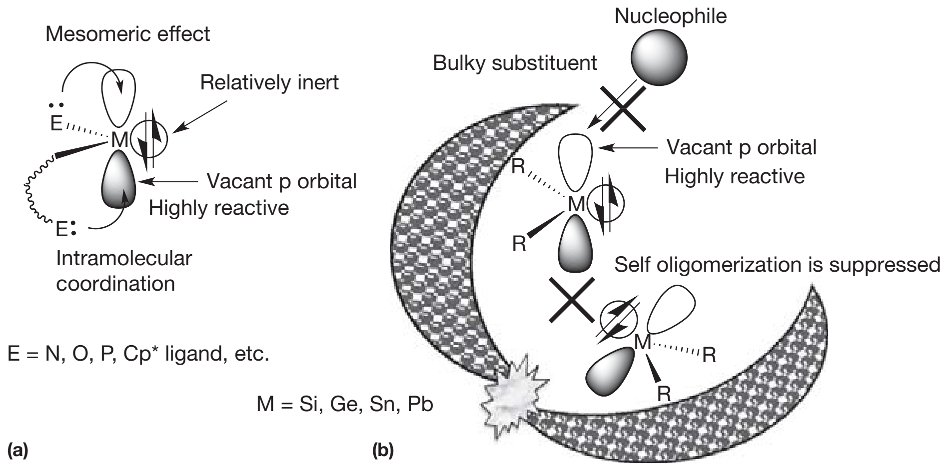
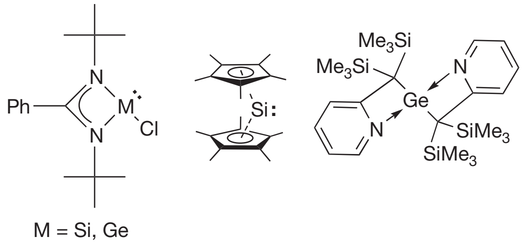


Figure 4 (a) Thermodynamic and (b) kinetic stabilization for metallylenes.



Scheme 1 Examples of stable $\sigma^{m(>3)}$, λ^2-metallylenes.

(ii) substitution reaction of M^{II} halides such as $GeCl_2$ (dioxane) as a starting material with ligand moieties such as RLi or ArLi as a nucleophile (Figure 5). In the former case (i), a few types of reduction reactions of R_4M species lead to the formation of R_2M: species: for example, (a) photochemical reductive elimination of a disilane from $R_2M(SiR'_3)_2$, (b) thermal and/or photochemical reductive elimination of an olefin or an alkyne from the three-membered ring systems, metalliranes, and metallirenes, (c) reduction of the corresponding dihalides R_2MX_2 (X = Cl, Br, and I) using reductive reagents such as lithium naphthalenide, KC_8, etc. On the other hand, the method (ii) can be applicable only in the case of germanium, since there is no available Si^{II} species, which can be easily handled as a starting material. In addition, the choice of the substituent 'R' should be of great importance for the purpose of the isolation of stable metallylenes and dimetallenes. As described above, when the metallylene thus generated is not very well sterically protected, it undergoes dimerization giving the corresponding double-bond compounds, dimetallenes.

In the 1980s, silylenes have been observed and/or isolated only in argon of hydrocarbon matrix at very low temperature (<77 K), and have been known to undergo ready oligomerization above the matrix temperature.[7] In contrast to the case of silicon, the divalent species of Ge, Sn, and Pb should be intrinsically stable when their vacant *n*p orbitals are stabilized by mesomeric π-coordination of the adjacent heteroatom such as a nitrogen atom. Indeed, diamino-substituted germylenes, stannylenes, and plumbylenes, $M[N(SiMe_3)_2]_2$ and $M[N(SiMe_3)(t\text{-Bu})]_2$ (M = Ge, Sn, Pb), have been isolated as stable compounds by Lappert's group in 1974.[8,9] By contrast, $Si[N(Me_3Si)_2]_2$ was found to be stable only at low temperature and undergoes ready decomposition above 0 °C giving uncharacterized products (Scheme 2).[10] Furthermore, Kira et al. reported that $Si[N(i\text{-Pr})_2]_2$ was found to exist as an equilibrated mixture between $Si[N(i\text{-Pr})_2]_2$ and the corresponding dimer, $[(i\text{-Pr})_2N]_2Si{=}Si[N(i\text{-Pr})_2]_2$, in solution.[11] Thus, acyclic and cyclic diaminogermylenes have been isolated and investigated in detail, but the chemistry of silylenes has not been developed

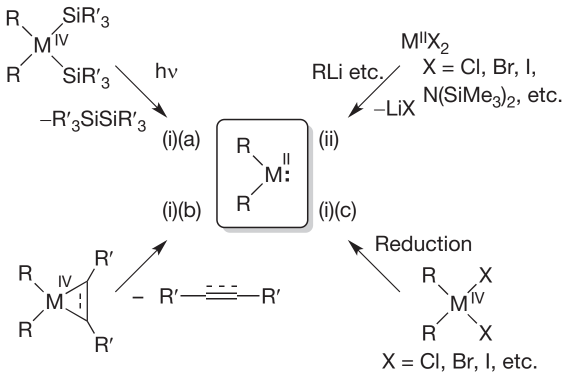
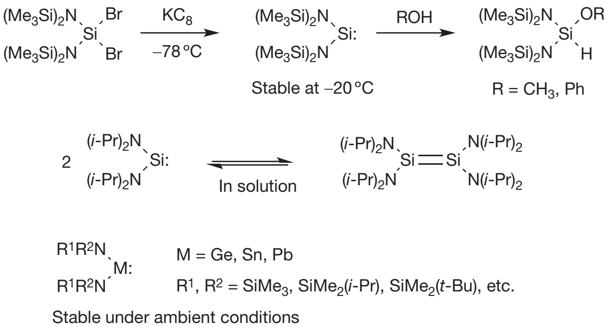


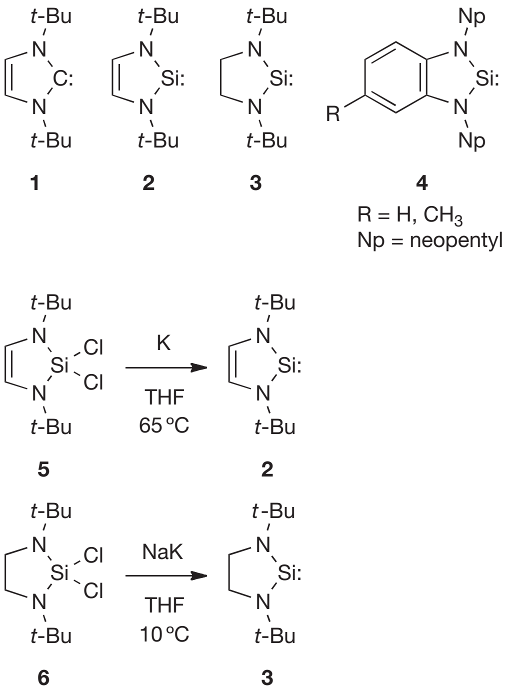
Figure 5 Synthetic methods for metallylenes.



Scheme 2 Acyclic diaminometallylenes.

due to the lack of a stable example. In 1991, isolation of the first stable carbene, NHC **1**, was reported by Arduengo and coworkers.[12] Just after this sensational work, Denk and West have succeeded in the synthesis of the first stable silylene, *N*-heterocyclic silylene (NHSi) **2**, by the reduction reaction of the corresponding dichlorosilane with potassium in tetrahydrofuran (THF) at 65 °C.[13] The isolation of stable silylene **2** was followed by the synthesis of its saturated and benzo-fused analogs, **3** and **4**.[2,5,14] These stable silylenes were synthesized by the reduction in the corresponding dichlorosilanes, that is, the synthetic method (i)(c) (Scheme 3). Of course, these silylenes **2**–**4** should be stabilized by the mesomeric coordination of the lone pairs of the adjacent nitrogen atoms. Thus, it should be a key factor to isolate a stable metallylene that the vacant *n*p orbitals should be stabilized by the π-electron donation of the adjacent heteroatoms.

Interestingly, silylene **2** with the unsaturated ring system is stable under ambient conditions without any decomposition, but silylene **3** with the saturated ring system is only marginally stable. It has been discussed why unsaturated silylene **2** is much more stable and much more inert than saturated silylene **3** even though both of the silylenes seem to be stabilized by the mesomeric effects of the adjacent nitrogen atoms. Steric hindrance may play an important role in stabilization of silylenes, but the steric situation of **2** and **3** seems not to be different. Further, steric hindrance is unlikely to be a major factor in stabilization in these cases, because Si atoms of silylenes **2** and **3** seem not to be effectively protected by the *tert*-butyl groups (Figure 6). As described above, the mesomeric π-electron donation from the adjacent nitrogen atoms toward the vacant p orbitals on the silicon atoms should be strong stabilizing factor in both cases of compounds **2** and **3**. The nitrogen atoms of saturated silylene **3** are thought to be much more basic than those of unsaturated silylene **2**, because the lone pair of the nitrogen atoms would be conjugated with the unsaturated C=C bond. Indeed, the Si–N bonds of saturated silylene **3** (1.719 Å) are shorter than those of unsaturated silylene **2** (1.753 Å), showing strong π-electron donation in **3** as compared to **2**. Simply thinking, one can guess that saturated silylene **3** would be more stable than unsaturated silylene **2** due to the strong π-electron donation, conflicting with the experimental results. On the basis of recent detailed experimental results and the theoretical calculations, it can be concluded that stabilization energy would be gained by the aromatic delocalization over the 6π electrons on the C_2N_2Si five-membered ring system in unsaturated silylene **2**, and such stabilization should not be afforded in saturated silylene **3** (Figure 7). Several experimental evidences for the aromatic character of unsaturated



Scheme 3 Stable silylenes.

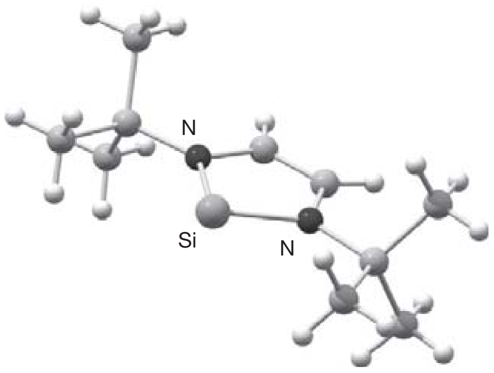


Figure 6 Structure of NHSi **2**.

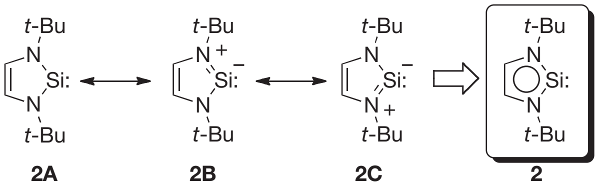


Figure 7 6π-electron system of NHSi **2**.

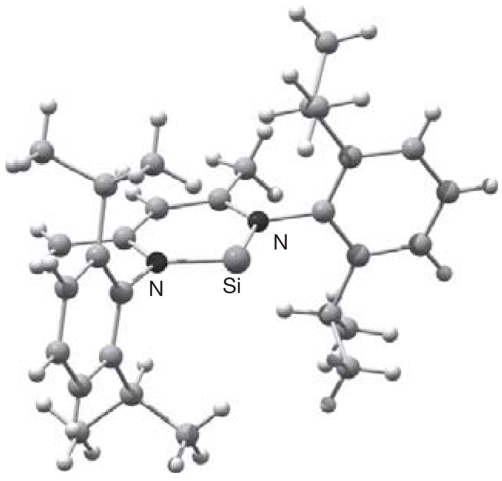
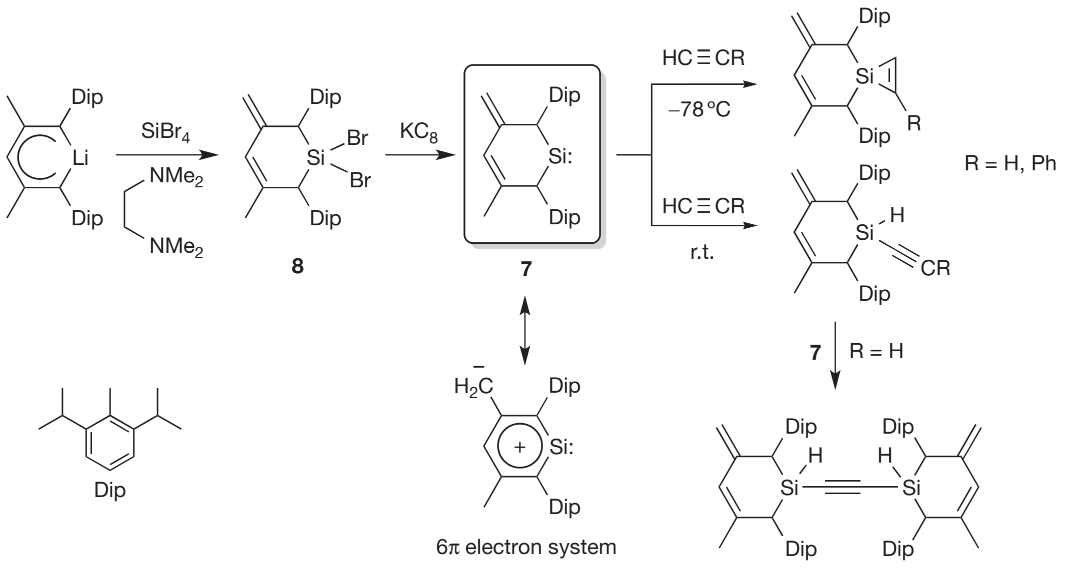
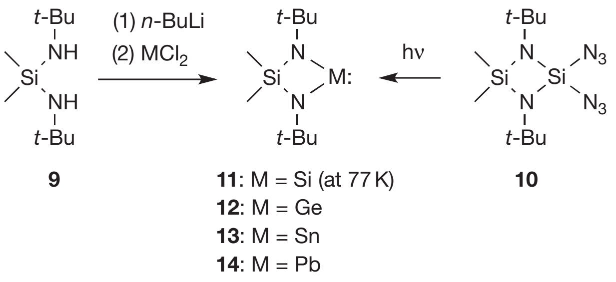


Figure 8 Structure of NHSi **7**.



Scheme 4 A new family of stable silylene **7**.



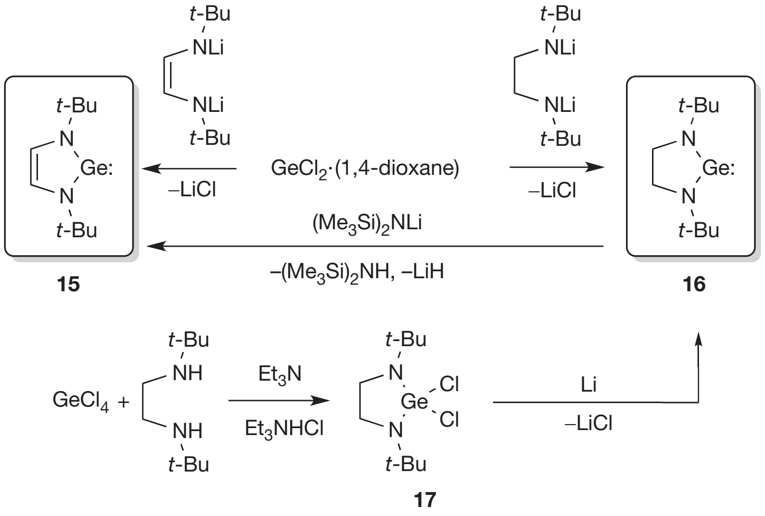
Scheme 5 Synthesis of N-stabilized metallylenes with four-membered ring systems.

silylene **2** were found. For example, the down-field shift of the H–C=C protons in ^{1}H NMR spectra as compared to those of dichlorosilane precursor **5** indicates the diamagnetic ring current effect in the C_2N_2Si five-membered ring of silylene **2**. On the basis of theoretical calculations on the isodesmic reaction schemes and Nucleus-Independent Chemical Shift the aromaticity, aromatic resonance energy, in unsaturated silylene **2** was estimated to be about 50–60% of that in benzene, C_6H_6.

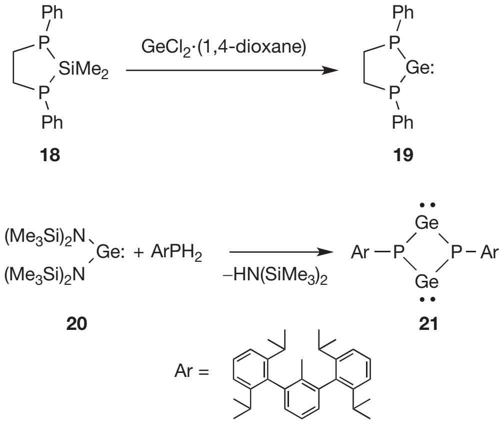
Thus, there are many examples of stable N-stabilized silylenes at present. Recently, a new family of NHSis, silylene **7**, has been reported by Driess's group (Figure 8), which is stabilized not only by the adjacent nitrogen atoms but also by the zwitterionic 6π-aromatic resonance (Scheme 4).[5,15] This new silylene **7** was found to show unique reactivity toward small molecules such as alkynes, alkenes, NH_3, and so on, demonstrating its potential ability of catalytic activation of small molecules. The possible trigger of such unique reactions would be due to the Lewis acidic properties of the stable silylenes. Even though the adjacent nitrogen atoms would stabilize the vacant p orbital of the stable silylene, the silylene center should be still highly Lewis acidic. The chemistry of silylene **7** was summarized in a recent review.[5,15]

Since acyclic diaminogermylenes are stable enough to be treated under ambient conditions as described above, the synthesis and isolation of N-heterocyclic germylenes (NHGes), heavier congeners of Arduengo's stable carbene and West's stable silylene, are somewhat lately achieved in 1992. Before the synthesis of first stable carbenes (NHCs) and silylenes (NHSis), Veith reported the stable germylene **12** bearing –N–Ge–N– four-membered ring system as shown in Scheme 5.[16] Although germylene **12** and its tin (**13**) and lead (**14**) analogs are stable under ambient conditions, the corresponding silylene **11** is detectable only in a glass matrix at 77 K.[17] Metallylenes **12**–**13** were readily synthesized by the reactions of the corresponding bis(lithium amide) prepared from bis(amine) **9** with the corresponding M(II) (M = Ge, Sn, and Pb) chlorides via the synthetic method (ii) in Figure 5. On the other hand, the silylene analog **11** was generated by the photolysis of silylazide **10** along with the elimination of nitrogen as well as by a synthetic method (i)(a) in Figure 5. After that, the first stable NHGes **15** (unsaturated) and **16** (saturated) were synthesized in 1992 by Herrmann's group.[18] Similarly to the case of NHSis, the corresponding dichlorogermanes were reduced by Li metal to give the stable germylenes. On the other hand, treatment of Ge(II) species of $GeCl_2\cdot$(1,4-dioxane) with the corresponding lithium amides easily gave the corresponding cyclic diaminogermylenes as shown in Scheme 5 (the synthetic method (ii) in Figure 5). The bonding situations of **9** and **10** are similar to the cases of stable silylenes **2** and **3**. That is, the Ge–N bond length in unsaturated germylene **9** (1.856 Å) is slightly longer than that of saturated germylene **10**, suggesting the aromatic 6π resonance in **9** and stronger N–Ge mesomeric π-donation in **10**. After that, several numbers of N-stabilized germylenes were synthesized and characterized (Scheme 6).[9,19]

Thus, the heteroatom substituents such as a nitrogen substituent can stabilize silylenes and germylenes via mesomeric coordination of the lone pair toward the vacant p orbital of the metallylene. While there is no stable example of σ^2,λ^2-silylenes bearing heteroatom ligands other than amido groups, many germylenes stabilized by the heteroatom ligands other than amido groups such as O, P, S, and halogeno-substituents



Scheme 6 Synthesis of stable *N*-heterocyclic germylenes **15** and **16**.



Scheme 7 Synthesis of stable P-substituted germylenes **19** and **21**.

have been reported so far.[2] It should be more difficult to stabilize a silylene than to stabilize a germylene, because the vacant p orbital of a silylene should exhibit higher reactivity than that of a germylene, and divalent species with $(n\text{s})^2(n\text{p})^2$ valence electron distribution should be more favorable in the case of germanium as compared with the case of silicon. Although a phosphorus-substituted silylene, a phosphorus analog of NHSis, is attractive species from viewpoint of its possible unique properties in theoretical calculations,[20] there is no stable example of such a phosphorus-substituted silylene. On the other hand, a few examples of stable P-heterocyclic germylenes bearing phosphorus substituents have been reported (Scheme 7).[21] Synthesis of these P-substituted germylenes **19** and **21** has been accomplished by the substitution reactions of Ge(II) species via method (ii) in Figure 5. The phosphorus atoms of the P-heterocyclic germylenes exhibit pyramidal geometry (Figure 9) in contrast to the NHGes, suggesting weaker mesomeric π-electron donation ability of a phosphorus atom as compared with a nitrogen atom. Other examples of heteroatom-stabilized germylenes are summarized in a recent review.[2]

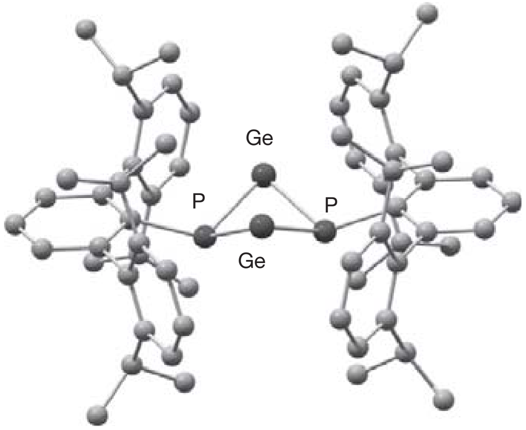
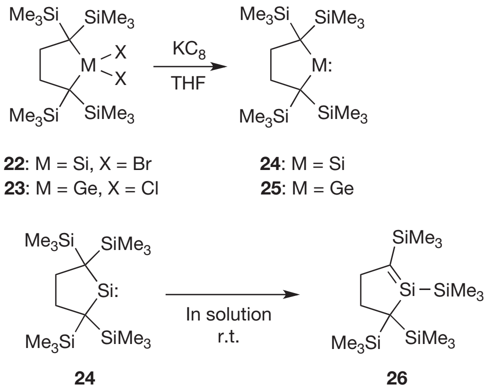


Figure 9 Structure of P-substituted germylene **21**. Hydrogen atoms are omitted for clarity.

Although the isolation of heteroatom-stabilized silylenes and germylenes opened the door to the new chemistry of metallylenes, the carbon-substituted stable metallylenes should tell us the intrinsic nature of a metallylene, because carbon substituents should lead to less electronic perturbation compared to heteroatom substituents such as N, O, and P. As shown in Figure 4, it is necessary to introduce sterically demanding aryl or alkyl substituents on to the central atom of a metallylene in order to isolate stable metallyenes. There are many reports on the trapping reactions of a carbon-substituted silylene, but such transient silylenes are mostly known to undergo dimerization giving the corresponding disilenes without any trapping reagents. In 1999, Kira et al. reported synthesis of the first stable dialkylsilylene **24** prepared by the reductive debromination reaction of the corresponding dibromosilane **22** (synthetic method (i)(c)) (Scheme 8 and Figure 10).[22] The reactive silylene center of **24** is not only sterically protected but also electronically stabilized by the two $SiMe_3$ groups attached to the α-carbons. That is, the bulky $SiMe_3$ groups should prevent its dimerization giving disilenes, and the C–SiMe$_3$ σ-bonds can stabilize the vacant p orbital of the silylene center of **24** via σ-conjugation. Silylene **24** exhibits monomeric structure in the solid state and is stable at 0 °C but undergoes slow isomerization to give silacyclopentene **26** in solution at room temperature via intramolecular 1,2-migration of a SiMe$_3$ group.

Stable dialkylsilylene **24** can be considered to exhibit characteristic feature reflecting intrinsic nature of a silylene due to less electronic perturbation of the carbon ligand toward the silylene center as compared with the nitrogen- or heteroatom-stabilized silylenes such as **2** and **7**. It should be noted that the ^{29}Si NMR chemical shift of silylene **24** is 567 ppm, which is comparable to the calculated values of ca. 740–780 ppm for simple silylenes such as H$_2$Si: and Me$_2$Si:.[14,22,23] In contrast, observed ^{29}Si NMR chemical shifts of N-stabilized silylenes **2** and **3** are 78.3 and 118.3 ppm, respectively, which are highly upper-field-shifted as compared with that of **24** probably due to the effective mesomeric coordination of the lone pairs toward the vacant p orbitals. In electronic spectra, a silylene is known to show its characteristic weak absorption due to the n–p electron transition, which is symmetry forbidden transition. The characteristic absorption maxima $\lambda_{\max}$ due to the n–p electron transition of stable alkyl silylene **24** is 440 nm (ε 500), which is comparable to that of Me$_2$Si: (453 nm)[7a] at 77 K in 3-methylpentane matrix and much longer than those of N-substituted silylenes (e.g., $\lambda_{\max}$ of **3** is 292 nm). Since $\lambda_{\max}$ values in electronic spectra and δ_{Si} values in NMR spectra are known to correlate inversely with the highest energy occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap energies in silylenes, the longer $\lambda_{\max}$ and lower-shifted δ_{Si} values of **24** should suggest its smaller HOMO–LUMO gap than those of diaminosilylenes, while HOMO and LUMO of a silylene generally consist of n and p orbitals of the silicon center. The chemistry of stable dialkylsilylene **24** was summarized in a recent review.[23]

Although there is only one example of a stable carbon-substituted silylene (**24**) at present, many stable germylenes bearing carbon substituents have been reported so far.[2] Since the lone pair of a germylene exhibits higher s character than that of a silylene, because the intrinsic nature of keeping its valence electron distribution as $(n\mathrm{s})^2(n\mathrm{p})^2$ is stronger than in heavier atoms, indicating weaker coordinating ability of the lone pair of a germylene toward the vacant p orbital as compared with the case of a silylene. Thus, many stable digermenes are generally known to be in equilibrium state with the



Scheme 8 Synthesis of stable dialkylsilylene **24** and dialkylgermylene **25**.

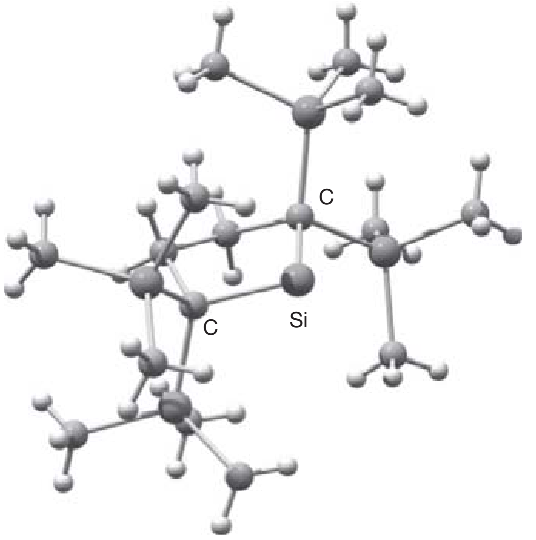
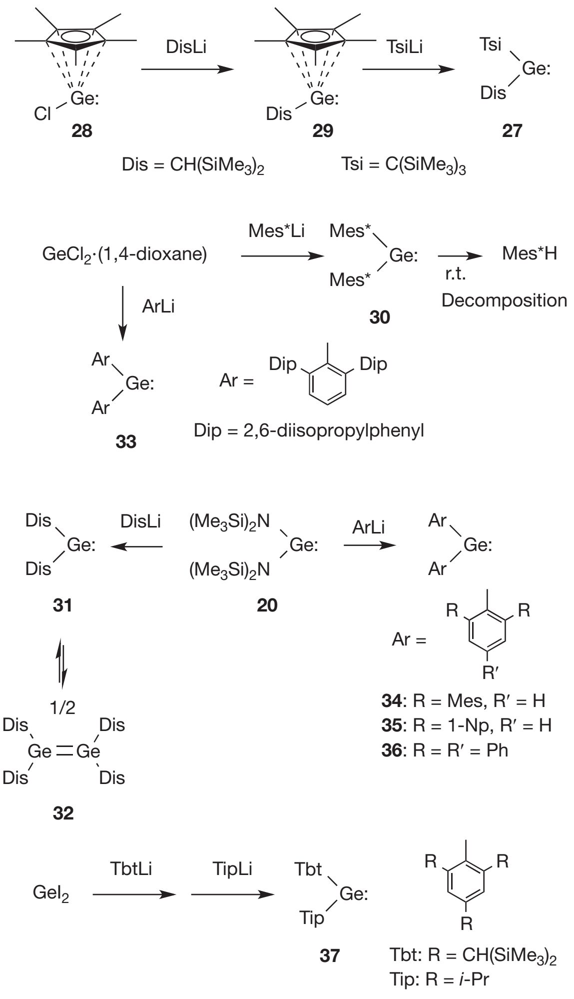


Figure 10 Structure of dialkylsilylene **24**.



Scheme 9 Synthesis of stable germylenes.

corresponding germylenes in solution, in contrast to the case of a silylene (a disilene). That is, a stable germylene can be isolated as a stable digermene in the solid state, which exhibits less reactivity than a germylene because a digermene has no reactive vacant p orbital. The synthetic methods for a germylene are similar to those for a silylene. For example, a germanium analog of silylene **26**, dialkylgermylene **25**, was synthesized by the reduction of dichlorogermane **23** as in the case of the synthesis of **24** (Scheme 8).[24] Thus, it has been demonstrated that the synthetic methods as shown in Figure 5 can be applicable toward the synthesis of stable germylenes. As described above, a few kinds of stable divalent species are available as precursors for the germylenes, in contrast to the case of silicon. The reaction of $GeCl_2 \cdot$(1,4-dioxane), GeI_2, and $[(Me_3Si)_2N]_2Ge$ with RLi and RMgBr (R = Dis ($CH(SiMe_3)_2$), Dip (2,6-diisopropylphenyl), etc.) afforded the corresponding germylenes, R_2Ge:, with elimination of insoluble salts (the synthetic method (ii) in Figure 5). The first stable dialkylgermylene **27** was synthesized by Jutzi's group (Scheme 9).[25] Germylene **27** was synthesized by a unique method, that is, twice nucleophilic substitution of different alkyl groups toward Cp* (=pentamethylcyclopentadienyl) and Cl-substituted germylene, Cp*(Cl)Ge: (**28**). Reaction of **28** with DisLi afforded the Cp*(Dis)Ge: (**29**) as a stable compound. Then, treatment of **29** with TsiLi gave germylene **27** with elimination of Cp*Li. Although Dis_2Ge: (**31**) (Dis = $CH(SiMe_3)_2$) exists as a monomer in solution and gas phase and as a dimer (digermene **32**) in the solid state, Dis(Tsi)Ge: (**27**) (Tsi = $C(SiMe_3)_3$) shows its monomeric structure both in solution and in the solid state. Thus, steric situation around the germylene center should effectively affect its structure. Furthermore, germylene **30** bearing two very bulky Mes* (=2,4,6-tri-*t*-butylphenyl) groups exists as a monomeric germylene even in the crystalline state on the basis of the x-ray crystallographic analysis,[26] though it undergoes decomposition to give Mes*H at room temperature. Diarylgermylenes **33–37** bearing extremely bulky aryl-substituents are stable crystalline compounds under ambient conditions (Figure 11).[27] These stable germylenes

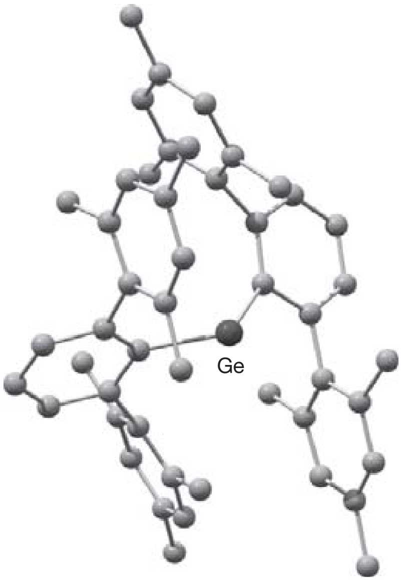
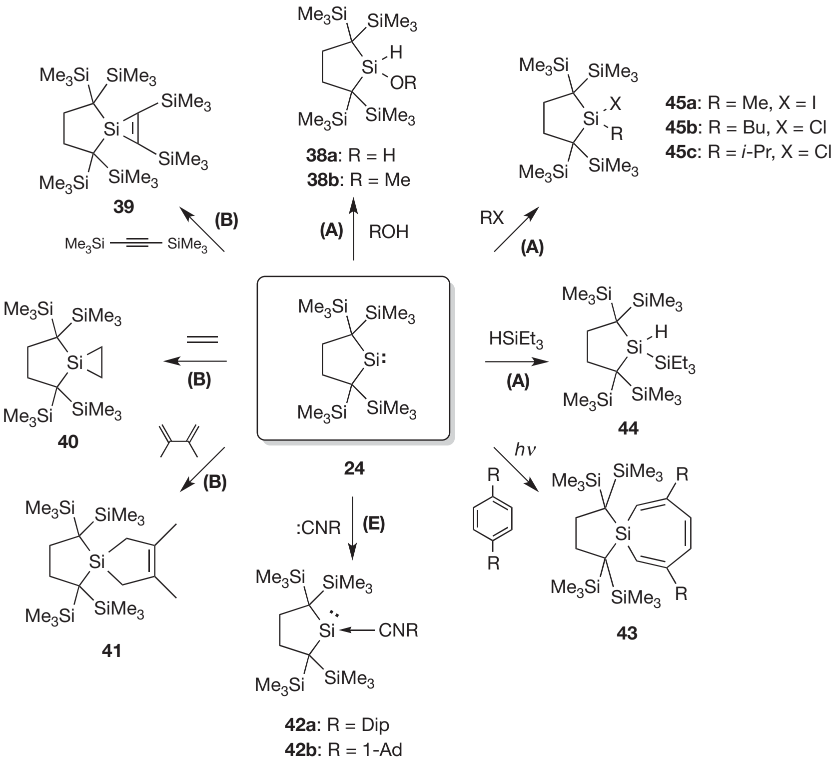


Figure 11 Structure of diaryldigermene **34**. Hydrogen atoms are omitted for clarity.



Scheme 10 Reactions of stable dialkylsilylene **24**.

are synthesized via method (ii) with using Ge(II) species such as $[(Me_3Si)_2N]_2Ge$ as a starting material.

1.18.4 Reactivity of Stable Silylenes and Germylenes

Several types of reactions of stable silylenes and germylenes as shown above have been reported. The reported reactivity contains unique reactions depending on the substituents and those reflecting intrinsic nature of metallylenes. The examples of the reactions of dialkylsilylene **24** are shown in Scheme 10 as representative.[23] The diverse reported reactivities of the stable silylenes and germylenes can be categorized in the following five types: (A) insertion reactions, (B) cycloaddition reactions, (C) reduction reactions, (D) oxidation reactions, and (E) coordination reactions. These reactions would reflect the intrinsic nature of a metallylene, that is, a silylene has low LUMO level due to low-lying vacant p orbital. Thus, reactions of a metallylene seem to be triggered by Lewis acidity of electrophilicity of a metallylene due to the vacant p orbital. A metallylene has two reactive sites, that is, the vacant p orbital and the lone pair on the basis of its singlet ground state. However, the lone pair should be relatively 'inert' as a nucleophile, since it exhibits high s character due to the inherent $(ns)^2(np)^2$ valence electron configuration. On the other hand, the vacant p orbital should make the metallylene highly electrophilic. Thus, almost all the reactivities of metallylenes should be initiated by the nucleophilic reaction of the reagents toward the vacant p orbital (Figure 12). Then, the lone pair of a metallylenes, electron density of which would be enhanced, can attack intra- or intermolecularly the electron-deficient moiety. For example, stable metallylenes (R_2M:) are known to readily react with water or alcohol (R′OH) to give the corresponding insertion products, $R_2M(H)(OR')$ (reactivity A). These insertion reactions can be rationalized as follows. In these reactions, R′OH behaves as a Lewis base, that is, the lone pair would attack the vacant p orbital of a metallylenes to give the oxonium complex, $R'(H)O^{+}\text{–}M^{-}R_2$. Then, the proton of the ROH moiety would be abstracted by the lone pair of $:MR_2$ moiety to give $R_2M(H)(OR')$. Similarly,

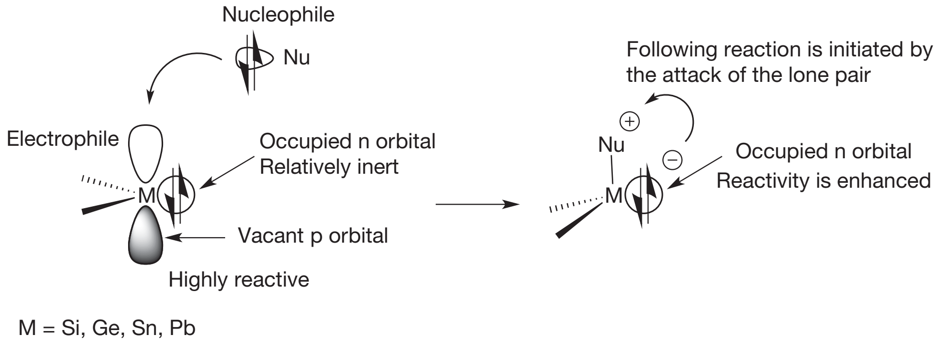
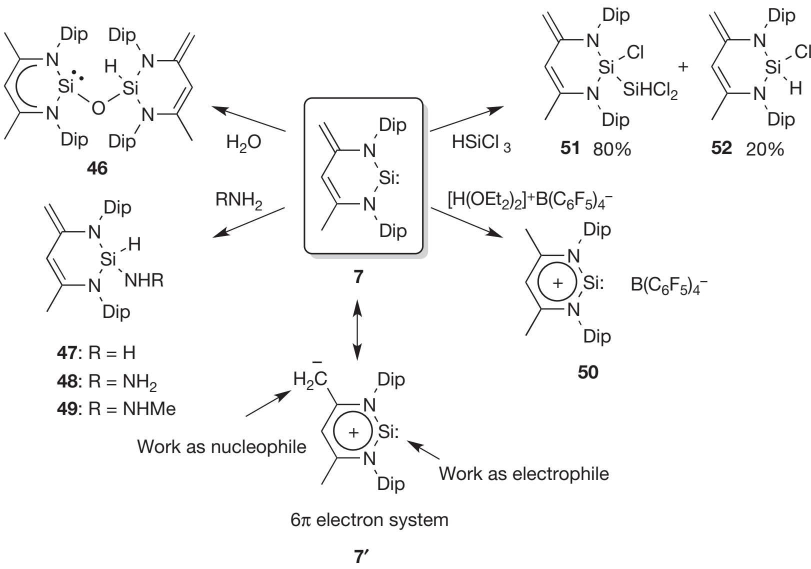
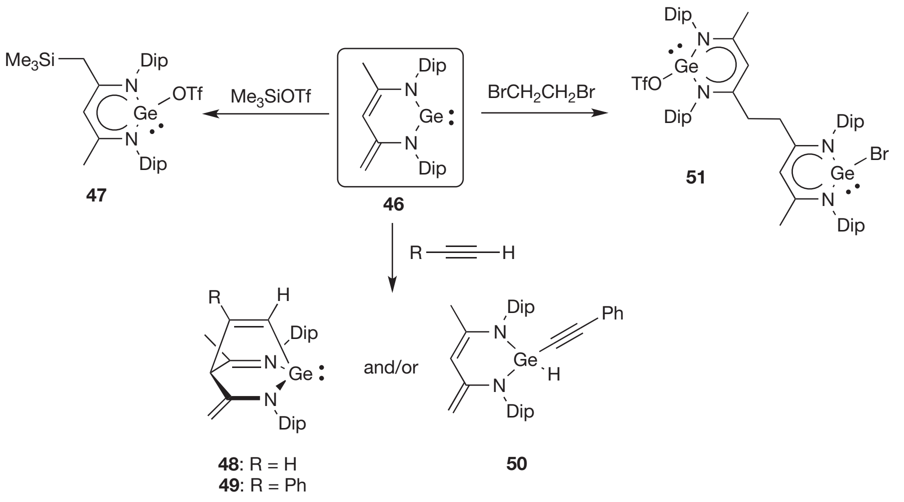


Figure 12 Typical mechanism of the reactions of metallylenes.



Scheme 11 Reactions of stable diaminosilylene **7**.



Scheme 12 Reactions of stable diaminogermylene **46**.

insertion reaction of a metallylene toward a haloalkane ($R'X$, $X = \text{halogen}$) to give $R_2M(X)R'$ can be most likely interpreted in terms of the initial nucleophilic attack of the lone pair of the haloalkane affording $R'X^+$–M^-R_2 followed by the nucleophilic attack of the lone pair of MR_2 moiety toward R^+ unit giving the final product of $R_2M(X)R'$.

From this point of view, a stable metallylene can activate X–Y chemical bonding such as C–C and C–H bond of the small molecules in the observed reactivity. As described above (Scheme 4), stable diaminosilylene **7** was reported to react with small molecules giving the corresponding adducts via bond activation.[15] In the case of **7**, the silylene center is still Lewis acidic even though the vacant p orbital is stabilized by the adjacent N atoms. Therefore, silylene **7** can work as reactive electrophile. However, **7** can work as a Lewis base not only at the silicon center like a general silylene but also at the anionic exo-methylene moiety due to its resonance structure **7′** as shown in Scheme 11. Such zwitter ionic property of silylene **7** should make it much reactive toward small molecules via bond activation. The germanium analog of **7**, N-stabilized germylene **46**, is also reported to show unique reactivities as shown in Scheme 12.[28]

Thus, a stable silylene and a germylene would be promising candidates as metal-free catalysts for the bond activation of small molecules. Recently, it can be thought that the low-coordinated species of heavier group 14 elements would exhibit unique behavior similar to those of transition metals.[29]

1.18.5 Conclusion

Metallylenes having +II oxidation states of heavier group 14 elements (Si, Ge, Sn, Pb) are neither imaginary species nor reactive intermediates but stable and isolable compounds when appropriately stabilized. Various substituents are applicable to stabilize metallylenes, and their substituent effects have been cleared. The study of metallylenes over last three decades revealed their basic and characteristic electronic structures involving the inert lone pair and a vacant p orbital. On the basis of the knowledge, the chemistry of stable analogs whose coordination numbers are more than 2, which were omitted in this chapter, showed a marked development recently. Appropriate selections of substituent and ligand make it possible to synthesize highly stable compounds retaining metallylene characters. For related chapters in this Comprehensive, we refer to Chapters 1.02, 1.03, and 1.11.

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1.19 Low-Coordinate Main Group Compounds – Group 14 (Sn, Pb)

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Glossary

Stannylene Tin analog of a carbene
Plumbylene Lead analog of a carbene
Distannene Tin analog of a olefin
Distannyne Tin analog of a acetylene
Diplumbyne Lead analog of a acetylene
Veith's metallylenes Heavier analogs of carbene bearing a —N(R)—Si(R_2)—N(R)— substituent
Arduengo's carbene Persistent carbenes bearing a —N(R)—C(R)—C(R)—N(R)— substituent

1.19.1 Introduction

Group 14 elements exist in two oxidation states, +II and +IV. In the case of carbon atom, low oxidation state, +II, is recognized as a carbene. Much attention has been focused on the heavier analogs of carbenes, which are called 'metallylenes,' that is, silylenes (R_2Si:), germylenes (R_2Ge:), stannylenes (R_2Sn:), and plumbylenes (R_2Pb:) from the viewpoint of the differences and similarities of the properties between those of carbenes.[1,2] Intrinsic nature of metallylenes including stannylenes and plumbylenes and their comparison with carbon, silicon, and germanium analogs are described in Chapter 1.15. The situations of stannylenes and plumbylenes are similar to each other, and different from those of silylenes and germylenes. In the case of tin and lead, the divalent species are easily in hand, since the +II species are intrinsically stable in the cases of M=Sn and Pb. Actually, stable divalent tin and lead compounds such as MCl_2 (M=Sn, Pb) are well known. However, these dihalides exist as polymer or ion pair in solution and in the solid state. In order to investigate the properties of 'monomeric' metallylenes, introduction of a various kinds of substituents to the metallylene centers has been attempted. Throughout these researches, many examples of stable and monomeric stannylenes and plumbylenes have been reported, and their characters are now becoming clear. Needless to say, the chemical characters of the metallylene center are highly affected by the substituents. In this section, therefore, the stannylenes and plumbylenes reported so far are classified by the substituents. As for 'formal' divalent species whose coordination number is higher than 2, numerous examples have been reported experimentally and theoretically and frequently reviewed.[3] We are not able to cover the whole results and focus on the recent and stable analogs whose coordination number is 2.

1.19.2 Stannylenes and Plumbylenes Bearing Two Carbon Substituents

1.19.2.1 Bearing Two Alkyl Substituents

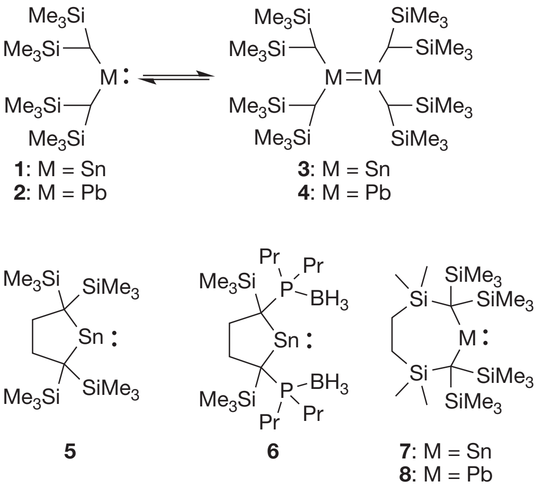
The first dialkyl stannylenes and plumbylenes **1** and **2** were reported in the 1970s (Scheme 1).[4] In solution, they are found to be in equilibrium between their monomers and the corresponding dimers **3** and **4** (double-bond compound, dimetallene). In the solid state, they exist as a dimetallene. Some examples **5–8** bearing bulkier alkyl substituents and a rigid ring skeleton have been reported so far, and they exist as a monomer either in solution or in the solid state.[5] These have been synthesized by the reaction with the anion of the substituent and MX_2 (M=Sn, Pb; X=Cl, $N(SiMe_3)_2$). It is noteworthy that compound **6** shows B–H···Sn agnostic interactions, which stabilize the electron-deficient tin center by 30–40 kcal mol^{-1}.

In the ^{119}Sn or ^{207}Pb NMR (nuclear magnetic resonance), their signals are observed in the extremely low-field region at 2328 (**1**), 2323 (**5**), 2299 (**7**), and 10 050 (**8**) ppm, respectively. The longest wavelengths of their ultraviolet/visible (UV/vis) spectra are 495 (**1**), 486 (**5**), 546 (**7**), and 610 (**8**) nm, which are assignable to the n–π* transitions. The value for lead analog

8 is dramatically red-shifted compared with the corresponding tin analog **7**. Reflecting the agostic interactions in compound **6**, its ^{119}Sn NMR chemical shifts (587 (*rac*-**6**) and 787 (*meso*-**6**) ppm) and the longest wavelengths of UV/vis spectra (338 (*rac*-**6**) and 360 (*meso*-**6**) nm) are significantly different from those of other dialkylstannylenes. The C–Sn–C bond angles of **5** and **7** are 86.7° and 118°, respectively, which are markedly different from each other. On the other hand, C–Pb–C angle of **8** is almost similar (117.1°) to the C–Sn–C angle of **7**.

1.19.2.2 Bearing Two Aryl Substituents

As for diarylstannylene and plumbylene, since the first report on the synthesis of Mes*$_2$Sn **9** in 1994[6] and Mes*$_2$Pb **10** in 1998[7] (Mes* = 2,4,6-tri(*t*-butyl)phenyl), a variety of diarylstannylenes and plumbylenes have been reported. In their synthesis, similarly to the synthesis of dialkylmetallylenes, introduction of aryl anions to MX_2 (M = Sn, Pb; X = Cl, $N(SiMe_3)_2$) is available. In addition, there are different methods from tin(IV) compounds by the reduction of dibromostannanes or desulfurization reactions of tetrathiametallolane (e.g., the syntheses of Tbt-substituted derivatives shown in Scheme 2).[8]

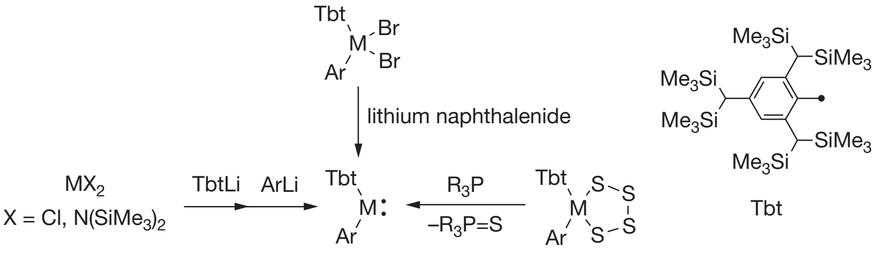


Scheme 1 Dialkylstannylenes and plumbylenes.

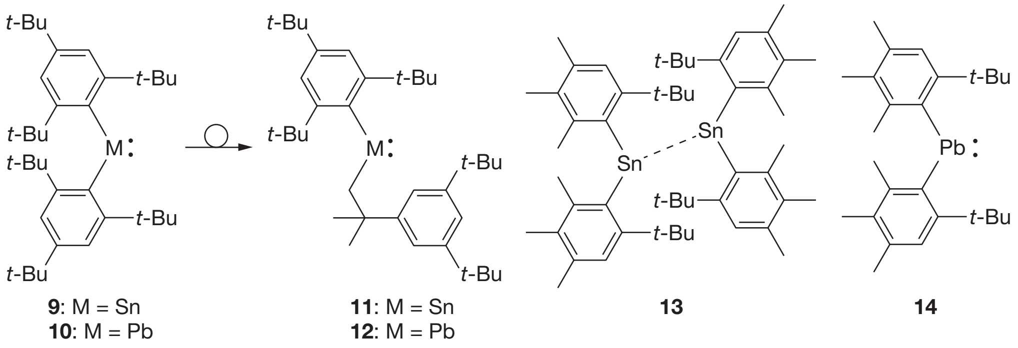
Compounds **9** and **10** are structurally characterized as monomers in the crystalline state, while the structure of **10** has not been determined yet. Moreover, compounds **9** and **10** are found to undergo intramolecular cyclization to afford alkyl (aryl)metallylenes **11** and **12** as stable metallylenes in both cases of M = Sn and Pb (Scheme 3). On the other hand, plumbylene **14** bearing two 6-*t*-butyl-2,3,4-trimethylphenyl groups, slightly smaller than Mes* group, is found to exist as a monomer in the crystalline state, although the stannylene **13** bearing the same ligands exhibits weak intermolecular interaction between the Sn atoms as a dimer in the crystalline state.[9] To date, many examples of stable diarylstannylenes and diarylplumbylenes bearing extremely bulky aryl ligands have been reported so far. Some of them have been structurally characterized (Scheme 4), showing that they exhibit the monomeric structures even in the solid state.[10,11]

1.19.2.3 Bearing Alkyl and Aryl Substituents

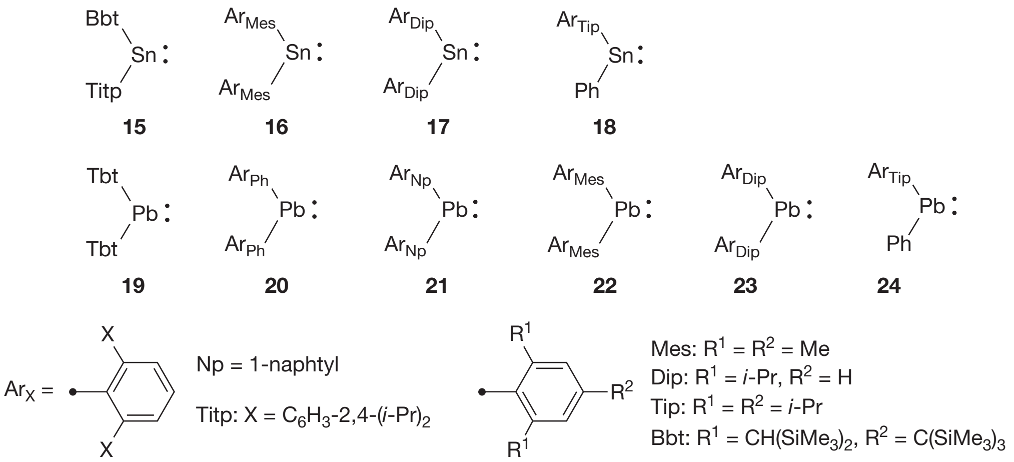
In addition to compounds **11** and **12**, the syntheses of heteroleptic alkyl(aryl)stannylenes and plumbylenes **25–27** have been achieved by utilizing terphenyl groups (Scheme 5).[11] Effective protection by terphenyl groups made it possible to introduce relatively small alkyl substituents. As an interesting example, diazomethylstannylene **28** is successfully synthesized and found to be converted into another cyclic stannylene **29** by the irradiation using 500 W high-pressure mercury arc lamp via



Scheme 2 Syntheses of diarylstannylene and plumbylene (M = Sn or Pb).



Scheme 3 Pioneering works on diarylstannylene and plumbylene.



Scheme 4 Established structures of diarylstannylenes and plumbylenes.

the generation of stannaacetylene intermediate **30**, which could also be postulated as a carbene-substituted stannylene **31** (Scheme 6).[12]

1.19.2.4 Bearing Alkynyl and Aryl Substituents

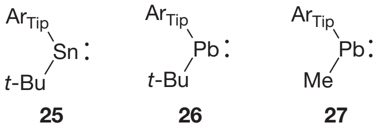
Alkynyl-substituted stannylenes **32** and **33** are monomeric in solution as judged by their NMR and UV/vis spectra (Scheme 7).[13] However, their structures in the solid state are completely different: the dimeric form **34** with orange-red color in the case bearing trimethylsilylethynyl substituent and stannylstannylene **35** with blue color in the case bearing *tert*-butylethynyl. This difference was considered to be a result of the packing effects.

1.19.2.5 Features of Aryl-Substituted Stannylenes and Plumbylenes

The spectral and structural features of aryl-substituted stannylenes and plumbylenes are highly affected by the nature of the substituents. In the ^{119}Sn NMR, the signals of diarylstannylenes have been observed around 2000 ppm. However, the ^{119}Sn NMR of **9** shows two signals at 961 and 1105 ppm, which are surprisingly high-field-shifted. In the cases of ^{207}Pb NMR, the reported chemical shifts for diarylplumbylenes are within the wide range of 6657–9751 ppm. Although the corresponding chemical shifts of alkyl(aryl)-substituted derivatives are in the similar region, compounds **11** and **12** show the signals in higher-field region at 980 (**11**) and 5067 (**12**) ppm, respectively. The longest wavelengths assignable to the n–π* transitions of their UV/vis spectra are also in the wide range of 400–600 nm. In their crystal structures, the angles of C–M–C (C: ipso-carbon of the substituent) are in the wide range of 97.7–117.6° (Sn) and 94.8–121.5° (Pb). Compared with the tin and lead analogs bearing same substituents, the angles are quite close.

1.19.3 Introduction of Heavier Group 14 Element as a Substituent

Introduction of silyl (germyl, stannyl, and plumbyl) substituents, which are more electropositive as compared with carbon substituent, is reported (Schemes 8–10).[14–16] The syntheses of bis-silyl derivatives have been typically achieved by the reaction of the divalent tin or lead source with the corresponding silyl anions. Germyl and stannyl derivatives and heteroleptic examples have been synthesized by similar substitution reactions using the corresponding anions. As a unique method, aryl(silyl)stannylene and plumbylene **39** and **40** have been synthesized by the substituent exchange reaction between the two symmetrically substituted stannylenes. In addition, bissilyl-, aryl(silyl)-, and amino(silyl)-stannylenes and plumbylenes **49–51** have been formed by the insertion reactions of diaminosilylene **52** into the M–N or M–C bonds.



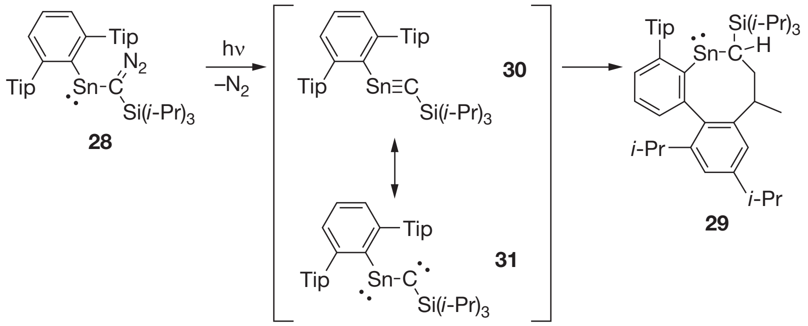
Scheme 5 Examples of alkylarylstannylene and plumbylene.

Silyl-substituted stannylenes **36** and **39** are equilibrated with the corresponding dimers (distannenes) **37** and **41** in solution, respectively, while they exist as dimers in the crystalline state. In contrast to the case of stannylene **36**, bissilylplumbylene **38** is found to exist as a monomer in the crystalline state.

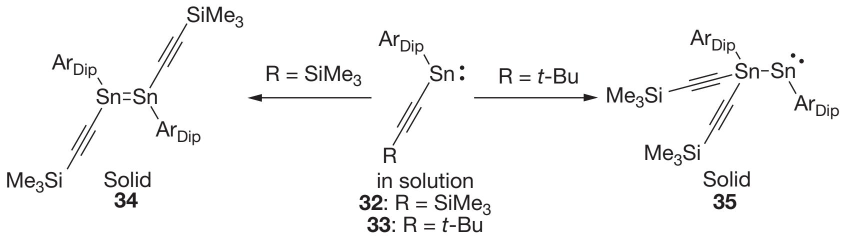
The heavier analogs of alkyne, triply bonded compounds between heavier group 14 elements (dimetallyne) **53** can be formulated as the resonance structures between the triply bonded compounds and the bis(metallylene) compounds **54**. Since the Pb–Pb bond of diplumbyne **55** is reported to feature single-bond character in the crystalline state, it should not be diplumbyne **53** but formulated as bis(plumbylene) **56**.[17] The bonding properties of the Sn–Sn bond of distannynes can be considered as triple bonds, but are sometimes discussed as biradical Sn=Sn character or bismetallylene :Sn–Sn: character with dependence on the electronic properties of the substituents.[18] In addition, the reaction of **56** with trimethylsilylazide affords cyclized plumbylplumbylene **57**.[19]

1.19.4 Halogen-Substituted Derivatives

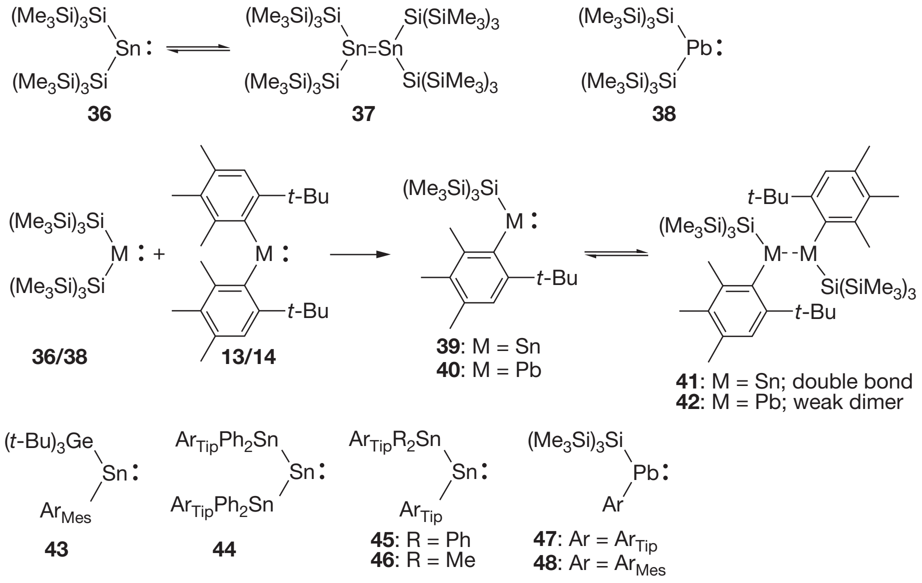
All stable halogen-substituted stannylenes and plumbylenes reported so far are monomeric species in solution on the



Scheme 6 Generation and intermediacy of a stannaacetylene to afford a cyclic stannylene.



Scheme 7 Alkynylstannylenes.



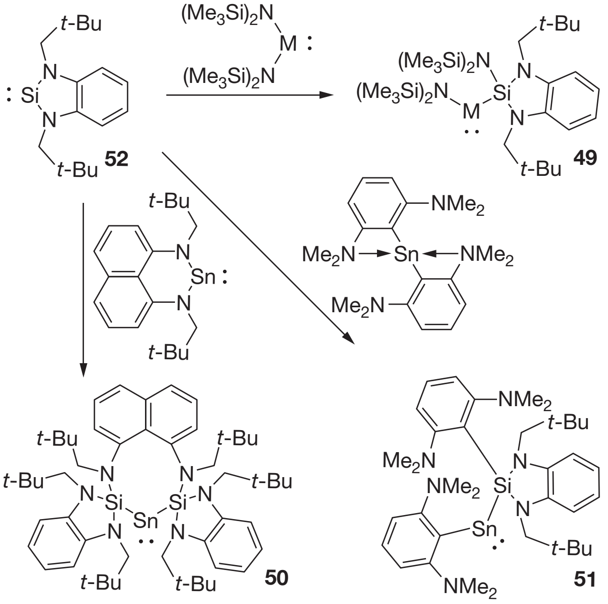
Scheme 8 Stannylenes and plumbylenes bearing silyl, germyl, and stannyl substituents.

basis of spectroscopic analysis and chemical reactivities. In the solid state, Ar_{Tip}-substituted chloro- and iodostannylenes **58**[20] and **59**[21] have been identified as a monomer. The other examples undergo dimerization in the crystalline state giving not the corresponding double-bond species but halogen-bridged dimers or trimer. Stannylenes **61–64** and plumbylenes **65–68** have been synthesized as stable compounds, whose crystal structures exhibited the halogen-bridged dimers. In the case of **59**, not only the monomeric form but also the Cl-bridged dimer **60** have been observed by the X-ray crystallographic analysis. These situations are completely different from the case of halosilylenes and halogermylenes, which never afford the halogen-bridged dimers. Bromoplumbylene **69** has been co-crystallized with pyridine to give monomeric crystalline structure with weak coordination of pyridine **70**.[11d] Unlike the compounds described above, chloroplumbylene **71** showed its trimeric structure **72** with $(PbCl)_3$ six-membered ring skeleton (Schemes 11 and 12).[22]

1.19.5 Hydrogen-Substituted Derivatives

The syntheses of hydrostannylenes **73** have been achieved by taking advantage of bulky terphenyl ligand.[23,24] In almost all cases, they form a hydride-bridged dimer in the crystalline state and in solution. The Sn–H–Sn bonds should be the 3-center-2-electron bonding, which should afford the intermolecular stabilization of the vacant p orbitals of the metallylene center. The syntheses of hydrostannylenes bearing various terphenyl ligands have been achieved by reduction of chlorostannylene with $LiAlH_4$ or $LiBH_4$ or the method via aminostannylenes **74**. Alternatively, the reactions of distannynes **75** with hydrogen molecule (H_2) afford the corresponding hydrostannylene dimers.[25] Although these methods are acceptable for various terphenyl-substituted ones, the case using C_6H-2,6-Tip_2-3,5-(i-Pr)$_2$ as a substituent affords stannylstannylene **76**, the hydrogen-migrated isomer of the bridged dimer of a hydrostannylene.[26] The difference of the products is interpreted in terms of the steric effect of the terphenyl ligands (Schemes 13 and 14).

In the lead case, interestingly, the reaction of bromoplumbylene **69** with $LiAlH_4$ afforded not the expected hydroplumbylene **77** but diplumbyne **55** (**56**).[17] In this reaction, the formation of **77** is considerable as an intermediate. Ready dimerization of **77** and the elimination of a hydrogen molecule could give **55** (Scheme 15).

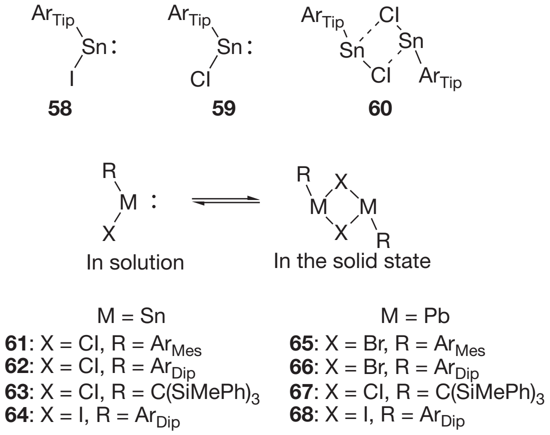


Scheme 9 Insertion reactions of diaminosilylene into M–N or M–C bonds.

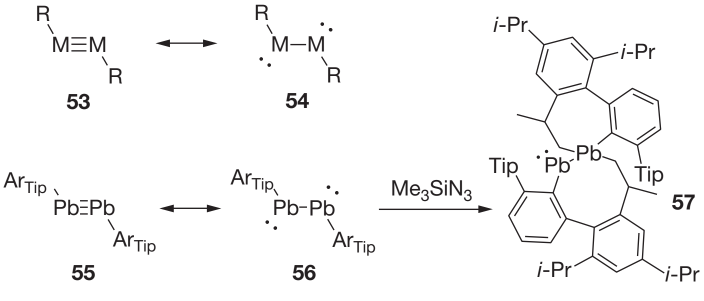
1.19.6 Heteroatom-Substituted Derivatives

Stabilization of metallylenes by using group 15 (N or P) and 16 (O or S) elements is highly effective, and the metallylenes stabilized by group 15 and 16 elements have longer history than the other types described above. Their frontier orbitals are strongly perturbed and stabilized by interactions with the orbitals of lone-pair electrons of the heteroatoms. Their structures and reactivities are quite unique and different from those of intrinsic singlet carbene analogs. So far, various kinds of heteroatom-substituted stannylenes and plumbylenes **78–82** have been reported and widely investigated (Scheme 16). Almost all of these compounds have monomeric central atoms as judged by NMR spectra, and in some cases by X-ray crystallographic analysis. However, compounds **79** bearing group 16 elements as a substituent have higher tendency to oligomerize than the diamino-substituted metallylenes represented by **78** probably due to the decrease in the number of substituents, and relatively bulky substituents are necessary to keep their monomeric form. Cyclic analogs **80** (Veith's metallylenes),[27,28] **81** (heavier analogs of Arduengo's carbene),[29] and **82**[29] are stabilized by chelating effects in addition to the perturbation by the nitrogen atoms. Since there are a number of reviews covering these compounds reported so far,[1] we limit ourselves here to some recent examples.

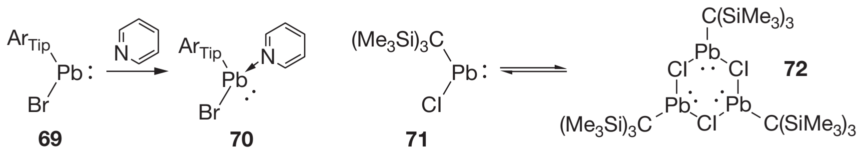
In recent years, their coordination abilities have extensively been investigated from the viewpoint of their σ-donor and π-acceptor characters toward transition metals, and their unique coordination modes have been revealed. For example,



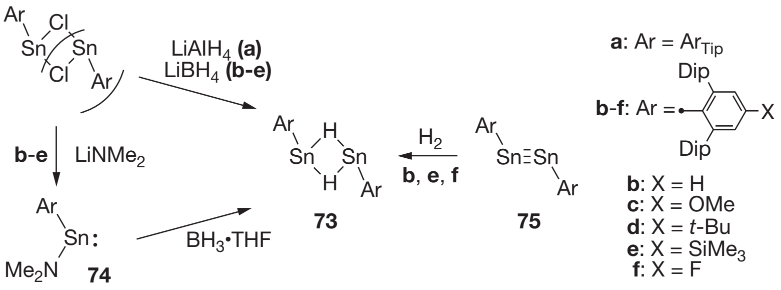
Scheme 11 Halogen-substituted stannylenes and plumbylenes.



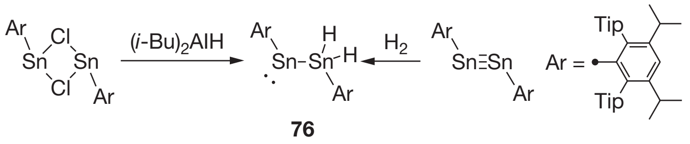
Scheme 10 Tin and lead analogs of alkyne.



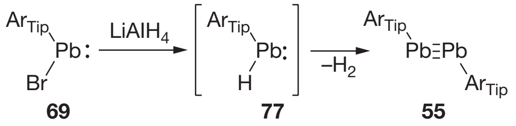
Scheme 12 Complexation and trimerization of haloplumbylenes.



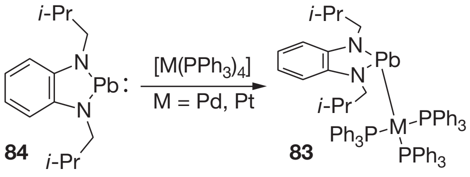
Scheme 13 Syntheses of hydrogen-substituted stannylenes.



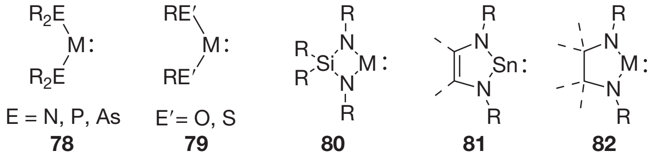
Scheme 14 Generation of stanylstannylenes.



Scheme 15 Intermediacy of hydroplumbylene to afford diplumbyne.



Scheme 17 Syntheses of plumbylene complexes.



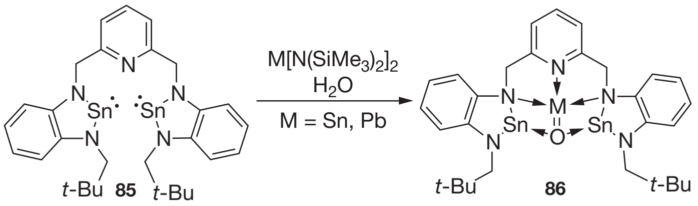
Scheme 16 Stannylenes and plumbylenes bearing heteroatom substituents.

the structures of Pd- and Pt-complexes **83** of plumbylene **84** show an angle of ca. 125° between the plumbylene plane and the Pd–Pb or Pt–Pb bond, indicating coordination of the transition metal to the empty π orbital of the Pb atom (Scheme 17).[30] Moreover, these types of ligands are useful for the main-group elements; bisstannylene **85** captured tin and lead analogs of carbon monoxide (**86**, Scheme 18).[31]

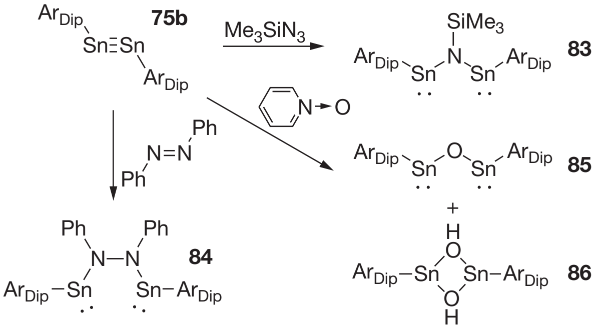
Tin–tin triple-bond compounds, distannynes, are important species in the chemistry of main-group elements themselves. In addition, they show unique reactivity giving novel tin-containing compounds. Especially, the compounds **83–85** containing a pair of two-coordinate Sn atoms have been successfully prepared by the reaction of distannyne **75b** with azide, azobenzene, and pyridine *N*-oxide, respectively (Scheme 19).[32,33]

1.19.7 Conclusion

In this chapter, the development of stabilization of stannylenes and plumbylenes is summarized based on the papers that have appeared in the last decade. The most important advances are the development of synthetic methods for heteroleptic metallylenes bearing substituents of various group elements and the elucidation of substituent effect toward metallylenes. Actually, the applications utilizing their unique electronic properties



Scheme 18 Capture of tin and lead analogs of carbon monoxide.



Scheme 19 Syntheses of stannylenes bearing heteroatom substituents from a distannyne.

and reactivity are noticeably increasing. These findings should be of some help for designing of tin- and lead-containing materials having novel functions and development of novel molecular transformations.

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1.20 Low-Coordinate Main Group Compounds – Group 15

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1.20.1 Nomenclature

Cations R_2P^+ and R_2As^+ are designated as phosphenium and arsenium ions rather than phosphanylium and arsanylium ions as recommended by IUPAC. The higher homologs are named accordingly as stibenium and bismuthenium ions, respectively. Neutral pnictogen(I) compounds R–E are referred to using the common non-IUPAC names as phosphinidenes (E=P), arsinidenes (E=As), and stibinidenes (E=Sb) rather than as phosphanylidenes, arsanylidenes, and stibanylidenes, respectively. Pnictogen is used as generic name for all group 15 elements, and generic cations R_2E^+ or neutral compounds R–E are thus referred to as pnictogenium cations or pnictinidenes, respectively.

1.20.2 Introduction

Low-coordinate compounds are defined in this chapter as derivatives of electronically and coordinationally unsaturated parent compounds that can be depicted as Lewis structures featuring a heavier group 15 element with an even number of

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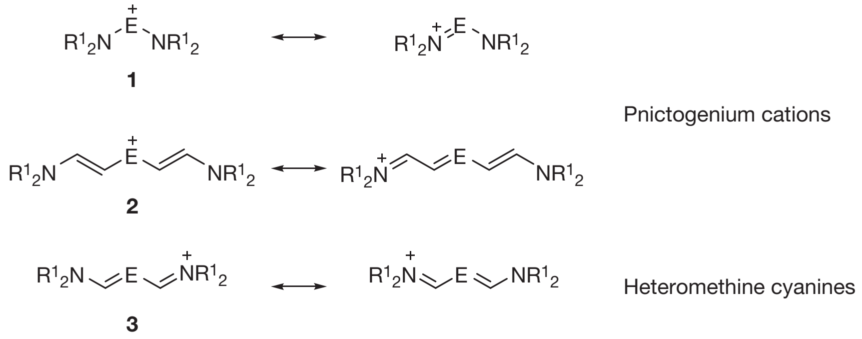


Scheme 1 Dominant canonical structures of amino-substituted pnictogenium cations and heteromethine cyanines.

$N<8$ valence electrons. This definition includes carbene-analog pnictogenium cations and neutral pnictogen(I) species which are derived from the parent six valence-electron species H_2E^+ and HE (E=P, As, Sb, Bi), and monocations (E^+) with a valence electron count of four. Radicals and compounds with multiple bonds involving pnictogen atoms are covered in **Chapters 1.12** and **1.13** respectively. Nitrogen analogs, such as nitrenium ions, nitrenes, and their complexes, are considered to belong to the realm of organic chemistry and will thus likewise be excluded.

Many heavier pnictogenium cations and virtually all neutral and cationic pnictogen(I) derivatives are only known as transient species but are readily converted into persistent or even isolable compounds by complexation with Lewis bases. Although these complexes are not low-coordinate or electronically unsaturated compounds in a strict sense, they are still capable of transferring a pnictogen(I) fragment to another substrate, and represent therefore synthetic equivalents of elusive pnictogen(I) species. Simple Lewis-base complexes of this type are thus included in this chapter, whereas complexes with more complicated frameworks involving catenation of group 15 elements are discussed in **Chapters 1.04** and **1.05**. On a similar basis, also transition metal complexes of neutral pnictogen(I) species constitute a borderline case between main group and coordination chemistry. This chapter focuses on stable or transient species with terminal pnictinidene ligands, and chemical reactions of these species, which are ligand centered rather than metal centered.

Although the systematic chemical exploration of molecular species featuring heavier group 15 elements in low-coordination states started off in the 1970s, this chapter mainly focuses on the more recent developments since the mid-1990s. The earlier literature, in particular on low-coordinate phosphorus compounds, has been extensively reviewed.[1–10]

1.20.3 Pnictogenium Cations

Pnictogenium cations R_2E^+ derived from the parent compound by formal replacement of the hydrogen by singly bonded substituents R are, as a consequence of the electron deficiency on the central atom, strong electrophiles and have only been observed as transient species in the gas phase. Isolable compounds are accessible when the electrophilic character is mediated by mesomeric interaction with suitable π-donor substituents, or by additional coordination of a Lewis base. The alleviating effect of π-donor groups is attributable to delocalization of the positive charge and introduces partial double-bond character into the R–E bonds.[1,3] The most widely used type of substituent to effect such stabilization are amino groups ($R^1{}_2N$), which are normally directly attached to the electrophilic center (**1**, **Scheme 1**) but may also be connected via an intervening double bond as in **2**; other types of π-donor substituents are thiolate (R^1S) or pentamethylcyclopentadienyl moieties. It is important to distinguish these stabilized pnictogenium cations from heteromethine cyanines **3** which lack any pronounced electrophilic character and exhibit rather different chemical behavior.[11] As it has recently been pointed out, phosphorus-containing species of this type may in certain cases be regarded as adducts of a phosphorus(I) cation with two carbon donor (i.e., carbene) moieties;[9] some aspects of these cations are addressed in **Section 1.20.5**.

1.20.3.1 Structure and Bonding

The electronic structure and bonding situation in both free pnictogenium cations and their complexes have been extensively investigated by computational studies at both *ab initio* and density functional theory (DFT) levels. A large part of these studies focused on the evaluation of π-interactions with the electron-deficient pnictogen center, and their implication on electronic ground states, frontier orbitals, and chemical reactivities and stabilities.

1.20.3.1.1 Free pnictogenium ions

Like the isoelectronic carbene-analog compounds with divalent group 14 elements, pnictogenium cations may exist in an electronic singlet ($^1A_1$) and triplet ($^3B_1$) state. Several topical quantum chemical studies at both *ab initio* and DFT level indicate a triplet ground state for the parent nitrenium cation, $NH_2{}^+$.[12] All cations with heavier elements exhibit, regardless of the substituents, singlet ground states.[13–23] The calculated singlet–triplet splitting energies, ΔE_{S-T}, increase in the series $EX_2{}^+$ (E=P, As, Sb; X=H, F, Cl, Br, I) generally with increasing atomic number of E (e.g., ΔE_{S-T} (kJ mol^{-1})=74.2 ($PH_2{}^{+14}$), 92.5 ($AsH_2{}^{+13}$), 105.0–106.3 ($SbH_2{}^{+13}$) at the complete active space-multi-configurational self-consistent field (CAS-MCSCF level)), and with increasing electronegativity of X (e.g., ΔE_{S-T}

(kJ mol^{-1}) = 51.5 (PH_2^+), 132.6 (PI_2^+), 174.9 (PBr_2^+), 208.8 (PCl_2^+[13]), 359.8 (PF_2^+[13]) at (p)MP4SDTQ/ECP-31 + g(d)//MP2/ECP-31 + g(d) + zpe level[22]). The singlet–triplet energy separation for the diaminophosphenium cation $P(NH_2)_2^+$ ($\Delta E_{S-T} = 274.1$ kJ mol^{-1}[22]) is somewhat lower than that calculated for PF_2^+ at the same level, and calculated splittings in substituted diaminophosphenium ions seem to decrease upon formal replacement of the phosphorus atom by arsenic.[26]

The molecular geometries in the electronic ground state are bent and exhibit acute bond angles (ranging from approximately 90° to 110° depending on the type of pnictogen atom, substituent, and computational method applied) and shorter E–X bonds than the corresponding anions, which is attributed to more favorable electrostatic interactions.[22] E–N bonds in amino-substituted cations exhibit additional shortening from π-conjugation effects and an appropriate increase in bond orders.[23–26] No such effect is observed in Ph_2P^+, presumably due to the effect that the gain in stabilization from π-conjugation cannot outweigh the loss of aromaticity in the phenyl ring.[26]

The connection between π-conjugation effects and cation stability has been studied to some extent for phosphenium ions. Cation stabilities were evaluated from computed energies of isodesmic group transfer reactions ΔE_{GT} (eqn [1]),[22,24,27] or from the transferred charge densities that accompany the formation of a donor–acceptor bond between a phosphenium ion and an arbitrary nucleophile (eqn [2]).[24] Both approaches allow to assess the affinity of a cation for attachment of a Lewis base in relation to a reference compound (usually the parent phosphenium ion, PH_2^+) in the gas phase. The results reveal that the stabilizing effect of a substituent R^1 increases in the series H < Cl < Me < SH, OH < Ph < NH_2.[24] A general increase in stability was further noted upon formal replacement of hydrogens in SH, OH, NH_2 fragments by alkyl groups[24] and, in the series of halogenated phosphenium ions, with decreasing substituent electronegativity (F < Cl < Br < I).[22] Ylide substituents –$CH(PH_3)$ exert an even stronger stabilizing effect than amino groups.[24] Analysis of appropriate group transfer energies revealed a correlation between increasing relative stabilities of halogenophosphenium cations PX_2^+ and the corresponding anions PX_2^- (X = F, Cl, Br, I).[22]

1

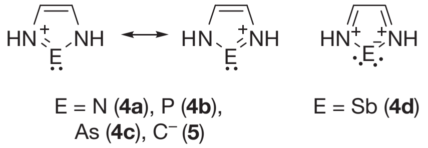
$$R^1_2P^+ + H{-}PH_2 \longrightarrow R^1_2P{-}H + {}^+PH_2 + \Delta E_{GT} \quad (1)$$

2

$$R^1_2P^+ + Nuc \longrightarrow R^1_2P \leftarrow Nuc \quad (2)$$

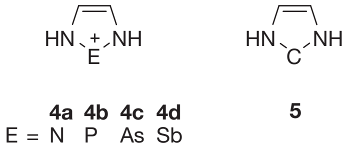
$Nuc = H^-, F^-, Cl^-, NMe_3, PMe_3$, ...

In a more detailed analysis, the stabilizing effect of a substituent was related to a combination of mesomeric stabilization by π-donor groups, which increases in the order OH < Cl < NH_2 < SH, and σ-bond polarization by electronegative substituents, which strengthens the contribution of the Coulomb term to the bond energy and increases in the order S ≈ Cl ≪ N < O. As a consequence, the higher overall stabilizing power of NH_2- with respect to OH- (which exert stronger Coulomb stabilization) or SH-groups (which are better π-donors) is due to a fortuitous balance of both effects.[24]



Scheme 2 Leading canonical structures for pnictogen analogs of imidazoyl carbenes.

A high degree of attention was dedicated to the role of π-electron delocalization in the heterocyclic pnictogenium ions **4** which are isoelectronic analogs of the neutral imidazoyl carbenes **5** (formula [I]). Comprehensive computational studies[28] indicated that all cations **4** display aromatic stabilization energies and magnetic properties (diatropic ring currents) that allowed us to attribute these systems some level of aromaticity. The nitrenium ion **4a** was found to display similar aromatic character as cyclopentadienide, $C_5H_5^-$, a true 6π-electron aromatic species, but the degree of aromaticity decreases with increasing atomic number of the pnictogen atom. The aromatic stabilization energy of phosphenium ion **4b** is lower than that of the parent phospholide, $C_4H_4P^-$,[24] which exhibits a similar degree of aromaticity as the isoelectronic $C_5H_5^-$, but still exceeds that of the parent carbene **5**,[24,28] thus leading to conclude that the aromaticities of both species are similar. Orbital analyses indicated that the leading Lewis structures of the lighter pnictogenium ions **4a–c** match that of carbene **5** and are characterized by the presence of a single lone pair on the low-valent main group element; the electronic structure of the stibenium cation **4d** is best approximated with a model in which the pnictogen element holds two electron pairs (**Scheme 2**).[28]



I

Analyses of the frontier orbitals of pnictogenium cations suggest that the lowest unoccupied molecular orbital (LUMO) is generally centered at the pnictogen atom. The type of the highest occupied molecular orbital (HOMO) varies depending on the substituent pattern, and may be represented by a molecular orbital (MO) centered predominantly at the pnictogen lone pair, a combination of lone pairs of electrons on adjacent atoms, or a delocalized π-orbital with a sizable coefficient at the pnictogen atom (**Figure 1**).[22,24,26–28] Although this diversity can help to explain differences in reaction patterns of pnictogenium cations that have been found in some cases,[23] the generally observed chemical reactivity patterns are far more uniform than anticipated. This is due to the fact that positively charged pnictogenium ions act predominantly as electrophiles, and the course of orbital-controlled chemical reactions is therefore dominated by the interaction of the strongly electrophilic pnictogen center with the HOMO of the nucleophile.[24] As a consequence, diamino-substituted pnictogenium cations exhibit electronic structures which bear close resemblance to those of isoelectronic and isolobal nucleophilic diaminocarbenes, and reactivity patterns which are better comparable to those of electrophilic carbenes.[24]

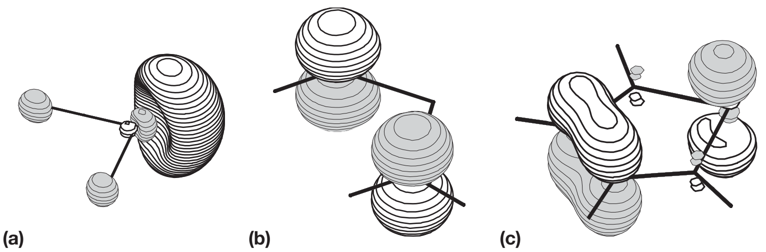
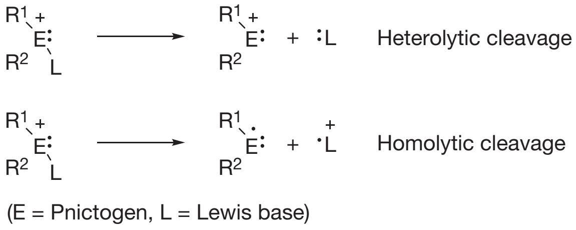


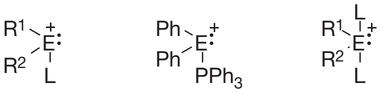
Figure 1 Isodensity representation of the HOMOs of (a) $[PH_2]^+$, (b) $[P(NH_2)_2]^+$, and (c) $[P(NHCH)_2]^+$.

1.20.3.1.2 Lewis-base complexes of pnictogenium ions

Pnictogen-centered cationic species **6** (formula [II]) can be formally disassembled into a cationic fragment $R^1R^2P^+$ and a neutral fragment L, and may thus be described as donor–acceptor complexes of a central pnictogenium cation $R^1R^2E^+$ and a Lewis base (L). Computational studies of hypothetical bond dissociation reactions (**Scheme 3**) indicated that this view is justified for various donor complexes derived from π-stabilized aminophosphenium or aminoarsenium ions ($R^1(R^2)E^+ = (CH_3)(NH_2)P^+$, $(CH_3)(NH_2)As^+$),[29] or Ph_2P^+.[30] Heterolytic bond cleavage is here energetically generally more favorable than homolytic cleavage, and the pnictogen–donor interaction was thus classified as a genuine dative bond.[31] Similar conclusions were also drawn from a topological analysis of the electron density of Lewis-base complexes of the phosphenium cations $(Me_2N)_2P^+$ and Ph_2P^+,[26,30] and from analyses of energy decomposition schemes and MOs of some PPh_3 complexes of pnictogenium cations (**7**).[32] For amine or phosphane adducts of more electrophilic cations, $(CH_3)_2E^+$ (E = P, As), homolytic bond cleavage was predicted to be energetically more favorable than heterolytic bond cleavage, and the pnictogen–donor bonds were considered normal covalent bonds. These compounds were thus referred to as pnictogenylphosphonium (or ammonium) ions rather than donor-stabilized pnictogenium cations.[29]



Scheme 3 Types of bond dissociation reactions of Lewis-base complexes of pnictogenium ions.



6 **7** **8**

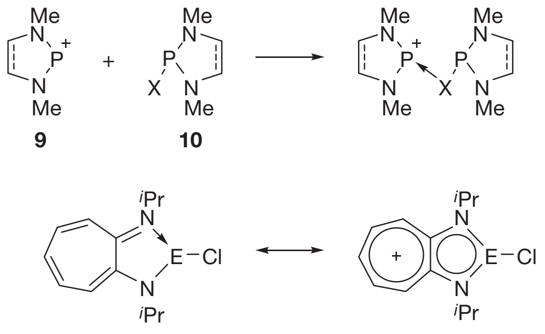
(E = P, As, Sb, Bi)

II

The interaction strength in pnictogenium cation/donor complexes has been evaluated by calculation of both 'adiabatic' and 'vertical' bond energies. Adiabatic energies correspond to the reaction energies of heterolytic bond cleavage processes (**Scheme 3**) in which the fragments formed are allowed to relax to their equilibrium geometries. In the calculation of vertical bond energies, the fragments remain frozen in the geometries they adopt in the complex. Calculated vertical bond energies for complexes of phosphenium ions with different types of donor molecules (phosphanes, amines, and carbenes) were similar or even larger than those of normal covalent bonds, in accord with the finding that calculated distances of dative bonds were close to the sum of covalent radii.[26] Similar trends were also noted for phosphane complexes of higher pnictogenium cations.[32] Energy decomposition analysis indicated that the principal attractive component of the pnictogen–donor bonding is generally contributed by the orbital term – which suggests that the bonds possess a high degree of covalent character – but that the importance of electrostatic contributions increases when the pnictogen atom moves down the group.[32] Phosphane donors induce a larger degree of charge transfer to an acceptor cation than amine donors, and trigger thus higher interaction energies and shortened dative bonds.[24,26,29] On the side of the cation, the strength of the dative bond decreases when the LUMO gets lower in energy and the intramolecular stabilization by π-donor substituents increases.[24,26,29] Energy decomposition analyses allowed to relate this trend to the effect that dative bond formation is associated with a breakdown of the π-delocalization in the cation, which becomes the more endothermic the higher the degree of mesomeric stabilization.[26]

Theoretical studies of the interaction between strongly π-stabilized diaminophosphenium ions **9** and P-halogenophosphanes **10** (**Scheme 4**), which may act as ambiphilic donors via the phosphorus or the halogen atom, suggest that the adduct formation is controlled by electrostatic rather than orbital interactions, and that creation of X → P dative bonds is energetically favored over P → P bonds.[33] In aminotropiminato-based cations **11**, formation of a robust N → E dative bond is supported by aromatic π-electron delocalization in the bicyclic ring system.[34] The reluctance of the heavier homologs **11b–11d** to form stable metal complexes was shown to be attributable to a combination of increasing stabilization of the nonbonding electron pair at E and the increase of the positive charge on the pnictogen atom due to increasing E–N and E–Cl bond ionicity.[34]

Computational studies of the interaction of the Lewis complexes **6** with a further donor molecule in the gas phase suggest that secondary complexes **8** (formula [II]) may form in an exothermic process without an intermediate barrier.[35,36] The coordination geometry in these specimens is based on a trigonal bipyramid in which one equatorial site is vacant and the donor groups occupy apical positions, so that the two dative bonds form a nearly linear array. Computed vertical or



9 **10**

11a **11b** **11c** **11d**
E = P As Sb Bi

Scheme 4 Selected intra- and intermolecular Lewis-base adducts of aminopnictogenium ions.

adiabatic bond dissociation energies of the dative bonds in these secondary complexes are by 40–60% lower than in the primary complexes **6**, and the attracting contribution is electrostatic rather than covalent.[32] The stability of the dative bonds increases, as expected, with increasing donor ability of the Lewis base and increasing electronegativity of the donor fragment in the primary complex,[35] thus epitomizing the importance of electrostatic interactions for the adduct formation.

1.20.3.2 Syntheses

1.20.3.2.1 Generation of pnictogenium ions in the gas phase

Isolated pnictogenium ions in the gas phase are accessible from fragmentation,[37–44] collision-induced dissociation,[45] or ion–molecule reactions[46,47] of precursor cations generated in the ion source of a mass spectrometer. The ions may be mass selected or stored in an ion cyclotron resonance (ICR) spectrometer or a quadrupole ion trap, and subjected to subsequent gas-phase reaction studies (see Section 1.20.3.4.5). Most studies have been dedicated to phosphenium or arsenium ions but cations EI_2^+ have been prepared for all heavier pnictogen elements.[45] Generation of pnictogenium ions via spontaneous or collision-induced fragmentation proceeds in most cases by cleavage of halogen, alkoxy, or phenyl radicals from suitable precursors (pnictogen trihalides, 2-chloro-1,3,2-dioxaphospholane, 2-chloro-1,3,2-benzodioxaphospholane, trimethyl phosphite, and triphenylphosphane, phenyldihaloarsanes). Arsenium–arene complexes have also been generated from AsI_3/benzene mixtures under chemical ionization conditions.[48] The aromatic phosphiranylium ion **12** (formula [III]) was produced by reaction of acetylene with a transient radical cation PBr^+ generated by fragmentation of PBr_3, and identified by computational studies and its reactions with acetylene and ethylene.[46] Solvent coordination of dithiolato-substituted cyclic bismuthenium cations was studied by atmospheric pressure chemical ionization mass spectrometry.[49]

12 III

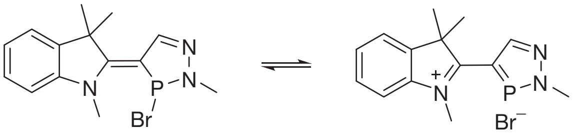
1.20.3.2.2 Syntheses of stable pnictogenium cations

Isolable or at least persistent pnictogenium cations can be generated in condensed phase and characterized by physical methods if the highly electrophilic low-coordinate main group center is stabilized by at least one strongly electron-donating substituent. Stabilizing groups are in most cases alkyl- or aryl-substituted amino or thiolato moieties; in special cases, PR_2[50] or cyclopentadienyl groups[51–54] have also been used. Most known pnictogenium ions are achiral, but some syntheses of optically active cations have also been reported.[55,56]

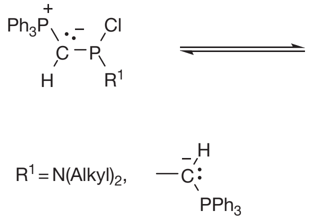
1.20.3.2.2.1 Synthesis via heterolytic cleavage of a pnictogen–element bond

The majority of pnictogenium cations known up to date were generated via cleavage of an anionic substituent from the tri-coordinate pnictogen atom of an appropriate neutral, electronically saturated precursor molecule. Halide ions were in most cases employed as leaving group but abstraction of amino substituents or hydride[57] has also been employed.

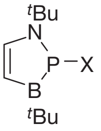
Pnictogen–halogen bond heterolysis requires generally the assistance of an electrophile. Spontaneous (partial or complete) self-dissociation is observed in a limited number of cases where the precursor either receives additional stabilization from the formation of a heteroaromatic delocalized π-electron system[58–61] as, for example, in **13** (eqn [3]), or contains strongly donating ylidyl substituents (eqn [4])[62]; the formed cations **14** are, however, better regarded as phosphonio-substituted phosphaalkenes rather than phosphenium cations.[63] *N*-heterocyclic phosphenium derivatives **15** (X = Cl, Br, I) (formula [IV]) are borderline cases which possess unusually long and polarizable P–X bonds (distances exceed those of normal covalent bonds by approximately 24% for X = Cl[59,64] and 30% for X = Br,[65] and the solid-state structure of the iodo derivative contains a one-dimensional coordination polymer of interacting phosphenium and iodide ions[65]). Measured dissociation constants (eqn [5]) are not compatible with complete ionization but suggest to describe these species as phosphenium halide contact ion pairs held together by predominantly ionic P–X bonds which still retain some covalent character.[64]



13 3

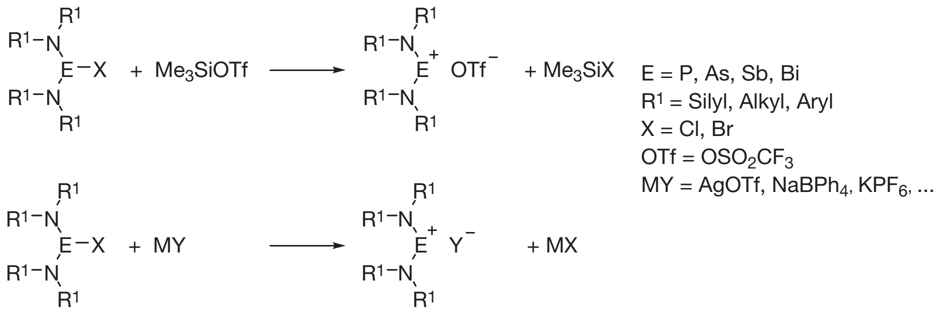


14 4

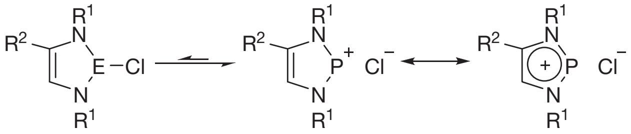


15 IV

X = F, Cl, Br, I



Scheme 5 Synthesis of pnictogenium ions by electrophile-assisted halide abstraction.



R^1	R^2	E	K (mol l^{-1})	Ref.
^{t}Bu	H	P	2.2(4) $\times 10^{-3}$	64
Mes	H	P	4.9(13) $\times 10^{-3}$	64
^{t}Bu	Cl	P	0.43(17)$\times 10^{-3}$	64
^{t}Bu	H	As	0.12(2) $\times 10^{-3}$	77

5

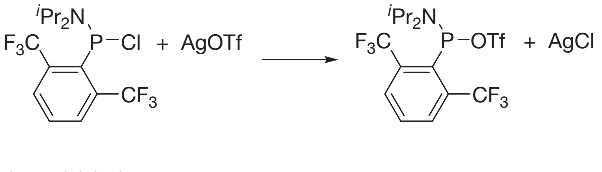
Reactions under electrophile-assisted cleavage of pnictogen–halogen bonds fall into two different categories. In the first group, the electrophile abstracts a halide from the neutral precursor to form the desired pnictogenium cation and a complex halide anion (eqn [6]). Transformations of this type were discovered as the first access to stable pnictogenium cations[66] and still remain one of the most used approaches. Starting materials and products form a dynamic equilibrium in which the added electrophile and the pnictogenium cation compete as Lewis acids for the Lewis basic halide ion; quantitative ion formation results if the added electrophile is a much stronger Lewis acid than the pnictogenium ion. These conditions are fulfilled when strong Lewis acids such as $AlCl_3$, $GaCl_3$, or $SbCl_5$ are used as electrophiles, and the formed pnictogenium cation is stabilized by one[67–69] or two[1,70–79] strongly π-donating amino or thiolato substituents (eqn [6]). The method is particularly useful to prepare cations with four- to six-membered heterocyclic rings which fix the donor substituents in a conformation allowing maximum π-interaction with the dicoordinate pnictogen atom.[66,76] Besides heterocyclic species with saturated and unsaturated[77] isolated rings, also fused systems containing annulated benzene[78] or naphthalene rings[72] are available. Additional stabilization by aromatic π-delocalization permits to accomplish quantitative formation of stable pnictogenium salts even with moderately strong Lewis acids such as $GeCl_2$ or $SnCl_2$.[79]

E = P, As, Sb, Bi
R^1 = Silyl, Alkyl, Aryl
R^2 = $(R^1)_2N$, R^1S, Aryl, Alkenyl
MX_n = e.g. $AlCl_3$, $GaCl_3$, $SbCl_5$

6

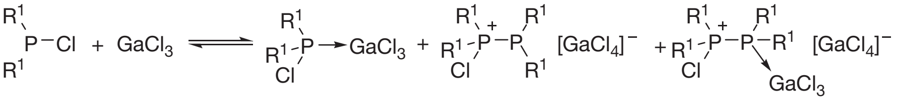
Insufficient electronic stabilization of the cation suppresses ion formation, or causes formation of side products. Dialkyl chlorophosphanes or Ph_2PCl react thus with $GaCl_3$ to give equilibrium mixtures which contain, depending on the nature of R^1 and the stoichiometric composition, different amounts of phosphane complexes **16**, phosphinophosphonium complexes **17**, or even a gallium complex **18** (only for R^1 = Me) of the latter (eqn [7]).[80]

As alternative to the reaction with Lewis acids, halide abstraction from pnictogen halides is accomplished by condensation with electrophiles such as trimethylsilyl triflate,[55–57,81] or by metathesis with salts containing weakly nucleophilic anions such as CF_3SO_3Ag,[82] $Ag[BF_4]$, $M[PF_6]$ (M = Tl, Ag, K),[61,81] $M[BAr^f_4]$ (M = Li, Na, Tl),[82,81] or $Na[BPh_4]$[83] (**Scheme 5**). Evaporation of volatile trimethylsilyl halide or precipitation of an insoluble salt makes cation formation practically irreversible, but the method still fails in cases of insufficient π-donor stabilization of the pnictogenium cation. In these cases, the reaction may not proceed at all, yield a covalent substitution product (eqn [8]),[68] a Lewis-base complex of a pnictogenium ion instead of the free cation (see **Section 1.20.3.2.3**), or result in anion degradation.



OTf = OSO_2CF_3

8



R^1 = Ph, Alkyl

16 **17** **18**

7

1.20.3.2.2.2 Synthesis via protonation or alkylation of double bonds

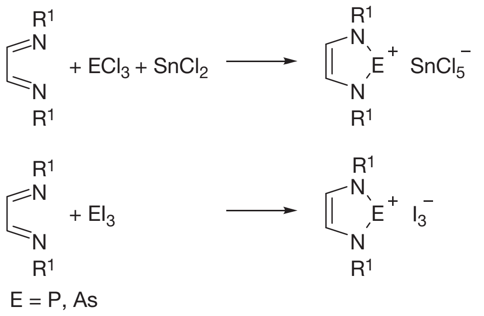
Isolable[3,84] or transient[85] phosphaalkenes and iminophosphanes react with triflic acid or methyl triflate via protonation or methylation of the double bonds. This approach allows straightforward synthesis of heterocyclic cations with unsymmetrical substitution patterns.[85] Methylation of the diphosphene Mes*PPMes* by a large excess of methyl triflate gives the isolable phosphenium salt [Mes*(Me)P–P$^+$Mes*]OTf with a cation that is stabilized by π-donation from a phosphino rather than an amino group.[50]

1.20.3.2.2.3 Synthesis via amination of a phosphadiazonium salt

Phosphadiazonium salt [Mes*N≡P]OTf reacts with Mes*OH and Mes*NH_2 via addition to the triple bond to give phosphenium salts [Mes*NH–P–NHMes*]OTf and [Mes*NH–P–OMes*]OTf.[86] The reaction is analogous to the synthesis of triazenes via amination of diazonium salts. Extension of this approach to prepare cations with higher pnictogens was so far prevented by the lack of appropriate higher diazonium analogs as starting materials.

1.20.3.2.2.4 Synthesis of heterocyclic cations via cycloaddition reactions

Phosphorus and arsenic trichloride react with tin dichloride to generate transient pnictogen(I) species which are trapped in the presence of 1,4-diazabutadienes via [1+4] cycloaddition to give penta- or hexachlorostannate salts of N-heterocyclic phosphenium and arsenium ions.[87,88] Phosphorus and arsenic triiodide react with 1,4-diazabutadienes even without additional reducing agent via spontaneous disproportionation to give N-heterocyclic phosphenium and arsenium triiodides (**Scheme 6**).[87,88] Similar reaction of pyridine-carbaldimines with PI_3 gives phosphenium triiodides with pyrido-annulated ring systems.[89] The triiodide anions can be exchanged for other anions such as OTf $^-$ or $[BPh_4]^-$ by subsequent anion metathesis.

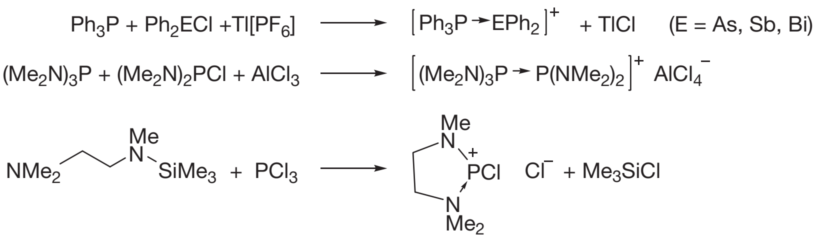


Scheme 6 Synthesis of heterocyclic phosphenium and arsenium ions via [1+4] cycloaddition.

1.20.3.2.3 Lewis-base-stabilized pnictogenium cations

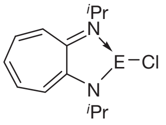
Lewis-base-stabilized pnictogenium cations represent the products of a chemical reaction between a free cation and a Lewis base, and this aspect is discussed in **Section 1.20.3.3**. In addition, however, stable Lewis-base complexes of pnictogenium cations are often accessible even when free cations (e.g., Ph_2E^+) are unavailable because of insufficient π-stabilization. Since these species are capable of transferring a pnictogenium unit to a different donor or other substrate, they may still serve as synthetic equivalents for a free R_2E^+ unit and offer thus a viable entry into pnictogenium cation chemistry. This section focuses on synthetic pathways to such pnictogenium ion equivalents which do not proceed via the free cations.

Neutral disubstituted pnictogen monohalides R_2EX may react with strong Lewis bases under formal replacement of the halide anion by a neutral nucleophile to give Lewis-base complexes of pnictogenium ions (**Scheme 7**). In cases where the pnictogen–halogen bonds remain intact, or dynamic mixtures of starting materials and products are obtained, the reaction equilibrium may be shifted to the side of the product by trapping the halide ions with suitable electrophiles such as $AlCl_3$, $GaCl_3$, Me_3SiOTf, or silver and thallium salts of anions of low nucleophilicity.[32,90–93] Spontaneous halide extrusion may occur if the attack of a suitable nucleophilic amine,[94] guanidine,[96] keto,[97] phosphane,[98] or thioether[99] function proceeds intramolecularly and enables formation of an entropically favored chelate ring. Chelation in pnictogenium complexes **11**, **19** (formula [V]) of aminotroponiminates or aminotroponates is supported by both the rigid molecular structure and aromatic π-delocalization.[100] β-Ketiminates (nacnac-ligands) yield, depending on the reaction conditions and the pnictogen halide employed, donor-stabilized pnictogenium ions featuring either *N*,*N*- (**21**)[101–103] or *N*,C-bound (**22**)[103,104] nacnac units. A guanidine-stabilized arsenium ion **23** reacts further under abstraction of the remaining chloride to give a multiply donor-stabilized dication **24** (**Scheme 8**).[96] Formation of dicationic complexes $[RP(Do)_2]^{2+}$ (R=Ph, Cy_2N; Do=DBN, DBU) occurs upon reaction of dichlorophosphanes $RPCl_2$ with the amidine bases DBU and DBN, respectively.[105] Likewise, arylpnictines Ph_3E (E=As, Sb) react with $BiCl_3$ or $PhBiCl_2$ and excess halide abstracting agent (Me_3SiOTf or $AlCl_3$) to give isolable dicationic complexes $[Ph_3E–BiR]^{2+}$ (E=As, R=Ph; E=Sb, R=Cl) which are stabilized in the crystalline state by additional intermolecular donor–acceptor interactions involving the counterions.[106] Alkylation of

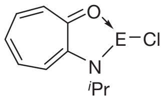


Scheme 7 Synthesis of Lewis-base stabilized pnictogenium ions.

donor–acceptor adducts between arsenium ions and an optically active phosphane has been employed for the selective synthesis of enantiomerically enriched tertiary arsines (**Scheme 9**).[91,92] *In situ* generation of a nucleophile is exploited during reactions of Ph_2PCl and $PhPCl_2$ with imidazolium carboxylates to give water-soluble phosphenium–carbene adducts.[107]

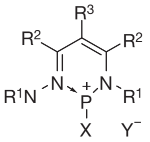


11



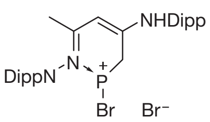
(E = P, As, Sb, Bi)

19



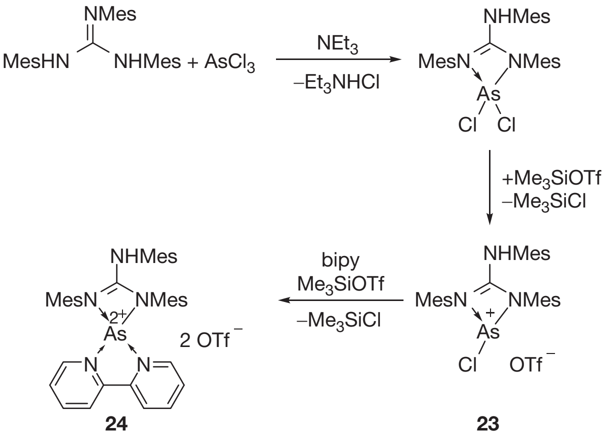
20

R¹=Dipp, C_6F_5
R², R³ = H, Me, Ar
X = Cl, I
Y = OTf, Br, I_3



21

V

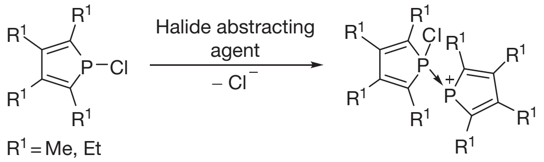


Scheme 8 Synthesis of a donor-stabilized As-dication.

The pnictogenium complex formation under creation of a donor/acceptor bond between the pnictogen atom and the nucleophile and spontaneous pnictogen–halogen bond heterolysis bears close mechanistic resemblance to associative or S_N2-type ligand displacement reactions in main group element compounds (e.g., transient adducts $[(R_2N)_2(Cl)P\cdots Cl^-]$ have been postulated as intermediates during halide exchange reactions of diamino chlorophosphanes[108]) or metal complexes. Formation of the dative bond not only mediates the electron deficiency at the pnictogen center but also provides an additional thermodynamic driving force. Bond heterolysis is therefore accomplished more easily than in the syntheses of free pnictogenium cations (**Section 1.20.3.2.2.1**) and may happen spontaneously,[94,97,100,107] or can be triggered by the choice of an appropriate solvent.[109] Evaluation of a negative entropy of activation of $\Delta S^{\neq} = -130 \pm 7.2\ \text{J mol}^{-1}\ \text{K}^{-1}$ and a low value of $\Delta H^{\neq} = 8.4 \pm 0.6\ \text{kJ mol}^{-1}$ for the equilibrium depicted in eqn [9] suggest that the reaction proceeds via an associative pathway and the energy barrier is entropically controlled.[109]

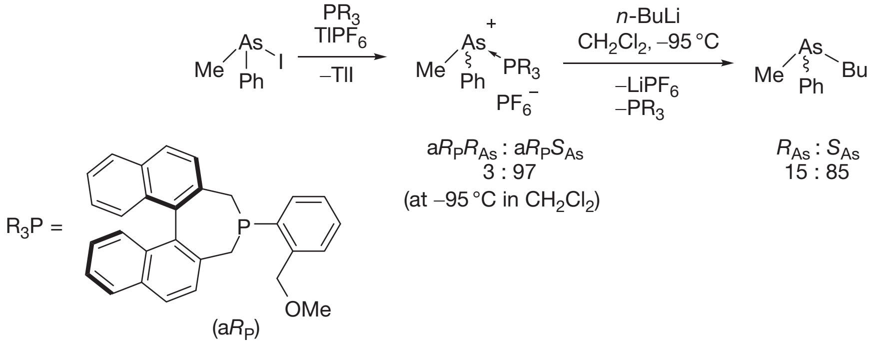
9

Lewis-base-stabilized pnictogenium cations have also been inadvertently obtained during attempts to generate highly unstable free cations via electrophile-induced halide abstraction from a neutral precursor in the absence of a dedicated nucleophile (eqn [10]).[110,111] Formation of base-stabilized cations under these conditions results from the fact that the pnictogen halide is itself a Lewis donor which supports halide abstraction from a second molecule of the starting material, thus leading to an overall reaction stoichiometry where the added electrophile consumes two rather than one equivalent of the neutral precursor.[80]

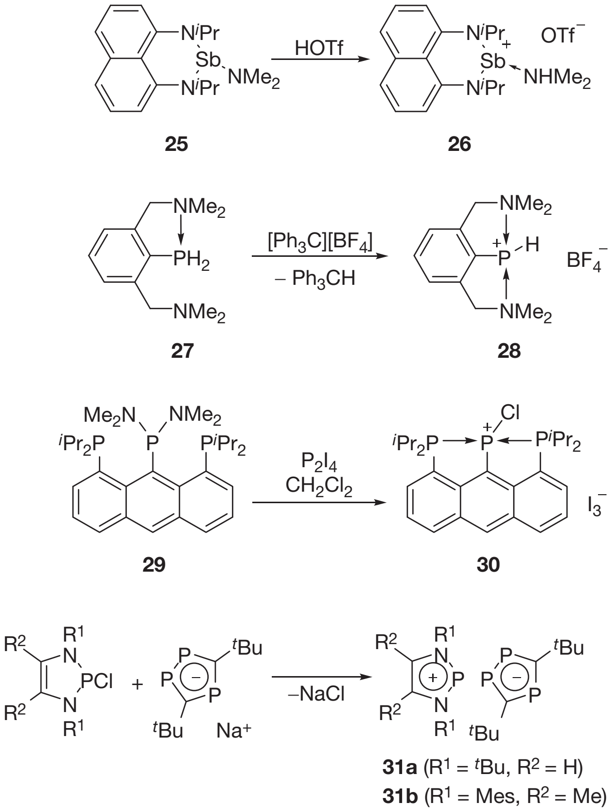


10

Some alternatives to the synthesis of Lewis-donor complexes of pnictogenium cations via halide abstraction are known (**Scheme 10**). Protonation of the dimethylamino



Scheme 9 Synthesis of an enantiomerically enriched tertiary arsine via a chiral arsenium ion – phosphane complex.

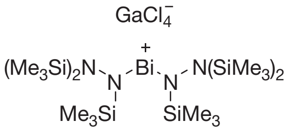


Scheme 10 Alternative pathways for the formation of Lewis-base adducts of pnictogenium ions.

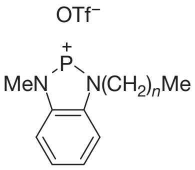
substituent in **25** yields amine complex **26**.[72] The intramolecularly donor-stabilized phosphenium cation **28** is prepared by hydride abstraction from the primary phosphane precursor **27**.[112] Substituent metathesis in the 1,8,9-tri(phosphino)anthracene **29** allows the synthesis of well-characterized phosphenium ion **30** stabilized by two intramolecular dative bonds.[113] Ion pairs **31** are prepared by metathesis of chlorodiazaphospholenes and a triphospholide and exhibit structural features reminiscent of frustrated Lewis pairs.[114]

1.20.3.3 Physical Properties

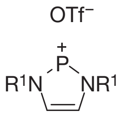
Most pnictogenium salts are solids that are thermally stable at ambient temperature under an inert atmosphere (N_2 or Ar; an exception is the bismuthenium salt **32** (formula [VI]) which must be handled at temperatures below −60 °C[75]) but decompose upon contact with air or upon dissolution in solvents that have not been rigorously dried. A thermoanalytic study of 1,3-dialkyl-benzo-1,3,2-diazaphospholenium triflates **33** disclosed the absence of any thermal decomposition up to 200 °C.[85] Like imidazolium salts, which find wide application as ionic liquids, the salts **33** exhibit low melting points <100 °C. Pnictogenium salts are generally readily soluble in polar aprotic organic solvents such as CH_2Cl_2 or $CHCl_3$ but insoluble in aliphatic hydrocarbons. Strongly electrophilic cations can attack ethers and aromatic hydrocarbons such as toluene, resulting in decomposition. Diazaphospholenium triflates **34** with cations that are strongly stabilized by aromatic π-delocalization behave in CH_2Cl_2 solution as 1:1 electrolytes,[64] whereas the triflates **35** with a lower degree of π-stabilization in the cations are classified as weak electrolytes that undergo a substantial degree of ion pairing.[56]



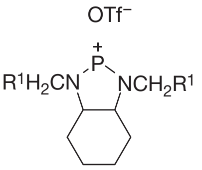
32



33
($n = 0–5$)



34
R^1 = alkyl, aryl

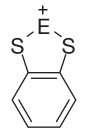


35
R^1 = aryl

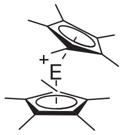
VI

1.20.3.3.1 Crystal structures

The majority of known single-crystal x-ray diffraction studies have been performed on phosphenium salts but structural data of cations based on heavier pnictogen elements are also known. The pnictogen atom carries in most cases at least one amino substituent; exceptions are phosphenium and arsenium cations **36** (formula [VII]) with two thiolate residues,[78,115] and metallocenium cations **37**.[51,53,54]



36a (E = P)
36b (E = As)



37a (E = As)
37b (E = Sb)
37c (E = Bi)

VII

The E–N distances in aminopnictogenium cations are intermediate between single and double bond lengths (Table 1) and reflect thus the partial multiple bond character which goes back to the intramolecular E–N–π-interactions. Bond angles at the pnictogen atom are, like in other types of singlet carbene analogs, generally far smaller than 120°, and become particularly low in heterocyclic derivatives because of the geometrical constraints imposed by the ring structure. Aminophosphenium ions show a bimodal distribution of P–N distances which is due to the fact that the effects of bond length equalization in heterocyclic cations with delocalized (aromatic) 6π-electron systems render the P–N bonds distinctly longer than average (Table 1).[28,61] The observed similarity of P–N bond lengths of mono-amino phosphenium ions $[R–P–N^iPr_2]^+$ (E = Cp*, Mes*; PN = 1.617–1.620) with those of nonaromatic

Table 1 Selected structural data of aminopnictogenium ions of general formula $[R^1R^2N–E–R^3]^+$ (R^1, R^2, R^3 = any substituent)

E	*E–N (Å)*		*N–E–R³ (°)*		*Number of compounds*
	Overall range	*Mean value*	*Overall range*	*Mean value*	
P (all data)	1.559–1.701	1.646	86.5–117.0	93.8	53
(aromatic)[a]	1.620–1.701	1.667	86.7–91.5	89.7	29
(nonaromatic)[b]	1.559–1.669	1.615			24
As	1.677–1.856	1.795	81.8–103.8	88.7	13
Sb	1.998–2.025	2.014	74.6–79.7	77.9	3
Bi	2.080–2.164	2.121	90.2–111.9	101.1	2

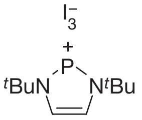
Data were obtained from the CSD database.

[a] 3,2-diazaphospholenium and benzo-1,3,2-diazaphospholenium cations with delocalized 6π- or 10π-electron systems.

[b] All other cations.

diaminophosphenium cations $[(R^1{}_2N)_2P]^+$ (**Table 1**) is at first glance surprising since the concentration of the double-bond character on a single R_2N group was expected[67] to result in relative bond shortening, but is in accord with theoretical predictions.[27]

Several crystal structures give evidence for intermolecular contacts between the electrophilic pnictogen element in the cation and the closest anion atoms that are substantially shorter than the sum of van der Waals radii[56,86] and suggest a contribution of intermolecular electrostatic effects to the cation stabilization. Distinct interion interactions leading to a supramolecular assembly of anions and cations are present in the structure of diazaphospholenium triiodide **38** (formula [VIII]).[65] The structure of $[(Mes^*NH)_2P][GaCl_4]$ contains one-dimensional stacks of cations and anion linked by P. . .Cl interactions and NH. . .Cl hydrogen bridges.[86] Despite the large and erratic variation in distances and number of contacts, and the large structural diversity of the species studied, aromatic 1,3,2-diazaphospholenium ions seem to show fewer short interion contacts which coincides with the particularly high cation stability of these species.[61,64,116]



VIII

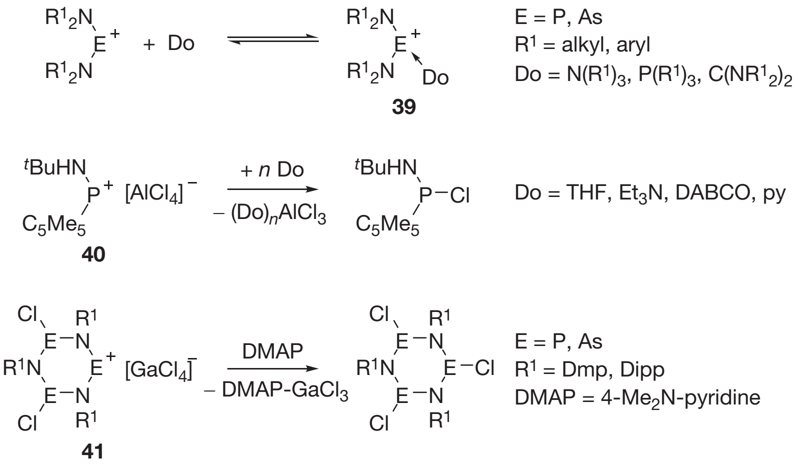
38

1.20.3.3.2 Spectroscopic properties

Pnictogenium cations of the heavier group 15 elements (As–Bi) show deep colors which arise from n–π* electronic transitions whose absorption energies lie in the visible range of the electromagnetic spectrum and decrease with increasing atomic number of the pnictogen.[75,76] Identification and analytical characterization of pnictogenium cations are preferably carried out by multinuclear nuclear magnetic resonance (NMR) spectroscopy. The ^1H NMR signals display normally a deshielding by 1–2 ppm with respect to the resonances of appropriate neutral precursors.[58,61,64] Variable-temperature ^1H NMR allows to monitor restricted rotation of *N*-aryl groups in cyclic diaminophosphenium ions.[82] ^{13}C NMR spectra of C_5Me_5-substituted cations exhibit dynamic signal averaging for the carbon atoms in the C_5Me_5 moiety due to rapid circumambulation of the pnictogen atom around the cyclopentadienyl ring.[51,52] The ^{15}N NMR signals of amino-substituted pnictogenium cations are by approximately 100 ppm less shielded than those of neutral chloro-substituted precursors and show a small anion dependence. The deshielding is attributable to the E–N multiple bond character.[61,64,77] The ^{31}P NMR signals of phosphenium are likewise strongly deshielded and are found in regions between approximately 520 and 195 ppm. Acyclic cations $[R_2N–P–X]^+$ (X = alkyl,[3] alkenyl,[69] aryl[67,68]) show the largest shifts ($\delta^{31}P = 520–395$ ppm), and cyclic cations featuring delocalized π-systems with aromatic character exhibit the most shielded resonances ($\delta^{31}P = 240–195$ ppm[1,58,61,64]). Solid-state ^{31}P NMR spectra of aminophosphenium ions reveal large chemical shielding anisotropies, the magnitude of which increases parallel with the chemical shift.[86] Both the deshielding and the large shielding anisotropy are not attributable to the effect of positive charge located at phosphorus but are related to the π-conjugation effects in the aminophosphenium moiety and reflect the partial multiple bond character of the P–N-bonds.[86] The occurrence of rapid dynamic exchange between pnictogenium ions and Lewis bases (frequently phosphanes or halide ions) induces signal averaging in solution NMR spectra and obstructs the determination of exact chemical shifts; the observed values represent in this case the population weighted average of the shifts of the pure components and change depending on the relative concentration of the equilibrating species.[33,82]

1.20.3.4 Reactivity

The chemical reactivity of all known pnictogen cations is dominated by their electrophilic character even if amino-substituted cations represent formal analogs of strongly nucleophilic, neutral amino carbenes. Prominent reactivity patterns of pnictogenium cations include therefore typical electrophile reactions such as the formation of donor/acceptor complexes with Lewis bases, bond insertion reactions (including CH activation), and cycloadditions with nucleophilic dienes. A certain ambiphilic character is epitomized by the formation of a variety of metal complexes where both L → M donation and M → L back donation contribute to the metal–ligand interactions. Accordingly, the cationic ligands are classified as (weak) Lewis-donor/(strong) Lewis-acceptor ligands in a similar



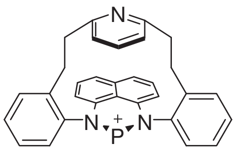
Scheme 11 Adduct formation vs. Anion degradation in the reaction of pnictogenium ions with Lewis-bases.

manner as CO, NO, or many electron-deficient nitrogen heterocycles.

1.20.3.4.1 Formation of Lewis-base adducts

Sufficiently Lewis acidic amino-pnictogenium cations interact with strong Lewis donors such as tertiary amines or pyridines,[117,118] tertiary phosphanes,[74,82] and carbenes[119], preferably under creation of a dative donor → pnictogen bond to give Lewis-base complexes **39** (Scheme 11). Exemptions are known in case of tetrachloroaluminate and tetrachlorogallate salts **40**, **41** which react with suitable O- or N-donors under anion degradation to yield mixtures of pyridine-MCl_3 adducts (M = Al, Ga) and neutral chloropnictogen compounds, respectively (Scheme 11).[52,120]

Formation of the cationic complexes **39** (Scheme 11) is an equilibrium reaction (cf. Section 1.20.3.2.3) which is shifted to the side of the fragments if the pnictogenium cation benefits from extensive intramolecular stabilization by π-donation or inductive effects,[64] if the Lewis base exhibits insufficient donor power,[82] or if adduct formation is hindered by steric congestion.[111] Amine or phosphane complexes of diaminopnictogenium ions exist thus sometimes as isolable species in the solid state but tend to undergo more or less complete dissociation in solution, or are not isolable at all.[64,82,118] Inhibition of the dissociation is feasible by intramolecular tethering of the Lewis acid–base interaction.[94,98] However, unfavorable preorganization of the donor and acceptor sites allows also to generate frustrated Lewis pair behavior like in **42** (formula [IX]) where the phosphenium and pyridine units are strong Lewis acceptor or donor functionalities in intermolecular reactions but intramolecular pairing is suppressed by the geometrical constraints of the macrocyclic ring.[121]

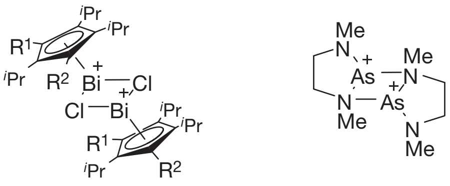


42

IX

Analyses of the Lewis acidities of isostructural pnictogenium ions based on different group 15 elements indicate that in some cases phosphenium ions are apparently stronger Lewis acids than homologous arsenium and stibenium cations,[118] while for other types of cations a reverse order is found.[77] Exchange of the coordinated Lewis donor on a phosphenium cation may follow both unimolecular (SN_1 pathway, preferable for strongly stabilized cations)[82] and bimolecular (SN_2 pathway, preferred for highly electrophilic Lewis acids) kinetics.[111]

Even if pnictogenium ions must, like isoelectronic carbenes and carbene analogs, be considered as ambiphilic, their oligomerization via mutual donor–acceptor interactions is obviously disfavored by repulsive electrostatic interactions and low Lewis basicities. Still, formation of stable dimers is observable in special cases, although the products are not isostructural to alkenes or their homologs with heavier group 14 elements. Chloro-substituted π-cyclopentadienyl bismuthenium cations **43** (formula [X]) exist as stable chloro-bridged dimers in both solid state and solution.[122] The topologically similar amido-bridged structure of the dimeric arsenium salt **44** is only stable in the solid state and dissociates completely in solution[115]; model calculations suggest that the cation is unstable toward fragmentation into two monomers in the gas phase, and its existence is explained to be a consequence of crystal-packing phenomena.[23]



43a ($R^1 = R^2 = Me$)
43b ($R^1 = H, R^2 = {}^iPr$)

44

X

1.20.3.4.2 Cycloaddition reactions

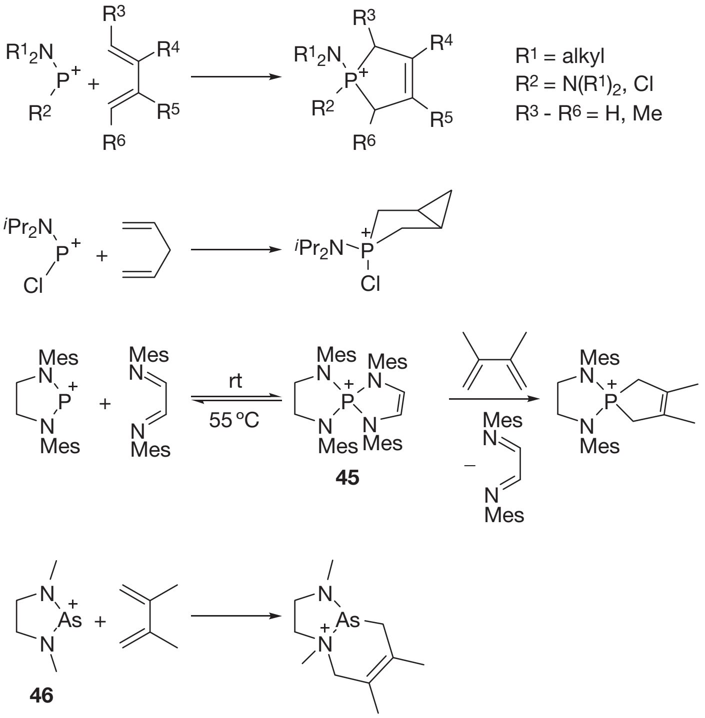
Stable or transient[123] phosphenium ions react readily as dienophiles. Reactions with nucleophilic 1,3-dienes and heterodienes (e.g., 1,4-diazadienes) produce [1+4]-cycloaddition products[1,124] and those with 1,4-dienes appropriate homo-[1+4]-cycloadducts (**Scheme 12**).[1,123] Product formation is facilitated by high electrophilicity and impeded by extensive intramolecular π-stabilization of the cation[125] or the presence of bulky substituents on either component.[124] The cycloaddition products are in most cases stable at ambient or higher temperature, but sterically congested **45** undergoes retro-addition with regeneration of the starting materials and reacts with dimethylbutadiene via formation of the corresponding phosphenium cation and release of 1,4-diazadiene (**Scheme 12**).[124] Reaction of diaminoarsenium ion **46** with dimethylbutadiene does not follow a similar pathway but gives a Diels–Alder analog [4+2] cycloaddition product (**Scheme 12**).[126] A quantum chemical study suggests that the different regioselectivity in the reactions of phosphenium and arsenium ions is controlled by the relative stabilities of the [2+4]- and [1+4]-cycloaddition products.[23]

Highly electrophilic stable or transient phosphenium ions undergo also [1+2] cycloaddition to electron-rich alkynes to give phosphirenium cations (**Scheme 13**)[127,128]; the transient cations are generated *in situ* from reaction of chlorophosphanes $RPCl_2$ or R_2PCl (R=alkyl, aryl) with $AlCl_3$, TlOTf,[128] or Me_3SiOTf[127] as activating electrophiles in the presence of alkynes as trapping reagents. Diaminophospheniums do not react. The formed phosphirenium ions react with external alkynes via exchange of the alkyne fragment.[127] A similar metathesis occurs also upon treatment of 1-phenyl-1-methylphosphiranium cation with alkynes to give the corresponding phosphirenium ions and ethylene.[128]

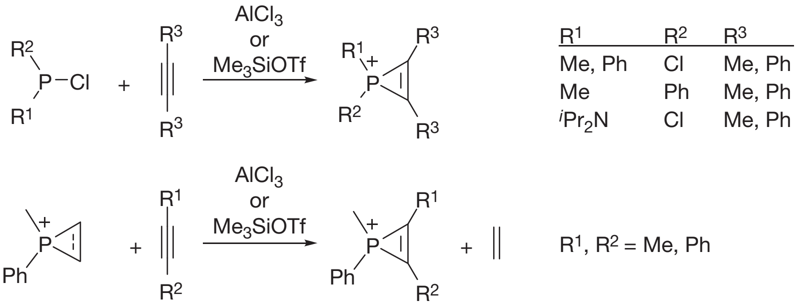
Comparable [1+*n*] or [2+*n*] cycloaddition reaction of stibenium or bismuthenium ions do not seem to have been studied, and appropriate adducts are unknown to date.

1.20.3.4.3 Insertion reactions

Insertion reactions of highly electrophilic phosphenium cations into reactive C–C and C–H bonds have appeared in occasional reports,[129] many of them in the older literature,[1,3,5] but do not seem to have been studied systematically. Some

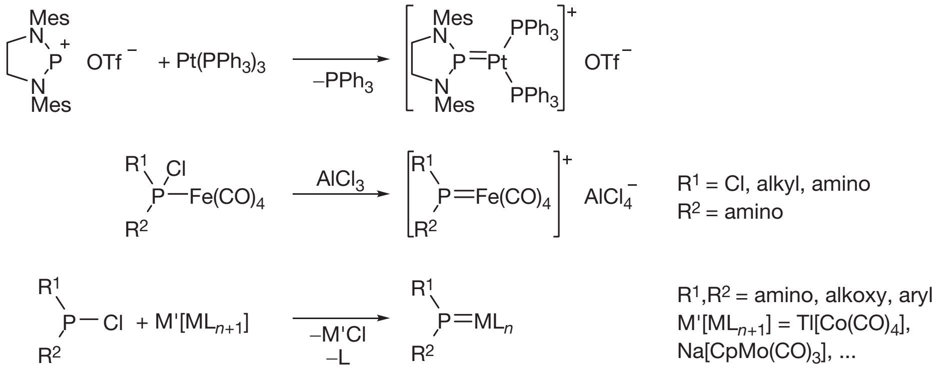


Scheme 12 Selected [n+4] cycloaddition reactions of pnictogenium ions.



R1	R2	R3
Me, Ph	Cl	Me, Ph
Me	Ph	Me, Ph
^{i}Pr$_2$N	Cl	Me, Ph

Scheme 13 Capture of transient pnictogenium ions via [1+2] cycloaddition reactions.

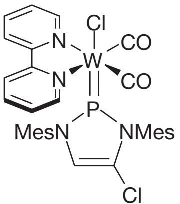


Scheme 14 Syntheses of cationic and neutral transition metal complexes of phosphenium ions.

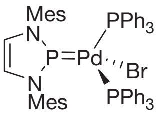
of the reactions reported are postulated to proceed via a transient phosphenium ion which is generated by reaction of a Lewis acid with a neutral chlorophosphane or phosphaalkene[130] precursor. The insertion of pnictogenium cations into pnictogen–pnictogen bonds to generate a variety of catena-pnictogen compounds is covered in Chapters 1.04 and 1.05.

1.20.3.4.4 Coordination chemistry

The ability to act as ligands in transition metal complexes is generally considered as a lucid illustration of the ambiphilic nature of pnictogenium cations. Known complexes can be divided into two categories depending on whether the cation is bound to a formally neutral or anionic metal fragment. Cationic complexes of the first type are generally prepared by direct interaction of a preformed pnictogenium cation with a suitable metal precursor capable of transferring a 14- or 16-valence electron ML_n fragment,[131] or by electrophile-induced abstraction of a substituent from a metal-coordinated neutral ligand (Scheme 14).[1,3,5,7,132] Cationic phosphenium complexes are also available via attack of an electrophile on a nucleophilic phosphinidene complex L_nMPR^1.[133] Neutral pnictogenium complexes are accessible via metathesis of pnictogenium salts (or neutral chloropnictogen compounds) with suitable metallate anions[1,3,5,7]; alternatively, they may also be prepared by various other routes not involving pnictogenium ions which are not reviewed here.[7] Pnictogenium complexes known to date contain late transition metals of groups 6–10 (Cr, Mo, W, Mn, Fe, Co, Rh, Ni, Pd, and Pt) with metal atoms in low oxidation states.[1,3,5,7,72,131,134,135] Some complexes such as **47** and **48** (formula [XI]) allow in particular stabilization of metal(0) halide fragments.[125,136]

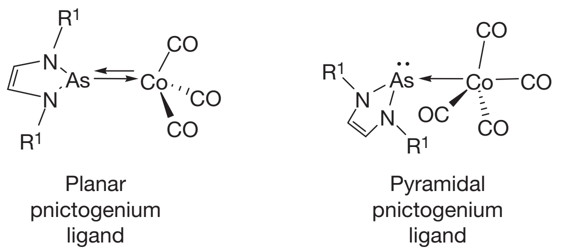


47



48

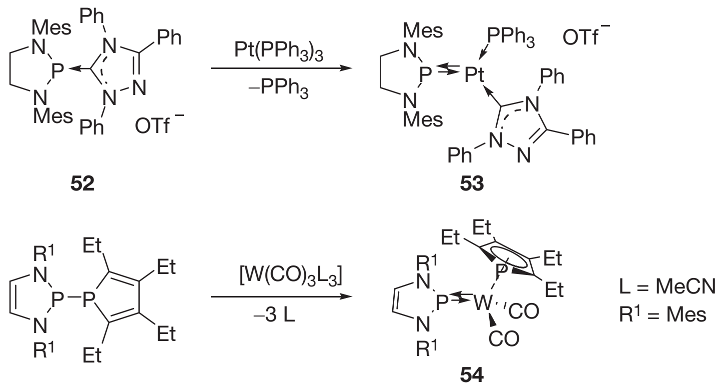
XI



Scheme 15 Metal-ligand interactions in complexes with planar and pyramidal pnictogenium ligands.

Most known pnictogenium complexes feature trigonal planar coordination at the pnictogen atom, and metal–ligand distances are distinctly shorter than in complexes with neutral donor ligands ER_3.[1,3,5,7] The bonding in these complexes is described by analogy to Fischer-type carbene complexes as resulting from a σ-donor/π-acceptor interaction between the ligand and metal fragments (Scheme 15).[1,5] In addition, several specimens with pyramidalized pnictogen coordination geometries and longer metal–pnictogen bond distances are known.[137–140] The bonding situation in these products has been addressed in terms of an 'inverse' donor–acceptor interaction where the metal fragment acts the donor and the pnictogenium ligand as the acceptor, and the metal-to-ligand charge transfer (MLCT) dominates (Scheme 15).[137,140] Both types of pnictogenium complexes bear a close relationship to analogous pnictido complexes with formally anionic R_2E^- ligands (e.g., for E=P: $[Mo(PCy_2)_4]$ or $[Cp_2M(PR_2)_2]$ with M=Zr, Hf; R=Et, Cy, Ph) which contain likewise both planar and pyramidal PR_2 moieties.[141] A distinction between complexes with anionic and cationic R_2E fragments is commonly drawn by considering common metal oxidation states (e.g., Zr (IV) in $[Cp_2Zr(PR_2)_2]$), or arguing with relative cation and anion stabilities of PR_2 ligands[27]; it is, however, conceivable that a clear-cut dividing line is lacking and, in a similar manner as in nitrosyl complexes, the partition of the electron density may change depending on the influence of ancillary ligands.

The reactivity of pnictogenium complexes is coined by a marked *trans*-effect of the cationic ligand which facilitates displacement of the metal ligand in trans position.[7] Neutral complexes behave as systems with formal metal–pnictogen double bonds and undergo addition or cycloaddition reactions, as well as various reactions under capture of a nucleophile (via both intermolecular reaction and intramolecular migration).[1,3,98,142] Detailed accounts of this chemistry have been given in several reviews.[1,3,7,143] Moreover, sporadic reports on the use of phosphenium cations as ligands for catalytic applications (hydroformylation[144] and arene carboxylation[145]) have appeared.



Scheme 16 Synthesis of phosphenium complexes via non-oxidative addition to a precursor complex.

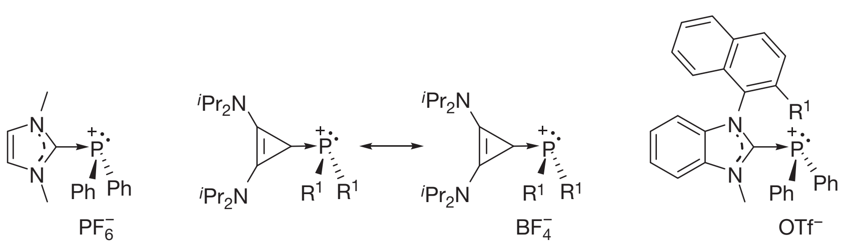
In addition to free pnictogenium cations, recently also their adducts with Lewis bases have received attention. Aminotroponato derivatives of heavier pnictogens **11** (E=As, Sb, Bi (formula [V])) are unsuitable as ligands,[34,100] but the corresponding phosphenium derivatives (**11**, E=P)[100] as well as phosphenium–carbene adducts such as **49**,[146] **50**,[147] or **51**[30,148] (formula [XII]) give stable metal complexes in which the ligands display pronounced π-acceptor character. Reaction of phosphenium–carbene adduct **52** with a platinum(0) precursor yields complex **53** under coordination of both the phosphenium and carbene fragment (**Scheme 16**).[134] As the metal increases its coordination number but retains its formal oxidation state, this reaction is addressed as a 'nonoxidative' addition similar to those of tetraaminoethylene to give metal–bis(carbene) complexes. Similar reactions yielding phosphenium–phospholide complexes (e.g., **54**) have also been performed with highly reactive diphosphanes.[149] Compound **51** releases a phosphenium cation fragment after reaction with chloride to give a carbene complex.[30]

1.20.3.4.5 Miscellaneous

Dimethoxyphosphenium cation reacts with diols in the gas phase via stereoselective[44] metathesis to give cyclic phosphenium cations.[43, 150] Analysis of specific fragmentation patterns of such ions generated in a mass spectrometer allows to distinguish between different stereoisomers of certain steroids.[42] Fragmentation of peptides by reaction with $[PCl_2]^+$ in the gas phase was studied by Fourier transform ion cyclotron resonance (FT-ICR).[41] Stable phosphenium ions can replace chlorophosphanes in nucleophilic substitution reactions; thus, $[(Cy_2N)_2P]^+$ reacts with a lithiated diazomethane to give a nitrile imine via attack of the nucleophilic reagent at the electron-deficient pnictogen atom,[151] and $[(^iPr_2N)_2P]^+$ reacts with a lithio-phosphaalkene to give a diphosphapropene[152] and with a phosphino-carbene to produce a bis(phosphonia)cyclopropanide.[153] The salt $[(^iPr_2N)_2P]OTf$ has been employed as stoichiometric oxidant which causes coupling of two molecules of a benzannulated σ^4-λ^5-[1,3,2]diazaphosphole via a yet unknown mechanism.[154]

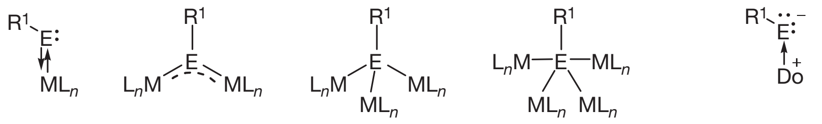
1.20.4 Neutral Pnictogen(I) Compounds: Phosphinidenes and Higher Homologs, and Their Transition Metal Complexes

Neutral molecular pnictogen(I) compounds of general formula R–E (pnictinidenes, E=P: phosphinidenes; E=As: arsinidenes; E=Sb: stibinidenes, and E=Bi: bismuthinidenes) are metastable and exist in free form only as transient species. Isolable derivatives are sometimes accessible if a pnictinidene can be stabilized by complex formation with a Lewis donor, a transition metal, or both. Known types of transition metal complexes of pnictinidenes exist as mononuclear species **55** with η^1-coordinated, terminal pnictinidene ligands, or as polynuclear derivatives in which pnictinidene ligands act as bridging ligands toward two to four metal nuclei (**56–58**, formula [XIII]). Mononuclear complexes can be straightforwardly described as Lewis donor–acceptor complexes and have found wide application in chemical synthesis. Polynuclear complexes are best described as species with delocalized



49 **50** (R1 = Ph, Cy, Ad) **51** (R1 = H, PPh2)

XII



Terminal (η^1) **55**

μ_2-bridging **56**

μ_3-bridging **57**

μ_4-bridging **58**

Lewis-donor complex **59**

XIII

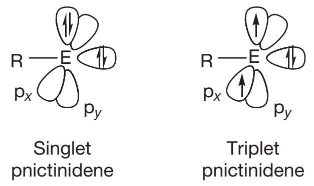
metal–pnictinidene multiple bond systems (complexes with μ_2-bridging ligands) or as pnictinidene–metal clusters (species with μ_3- or μ_4-bridging ligands) which differ in both their electronic structures and chemical behavior from the simple donor–acceptor complexes and are not covered in this chapter. Complexes **59** of pnictinidenes with Lewis donors represent ylide-like species. Their molecular structures span the whole range between labile pnictinidene–donor complexes, which readily transfer a pnictinidene moiety to another substrate, and stable ylides that show hardly any tendency to undergo pnictinidene transfer reactions. Such inert behavior is frequently encountered for highly resonance-stabilized derivatives and for anions that can be formally described as complexes of a pnictinidene with a negatively charged ligand. Whereas the chemistry of the labile species is addressed in this chapter, that of the stable ylides, which has in part been summarized in earlier reviews,[4,9] is excluded.

Although molecular pnictogen(I) compounds with all heavier group 15 elements are known, the chemistry of arsinidenes and higher homologs is still widely unexplored. In contrast, phosphinidenes and isolable and transient transition metal complexes of terminal phosphinidene ligands, as well as the application of both species in chemical synthesis, have extensively been studied. These aspects have been the subject of several earlier reviews.[2,6,8,155,156]

1.20.4.1 Structure and Bonding

1.20.4.1.1 Free pnictogen(I) compounds

Free pnictinidenes may exist, like pnictogenium ions or carbene-analog species, in either an electronic singlet ($^1\Delta$) or a triplet state ($^3\Sigma^-$). The electron configurations of both states are in a simplified picture described as featuring either two lone pairs of electrons and an empty p-orbital or one lone pair and two singly occupied p-orbitals at the pnictogen atom, respectively (**Scheme 17**). The energetic ordering of both states depends strongly on the substituents. Species with hydrogen, alkyl, or halogen substituents are unable to lift the degeneracy of the two p-orbitals and adopt a triplet ground state. The experimentally determined ($^3\Sigma^-$–$^1\Delta$) energy differences $\Delta E_{\mathrm{S-T}}$ of the parent EH compounds increase from −92 kJ mol^{-1} for PH[157] to −86 kJ mol^{-1} for AsH[158] and −82 kJ mol^{-1} for SbH.[159] Computational estimates of $\Delta E_{\mathrm{S-T}}$ are generally more negative than experimental values, ranging, for example, from −117 kJ mol^{-1} (QCISD(T)/6-311++G(3df,2p))[160] to −172 kJ mol^{-1} (MP2/LanL2DZ)[161] for PH, but reproduce the decrease in magnitude upon going from lighter to heavier elements (cf. the variation in $\Delta E(^3\Sigma^-–^1\Delta)$ from −138 (PH) to −109 (BiH) kJ mol^{-1} calculated at the B3LYP/LanL2DZp level[162]).



Scheme 17 Electronic states of pnictinidenes

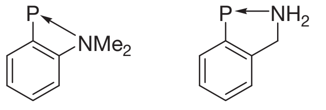
π-Donor substituents stabilize the singlet relative to the triplet state of a pnictidene, as the π-bonding interaction with one of the two degenerate p-orbitals lifts their degeneracy in the sense of a first-order Jahn–Teller distortion. In the limit of a sufficiently strong interaction, the ground state becomes a singlet pnictinidene which exhibits a strong dative π-bond formed by a transfer of charge density from the lone pair of the substituent into the empty p-orbital of the pnictogen atom. In a study of substituent effects on the singlet–triplet energy splitting in phosphinidenes,[160] Nguyen and coworkers estimated that $\Delta E_{\mathrm{S-T}}$ remains still substantial for phenyl phosphinidene (−92.0 kJ mol^{-1} vs. −133.9 kJ mol^{-1} for PH calculated at the QCISD(T)/6-311G(d,p)+ZPE level), but that the energy of the singlet state becomes similar, or even lower, than that of the triplet state for aminophosphinidenes (R_2N–P, $\Delta E_{\mathrm{S-T}}$ = −5.9–7.1 kJ mol^{-1} with R = H, CH_3) and phosphinophosphinidenes (R_2P–P, $\Delta E_{\mathrm{S-T}}$ = −16.3 to 15.4 kJ mol^{-1} with R = H, CH_3). A clear preference for a singlet ground state is predicted for phosphinidenes with strongly π-donating groups such as $(H_2N)_2P$–P ($\Delta E_{\mathrm{S-T}}$ = 34.4 kJ mol^{-1} at QCISD(T)/6-311G(d,p)+ZPE level),[160] FS–P ($\Delta E_{\mathrm{S-T}}$ = 84.5 kJ mol^{-1} at QCISD(T)/6-311G(d,p)+ZPE level),[160] or H_2CN–P ($\Delta E_{\mathrm{S-T}}$ = 242.7 kJ mol^{-1} at B3LYP/6-311+G** level).[163] From a practical viewpoint, amino (NR_2) and phosphino (PR_2) substituents with large alkyl groups R are considered the most plausible and feasible targets for preparing phosphinidenes with a closed-shell singlet ground state.[160]

Computed bond distances in diatomic pnictinidenes in the electronic ground state compare to single-bond distances in tervalent pnictogen compounds.[160] π-Donor substituents exert only a minor effect on P–R distances in triplet phosphinidenes (e.g., values of r_{PP} = 2.199 Å for H_2P–P and r_{PN} = 1.714 Å for H_2N–P calculated at the (U)MP2/6-31G(d,p) level remain still in the range of normal single bonds) but induce a substantial shortening of the bonds in the singlet state (r_{PP} = 1.945 Å for H_2P–P and r_{PN} = 1.643 Å for H_2N–P at the (U)MP2/6-31G(d,p) level) which reflects the increased π-conjugation between the empty pnictogen p-orbital and the lone pair on the substituent.[160] The computed distances in the linear C=N–P core of $H_2CN–P$ ($r_{CN} = 1.301$ Å, $r_{NP} = 1.567$ Å at the CCSD(T)/aug-cc-pVDZ-level) highlight the extreme degree of π-conjugation in this molecule and suggest that the bonding situation is closer to a zwitterionic allenic or ylidic structure (i.e., $H_2C{=}N^{(+)}{=}P^{(-)}$) than a genuine phosphinidene.[163]

1.20.4.1.2 Complexes of pnictogen(I) compounds

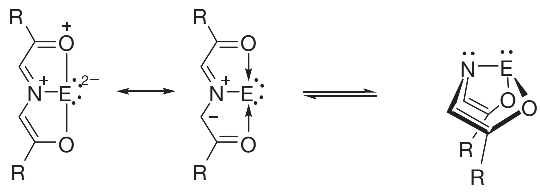
1.20.4.1.2.1 Lewis-donor complexes

Phosphanes are potent Lewis donor that can stabilize an electrophilic pnictinidene by formation of donor–acceptor complexes of type **59** (formula [XIII]). Phosphinidene derivatives (Do = PR_3, E = P) are named phosphinylidene phosphoranes[4] or, owing to their structural relation to the Staudinger complexes R_3PNR and Wittig reagents R_3PCR_2, 'phospha-Wittig reagents'. The corresponding arsinidene adducts are also known.[164] The ylide nature of the phosphinidene adducts is highlighted by a computational study which shows the presence of a short P–P bond (2.087 Å at MP2/6-31G* compared with 2.064 and 2.210 Å for *trans*-HPPH and $H_2P–PH_2$ at the same level) with a strong Coulombic contribution for parent $H_3P^{(+)}–P^{(-)}H$ (**60**).[165] Although **60** is by 116 kJ mol^{-1} (at MP4/6-31G*) higher in energy than the isomeric diphosphane $H_2P–PH_2$, it also has a high kinetic stability as conversion to the more stable isomer is hindered by a barrier of 149 kJ mol^{-1}. A slightly lower binding energy between the phosphinidene and the donor fragment as in the phospha-Wittig ylide **60** is also calculated for the analogous amine complex $H_3N^{(+)}–P^{(-)}H$ **61** (176 kJ mol^{-1} for **61** vs. 225 kJ mol^{-1} for **60** at MP4/6-31G* + zpe). Complex **61** is predicted to be only by 10.9 kJ mol^{-1} higher in energy (at MP4/6-31G* + zpe) than the isomeric Staudinger adduct H_3PNH despite the presence of a very long N–P bond distance of more than 1.95 Å.[165] Similar results are also obtained for complexes of a series of other phosphinidenes with NH_3 and PH_3.[166] Amine coordination of the univalent phosphorus atom at distances around 1.95 Å with a concomitant stabilization of a singlet ground state is also suggested by computational studies of the functionalized phosphinidenes **62** and **63** (formula [XIV]).[8]



62 **63** XIV

A very special case are the 'hypervalent pnictogen(I) compounds' **64** (Scheme 18, R = ^{t}Bu).[167–169] The planar molecular structures with a T-shaped coordination geometry at the central pnictogen atom are intuitively explained in terms of a pseudo-trigonal bipyramidal (ψ-tbp) coordination with a valence electron count of 10 and two nonbonding electron pairs at the pnictogen atoms (leading to a description as 10-E-3 where E = P, As, Sb). *Ab initio* computational studies[170,171] suggested to describe **64**, in line with this perception, as amino-substituted pnictinidenes which are stabilized by donor–acceptor interactions with two axial oxygen atoms. Computed bond lengths and electron density[171] support a description of the bonding in the axis as four-electron-three-center bond with partial ionic character. Compounds **64** convert upon geometric distortion into isomers **65** featuring pyramidal tri-coordinate pnictogen atoms and a bonding situation that obeys the octet rule (the isomerization involves only a change in orbital occupancy and molecular geometry and was therefore called 'electromorphic').[167] MP2 calculations on the parent phosphorus compound (with R = H) suggest that the planar isomer **64a** is by 58.2 kJ mol^{-1} more stable than the pyramidal isomer **65a**[171]; this stabilization is mainly attributable to electron correlation effects. Conversion of the planar into the pyramidal geometry is despite such a large energy difference observable after coordination of the phosphorus atom to a transition metal.[171]



64a (E = P)
64b (E = As)
64c (E = Sb)

65a (E = P)
65b (E = As)
65c (E = Sb)

Scheme 18 Electromorphic rearrangement between planar and pyramidal isomers of 'hypervalent' pnictogen(I) compounds.

1.20.4.1.2.2 Transition metal complexes

Coordination of a pnictinidene ligand to a 16-electron transition metal fragment ML_n – prototypical species are $M(CO)_5$ or Cp_2M with M = Cr, Mo, W – lifts the degeneracy of the two p-orbitals in a free pnictinidene by involving one of them in metal–ligand bonding. Systematic investigations of the electronic structure have been carried out for phosphinidene complexes **55** (E = P) (formula [XIII]). These species are isoelectronic to carbenes and carbene-analog compounds, and feature likewise bent structures with bond angles at the pnictogen atom that are smaller in the singlet than in the triplet state.[172,173] Theoretical studies substantiate that phosphinidene complexes have generally singlet ground states. The singlet–triplet energy gap depends, as in the case of free phosphinidenes, on the substituent at phosphorus, and increases when electron-donating groups are present. For example, calculated (at the DFT level using a large triple-*z* polarized (TZP) basis and the economical Becke88-Perdew86 (BP) density functional) values of ΔE_{S-T} for $(OC)_5W–PR$ increase from 29.7 kJ mol^{-1} for R = H to 95.0 kJ mol^{-1} for R = OH and to 125.1 kJ mol^{-1} for R = NH_2.[172] Complex $(OC)_5WP–P(NH_2)_2$ is an exemption; the singlet–triplet energy gap is here even smaller than in the free phosphinidene, and the phosphorus-containing ligand is according to the results of a population analysis considered a nucleophilic phosphide rather than an electrophilic phosphinidene.[174]

Analysis of metal–ligand interactions in complexes $M(CO)_5$-PR with an energy decomposition scheme separates the total bond energy into contributions from electrostatic interaction, Pauli repulsion, and σ- and π-type orbital interactions. This scheme allows a quantitative estimate of σ- and π-bond strengths, and enables to interpret the donor–acceptor bonding within the Dewar–Chatt–Duncanson model.[172] Phosphinidines are accordingly considered strong π-acceptors and even stronger σ-donors, and the metal–phosphorus bonds have substantial multiple bond character and quite high bond dissociation energies. The calculated energy for the dissociation of

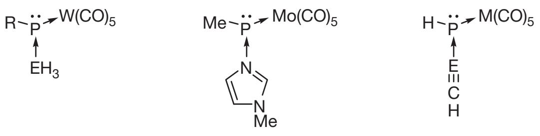
$(OC)_5WPH$ into $W(CO)_5$ and ^1PH of 325.7 kJ mol^{-1} at the BP/TZP level of theory is higher than the experimental value of 192.6 kJ mol^{-1} for the first W–CO bond dissociation energy of $W(CO)_6$.[172] The π-back donation from the metal decreases if the phosphinidene carries π-donor substituents. For example, the calculated (at BP/TZP level) σ- and π-components of the orbital interaction term in $(OC)_5CrPH$ are 261.0 (σ-donation) and 171.1 kJ mol^{-1} (π-back donation); formal replacement of the hydrogen by an amino group has a negligible effect on the σ-component but reduces the π-component to 89.1 kJ mol^{-1}.[172]

Transition-metal-bound phosphinidenes may show electrophilic or nucleophilic character.[175] This 'philicity' is according to a DFT study on phosphinidene complexes L_nMPH (M = group 4 to group 9 metals; L = CO, PH_3, Cp) mainly influenced by the spectator ligands L whereas the metal M is less important. Strong σ-donor ligands raise the π*(MP)-orbital energy, increase the electron density on the phosphorus atom, and enhance thereby its nucleophilicity, whereas strong π-acceptor ligands lower the charge on phosphorus and the π*(MP)-orbital energy, and enhance thus the electrophilicity of the phosphinidene. The distinction between nucleophilic and electrophilic phosphinidene complexes mirrors the well-known dichotomy between Fischer- and Schrock-type carbene complexes,[8] but it has been pointed out that the two types of carbene complexes are usually related to species arising from a singlet–singlet or a triplet–triplet combination of metal fragment and ligand, and that this comparison is, in view of the strongly preferred triplet state of R–P and the MP bond analysis, therefore rather schematic.[175]

Computational studies on complexes of phosphinidenes with 14-electron transition metal fragments predict bent structures for nucleophilic phosphinidene complexes such as Cp_2MPH (M = Ti, Zr, Hf)[175] and practically linear structures with still shorter P–M bonds for electrophilic phosphinidene complexes such as $[Cp(CO)_2M{\equiv}PMe]^+$ (M = Cr, Mo, W).[176] Energy decomposition analysis suggests that the metal–ligand interaction in the linear complexes can be described as a pseudo-triple bond which includes a dative interaction of the former phosphorus lone pair with the metal atom and exhibits a higher degree of covalent and a lower degree of electrostatic interaction than the metal–ligand bond in bent phosphinidene complexes. The higher formal bond order coincides with a concomitant increase in bond dissociation energies by nearly 89–140 kJ mol^{-1}.

1.20.4.1.2.3 Complexes with metals and Lewis bases

Electrophilic phosphinidene complexes retain still significant Lewis-acid character and can undergo, like free phosphinidenes, an additional donor–acceptor interaction with a Lewis base. Formation of complexes such as **66**[174] or **67**[177] (formula [XV]) is less exothermic than for the corresponding free phosphinidenes (calculated binding energies range from 34 to 87 kJ mol^{-1} for **66** at B3LYP/SBK-31(d) level,[174] depending on the substituent). Still lower binding energies (49–55 kJ mol^{-1} at the same B3LYP/SBK-31(d) level) are calculated for complexes **68** with weak Lewis bases PCH and NCH, respectively, suggesting that these species may not exist as stable species but exist in equilibrium with the separated fragments.[174] The dative P → M and donor → P bonds in the computed molecular structures of **66**–**68** are approximately orthogonal, leading to a strongly pyramidalized coordination environment at phosphorus, and the phosphorus–metal bonds are much longer than in the donor-free phosphinidene complexes (cf. W–P 2.423 Å in $(OC)_5WPH$ vs. 2.637 Å in $(OC)_5WP(H){\leftarrow}PH_3$ at B3LYP/SBK-31(d)[174]).



66
R = H, Me, NH_2, PH_2, PF_2
E = N, P

67

68
M = Cr, Mo, W
E = N, P

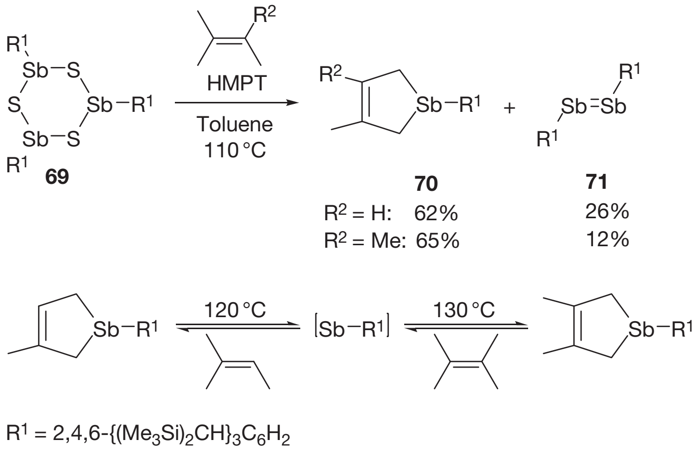
XV

1.20.4.2 Syntheses

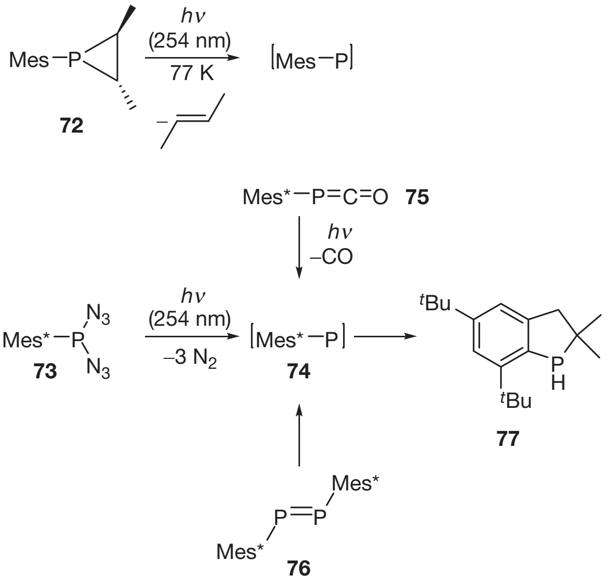
1.20.4.2.1 Generation of transient pnictogen(I) compounds

Reports on the generation of pnictinidenes with heavier group 15 elements (As, Sb, and Bi) are sparse. Diatomic species EH or EX (E = As, Sb, Bi; X = F, Cl, Br, I) have been produced at high temperature in the gas phase from vaporized pnictogens and hydrogen or halogen atoms in fast flow systems,[158,159,178] or by electrical glow discharge from suitable volatile precursors (e.g., AsH from AsH_3),[179] and characterized by spectroscopic methods (see Section 1.20.4.3.2). Tokitoh et al. reported on the deselenation of 1,3,5-triselena-2,4,6-tristibane **69** in the presence of 1,3-butadienes to give mixtures of heterocycles **70** and distibene **71**, and the thermally induced diene exchange of **70** with another butadiene (Scheme 19); both reactions were explained by invoking a transient stibinidene as intermediate.[180]

Attempts to create phosphinidenes have been more frequent, but much of the earlier work – in particular, chemical transformations starting from polyphosphanes – has been considered as erratic and gave no conclusive evidence for the generation of phosphinidenes under synthetically acceptable conditions.[8] Direct experimental proof for the generation of a phosphinidene was obtained during photolysis of phosphirane **72** with ultraviolet (UV light) (254 nm) in a glassy argon matrix at 77 K which proceeds via cheletropic [2 + 1] retro-addition of the phosphirane ring to produce spectroscopically characterized mesityl phosphinidene (Scheme 20).[181,182] Transient supermesityl phosphinidene **74** is postulated to be formed during photolysis reactions of diazidophosphane **73**, phosphaketene **75**, or diphosphene **76**, and to decay subsequently via intramolecular insertion of the phosphorus atom into a CH bond of one *ortho-tert*-butyl group to give high yields of phosphaindane **77** (Scheme 20).[183] Photolysis of phosphinidene–phosphane complexes **78**, which are readily synthesized by Mg or Zn reduction of sterically hindered aryl dichlorophosphanes in the presence of PMe_3,[184,185] is assumed to produce a mixture of PMe_3 and transient phosphinidenes **79** which are then quenched to give, depending on the substituent, either phosphaindene **77** or phosphafluorene **80** via intramolecular CH bond insertion, or diphosphene **81** via bimolecular reaction with excess **78** (Scheme 21).[186] Arsinidene–phosphane adduct **82** is accessible by analogy to **78** from a bulkily substituted dichloroarsine and undergoes thermally induced fragmentation at or above room temperature to give diarsene



Scheme 19 Reactions involving capture of a transient stibinidene.



Scheme 20 Photochemical generation of transient phosphinidenes.

83 (Scheme 21); analogs of **82** with sterically less demanding substituents seem to exist only as transient species that are thermally unstable toward formation of diarsenes.[164] Thermal reaction of the phosphinylidene phosphorane **84** with alkenes and 1,3-dienes to give cyclic phosphanes **86**, **87**, **88** is assumed to proceed via transient singlet phosphinidene **85** as key intermediate (Scheme 22).[187] Precursor **84** is accessible by oxidation of $({}^t\mathrm{Bu})_2\mathrm{P{-}P(Li){-}P}({}^t\mathrm{Bu})_2$ with 1,2-dibromoethane[187] and can be converted into analogous derivatives by alkylation of the PBr function.[188]

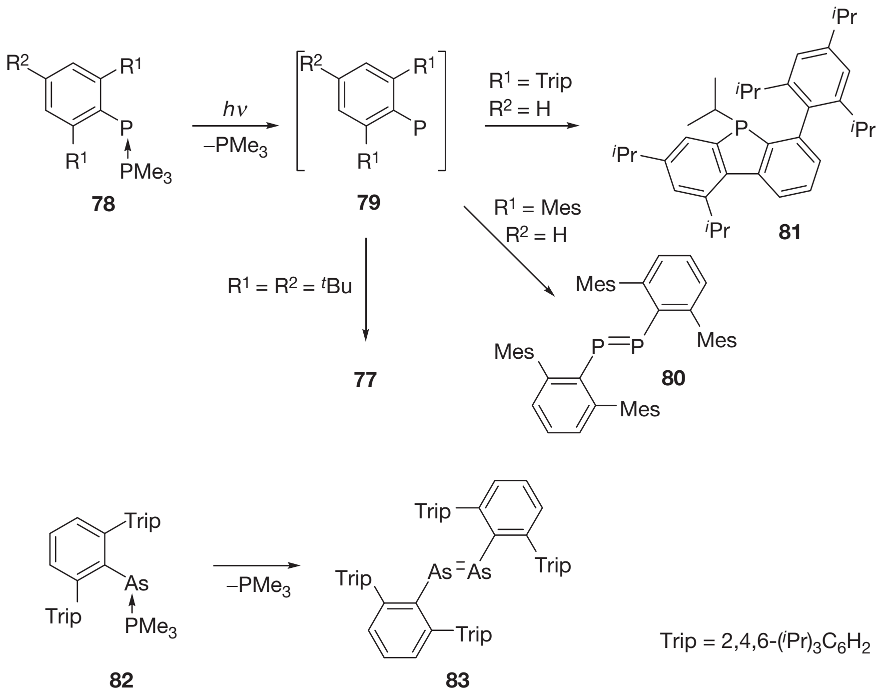
Photolysis of phospholenes[181] or thermolysis of triazaphospholenes or oxazaphospholenes[189] presumably also render phosphinidenes, but the synthetic applicability of these methods has remained limited. Thermally induced cheletropic fragmentation of five-membered fused 1,3,2-diazaphospholene rings has been proposed as an alternative approach to phosphinidenes but this still awaits experimental verification.[190]

1.20.4.2.2 Generation of transient transition-metal-stabilized pnictogen(I) compounds

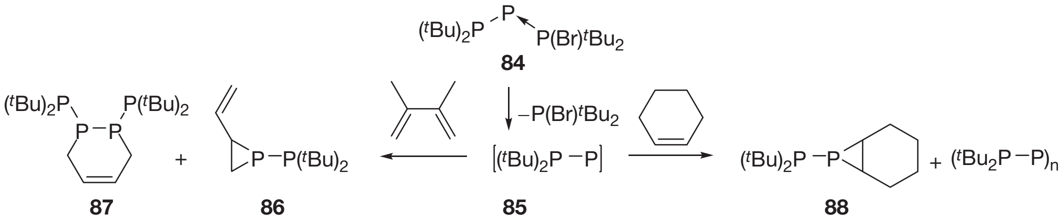
Generating transient electrophilic phosphinidene complexes $\mathrm{RPM(CO)_5}$ (M = Cr, Mo, W) or $\mathrm{RPFe(CO)_4}$ in the presence of suitable trapping reagents that are capable of capturing the subvalent species in a controlled chemical reaction has been established as an efficient approach in synthetic chemistry (see Section 1.20.4.4). Although these complexes are normally too short-lived to be detectable by conventional spectroscopic methods, their intermediacy has been inferred from kinetic data,[191] and formation of a phosphinidene complex with a cationic substituent R has been directly confirmed by mass spectrometry.[192]

Generally applicable methods for the *in situ* synthesis of transient phosphinidene complexes $\mathrm{RPM(CO)}_n$ involve thermal decomposition of suitable precursors such as phosphanorbornadiene complexes **89**,[193] which are historically the first and, to date, still the most widely phosphinidene source, or benzophosphepine complexes **90**,[194] which release a phosphinidene complex via a bicyclic phosphanorcaradiene intermediate **91** (Scheme 23).

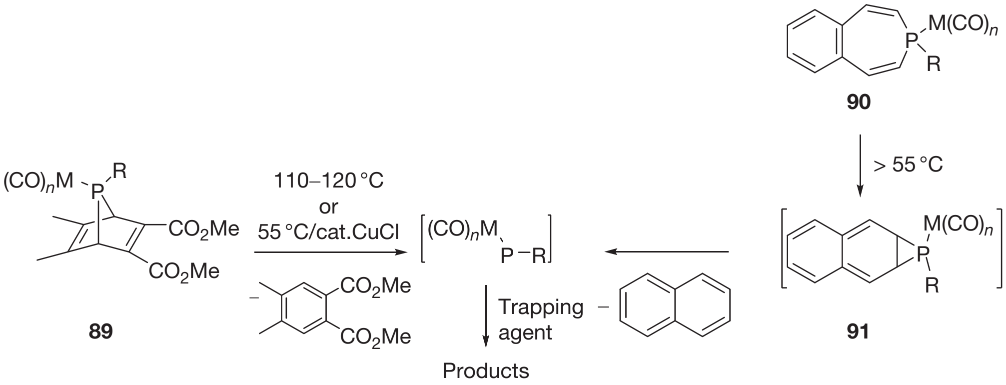
Formation of transient phosphinidene complexes via cheletropic fragmentation of 7-phosphanorbornadiene (7-PNBD) complexes is applicable to precursors with a wide range of substituents and exhibits a great functional group tolerance. This method is therefore suitable to access functional transient phosphinidene complexes such as superelectrophiles $\mathrm{(OC)_5WPCl}$[195] or $\mathrm{(OC)_5WPF}$,[196] which allow further derivatization of trapping products, or various alkenyl-substituted phosphinidene complexes, which may be trapped by intramolecular cycloadditions to give bi- or polycyclic phosphane complexes.[197,198] Uncatalyzed fragmentation of 7-PNDB precursors requires generally temperatures between 100 and 120 °C, although formation of a reactive transient complex such as $\mathrm{(OC)_5WPCl}$ may commence at 60 °C.[195] Reaction temperatures of 55 °C or less are reached if the transformation is conducted in the presence of a catalytic amount of CuCl.[2,6] The transient species formed during copper-catalyzed fragmentation of a 7-PNBD-$\mathrm{W(CO)_5}$ complex is according to a recent computational study a bimetallic species with molecular structure **92** (formula [XVI]).[199] Stabilization of the copper center by the additional alkene donor (or a solvent) is



Scheme 21 Pnictinidenes from thermally or photolytically induced cleavage of pnictinidene-phosphane complexes.



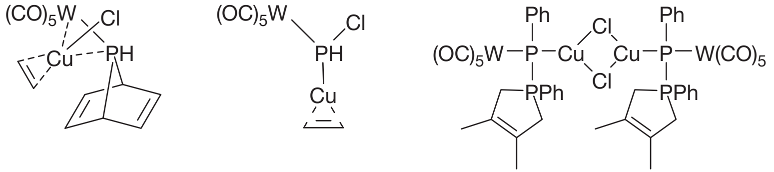
Scheme 22 Generation and Capture of a transient phosphanyl-phosphinidene.



Scheme 23 Generation of transient electrophilic phosphinidene complexes by cycloreversion reactions.

predicted to induce chloride migration to phosphorus to give **93**; the chloride migrates presumably back to the copper atom if an incoming substrate (e.g., an alkene in a cycloaddition sequence) interacts with the phosphorus atom in a later stage of the reaction. Experimental support for the postulated copper coordination is inferred from the isolation of a dimeric complex **94** from reaction of a transient phosphinidene complex with a phospholene.[200]

Cleavage of a phosphinidene complex from a benzophosphepine complex occurs even without a catalyst at lower temperatures (75–85 °C, onset of the reaction observed around 55 °C) than fragmentation of 7-PNBDs, with the exact conditions depending more on the nature of the substituent than on the coordinated metal at phosphorus.[194,201] Formation of transient phosphinidene complexes is supported by kinetic studies.

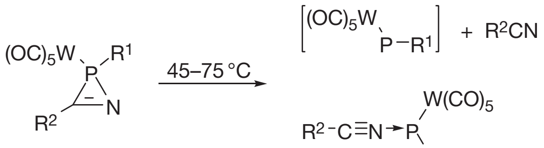


92 **93** **94**

XVI

The activation energy for formation of $(OC)_5WP{-}Me$ from a benzophosphepine precursor **90** (Scheme 23, R=Me, M=W, $\Delta E^{\neq} = 113.0 \pm 1.3\ \mathrm{kJ\ mol^{-1}}$) is by $25\ \mathrm{kJ\ mol^{-1}}$ lower than for the generation of the same phosphinidene complex from a 7-PNBD source; trapping of the transient species gives the same products, but in better yield, and thermolysis of benzophosphepines without a trapping agent results in addition of the formed phosphinidene complex to a CC bond of another phosphepine ring.[201] Computational studies predict that the phosphinidene complex is formed via electrocyclic isomerization of the benzophosphepine ring to a bicyclic phosphanorcaradiene **91** which then produces the transient phosphinidene complex by cheletropic fragmentation of the three-membered ring (Scheme 23). These studies highlight also the importance of benzannulation: since free benzophosphepines are protected toward spontaneous fragmentation as their isomerization to bicyclic phosphanorcaradienes is endergonic, they can therefore be isolated, purified, and further converted into the complexes which are then used as sources of singlet phosphinidene complexes; in contrast, nonbenzannulated benzophosphepines isomerize in an exergonic reaction and are thus liable to undergo fragmentation to give synthetically less useful triplet phosphinidenes.[201,202]

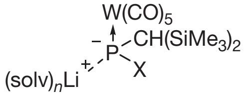
Some reaction schemes giving access to special types of phosphinidene complexes have been reported. Thermal ring opening of an azaphosphiridine complex generates a mixture of a transient phosphinidene complex and its donor adduct (eqn [11]).[203] Metathesis of Collman's reagent $Na_2[Fe(CO)_4]$ with $Et_2N{-}PCl_2$ produces transient phosphinidene iron complex $(OC)_4FeP{-}NEt_2$ which is trapped by cycloadditions with alkynes and terminal alkenes.[204] Conversely, the 'trappable' aminophosphinidene complex $(OC)_5WP{-}NEt_2$ is produced by retro-cycloaddition of Et_2N-substituted phosphiranes at 70–90 °C; fragmentation of precursors with other substituents requires higher temperatures which typically induce thermal degradation, and provides therefore a less effective phosphinidene source.[205] A transient nucleophilic phosphinidene complex was generated by thermolytic elimination of methane from a Hf-alkyl phosphido complex $[Cp^*CpHf(CH_3)\{P(H)Ph\}]$ and intercepted by cycloaddition with butene.[206] A transient stibinidene complex is believed to be involved in the zirconocene- and hafnocene-catalyzed dehydrocoupling of primary aryl stibines $ArSbH_2$ (Ar=Mes, 2,6-$Mes_2C_6H_3$) to give $(ArSb)_n$ and H_2.[207]



$R^1 = CH(SiMe_3)_2$; R^2 = aryl

11

A further reaction scheme allowing formal transfer of a phosphinidene complex to a substrate is the phospha-Wittig reaction (Scheme 24) of neutral or anionic metal complexes of phosphoranylidene phosphanes (Me_3PPR) or phosphoryl phosphides such as **95** which has recently been reviewed in some detail.[185] The reactivity pattern of the phospha-Wittig reagents reflects, however, mainly nucleophilic character; free phosphinidene complexes are most likely not involved. The same may hold true for reactions of phosphinidenoid complexes **96** (formula [XVII]),[208] although further studies of their chemistry are needed for a final assessment.

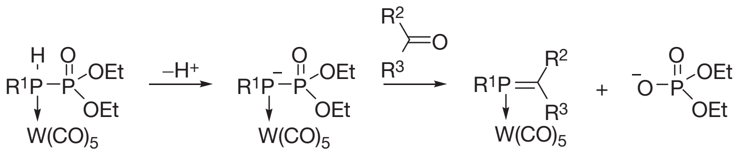


96 (X=F, Cl)

XVII

1.20.4.2.3 Synthesis of stable pnictogen(I) transition metal complexes

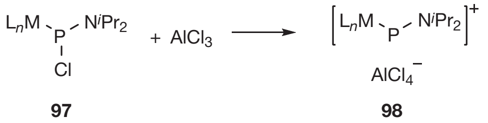
Metallophosphanes **97** with group 6 to group 9 transition metals react with $AlCl_3$ via halide abstraction to give isolable or persistent cationic complexes **98** (eqn [12]).[209–213] The products are crystalline compounds that are thermally stable at ambient temperature but extremely sensitive to air and, in particular, moisture, and display a similar reactivity as transient



95

Scheme 24 Synthesis of phosphaalkene complexes via the phospha-Wittig reaction.

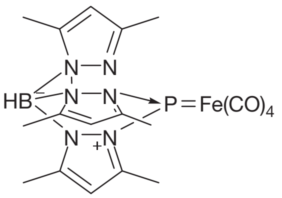
electrophilic phosphinidene complexes. Using an excess of $AlCl_3$ during the synthesis helps to remove the last traces of water from the reaction mixtures and thus to maintain the rigorously anhydrous conditions that are essential for the successful isolation of the target molecules. The heteroatom stabilization seems to be essential for the stability of the products; using the same protocol to generate a transient cationic alkyl phosphinidene complex produces only a transient species which can be trapped by cycloaddition or insertion reactions (see **Section 1.20.4.4**) but not isolated.[214]



12

L_nM	$Cp^*M(CO)_3^+$	$M(CO)_5^+$	$Cp^*M(CO)_2^+$	$(Ph_3P)M(CO)_3^+$
M	Mo, W	Re	Fe, Ru, Os	Co

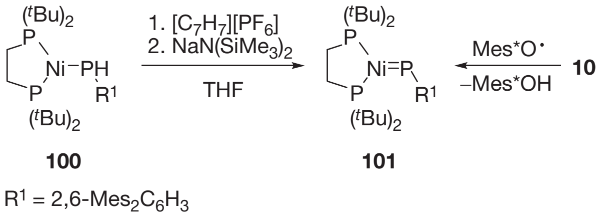
Isolable neutral phosphinidene complexes $[Cp(OC)_3VPR]$ ($R{=}N^iPr_2$, NCy_2) are obtained from metathesis of $RPCl_2$ with $Na_2[CpC(CO)_3]$.[215] Due to compensation of the strongly electron-donating influence of the Cp ligand by the electron-withdrawing carbonyls, the chemical behavior of these products reflects the remaining electrophilic character of the phosphinidene unit. Analogous metathesis of a pyrazolylborato dichlorophosphane with Collman's reagent gives a donor-stabilized phosphinidene complex **99** (formula [XVIII]). A borderline case between electrophilic and nucleophilic phosphinidene complexes is the isolable **101** which was first prepared by oxidation of Ni(I) phosphido complex **100** with tropylium cation and deprotonation.[217] The conversion is also feasible in one step by hydrogen atom abstraction with a suitable radical (**Scheme 25**).[218]



XVIII

99

Stable nucleophilic phosphinidene complexes[155] are distinguished by the presence of strongly electron-donating ancillary ligands (often Cp or Cp*, possibly in combination with other strong donors such as phosphanes or carbenes) and were the first isolable phosphinidene complexes to be prepared in the late 1980s.[219] Initial studies focused mainly on complexes of early transition metals, but to date derivatives featuring transition metals from group 3 to 9 as well as lanthanides (Nd[220] and Lu[221]) and actinides (U[222]) are known. Most isolable nucleophilic phosphinidene complexes exhibit 18-electron configuration at the transition metal, but species with lower electron counts of 16 or even 14 are transient intermediates in many reactions, and are in special cases spectroscopically observable (i.e., as solvate $Cp^*(CH_2Cl_2)IrP(2,6\text{-}Mes_2C_6H_3)$ stabilized by a methylene chloride[223] or as unsolvated complexes $Cp^*{}_2ZrPR$ ($R{=}Mes$, Mes*, Ph, Cy, $SiPh_3$)[224,225]) or even isolable.[226]

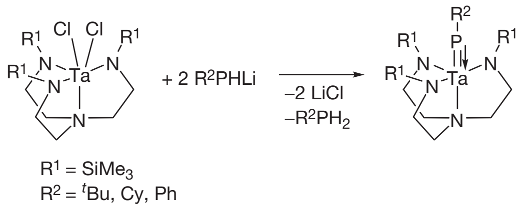


Scheme 25 Syntheses of a low coordinate nickel phosphinidene complex.

The most common synthetic protocol relies on the dehydrohalogenation of phosphido complexes which either are prepared as isolable precursors or form merely transient intermediates. The reaction can be accomplished in several ways.[155] Salt elimination can be achieved by treatment of a lithiated metalate with a dichlorophosphane (eqn [13])[219] or by reaction of a complex transition metal halide with a lithiophosphane.[227] Conversion of the intermediate phosphido complexes is often conveniently accomplished by employing a second equivalent of the lithiophosphane as a base (eqn [14]). Some reactions require the presence of an additional stabilizing ligand (eqn [15]); frequently, phosphanes[224,225,228,229] or carbenes[229] are used for transition metals, and $OPMe_3$ for uranium.[222] Alternatives to salt elimination are dehydrohalogenation of complex transition metal dihalides carrying a primary phosphane ligand by strong amidine bases in the presence of an additional donor ligand (eqn [16])[229,230] or carbenes (in this case, excess carbene acts as the same time as stabilizing ligand),[231] dechlorosilylation of an intermediate silylphosphido complex (eqn [17]),[228] or elimination of methane from methyl phosphido complexes (eqn [18]).[206] The last approach allows also to prepare an isolable terminal stibinidine complex.[232]

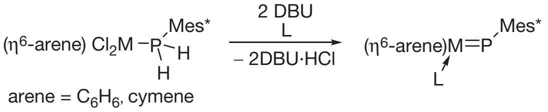
$$1/4\ [(Cp_2MHLi)_4] + RPCl_2 \xrightarrow[-LiCl\ -HCl]{} Cp_2M{=}PR \qquad 13$$

M = Mo, W
R = Mes*, $CH(SiMe_3)_2$



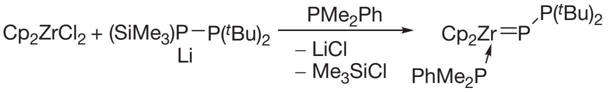
14

$$Cp_2ZrCl_2 + 2\ Mes^*PHLi \xrightarrow[-2\ LiCl\ -Mes^*PH_2]{PMe_3} Cp_2(Me_3P)\,Zr{=}PMes^* \qquad 15$$



16

arene = C_6H_6, cymene
M = Ru, Os
L = PPh_3, PMe_3, ^tBuNC, CO



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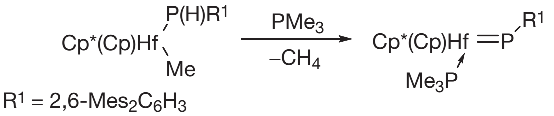


18

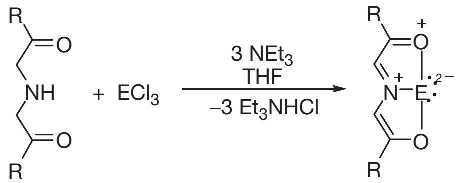
Although the dehydrohalogenation approach seems to be rather general, it does not work in all cases. Reactions of $[(Cp^*)_2HfX(PHR)]$ (X = Cl, I; R = Cy, Ph) with anion bases give product mixtures rather than the desired phosphinidene complexes,[233] and the failure of attempts toward dechlorosilylation of $[Cp_2ZrCl\{P(SiMe_3)Mes^*\}]$[234] is presumably owing to the absence of an additional stabilizing ligand.[6] The outcome of many synthetic protocols was also found to depend crucially on steric requirements of the ligands at the metal and phosphorus atoms.[225]

In addition to metathesis and elimination reactions, some further approaches to individual nucleophilic phosphinidene complexes of early transition metals are known. Oxidative addition of phenyl phosphane to the electron-deficient complex $[(^tBu_3SiO)_3Ta]$ to give an intermediate phosphido complex and subsequent 1,2-H_2 elimination is a viable route to phosphinidene complex $[(^tBu_3SiO)_3TaPPh]$.[235] Complex $[Cp(^tBu_3PN)Ti(PMe_3)=PMes^*]$ is formed via an analogous reaction starting from an *in situ* generated, transient Ti(II) species.[236] Prototropic shift of a metal hydride to the nitrogen atom of a PN double bond produces the phosphinidene unit of spectroscopically detectable, but not isolable, complexes $[(Cp^*)_2MP\text{–}NHMes^*]$ (M = Mo, W) in the coordination sphere of the transition metal.[237] Isolable products $[(nacnac)M(CH_2{}^tBu)=PR]$ (M = Ti, V; R = Is, Mes) with quasi-linear phosphinidene units are formed by reacting metal alkylidene complexes $[(nacnac)(X)M=CH^tBu]$ (M = Ti, V; X = I, OTf) with LiP(H)R to give transient alkylidene–phosphido complexes which then undergo spontaneous 1,3-H-shift to give the phosphinidene complexes.[238] Assembly of the phosphinidene unit on a metal by P-alkylation of an anionic terminal phosphido complex gives way to niobium phosphinidene complexes $[\{Np(Ar)N\}_3Nb\equiv PR]$ ($Np = {}^tBuCH_2$, $Ar = 3,5\text{-}Me_2C_6H_3$; $R = SiMe_3$, $SnMe_3$, PPh_2, P^tBu_2) with quasi-linear phosphinidene units.[239]

Last, but not least, a couple of stable phosphinidene complexes are accessible via transfer of a phosphinidene group RP to a suitable transition metal precursor. Phosphaketene $Mes^*P=C=O$ reacts with $[L_4WCl_2]$ ($L = Ph_2MeP$) to give *cis*-$[L_2Cl_2(CO)W\equiv PMes^*]$ with a linear phosphinidene unit.[240] The product is special as both the RP and CO units of the phosphaketene end up in the metal complex (analogous reaction of a phosphacarbodiimide $Mes^*P=C=NPh$ gives a thermally unstable phosphinidene–isocyanide complex). The phospha-Wittig reagents Me_3PPAr (Ar = Mes*, 2,6-$Mes_2C_6H_3$) are able to deliver their phosphinidene unit to low-valent early transition metal complexes; e.g., reaction with $[Cp_2Zr(PMe_3)_2]$ gives $[Cp_2(Me_3P)ZrPAr]$.[241]

1.20.4.2.4 *Synthesis of hypervalent pnictogen(I) compounds*

The 'hypervalent' pnictogen(I) compounds **64a–c** (see Section 1.20.4.1.2.1) are readily obtained by base-induced condensation of ECl_3 with di-β-keto-amines (eqn [19])[167–169]; the formal reduction of the pnictogen atom during this transformation is compensated for by an appropriate oxidation of the ligand. Bismuth trichloride reacts under the same conditions to give a complex consisting of a nona-coordinate Bi^{3+} cation and three monoanionic ligands; a tri-coordinate Bi(I) analog of **64** is not observable.[242]



(R = ${}^tBu$)

64a (E = P)
64b (E = As)
64c (E = Sb)

19

1.20.4.3 Physical Properties

Isolable donor adducts and transition metal complexes pnictinidenes are generally thermally stable at ambient temperature (a known exception is ${}^tBu_2(Br)PP\text{–}P^tBu_2$ (**84**) which decomposes slowly at room temperature[187]) but highly sensitive to air and moisture and must thus be handled under an inert atmosphere and in rigorously dried and degassed solvents. Most derivatives are readily soluble in aprotic organic solvents.

1.20.4.3.1 *Crystal structure studies*

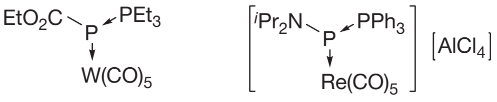
Due to the transient nature of pnictidenes, available crystal structure data are limited to their isolable complexes with Lewis donors or transition metals. Up to date, all available studies have been devoted to phosphinidene derivatives.

The molecular structures of phospha-Wittig reagents of general type $(R^1)_3PPR^2$ exhibit P–P bond distances of 2.08–2.13 Å that are close to the short end of the range of P–P single bonds, and bond angles of 100–107°.[188,243] The range of P–P distances is in accord with the theoretical prediction of an ylidic bond which benefits from substantial electrostatic interaction between the oppositely charged phosphorus atoms (see Section 1.20.4.1.2.1).

Crystal structures of terminal phosphinidene complexes reveal distinct differences between complexes with electrophilic and nucleophilic RP units. Cationic complexes $[L_nMP\text{–}N^iPr_2]^+$ (L_nMCp*$(CO)_3$M with M = Mo, W; Cp*$(CO)_2$M with M = Fe, Ru, Os; $(CO)_5$Re) and the neutral specimen $Cp(CO)_3VP\text{–}N^iPr_2$ exhibit P–N bonds of 1.62–1.65 Å that are intermediate between single and double bonds and suggest a significant degree of phosphorus–nitrogen π-interaction.[209–215] The M–P bonds in complexes with M = Mo, W, Re, Ru, Co are only slightly shorter than the corresponding distances in Me_3P complexes of these metals, which led to conclude that the σ-donor/π-acceptor properties of the phosphinidene ligand in these complexes match those of phosphanes. The M–P distance in the iron complex is somewhat shorter but is still intermediate between a single and a double bond.[211] The bond angles at the phosphorus atoms are in all complexes close to 120°.

Nucleophilic phosphinidene complexes are divided into species with bent (bond angles 100–145°) or quasi-linear (bond angles 160–180°) coordination geometries at phosphorus. Both types of complexes exhibit very short phosphorus–metal bonds (currently known values for individual compounds are listed in a recent review[155]) which indicate the presence of metal–phosphorus double bonds or pseudo-triple bonds (due to formation of an additional dative bond through interaction of the phosphorus lone pair with the metal). The clear-cut distinction between the bonding of a nucleophilic phosphinidene unit and a phosphane ligand to the same central metal is illustrated by the comparison of the two different bond lengths (ZrP 2.505(4) Å, Zr–PMe_3 2.741(5) Å) in the bent (Zr–P–C 101.4(1)°) phosphinidene complex $[Cp_2(Me_3P)ZrPMes^*]$.[244]

Molecular structures of a few phosphinidene complexes such as **102**[245] and **103**[213] (formula [XIX]) featuring stabilization of the phosphinidene ligand by both a transition metal and a Lewis donor show a lengthening of both P–P(phosphane) and P–M bonds compared to pure phosphinidene–donor or phosphinidene–metal complexes, respectively, and a strongly pyramidalized phosphorus atom.



XIX

102 **103**

1.20.4.3.2 Spectroscopic studies

Information of the physical properties of transient diatomic pnictinidenes stems mainly from spectroscopic studies using different methods (UV–vis, infrared (IR)-laser magnetic resonance, IR, microwave spectroscopy) of isolated molecules in the gas phase.[158–179,246] The results allow to determine, for example, singlet–triplet splitting energies ΔE_{S-T} (see also Section 1.20.4.1.1), or equilibrium geometries (Table 2). Transient mesityl phosphinidene was characterized by matrix isolation UV–vis, IR, and electron paramagnetic resonance (EPR), which confirmed also the triplet ground state of this molecule.[181,182]

Isolable or persistent pnictinidene derivatives are routinely characterized by IR and NMR data. ^{31}P NMR data are particularly useful for the structural assessment of phosphinidene derivatives. The low coordinate phosphorus atoms in phosphinidene-donor adducts $(R^1)_3PPR^2$ exhibit negative chemical shifts whereas those in phosphinidene complexes appear generally at lower fields. Regardless of the electrophilic or nucleophilic nature of the ligands, the signals of bent complexes appear strongly deshielded ($\delta^{31}P$ approximately 500–1100 ppm) and are clearly distinguishable from the more shielded ones of linear complexes ($\delta^{31}P$ approximately 160–300 ppm).[6,155,156,176,209–214] ^1H and ^{13}C NMR data enable insights into the conformational dynamics of some bent phosphinidene complexes. The perseverance of the chemical equivalence of the two P^tBu_2 donor units in **96** at low temperature in solution indicated a low barrier for rotation (or inversion) of the bent phosphinidene ligand.[217] Observation of diastereotopic methyl groups of $^iPr_2N$ substituents in electrophilic aminophosphinidene complexes at room temperature reveals restricted P–N bond rotation and underlines the substantial phosphorus–nitrogen double-bond character.[209–215]

Table 2 Spectroscopically determined equilibrium distances of parent pnictinidenes E–H in their electronic ground state

E–X	*R_e (Å)*	*References*
P–H	1.432846(7)	247
As–H	1.52320(6)	158
Sb–H	1.70187	159
Bi–H	1.791	246

Both nucleophilic and electrophilic phosphinidene complexes are frequently deeply colored. However, even though UV–vis spectra have been recorded in some cases, no systematic evaluation of the electronic spectra of these compounds has as yet been undertaken.

1.20.4.4 Reactivity

Studies on the chemical reactivity of pnictinidenes focused mainly on phosphinidenes, their donor adducts, and, in particular, terminal phosphinidene complexes. The chemical properties of the higher homologs remain widely unknown, although the sparse available data[180,232] indicate that these species may behave similarly.

The chemistry of triplet phosphinidenes is described as very erratic, and not synthetically useful.[6,8] This assessment agrees with theoretical studies which predict that phosphinidenes react indeed less selective in the triplet than in the singlet state.[248] A possible explanation for the erratic behavior is provided by the hypothesis that free phosphinidenes may in some reactions not be generated at all and alternative pathways are invoked.[8,156,248] In contrast to the unclear status of triplet phosphinidenes, there is an extensive chemistry of singlet phosphinidene derivatives which is clearly related to the P(I) oxidation state and allows a clear distinction of the behavior of nucleophilic and electrophilic species.[6]

1.20.4.4.1 Reactivity of electrophilic pnictinidene derivatives

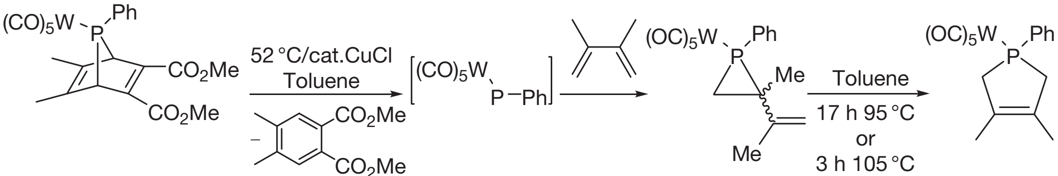
Chemical studies focused mainly on terminal electrophilic phosphinidene complexes and established that the reactivity of these species is dominated by typical electrophile reactions such as cycloadditions to multiple bond systems, insertion into single bonds, and, in the absence of trapping reagents, oligomerization. Investigations on reactivities of free phosphinidenes are confined to a study of transient $^tBu_2P$–P (**85**), which is presumed to have a singlet ground state[160] and shows a similar behavior as transient complexes $(OC)_5MPR$.[187] The close resemblance of the reactions of electrophilic phosphinidene complexes to that of electrophilic singlet carbenes and carbene-analogs is suggested by small and negative Hammett reaction constants for transient complexes $(OC)_5WPR$ (−0.76 for R = Ph, −0.60 for R = Me, −0.55 for R = MeO) in the CuCl-catalyzed addition to styrenes.[249] Moreover, the energy profiles of the reactions of parent singlet phosphinidene ^1PH with ethylene, H_2O, H_2S, HF, and HCl are according to computational studies very similar to those of X–H bond insertion processes of other carbene-analog species such as $^1CH_2$, $^1SiH_2$, or ^1NH.[6] The exothermic reaction between ^1PH and ethylene to give phosphirane shows likewise no enthalpic barrier.[250] Reactions of ^1PH with the remaining substrates proceed via initial van der Waals or donor–acceptor complexes (only the HP–SH_2 complex shows some ylide character) which have to overcome only very small barriers to react via hydrogen migration to the thermodynamically much more stable phosphanes.[251]

The best-studied reaction of phosphinidene complexes is the 1,2-cycloaddition with alkenes, alkynes, or heteronuclear CN,[203,252,253] CO,[203,252] CS,[255] CP,[256] or CSi[254] multiple bonds to give three-membered phosphiranes, phosphirenes, or heterophosphiranes. The addition step is reversible, allowing interconversion of three-membered rings via transfer of a phosphinidene complex between different multiple bond systems.[181,203,252] Cycloadditions to alkenes occur with retention of the configuration of the double bonds[191] but show little or no selectivity toward different competing substrates,[257] in accord with the conception that generating the phosphinidene complex is the rate-determining step in the overall reaction.[191] Reaction of phosphinidene complexes with exocyclic alkenes gives stable spiro compounds.[258,259] Allenes[260] or phosphaallenes[261] react to give complexed methylenephosphiranes or methylenediphosphiranes, respectively. Additions to cummulenes occur preferably to the terminal double bond to give complexes of vinylidene phosphiranes which rearrange to phospha[3]radialenes.[262] Comprehensive accounts discussing the full synthetic scope and application of the cycloaddition reactions of phosphinidene derivatives have been given in several reviews[2,6,8,156,256] and will not be repeated here.

Trapping of transient phosphinidene complex $(OC)_5WPPh$ by 1,3-dienes gives a mixture of complexed vinylphosphiranes (major products) and phospholenes (minor product) arising from formal [1+2] and [1+4] cycloaddition, respectively.[6] Detailed studies indicated that phosphiranes (**104**) form as initial products when the reaction is carried out under mild conditions (**Scheme 26**).[263] Vinylphosphiranes with anti-configuration may epimerize to the syn-isomers, likely via a biradical intermediate, which rearrange then via 1,3-sigmatropic shift to give thermodynamically more stable phospholenes (**105**).[264] The vinylphosphirane–phospholene conversion follows, according to a kinetic study in the absence of a catalyst, a biradical pathway, and in the case of a CuCl-catalyzed process a concerted pathway.[265] Computational studies suggest that both reaction channels are close in energy, and that the transition state displays as in the vinylcyclopropane–cyclopentene rearrangement of hydrocarbons some biradical character the extent of which varies as a consequence of substituent-induced steric congestion.[266] When the [1,3]-shift of the initially formed vinylphosphirane is inhibited, addition of a second phosphinidene to give bisphosphiranes may be observed.[267] Multiple addition is also feasible in reactions of transient phosphinidene complexes with alkynes, and stepwise addition of phosphindene complexes to alkynyl phosphirene **106** enables to construct oligophosphirene complexes **107** and **108** (**Scheme 27**).[268]

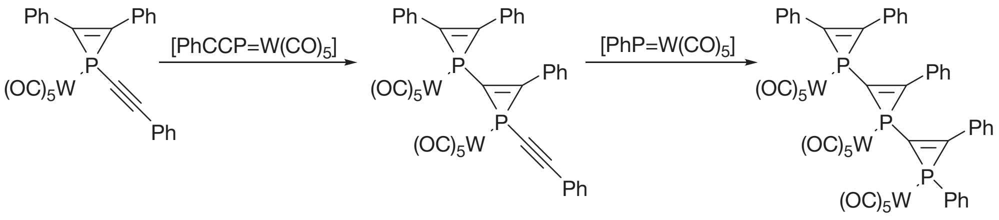
A preference for 1,2-addition is also evident in the reaction of transient $^tBu_2P$–P with cyclohexadiene,[187] but reactions of transient phosphinidene complexes with α,β-unsaturated ketones[263] and 1-azadienes[269] yield only 1,4-addition products. Exclusive [1,4] addition is likewise observed for reactions of a stibinidene with butadienes.[180]

Insertion reactions of phosphinidene complexes have been much less studied than cycloadditions but examples for the insertion of transient $(OC)_5WPPh$ or isolable electrophilic phosphinidene complexes into CH,[270] SiH,[271] or CX[272] bonds are known. Several other CH or CX insertion reactions are likely to occur via intermediate phosphinidene donor complexes (*vide infra*), and, in some cases, conversion of transient phosphinidene complexes to phosphane complexes via formal insertion of the phosphorus atom into a single bond follows obviously a more complicated mechanism than simple oxidative addition.[272] Reactions of transient electrophilic phosphinidene complexes in the absence of trapping agents either



104 **105**

Scheme 26 Trapping of a transient phosphinidene complex by a 1,3-diene and vinylphosphirane-phospholene conversion.



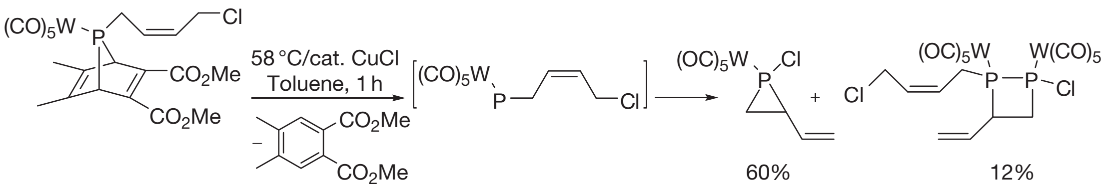
106 **107** **108**

Scheme 27 Stepwise construction of oligophosphirene complexes.

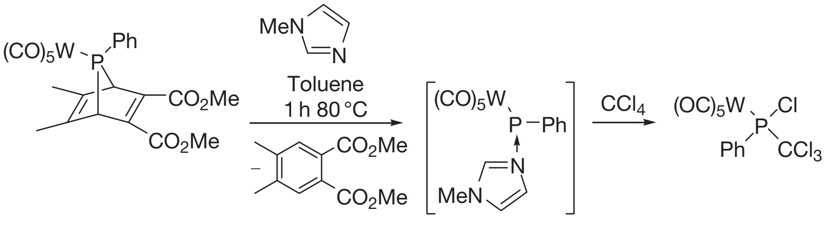
proceed via intramolecular attack, if suitable functional groups are present (e.g., the synthesis of a chloro-vinylphosphirane complex from a transient chlorobutenyl-phosphinidene complex, **Scheme 28**[198]), or yield complexes of dimers (diphosphenes) or higher oligomers (cyclophosphane oligomers $(RP)_n$ with $n>2$), the nature of which depends on the reaction conditions and the type of metal atom and substituents in the starting material.[191,273] The recent isolation of diphosphene complexes from CuCl-catalyzed thermolysis of 7-phosphanorbornadiene–$W(CO)_5$ complexes[273] nicely illustrates this reactivity and marks a close parallel to the formation of compounds R_2EER_2 with double bonds between two group 14 elements from carbene-analog precursors ER_2.

A particular interesting aspect of the chemistry of electrophilic phosphinidene complexes deals with attempts to make the phosphorus center to react as a nucleophile rather than an electrophile ('Umpolung').[8] This goal is readily achieved by generating a transient phosphinidene complex in the presence of a strong nucleophile like *N*-methylimidazole.[177] The nitrogen heterocycle acts then as a base which stabilizes the univalent phosphorus atom by formation of a donor–acceptor bond to give transient (singlet) phosphinidene–Lewis-base adduct **109** (**Scheme 29**). Electron donation by the Lewis base is sufficient to make the phosphinidene unit undergo reactions which are quite untypical for electrophilic phosphinidenes, like formation of a chlorotrichloromethyl phosphane with CCl_4.[177]

Transient phosphinidenes featuring synergistic stabilization by both a Lewis donor and a Lewis acceptor are generated during thermal ring opening of azaphosphirene complexes. The reaction affords, besides phosphinidene complexes, transitory nitrilium phosphanylides **110** (performing the reaction in the presence of stronger Lewis donors permits also to replace the coordinated nitrile by a different donor unit) which can be subsequently trapped by various cycloaddition reactions (**Scheme 30**).[203,252] This approach has been elaborated into a versatile synthetic route to numerous phosphorus heterocycles, and the results of these studies have been comprehensively reviewed.[252] Isolable Lewis donor/acceptor adducts of phosphinidenes are accessible via different routes, involving complexation of a stable phosphinidene–Lewis adduct with a suitable transition metal (e.g., **111**,[274] eqn [20]), treatment of a stable electrophilic phosphinidene complex with a Lewis donor (e.g., **112**, eqn [21][275]), or, finally, from reaction of a 7-phosphanorbornadiene with a cyclopropylidene carbene at room temperature (**113**, eqn [22][276]). The nucleophilic character of the phosphorus atom in **113** is demonstrated by reactions involving protonation or alkylation at phosphorus, formation of a CS_2 insertion product, and cycloaddition with electron-poor α,β-unsaturated ketones or quinones to give oxaphospholene derivatives.[276]



Scheme 28 Intramolecular trapping of a transient phosphinidene complex.



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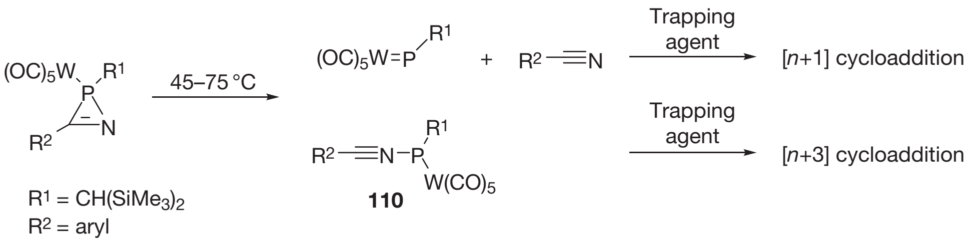
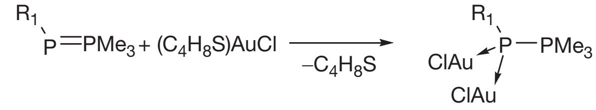
Scheme 29 Umpolung of the reactivity of an electrophilic phosphinidene complex by formation of a transient Lewis-base adduct.



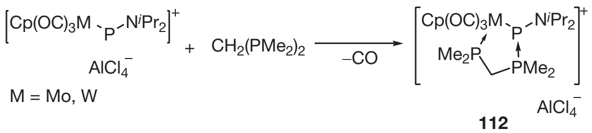
Scheme 30 Trapping of transient phosphinidene intermediates during the thermal ring opening of azaphosphirene complexes.



$R^1 = 2,6\text{-}Mes_2C_6H_3$

111

20



M = Mo, W

112

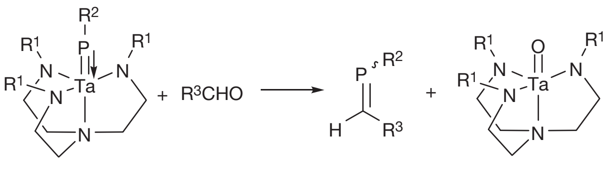
21

1.20.4.4.2 Reactivity of nucleophilic pnictinidene derivatives

Prominent reaction channels for nucleophilic phosphinidene complexes are metathesis reactions under transfer of the phosphinidene unit to another substrate, cycloaddition to the PM double bond, or insertion into the MP bond. Nucleophilic phosphinidene complexes behave in many of these reactions as synthetic equivalent of $[RP^{2-}]$ dianions,[8] and their (cyclo) addition reactions with alkenes and alkynes, although still limited in number, differ clearly from the reaction patterns of electrophilic phosphinidene complexes and seem more related to analogous reactions of alkylidene transition metal complexes.

Metathesis with carbonyl compounds under formation of a phosphaalkene and a metal oxo species ('phospha-Wittig' reaction) is to date the most characteristic reaction of nucleophilic phosphinidene complexes and works best for complexes of oxo- or halophilic transition metals.[181] The reaction was first discovered for tantalum complex **115** (eqn [23]).[227] A particularly versatile phosphinidene transfer reagent is $[Cp_2(Me_3P)ZrPMes^*]$ (**116**) which reacts with aldehydes and ketones via phospha-Wittig reaction, presumably via an intermediate four-membered metallacycle, to give phosphaalkenes together with polymeric zirconocene oxide $[\{Cp_2ZrO\}_n]$ and PMe_3, with phenylisothiocyanate to give heteroallene $PhN{=}C{=}PMes^*$ and $[\{Cp_2Zr(\mu\text{-}S)\}_2]$, with epoxides to give phosphiranes by P/O exchange, and with geminal or α,ω-dihalides to give Cp_2ZrCl_2 together with the corresponding phosphaalkenes or appropriate phosphorus heterocycles, respectively.[225,277]

Complexes $Cp(Ph_3P)MPMes^*$ with group 9 metals (M = Co, Rh, Ir) give phosphaalkenes upon reaction with dihalomethanes but not with carbonyl compounds.[278] Computational[279] and kinetic studies[229,231,278] of phosphinidene transfer reactions of **116** and other phosphinidene complexes with dihalides indicate that the rate of product formation depends on the halogen atom of the substrate, the halophilicity of the transition metal, and the donor properties of the ancillary ligand (a strongly electron-donating carbene being more effective than PPh_3).



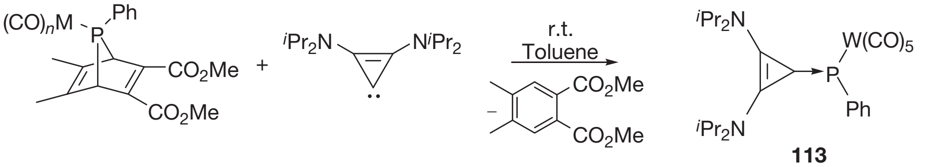
115

$R^1 = SiMe_3$, $R^2 = Ph$, ^tBu, $R^3 = Ph$, Fc

23

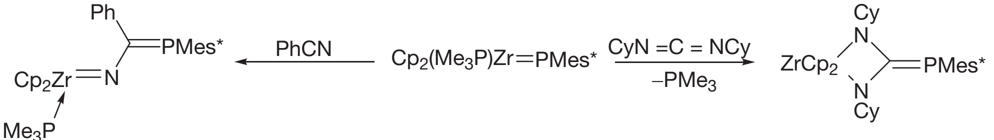
Reactions under insertion of substrate molecules into the MP bond of a phosphinidene complex are few and include formation of phosphaimido- and phosphaguanidino complexes **117**, **118** via insertion of benzonitrile or dicyclohexylcarbodiimide into the ZrP bond of **116** (Scheme 31),[225] and the generation of marginally stable η^2(N,C)-phosphaazaallene (**119**) and phosphinylimide complexes (**120**) from *t*-butyl isonitrile or diphenyl diazomethane and coordinatively unsaturated titanium complex $[(nacnac)(Np)TiPMes^*]$ (Np = neopentyl, Scheme 32).[238]

Cycloaddition to the MP bond of nucleophilic phosphinidene complexes is observed in various reactions with alkynes and isonitriles. Transient $[Cp_2ZrPMes^*]$, which is accessible by cleavage of PMe_3 from isolable **116** or via spontaneous loss of methane from the phosphido complex $[Cp_2Zr(Me)(PHMes^*)]$, is intercepted by alkynes in a [2+2]-cycloaddition to give phosphametallacyclobutenes **121** (Scheme 33).[280] The cycloaddition is reversible, allowing **121** to react with PMe_3 under regeneration of **116** and release of the alkyne, and to undergo exchange reactions with other alkynes. Reversible addition of phosphaalkynes is reported for transient Ir and Ru phosphinidene complexes with ancillary carbene ligands.[281] Reaction of **101** with ethylene gives



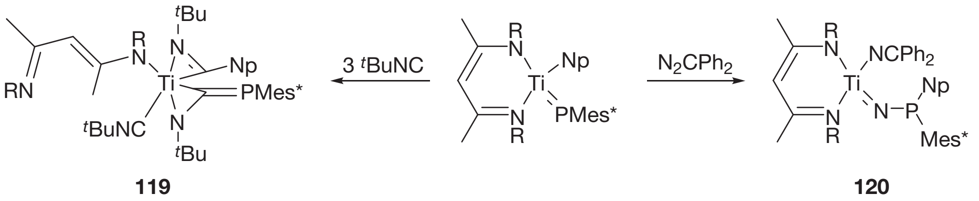
113

22

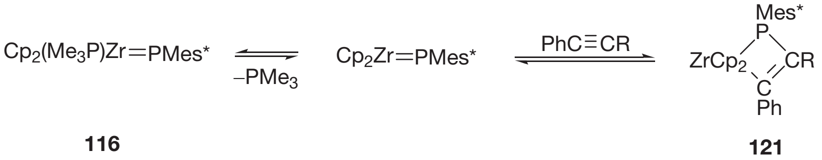


117 **116** **118**

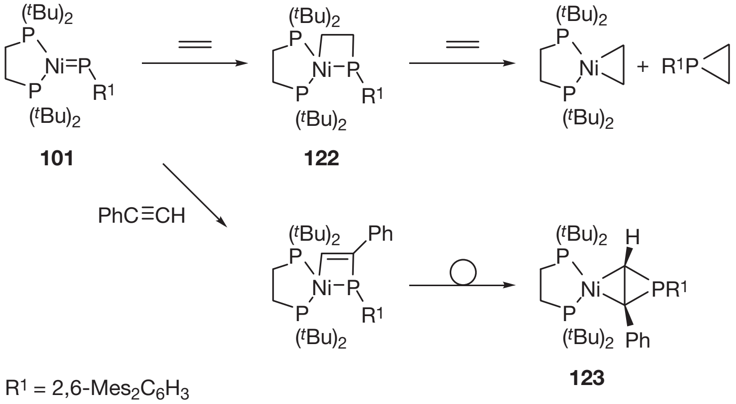
Scheme 31 Nitrile and carbodiimide insertion into the Zr=P bond of a nucleophilic zirconium phosphinidene complex.



Scheme 32 Isonitrile and azoalkane insertion into the Ti=P bond of a nucleophilic phosphinidene complex.

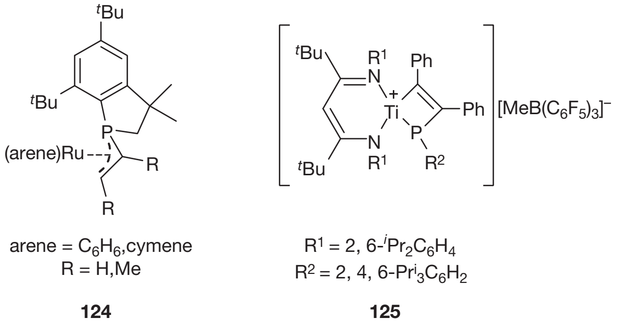


Scheme 33 Reversible alkyne addition of a nucleophilic phosphinidene complex.



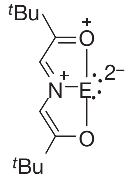
Scheme 34 Irreversible addition of ethene and alkynes to a phosphinidene nickel complex.

spectroscopically detectable phosphametallacyclobutane **122** which is cleaved by excess C_2H_4 to give a phosphirane and a Ni–C_2H_4 complex (Scheme 34); reaction with *E*-d_2-ethylene proceeds with retention of the stereochemistry at the double bond.[282] Alkynes and **101** produce an uncommon metallaphosphabicyclobutane **123** by way of a putative [2+2]-cycloaddition product as intermediate (Scheme 34).[283] Initial formation of phosphametallacyclobutenes via [2+2]-cycloaddition is postulated to explain the reactions of *in situ* generated 16-electron complexes [(η^6-arene)RuPMes*] (arene= C_6H_6, cymene) with alkynes to give vinyl-phosphaindane complexes **124** (formula [XX]) as stable end products,[133,230] and is further considered as a key step in the catalytic hydrophosphination of diphenyl acetylene with $PhPH_2$; the active catalyst in this reaction is presumably formed via Ar–P metathesis between $PhPH_2$ and zwitterionic precatalyst **125**.[284] The stepwise addition of two aryl isocyanides to transient 16-electron complexes [Cp*IrP–R] (R=Mes, Mes*, Dmp) proceeds via coordination of the first isocyanide to give 18-electron phosphinidene complexes [Cp*(ArNC)IrP–R] (Ar=xylyl) which then react with a further isocyanide under [2+1]-cycloaddition to the MP bond.[223]

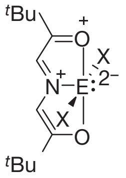


XX

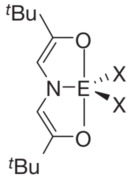
The 'hypervalent' pnictinidene–Lewis donor adducts **64a–c** (formula [XXI]) react, as a consequence of the electronic saturation of the low-valent central atoms by the two axial Lewis donor units, mainly as nucleophiles. The resulting reactivity of **64a** has been comprehensively reviewed.[171] Oxidation of **64a–c** with halogens yields either ψ-octahedral dihalides **126** (for E=P, X=F[285] and E=Sb, X=Cl, I[170]) or species **127** with distorted tbp-coordination of the central atom (E=P, X=Cl, Br[170]). The molecular structures of **126** suggest that a nonbonding electron pair is retained on the central atom, and



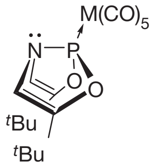
64a (E = P)
64b (E = As)
64c (E = Sb)



126a (E = P, X = F)
126b (E = Sb, X = Cl)
126c (E = Sb, X = I)



127a (E = P, X = Cl)
127b (E = P, X = Br)



128 (M = Cr, W)

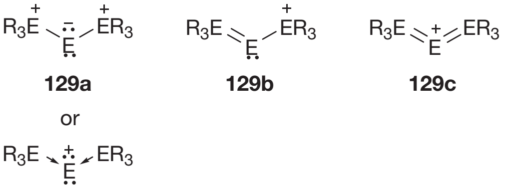
XXI

highlight the character of **64** as pnictogen(I) compounds, whereas the central atoms in **127** are best described as a phosphorus(V) centers. The implication of this dichotomy – that the central atom in **64** can switch rather easily between a formal pnictogen(I) and a pnictogen(III) valence state – is further emphasized by the easily observable change from ψ-tbp to pyramidal configuration of the bicyclic framework after coordination of the phosphorus atom to a transition metal (**128**).[171] Compounds **64** do not seem to exhibit any reactivity as pnictinidene transfer reagents.

1.20.5 Derivatives Containing Donor-Stabilized Pnictogen(I) Cations

As an alternative to stabilize an electron-deficient pnictidine R–E by a Lewis donor L in a neutral pnictinidene(I) complex, one can conceive interaction of a pnictidine(I) cation with two Lewis donors, $[L \rightarrow E \leftarrow L]^+$. If the donor atoms are likewise based on pnictogen atoms, such complexes may be given the generic name of tripnictogenium cations. Since isolated pnictidine(I) cations exhibit a valence electron count of four, tripnictogenium ions and neutral L→E–R complexes are isoelectronic. Due to the possibility to represent tripnictogenium ions by very different valence structures (**Scheme 35**),[4,9] there is some ambiguity in assigning a distinctive oxidation and valence state for the central dicoordinate pnictogen atom. Although the description as a pnictogen(I) species **129a** had been realized in the first report on the synthesis of a triphospheniumion,[286] tripnictogenium cations have thus often been perceived as ylidic pnictogen(III) (**129b**) rather than pnictogen(I) compounds.[4] As a consequence, the prospect of using such species to develop a unique pnictogen (I) chemistry was for a long time widely neglected, and is only recently receiving renewed recognition.[9]

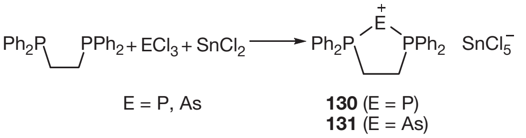
The outline of the chemistry of donor-stabilized pnictogen(I) cations in the following section focuses mainly on compounds with pnictogen-based donor units. The important case of stabilizing cations with N-heterocyclic carbenes will be briefly mentioned but is more comprehensively covered in **Chapter 1.16**.



Scheme 35 Canonical structures for the representation of donor-stabilized pnictogen(I) cations.

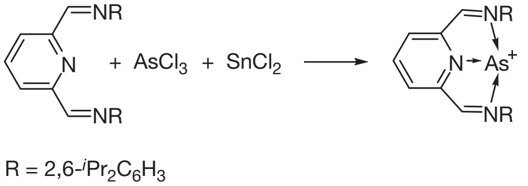
1.20.5.1 Syntheses

Salts with donor-stabilized pnictogen(I) cations are generally accessed by reduction of a pnictogen trihalide in the presence of a suitable ligand, or by transmutation of a preformed donor-stabilized pnictogen(I) cation via ligand exchange. Reduction of PCl_3 with $SnCl_2$ in the presence of the chelating bis(diphenylphosphino)ethane (dppe) gives triphosphenium salt **130** as the first derivative of this type ever isolated (eqn [24]).[286] Tin(II) bromide can likewise be used as a reducing agent, and employing bifunctional phosphanes with different saturated and unsaturated backbones gives rise to cations with four- to seven-membered chelate rings.[287–290] Many of the products have only been identified *in situ* by their characteristic ^{31}P NMR data, but detailed protocols for the synthesis of isolable triphosphenium salts are available.[291] Phosphane-stabilized As(I) cations such as **131** (eqn [24]) are accessible by the same route starting from $AsCl_3$[287,289,292] but antimony(I) or bismuth(I) compounds have not been prepared, presumably because of the tendency of the heavier pnictogen trihalides to be reduced to the elements under the reaction conditions.[9] Using α,α′-diimines (1,4-diazabutadienes) rather than phosphanes as donor gives heterocycles which are best described as N-heterocyclic pnictogenium cations (**Section 1.20.3.2.2.4**), indicating that the diimine is reduced to a diamide fragment and the pnictogen(III) center is retained.[87,88] Products containing genuine donor-stabilized As(I) centers are, however, accessible when less easily reducible pyridine-imines are employed (eqn [25]).[293]



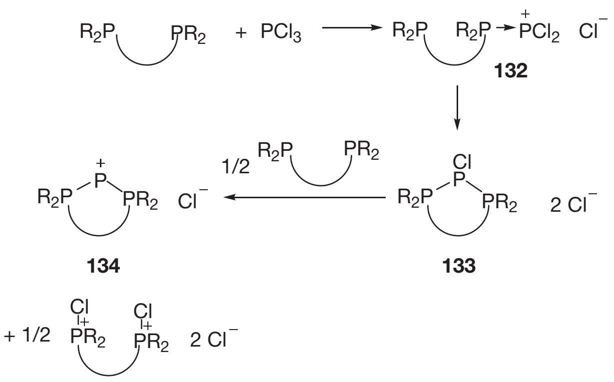
130 (E = P)
131 (E = As)

24



25

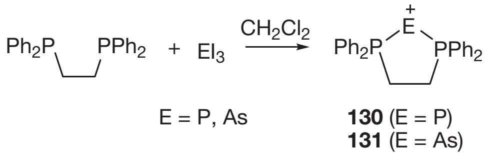
As an alternative to the use of tin(II), reduction of PCl_3[288,289,294,295] and $AsCl_3$[289,296] is feasible by employing an additional equivalent of the ligating phosphane which is thereby oxidized from P(III) to P(V). The higher homologs, $SbCl_3$ and $BiCl_3$, do not undergo redox reactions in the presence of donors but yield complexes of the E(III) cations instead.[9] Formation of cyclic triphospheniumions commences



Scheme 36 Formation of cyclic triphosphenium ions from diphosphanes and PCl_3.

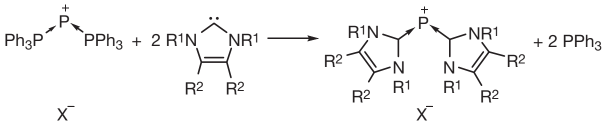
according to ^{31}P NMR studies with nucleophilic attack of the chelate ligand at PCl_3 to give a donor-stabilized phosphenium cation **132**, which subsequently cyclizes to a dication **133** by loss of halide, and is finally reduced by a second molecule of the phosphane donor to produce monocation **134** and a chlorophosphonium ion (Scheme 36).[297] A drawback of this approach as a preparative method is that the chlorophosphonium byproducts are difficult to separate as their solubility is often very similar to that of the desired products; many cations prepared by this method have thus only been characterized by ^{31}P NMR.[288,289] The ligand oxidation approach gives access to acyclic cations when monofunctional phosphanes such as PPh_3 or $P(NMe_2)_3$ and PCl_3 are reacted in the presence of a strong Lewis acid such as $AlCl_3$ or $GaCl_3$ which intercept the formed halide ions by formation of complex anions.[291,294,295] The reaction between $P(NMe_2)_3$, PCl_3, and $AlCl_3$ is special as its outcome depends subtly on the reaction conditions: dissolving $P(NMe_2)_3$ and $AlCl_3$ in CH_2Cl_2 at 0 °C and subsequently adding PCl_3 gives the triphospheniumion $[(Me_2N)_3P\text{–}P^{(+)}\text{–}P(NMe_2)_3]$, while phosphenium salt $[(^iPr_2N)_2P][AlCl_4]$ is formed when $AlCl_3$ is added to a previously prepared solution of PCl_3 and $P(NMe_2)_3$; both products are not interconvertible.[295] Ligand disproportionation is also observed in the reaction of PCl_3 with stable N-heterocyclic carbenes to give a phosphamethine cyanine, which is in this case is described as P(I)-carbene adduct, and a chloroimidazolium cation.[298]

In a further variation, P(I) and As(I) species can be generated by disproportionation of PI_3 or AsI_3 in the presence of a chelating phosphane in a nondonating solvent such as CH_2Cl_2 (eqn [26]).[292,299,300] Iodine formed as byproduct is easily removed, and the remaining iodide counterion can be readily displaced by anion metathesis. Instead of PI_3, also P_2I_4 has been used.[292,301] Analogous formal disproportionation of PCl_3 or PBr_3 in the presence of chelating bis-phosphanes to give cyclic triphosphenium halides can be induced by addition of cyclohexene as halogen scavenger.[302]



26

Acyclic triphosphenium ion $[Ph_3P\text{–}P^{(+)}\text{–}PPh_3]$ reacts with more basic phosphanes R_3P via ligand exchange to give unsymmetric and symmetric acyclic cations $[R_3P\text{–}P^{(+)}\text{–}PPh_3]$ and $[R_3P\text{–}P^{(+)}\text{–}PR_3]$[294]; by analogy, bi- or tetradentate phosphanes yield cyclic[289] or spirocyclic triphospheniumions.[303] The synthetic utility of this approach is somewhat restricted by the occurrence of side reactions which may preclude product isolation.[294,303] Phosphane replacement in reactions between triphosphenium cations and tetraaminoalkenes[304] or N-heterocyclic carbenes[298] enables the synthesis of phosphamethine cyanine cations[11] (eqn [27]). Considering that phosphamethine cyanines are conventionally prepared from iminium chlorides and a masked PH_3 source such as $P(CH_2OH)_3$ or $P(SiMe_3)_3$, these results indicate that these cations may likewise exhibit a dichotomy between P(I) and multiply bonded P(III) species which are discussed further in Section 1.20.5.2.



X = I, PHh_4; R^1 = alkyl; R^2 = H, Me

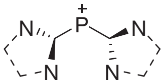
27

1.20.5.2 Physical Properties, Structure, and Bonding

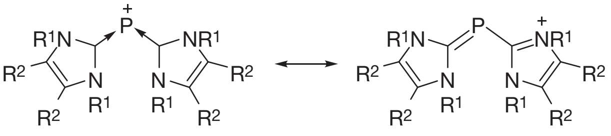
Crystal structure studies of tripnictogenium cations reveal rather short bonds between the central and ligating pnictogen atoms (P–P bonds in P–P–P frameworks 2.10–2.13 Å, As–P bonds in P–As–P frameworks 2.24–2.27 Å[9]) which are intermediate between single- and double-bond distances. Bond angles at the di-coordinate central atoms are very acute (P–P–P 86–106°, P–As–P 85–93°[9]), which owes presumably in part to the constraints of the cyclic framework of many specimens. Phosphorus(I)–carbene adducts (phosphamethine cyanines) exhibit P–C bonds that are only little shorter than single bonds (1.75–1.82 Å[9,298]), and display a pronounced twisting of the coordination planes of the two carbon atoms in the terminal carbene units with respect to the central C–P–C plane (torsion angles 50–60°,[298] see Scheme 37). As this torsion diminishes the π-overlap between the filled p-orbital at the central atom and the formally empty p-orbitals at the carbene C-atoms, the observed structures were perceived as carbene-stabilized phosphorus(I) compounds **135a** rather than genuine multiple bond systems **135b** (Scheme 38).[9]

Spectroscopic studies of donor-stabilized pnictogen(I) cations focused very much on ^{31}P NMR investigations of phosphorus-containing species. The coordination shifts of the donating P-atoms in triphosphenium ions and the homologs containing As(I) are positive in the case of alkyl/aryl phosphanes but negative for ligands containing P–N or P–O bonds (a compilation of chemical shift data is given by Ellis and Macdonald[9]). The signals of central P(I) atoms in triphosphenium cations are further strongly shielded ($\delta^{31}P = -160$ to -290 ppm[9]) and exhibit large $^1J_{PP}$ couplings (330–510 Hz). The ^{31}P NMR signals of phosphamethine cyanines are less shielded and depend more strongly on the substituents ($\delta^{31}P = -120$ to 155[9,11]). Tripnictogenium cations are mostly colorless or at best weakly colored, and no systematic exploration of electronic spectra seems to have been performed. Phospha- and arsamethine cyanines – in particular those containing extended π-systems in the carbene units – show a strong absorption band in the visible region ($\lambda_{max}=490$–650 nm with $\varepsilon_{max}=3$–5×10^4 l mol^{-1} cm^{-1} for As- and $\lambda_{max}=420$–570 nm with $\varepsilon_{max}=3$–4×10^4 l mol^{-1} cm^{-1} for P-containing compounds; see Ellis and Macdonald[9] and Slootweg and Lammertsma[11] for more detailed data compilations) and have been investigated for their properties as dyes.

Computational studies on triphosphenium and analogous amine-stabilized phosphorus(I) cations[299,300] confirm the presence of short single bonds and bent coordination of the central atom that had been observed in the crystallographic studies. The computed LUMO energies of model compounds $[(H_3N)_2P]^+$ and $[(H_3P)_2P]^+$ are similar but the HOMO of the phosphane adduct receives substantial stabilization from π-interaction between the $3p_x$-orbital at the central phosphorus atom and σ*(PH) antibonding orbitals of the PH_3 units. This back-donation reduces the electron population of the $3p_x$-orbital and is seen as a major prerequisite for the increased stability of triphosphenium ions with respect to the still unknown P(I)-amine complexes.[9] DFT calculations on bis-NHC-substituted phosphorus(I) cations at the B3PW91 level[298] reproduce the experimentally observed, twisted arrangement of the carbene units with respect to the central C–P–C plane and show that a coplanar arrangement of carbene ligands in the plane of the central C–P–C framework with C_{2v} symmetry is no minimum on the potential energy hypersurface. Moreover, calculated P–C bond lengths are only marginally smaller than P–C single-bond distances. At the same time, population analyses reveal substantial back bonding from the occupied $3p_x$-orbital on phosphorus into π*-type orbitals on the carbene units which induces a sizable amount of π-electron delocalization and explains the dye-like properties of these species.[9,298] Interpretation of the computational results led to the conclusion[9] that the model of phosphorus(I)–Lewis donor complexes provides the most accurate and most appropriate description for both triphosphenium ions and phosphamethine cyanines, but that an important contribution from ylide (triphosphenium ions) or multiply bonded (phosphamethine cyanine) structures containing trivalent phosphorus atoms cannot be neglected. As a consequence, the cationic species are addressed as hybrids between P(III) and P(I) compounds, thus underlining the problems[9] arising with the assignment of defined oxidation states in the presence of strong covalent bonding contributions in these compounds.



Scheme 37 Twisted structures of phosphorus(I)-carbene adducts.



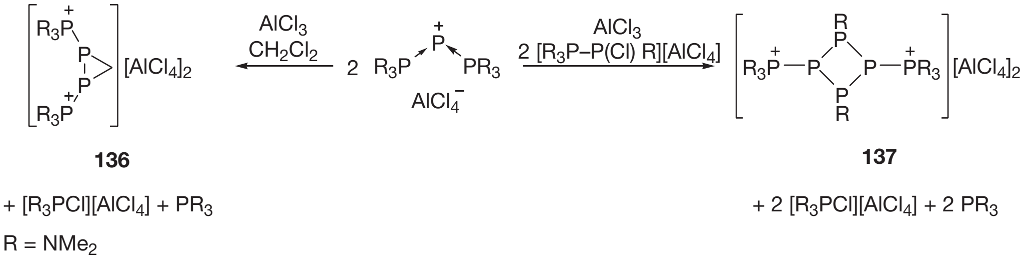
135a **135b**

Scheme 38 Leading anonical structures for carbene-stabilized P(I)-compounds.

1.20.5.3 Reactivity

Although triphosphenium and related arsenium cations are generally prepared under inert atmosphere, some of the products are air stable.[288,292] In contrast, the salt [(dppe)As]I reacts with atmospheric oxygen to give the isolable product $[Ph_2P(O)CH_2CH_2P^+(OH)Ph_2][As_6I_8]$.[292] Reactions of acyclic tripnictogenium cations with neutral nucleophiles have already been discussed in the context of the synthesis of tripnictogenium cations via ligand metathesis (**Section 1.20.5.1**) and are considered to highlight the character of the cations as donor-stabilized pnictogen(I) derivatives[9] (although an alternative interpretation as ylide transfer reactions is also conceivable). Similar displacement of a ligating phosphane occurs in reactions of triphosphenium cations with anionic nucleophiles X^- (e.g., X^-=chloride, cyanide, and phosphides)[4,291]; the formed neutral phosphinylidene phosphoranes of the type X–$P\leftarrow PR_3$ lose, more or less easily, the remaining phosphane to give insoluble materials which have not been characterized (a rationale for this behavior becomes feasible by considering phosphinylidene phosphoranes as phosphane complexes of phosphinidenes, see Section 1.20.4.1.2.1).

Despite their positive charge, triphospheniumions behave also as nucleophiles that are protonated/alkylated at the low-valent pnictogen atom (acyclic derivatives more readily than cyclic ones) by reaction with HCl, HOTf, ^{t}BuCl/$AlCl_3$, or MeOTf.[290,305,306] Amino-substituted triphosphenium ions react with a combination of $AlCl_3$ and a second electrophile such as CH_2Cl_2 or the in situ formed complex $[Me_2NP(Cl)$–$PPh_3]^+$ as source of a cationic $[R_3P$–$P]^+$ moiety to give phosphonio-substituted three- or four-membered heterocycles **136**, **137** (**Scheme 39**).[291,307] A well-defined reaction of both P(I)- and As(I)-containing tripnictogenium cations is their reaction with an excess of Schwartz's reagent $[(Cp_2ZrHCl)_4]$



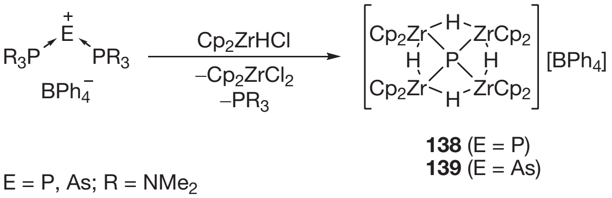
136 **137**

+ $[R_3PCl][AlCl_4]$ + PR_3

R = NMe_2

+ 2 $[R_3PCl][AlCl_4]$ + 2 PR_3

Scheme 39 Reactions of a triphosphenium ion with electrophiles.



138 (E = P)
139 (E = As)

Scheme 40 Reaction of tripnictogenium ions with Schwartz's reagent.

to give cations **138**, **139** with a planar tetracoordinate pnictogen atom (**Scheme 40**).[295,308] Whereas the reaction of the triphosphenium ion to give **138** is straightforward, the As(I)-containing tripnictogenium ion yields, quite surprisingly, a mixture of 'both' **138** and **139**, indicating the occurrence of a redox reaction, the mechanism of which is still unknown.[296]

1.20.6 Conclusion

The chemistry of low coordinate compounds of group-15 elements has seen a tremendous development during the last few decades. This progress is intimately connected with the advances in both experimental techniques, which provided tools to generate and handle increasingly labile and reactive species, and computational chemistry, which was indispensable for establishing a rational understanding of physical properties and reactivities.

The chemistry of pnictogenium cations $[R_2E]^+$ and pnictinidenes [RE] has meanwhile reached a certain maturity. Pnictogenium ions of all heavier group-15 elements have been accessed as isolable species by various synthetic routes. They exhibit singlet ground states, and their reactivity is controlled by a pronounced electrophilic character which allows them to form complexes with Lewis-bases and electron rich transition metal fragments with sufficient back-donation capability to support retro-dative M→E dative bonds. Phosphenium ions exhibit also some lingering nucleophilic character which makes them ambiphiles that can undergo typical carbene-like reactions like oxidative addition or bond insertion. Pnictinidenes still remain transient molecules which have generally triplet ground states. Detailed studies have so far mainly focused on phosphorus-containing species, and allowed to establish that the singlet-triplet energy gap can be controlled by intramolecular p-donation or complexation by external Lewis-bases or/and transition metals. Free phosphinidenes exhibit (like all pnictinidenes) strong s-donor and p-acceptor qualities and must be considered ambiphiles. Coordinated phosphinidenes may show electrophilic or nucleophilic character depending on how their "philicity" is mediated by intramolecular interactions. The taming of the electrophilic character seems to be crucial to obtain isolable compounds; accordingly, stable nucleophilic phosphinidene transition metal complexes and Lewis-donor adducts have been prepared, whereas electrophilic phosphinidene complexes still remain elusive transient species. The reactivity of triplet phosphinidenes is erratic. Electrophilic singlet phosphinidene derivatives undergo predominantly oxidative addition processes like [n+1]-cycloaddition and bond insertion. Nucleophilic phosphinidene complexes react predominantly under metathesis and transfer of the phosphinidene unit to another substrate, cycloaddition to the P═M double bond, or insertion into the M═P bond, and behave in many cases as synthetic equivalent of $[RP^{2-}]$ dianions. Both pnictogenium cations and electrophilic and nucleophilic phosphinidene derivatives find various uses in heterocycle synthesis. In addition, the first applications in catalysis have been reported. It is envisaged that further exploration of these areas as well as widening the focus on the chemistry of complexes of higher pnictidenes will have great prospect for future developments.

In contrast, the chemistry of donor stabilized pnictogen(I) cations $[L{\rightarrow}E{\leftarrow}L]^+$ is still in its early stages. Although species of this type have been known for some time, their perception was long veiled by the possibility of a description as ylidic pnictogen(III) rather than pnictogen(I) species. The recently renewed recognition of this area is closely connected with the introduction of *N*-heterocyclic carbenes as new type of stabilizing ligands and has led to sharpen the profile of appropriate phosphorus- and arsenic-containing derivatives as coordination compounds of low-valent main-group elements. It remains to be seen which impact the intentional future development of this chemistry will have. For related chapters in this Comprehensive, we refer to **Chapters 1.05**, **2.05**, and **2.06**.

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1.21 Low-Coordinate Main Group Compounds – Group 16

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Nomenclature

AACVD	Aerosol-assisted chemical vapor deposition
Ad	Adamantyl
BDTA	Benzodithiazolyl
BIAN	Bisiminoacenaphthene
Bipy	2,2′-Bipyridine
Ch	Chalcogen; group 16 element (O, S, Se, Te, Po)
CV	Cyclic voltammetry
DAB	Diazabutadiene
DCM	Dichloromethane
DFT	Density functional theory
DIMPY	2,6-Diiminopyridine
Dipp	2,6-Diisopropylphenyl
4-DMAP	4-Dimethylaminopyridine
DMP	2,6-Dimethylphenyl
dtc	Diethyldithiocarbamate
DTDA	1,2,3,5-Dithiadiazoyl
EPR	Electron paramagnetic resonance
GPx	Glutathione peroxidase
^{i}Pr	*iso*-Propyl
***m*CPBA**	*meta*-Chloroperbenzoic acid
MBDTA	Methylbenzodithiazolyl
MeCN	Acetonitrile
Mes	2,4,6-Trimethylphenyl
^{n}Bu	*n*-Butyl
NHC	*N*-Heterocyclic carbene, R_2IM
NMR	Nuclear magnetic resonance
OTf	Trifluoromethanesulfonate
SEEPR	Simultaneous electrochemical electron paramagnetic resonance
SQUID	Superconducting quantum interference device
^{t}Bu	*tert*-Butyl
T_C	Ferromagnetic ordering temperature
THF	Tetrahyrdrofuran
TIP	Tetrakis(imino)pyracene
TMEDA	Tetramethylethylenediamine
TMS	Trimethylsilyl
tmtu	Tetramethylthiourea
tu	Thiourea
UV–vis	Ultraviolet–visible
VSEPR	Valence shell electron pair repulsion
XRD	X-ray diffraction

1.21.1 Introduction

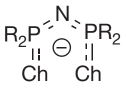
The low-valent chemistry of the group 16 elements (the chalcogens; Ch = O, S, Se, Te, and Po) has witnessed continuous expansion over the past several decades. Typically thought of as being electron rich, these electronegative elements are usually found in functional groups of organic molecules and/or as electron donors for transition metals. While there is presently new and interesting chemistry with these more traditional areas of group 16, a new realm of electrophilic and polycationic chalcogen chemistry has also begun to develop.

1.21.2 Dichalcogenido Imidodiphosphinates

1.21.2.1 Introduction and Synthesis

The chemistry of dichalcogenido imidophosphinates $[N(PR_2Ch)_2]^-$ (**1Ch**) has a long history and is still continuing to progress. Since their discovery in the 1960s,[1–3] the oxygen, sulfur, and selenium derivatives have been extensively studied (**Figure 1**).[4,5]

The resulting metal complexes have found use in several applications, including nuclear magnetic resonance (NMR) shift reagents, luminescent complexes in photonic devices or in metal extraction processes.[6] However, it is the recent discovery of the use of certain metal complexes of $[N(P^iPr_2Se)_2]^-$ as single-source precursors for the production of thin semiconducting binary selenide films that has revitalized the use of these materials.[7–10] The synthesis of these compounds is readily performed either by adding elemental chalcogen to the neutral amine ($HN(PR_2)_2$) (Ch = S, Se)[11,12] followed by deprotonation or by generating the anion $[N(PR_2)_2]^-$ prior to the addition of chalcogen metal (Ch = Te)[13,14] (**Scheme 1**). The protocol can also be adapted to synthesize the mixed chalcogen ligands.[15]



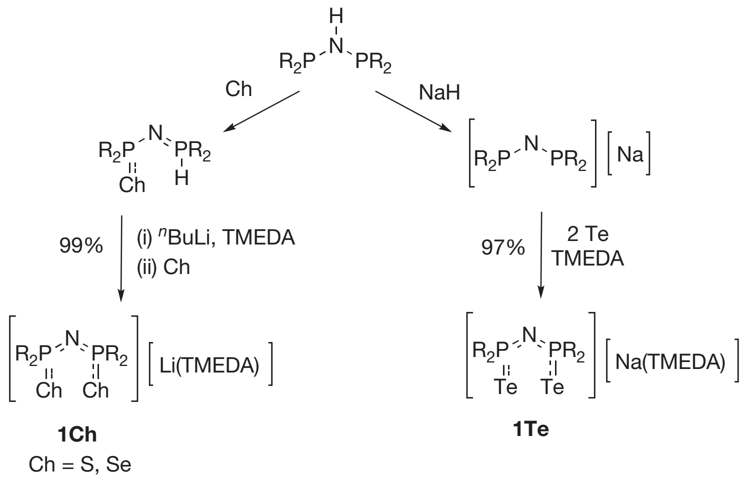
1Ch

Ch = O, S, Se, Te
R = alkyl, aryl

Figure 1 The general structure of the dichalcogenido imidophosphinate ligand, **1Ch**.

1.21.2.2 Redox Behavior

Chivers et al. have investigated the redox behavior of these types of ligands thoroughly in a series of publications. The one-electron oxidation of the sodium salts of $[N(PR_2Ch)_2]^-$ (Ch = S, Se, Te; R = ^{i}Pr, ^{t}Bu) with I_2 results in dimers in the form of either dichalcogenides (**2Ch**) or spirocyclic contact ion pairs (**5Ch**, **6Ch**) (**Figure 2**).[16,17] Interestingly, the dichalcogenide with a Te–Te bond (**3**,**4**) is formed exclusively after the one-electron reduction of the mixed cation $[N(P^iPr_2Te)(P^iPr_2Ch)]^+$ (Ch = S and Se) with cobaltocene.[18] The solid-state structures exhibit slightly elongated Ch–Ch bonds, consistent with density functional theory (DFT) calculations performed on the model compounds. The two-electron oxidation of $[N(PR_2Ch)_2]^-$ (Ch = S, Se, Te; R = ^{i}Pr, ^{t}Bu) with I_2 readily results in the generation of a cyclic cationic five-membered ring (**7Ch**, **8**, **9**).[18,19] It was found that the substituent on the phosphorus center plays a role in the three-dimensional (3D) structure of the compound. For example, when R = ^{t}Bu, the sulfur derivative is an ion-separated monomer in the solid state with an I_3^- anion while the selenium and tellurium



Scheme 1 The synthesis and structure of dichalcogenido imidophosphinate ligands.

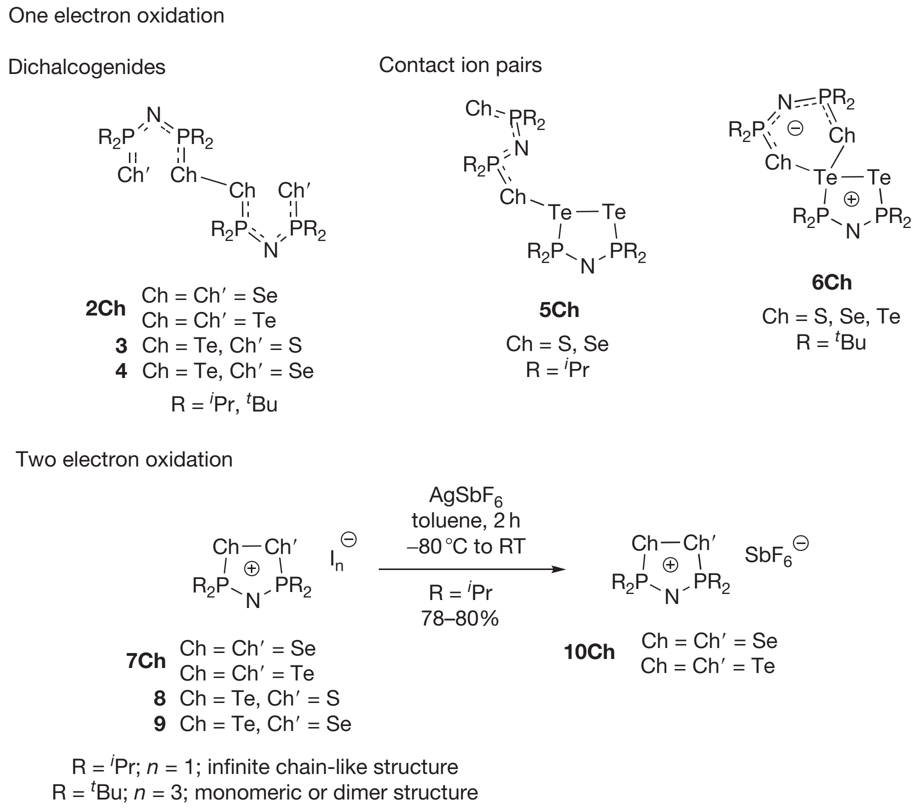


Figure 2 Products resulting from the one-electron or two-electron redox activity of the dichalcogenido imidophosphinate ligands.

analogs form dimers with close Ch–Ch contacts. When R = ^{i}Pr, the iodide anion interacts with one of the chalcogen centers to form an infinite chain-like structure. Anion exchange can also be performed with $AgSbF_6$ to eliminate the chalcogen halide interactions and form **10Ch**.[20]

1.21.2.3 Coordination Chemistry

The coordination chemistry of **1Te** exhibits some significant differences from the sulfur and selenium derivatives. The discussion of this section focuses on the tellurium analogs as a majority of them have been prepared since 2005 while the other chalcogen species have been covered previously.[4,5] Transition metal, lanthanide, actinide, and main group halides are ideal precursors for the metathesis reaction with the anionic ligand to form the homoleptic metal complexes $M[N(P^iPr_2Te)_2]_n$.[21] The various structures of the ligand coordinated to the metal center are summarized in Figure 3. Different geometries are observed based on the metal center, for example, the group 10 metals form square planar geometries

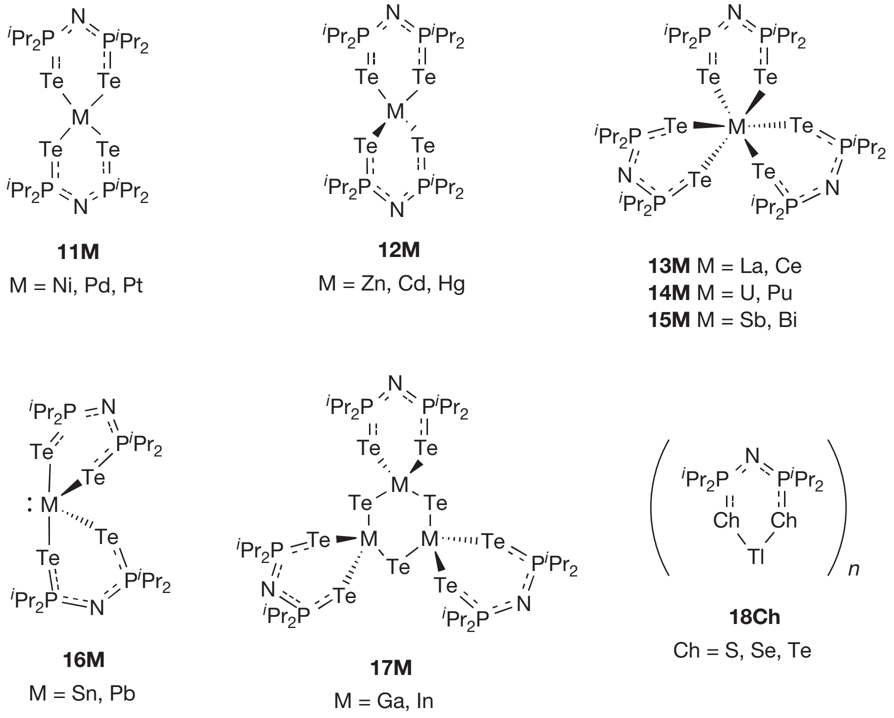


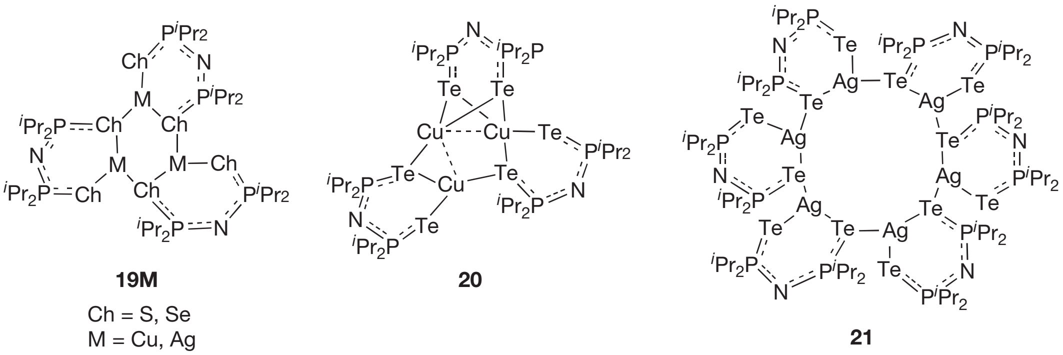
Figure 3 The different coordination geometries of metals complexed by $[N(P^{i}Pr_2Te)_2]$.

about the metal center (**11M**, M = Ni, Pd, and Pt, *n* = 2).[22–24] Noteworthy is that the related mixed dichalcogenide group 10 metal complexes $M[N(P^{i}Pr_2Te)(P^{i}Pr_2Ch)]_2$ (M = Ni, Pd, and Pt; Ch = S and Se) exist in the *trans*-conformation for Ni, but a mixture of the *cis*- and *trans*-isomers is observed in solution for Pd and Pt. Distorted tetrahedral geometries are observed for group 12 transition metals (**12M**, M = Zn, Cd, and Hg; *n* = 2),[25] while distorted octahedral geometries are observed for representative lanthanides (**13M**, M = La and Ce, *n* = 3), actinides (**14M**, M = U, and Pu, *n* = 3),[26,27] and heavy group 15 elements (**15M**, M = Sb and Bi, *n* = 3).[25] Group 14 complexes (**16M**, M = Sn and Pb, *n* = 2) adopt a pseudo-trigonal bipyramidal geometry, consistent with an AX_4E configuration, reflecting the stereochemical influence of a lone pair of electrons on the metal.[28] The group 13 elements exhibit interesting reactivity in the fact that reaction of GaI or InCl with $(TMEDA)[Na][N(P^{i}Pr_2Te)_2]$ results in complex mixtures. However, adding elemental tellurium to the reaction mixture results in the formation of heteroleptic complexes (**17M**, M = Ga and In) with one **1Te** bound to each metal in a central M_3Te_3 ring.[29] The reaction of TlOEt with tetramethylethylenediamine $(TMEDA)[Na][N(P^{i}Pr_2Ch)_2]$ (Ch = S, Se, Te) results in the formation of coordination polymers (**18Ch**).[30] For the tellurium species (**18Te**), the structure possesses six-coordinate thallium centers bridged with two ligands almost perpendicular to each other. The selenium derivative (**18Se**) has a similar structure with both five- and six-coordinate thallium centers while the sulfur analog (**18S**) has four-coordinate thallium centers in a ladder-like polymer. It should be noted that this chemistry generally proceeds very cleanly and that the products are all isolated in good yields.

Coinage metals also exhibit interesting structural differences (Figure 4), mostly as a result of the tendency of **1Te** to adopt a doubly bridging bonding arrangement.[31] This is observed using copper where **1S** and **1Se** behave as singly bridging ligands and the three copper atoms form an equilateral triangle (**19Cu**),[32,33] while with **1Te** the copper complex (**20**)[31] has two short (2.63 Å) and one long (3.58 Å) Cu–Cu bond. The silver complex with **1Te** forms a hexameric structure (**21**)[31] comprised of an Ag_6Te_6 ring while the selenium analog is trimeric (**19Ag**).[33] The substituents on phosphorus can also cause dramatic changes to the structure. For example, simple variation of the ^{i}Pr groups to Ph groups results in a tetrameric structure with an Ag_4Te_4 ring and a doubly bridged ligand causing a short transannular Ag–Ag contact.[31]

1.21.2.4 As Single-Source Precursors for Thin Films

Several of these molecules have also been employed as single-source precursors for binary metal tellurides – compounds that have potential in low-band-gap semiconducting materials, thermoelectric devices, and telecommunication.[34] The library of metal complexes was tested by aerosol-assisted chemical vapor deposition (AACVD) procedures to determine if these compounds were suitable for the formation of thin films. The reactions to form CdTe,[35] Sb_2Te_3,[36] In_2Te_3,[37] PbTe,[28] and $NiTe_2$[22,38] were successful under the proper conditions while some of the other complexes were unsuccessful and resulted in the deposition of elemental tellurium. Nevertheless, this class of compounds demonstrates real utility in material applications and continues to be investigated in this regard.



19M

Ch = S, Se
M = Cu, Ag

20

21

Figure 4 The structural differences of **1Te** in comparison to **1S** and **1Se** with regard to the coinage metals.

1.21.2.5 Isoelectronic Carbon-Bridged Analogs

The isoelectronic carbon-bridged derivative $[C(PPh_2S)_2]^{2-}$ (**22**) has also been investigated in conjunction with the chalcogens. Le Floch et al. prepared the dilithiated salt in 2004,[39] which has served as an excellent reagent to undergo metathesis with a variety of metals (Pd, Ru, Zr, Tm, Sm, and U) and main group halides (Ge, Sn, and Pb).[40–47] The common mode of binding to the metal center is through S,C,S′ chelation and noticeably strong interaction from the carbene.[48] The treatment of **22** with mild oxidizing agents produces either monomeric (**23**) or dimeric carbenoids (**24**).[49,50] The carbene center has also been shown to have nucleophilic character in the reaction with CS_2 to give $[S_2C{=}C(PPh_2S)_2]^{2-}$ (**25**).[51] The same researchers also reported the clean synthesis of $Ph_2C{=}C(PPh_2S)_2$ (**26**) from the reaction of benzophenone with the Sm, Tm, or Zr metal complexes.[40,43,44] The isolation of **26** also demonstrates the nucleophilic character at carbon and this product could not be isolated from the dilithiated salt **22**. While the isoelectronic diseleno monoanion (**27**) was first prepared in 1971 and metal complexes were formed in situ,[52] an efficient synthesis was not reported until 2009.[53] Reactions with $ZnCl_2$ and $HgCl_2$ form the homoleptic metal complexes (**28M**),[53] while reactions with $SnCl_2$ and a $TeCl_2$ source in a 1:2 ratio form oxidized homoleptic metal(IV) complexes, **29** and **30**, of the triselenodianion $[SeC(PPh_2Se)_2]^{2-}$.[54] The redox behavior of these unusual dianions (**31** Ch = S and Se) has also been recently investigated. The one-electron oxidation with I_2 results in the formation of dimers (**33**) of the corresponding anion radicals (**32**).[55,56] The protonated monoanion (**34**) is generated either by the further oxidation with iodine (Ch = S), or simply by leaving the dianion in solution (tetrahydrofuran (THF), CH_2Cl_2, and CH_3CN) or reacting with 12-crown-4 (Ch = Se; Figure 5).[57] The nature of the few metal complexes already characterized as well as their redox chemistry suggests that prosperous coordination chemistry for these ligands is in store.

1.21.3 Phosphorus–Selenium Heterocycles

1.21.3.1 Synthesis

Woollins reagent (**35**), which is analogous to Lawesson's reagent (**36**), was first synthesized in 1988 by the treatment of homocyclic phosphorus pentamers $(PPh)_5$ with ten stoichiometric equivalents of elemental selenium.[58–60] A new synthesis from $PhPCl_2$ and Na_2Se in liquid ammonia allows for the clean large-scale production, *ca.* 150 g, in better yield than the original method (Scheme 2).[61] The compound is now commercially available so any researcher can utilize the chemistry this reagent provides.

1.21.3.2 Reactivity

The primary use of these compounds is the selenation or thiolation of organic electrophiles (Scheme 3). While **36** has been studied for some time and its reactivity is well understood,[62] **35** is continuously demonstrating novel chemistry. For example, **35** will undergo selenation reactions to form selenoketenyl (**36**),[63] selenoamides (**37**),[64] selenoaldehydes (**38**),[65] and selenoacetic acids (**40**).[66,67]

Furthermore, novel phosphorus–selenium heterocycles can be formed by treatment of **35** with unsaturated substrates such as alkenes, alkynes,[68–71] and cyanamides[72] or dibasic nucleophiles (Scheme 4).[73] However, multiple products are often observed and need to be separated. The nature of the products varied greatly with the substituents on the organic substrate, unfortunately with no obvious trend. On the contrary, it does provide countless possibilities.

Unique, large rings with diselenide linkages (Figure 6) have been formed from the reaction of **35** and simple organic substrates (diols for **46** and **47**,[74] and dichloromethane for **48**)[75] in the presence of primary or secondary amines. The utility of **35**, which has recently been reviewed,[76] will continue to expand for both the transformation of organic substrates as well as preparation of inorganic heterocycles.

1.21.4 Chalcogen Diimides

1.21.4.1 Selenium: Synthesis and Coordination Chemistry

The coordination chemistry of chalcogen diimides has a rich history and is still expanding. While the stable monomeric sulfur derivatives (**49**) have long been known to bind to a number of transition metals in different bonding modes, the selenium and tellurium analogs have seen slower development (Figure 7).[77,78] The first example of a selenium diimide (**50^{t}Bu**), $(Se(N^tBu)_2)$, was reported by Sharpless et al. in 1976;[79] however, structural characterization was not obtained as the compound decomposes at room temperature to give a six-membered ring $(SeN^tBu)_3$ among other products.[80]

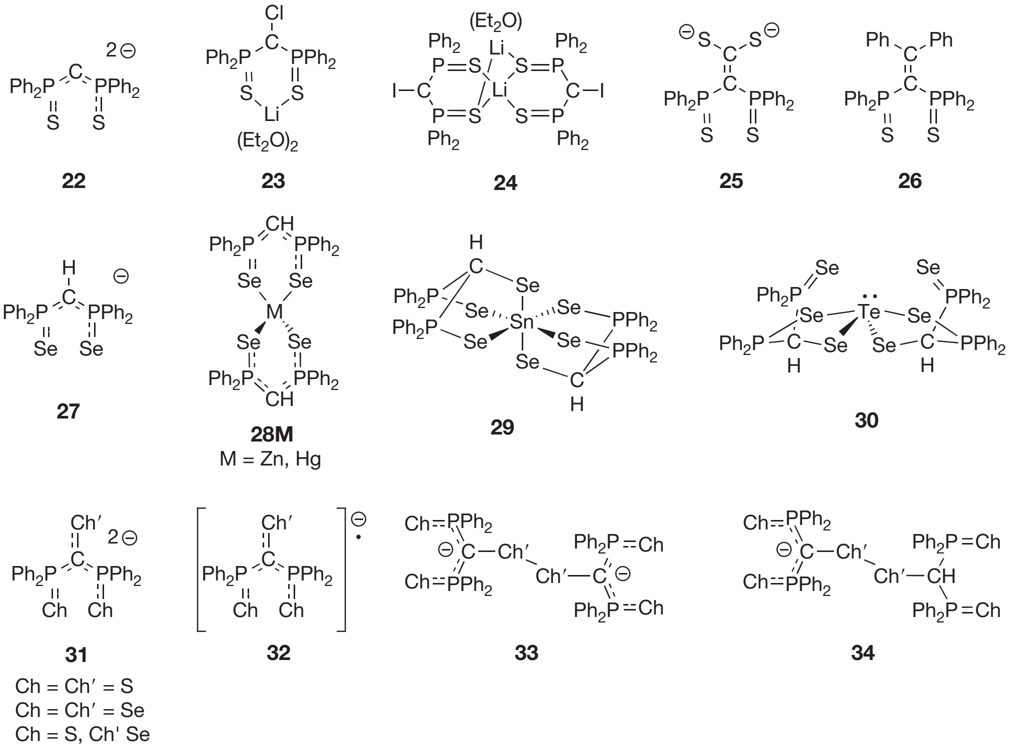
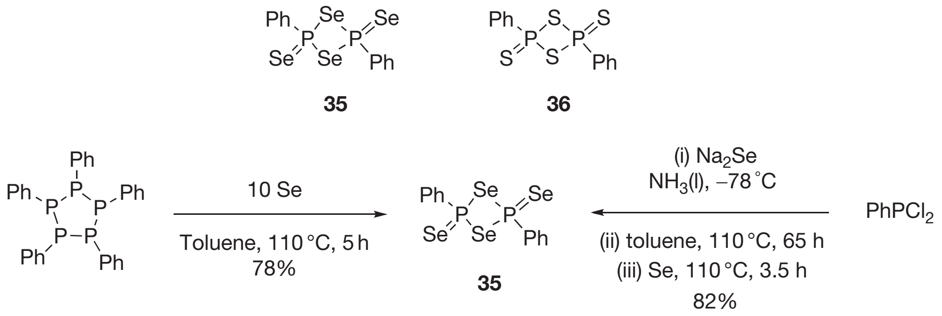
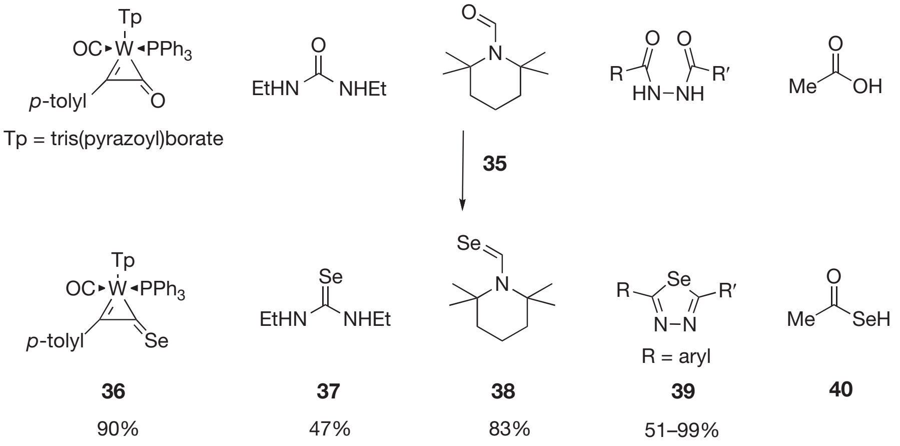


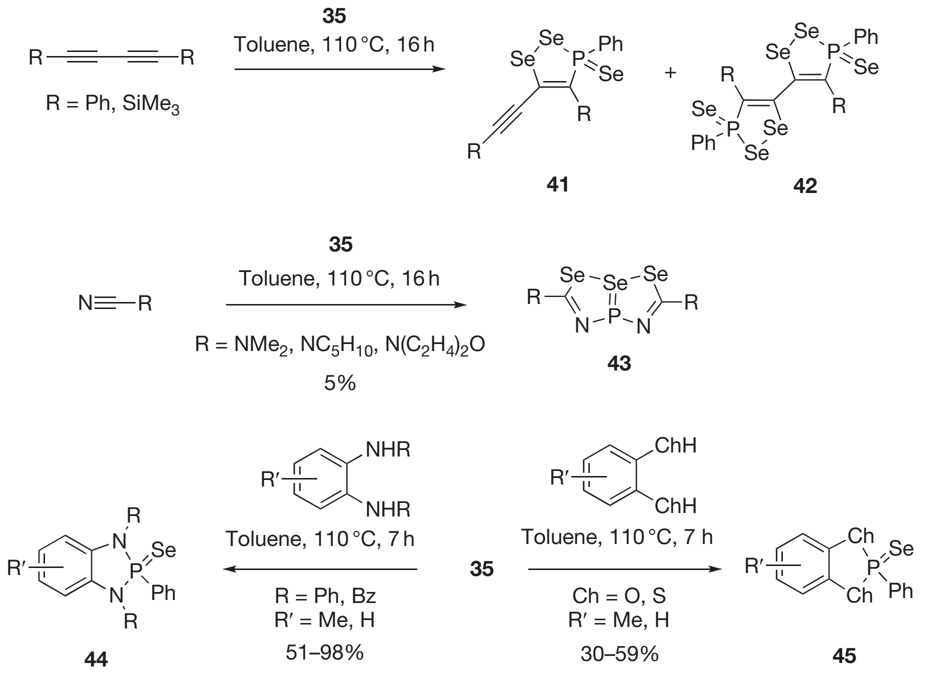
Figure 5 Structures of dichalcogeno carbophosphinate ligands, **22** and **27**, examples of metal complexes, and products of redox chemistry.



Scheme 2 The structure of Woollins reagent **35**, Lawesson's reagent **36**, and the two synthetic procedures to prepare **35**.



Scheme 3 Selenation of various organic functional groups using **35**.



Scheme 4 Sampling of reactions of **35** with unsaturated substrates and dibasic nucleophiles.

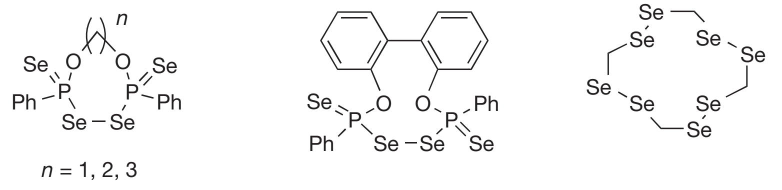


Figure 6 Examples of large ring systems obtained from **35**.

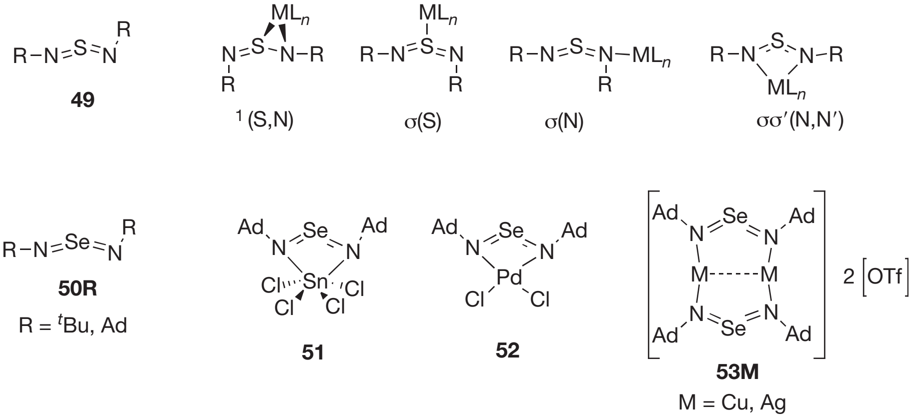


Figure 7 The structure of sulfur diimides (**49**) in various bonding modes, the selenium diimide (**50R**), and the structure of its coordination complexes (**51–53M**).

In 2002, Chivers et al. reported the solid-state structure of the adamantyl derivative, **50Ad**, which possesses a *Z*,*E*-configuration in the solid state.[81] The compound was prepared by treating SeCl$_4$ with AdNHLi in THF at −78 °C, where excess AdNHLi is needed to deprotonate the amine and form the chalcogen diimide. The Se–N bond lengths are significantly different at 1.68 and 1.73 Å, which is slightly longer than the predicted double bond length of 1.65 Å. Coordination complexes were formed using **50Ad** with different late transition-metal centers and it was found that the nature of the ligand depends on the metal. For example, the reaction of **50Ad** with $PdCl_2(NCPh)_2$ or $SnCl_4$ results in the monomeric N,N′ chelate (**51**, **52**)[82,83] while reaction with AgOTf and CuOTf results in a dimer (**53M**)[84] with a metal–metal interaction. The chloride-bridged cobalt dimer was also prepared.[85]

1.21.4.2 Tellurium: Synthesis and Coordination Chemistry

While the lighter chalcogen diimides are monomeric in the solid state and in solution, the tellurium analog (**54^{t}Bu**) exists as a dimer with a Te_2N_2 ring and two exocyclic Te–N bonds (**Figure 8**).[86] Investigation of the solid-state structure reveals Te–N bond lengths of 2.08 Å in the ring core and 1.88 Å for the diimide bonds. The ^{t}Bu groups are in the *cis*-orientation with respect to the ring. The related species with adamantyl groups, **54Ad**, was observed to exist in the *trans*-conformation in the solid state, showing that the geometry of the major product can be adjusted by the substituents on nitrogen. Metal complexes that display versatile ligand behavior have been formed with the examples of some structures (**54**, **55**) shown in **Figure 8**.[87–89]

1.21.4.3 Reactivity

The nature of the structure (monomeric vs. dimeric) of chalcogen diimides has also been subjected to DFT calculations.[90,91] The Chivers research group has also investigated the reactivity of these novel compounds (**Figure 9**). For example, the selenium and tellurium diimides can undergo hydrolysis, and cycloaddition in the case of Se, to form chalcogen oxides (**57Ch** and **58Ch**).[80,81,91–93] The reaction of **54** with $B(C_6F_5)_3H_2O$ results in sequential hydrolysis of the exocyclic nitrogen centers to form the telluroxane Lewis acid adduct (**59**).[91,94] In a separate publication, it was shown that hydrolysis can occur at one tellurium center (**60**) and form a spirocyclic metal complex.[89] Commonly observed in the reactions to form the chalcogen diimides, several chalcogen nitrogen ring systems (**61Ch**, **62**, **63**) have been identified and characterized by multinuclear NMR studies (^{77}Se and ^{125}Te) and single-crystal X-ray diffraction experiments.[80,86,93] Lastly, it was shown that either one or both of the diimide functionalities can be replaced by halogen or alkoxide substituents, respectively.[95]

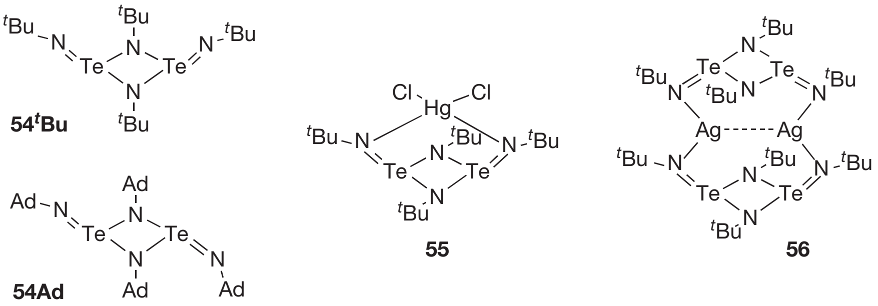


Figure 8 Structure of the tellurium diimide dimer (**54**) and two metal complexes (**55**, **56**).

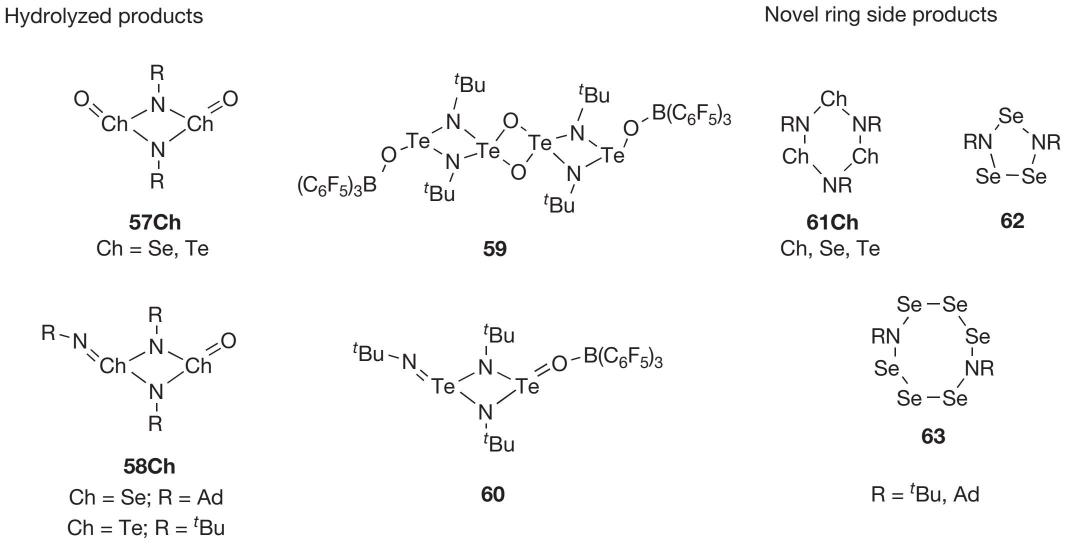


Figure 9 Select examples of other compounds formed from various chalcogen diimides.

1.21.5 Chalcogen–Nitrogen-Based Radicals

1.21.5.1 Introduction

There are several forms of chalcogen–nitrogen (Ch = S and Se)-based radicals (**Figure 10**; **64–72**), which are thought of as useful small building blocks for molecular materials (Chapter 1.14). A majority of these types of radicals have been extensively studied with several reviews on their synthesis, characterization, and electronic properties.[77,96–101] There are also numerous reports of metal complexes in the literature showing versatile binding and flexibility about the chalcogen and nitrogen atoms in the ring core.[102] A nice example of this is in the reaction of thiazyl radicals with $(Cp)Cr(CO)_3$. Two different bonding modes are observed depending on the substituents on carbon; η^1-coordination via the sulfur atom and three carbonyl groups about chromium (**73**) and η^2-coordination about sulfur and the adjacent nitrogen atom with two carbonyl group bound to chromium (**74**).[103]

1.21.5.2 Sulfur–Nitrogen-Based Radicals

The study of 1,2,3,5-dithiadiazolyl (DTDA) radicals (**65**) for use as magnetic materials has received quite a bit of attention.[104–108] Recent ultraviolet–visible (UV–VIS) studies are in agreement with electron paramagnetic resonance (EPR) experiments, which reveal a very high dimerization enthalpy (35 kJ mol^{-1}) and thus adopt a π*–π* dimer motif, which quenches the paramagnetism in the solid state.[109,110] Dimerization has been suppressed and long-range magnetic order has been observed in a small number of cases. Rawson et al. reported the synthesis of DTDA radicals with chlorinated aromatics substituted on the carbon atom (**75**, **76**).[111] The chloro–aryl groups π stack in the solid state and the superconducting quantum interference device (SQUID) magnetic measurements reveal the onset of paramagnetism above 150 °K. The EPR studies suggest two differing microscopic mechanisms for the increase in bulk paramagnetism. The π*–π* dimer breaks down in the monochlorinated derivative to generate an increasing number of radicals with $S = ½$, while the dichlorinated dimer sees a thermal population of the excited triplet state in the π*–π* dimer (**Figure 11**).

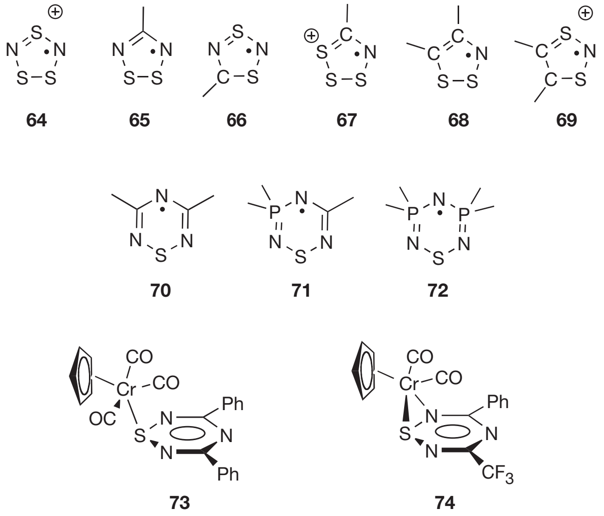


Figure 10 Examples of 7π electron sulfur nitrogen-based radicals and one recent example of a metal complex, **73** and **74**.

It was also shown by Rawson et al. that benzodithiazolyl (BDTA), **77**, and methylbenzodithiazolyl (MBDTA), **78**, radicals can be incorporated in porous hybrid frameworks by gas-phase diffusion (**Figure 12**).[112] The inclusion of thiazyl radicals in porous coordination materials had not been established previously and provides potential for communication between the radical guest and paramagnetic framework. Powder x-ray diffraction (XRD) and EPR studies are consistent with dimer motif for BDTA within the MIL53(Al) structure, while MBDTA is a monomer. The host–guest structures are stable for months and allow for modification of the BDTA radical π*–π* mode of association, resulting in an increase in sample paramagnetism. Furthermore, the radical guests can be released when desired by addition of dichloromethane to the material.

1.21.5.3 Sulfur-, Selenium-, and Nitrogen-Based Radicals

Several researchers have focused synthetic efforts on the use of highly delocalized organic systems, which possess a low value of the Mott–Hubbard onsite Coulomb potential (U) as well as the incorporation of heavy heteroatoms, which can lead to an enhanced bandwidth (W). Oakley et al. utilize the resonance-stabilized heterocycles (**Figure 13**) as highly delocalized spin systems, which display low gas-phase disproportionation energies (ΔH_{disp}) and electrochemical cell potentials (E_{cell}), indicative of a low U.

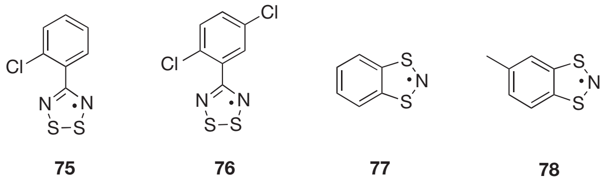


Figure 11 Structures of chlorinated aryl-substituted DTDA radicals (**75**, **76**) and structures of the BDTA radicals used for vapor diffusion into MIL53(Al) (**77**, **78**).

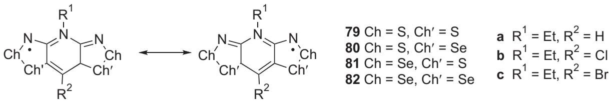
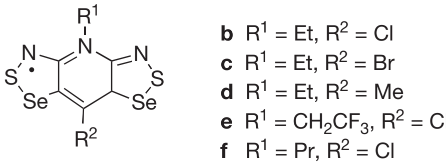


Figure 12 Structure of the highly delocalized radicals utilized by Oakley et al.



80b-f

Figure 13 The isostructural variants of **80** that show different degrees of slippage in the π-stacking and thus their radical properties.

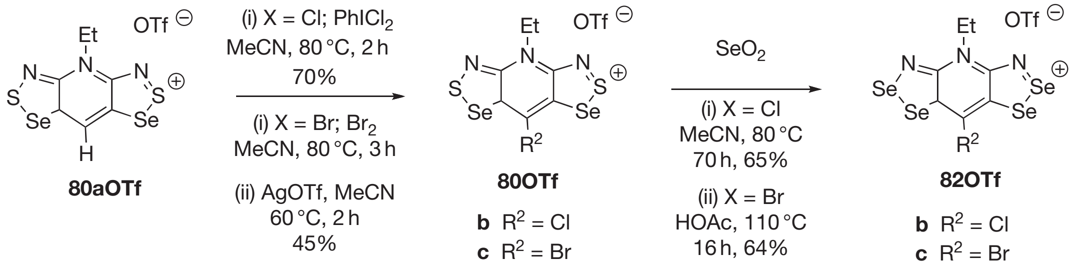
This system allows for alteration in both intermolecular magnetic and electronic interactions, either through variation of the exocyclic substituents or by replacing sulfur with its heavier congener selenium.[113–116] Incorporating selenium proved to lead not only to significant enhancements in conductivity but also to some remarkable magnetic effects. The greater spatial extension of 4p-orbitals on selenium relative to 3p-orbitals on sulfur allows for this enhancement in conductivity and performance. For example, **81a** and **82a** were observed to order as spin-canted antiferromagnets, while **80b** and **82b** were found to order as bulk ferromagnets and display coercive fields.[117–119]

Understanding of the relationship between crystal structure, electronic structure, and bulk property can allow for improvements in conductivity, ordering temperature, and coercivity.[120] Oakley et al. investigated the effect of variations in the molecular packing found for **80b**, using four isostructural variants (Figure 13), where the modification of the substituents was small enough to maintain the tetragonal space group. Two of the molecules (**80c** and **80d**) ordered as ferromagnets, while the other two (**80e** and **80f**) showed no indication of ordering above 2 K illustrating the use of chemical pressure to modify structure and properties.[121]

Furthering the strategy to invoke physical pressure, Oakley et al. showed that by applying relatively mild pressures, the crystal structure and ordering temperature of **82b** could be modified.[122] However, a decrease in ferromagnetic ordering temperature (T_C) at more elevated pressures (greater than 1 GPa) was observed, which correlates with a decrease in slippage of the π-stacking of the radical. This slippage process produces an initial increase in T_C, observed at pressures less than 1 GPa, followed by the ensuing decrease in the π-stacking interaction, which causes the intermolecular magnetic exchange. The effect of increased pressure (>5 GPa) on the crystal structure and charge transport properties of **82b** was recently investigated.[123] The synthesis of the radical precursors (**80OTf** and **82OTf**) is shown in Figure 14, and the bulk reduction using *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPDA) or octamethylferrocene affords the radicals **80b,c** and **82b,c** in excellent yields (>86%). The bromo-substituted bisdiselenazolyl **82c** is isostructural to **82b** and is a bulk ferromagnet with relatively mild compression (<5 GPa). While **82c** undergoes similar structural and magnetic changes to those observed for **82b**, the maximum T_C (24 K at 2 GPa) is higher. Interestingly, these neutral radical conductors are also the first to exhibit a pressure-induced metallization as observed by compression beyond the region where magnetic ordering is quenched, 7 GPa and 9 GPa for **82b** and **82c**, respectively (Scheme 5).[123]

1.21.5.4 Binary Sulfur–Nitrogen-Based Radicals

The unsaturated binary sulfur–nitrogen compounds are well known to undergo redox activity that cause unique structural



80aOTf

80OTf
b $R^2 = Cl$
c $R^2 = Br$

82OTf
b $R^2 = Cl$
c $R^2 = Br$

Scheme 5 Synthesis the radical precursors **80OTf** and **82OTf**.

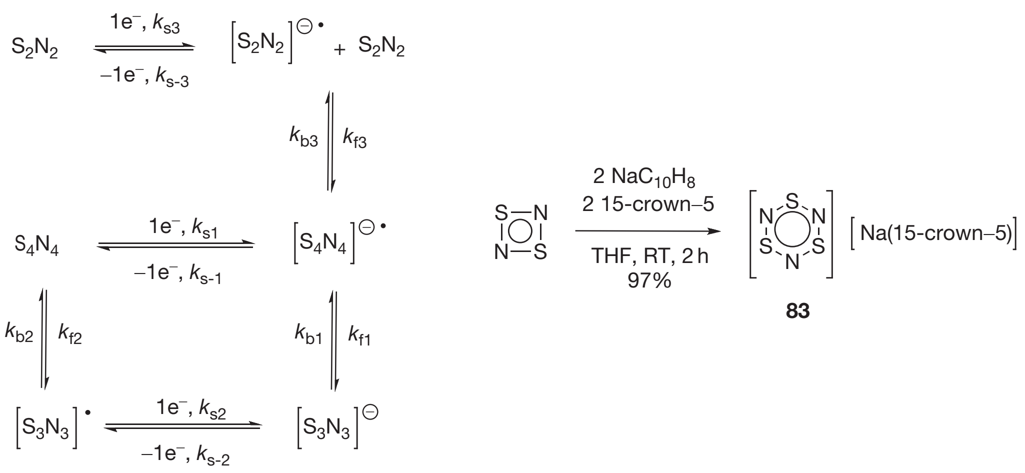


Figure 14 The proposed mechanism for the formation of $[S_3N_3]^-$ originating from S_2N_2 or S_4N_4 (left) and the chemical reduction to form the S_3N_3 anion (**83**) (right).

changes, which continue to challenge our understanding of the mechanistic pathway. While the redox chemistry of S_4N_4 has been subjected to several studies, Boerê et al. very recently applied simultaneous electrochemical electron paramagentic resonance (SEEPR) spectroscopy and modern digital simulation of the cyclic voltammetries (CVs) to this molecule.[124,125] The one-electron reduction of S_4N_4 produces $[S_3N_3]^-$ via $[S_4N_4]^-$, which was confirmed by CV studies of the salts. The mechanism was determined to fit well into a square scheme with first-order decay of both redox products. This work was supported by another publication involving the electrochemical and chemical reduction of S_2N_2, another well-studied molecule as well as a precursor to poly(sulfurnitride).[126] The one-electron reduction of S_2N_2 forms $[S_2N_2]^{-\cdot}$ which equilibrates with another S_2N_2 to form $[S_4N_4]^{-\cdot}$, an intermediate prior to the formation of $[S_3N_3]^-$. The EPR studies support this mechanism, as does the chemical reduction of S_2N_2 where the sodium crown ether salt of $[S_3N_3]^{-\cdot}$ (**83**) is formed quantitatively and structurally characterized.[126] The S_3N_3 ring is nearly planar, with only a slight distortion toward a chair conformation and also has a significant Na–N contact.

1.21.6 Chalcogen *peri*-Substituted Naphthalenes

1.21.6.1 Synthesis and Reactivity of Unsubstituted Dichalcogenoles

Double substitution in the 1- and 8-position of a naphthalene ring is known as *peri*-substitution. The ideal *peri*-distance of 2.5 Å that results from the rigid aromatic backbone causes inherent strain about the two *peri*-atoms.[127] The general preparation of the chalcogen-substituted compounds **85Ch** involves the treatment of 1,8-dilithionaphthalene with elemental chalcogen, to form **84Ch**, followed by quenching with acid in air.[128,129] Interestingly, the Ch–Ch solid-state bond lengths of **85S** (2.09 Å) and **85Se** (2.36 Å) are slightly longer than in the unconstrained disulfides (2.03 Å) and diselenides (2.29 Å) (PhChChPh), respectively.[130] This is consistent with the rigid backbone pulling the bonded *peri*-atoms away from each other and closer to the ideal *peri*-distance. Sequential lithiation and chalcogen addition of 1,8-dibromonaphthalene can controllably give all possible permutations of the mixed chalcogen species **86a–c** (Ch = S, Se, Te).[131] The dichalcogenoles can be carefully reduced to **84Ch** using $LiAlH_4$ but exposure to air for prolonged periods of time will revert them back to **85Ch** (Scheme 6).[132]

The reactivity of these species has been well documented (Scheme 7), in particular their oxidation chemistry,[133–136] typically with *m*-chloroperbenzoic acid (*m*CPBA), and substitution of the 2- and 7-position of the naphthalene ring via Friedel Crafts alkylation.[128,137] New reactivity is also being discovered, for example, **84Ch** (Ch = S and Se) or **85a** reacts with Woollins reagent, **35**, to form unique heterocycles with a Ch–P(Se)–Ch′ bonding motif (**93a–c**).[138]

1.21.6.2 Synthesis and Reactivity of Dichalcogenylnaphthalenes

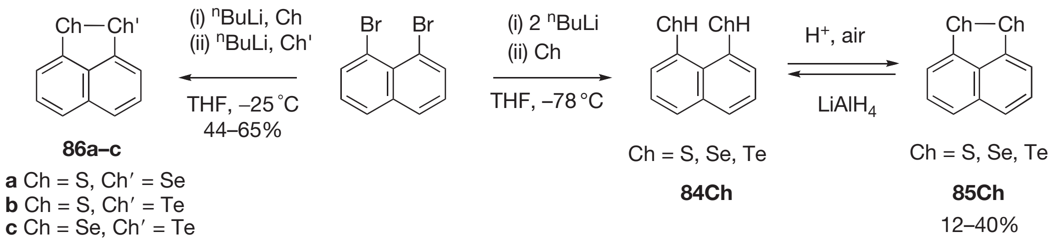
The 1,8-bis(phenylchalcogenyl)naphthalenes **94Ch** (Ch = S, Se, and Te) can be synthesized using a similar approach as outlined for **84Ch**. The TMEDA-stabilized dilithionaphthalene readily reacts with diphenyldisulfide and diphenyldiselenide to give the desired products in variable yields (Scheme 8).[139–141] The tellurium derivative can only be isolated from a dilithio-precursor that has no TMEDA present. Monolithiation/coupling reactions can be performed to prepare the mixed species (**95a–c**).[140,141] Analysis of the solid-state structures of these compounds reveals that larger chalcogen atoms in the *peri*-positions enhance the interactions of the substituents.[141] This can be rationalized by the repulsion of the bulky chalcogen atoms, which forces the naphthalene backbone to distort away from the ideal planar geometry to accommodate a longer Ch–Ch bond distance.

Treatment of the mixed chalcogen compounds **95a–c** with sulfuric acid results in a significant downfield shift in the ^{77}Se and ^{125}Te NMR resonance.[140,142] This shift is indicative of the formation of a 1,2-dication in each case (**97Ch**, **98a–c**) (Scheme 9). Similar dications of the type **99Ch** (Ch = S, Se, Te) have been extensively studied and are highlighted in a review.[143] A separate study focused on the reactions of halogens with the library of **94Ch** and **95a–c**. Diverse reactivity is observed, depending on the chalcogen and halogens atoms present, with the results summarized in Scheme 9.[128] The results of these two studies highlight the fact that this class of compounds can display uniform or very distinct reactivity. There is great tunability in this system that will allow for the functionalization of the *peri*-atoms, thus allowing for the potential of novel reactivity due to the inherent strain.[144]

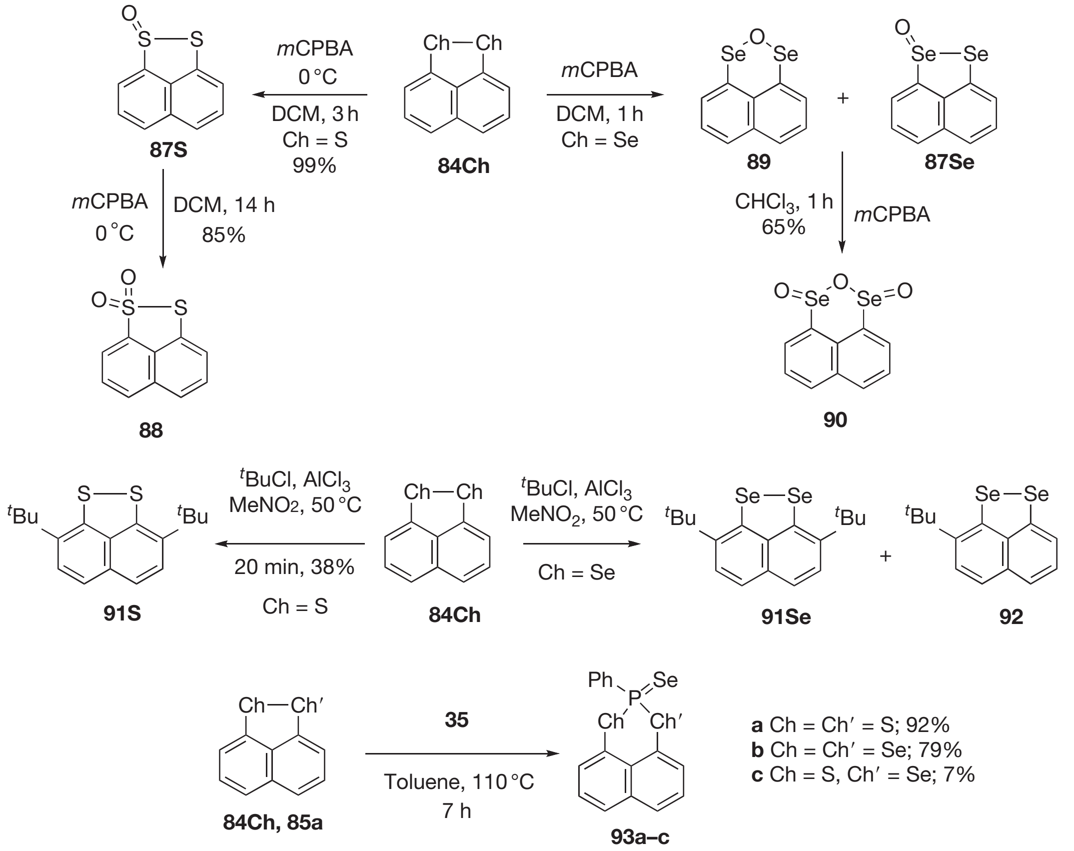
1.21.7 Organochalcogens with Intramolecular Stabilization

1.21.7.1 Introduction

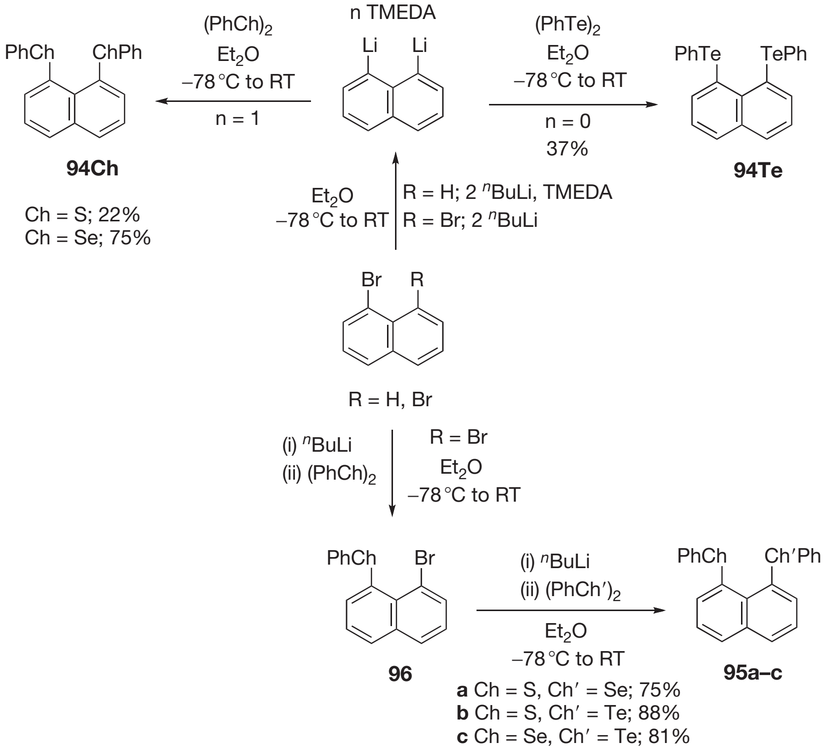
The use of adjacent donating atoms to stabilize electrophilic sulfur centers is a well-developed area of research. However,



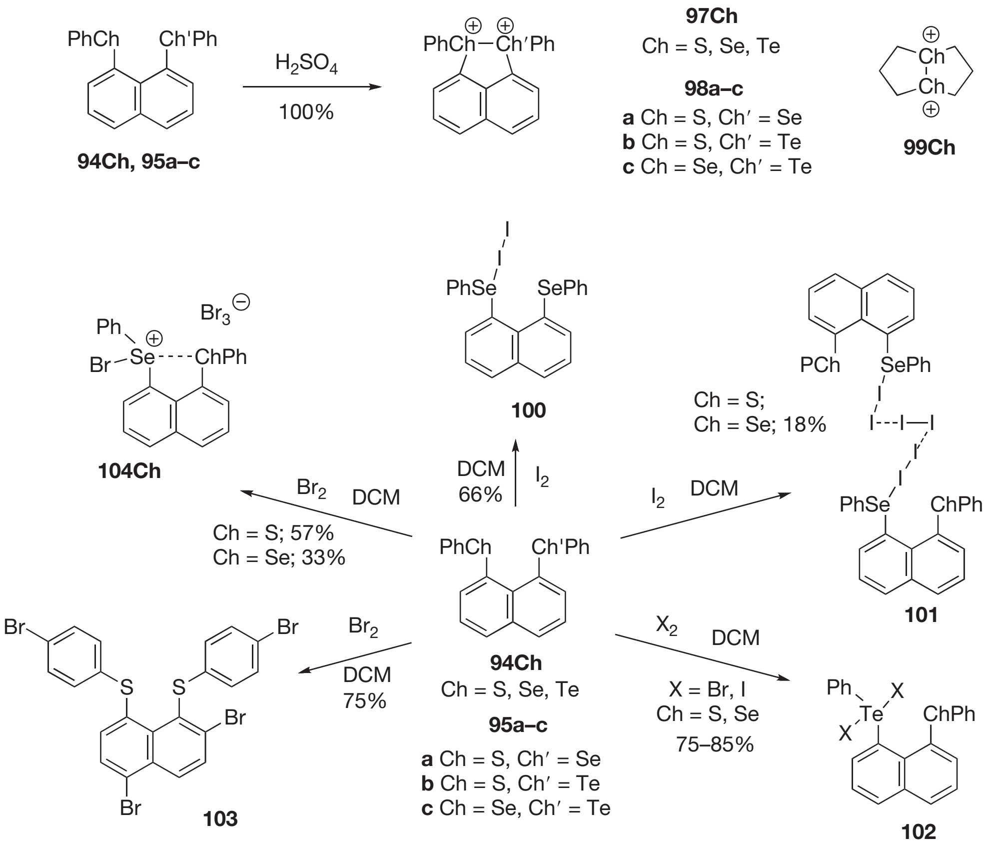
Scheme 6 Synthesis of unsubstituted dichalcogenoles.



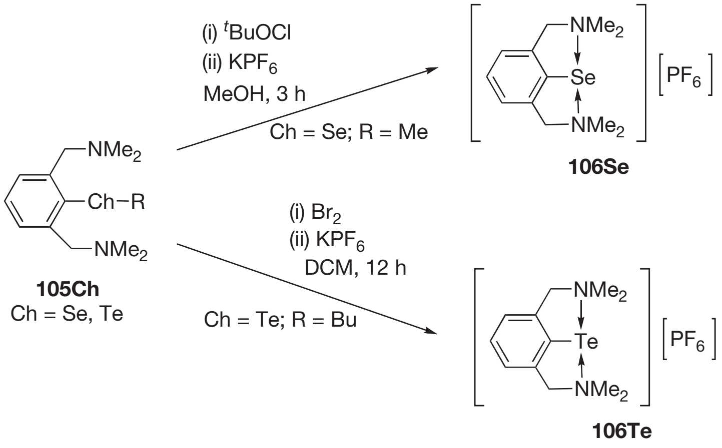
Scheme 7 Examples of reactivity of unsubstituted dichalcogenoles.



Scheme 8 Synthesis of the bisphenyl dichalcogenoles.



Scheme 9 Reactivity of the bisphenyl dichalcogenoles with sulfuric acid (top) and the halogens (bottom).



Scheme 10 The base-stabilized chalcogenenium cations prepared by Furukawa (**106Ch**).

the first real isolation and crystallographic characterization of heavy chalcogenium (**106Ch**, Ch=Se and Te) cations was by Furukawa et al. in 1995 (Scheme 10).[145] Two neighboring amino groups were used to stabilize the reactive fragment, which is formed by removing an alkyl substituent from the chalcogen on **105Ch** with an oxidant, followed by anion exchange with KPF_6. The Se–N bond lengths are significantly larger than standard single bonds (av. 2.16 Å cf. 1.87 Å), and the multinuclear NMR spectra of **106Ch** show a significant downfield shift from the starting material, indicative of dative stabilization of the electrophilic chalcogen center.

1.21.7.2 Selenium

Since this discovery a variety of related selenium and tellurium species have been prepared and characterized.[146–168] These types of compounds have shown to be useful as starting materials for organochalcogen chemistry as well as ion-radical salts with high conductivity. Several selenium-based compounds of this type have been shown to possess glutathione peroxidase (GPx)-like activity.[169] The nature of the Se–N interaction was found to correlate with the GPx activity where weak interactions showed high activity while strong interactions showed no activity. Singh et al. and Mugesh et al. who have prepared an overwhelming majority of these compounds (Figure 15) have also extensively studied their reactivity, redox chemistry, decomposition, and substituent effect.[147–166] An illustration to higher stability of these types of low-valent selenium centers is the fact that a terminal selenyl azide (**119**) can be isolated and characterized in the solid state with the aid of intramolecular interactions.[170] A similar type of compound was even shown to undergo click chemistry with phenylacetylene to form **120**.[171]

1.21.7.3 Tellurium

This idea can be extended to tellurium as Singh et al. prepared a base-stabilized diaryltelluride (**121**) by simple mixing of tellurium powder with the lithiated amino-naphthalene-starting material.[172] Using similar reaction conditions, Beckmann et al. were able to isolate a diaryl tritelluride (**122**) in 42% yield.[173] Interestingly, ^{125}Te NMR spectroscopy suggests that **121** is in equilibrium with **122** in solution (Figure 16). Singh et al. have also prepared related tellurium compounds (**123**–**126**),[174–176] and the hydrolysis products.[175] These low-valent compounds can be thought of as useful starting materials for the generation of hypervalent oxotellurides, which are known to be suitable oxidizing agents, catalysts, and oxygen-transfer reagents.[177–180]

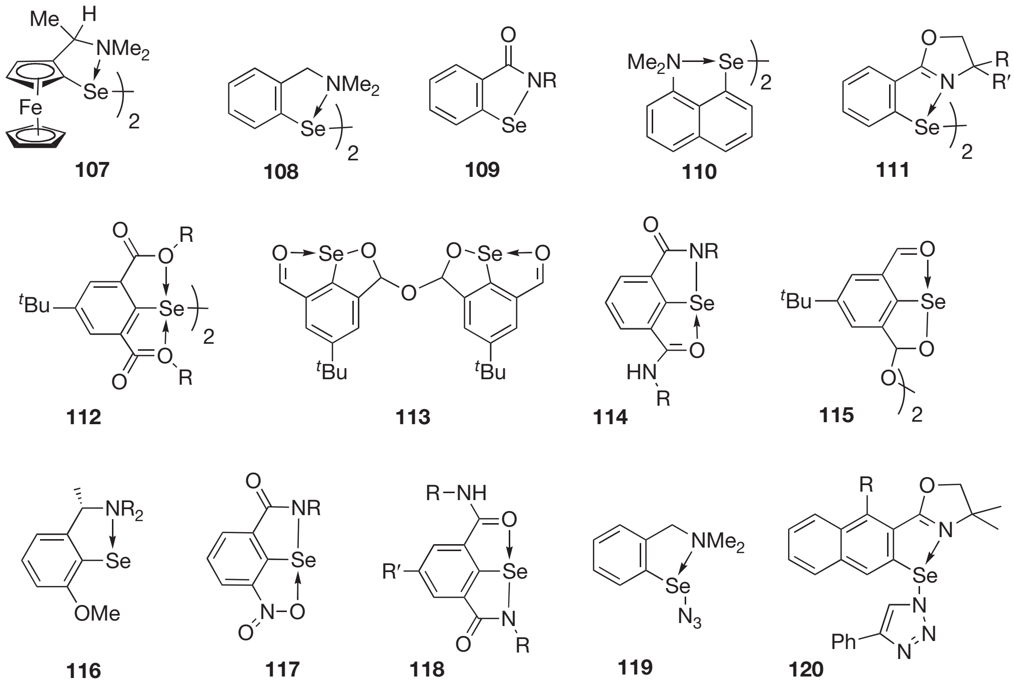


Figure 15 Examples of intramolecular base-stabilized organoselenium compounds.

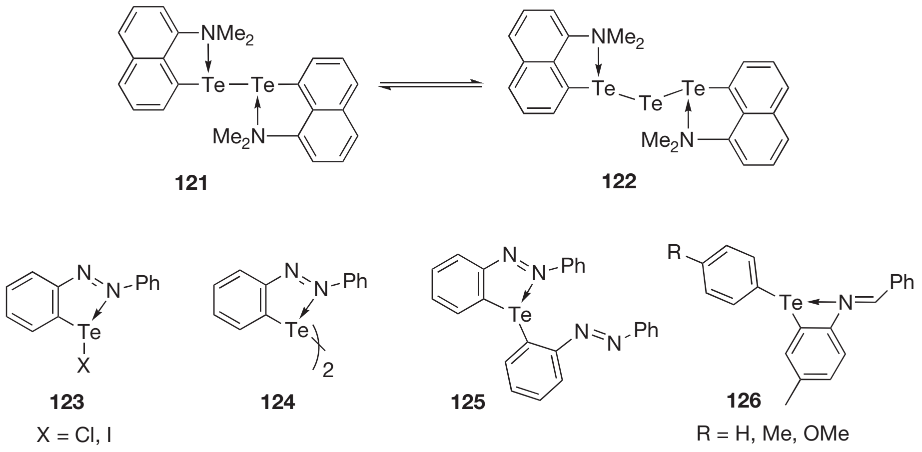


Figure 16 Examples of intramolecular base-stabilized organotellurium compounds.

1.21.8 Chalcogen–Nitrogen Secondary Bonding Interactions

Low-valent chalcogen centers in the form of 1,2,5-chalcogenadiazoles have (**127Ch**) been shown to possess secondary bonding interactions, which can act as a tool for the spontaneous formation of larger molecular building blocks.[181,182] The interaction is dominated by the orbital mixing of the nitrogen lone pair and the chalcogen-centered antibonding orbitals with a smaller, but still important, electrostatic interaction.[183,184] In this context, the tellurium derivatives typically have the strongest association energies due to the more polar character and lower-lying antibonding orbitals with respect to the lighter chalcogens.[184–186] Depending on electronic or steric nature of the compounds, the structure can vary from dimer (**128Ch**) to a ribbon polymer (**129Ch**) in the solid state (Figure 17). For example, **127Te** (R=H) and **130a** exist as ribbon polymers,[187] while **130b** and **130c** form dimers.[187,188] Of particular note is 4,5,6,7-tetrafluorobenzo-2,1,3-telluradiazole (**130d**) which can exist in three crystalline phases and displays supramolecular chromotropism.[189] The most stable red phase consists of a puckered ribbon polymer while the metastable yellow phase consists of a ribbon polymer with alternating short and long intermolecular Te — N distances. At 127 °C, the yellow phase is converted to the red phase irreversibly. Crystals grown in the presence of pyridine consist of dimers with pyridine solvates, which transforms to the red phase after the crystals effloresce. Computational studies confirm that the optical properties are related to the intermolecular π-orbital mixing and the supramolecular symmetry.

1.21.9 Reactions of N-Heterocyclic Carbenes with ChX_4

The reaction of an N-heterocyclic carbene (NHC) with the chalcogen tetrahalides results in redox activity forming a ChX_2 (Ch=Se and Te; X=Cl, Br, and I) carbene complex and an oxidation byproduct being elemental halogen.[190] This is undesirable as the liberated X_2 can then react with starting material or the product producing complex mixtures and hampers the yields. For example, using $SeCl_4$ the eliminated Cl_2 is immediately consumed by unreacted NHC to give a chloroimidazolium salt with a $[SeCl_6]$ dianion (**132**) as well as the $SeCl_2$ carbene complex (**131Se**) (Scheme 11). The same reaction using $SeBr_4$ gives the desired $SeBr_2$ adduct only with several byproducts that can fortunately be separated by solvent extraction. Kuhn and coworkers illustrated that heavier halides

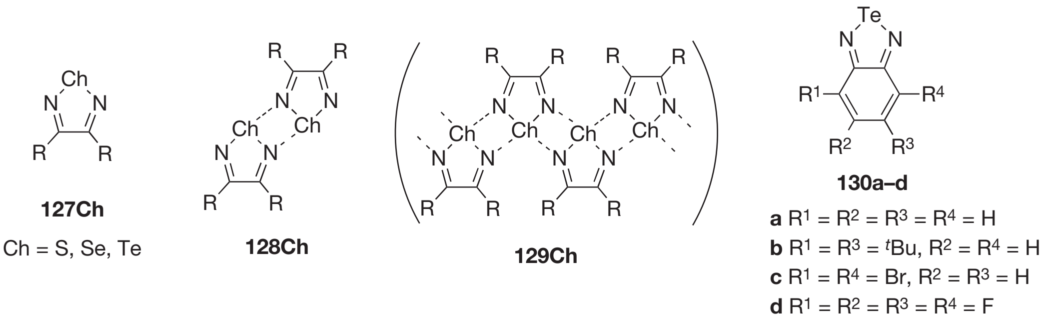
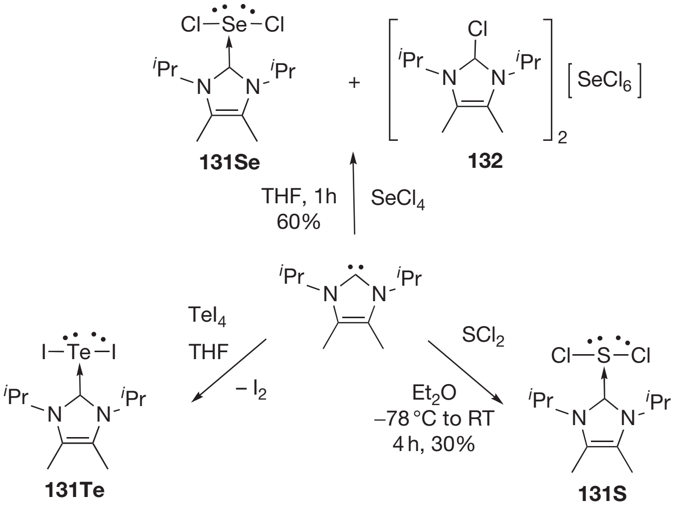


Figure 17 Illustration of 1,2,5-chalcogenadiazoles (**127Ch**) and their secondary bonding interactions.



Scheme 11 Spontaneous reduction of chalcogen tetrahalides (Ch=Se and Te) in the presence NHC to form **131Ch** and the formation of the analogous **131S** using SCl_2.

provide less of a problem, by demonstrating that treating TeI_4 with a stoichiometric equivalent of NHC only gives the TeI_2 carbene Lewis acid–base adduct (**131Te**) (**Scheme 11**).[191] While the released I_2 is not involved in side reactions, using $TeCl_4$ or $TeBr_4$ results in the formation of several other products. There is some precedent for the formation of these types of compounds in the literature, via a different protocol. Instead of reducing the chalcogen center from the +4 oxidation state to the +2 oxidation state, it was found that the oxidation of a seleno- or tellurourea with molecular X_2 formed the same product (**131Ch**).[192–194] It should also be noted that sulfur dichloride reacts with the same carbene to form the analogous SCl_2 coordination complex, **131S**.[195]

1.21.10 ChX$_2$ Synthons

1.21.10.1 Stability and Disproportionation

Some of the simplest low-valent group 16 species are the binary chalcogen dihalides. These species are thermally unstable and decompose by disproportionation (eqns [1]–[4]). While SCl_2 is stable for weeks at −30 °C,[196] $SeCl_2$ and $SeBr_2$ must be generated in situ and used immediately as they decompose within hours or minutes, respectively.[197,198] It is generally thought that free TeX_2 is so unstable, disproportionating at ambient temperatures,[199] that it could only be observed within a gas matrix. However, this is controversial as there are old reports of solid $TeCl_2$ being isolated,[200,201] and also separate publications of its existence being refuted.[202–204] Furthermore, there is a recent report claiming the utilization of $TeCl_2$ as a Te(II) source[205] in reactivity similar to the sulfur and selenium dihalides. Zotov et al. performed a recent X-ray diffraction study of the amorphous, and more stable, tellurium halides ($TeCl_{2-x}I_x$; $x=0.5$ and 0.1) and determined that both the tellurium tetrahalides and tellurium subhalides were present in the glassy solids, and thus do not contain discernible TeX_2 units:[206]

$$2\,SCl_2 \longrightarrow S_2Cl_2 + Cl_2 \qquad [1]$$

$$3\,SeCl_2 \longrightarrow Se_2Cl_2 + SeCl_4 \qquad [2]$$

$$2\,SeBr_2 \longrightarrow Se_2Br_2 + Br_2 \qquad [3]$$

$$2\,TeCl_2 \longrightarrow TeCl_4 + Te(0) \qquad [4]$$

Equations [1]–[4] are disproportionation reactions of the chalcogen dihalides.

1.21.10.2 Preparation

The known methods for preparing ChX_2 are illustrated in eqns [5]–[10]. Sulfur dichloride is prepared in multigram quantities from the addition of Cl_2 gas to S_2Cl_2 followed by distillation in the presence of PCl_3. The obvious method for SeX_2 production, Se^0 and X_2, generates a mixture of selenium halides until the eventual excess of halogen gives the more stable SeX_4. This trait is contrary to what is observed with sulfur, where SCl_2 is more stable than SCl_4, and is inconsistent with the inert pair effect. Stoichiometric addition of Se^0 and SO_2Cl_2 in THF gives $SeCl_2$ and SO_2 gas as the only byproduct.[197] This method is generally used for large $SeCl_2$ production, as it is difficult to handle small amounts of liquid SO_2Cl_2. Another approach involves reducing $SeCl_4$ with Ph_3Sb resulting in the generation of $SeCl_2$ and Ph_3SbCl_2.[207] This method works well for small-scale reactions provided the other reagents in onward transformations do not react with the chlorostiborane byproduct. The less stable $SeBr_2$ can be generated by comproportionation reaction of Se^0 and $SeBr_4$ in THF or MeCN solution in 10 min.[208] Treating $SeCl_2$ with trimethylsilyl bromide (TMSBr) can also generate selenium dibromide via a metathesis route.[197] $TeCl_2$ is generated from the reduction of $TeCl_4$ by bis(trimethylsilane) with the generated trimethylsilyl chloride (TMSCl) being removed *in vacuo*, and isolated in 60% yield.[209,210] The authors are careful to point out that the solid obtained is not completely $TeCl_2$, but it does act as a stoichiometric equivalent in the next step of their reaction sequence:[205]

$$S_2Cl_2 + Cl_2 \xrightarrow{PCl_3} 2\,SCl_2 \qquad [5]$$

$$Se^0 + SO_2Cl_2 \longrightarrow SeCl_2 + SO_2\,(g) \qquad [6]$$

$$SeCl_4 + SbPh_3 \longrightarrow SeCl_2 + SbPh_3Cl_2 \qquad [7]$$

$$Se^0 + SeBr_4 \longrightarrow 2\,SeBr_2 \qquad [8]$$

$$SeCl_2 + 2\,Me_3SiBr \longrightarrow SeBr_2 + 2\,Me_3SiCl \qquad [9]$$

$$TeCl_4 + (Me_3Si)_2 \longrightarrow TeCl_2 + 2\,Me_3SiCl \qquad [10]$$

Equations [5]–[10] are the different synthetic approaches to generate ChX_2 (Ch=S, X=Cl; Ch=Se, X=Cl, Br; Ch=Te, X=Cl).

1.21.10.3 Reactivity

There have only been a handful of synthetic transformations using free ChX_2 synthons (**Figure 18**). The most popular, and oldest, is likely the reaction of SCl_2 with ethylene to produce sulfur mustard (**133**).[211] Selenium dihalides can also undergo addition reactions with olefins in a similar manner, with a nice example being the recent preparation of the conducting polymer (**134**) via a selenophene monomer prepared from

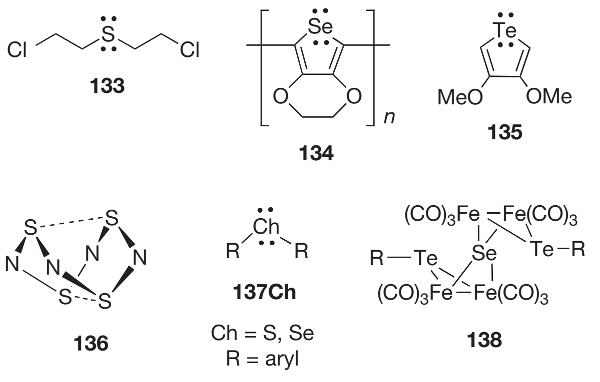


Figure 18 Examples of compounds prepared from ChX_2.

$SeCl_2$.[212] This methodology has been utilized in several instances by synthetic chemists to install thio- or selenoether functionalities to organic molecules.[213–215] Furthermore, $TeCl_2$ was shown to undergo similar reactivity in the preparation of a parent tellurophene (**135**),[205] which is of interest because polytellurophenes are considered to be highly stable, low-band-gap polymers and candidates for solar cell applications.[216] It should be noted that the synthesis of **135** from $TeCl_2$ proceeds in 5% isolated yield,[205] significantly lower than transformations with the lighter chalcogen dihalides. Polar solvents such as Et_2O or THF instead of hexane gave even worse results while SeX_2 (X = Cl and Br) is quantitatively prepared in those solvents. Sulfur dichloride can also be treated with ammonia to give tetrasulfur tetranitride (S_4N_4, **136**),[217] a common precursor to several sulfur, nitrogen-containing molecules. The related 1,5-$Se_2S_2N_4$ molecule can be prepared using $SeCl_2$ and could find use as an exact source of sulfur, selenium, and nitrogen in 1:1:2 stoichiometric equivalents respectively.[218,219] A simple, one-pot transformation involves the synthesis of ChR_2, reagents often useful for organic chemists, (**137**) by a Grignard reaction with ChX_2.[220] One other common use of these materials is metathesis to transfer the chalcogen to some anionic fragment. A case in point is the use of $SeCl_2$ in the formation of double butterfly complexes (**138**).[221,222]

1.21.11 Reactivity of Chalcogen Halides with Nitrogen-Based Ligands

1.21.11.1 Introduction

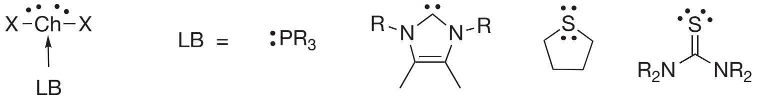
Synthetic and stoichiometric equivalents of ChX_2 that could be easily stored and manipulated would provide an advance in the field of low-oxidation-state and low-valent chalcogen chemistry. There are several examples of this that have been achieved over the past several decades, generally described as **139–142ChX$_2$** in **Figure 19**. Foss et al. pioneered the oldest method which is the simple Lewis base coordination of in situ generated ChX_2 by treating it with various sulfur donors (**141,142ChX$_2$**).[197,223–230] The oxidative additions of X_2 to phosphane selenide (**139SeX$_2$**), or selenourea (**140SeX$_2$**) precursors are approaches utilized by Godfrey et al.,[231–233] Kuhn et al.,[191,194,195] and others.[234–236] The conflicting reports on free TeX_2 have resulted in the simplest route to these types of compounds being either a spontaneous reduction of TeX_4 to Te(II),[237] or oxidative addition using X_2.[230,238,239] Treating TeO_2 with HCl in the presence of a Lewis base, in this case the thiourea (**142TeX$_2$**), has also proved to be successful.[229,240,241]

Nitrogen-based ligands can also stabilize low-valent chalcogen halide fragments, where the chalcogen oxidation state, halide present, as well as the substituents on the ligand can play a crucial role in the reactivity and thus the outcome of the onwards chemistry when utilizing these synthons.

1.21.11.2 Alkyl DAB: Formation of 1,2,5-Chalcodiazolium Cations

The direct reaction of ^{t}Bu$_2$DAB (DAB = diazabutadiene) with SeX_4 results in the formation of a unique 1,2,5-selenadiazolium cation with $[SeX_6]$ dianion (**144X**; X = Cl and Br) (**Scheme 12**).[242] The two-electron reduction of selenium was observed along with the loss of *tert*-butyl halide via the elimination of X_2. A break in symmetry is observed in the ^{1}H NMR spectrum as the backbone protons have separate resonances that integrate in a 1:1:9 fashion with respect to the *tert*-butyl singlet. The use of a X_2 trap, cyclohexene, which has been used successfully in reactions with phosphorus trihalides,[243,244] increased the isolated yields from 30–35% to 80–90%. These anions are not uncommon when working with ChX_4; however, they are redox active and can act as a chloride source. The use of $SeCl_2$ circumvents this issue and results in the cleaner reaction to the 1,2,5-selenadiazolium chloride product (**145**).[245] The much simpler chlorine atom can easily undergo metathesis and be replaced with the more inert triflate anion (**143Se**). In the case of sulfur, the 1:2 stoichiometric addition of SCl_2 and trimethylsilane trifluoromethanesulfonate (TMSOTf) results in a $S(OTf)_2$ synthon that can then be treated with ^{t}Bu$_2$DAB to form 1,2,5-thiadiazolium triflate salt (**143S**) in 60% yield.[246] In contrast to the selenium derivative, the sulfur analogs are unstable and decompose within 30 min, even in the solid state under nitrogen atmosphere. The reaction of the same ligand with TeX_4 results in the Lewis acid–base adduct (**146**), isolated in greater than 90% yield, as opposed to reduction of Te.[245] Treatment with the halide extraction agent TMSOTf, however, results in the spontaneous reduction to the tellurium triflate analog (**143Te**).[247] The production of several other side products, arising from the released X_2, causes the isolated yield to be low at 30%, much worse than reaction with the sulfur and selenium dihalides.

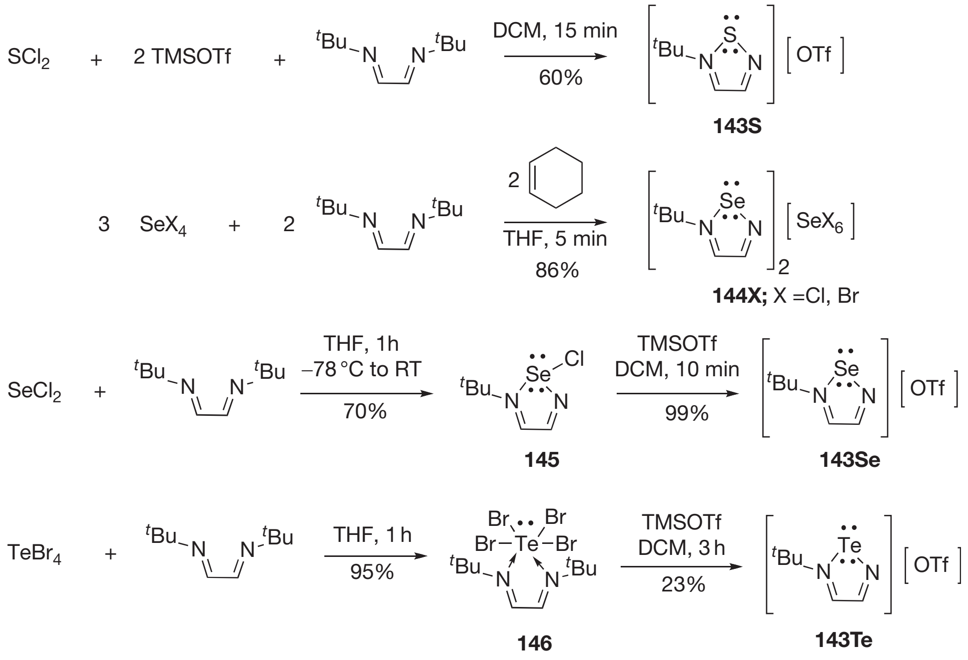
The donor–acceptor chemistry of the **143Ch** (Ch = Se and Te) cation was explored by using a variety of Lewis bases, including phosphanes, N-heterocyclic carbene, and 4-dimethylaminopyridine.[247] In all cases the resulting compounds (**147Do** and **148Do**) can be described as a coordinative interaction between the two-electron donor and the electrophilic chalcogen center (**Figure 20**). The bond lengths in the solid-state structures support a dative bonding model as does the fact that the donor molecule can be displaced with a superior Lewis base in nearly quantitative yields.



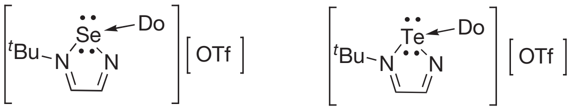
139-142ChX$_2$ **139** **140** **141** **142**

Ch = S, Se, Te
X = Cl, Br, I

Figure 19 Early examples of Lewis base-stabilized ChX_2 compounds.



Scheme 12 Reactions of ^{t}Bu$_2$DAB with chalcogen halides.



147Do

Do = PEt$_3$, PBu$_3$, PCy$_3$, PPh$_3$, 4-DMAP,^{i}Pr$_2$IM

148Do

Do = PCy$_3$, PPh$_3$, 4-DMAP, ^{i}Pr$_2$ IM

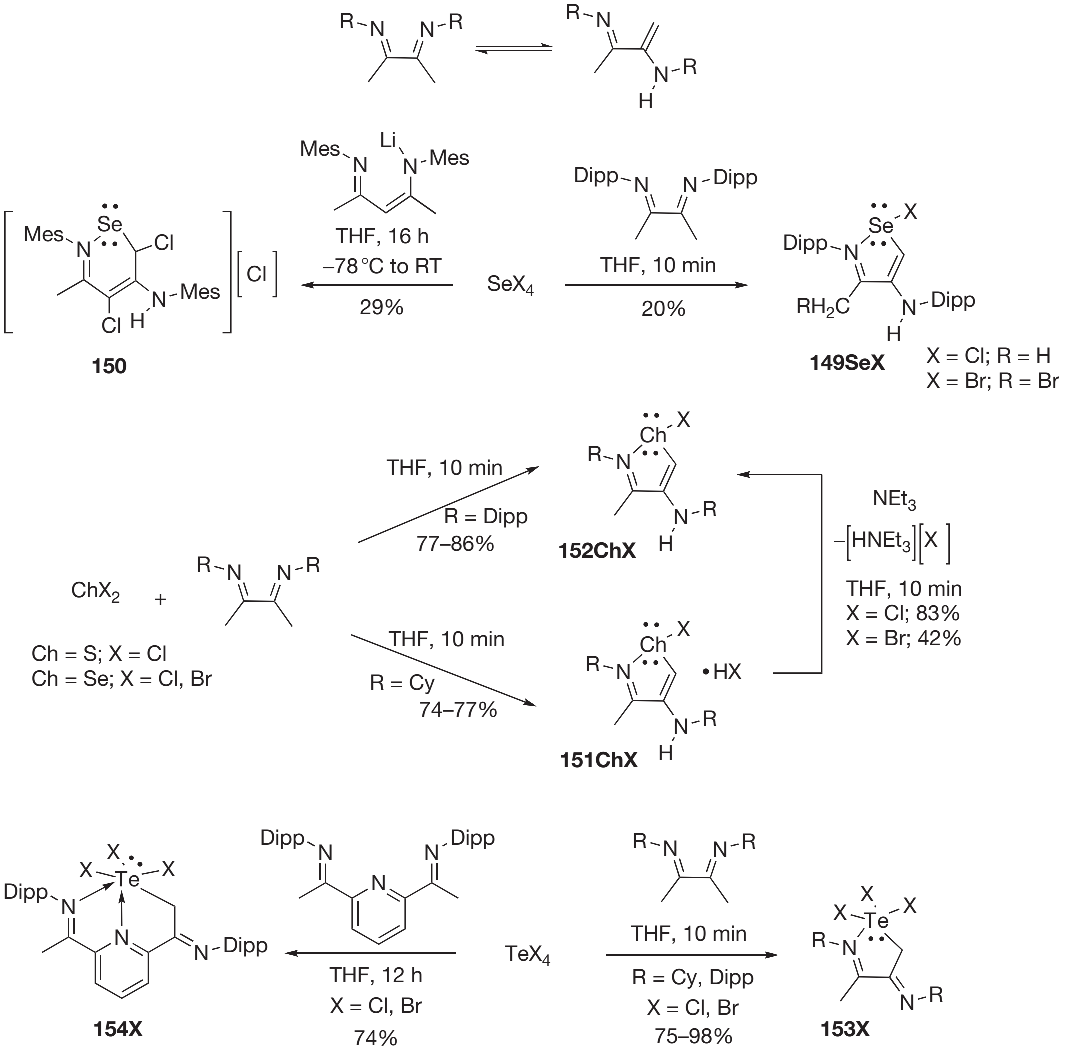
Figure 20 Illustration of the donor–acceptor chemistry of **143Ch** (Ch = Se and Te).

1.21.11.3 R$_2$Me$_2$DAB: Rearrangement and the Formation of N-Ch-C Heterocycles

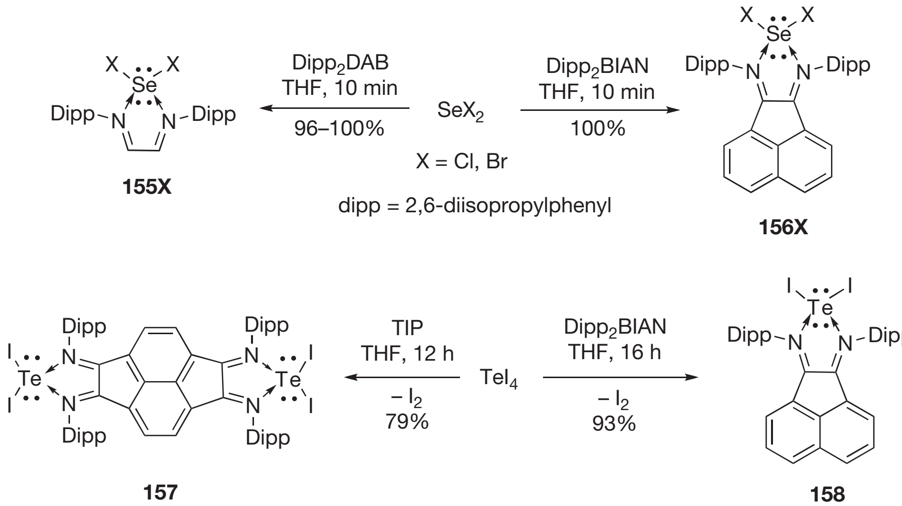
Substituting the hydrogen atoms on the DAB backbone with methyl groups (R$_2$Me$_2$DAB) results in attack of the enamine tautamer when treated with chalcogen halides. Reaction of SeX$_4$ (X = Cl and Br) gives the N,C-bound Se(II) compounds (**149SeX**) along with the elimination of X_2 (Scheme 13).[248] A break in symmetry is again observed in the ^{1}H NMR spectrum with the amine and olefinic protons clearly visible. In both cases the isolated yields are less than 20%, and in the case of Br there is halogenation of the ligand backbone. Similar reactivity was observed by Richards and coworkers with the reaction of the related β-diketimate ligand and SeCl$_4$ (**150**).[249] In this situation, the production of Cl$_2$ results in the unpredictable halogenation of the ligand backbone depending on the substituents and reaction solvent. The redox activity, subsequent halogenation, and low yields can be eliminated with the use of SCl$_2$ or SeX$_2$ (X = Cl, Br). In all cases, the N,C-bound heterocycle (**151ChX**, **152ChX**, Ch = S and Se) is formed in nearly quantitative yields. Varying the nitrogen substituents with alkyl (cyclohexyl) or aryl (Dipp = 2,6-diisopropylphenyl) groups allows for tuning the sterics and electronics of the ring. In the case of cyclohexyl, HX was observed in the product for both sulfur and selenium (**151ChX**), which was subsequently removed by treatment with base (**152ChX**). The reaction of TeX$_4$ (X = Cl and Br) with R$_2$Me$_2$DAB results in no reduction of tellurium and instead the N,C-bound tellurium (IV) species (**153X**) with three covalently bound halides (Scheme 13).[248] The mechanism for the reaction was proposed using evidence from the Dipp$_2$Me$_2$DAB with deuterated methyl groups. A product of this type (**154X**) is not uncommon, as similar reactivity has been observed in the reaction of TeX$_4$ (X = Cl and Br) with a diiminopyridine (DIMPY) ligand.[237]

1.21.11.4 Ar$_2$DAB: Generation of SeX$_2$ in a Bottle

To generate bottleable sources of the selenium(II) halides, the 1:1 stoichiometric addition of SeX$_2$ with Dipp$_2$DAB or Dipp$_2$-BIAN (BIAN = bisiminoacenapthene) resulted in the generation of SeX$_2$ α-diimine chelates (**155X**, **156X**) in nearly quantitative yields (Scheme 14).[250] This is in contrast to the *tert*-butyl-substituted DAB, which underwent redox activity. Examination of the solid-state structures revealed the selenium atom to be in a square planar geometry, consistent with AX$_4$E$_2$ predicted by valence shell electron pair repulsion (VSPER) theory. The Se–N bond lengths are significantly longer than the standard Se–N single bonds (2.26-2.35 Å cf . 1.85 Å) indicative of a dative interaction. The C–N and C–C metrical parameters are consistent with the free ligand, supporting the proposed coordination bonding model with no reduction of the ligand framework. Remarkably, these compounds were found to be stable when stored under ambient atmosphere in the laboratory for at least 2 months (confirmed by Fourier transform (FT)–Raman spectroscopy) and indefinitely stable when stored under N$_2$.[250] Cowley and coworkers reported that Dipp$_2$BIAN or the related Dipp$_4$TIP ligand (TIP = tetrakis



Scheme 13 Reactions of chalcogen halides with enamine tautomers.



Scheme 14 The reactions to form the ChX_2 α-diimine adducts.

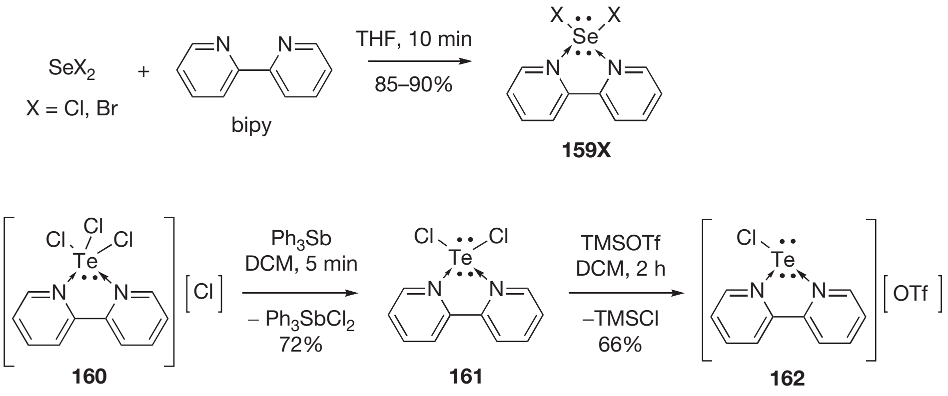
(imino)pyracene) could stabilize a TeI_2 fragment (**157**, **158**) via the high-yielding reductive elimination of I_2 from TeI_4 in the presence of the ligand (Scheme 14).[237,251] Similar to the selenium derivatives, the tellurium atom is square planar in the solid state, exhibiting long Te–N bonds (2.40 Å cf. 2.03 Å), and unchanged bond lengths in the ligand framework. It should be noted that SCl_2 does not form a complex with $Dipp_2DAB$ at room temperature as only free ligand is observed in the ^1H NMR spectrum.

1.21.11.5 Bipy-Stabilized ChX_2

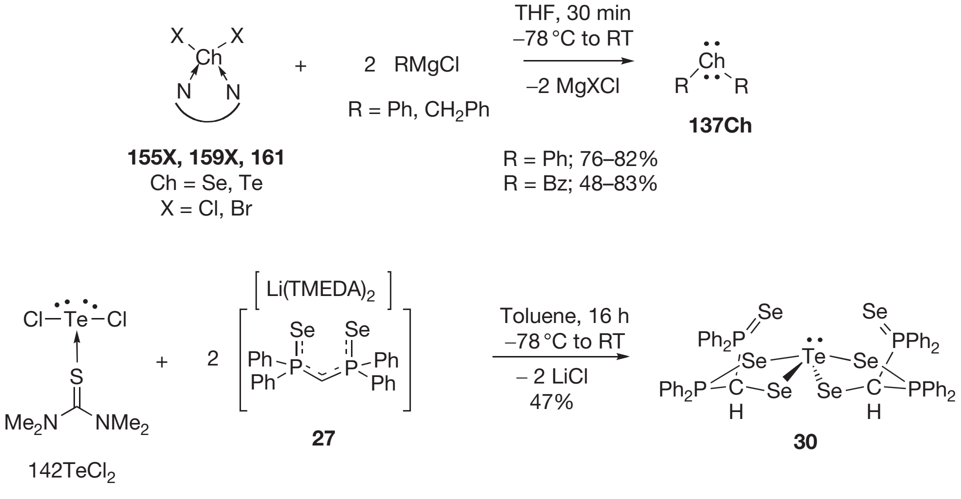
The ubiquitous 2-2′-bipyridine (bipy) ligands can also be used to stabilize ChX_2 fragments, representing surprisingly rare selenium and tellurium bipy complexes (Scheme 15). The SeX_2 adducts (**159X**) are formed by the direct reaction of the binary halide and bipy in a 1:1 stoichiometry.[250] As was the case with the α-diimines, the selenium center is in a square planar geometry. The related tellurium species (**161**) had to be prepared from the reduction of the $TeCl_4$bipy coordination complex (**160**) by Ph_3Sb. Single crystals of **161** could not be obtained so a cationic derivative (**162**) was synthesized. Single-crystal X-ray analysis revealed a T-shaped geometry about tellurium, consistent with the AX_3E_2 electron pair geometry, confirming the reduction to Te(II) from Te(IV).[250]

1.21.11.6 Reactivity of Base-Stabilized ChX_2

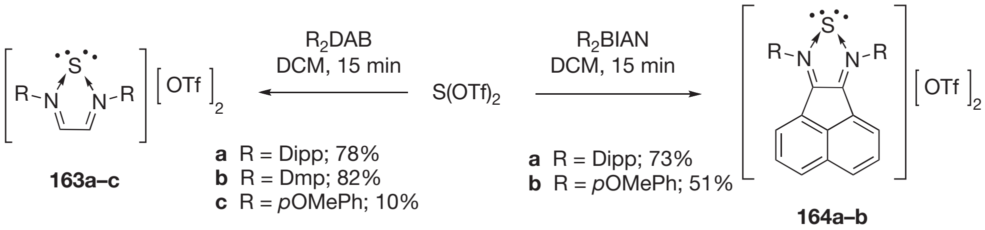
Utilizing these compounds as synthetic sources of ChX_2 was illustrated in reactions with aryl Grignards. The same diarylselenides reported for reactions with free $SeCl_2$[220] were prepared from **155Cl** as a $SeCl_2$ synthon in comparable yields (Scheme 17).[250] However, the liberated ligand and its decomposition products had to be removed from the reaction mixture by column chromatography. Under the same reaction conditions, **159Cl** was able to avoid similar decomposition products due to the fact that the bipy framework is more robust than the DAB. The formation of the insoluble coordination complex between bipy and the $MgCl_2$ byproduct allows for simple filtration and solvent removal to isolate the target product (**137Se**) (Scheme 16).[250] The analogous diaryl tellurides (**137Te**) were prepared in good yields from reagent **161**. It was also demonstrated that the bipy ligand could be displaced in a ligand exchange reaction with an NHC to form the easily isolated $TeCl_2$NHC complex,[250] thus circumventing the reductive elimination approach established by Kuhn.[191] While the



Scheme 15 Reactions to form the bipy complexes of ChX_2.



Scheme 16 Examples of the use of base-stabilized ChX_2 for onward chemistry.



Scheme 17 The synthesis of the sulfur analogs of the NHC.

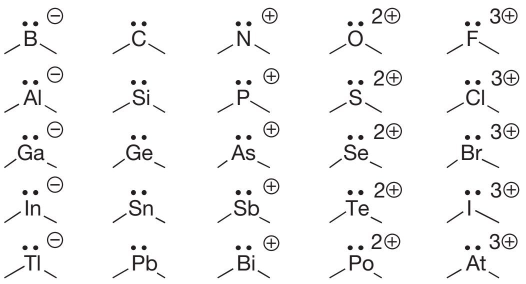


Figure 21 Illustration of the main group carbene analogs.

TeI_2 compound could be isolated, reactions to form the Cl and Br derivatives resulted in complex mixtures and products were unable to be isolated using redox. Chivers et al. have also utilized a synthetic source of $TeCl_2$ for onward chemistry (**163**) (Scheme 17),[54] in this case the $TeCl_2$tmtu (tmtu = tetramethylthiourea) compound (**142TeCl₂**) prepared by Foss.[229]

1.21.12 Group 16 N-Heterocyclic Carbene Analogs

1.21.12.1 Introduction

Since the discovery of the Arduengo carbene[252] in 1991, the race has been on for the synthesis of the other main group analogues (Figure 21). While a majority of the group 13, 14, and 15 analogs have since been prepared; the group 16 analogs had remained elusive.[253]

1.21.12.2 Sulfur

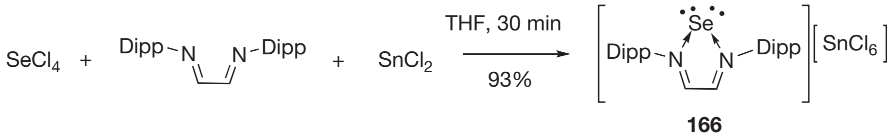
The 1:1 stoichiometric reaction of freshly prepared $S(OTf)_2$ with DAB or BIAN ligands with aryl substituents (Dipp, Mes) on the nitrogen atom resulted in the formation of the sulfur(II) dication N,N′ chelate (**163a–c**, **164a–b**) (Scheme 17).[246,254] Prior to this discovery, rare examples of sulfur dications had been limited to the higher oxidation state S(IV) compounds isolated by Furakawa.[255] Furthermore, these compounds were the first sulfur containing structural mimics of the N-heterocyclic carbene. Examination of the solid-state structure reveals the S–N bonds to be slightly shorter than the standard distance for a single bond (average in **163a–c** 1.68 Å cf. 1.76 Å), an indication of the electrophilicty about sulfur.[254] The C–N and C–C bonds in the ligand are consistent with double and single bonds respectively, which is consistent with previous calculations done on related compounds.[256] There are weak sulfur triflate contacts; however, the fact that the three sulfur – oxygen bonds in the triflate anion are not distorted suggests that there are no covalent interactions. The use of $^{19}F\{^{1}H\}$ NMR spectroscopy is quite diagnostic in determining the covalent/ionic nature of triflate in various chalcogen complexes. For example, the difference between a known covalent triflate, H_3COTf ($\delta_F = -75$), and a known ionic triflate, $NOct_4OTf$ ($\delta_F = -79$ in DCM, $\delta_F = -78.5$ in MeCN) is quite distinguishable and can provide insight into whether the triflate oxygen is bound or detached from the chalcogen center in solution. In the case of **163a–c** and **164a–b**, the $^{19}F\{^{1}H\}$ NMR spectra are consistent with ionic triflates.[246,254] Facile exchange of the triflate anions with the tetrakis(pentafluorophenyl)borate anion, to give **165**, was achieved in high yields and provided a complex with minimal cation–anion interactions.

1.21.12.3 Selenium and Tellurium

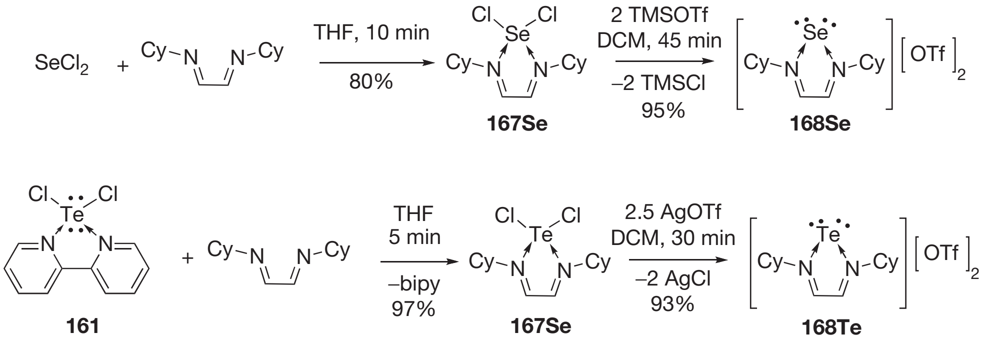
The first selenium NHC analog (**166**) was prepared by the reaction of one stoichiometric equivalent of $SeCl_4$ with $Dipp_2DAB$ and $SnCl_2$ (Scheme 18).[257] The solid-state structure revealed Se–N bond lengths consistent with a single bond (average in **166** 1.89 Å cf .1.85 Å) while the bond lengths in the ligand framework are consistent with the formation of a $[Se]^{2+}$ chelate as opposed to having undergone intramolecular charge transfer. Calculations also support the proposed bonding arrangement.[256] The potential of redox activity with the $SnCl_6$ dianion hindered the study of further chemistry for this compound so a related species with more inert anions was pursued.

Halide abstraction attempts with TMSOTf or AgOTf on the $Dipp_2DAB$-stabilized $SeCl_2$ resulted in no reaction. However, by simply replacing the diisopropylphenyl groups on the DAB framework with cyclohexyl groups, the subtle change in the electronic structure of the ligand allowed for the facile chloride abstraction of the $SeCl_2Cy_2DAB$ adducts (**167Se**) with TMSOTf to form the base-stabilized selenium dication (**168Se**).[258] The tellurium analog could also be prepared by utilizing the same ligand set; **161** readily undergoes ligand exchange with Cy_2DAB to form **167Te**, which then undergoes halide abstraction with AgOTf to form the tellurium dication (**168Te**) (Scheme 19).[259] Examination of the solid-state structures reveals C–N and C–C bond lengths consistent with what has already been observed for these types of compounds. Both the selenium and tellurium examples maintain weak triflate interactions in the solid state, which is not observed in solution as observed by $^{19}F\{^{1}H\}$ NMR spectroscopy.

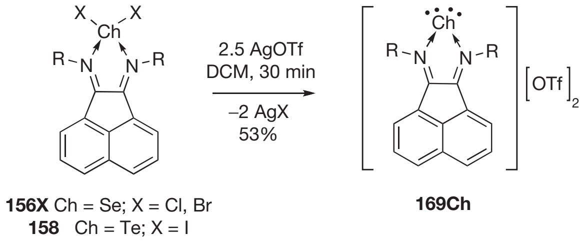
Cowley's TeI_2 compound (**158**) can also readily undergo halide abstraction by treatment with excess AgOTf in DCM (Scheme 20).[260] The color change from dark blue to orange



Scheme 18 The synthesis of the first selenium analog of the NHC.



Scheme 19 Formation of selenium and tellurium NHC analogs with inert triflate anions.



Scheme 20 Halide abstraction of ChX_2 BIAN complexes.

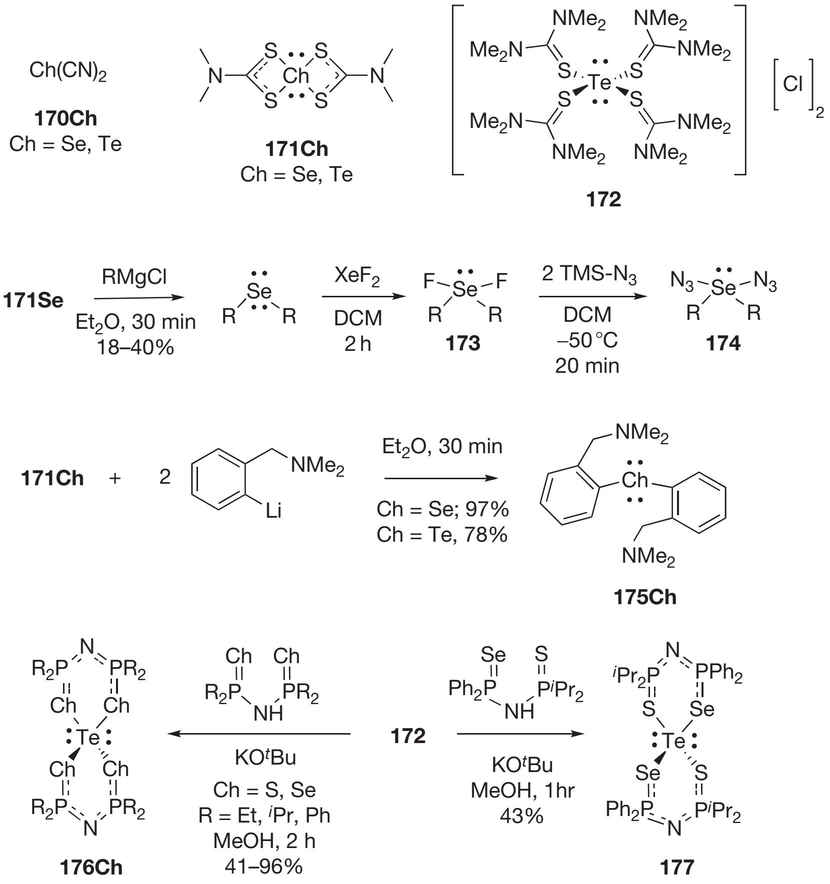
is observed in minutes and the triflate salt (**169Ch**) is isolated in good yields. The solid-state structure possesses long bond lengths between Te and the triflate oxygen (Te–O = 2.32–2.48 Å cf. 2.0 Å for a standard Te–O bond). However, $^{19}F\{^{1}H\}$ NMR spectroscopy reveals that the triflates are covalently bound to the Te center in solution. The electrophilicity about tellurium can be inferred from the $^{125}Te\{^{1}H\}$ NMR spectrum, where a downfield resonance is observed ($\delta_{Te} = 2853$). This approach has been successful for the SeX_2-BIAN species, **156X** (X = Cl, Br); however, no solid-state structure was obtained.[258] These compounds are appealing as the protons on the DAB backbone are considerably more acidic than the BIAN backbone – a feature that can hinder the onward chemistry of these complexes.

1.21.13 $[Ch]^{2+}$ Synthons: Unique Route to Unprecedented Bonding of the Chalcogens

1.21.13.1 Introduction

There are rare reports of dicationic chalcogen synthons, $[Ch]^{2+}$, although growth in the area is beginning to occur. These materials are desirable as they can be considered a naked chalcogen source without the accompanied reactivity of the included halides. Therefore, $[Ch]^{2+}$ sources can prove to be useful in studying new structure, bonding, and reactivity within group 16. The first example of a $[Ch]^{2+}$ compound is the selenium and tellurium binary cyanides, $Ch(CN)_2$ (**170Ch**); however, chemistry with these molecules beyond their stabilization and structural characterization has not been explored.[261–264] Over the course of three decades, beginning in 1950, Foss and coworkers published a series of $[Ch]^{2+}$ materials stabilized by sulfur-based ligands.[225,230,240,241,265,266] There are a few examples for both selenium and tellurium where these compounds were utilized as a chalcogen(II) source (Scheme 21). Klapotke et al. employed a $Se(dtc)_2$ complex (**171Se** dtc = diethyldithiocarbamate) and were able to form a variety of diorganoselenides via a Grignard reaction. The resulting product was oxidized using XeF_2 to R_2SeF_2 (**173**), and the fluorides were subsequently abstracted with trimethylsilyl azide ($TMSN_3$) to form diorganoseleniumdiazides (**174**).[267] Singh and coworkers have also used **171Ch** in organolithium reactions in a different, and high yielding, approach for preparing new Ch–C bonds (**175**).[268] Another utilization of a $[Te]^{2+}$ synthon was illustrated by Woollins and coworkers by taking Foss' $[Te(tmtu)_4][Cl]_2$ complex[241] (**172**; tmtu = tetramethylthiourea) and treating it with an imidophosphinate ligand in the presence of $KO^{t}Bu$ to form **176Ch**.[269] Ibers has also utilized this methodology to form similar Te(II)-centered compounds (**177**) stabilized by sulfur and selenium.[270] In all these cases, a cation is required to displace the Ch(II) fragment and drive the reaction to the new product (Scheme 21).

The group 16 N-heterocyclic carbene structural mimics can be considered $Ch(OTf)_2$ synthons for sulfur, selenium, and tellurium. The neutral ligands allow free access to the chalcogen center without the necessary cation exchange as observed in the previous examples. Furthermore, the in situ-generated $S(OTf)_2$ can also be used directly as a source of S^{2+} without the potential implications of having another ligand present in the reaction mixture.



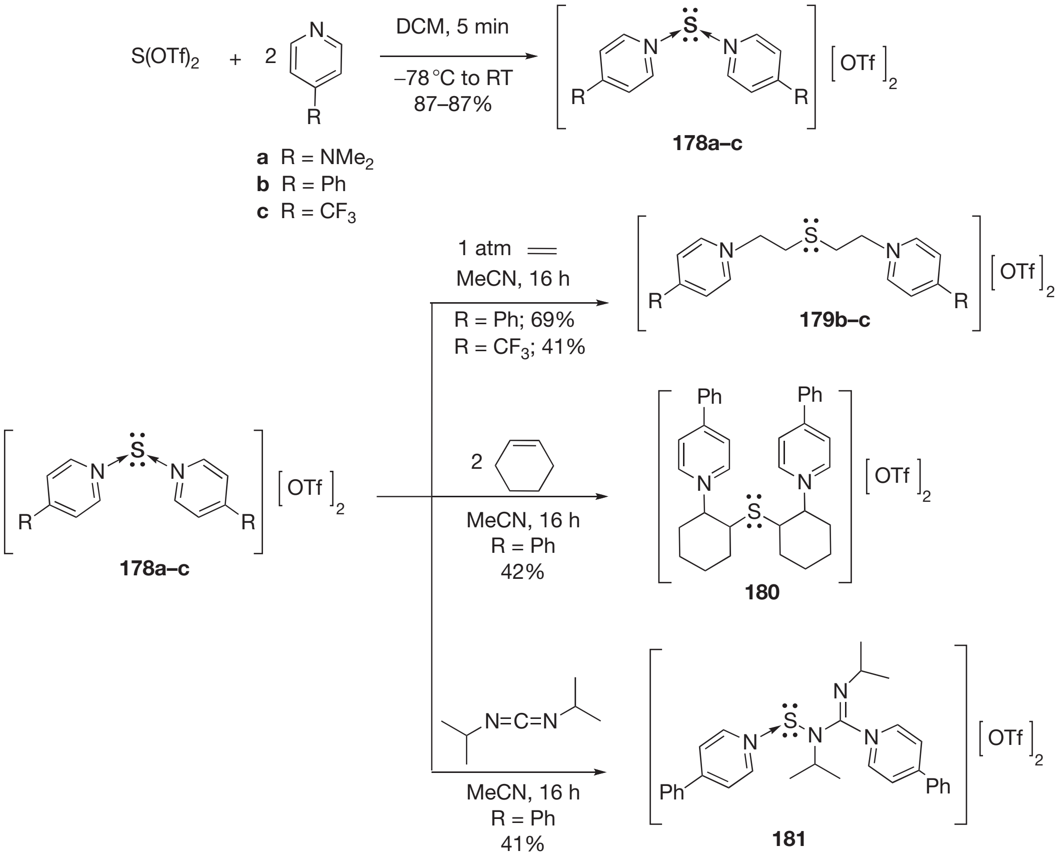
Scheme 21 Transfer of $[Ch]^{2+}$ via Foss' chalcogen sources.

1.21.13.2 Reaction of $S(OTf)_2$ with Pyridines and Onward Reactivity

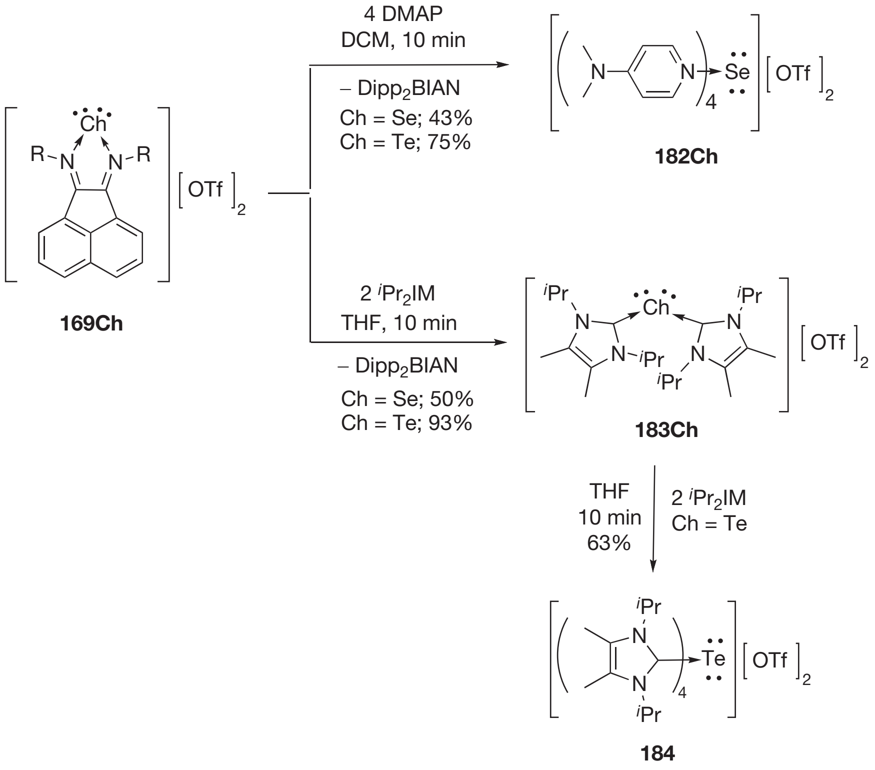
This strategy has been utilized for the synthesis of compounds with different coordination environments about sulfur. For example, treatment of SCl_2, TMSOTf, and various pyridine ligands (4-dimethylaminopyridine (DMAP), 4-phenylpyridine, and 4-trifluoromethylpyridine) in a 1:2:2 stoichiometric ratio results in S(II) dications with pyridine donors (**178a–c**; **a** = NMe_2, **b** = Ph, and **c** = CF_3) (Scheme 22).[271] The solid-state structures revealed an AX_2E_2 geometry about sulfur and S–N bonds slightly shorter than the standard single bond length (1.717 Å for **178a**, 1.737 Å for **178b** cf. 1.76 Å). The triflate anions deviate from the ideal square planar geometry and show no distortion in the S–O bond lengths and therefore do not interact with the electrophilic sulfur dication. Interestingly, the Ph- and CF_3-substituted pyridine derivatives were capable of reacting with olefins. Treating **178b** and **178c** with one atmosphere of ethylene resulted in the complete conversion of the insertion of ethylene into the S–N dative bond (Scheme 22).[271] It should be noted that the identical reaction conditions with **178a** resulted in no reaction, likely due to the increased donor ability of the 4-DMAP ligand. Two other unsaturated substrates, cyclohexene and diisopropylcarbodiimide, were shown to react with **178b** to give insertion products (**179–181**).[271] In all cases, confirmation of the structure and connectivity was obtained by single-crystal X-ray analysis. A mechanism was proposed on the basis of the ^1H and $^{19}F\{^1H\}$ NMR data obtained throughout the reaction and described in detail in the publication.

1.21.13.3 Transfer of $Ch(OTf)_2$ to Novel Coordination Environments

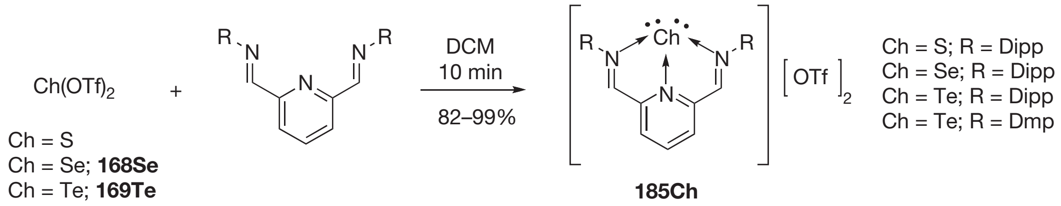
The $Se(OTf)_2$ and $Te(OTf)_2$ complexes **168Se** and **169Ch** were found to be susceptible to ligand-exchange reactions with different Lewis bases of higher donor ability.[258,260] The reaction of the $[Ch]^{2+}$ source with either 4-dimethylaminopyridine (4-DMAP), or an NHC (1,3-diisopropylimidazol-2-ylidene, $^iPr_2IM$) gives new selenium- and tellurium-centered dications (Scheme 23). In the case of 4-DMAP, rare main group 4-coordinate pinweel structures are obtained (**182Ch**) with nearly ideal D_{4h} symmetry. With the NHC, 2-coordinate complexes are obtained (**183Ch**) which can be considered dicationic chalcogen structural mimics of the recently reported bent allenes or carbodicarbenes.[272] The C–Ch–C bond angle is almost exactly 90° reflecting the use of unhybridized p-orbitals to form the Ch–C bonds.[258,260] In contrast, the C–C–C bond angle in carbodicarbenes is 134° consistent with some multiple bond character between the carbon centers.[272] Furthermore while the C(0) complex has been shown to be a strong donor for transition metals, the Te(II) complex is electrophilic as further addition of two equivalents of NHC gives the



Scheme 22 The synthesis of sulfur(II) dications featuring monodentate ligands and the insertion reactions with olefins.



Scheme 23 Transfer of Ch^{2+} to DMAP and NHC coordination complexes.



185Ch

Scheme 24 Synthesis of remarkably stable chalcogen R$_2$DIMPY complexes.

4-coordinate square planar 'paddlewheel' complex (**184**).[260] Compound **184** bears D_4 symmetry and possesses much longer Ch–C bonds due to the strong *trans*-influence and the steric demands of four carbene molecules about a single Te atom. The selenium derivative, **183Se**, does not react with further equivalents of NHC. In all cases, the solid-state structures, as well as the multinuclear NMR data, are consistent in describing these molecules as base-stabilized chalcogen dications. It should be noted that on the whole ligand exchange is not common reactivity for group 16 elements; however, it does occur readily and quantitatively with the highly electrophilic chalcogen coordination complexes.

1.21.13.4 Taming [Ch]$^{2+}$ with the DIMPY Ligand

A separate series of group 16 dications was prepared by treatment of the Ch(OTf)$_2$ synthons (Ch = S, Se, Te) with the ubiquitous diminopyridine ligand to form the first *N*,*N*′,*N*″ R$_2$DIMPY chalcogen coordination complexes, **185Ch** (Scheme 24).[273] To avoid the previously observed reactivity of the enamine tautomer, the less common proton-substituted ligand was prepared. The solid-state structures revealed a T-shaped geometry about the chalcogen center, consistent with the AX$_3$E$_2$ electron pair configuration. The pyridine nitrogen occupies the equatorial site while the two imine nitrogen atoms occupy the axial sites. The Ch–N metrical parameters support a delocalized hybrid structure to stabilize the dicationic charge. Fascinatingly, all the solid samples showed no signs of decomposition upon exposure to the open air for at least 3 weeks.[273] This is in stark contrast to all previously studied chalcogen dications stabilized by monodentate and bidentate donors that decompose immediately when exposed to air. The sulfur derivative is even stable after the addition of water for over an hour, which is a remarkable feature.

1.21.14 Conclusion

Several influential reports in the realm of low-valent group 16 chemistry have surfaced in the past 10 years and the chemistry in this field will continue to expand. Numerous examples of novel main group, transition metal, and lanthanide and actinide complexes with chalcogenidophosphinate ligands have been formed displaying differing coordination modes about the central atom. Tuning the ligand framework will give rise to additional structures, and the potential use of these materials as single-source precursors for binary metal selenides and tellurides is well underway. Chalcogen diimides also have great potential as ligands for a variety of metal centers. Radical-based chalcogen chemistry has been around for some time and has seen sustained growth with examples ranging from fundamental understanding of relatively simple molecules to compounds being used for magnetic devices. A number of base-stabilized organoselenium compounds have been shown to possess glutathione peroxidase (GPx) activity while tellurium derivatives are very recently getting attention as precursors for telluroxanes. Unique heterocycles have been formed, often in high yields, using DAB or BIAN ligands and the chalcogen halides. The 'trapped' ChX$_2$ (Ch = Se and Te) compounds have already been shown to be capable Ch(II) delivery sources, where the free binary halides are significantly less stable. The [Ch]$^{2+}$ synthons are excellent Ch(II) precursors to more complicated molecules, while avoiding the detrimental reactivity a halogen anion can possess. The next step figures to be the utilization of these newly developed synthetic strategies in innovative areas of chalcogen chemistry. Moving from novel structure and bonding to the exploitation of these compounds in organic synthesis, bond activation, and materials chemistry is paramount for the continued development in this area. In all the discussed examples, the molecular design is critical as subtle changes in sterics and electronics can bestow significantly different reactivity. This observation signifies the great potential chalcogen-centered molecules have as useful compounds for synthetic chemists as well as in functional materials.

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