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Coordination Chemistry Reviews
210 (2000) 73–99

COORDINATION CHEMISTRY REVIEWS

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Unusual structures of main group organometallic compounds containing *m*-terphenyl ligands

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Received 29 September 1999; accepted 1 December 1999

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PII: S0010-8545(00)00317-9

Abstract

The use of the *m*-terphenyl substituent has facilitated the synthesis of numerous unusual molecules containing main group elements. This review reports these advances as well as highlights potential synthetically useful derivatives. Finally, future applications for this ligand design are suggested.

Keywords: Main group organometallic compounds; *m*-Terphenyl ligands; Ligand design applications

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1. Introduction

The quest for molecules possessing main group elements in low coordinate environments (i.e. a molecule with a main group element engaging in multiple bonds or an element with a low coordination number) has been an important area of research for the past 20 years [1]. This is due, in part, to the potential synthetic versatility of these compounds in chemical reactions (via addition reactions) as well as for the synthetic hurdles that must be overcome to prepare and isolate them given their reactive nature.

In many cases, molecules with elements exhibiting unusual bonding modes can be isolated when the center of interest possesses at least one sterically demanding substituent. Stability with respect to cyclic or oligomeric alternatives can be imposed by sterically demanding groups [2]. This is perhaps best illustrated by the phosphinidene fragment (RP) which, with small alkyl or aryl substituents (R), cyclic species are isolated (i.e. $R = P$, $(PhP)_{5,6}$ whereas with large groups, such as (Mes* = 2,4,6-tri-*tert*-butylphenyl), lower oligomers are isolated [1]. An example of a ‘dimer’ is Mes*P = PMes* [3]. This molecule represented a watershed in synthetic main group chemistry since it was one of the first examples of a molecule possessing a bona fide double bond between two heavy main group elements. Predictably, the synthetic strategy of incorporating bulky ligands into molecules to stabilize unusual bonding modes has been used extensively, and to date numerous molecules possessing reactive moieties have been prepared using this approach. The synthesis and reactivity of these unusual molecules has been reviewed [4].

2. Ligand designs

Numerous ligand designs have been used to prepare molecules with elements in unusual bonding modes, and sometimes the chemistry observed for these systems is ligand dependent. Alkyl and aryl substituents that have been extensively employed include $(SiMe_3)_2CH$ [5], Mes*(2,4,6-tri-*tert*-butylphenyl) [3], Trip (tri-*iso*-propylphenyl) [6], Dipp (di-*iso*-propylphenyl) [6] and Bmt ((4-*tert*-butyl-2,6-bis[(2,2″,6,6″-tetramethyl-*m*-terphenyl-2′-yl)methyl]phenyl) [7]. For the most part, these ligands are readily prepared, and some are commercially available.

A relatively new ligand design is the generalized *m*-terphenyl ligand **1**. A series of these ligands, which will be referred to extensively throughout this review, is presented in Fig. 1. These substituents are easily prepared and they are extremely robust [8]. This general ligand type is one of the bulkiest yet devised, and it appears to offer the most synthetic utility, since, for the most part, substitution in the 1 position of the central phenyl group (C_{Ar}) is facile and often proceeds in high yield (vide infra). Substituents in this position are effectively in a 'pocket' between the two *ortho* aryl groups and they can often experience strong associations to the *ortho* aryl groups via a π-arene interaction.

The purpose of this review is to illustrate the extensive use of these ligands in the synthesis of organometallic compounds containing *s* and *p* block elements. Generally, only molecules containing C_{ar}–M bonds are discussed; aryloxides and thiolato compounds are excluded. Finally, this review is primarily restricted to those compounds that have been crystallographically characterized. For important compounds, diagrams showing the geometry of the element of interest have been drawn with relevant bond lengths and bond angles (Figs. 2–28). Furthermore, emphasis is placed upon compounds with demonstrated or potential synthetic utility.

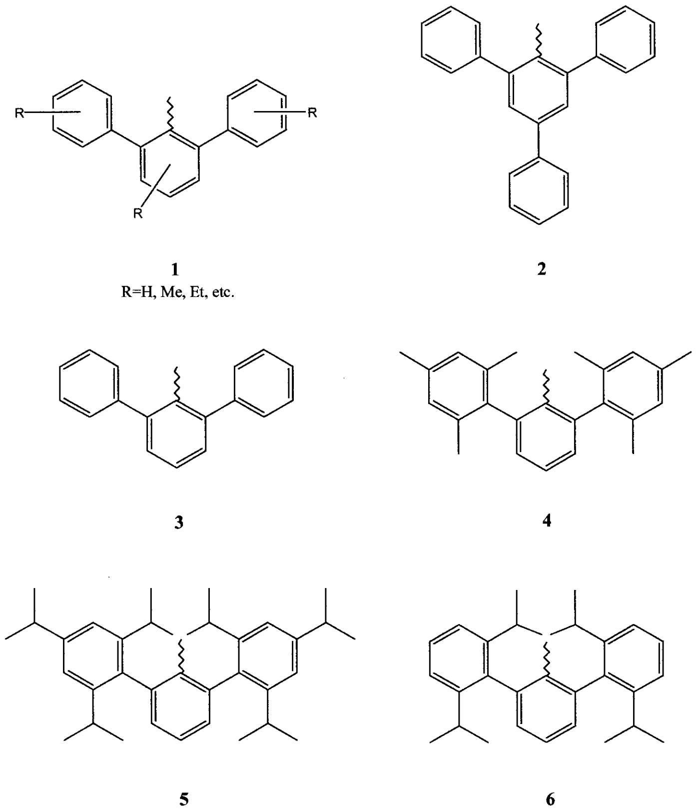


Fig. 1. Generalized **1** and specific **2**–**6** *m*-terphenyl ligands discussed in this review.

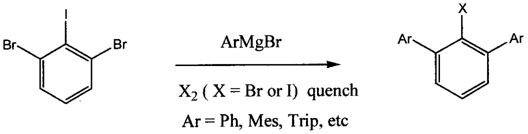
3. Synthesis of *m*-terphenyl substituents

The preparation of the *m*-terphenyl substituent **1** is best achieved through a one-pot synthesis from a suitable trihalobenzene [8]. These polyhalogenated benzenes are readily prepared from 2,6-dihaloanilines through diazotization followed by iodine or bromine quench. Preparation of the *m*-terphenyl is typically achieved through the reaction of dihaloiodobenzene with three equivalents of an aryl Grignard reagent followed by a halogen (iodine and bromine) quench (Scheme 1). This reaction, which is believed to proceed through an aryne intermediate, results in the formation of the generalized 1-halide substituted terphenyl **1**. Numerous aryl Grignard reagents have been used providing a general route to a wide variety of *m*-terphenyls, (i.e. **3**–**6**), and their isolated yields are often in excess of 60% (based on trihalobenzene). An alternative starting material to 2,6-dibromoiodobenzene is 2,6-dibromo-4-methyliodobenzene. This 4-methylated derivative is cheaper, but it has not been used as extensively as the unsubstituted derivative [9].

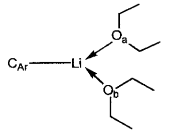
4. Group 1: organolithium and organosodium compounds

The extensive use of organolithium reagents in the synthesis of organic, inorganic and organometallic compounds has prompted studies into their solid-state structure. The lithium derivative of ligand **2** provided the first indications of the synthetic versatility of *m*-terphenyls as well as suggested the potential structural diversity presented by this ligand design [10,11]. Lithiation of **2**-Br with *n*-butyllithium in hexanes affords **2**-$Li(OEt_2)_2$ [10]. The solid-state structure of **2**-$Li(OEt_2)_2$ consists of a lithium atom, which has a trigonal planar geometry and which is coordinated to two diethyl ether molecules. The coordination of ether molecules to the lithium atom prevents aggregation (i.e. base stabilization) and the complex is a rare example of a monomeric organolithium reagent.

Lithiation of the larger ligand **5**-Br in Et_2O also affords a monomeric aryl lithium compound with a molecular formula of **5**-$Li(OEt_2)$ [12]. The metal center is dicoordinate and the lithium atom engages in bonds to carbon as well as with oxygen from the coordinated ether molecules. The larger steric bulk of **5** rather than **4** is suggested by the isolation of a mono etherate complex **5**-$Li(OEt_2)$ that is formed via lithiation of **5**-Br in ether. Lithiation of **4**-I with *n*-butyllithium in

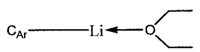


Scheme 1. Reaction of a trihalobenzene with an aryl Grignard reagent producing a generalized *m*-terphenyl ligand.



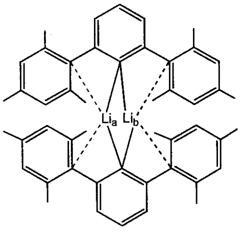
2-Li(OEt$_2$)$_2$

C_{Ar}-Li	2.074(16)
Li-O_a	1.954(18)
Li-O_b	1.971(18)
O_a-Li-O_b	111.9(7)



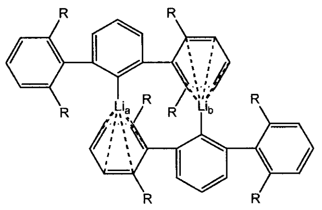
5-Li(OEt$_2$)

C_{Ar}-Li	2.017(7)
Li-O	1.850(7)
C_{Ar}-Li-O	171.9(5)



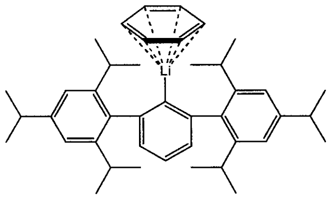
(4-Li)$_2$

Li-C_{Ar}	2.16(1)-2.20(1)
Li-C_{ipso}	2.51(1)-2.56(1)
Li_a-C_{Ar}-Li_b	63.2(5)
C_{Ar}-Li-C_{Ar}	116.8(15)



(6-Li)$_2$ R = *i*Pr

Li_a-C_{Ar}	2.069(6)
Li_b-C_{Ar}	2.067(6)
Li_a···C_{Ar}	2.366(7)-2.5334(6)
Li_b···C_{Ar}	2.385(7)-2.526(6)

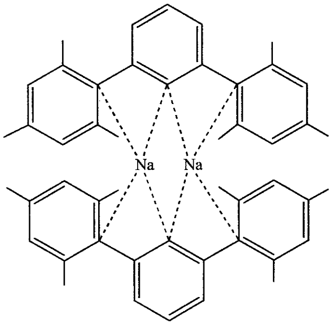


C_{Ar}-Li	2.03(2)
Li-$C_{benzene}$	2.33(2)-2.36(2)
C-C_{Ar}-C	115.0(9)

5-Li • benzene

Fig. 2. Selected bond lengths (Å) and bond angles (°) for organolithium compounds stabilized by *m*-terphenyl substituents.

hexanes affords the unsolvated lithium aryl compound **4**-Li [13]. In the solid state **4**-Li exists as a dimer (**4**-Li)$_2$ (see Fig. 1) with σ-interactions through Li–C_{Ar} bonds, as well as longer π-type interactions (Li–C_{ortho}) of the mesityl arm of **4** [13]. The lithium atoms are μ_2 with respect to their aryl substitution. The compound **6**-Li also exists as a dimer (**6**-Li)$_2$, but in this case exhibits a η^1 Li–C σ-interaction as well as an η^6 π-interaction with one of the pendent aryl rings of **6** [14]. Dissolution of **5**-Li in benzene, followed by subsequent recrystallization, affords a monomeric aryl lithium compound, **5**-Li · benzene [14]. This compound exhibits a Li–C σ-bond to the terphenyl ligand, as well as an η^6 π-interaction to the coordinated benzene. The molecular structure of **6**-Li is unique in that it is the first example of a monomeric σ-bonded organolithium compound stabilized through only steric effects and weak solvation. The importance of these π interactions with the *ortho* aryl substituents on the *m*-terphenyl will be discussed in Section 9.



C_{Ar}-Na	2.572(2), 2.609(2)
C_{ipso}-Na	2.595(2)-2.663(2)
Na---Na	2.874(2)
C_{Ar}-Na-C_{Ar}	111.40(10),113.82(10)

Fig. 3. Selected bond lengths (Å) and bond angles (°) for (**4**-Na)$_2$.

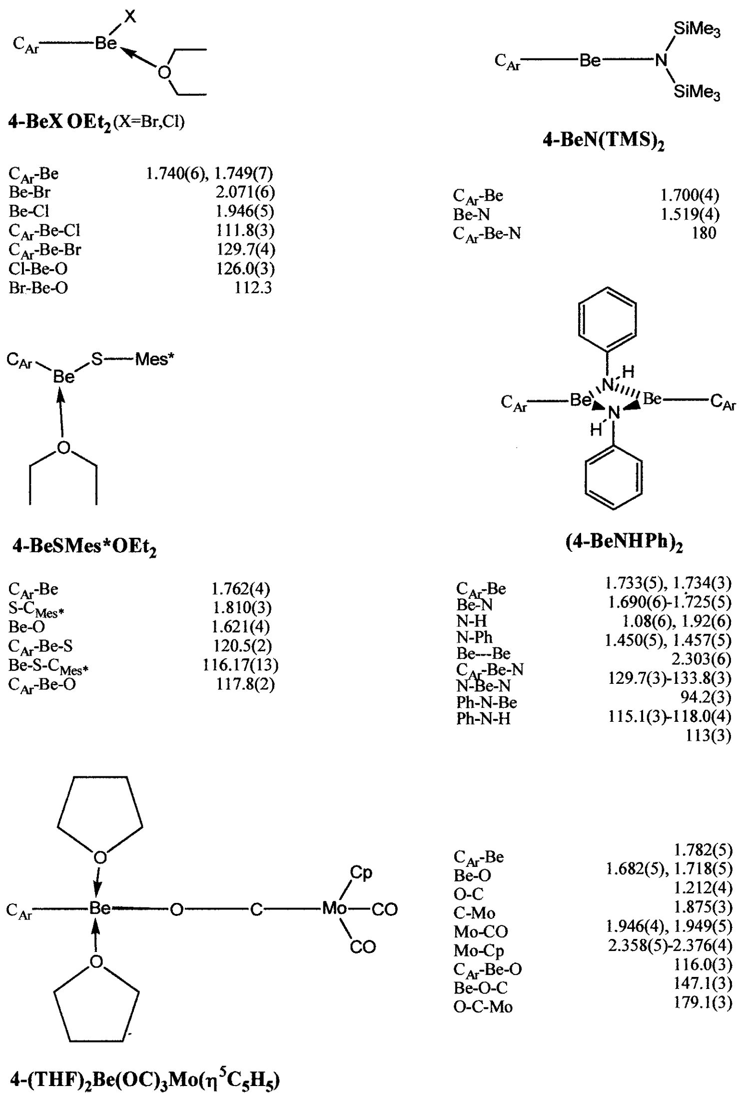
The synthesis of the first solvent-free sodium aryl (**4**-Na)$_2$ was achieved by the reaction of **4**-Li with an excess of sodium *tert*-butoxide [15]. Attempts to prepare the analogous potassium derivative were unsuccessful. The solid-state structure of (**4**-Na)$_2$ was determined by X-ray crystallography. The dimeric structure of (**4**-Na)$_2$ differs from that of (**4**-Li)$_2$. For (**4**-Li)$_2$, the interaction with the *ipso* carbon of the mesityl rings are longer than the interactions with the *ipso* carbon (i.e. C_{Ar}) of the phenyl rings, whereas in (**4**-Na)$_2$ the sodium atom engages in four nearly equidistant Na···C interactions.

5. Group 2: organoberyllium compounds

The chemistry of beryllium is perhaps not as well established as that of other Group 2 elements, and this is due, to a large degree, to the high toxicity of this element. Nevertheless, ligand **4** has been used to greatly expand the organometallic chemistry of this poorly studied element [16].

Metathesis reactions, starting with BeX_2 (X = Cl, Br) and **4**-Li, produced the organoberyllium halide **4**-BeX(OEt_2) (X = Cl, Br) that can be isolated in 65% yield [16]. The reactive Be–X fragment is an ideal candidate for further substitution reactions via metathesis reactions with suitable nucleophiles. Using standard methodology, these two beryllium halides (**4**-BeX(OEt_2) (X = Cl, Br)) can be used to prepare a wide range of compounds, and these include **4**-BeSMes*, **4**-Be[(NHPh)]$_2$, **4**-BeNHSiPh$_3$ and **4**-BeN(SiMe$_3$)$_2$ [16]. Structural features of these compounds are summarized in Fig. 4.

A few comments concerning this series of beryllium compounds are worth mentioning. First, compounds **4**-BeX · OEt_2 (X = Cl, Br) are the first crystallographically characterized molecules to display bonding between three-coordinate beryllium and halogens. These molecules are base stabilized through coordination to ether. Structural parameters for both compounds, with the exception of Be–X bond distances, are similar. Another unusual compound in this series is **4**-BeN(SiMe$_3$) which is the first dicoordinate beryllium compound in the solid state.



4-BeX OEt$_2$(X=Br,Cl)

C_{Ar}-Be	1.740(6), 1.749(7)
Be-Br	2.071(6)
Be-Cl	1.946(5)
C_{Ar}-Be-Cl	111.8(3)
C_{Ar}-Be-Br	129.7(4)
Cl-Be-O	126.0(3)
Br-Be-O	112.3

4-BeN(TMS)$_2$

C_{Ar}-Be	1.700(4)
Be-N	1.519(4)
C_{Ar}-Be-N	180

4-BeSMes*OEt$_2$

C_{Ar}-Be	1.762(4)
S-C_{Mes*}	1.810(3)
Be-O	1.621(4)
C_{Ar}-Be-S	120.5(2)
Be-S-C_{Mes*}	116.17(13)
C_{Ar}-Be-O	117.8(2)

(4-BeNHPh)$_2$

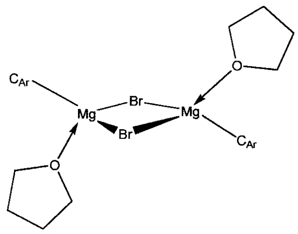
C_{Ar}-Be	1.733(5), 1.734(3)
Be-N	1.690(6)-1.725(5)
N-H	1.08(6), 1.92(6)
N-Ph	1.450(5), 1.457(5)
Be—Be	2.303(6)
C_{Ar}-Be-N	129.7(3)-133.8(3)
N-Be-N	94.2(3)
Ph-N-Be	115.1(3)-118.0(4)
Ph-N-H	113(3)

C_{Ar}-Be	1.782(5)
Be-O	1.682(5), 1.718(5)
O-C	1.212(4)
C-Mo	1.875(3)
Mo-CO	1.946(4), 1.949(5)
Mo-Cp	2.358(5)-2.376(4)
C_{Ar}-Be-O	116.0(3)
Be-O-C	147.1(3)
O-C-Mo	179.1(3)

4-(THF)$_2$Be(OC)$_3$Mo($\eta^5C_5H_5$)

Fig. 4. Selected bond lengths (Å) and bond angles (°) for organoberyllium compounds stabilized by *m*-terphenyl substituents.

Finally, since the synthetic value of the beryllium halide **4**-BeCl was demonstrated through the metathesis reactions with main group nucleophiles, an attempt to prepare a molecule possessing a transition metal–beryllium bond was made using a transition metal based nucleophile. Reaction of **4**-BeCl with NaMo(η^5-C_6H_5)(CO)$_3$ does not produce a compound with a Be–Mo bond, but rather produces an isocarbonyl **4**-Be(THF)$_2$OCMoCp(CO)$_2$ [16].



C_{Ar}-Mg	2.132(6)
Mg-Br	2.559(2), 2.579(2)
Mg---Mg	3.621(2)
Br-Mg-Br	90.4(1)
Mg-Br-Mg	89.6(1)
Br-Mg-C_{Ar}	125.0(2), 126.3(2)

[4MgBr(THF)]$_2$

Fig. 5. Structural features for the *m*-terphenyl substituted Grignard reagent [**4**-MgBr(THF)]$_2$.

5.1. Grignard reagents

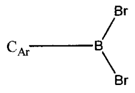
The synthetic value of Grignard reagents cannot be ignored, and numerous studies have examined their synthesis, structure and reactivity. Of relevance to this review is [**4**-MgBr(THF)]$_2$ crystals of which were serendipitously isolated from the reaction of **4**-I with Mg in the presence of $MgBr_2$ [17]. The structural aspects of [**4**-MgBr(THF)]$_2$ reveal a compound with a coordination geometry at magnesium consisting of a Mg–C bond, two bridging Mg–Br bonds, as well as an interaction with THF. This produces an overall four coordinate distorted tetrahedral geometry at magnesium.

6. Group 13: halides and halide derivatives of organoboron compounds

The effects of sterically demanding substituents are perhaps best illustrated by the chemistry of Group 13 (B, Al, Ga, In, Tl). Tricoordinate Group 13 centers are characterized by high electrophilicity and hence, in the absence of a bulky ligand, tetracoordinate species are typically observed. For most derivatives, this coordination environment can be achieved through dimerization (i.e. via halide bridge formation) or by coordination of donor solvents (i.e. Et_2O or THF) to the Group 13 metal centers.

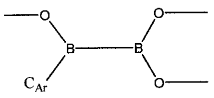
Sterically demanding aryl boron dihalides, **4**-BCl_2 and **4**-BBr_2, are prepared by direct reaction of **4**-Li with BX_3 ($X = Cl$, Br) [18]. These reactions proceed in high yield and afford the boron dihalides **4**-BX_2 ($X = Cl$ or Br). X-ray crystallographic studies on these compounds reveal that the boron centers are tricoordinate; all other structural features are unremarkable.

Compounds **4**-BX_2 ($X = Cl$ or Br) are ideal synthons, and they can be used to prepare boronfluorenyl compounds via reduction with alkali metals. Formation of these ring structures is believed to proceed through a B(I) species which, due to its high electrophilicity, engages in cyclization reactions and provides a unique example of a boron insertion reaction into a C–C bond. This reduction behavior contrasts greatly with that observed for the related gallium compound **4**-$GaCl_2$ (vide infra).



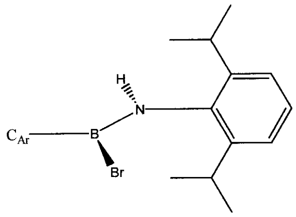
4-BBr_2

C_{Ar}-B	1.565(11)
B-Br	1.902(5)
C_{Ar}-B-Br	121.8(2)
Br-B-Br	116.3(4)



4-B(OMe)$B(OMe)_2$

C_{Ar}-B	1.599(4)
B-B	1.718(5)
B-O	1.359(4)-1.364(4)
C_{Ar}-B-O	112.8(3)
C_{Ar}-B-B	124.0(2)
O-B-O	116.0(3)



(4-$BBrNHiPr_2C_6H_3$)

C_{Ar}-B	1.56(3)
B-Br	1.93(2)
B-N	1.34(3)
N-C	1.45(2)
N-B-C_{Ar}	124.8(18)
N-B-Br	116.8(17)
C_{Ar}-B-Br	118.3(15)
B-N-C	128.1(16)

Fig. 6. Selected bond lengths (Å) and bond angles (°) for *m*-terphenyl substituted boron containing compounds.

Reaction of **4**-Li with $B_2(OMe)_4$ produces, in reasonable yield, **4**-B(OMe)B(OMe)$_2$. Attempts to prepare the disubstituted derivative **4**-B(OMe)B(OMe)-**4** were made at elevated temperatures, but only **4**-B(OMe)$B(OMe)_2$ could be isolated. This observation would suggest that double substitution is probably prevented for steric reasons. Reduction of **4**-B(OMe)B(OMe)Mes also produces cyclic products [19].

Metathesis reactions are of great importance in organometallic chemistry. The synthetic potential of **4**-BBr_2 was demonstrated in the synthesis of (**4**-$BBrNH^iPr_2$-C_6H_3) which possesses a degree of N–B π-bonding [20].

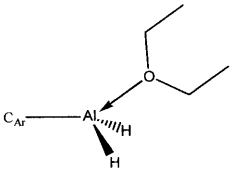
6.1. Halide and hydride derivatives of aluminum, gallium, and indium

Aluminum halides and hydrides are important due to their reactivity and unusual structural features. The hydrides of aluminum and heavier elements, compared to that of boron, are relatively unknown. Preparation of Al–X (X = halide or hydride) fragments can easily be achieved through the use of *m*-terphenyl substituents

The synthesis of **4**-$AlH_2(OEt_2)$ can be accomplished through several steps. Reaction of (**4**-Li)$_2$ with AlH_3NMe_3 in ether results in the formation of [**4**-

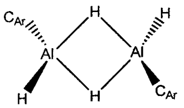
$AlH_3Li(OEt_2)]_2$. Treatment of [**4**-$AlH_3Li(OEt_2)]_2$ with chlorotrimethylsilane in an ether–hexane mixture yields the monomeric base stabilized aluminum hydride **4**-$AlH_2(OEt_2)$ [21]. Warming powdered crystalline **4**-$AlH_2(OEt_2)$, under vacuum produces (**4**-$AlH_2)_2$ which can be crystallized from benzene or toluene. All three compounds have been crystallographically characterized, and structural details are presented in Fig. 7. The synthesis and structure of the related derivatives **5**-$AlH_2(OEt_2)$ and (**5**-$AlH_2)_2$ were also reported. Their structural features are reminiscent of those using ligand **4**. On a related note, the synthesis of the aluminate [**2**-$AlH_3Li(OEt)_{1.5}]_2$ can be achieved by direct reaction of **2**-Li with $LiAlH_4$ and it has been structurally characterized [22].

Direct reaction with $AlCl_3$ and **4**-Li is not a viable synthetic approach to the sterically encumbered aluminum halide **4**-$AlCl_2$. Rather, synthesis of **4**-$AlCl_2(OEt_2)$



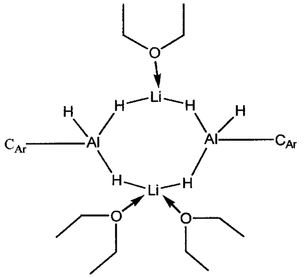
4-$AlH_2(OEt)_2$

C_{Ar}-Al	2.002(3)
Al-O	1.922(3)
Al-H	1.45(4)-1.62(4)
C_{Ar}-Al-H	120.8(14)-120(2)
C_{Ar}-Al-O	103.60(14)



(4-$AlH_2)_2$

C_{Ar}-Al	1.956(3)
Al-H	1.44(4)-1.65(5)
Al---Al	2.630(2)
C_{Ar}-Al-H	108.9(5)-133(2)
H-Al-H	74.7-107.9(14)



[2-$AlH_3Li(OEt)_{1.5}]_2$

C_{Ar}-Al	2.018(4)
Al-H_{bridge}	1.62(4)
Al-$H_{terminal}$	1.545(41)
Li-H	1.77(4)
Li-O	1.892(11)-1.954(6)
C_{Ar}-Al-H_{bridge}	106.7(1.5)
H-Li-H	107.4(1.8)

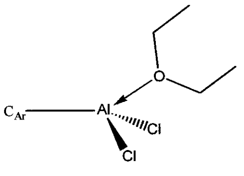
Fig. 7. Selected bond lengths (Å) and bond angles (°) for aluminum hydride derivatives substituted with *m*-terphenyl substituents.

is best achieved through the reaction of **4**-$AlH_2(OEt_2)$ with trimethylsilylchloride, which produces the desired compound in good yield [21]. X-ray analysis of solid samples of **4**-$AlCl_2(OEt_2)$ indicate that the fourth coordination site on aluminum is occupied by coordinated Et_2O, and, not surprisingly, this compound is monomeric in the solid state. Ether is easily removed from this complex by refluxing in hexanes to give (**4**-$AlCl_2)_2$. This compound is a dimer, possessing chloride bridges [21]. The potentially synthetically useful aluminum bromide derivative **2**-$AlBr_2(OEt_2)$ can be prepared by direct reaction of **2**-Li and $AlBr_3$ and it can be isolated in moderate yield [21].

An interesting reaction occurs when **4**-Li reacts with $AlBr_3$ in ether. The product isolated from these reaction mixtures has been structurally characterized as (**4**-$AlBr_3Li)_2$ [23]. This compound possesses an Al–Br–Li–Br–Al bridge and can be viewed as the LiBr addition product of **4**-$AlBr_2$. Reaction of (**4**-$AlBr_3Li)_2$ with $Li(NH^iPr_2C_6H_3)$ results in the formation of neutral **4**-$Al(NH^iPr_2C_6H_3)_2$ which exhibits a sterically enforced trigonal planar geometry at aluminum [23].

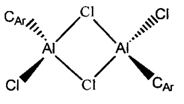
A wide range of *m*-terphenyl substituted gallium halide derivatives have been reported, and many of these have been prepared using the standard metathesis approach. Direct reaction of **4**-Li with $GaCl_3$ in ether yields **4**-$GaCl_2$ in modest yield. This compound is dimeric in the solid state (**4**-$GaCl_2)_2$ [24]. The steric crowding in this molecule forces the gallium centers to be distorted from an ideal tetrahedral geometry.

The synthetic utility of **4**-$GaCl_2$ is suggested by its reaction with MesLi which produces **4**-$GaMes_2$ in high yield. This compound possesses extreme steric crowding at the gallium center [24]. Reaction of (**4**-$GaCl_2)_2$ with [**2**-$Me_2NCH_2)C_6H_4$]Li results in the formation of an intramolecularly base-stabilized gallium halide **4**-GaCl[**2**-



4-$AlCl_2(OEt_2)$

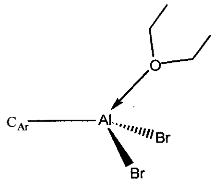
$Al-C_{Ar}$	1.992(3)
Al-O	1.877(2)
Al-Cl	2.132(2), 2.140(1)
$C_{Ar}-Al-Cl$	118.60(8), 121.09(8)



(4-$AlCl_2)_2$

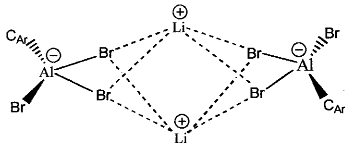
$Al-C_{Ar}$	1.937(15)
$Al-Cl_{terminal}$	2.125(5)
$Al-Cl_{bridge}$	0.07
$C_{Ar}-Al-Cl_{bridge}$	113.5(3)-121.5(4)
$Cl_{brid.}-Al-Cl_{term.}$	89.6(2)-90.0(2)

Fig. 8. Selected bond lengths (Å) and bond angles (°) for aluminum halides substituted with *m*-terphenyls.



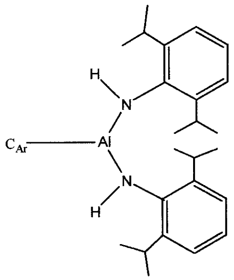
2-AlBr$_2$OEt$_2$

C_{Ar}-Al	1.983(9)
Al-Br	2.297(3)-2.302(3)
Al-O	1.868(8)
C_{Ar}-Al-Br	113.5(3)-119.2(3)
Br-Al-Br	109.41(12)
C_{Ar}-Al-O	106.7(4)



(4-AlBr$_3$Li)$_2$

C_{Ar}-Al	1.96(2)
Al-Br	2.285(6)-2.398(5)
Br-Li	2.52(3)-2.80(3)
Li---Li	3.41(5)
C_{Ar}-Al-Br	111.1(5)-122.2(5)
Al-Br-Li	84.9(7)-106.1(8)



4-Al(NH*i*Pr$_2$C$_6$H$_3$)$_2$

C_{Ar}-Al	1.978(11)
Al-N	1.788(6)
N-iPr$_2$C$_6$H$_3$	1.436(10)
C_{Ar}-Al-N	116.4(2)
N-Al-N	127.3(5)
Al-N-iPr$_2$C$_6$H$_3$	138.1(6)

Fig. 9. Selected bond lengths (Å) and bond angles (°) for organoaluminum compounds substituted with *m*-terphenyl ligands.

$Me_2NCH_2)C_6H_4]$, thus illustrating the synthetic utility of this molecule [24]. The geometry at gallium is of distorted tetrahedral geometry. Finally, reaction of **5**-Li with $GaCl_3$ produces monomeric **5**-GaCl$_2$ whereas, under similar reaction conditions, **5**-Li reacts with $InCl_3$ to produce dimeric (**5**-InCl$_2$)$_2$ [25].

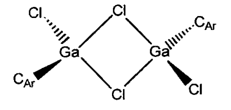
In contrast to boron and aluminum, two *m*-terphenyl substituents can be placed around the heavier Group 13 elements. For example, reaction of two equivalents of **4**-Li with $GaCl_3$ in ether, affords the diaryl gallium chloride **4**$_2$-GaCl [26]. X-ray crystallographic studies of crystalline **4**$_2$-GaCl reveal the extreme steric crowding at the gallium center and T-shaped geometry at gallium. The bromide **4**$_2$-GaBr was prepared in a similar fashion and is isostructural with **4**$_2$-GaCl [24]. The related indium halide **4**$_2$-InBr was reported, and it also has a sterically enforced T-shaped geometry [27]. Two synthetic routes to this compound were described: direct arylation of $InBr_3$ with **4**-Li and reaction of **4**-Li with In_2Br_4 which produces **4**$_2$-InBr via a disproportionation reaction.

6.2. Unusual compounds containing Group 13 elements

Homonuclear metal–metal bonds between heavy main group elements are not unknown, although they remain rare. Examples of ring systems containing these elements are noticeably few, and of importance to this review are the handful of examples that are primarily stabilized by ligands such as **1**.

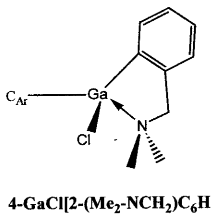
In 1995 a remarkable report described a novel ring containing compound of gallium. Reduction of **4**-$GaCl_2$ with sodium in ether results in the formation and isolation of Na_2(**4**-Ga)$_3$, a molecule with a Ga_3 core [28]. The potassium derivative K_2(**4**-Ga)$_3$ has also been reported [29]. Structural features for the potassium derivative are similar to that of the sodium compound.

The plane of gallium atoms (Ga–Ga–Ga angles 60.0(1)°) is capped by a sodium atom located 3.220(2) Å above the centroid of each face. The gallium–gallium bonds are short (2.44(1) Å), and these are significantly shorter than a single Ga–Ga bond (2.541(1) Å in $(Disyl)_2Ga–Ga(Disyl)_2$ and also shorter than in the radical anion $[Trip_2Ga–GaTrip_2]$ [30]. In view of this, it was suggested that there is significant σ-bonding within the gallium core. From a more interesting perspective, the three-membered gallium ring is a dianion with two delocalized π electrons. Therefore, this ring is formally isoelectronic with a cyclopropenium carbocation, which possess a Hückel number of delocalized electrons. With this in mind, it was argued that Na_2(**4**-Ga)$_3$ possesses aromatic character and that the planarity and short bonds observed for the gallium ring are consistent with metalloaromaticity. Theoretical calculations on model compounds such as $Na_2(GaH)_3$ and $K_2(GaH)_3$ support the aromatic character of this dianion [29].



(4-GaCl$_2$)$_2$

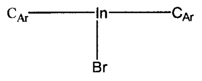
C_{Ar}-Ga	1.934(1), 1.96(1)
Ga-Cl_{bridge}	2.320(4)-2.333(5)
Ga-$Cl_{terminal}$	2.172(5), 2.290(4)
C_{Ar}-Ga-Cl_{bridge}	114.8-116.2(4)
Cl_{bridge}-Ga-Cl_{bridge}	86.8(2), 87.1(2)
C_{Ar}-Ga-$Cl_{terminal}$	126.0(4), 126.6(4)



4-GaCl[2-(Me$_2$-NCH$_2$)C$_6$H$_4$]

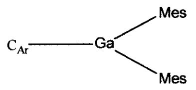
C_{Ar}-Ga	2.008(4)
Ga-Cl	2.229(2)
Ga-N	84.7(2)
Ga-C	1.991(5)
C_{Ar}-Ga-C	134.2(2)
C_{Ar}-Ga-Cl	109.63(14)
C_{Ar}-Ga-N	119.5(2)

Fig. 10. Selected bond lengths (Å) and bond angles (°) for organogallium compounds substituted with *m*-terphenyl ligands.



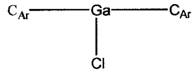
4_2-InBr

C_{Ar}-In	2.166(26), 2.171(25)
In-Br	2.505(4)
C_{Ar}-In-Br	98.7(6), 103.9(6)
C_{Ar}-In-C_{Ar}	157.3(8)



4-GaMes$_2$

C_{Ar}-Ga	1.998(7)
Ga-Mes	1.998(5)
C_{Ar}-Ga-Mes	124.15(13),124.15(14)
Mes-Ga-Mes	111.7(3)



4_2-GaCl

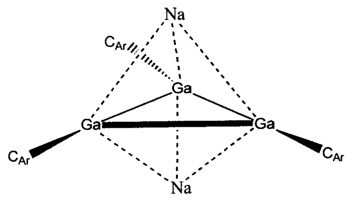
C_{Ar}-Ga	1.956(16)-2.001(16)
Ga-Cl	2.177(5)
C_{Ar}-Ga-C_{Ar}	153.5(5)
C_{Ar}-Ga-Cl	103.2(4)-103.4(4)

Fig. 11. Selected bond lengths (Å) and bond angles (°) of extremely crowded gallium and indium compounds substituted with *m*-terphenyl ligands.

6.3. Gallium-element triple bonds

Multiple bonds between heavy main group elements are of continued interest due to their synthetic potential via addition reactions as well as through a fundamental interest, recognizing the scarcity of structurally authenticated examples of these unusual compounds. Whereas reduction of **4**-GaCl with sodium resulted in the formation of Na_2(**4**-Ga)$_3$, reduction of the slightly larger aryl gallium dichloride **5**-$GaCl_2$ with metallic sodium resulted in the isolation of a compound that can be formulated as Na_2(**5**-Ga)$_2$ [31]. This molecule was reported to contain a Ga≡Ga triple bond. Significant structural features of this molecule include the Ga–Ga bond distance of 2.319(3) Å as well as the geometry around each gallium center which is bent (C_{ar}–Ga–Ga, 128.5(4) and 133.5(4)°). This contrasts to the anticipated linearity expected for an alkyne derivative. Also of note are interactions between Na^+ ions and the *ortho* mesityl rings and these should stabilize the Ga/Na cluster.

A recent article draws attention to the non-linearity of Na_2(**5**-Ga)$_2$ as well as other structural features and concludes that this compound can best be viewed as possessing a localized double bond, not a triple bond. This conclusion is based upon DFT calculations [32].



Ga-Ga	2.441(1)
Ga-Na	3.229(2)
Ga_3 Centroid ---Na	3.220(2)
C_{Ar}-Ga-Ga	133.7(1)
Ga-Ga-Ga	60.0(1)

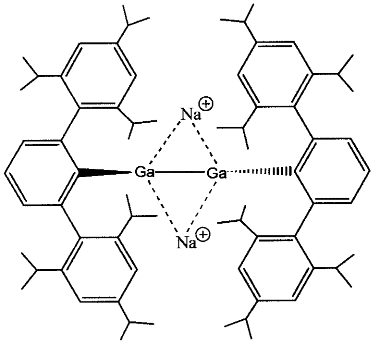
Fig. 12. Selected bond lengths (Å) and bond angles (°) for Na_2(**4**-Ga)$_3$.

Another molecule that has gained attention recently is **4**-GaFe(CO)$_4$, a molecule with a possible Ga≡Fe triple bond [33]. This compound was prepared in high yield by the reaction of **4**-GaCl$_2$ and Na$_2$[Fe(CO)$_4$]. Crystallographic studies were performed and revealed the shortest Ga–Fe bond yet reported (2.2248(7) Å). It has a linear geometry around gallium and thus it was formulated as a Ga≡Fe triple bond (Fig. 14(A)). This bonding description has been refuted based upon qualitative arguments as well as through DFT calculations. A model involving a dative Ga–Fe bond (Fig. 14(B)) was proposed, in which the iron has an 18-electron configuration. This is typical of LFe(CO)$_4$ compounds [34]. Finally, a bonding description intermediate between these two polarized views was reported [35].

6.4. Indium(I) and thallium(I) compounds

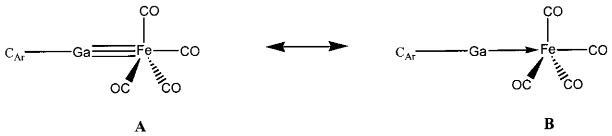
Consistent with periodic trends, the dominant oxidation state of the lighter Group 13 elements is three. As one proceeds down the group, the lower oxidation states become more stable with respect to disproportionation reactions to M^0 and M^{III}. Indium(I) forms a number of organometallic compounds which exhibit aggregation in the solid state. Crystallographically characterized examples include [In(Cp)]$_\infty$, which adopts a polymeric zigzag arrangement [36] as well as InCp* which exists in the crystal as a hexameric structure [37]. [38]

An example of a bona fide monomeric indium(I) compound has recently been reported. Reaction of InCl with **5**-Li results in the formation of a bright orange



C$_{Ar}$-Ga	2.028(14), 2.06(2)
Ga-Ga	2.319(3)
Ga-Na	3.085(7), 3.106(7)
C$_{Ar}$-Ga-Ga	128.5(4), 133.5(4)
C$_{Ar}$-Ga-Na	101.7(5)-107.0(6)
Ga-Ga-Na	66.76(13), 68.1(2)

Fig. 13. Selected bond lengths (Å) and bond angles (°) for Na$_2$(**5**-Ga)$_2$.



C$_{Ar}$-Ga	1.943(3)
Ga-Fe	2.2248(7)
Fe-CO	1.758(7)-1.766(5)
C$_{Ar}$-Ga-Fe	179.2(1)

Fig. 14. Resonance structures and pertinent structural data for **4**-GaFe(CO)$_4$.

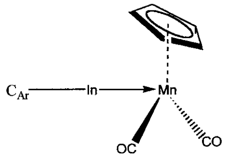
crystalline compound that has been characterized as **5**-In [39]. There are no In···In interactions (nearest In···In distance 6.890(2) Å). Confirmation or the Lewis basic nature of **5**-In is supported by its reactivity with electron pair acceptors such as η^5-Cp(CO)$_2$Mn(THF). The solid-state structure of the resulting complex **5**-InMnCp(CO)$_2$ has been determined. This compound exhibits linear geometry at indium. The infrared data for the carbonyl stretching frequencies indicate that the π-acceptor characteristics of **5**-In are weak.

A structurally related derivative **5**-Tl was reported and it is prepared through the facile reaction of **5**-Li(OEt$_2$) with TlCl in diethyl ether. Bright orange thermally unstable crystals of **5**-Tl can be isolated in good yield and the structure is consistent with a monomeric aryl thallium compound with no thallium···thallium interactions. The C_{Ar}–Tl bond length is 2.34(1) Å. Little interaction with the *ortho* tri-*iso*-propylphenyl rings was suggested [40].

7. Group 14: silicon halides, hydrides and amides

The chemistry of silicon halides and hydrides is an extensive field of study, and this is primarily due to their importance in polymeric systems and organic synthesis. Molecules central to this research area include silanes and chlorosilanes. The *m*-terphenyl ligand has been used to prepare several potentially synthetically useful silanes and chlorosilanes. Metathesis reactions of the corresponding alkylithium **4**-Li and **5**-Li and a halosilane compound afford in good yield **4**-SiCl$_3$, **5**-SiCl$_3$, **4**-SiHCl$_2$, **5**-SiHCl$_2$, **4**-SiH$_3$, **5**-SiH$_3$ and **4**-SiCl$_2$SiCl$_3$ [41]. Three compounds were crystallographically characterized namely **4**-SiCl$_3$, **5**-SiCl$_3$ and **4**-SiCl$_2$SiCl$_3$. Their solid-state structures reveal no unusual features.

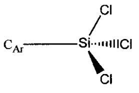
The synthesis of **2**-SiCl$_3$ was reported as part of an interesting study of silyl amines. Reaction of **2**-Li with SiCl$_4$ followed by aminolysis produces **2**-Si(NH$_2$)$_3$ which can be isolated as a crystalline solid in good yield. X-ray analysis of this material shows the anticipated geometry around silicon, but also shows the nitrogens in an unusual pyramidal geometry [42]. This contrasts with previously characterized Si–NH$_2$ containing compounds, which possess planar nitrogen centers. Planarity at nitrogen for Si–N compounds is believed to be the result of a Si–N π-bonding component either lp → σ* type or 1p → d type (lp = lone pair).



5-InMnCp(CO)$_2$

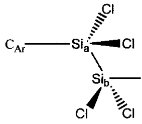
C_{Ar}-In	2.155(3)
In-Mn	2.4102(9)
Mn-(η^5-C_5H_5)	2.115(3)-2.311(4)
Mn-C	1.785(4)-1.774(4)
C-O	1.168(5)-1.167(5)
C-C_{Ar}-In	123.8(2)
C_{Ar}-In-Mn	175.39(9)

Fig. 15. Selected bond lengths (Å) and bond angles (°) for **5**-InMnCp(CO)$_2$.



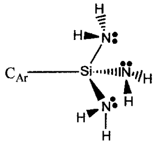
4-SiCl$_3$

C_{Ar}-Si	1.872(3)
Si-Cl	2.081(11)-2.0355(13)
C_{Ar}-Si-Cl	110.86(10)-116.03(10)



4-SiCl$_2$SiCl$_3$

C_{Ar}-Si(a)	1.874(4)
Si(a)-Cl	2.042(2)-2.050(2)
Si(a)-Si(b)	2.358(2)
Si(b)-Cl	2.027(2)-2.053(2)
C_{Ar}-Si(a)-Cl	110.43(14)-111.10(14)
C_{Ar}-Si(a)-Si(b)	128.62(14)



2-Si(NH$_2$)$_3$

Si-N	1.708(7)-1.710(7)

Fig. 16. Selected bond lengths (Å) and bond angles (°) for organosilicon compounds substituted with *m*-terphenyl ligands.

7.1. Low coordinate germanium, tin and lead compounds

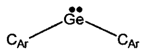
Dicoordinate Si, Le, Sn and Pb compounds are of interest due to their structural and electronic relationships to carbenes. The use of ligands **4** and **5** has resulted in the preparation of a whole series of new low-coordinate Ge, Sn and Pb compounds. For example, treatment of **4**-Li with MCl_2 ($M = Ge$, Sn or Pb) leads to the formation of **4**$_2$-M [43]. X-ray crystal structures have been determined and all three compounds are monomeric in the solid state. The metal centers in these compounds show no short contacts, the nearest metal centers being over 8 Å away.

Reaction of **4**$_2$-Ge with $GeCl_2$ results in ligand redistribution to form (**4**-GeCl)$_2$ which can be isolated in excellent yield [43]. This compound exhibits Ge–Ge association in the solid state (2.443(2) Å). Similar results were obtained from the reaction of **4**$_2$-Sn and $SnCl_2$ to produce (**4**-SnCl)$_2$. Both compounds are of great synthetic value since they possess a reactive M–X bond. The related compounds (**5**-GeCl)$_2$ and (**5**-SnI)$_2$ were also reported and possess no unusual structural features [44]. The synthetic versatility of the aryl metal halides was demonstrated by the synthesis of **5**-SnN(SiMe$_3$)$_2$, also reported to be easily prepared directly from **5**-Li and Sn[N(SiMe$_3$)$_2$]$_2$ [44].

A structural feature common for all LMX compounds (L = **4**, **5**, M = Ge, Sn, Pb, X = Cl, I) is significant distortions of the C_{aryl}–M bond. These manifest themselves as an approach of the central atom to one of the two closest flanking aryl rings. These interactions are reminiscent of Menshutkin complexes, which are well known for Group 14 elements in oxidation state II (vide infra).

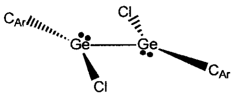
7.2. Unusual Group 14 compounds

Reduction of **4**-GeCl with one equivalent of KC_8 affords the cyclotrigermenyl radical (**4**-Ge)$_3$ [45]. This molecule was characterized by ESR spectroscopy and by



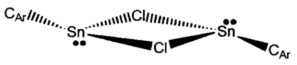
4_2-Ge

C_{Ar}-Ge	2.033(4)
C_{Ar}-Ge-C_{Ar}	114.4(2)



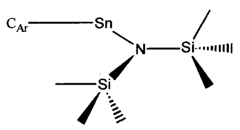
(4-GeCl)$_2$

C_{Ar}-Ge	2.000(6)
Ge-Ge	2.443(2)
Ge-Cl	2.120(2)
C_{Ar}-Ge-Cl	113.7(2)
Ge-Ge-Cl	107.49(8)



(4-SnCl)$_2$

C_{Ar}-Sn	2.222(5)
Sn-Cl	2.600(2), 2.685(2)
C_{Ar}-Sn-Cl	92.35(14), 102.11(14)
Sn-Cl-Sn	98.28(6)
Cl-Sn-Cl	92.35(14)



5-Sn[N(TMS)$_2$]

C_{Ar}-Sn	2.225(5)
Sn-N	2.094(5)
N-Si	1.736(5), 1.756(4)
N-Sn-C_{Ar}	108.4(2)
Si-N-Si	125.7(3)
Sn-N-Si	106.1(2), 123.9(2)

Fig. 17. Selected bond lengths (Å) and bond angles (°) for organogermanium and tin compounds, stabilized by *m*-terphenyl substituents.

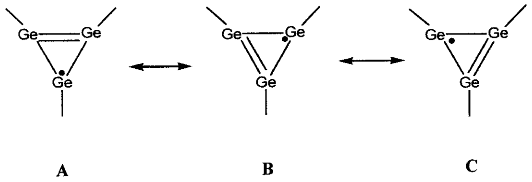
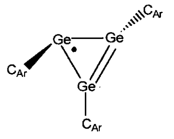


Fig. 18. Resonance structures of the cyclotrigermenyl radical (**4**-Ge)$_3$ showing bond lengths (Å) and bond angles (°).

X-ray crystallography, and possesses a delocalized π-bond as well as a delocalized unpaired electron and the average Ge–Ge distance is 2.35(7) Å. Likewise, reduction of **4**-GeCl with two equivalents of KC_8 produces the anionic trigermenyl anion K(**4**-Ge)$_3$ [45]. This compound can be viewed as the ring-opened product of cyclic radical (**4**-Ge)$_3$. The Ge–Ge bond length is 2.422(2) Å with a Ge–Ge–Ge angle of 159.19(10)°. The geometrical features are consistent with the description of an alkyl anion analogue.

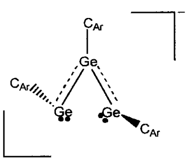
Finally, reaction of **4**-GeCl with Na[Mo(η^5Cp)(CO)$_3$] results in the formation of **4**-GeMo(η^5Cp)(CO)$_2$ [46]. The Mo–Ge bond is short, 2.271(1) Å, and the geometry around germanium is almost linear. (Mo–Ge–C, 172.2(21)°). The structural data and the electronic configuration of this species allows for the assignment of a Mo≡Ge triple bond (i.e. a germylyne complex).

The radical anion [**5**-SnSn-**5**]$^{-\bullet}$ was synthesized via the reduction of **5**-SnCl in THF using KC_8 [47]. This anion has been characterized as the salt of two different cations, namely $[K(THF)_6]^+$ and $[K(\text{dibenzo-18-crown-6})(THF)_3]^+$. There are no significant structural differences for the anion in these two salts The Sn–Sn distance is 2.8123(9) Å, and the Sn–Sn–C_{Ar} angle is 95.20(13)°. Structural data for this molecule support the assignment of this molecule as having a bond order of 1.5 (i.e. a π bond plus a half-filled σ bond).



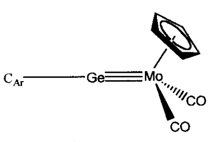
(4-Ge)$_3$

Ge-Ge(av)	2.35(7)



(4-Ge)$_3^-$

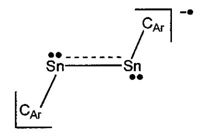
Ge-Ge	2.422(2)
Ge-Ge-Ge	159.19(10)
C_{Ar}-Ge-Ge	111.3(3)



4-GeMoη^5Cp(CO)$_2$

C_{Ar}-Ge	1.933(7)
Ge-Mo	2.271(1)
Mo-η^5(C_5H_5)	2.30(1)-2.379(12)
Mo-Ge-C_{Ar}	172.2(2)

Fig. 19. Selected bond lengths (Å) and bond angles (°) for unusual organogermanium compounds stabilized by *m*-terphenyl substituents.



Sn-Sn	2.8123(9)
C_{Ar}-Sn	2.236(5)
Sn-Sn-C_{Ar}	95.20(13)

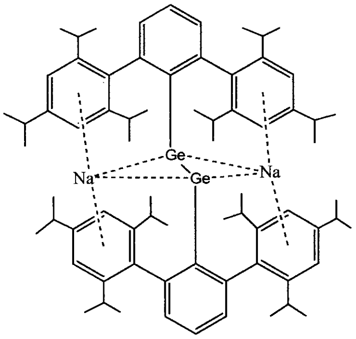
Fig. 20. Selected bond lengths (Å) and bond angles (°) for [**5**-SnSn-**5**]$^{-\bullet}$.

Reduction of **6**-MCl (M = Ge or Sn) with alkali metals (Na or K) produces doubly reduced compounds. Two derivatives were crystallographically characterized. Na_2(**5**-Ge)$_2$ and K_2(**5**-Sn)$_2$. These provide interesting comparisons to the previously described radical anion [**5**-SnSn-**5**]$^{-\bullet}$ [48]. The doubly reduced species possesses formal M=M double bonds (i.e. a π bond plus a filled σ bond) and as a result are formally isoelectronic to dipnictenes (vide infra). Also noteworthy, is the presence of η^6-arene···Na^+ and η^6-arene···K^+ interactions.

8. Group 15: halides, hydrides and derivatives

Synthesis of the synthetically valuable phosphorus halide **4**-PCl_2 proceeds in high yield via the reaction of **4**-Li and PCl_3 in THF [49]. This molecule is water sensitive and the phosphinic acid, **4**-P(O)(OH)H, has been isolated and comprehensively characterized. Conversion of **4**-PCl_2 to the air stable primary phosphine **4**-PH_2 can be easily achieved through reaction with $LiAlH_4$ followed by aqueous work-up [49].

The phosphine **4**-PH_2 reacts readily with metallic potassium to give the solvent free phosphide, **4**-P(H)K, which in the solid state, is a tetramer (**4**-P(H)K)$_4$ [50]. The solid-state structure is a '4-step' ladder. Each phosphorus atom interacts with as many as three K^+ atoms and the potassium atom interacts with as many as three phosphorus atoms. Each K^+ cation also exhibits η^6 π-interactions to the mesityl rings of ligand **4**. Substitution of both hydrogen atoms on phosphorus by alkali metals has not been observed, although it has been observed for the smaller ligands **2**-PH_2 and **3**-PH_2. Finally it is interesting to note that **4**-PH_2 does not undergo bis-metallation which is in contrast with, for example, $MesPH_2$.



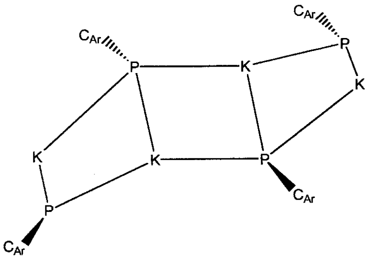
Ge-Ge	2.3943(13)
C_{Ar}-Ge	2.065(3)
Ge-Na	3.074(3)-3.121(3)
Ge-Ge-C_{Ar}	102.37(8)
Na-C_{ipso}	2.799(3)-2.813(3)

Fig. 21. Selected bond lengths (Å) and angles (°) for Na_2(**5**-Ge)$_2$.

Under similar reaction conditions as those for the metallation of **4**-PH$_2$ with potassium, reaction of **4**-PH$_2$ with Rb and Cs produced the related compounds, **4**-P(H)Rb and **4**-P(H)Cs [51]. X-ray crystallographic analysis of crystals isolated from the reaction mixtures indicate the formation of the phosphide (**4**-P(H)Rb)$_4$ $\cdot$ C$_7$H$_8$ and the complex phosphide salt $\{$Cs$^+$[**4**-P(H)Cs$_2$]$^-$ $\cdot$ 1/3C$_7$H$_8\}_x$ [51]. The rubidium salt (**4**-P(H)Rb)$_4$ $\cdot$ C$_7$H$_8$ is a tetramer with a cubic arrangement of Rb and P atoms. The cesium salt $\{$Cs[**4**-P(H)Cs$_2$] $\cdot$ 1/3C$_7$H$_8\}_x$ is a polymeric two-dimensional framework of Cs$^+$ and$\{$[**4**-P(H)]$_3$Cs$_2$] contact ion pairs. Again evident are η^6 π-interactions between the Cs$^+$ and Rb$^+$ cations and the *ortho* mesityl groups of **4**.

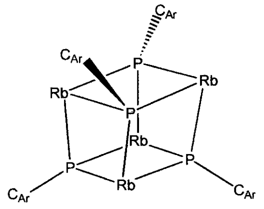
The syntheses and structures of the heavier *m*-terphenyl dihalopnictogens have also been reported. Of particular interest are the structures of **6**-AsCl$_2$, **5**-SbCl$_2$, and **4**-BiCl$_2$ [52]. For **6**-AsCl$_2$, **5**-SbCl$_2$ and **4**-BiCl$_2$ the solid-state structures are monomeric (i.e. no M···Cl interactions). Both of these compounds exhibit M···Aryl interactions which are evident between the *ortho* mesityl rings and the metal center. Furthermore, the bismuth derivative has two crystal forms and the formation of these is solvent dependent. For example, recrystallization of **4**-BiCl$_2$ from benzene yields the monomeric form. The dimeric form is obtained by recrystallization of **4**-BiCl$_2$ from ether giving a product possessing Bi···Cl bridges, and as such, is related to **2**-BiCl$_2$.

Finally, reaction of **2**-Li in THF with BiCl$_3$ yields **2**$_3$-Bi, which was characterized by X-ray crystallography [53]. The structure is similar to that found for other BiR$_3$ compounds. Finally the synthesis of (**2**-BiCl$_2$)$_2$[53] was also reported. The structure of (**2**-BiCl$_2$)$_2$ is dimeric in the solid state with two terminal and two bridging chloride substituents [54]. Finally, the synthesis of **2**-BiCl$_2$ was reported [54]. This compound is dimeric in the solid state (i.e. (**2**-BiCl$_2$)$_2$) and the bismuth center possess one terminal Bi–Cl bond and two bridging chloride interactions.



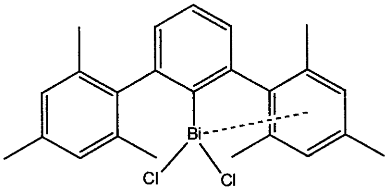
K-P	3.043(2)-3.438(2)
C$_{Ar}$-P	1.800(5)

Fig. 22. The '4-step' ladder core of (**4**-P(H)K)$_4$.

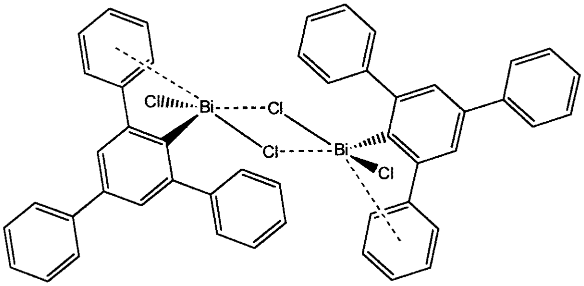


P-Rb	3.399(2)-3.756(2)
Rb---Rb	4.2896(10)-5.3954(12)
P-Rb-P	79.31(5)-106.11(5)

Fig. 23. Pertinent structural data for [**4**-P(H)Rb]$_4$C$_7$H$_8$.



4-BiCl$_2$	Bi-Centroid	3.472
	C$_{Ar}$-Bi	2.267(5)
	Bi-Cl	2.501(1), 2.539(1)
	C$_{Ar}$-Bi-Cl	94.3(1), 102.3(1)
	Cl-Bi-Cl	88.20(5)



(2-BiCl$_2$)$_2$	Bi-C$_{Ar}$	2.266(4)
	Bi-Cl$_{terminal}$	2.529(13)
	Bi-Cl$_{bridging}$	2.5305(12), 3.0738(12)
	Bi-Centroid	3.527
	C$_{Ar}$-Bi-Cl$_{bridging}$	79.05(12)
	Cl$_{briding}$-Bi-Cl$_{briding}$	79.72(4)
	Bi-Cl$_{briding}$-Cl$_{briding}$	100.28(4)

Fig. 24. Selected bond lengths (Å) and bond angles (°) for **4**-BiCl$_2$ and (**2**-BiCl$_2$)$_2$.

8.1. Multiple bonds involving Group 15 elements

Group 15 dipnictenes (i.e. those which feature E=E double bonds) have been extensively studied, and many of these have been isolated for phosphorus and arsenic. The heavier congeners are more rare [55,56]. The first diphosphene possessing terphenyl substituents was **4-P=P-4** and it was prepared by the reductive coupling of **4**-PCl$_2$ with magnesium in THF. This molecule possesses a short P=P double bond (1.985(2) Å) [49]. Surprisingly reduction of **5**-PCl$_2$ with magnesium produces **5-P=P-5** as well as a small amount of the cyclic phosphine shown in Fig. 25 [52].

Two homologous series of dipnictenes were prepared by reductive coupling of **4-E=E-4** compounds (E = As, Sb and Bi) and **5-E=E-5** were also reported and structural data are given in Fig. 26. All were prepared in high yield (< 80%) [52].

Unsymmetric dipnictenes were also prepared by a new synthetic route. Direct reaction of $MesPLi_2$ with **5**-$AsCl_2$ or **5**-$SbCl_2$ yields the phosphaarsene MesP=As-**5** and the first crystallographically characterized phosphastibene MesP=Sb-**5** [57]. All structural parameters are in agreement with anticipated values.

9. Stabilization of unusual molecules with *m*-terphenyls

The kinetic and thermodynamic consequences of bulky substitution have been examined [2]. Using a simple model, it was shown that while large groups kinetically stabilize molecules (i.e. provide large activation energies to prevent rearrangement through dimerization, etc.), they can also influence the relative energetics between, for example, monomeric and dimeric structural alternatives through the release of substituent steric strain. These thermodynamic and kinetic considerations are true for the generalized *m*-terphenyl ligand **1**.

Examination of the data collected for the review indicates the suitability of *m*-terphenyls to stabilize electron rich (anionic) species as well as neutral species. Particularly for the anionic species, formation of close anion/cation pairs is generally observed with terphenyl substituents. This allows close electrostatic interactions between the cations (such as Li^+, Na^+, K^+, Cs^+ and Rb^+) and the anionic centers of the molecules. Also evident are η^6 π-interactions between the cation and the *ortho* aryl rings as is observed for (**4**-Li)$_2$, K_2(**4**-Ga)$_3$, Na_2(Ga-**5**)$_2$ and **4**-P(H)K. Thus, in many cases, a cluster of metals is observed, with M···cation interactions evident, as well as cation···arene interactions. Furthermore, compounds such as **4**-MCl_2 (M = As, Sb, Bi) exhibit metalloid···arene interactions which are reminiscent of Menshutkin complexes [58]. The significance of these interactions between central atoms (or functional groups) and the two *ortho* aryl rings on *m*-terphenyl ligands has been the subject of an elegant NMR study [59].

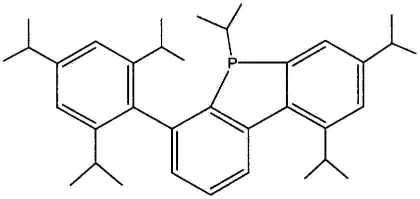
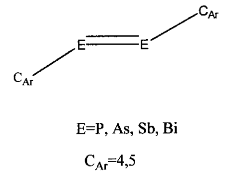
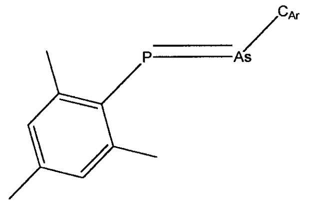


Fig. 25. The cyclic by-product produced by the reduction of **5**-PCl_2.



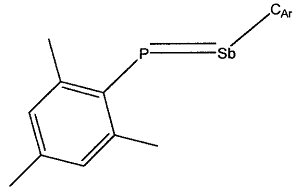
	E-E	E-E-C_{Ar}
4-P=P-4	1.985(2)	97.5(1), 109.8(1)
4-As=As-4	2.276(3)	98.5(4)
4-Sb=Sb-4	2.6558(5)	94.1(1)
4-Bi=Bi-4	2.8327(14)	92.5(4)
5-As=As-5	2.285(3)	96.4(2), 107.8(2)
5-Sb=Sb-5	2.668(2)	98.9(2)

Fig. 26. Symmetrical dipnictenes stabilized by *m*-terphenyl substituents showing relevant bond lengths (Å) and angles (°).



C_{Ar}-As	1.975(6)
As-P	2.134(2)
C_{Ar}-As-P	101.4(2)
C_{Mes}-P-As	96.7(2)

MesP=As-5

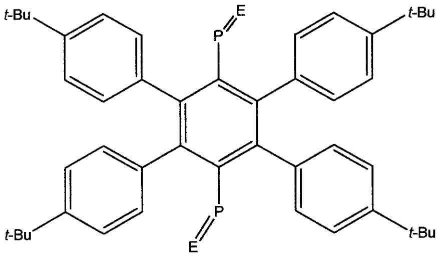


C_{Ar}-Sb	2.174(7)
Sb-P	2.335(2)
C_{Ar}-Sb-P	100.9(2)
C_{Mes}-P-Sb	95.7(3)

MesP=Sb-5

Fig. 27. Unsymmetrical dipnictenes stabilized by *m*-terphenyl substituents showing relevant bond lengths (Å) and angles (°).

Recognising these facts, compounds which exhibit M···Aryl associations represent a novel class of 'base stabilized' compounds. Previous to this, base stabilization was achieved through σ-donation (most commonly from a nitrogen or oxygen donor) to a reactive metal site. In ligands such as **1**, base stabilization is achieved through π-interactions which add stability to the observed complexes between cations (i.e. K^+, Na^+, Cs^+) as well as heavy metalloids (i.e. Sn, Pb, As, Sb, Bi). It is clear then, that terphenyl ligands provide both kinetic stabilization (steric bulk), as well as thermodynamic stabilization (i.e. through η^6 arene σ-bond formation) .



E= 4-P and C_6H_5-C(H)

Fig. 28. Diagram of a bifunctional low-coordinate phosphorus compounds stabilized by a 1,4-disubstituted tetraarylbenzene core.

10. Conclusions and outlook

m-Terphenyl ligands have been shown to be effective substituents for the stabilization of numerous unusual bonding arrangements. Future applications of these large substituents are likely to occur, and three exciting possibilities are described here.

Perhaps one of the greatest synthetic challenges remaining in main group chemistry is the synthesis of bona fide E≡E triple bonds. Such alkynic derivatives, particulary those involving triple bonds to carbon, are well known for phosphorus and arsenic [1], but they remain elusive for Si, Ge, Sn, Pb, Sb and Bi. Ligands such as **1** may facilitate the isolation of these heavy element containing alkyne congeners.Bifunctional main group compounds are rather rare, and it is likely that significant developments will occur using terphenyl ligands. A recent development describes the synthesis of bis(diphosphenes) and bis(phosphaalkenes) using (*p*-*tert*-butylphenyl)$_4C_6X_2$ as the central unit (Fig. 28) [60]. These compounds may have numerous applications, including molecular wires as well as interesting polymeric materials. They may also exhibit unusual coordination behavior to transition metals.

The chemistry of main group arylamides and aryloxy compounds is a wide and diverse field of study. As with the phosphide **4**-PH_2, numerous exciting advances are expected with the sterically demanding amine and phenol **4**-NH_2 and **4**-OH, respectively [61].

Acknowledgements

The authors would like to thank Acadia University and the Natural Science and Engineering Research Council of Canada (NSERC) for financial support. We are also grateful to Matthew Hopkins, Tamara Hamilton and Carla Dumaresque for help in the preparation of this manuscript.

Note: an excellent review of the same material described above has recently been published [62]. Although the material covered is the same, the authors hope that the synthetic inorganic community will find them complementary.

Appendix A. Abbreviations

Bmt	(4-*tert*-butyl-2,6,-bis[2,2″,6,6″-tetramethyl-*m*-terphenyl-2′-yl)methyl] phenyl)
C_{Ar}	carbon center on the central aryl ring
C_{ipso}	*ipso* carbon on the 2 or 6 aryl ring
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl

Dipp	2,6-di-*iso*-propylphenyl
Et	ethyl
Et_2O	diethyl ether
${}^{i}Pr$	*iso*-propyl
Me	methyl
Mes	2,4,6-trimethylphenyl
Mes*	2,4,6-tri-*tert*-butylphenyl
Ph	phenyl
Trip	2,4,6-tri-*iso*-propylphenyl

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