FEATURE ARTICLE

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Silicon, germanium, tin and lead analogues of acetylenes

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Recent experimental results which have described the characterization of the first, stable heavier group 14 element analogues of acetylenes are outlined. It is shown that the use of large terphenyl substituents allows the isolation of transition metal-heavier group 14 element complexes that can achieve essential triple bonding by a three-fold orbital interaction between the transition metal and group 14 moiety. On the other hand the alkyne analogues RMMR (R = Ge, Sn or Pb) display increasing distortions from linearity to *trans*-bent geometry due to the accumulation of non-bonding electron density at the group 14 element. The non-bonding electron density comes at the expense of electron density in the bonding region between the group 14 elements. Accordingly the bond orders are decreased to values that are near double for the germanium and tin derivatives and single for the lead compound.

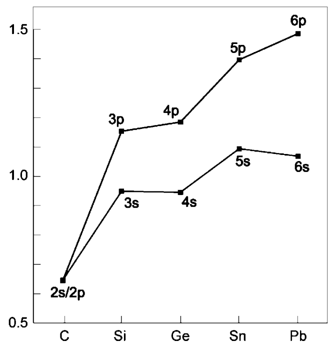

Fig. 1 Variation in the most probable radii of the s and p valence orbitals in group 14 elements.[2]

1 Introduction

The study of stable compounds with multiple bonds between heavier main group elements has been guided almost exclusively by the pursuit of molecules (generally stabilized by large substituents) that are iso-structural to their carbon analogues. However, it has become increasingly clear that this goal is difficult, if not impossible, to attain for reasons which are inherent to the electronic structure of the heavier main group elements where orbital mixing (hybridization) occurs to a much lesser extent than in the lightest element in each group.[1] This phenomenon is most easily understood in terms of the radii of the s and p orbitals as illustrated for group 14 elements (tetrels) in Fig. 1.[2] For carbon the most probable radii of the 2s and 2p orbitals are almost the same owing to the absence of Pauli repulsions from non-existent 1p electrons. In contrast, the radii of *n*s and *n*p (*n* = 3–6) orbitals of the heavier congeners Si–Pb differ considerably. This makes orbital mixing in these elements more difficult. The result is that the more stable, lower energy s-electrons are increasingly excluded from bonding. In effect, the valence s electrons become increasingly lone pair in character as each group is descended and this has profound bonding and structural consequences. The group 14 element alkene analogues, first synthesized by Lappert,[3] West[4] and Brook,[5] provide a striking illustration of the changed bonding where, instead of the planar D_{2h} geometry typically seen in alkenes, increasingly *trans* pyramidal geometries (C_{2h}) and decreased bond shortenings are observed on proceeding from the silicon to the lead compounds.[6] In fact, for the tin, lead and many of the germanium alkene congeners dissociation takes place in hydrocarbon solution to give monomeric **:**MR_2 molecules (M = Ge, Sn or Pb, R = hydrocarbyl or related group). The silicon derivatives (disilenes) generally do not dissociate at room temperature, their geometries usually display only modest deviations from planarity and the Si–Si bond lengths are consistent with double bonds. In addition, solid state ^{29}Si NMR data for a range of disilenes lend experimental support to the classical σ- and π-bonded model for the Si–Si double bond.[7] At present, about forty of the heavier tetrel alkene analogues have been structurally characterized and their chemistry has been examined in some detail.[6] In general, the chemistry of the heaviest derivatives also supports the weak bonding picture suggested by the structural data and solution behavior.

In spite of the large body of experimental data now known for the Si–Ge alkene analogues, stable alkyne congeners RMMR (M = Si–Pb) have remained unknown until recently. One of the reasons for their absence has been the greater steric requirements for the R group since each tetrel now carries only one substituent. Another has been the scarcity of suitable precursors that could be smoothly converted to stable RMMR molecules. Nonetheless, since the early 1980s there have been numerous

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calculations on their hypothetical hydrogen or methyl derivatives in particular those of silicon and germanium.[8,9] The unique hydrogen species were calculated to possess energetically low lying doubly bridged, monobridged or vinylidene structures in preference to a *trans*-bent or linear triply bonded form. Spectroscopic studies on Si_2H_2 have identified both the mono- and dihydrogen bridged structures HSi(μ-H)Si and $Si(\mu\text{-}H)_2Si$ which have short Si–Si distances of 2.119 and 2.2079 Å (*cf.* Si–Si = 2.34 Å in elemental silicon).[10] Computational data for methyl derivatives[8,9,11] have clearly shown that the vinylidene and planar *trans*-bent C_{2h} structures are the lowest energy isomers. With large substituents the vinylidene form is disfavored for steric reasons, and the planar, *trans*-bent isomer is the most stable. The *trans*-bent structure is favored over the linear structure for similar reasons to the preference for *trans*-pyramidal C_{2h} structures in the alkene analogues. The calculations have also shown that the electronic properties of the substituents can exert a large effect.[11,12] Although in all cases the *trans*-bent geometry is more stable than the linear, in some cases by as much as 37 kcal mol^{-1}, the use of σ-donor substituents such as silyls can lower the energy difference to as little as *ca*. 4 kcal mol^{-1} in RSiSiR molecules[12] so that a disilyne which has nearly linear geometry should be isolable at room temperature.[13]

In addition to the computational results a number of experiments have indicated the existence of alkyne-like transient species such as MeSiSiMe,[14] $2,6\text{-}Mes_2H_3C_6SiSiC_6H_3\text{-}2,6\text{-}Mes_2$[15] (Mes = C_6H_2-2,4,6-Me_3), R*SiSiR*,[16] R_2*MeSiSiSiSiMeR*$_2$ (R* = $SiBu^t_3$),[17] HCSiX (X = F or Cl) or $Me_3SiCGeC_6H_3\text{-}2,6(CH_2NPr^i_2)_2$.[18] They were either detected spectroscopically or their existence was inferred on the basis of plausible reaction schemes. None has been isolated however. The main purpose of this feature article is to summarize the most prominent recent experimental developments in the characterization of stable heavier group 14 element alkyne-like derivatives, and to discuss their bonding and its impact on the current debate on the nature of triple bonds in heavier main group compounds.

2 Stable compounds with transition heavier group 14 element triple bonds: isolobal analogies

The first stable compound to feature triple bonding to a heavier tetrel was the molybdenum–germanium derivative $(\eta^5\text{-}C_5H_5)(CO)_2MoGeC_6H_3\text{-}2,6\text{-}Mes_2$.[19] This species was synthesized by the reaction given in eqn. (1).

This route involved elimination of NaCl and CO to generate $(\eta^5\text{-}C_5H_5)(CO)_2Mo{\equiv}Ge\text{–}C_6H_3\text{-}2,6\text{-}Mes_2$ under mild conditions. The facile elimination of CO is probably due to steric congestion caused by the large size of the terphenyl substituent. An X-ray crystal structure (Fig. 2) showed that the germanium was two-coordinate and it had a wide Mo–Ge–C interligand angle of 172.2(2)°. Moreover, the Mo–Ge bond length of 2.271(1) Å was quite short in comparison to single bonds (*ca.* 2.65 Å) in other molybdenum-germanium complexes. These structural parameters were consistent with the presence of an Mo–Ge triple bond—a germylyne complex. This bonding description was also justified on the basis of a three fold interaction between the three frontier orbitals (of a and e symmetry) of the 15-electron fragment $Mo(\eta^5\text{-}C_5H_5)(CO)_2$ and the isolobal, three electron GeAr moiety as shown in Fig. 3. Subsequent work expanded the original result for molybdenum to the chromium and tungsten analogues as well as species with the larger $\text{–}C_6H_3\text{-}2,6\text{-}Trip_2$ (Trip = $C_6H_2\text{-}2,4,6\text{-}Pr^i_3$) substituent at germanium.[20] In addition, the corresponding chromium and tungsten singly bonded tricarbonyl derivatives of GeAr were isolated by performing the reaction at lower temperature. Important structural parameters for these complexes are summarized in Table 1. It is clear that the triply bonded species have M–Ge bonds that are more than 0.4 Å shorter than those in the singly bonded complexes. Also, the narrower M–Ge–C angles (< 120°) in the singly bonded complexes are consistent with the presence of a lone pair at germanium.

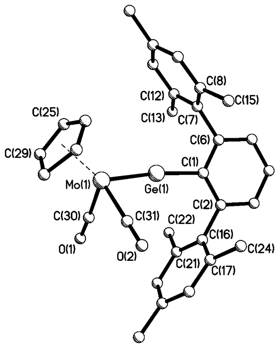


Fig. 2 Drawing of the X-ray crystal structure of $(\eta^5\text{-}C_5H_5)(CO)_2Mo{\equiv}Ge\text{–}C_6H_3\text{-}2,6\text{-}Mes_2$ showing the almost linear geometry for the Mo–Ge–C moiety. Hydrogen atoms are not shown.[19]

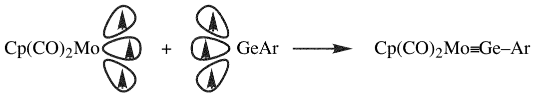


Fig. 3 Schematic drawing of the orbital interactions between the fragments $Cp(CO)_2Mo$ and ArGe.

Table 1 Selected structural data for singly bonded $(\eta^5\text{-}C_5H_5)(CO)_3M\text{–}Ge\text{–}Ar$ (M = Cr or W) and triply bonded $(\eta^5\text{-}C_5H_5)(CO)_2M{\equiv}Ge\text{–}Ar$ (M = Cr, Mo or W) Complexes[19,20]

	Cr	Mo	W
$(\eta^5\text{-}C_5H_5)(CO)_3M\text{–}Ge\text{–}Ar$			
M–Ge/Å	2.590(2)[a]	—	2.681(3)[a]
M–C/Å	1.989(8)	—	1.99(2)
C–Ge–M/°	117.8(2)	—	114.7(6)
$(\eta^5\text{-}C_5H_5)(CO)_2M{\equiv}Ge\text{–}Ar$			
M–Ge/Å	2.1666(4)[a]	2.272(8)[a]	2.277(1)[b]
M–C/Å	1.951(2)	1.936(5)	1.916(11)
C–Ge–M/°	175.99(6)	174.25(14)	170.9(3)

[a] Ar = $C_6H_3\text{-}2,6\text{-}Trip_2$. [b] Ar = $C_6H_3\text{-}2,6\text{-}Mes_2$.

The reaction, by Filippou and coworkers, of Ge(X)Cp* (X = Cl, Br or I; Cp* = cyclo-C_5Me_5) with *trans*-$[M(dppe)_2(N_2)_2]$ (M = Mo or W; dppe = $Ph_2PCH_2CH_2PPh_2$) as shown in eqn. (2)[21,22] has provided an alternative synthetic approach to germylyne complexes *via* an oxidative addition–displacement reaction. The products obtained were *trans*-X(dppe)$_2$M≡GeCp* (M = Mo; X = Cl or Br; W, X = Cl, Br or I) wherein the Cp* is η^1 bonded to germanium and which featured M–Ge triple bond distances and angles in the range 2.293(1)–2.3185(6) Å and 171.23(3)–174.04(3)°. Density functional calculations were performed on model complexes of the type *trans*-$[Cl(L)_4W{\equiv}ECp]$ (L = CO, PH_3; E = C, Ge; Cp = $\eta^1\text{-}C_5H_5$). The complexes were predicted to have an η^1-bound Cp

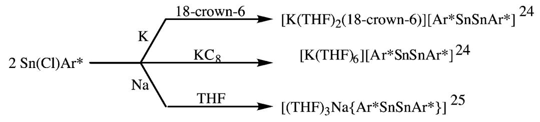
$$\mathrm{Na}\left[\mathrm{Mo}\left(\eta^5\text{-}\mathrm{C_5H_5}\right)\left(\mathrm{CO}\right)_3\right] + \mathrm{Ge}\left(\mathrm{Cl}\right)\mathrm{C_6H_3\text{-}2,6\text{-}Mes_2} \xrightarrow{50\ ^\circ\mathrm{C}} \left(\eta^5\ \text{-}\mathrm{C_5H_5}\right)\left(\mathrm{CO}\right)_2\mathrm{Mo} \equiv \mathrm{Ge\text{-}C_6H_3\text{-}2,6\text{-}Mes_2} + \mathrm{CO} + \mathrm{NaCl} \qquad (1)$$

$$\textit{trans}\text{-}\left[\mathrm{M}\left(\mathrm{dppe}\right)_2\left(\mathrm{N_2}\right)_2\right] + \mathrm{Ge}\left(\mathrm{X}\right)\mathrm{Cp}^* \rightarrow \textit{trans}\text{-}\mathrm{X}\left(\mathrm{dppe}\right)_2\mathrm{M} \equiv \mathrm{Ge\text{-}Cp}^* + 2\mathrm{N_2} \qquad (2)$$

substituent and there was fair agreement between the experimental and theoretical W≡Ge bond distances (to be calculated 2.347 and 2.374 Å).[21,22] The calculations showed that the germylyne ligand is a poorer σ-donor than a carbyne but an equally good π-acceptor. However, comparison of the carbonyl stretching frequencies of the triply bonded complexes in Table 1 showed that they were significantly (45–65 cm^{-1}) lower than those in related carbyne complexes. This difference may be interpreted in terms of a higher σ-donor/π-acceptor ratio for the germylyne ligand. This may be a result of the higher electropositive character of germanium which may permit stronger σ-bonding to the metal through an orbital that may have considerable sp character and is relatively low in energy. The sp hybridization at germanium is supported by the observation of J_{CW} = ^{13}C–^{183}W coupling in the range 46–48 Hz for the *ipso* carbon of the terphenyl ligand, which is very similar to the 38 Hz coupling reported for (η^5-C_5H_5)(CO)$_2$W≡C–C_6H_3-2,6-Me_2.[23] On the other hand, the germanium p-orbitals are expected to be at a significantly higher energy which may result in less efficient π-interaction with the frontier orbitals of the metal fragment (but see later in section 7). Irrespective of which bonding picture is more accurate, the interaction between the germanium and transition metal moieties is essentially a triple one that ensures very short Ge–M distances and a near linear germanium coordination. Their designation as germylyne complexes is thus a relatively accurate description of their bonding. In essence, the Ge–M bond is composed of three electron pairs in orbitals that are localized mostly in the region between the germanium and transition metal. Furthermore, the geometry at germanium closely resembles the linear arrangement found at carbon in alkynes.

3 Reduction of M(Cl)Ar* to the mono and dianions [Ar*MMAr*]$^{\cdot-}$ and [Ar*MMAr*]$^{2-}$ (M = Ge or Sn)

The isolation of transition metal complexes with triple bonds to an almost linearly coordinated germanium suggested that stable compounds of the general formula RMMR (R = alkyl or aryl group; M = Si–Pb) were an attainable goal. The first experiments directed toward this objective involved the reduction of the aryltin(II) halide Sn(Cl)Ar* (Ar* = C_6H_3-2,6-$Trip_2$) with potassium or sodium in accordance with Scheme 1.[24,25] It is noteworthy that organotetrel(II) halide reduction substrates themselves, *i.e.* species of the formula M(X)R (M = Ge, Sn or Pb, R = monodentate alkyl or aryl group), had been extremely rare and confined to a number of $C(SiMe_3)_3$ derivatives.[24] The use of terphenyl groups as R substituents showed that they could possess quite a wide structural diversity. Unusual halide substituted alkene like structures observed for germanium, chloride bridged dimers were obtained for tin and monomeric structures were observed for derivatives of lead.[26–28]



Scheme 1 Reduction of Sn(Cl)Ar* with Na, K or KC_8.

It can be seen in Scheme 1 that even when stoichiometric quantities of reductant were used, singly reduced salts were crystallized in each case. It was also shown that stirring Sn(Cl)Ar* with excess potassium for longer periods gave the novel doubly reduced complexes K_2Ar*SnSnAr*.[29] Important bond distances and angles for the various reduced tin species are given in Table 2. The singly reduced compounds contain one unpaired electron and EPR spectroscopy showed that the hyperfine coupling to the $^{119/117}$Sn isotopes was small (*ca.* 8–9 G) and consistent with the location of the odd electron in a π-orbital. The Sn–Sn bond lengths in the monoanions were near 2.81 Å (*cf.* 2.80 Å in gray tin)[30] and featured Sn–Sn–C angles in the range 93.6–98.0°, *cf.* structure of [(THF)$_3$Na{Ar*SnSnAr*}] in Fig. 4.[25] Due to the relatively narrow Sn–Sn–C angles in these compounds, they were viewed as a singly reduced form IV of the singly bonded valence isomer(III) of the distannyne(I) as shown in Scheme 2

Table 2 Selected Bond Distance and Angles for Singly and Doubly Reduced Ar*MMAr* (M = Ge or Sn) Species

	M–M/Å	M–M–C/°	Ref.
[K(THF)$_6$][Ar*SnSnAr*]	2.8123(9)	95.20(13)	24
[K(18-crown-6)(THF)$_2$]	2.7821(4)	93.6(4), 95.0(4)	24
[Ar*SnSnAr*]	2.8236(14)	97.3(2)	
[(THF)$_3$Na{Ar*SnSnAr*}]	2.8107(13)	97.93(3), 98.1(4)	25
K_2Ar*SnSnSnAr*	2.7763(9)	107.50(14)	29
Na_2Ar*GeGeGeAr*	2.394(1)	102.37(8)	29

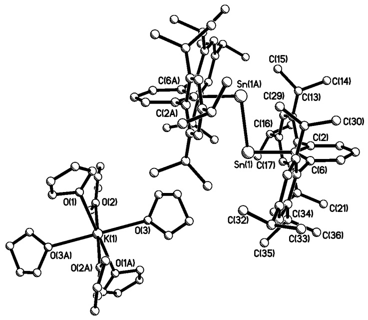
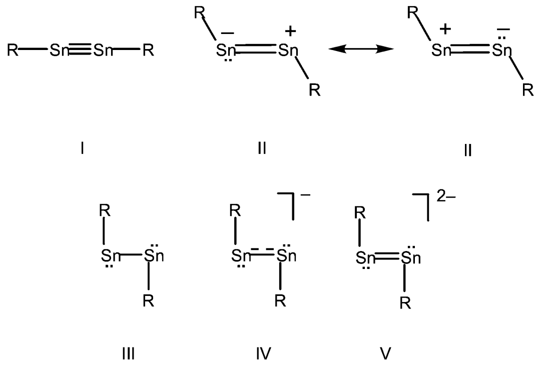


Fig. 4 The X-ray crystal structure of [K(THF)$_6$][{Ar*SnSnAr*}] illustrating the *trans*-bending of the CSnSnC framework. Hydrogen atoms are not shown.[24] Structural data are given in Table 2.

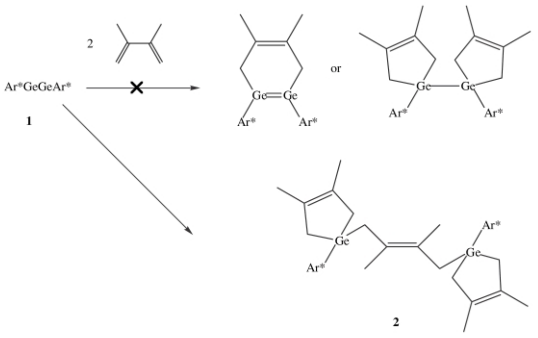


Scheme 2 Schematic drawing of some bonding possibilities in neutral and reduced RSnSnR compounds.

Although the formal bond order in IV is 1.5, the absence of shortening with respect to the single bond in elemental tin could be rationalized on the basis that the Sn–Sn σ bond results from overlap of p-orbitals which, due to their larger average radii,[2] cause it to lengthen. Further reduction to K_2Ar*SnSnAr*, which contains a formal Sn–Sn double bond (by analogy with isoelectronic $Ar^*\ddot{S}b{=}\ddot{S}bAr^*$),[31] as illustrated in the dianion V, causes the Sn–Sn bond to shorten slightly to 2.7763(9) Å and the Sn–Sn–C angle to widen to 107.50(14)°. The K$^+$ ions are complexed to the dianion and sandwiched between Trip rings. Parallel work involving the reduction Ge(Cl)Ar* afforded Na_2Ar*GeGeAr* which had a Ge–Ge bond length of 2.394(1) Å (*cf.* Ge–Ge single bond in elemental Ge = 2.44 Å) and a Ge–Ge–C angle of 102.37(8)°.[29] The relatively modest shortening of the formal Ge–Ge and Sn–Sn double bonds in comparison to single bonds is probably due to the presence of Coulombic repulsions within the dianions $[\mathrm{Ar^*MMAr^*}]^{2-}$ (M = Ge or Sn).

4 Neutral ArMMAr (M = Ge, Sn or Pb; Ar = terphenyl group) alkyne analogues: experimental and calculated structures

Further investigations of the reduction of M(Cl)Ar* (M = Ge or Sn; Ar* = $\mathrm{C_6H_3}$-2,6-$\mathrm{Trip_2}$) with exactly one equivalent of sodium or potassium, for periods of 2–3 days, showed that quantities of the singly reduced salts Na or K{Ar*MMAr*} with various degrees of complexation by the donor solvent were often produced. The solubility of these ionic species is lower than neutral Ar*MMAr* so that such salts are precipitated first. It was found that the more soluble, neutral Ar*MMAr* (M = Ge or Sn) species could also be obtained as red or green crystals once the monoanion salts had been removed. However, the crystals obtained with the Ar* ligand were found to be unsuitable for X-ray crystallography, although they could be characterized spectroscopically and analytically. Crystalline products were obtained by the addition of two equivalents of 2,3-dimethyl-1,3-butadiene as shown in Scheme 3 which afforded the unusual product $[\mathrm{Ar^*Ge\{CH_2C(Me)C(Me)CH_2\}CH_2C(Me){=}}]_2$ derived from the reaction of Ar*GeGeAr* with three equivalents of butadiene.[32] The formation of the 'bridged' product is unusual. Initially it was expected that a digermacyclohexadiene product depicted in the upper line of Scheme 3 would be obtained but this is sterically disfavored owing to the *cis*-orientation of the large Ar* ligand. The formation of a cyclopentene ring at each germanium is also a possibility but this molecule would also be extremely crowded so that dissociation to give $\{\mathrm{Ar^*GeCH_2C(Me)C(Me)CH_2}\}^{\cdot}$ radicals could occur to add a further diene to yield the product obtained.



Scheme 3 Reaction of Ar*GeGeAr* with 2,3-dimethyl-1,3-butadiene.[32]

While efforts to obtain X-ray quality crystals of the neutral Ar*GeGeAr* and Ar*SnSnAr* compounds continued, parallel work on divalent metal hydrides of heavier group 14 elements provided an unexpected route, [eqn. (3)], to the first heavier group 14 element analogue of an alkyne whose crystals were of sufficient quality for a structure determination.[33]

$$2\ \mathrm{Pb(Br)Ar^*} \xrightarrow{\mathrm{LiAlH_4,\ Et_2O}} \mathrm{Ar^*PbPbAr^*} \qquad (3)$$

The compound Ar*PbPbAr* was isolated as amber-green dichroic crystals in *ca*. 10% yield by this route. The isolation of this product is in contrast to the analogous reduction with Sn(Cl)Ar* where the unusual hydride $\{\mathrm{Sn}(\mu\text{-H})\mathrm{Ar^*}\}_2$ was obtained.[34] It is possible that the reduction of Pb(Br)Ar* also proceeds through a lead(II) hydride intermediate which could convert rapidly to Ar*PbPbAr* with elimination of hydrogen. The most important structural parameters of the dimer are the Pb–Pb bond length, 3.1881(1) Å, the planar, *trans*-bent CPbPbC core arrangement, and the Pb–Pb–C angle, 94.26(4)° (Fig. 5).

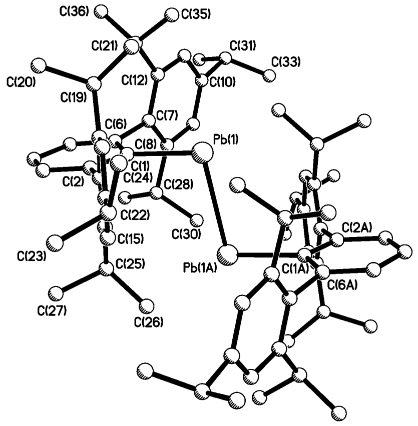
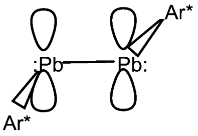


Fig. 5 The structure of Ar*PbPbAr* illustrating the almost 90° Pb–Pb–C angles.[33] H atoms are not shown. Some important bond distances and angles are given in Table 3.

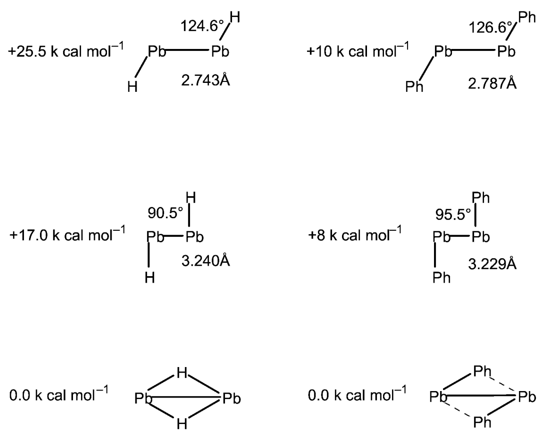
The Pb–Pb bond distance is much longer than those found in diplumbanes which are usually in the range 2.85–2.95 Å.[30] However, it is significantly shorter than the interatomic distance of 3.49 Å found in metallic lead. Owing to the near 90° Pb–Pb–C angle, the structure of Ar*PbPbAr* corresponds to a diplumbylene (rather than a diplumbyne species) which carries a lone pair at each lead and empty p orbitals that lie perpendicularly to the CPbPbC plane as shown.



diplumbylene

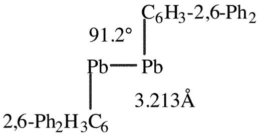
Although it is not possible to infer bond hybridization from interbond angles, the structure strongly suggested that the lead employed 6p orbitals to form bonds to its metal partner as well as the terphenyl ligand, while the lone pair occupied a 6s orbital. The relatively long Pb–Pb and Pb–C (2.303(2) Å, *cf*. 2.22(2) Å in $\mathrm{Pb_2Ph_6}$)[30] bonds are consistent with the use of 6p orbitals for σ-bonding. The apparent lack of significant involvement of the 6s electrons in the bonding can be attributed in part to their further stabilization and contraction by relativistic effects. Nonetheless, the bonding is not as simple as it is depicted in this scheme and high level calculations on various model species have allowed further insights. Thus, calculations[35] on the hydride $\mathrm{Pb_2H_2}$ and phenyl derivative $\mathrm{Pb_2Ph_2}$ showed that the terminally bonded *trans*-bent isomers were higher lying transition states than the doubly hydrogen or phenyl bridged global minima at 0.0 kcal $\mathrm{mol^{-1}}$ (Scheme 4).

The experimentally observed stability of the Ar*PbPbAr* structure does not appear to be a result of the electronic effects of the aryl substituents. Instead, steric effects seem to play a key role. Thus, calculations on the more elaborate model species $\mathrm{Pb_2(C_6H_3\text{-}2,6\text{-}Ph_2)_2}$, which incorporated the bulkier terphenyl ligand -$\mathrm{C_6H_3}$-2,6-$\mathrm{Ph_2}$, showed that the bridged structure was destabilized by the ligand size. Furthermore, the calculations showed that the strongly *trans*-bent structure depicted schematically by the representation is an energy minimum rather than a transition state as it is in the $\mathrm{Pb_2Ph_2}$ species. Moreover, the calculated Pb–Pb distance, 3.213 Å, and the Pb–Pb–C angle, 91.2°, are in good agreement with those experimentally observed. In effect, the bulkier terphenyl ligand stabilizes a structure that would normally be a transition state if a less bulky



Scheme 4 Relative energies of various arrangements of Pb_2H_2 and Pb_2Ph_2.[35]

substituent were employed. The calculations confirmed that there was no Pb–Pb π-bond and that the Pb–Pb bond was purely of σ character as originally proposed.



Like Pb_2H_2, numerous calculations on the silicon and germanium congeners Si_2H_2 and Ge_2H_2 have confirmed that the global minimum in each case is a dihydrogen bridged structure similar to the lead compound.[8,9] Unlike Pb_2H_2 however, the *trans*-bent multiply bonded arrangement with terminal hydrogens is not a transition state but is a higher lying local minimum for both silicon and germanium. Calculations for the methyl derivative Si_2Me_2[36] showed that the dimethyldisilavinylidene isomer Me_2SiSi and the *trans*-bent isomer of MeSiSiMe were the lowest lying minima with the *trans*-bent arrangement lying 12 kcal mol^{-1} above Me_2SiSi.[36] However, it is probably safe to assume that the use of larger substituents would favor a *trans*-bent isomer for steric reasons. The calculated Si–Si and Ge–Ge bond lengths in the *trans*-bent isomers were 2.090[36] and 2.197 Å[37] with Si–Si–C and Ge–Ge–C angles of 129.9°.[8] Unlike in the lead species Ar*PbPbAr*, the M–M distances are much shorter than those expected for the single bonds Si–Si = 2.34 and Ge–Ge = 2.44 Å and suggest considerable multiple character. In fact, such bonds are slightly shorter than the shortest bond distances measured experimentally for Si–Si (2.138(2) Å) and Ge–Ge (2.213(2) Å) double bonds.[6] The linear forms of MeSiSiMe or MeGeGeMe lie at higher energies.[36–38] They are not minima, however, but are transition states, even though they were calculated to have even shorter Si–Si and Ge–Ge distances of 1.937 and 2.073 Å, respectively. It has been calculated that the bond orders in the *trans* structures of the silicon and germanium with various substituents vary between 1.74 and 2.37 (*vide infra*).[11]

In order to obtain crystals of the digermanium and ditin diaryls that were suitable for X-ray crystallography, we tested several ligands, and it was found that the ligand -C_6H_3-2,6-$Dipp_2$ (Dipp = C_6H_3-2,6-$\mathrm{Pr^i}_2$), which is closely related to Ar* and differs only in the absence of *para* $\mathrm{Pr^i}$ groups from the flanking aryl rings, readily yielded well-formed crystals that could be structurally characterized. Although *para* substituents at aryl rings generally have little steric effect at the *ipso* position, this is not so in the case of terphenyl substituents as demonstrated by the structures of the lithium derivatives C_6H_6·LiAr* and $(LiAr')_2$ (Ar′ = C_6H_3-2,6-$Dipp_2$)$_2$.[39] When crystallized from benzene LiAr* has a monomeric structure in which the lithium is η^6-coordinated to benzene and the *ipso* carbon of the terphenyl ligand. In contrast, LiAr′ is a dimer, even in the presence of benzene, and affords the unusual structure shown on the right hand side of Fig. 6. We reasoned therefore that the use of the Ar′ ligand might allow stronger dimerization to occur while permitting adequate steric protection for the tetrels, as well as inducing crystals to form in a manner that would be useful for X-ray crystallographic study. Treatment of the aryl tetrel(II) halide with potassium as shown in eqn. (4) afforded the compounds Ar′GeGeAr′[40] and Ar′SnSnAr′[41] in moderate yield. The analogous lead compound Ar′PbPbAr′ could also be obtained in good yield by treatment of Pb(Br)Ar′ with $\mathrm{HAlBu^i}_2$. No problems were encountered in obtaining data sets for the germanium or tin compounds. The structures may be illustrated by the germanium species shown in Fig. 7. Structural data for the compounds as well as the neutral lead dimer are given in Table 3.

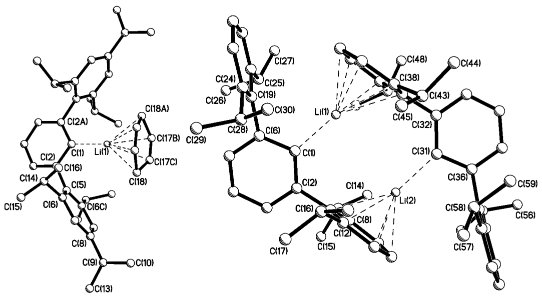


Fig. 6 The monomeric and dimeric structures of C_6H_6·LiAr* and $(LiAr')_2$. H atoms are not shown.[39]

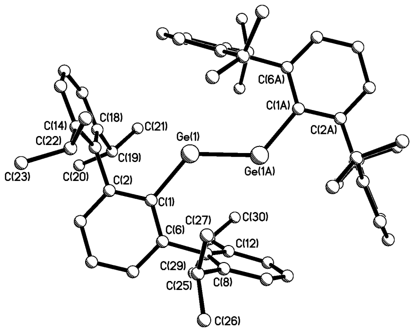


Fig. 7 The structure of Ar′GeGeAr′ illustrating the planar *trans*-bent C(1)Ge(1)Ge(1A)C(1A) skeleton. Hydrogen atoms are not shown.[40] Structural data are given in Table 3.

$$2\mathrm{M(Cl)Ar'} \xrightarrow{2\mathrm{K}} \mathrm{Ar'MMAr'} + 2\mathrm{KCl} \qquad (4)$$

(M = Ge or Sn; Ar′ = C_6H_3-2,6-$Dipp_2$; Dipp = C_6H_3-2,6-$\mathrm{Pr^i}_2$)

The main structural features of interest are obviously the planar, *trans*-bent CMMC core, the M–M distance and the M–M–C angle. It can be seen that the Ge–Ge and Sn–Sn bond lengths are much shorter than the distances expected from normal single bonds of 2.44 Å (Ge) and 2.81 Å (Sn). The M–M–C angles are much wider than the corresponding angles in lead. The measured parameters suggest considerable multiple character. The Ge–Ge distance and Ge–Ge–C angle may also be compared to the 2.22 Å and 123.0 or 124.0° recently calculated for parent *trans*-HGeGeH[11] or the 2.197 Å and 124.1° calculated for MeGeGeMe.[37] The longer Ge–Ge bond and wider Ge–Ge–C angle experimentally measured for Ar′GeGeAr′ may be a consequence of the large size of the Ar′ group. A calculation[11] for the *trans*-bent isomer of HSnSnH revealed a

Table 3 Selected bond distance and angles for Ar′MMAr′ (M = Ge or Sn) and Ar*PbPbAr*

	M–M/Å M–C/Å	M–M–C/°	Torsion angle/°	Ref.
Ar′GeGeAr′	2.2850(6) 1.996(3)	128.67(8)	0.4	39
Ar′SnSnAr′	2.6675(4) 2.191(3)	125.24(7)	3.5	40
Ar*PbPbAr*	3.1881(10) 2.303(2)	94.26(4)	3.4	41

Sn–Sn distance of 2.65 Å and an Sn–Sn–H angle of 122° which agree more closely with those measured in Ar′SnSnAr′.

Calculations have also been carried out on the structurally uncharacterized terphenyl compounds Ar*GeGeAr* and Ar*SnSnAr* and on the sterically crowded, as yet unsynthesized, species TbtMMTbt (M = Ge or Sn; Tbt = C_6H_2-2,4,6-$\{CH(SiMe_3)_2\}_3$.[42] These were density functional calculations at the B3LYP level with a smaller 3–21G* basis set (owing to the size of the molecules) and the Gaussian 98 program. However, calibration calculations on HGeGeH at the B3LYP/6–311G (2d,2p) and MP2/6–311G (2d,2p) levels suggested that the lower level calculations ensure relatively accurate results. For Ar*GeGeAr* the *trans*-bent isomer is 29.5 kcal mol^{-1} more stable than the vinylidene GeGeAr*$_2$ for steric reasons. In the *trans*-bent Ar*GeGeAr* was calculated to be 2.277 Å which is in very good agreement with the experimentally measured 2.2850(6) Å. The Ge–Ge–C angle was calculated to be 123.2° or *ca*. 5° narrower than the measured value. However, the CGeGeC core was calculated to be twisted by 22.4° around the Ge–Ge bond. It is possible that these angular differences are due to the presence of para Pr^i groups in Ar*GeGeAr*. A less *trans*-bent and less twisted structure with a shorter Ge–Ge distance of 2.218 Å was also located but this is 46.3 kcal mol^{-1} less stable than the structure above. Upon replacement of Ar* by C_6H_3-2,6-Ph_2 substituents, a more highly *trans*-bent (Ge–Ge–C = 99.2°) and twisted (88.5°) structure, in which the germaniums interact with the aryl rings of the terphenyl group was calculated. This structure also featured a long Ge–Ge bond distance of 2.509 Å. With phenyl groups at germanium, a dibridged structure similar to that calculated for Pb_2Ph_2 was obtained. For the tin compound, the Ar*SnSnAr* structure was calculated to have a more *trans*-bent (Sn–Sn–C = 111.0°) and twisted (54.7°) skeleton with a long Sn–Sn bond of 2.900 Å. These parameters are quite different from those experimentally observed for Ar′SnSnAr′. In contrast, calculations for TbtSnSnTbt afforded the parameters Sn–Sn–C = 122.0°, twist angle 10.7° and Sn–Sn = 2.659 Å which are in good agreement with the experimental data for Ar′SnSnAr′.[42]

5 Bonding models and approximations

The bonding in compounds thought to have homonuclear triple bonds between heavier main group elements has been debated exhaustively over the last five years, especially in the case of gallium compounds. One bonding model[43,44] advocated for the existence of triple bonding between heavier main group elements with a *trans*-bent geometry viewed the bond as a threefold interaction between two doublet fragments as represented in Chart 1.

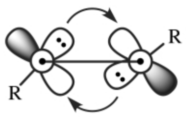


Chart 1

In this way the bond can be considered a triple one since it consists of two donor–acceptor, polar-dative (paw-paw) bonds involving the lone pairs (indicated by arrows), plus a π-bond due to coupling between the unpaired electron in the p-orbital on each element (indicated by the central line between the p-orbitals in an end-on view). This bonding model has the advantage that it is simple to visualize. Yet, there are difficulties with it because if the *trans*-bending is increased to *ca*. 90°, as it is in the lead compound Ar*PbPbAr*, the donor–acceptor bonds are undone and the model assumes a structure shown in Chart 2 in which the metals are formally linked by a single bond.

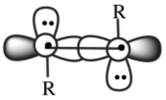


Chart 2

However, the drawing implies that this is a π-bond and not a σ-bond even though σ-bonding is also possible through head to head overlap of p orbitals. There has been no evidence to suggest that π-bonding is stronger than σ-bonding between heavier main group elements. Indeed, calculations on the model compounds for Ar*PbPbAr* featured Pb–Pb–C angles that were close to 90° and showed them to be σ-bonded in this configuration.[35] Thus, the above model, which leads to a single π-bond when the *trans*-bending is 90°, is not in agreement with theoretical data, or what is currently known about the relative strengths of σ and π bonds in main group compounds. Even if it were conceded that a σ bond is indeed present in the singly bonded species, it is not readily apparent how the transformation from π → σ bonding occurs upon narrowing the bending angle by this simple model. Nonetheless, theoretical support for the triple bonding model has been reported. It has come mainly from calculations on related species such as $[HGaGaH]^{2-}$ or $[MeGaGaMe]^{2-}$ which are models for $[Ar*GaGaAr*]^{2-}$—a gallium dianion that is isoelectronic to neutral Ar*GeGeAr*. By use of localized molecular orbitals (LMOs), three bonding molecular orbitals, that correspond to two polar-dative and one σ-bond, can be calculated.[43b] The two dative bonds were described as weak interactions. The predicted behavior of the p-orbital when a *trans*-bending angle of *ca*. 90° is enforced has remained undefined.

The other bonding model for heavier main group acetylene analogues is based on the MO approximation and involves canonical molecular orbitals (CMOs).[8,11] There is a second order Jahn–Teller mixing of M–M σ* and π levels and, to a much lesser extent, π* and σ levels (since they are much further apart energetically) to give a molecular orbital that is non-bonding or nearly so. In this way the M–M bond is transformed from a triple to a double one. The model also demonstrates how a triple bond can be transformed into a σ-bond with lone pairs at each group 14 element upon bending the geometry through 90°. This model is, perhaps, more difficult to conceptualize than the triple bonded one described above, but is more flexible in its applicability in terms of energy levels and the reconciliation of bond lengths and bond orders. The orbital mixing is possible since the energy levels are closer to each other in the heavier elements as a result of weaker M–M bonds and the equivalent symmetry of the orbitals in *trans*-bent C_{2h} symmetry. These interactions are illustrated in the correlation diagram in Fig. 8. In this scheme, one of the two π bonds in the linear molecule is transformed into a lone-pair like b_u orbital so that the number of bonding orbitals associated with the M–M bond decreases from three to approximately two. However, this model as shown is also oversimplified since it does not adequately illustrate the s–s orbital combination which has a_g symmetry slightly mixed into the p_z–p_z a_g combination and mainly provides the lone pair combinations when the bending angle is 90°. Nonetheless, the

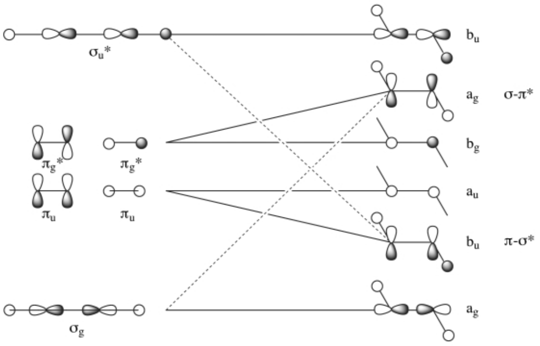


Fig. 8 Schematic diagram of the orbital interactions in linear and *trans*-bent HMMH model species.

model does show that bending weakens the M–M bond through gradual transformation of a π-bonding orbital into a non-bonding, lone pair orbital. The σ-bond is also weakened through a less efficient overlap. The weakening and lengthening of the bonds together with the appearance of lone pair character at the heavier main group element, as manifested by the *trans*-bent, geometry corresponds to a reduction in bond order from three to roughly two.

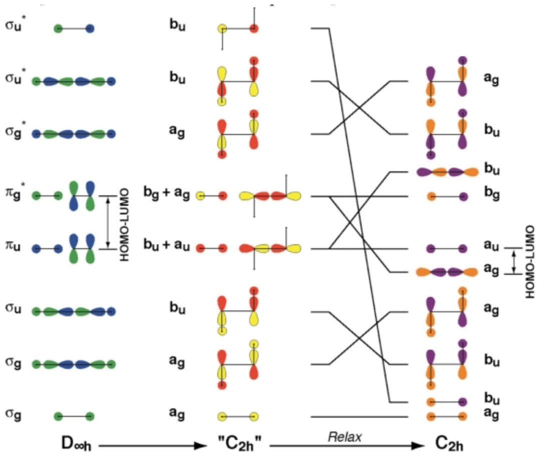


Fig. 9 Schematic diagram of the orbital changes upon 90° bending of the HMMH geometry.

Upon bending the HMMH skeleton through 90° the correlation diagram in Fig. 9 is applicable. At the left the (unhybridized) molecular orbitals for the linear geometry are illustrated, and five electron pairs occupy the $2\sigma_g$, σ_u and $2\pi_u$ levels corresponding to an M≡M triple bond and two M–H bonds. Upon bending through 90°, the in-plane π_u orbital is converted to an a_u σ*-orbital while the out of plane π_u orbital remains essentially unaffected although its symmetry designation is b_u in the C_{2h} point group. Similarly, the most stable σ_g orbital overlap is unaffected, becoming a_g in C_{2h} symmetry. In contrast, the next highest σ_g and σ_u orbitals, upon rotation through 90°, become a_g and b_u orbitals which are both bonding with respect to the M–H interaction but antibonding and bonding respectively with respect to the M–M interaction. In sum, the lowest a_g orbital and the a_u orbital are sigma bonding and antibonding, whereas the remaining a_g and lower b_u orbital are π-antibonding and bonding respectively. To a first approximation the bonding effects of these four orbitals cancel each other leaving only the b_u π-level as a net π-bonding orbital. The central set of orbitals seemingly supports the view that the metals are indeed connected by a π-bond in this case. However, upon "relaxation", which is necessitated by the degree of bonding character or stabilization of each orbital, the orbital sequence on the right hand side is obtained. Of great importance is the realization that where strong *trans*-bending occurs one is dealing with the heaviest elements of the group 14 where the s-electrons are increasingly non-bonding in character. Where M is Pb the assumption of non-bonding character for the 6s-electrons is a reasonable approximation. The lack of bonding by the 6s-electrons implies that the symmetric (a_g) and unsymmetric (b_u) combinations are, in effect, lone pair orbitals which lie close to each other in energy. Thus the five occupied molecular orbitals become a_g (lone pair), b_u (lone pair), b_u (M–H σ-bonding, M–M π-bonding), a_g (M–H, σ-bonding, M–M, π-antibonding), a_g (M–M, σ-bonding) and the LUMO is a π-level of a_u symmetry that lies perpendicularly to the HMMH plane. The net effect of these is an M–M single (σ) bond and a molecule which, upon reduction accommodates the extra electrons in a LUMO (π-bonding) level. This is consistent with the experimental findings.

6 Bond orders

In section 4 it was shown that calculations could, in many instances, reproduce the experimentally measured core structural parameters fairly accurately. In section 5 the two main bonding models were outlined and briefly discussed. The localized molecular orbital (LMO) scheme led to a triply bonded *trans*-bent molecule. However, the advent of the single bonded lead compound Ar*PbPbAr*, which has a Pb–Pb σ-bond, showed that simple extrapolation to a single π-bond obtained by 90° bending was not observed in practice.[33,34] On the other hand, the canonical molecular orbital (CMO) model incorporating the mixing of bonding and antibonding orbitals to yield orbitals of non-bonding character affords a bond order that is less than three. In particular, the character of the b_u HOMO arising from mixing of a π and a σ* orbital is crucial to the assignment of the Ge–Ge bond order in the model species *trans*-bent MeGeGeMe.[37] This orbital is illustrated by the contour diagram in Fig. 10 where it can be seen that its shape differs significantly from that expected for a π-bond, it is closer in character to a lone pair orbital. The minor correlation of the lone pair across the MeGeGeMe molecule is with the Ge–C σ-bond rather than a p-orbital in the other germanium atom. This approach leads to a bond order of approximately two for the Ge–Ge bond and this is in harmony with the 2.097 bond order calculated using AIM theory.[37] These conclusions are in

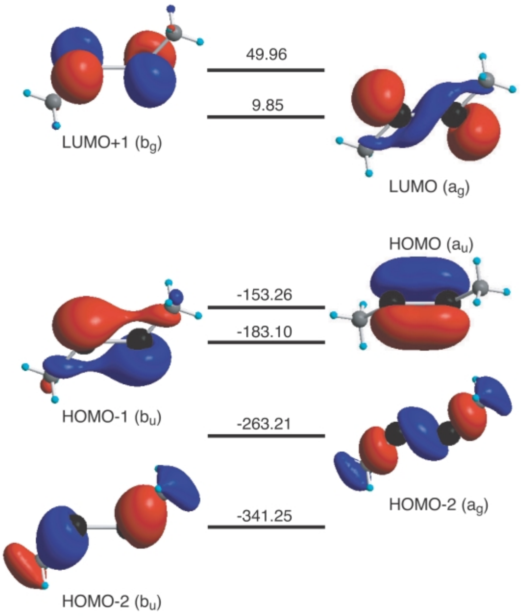


Fig. 10 Molecular orbital diagram for *trans*-MeGeGeMe obtained with a 6-31G(d) basis set. The energies given are in kcal mol^{-1}.[37]

essential agreement with earlier findings[45] for the isomers of Ge_2H_2 which showed that the linear form HGe≡GeH (Ge–Ge = 2.024 Å) is not a minimum on the potential energy surface but lies about 25 kcal mol^{-1} above the *trans*-bent (C_{2h}) form (the most stable structure is a dihydrogen bridged species Ge(μ-H)$_2$Ge which lies *ca.* 18 kcal mol^{-1} below the C_{2h} form). The Ge–Ge distance in the C_{2h} structure – 2.204–2.215 Å (depending on the basis set), is very similar to the 2.197 Å calculated for *trans*-bent MeGeGeMe.

The Ge–Ge bonding in the *trans*-bent HGeGeH may also be represented as resonance hybrids described by

$$\mathrm{H\overset{-}{\ddot{G}}e{=}\overset{+}{Ge}H \leftrightarrow H\overset{+}{Ge}{=}\overset{-}{\ddot{G}}eH}$$

in which the Ge–Ge bond is a double one. This representation has strong parallels with the resonating lone pair depiction of the bonding illustrated by the structure of II in Scheme 2. These resonance forms are related to those originally proposed by Lappert,[3b] and later by Pauling[46] for the heavier tetrel analogues of alkenes. The existence of Ge–Ge double bonds in RGeGeR compounds is also supported by the fact that Ge–Ge bond lengths calculated for the *trans*-bent forms of HGeGeH and MeGeGeMe are similar to those at the lower end of the range experimentally observed 2.213(2)–2.347(2) Å for germanium alkene analogues. Nonetheless, they are shorter than the 2.2850(6) Å observed for Ar′GeGeAr′ and it is possible that experimental Ge–Ge distance in this compound is longer for steric reasons. The negligible torsion angle between the CGeGeC core and the planes of the central aryl rings show that conjugation involving the aryl rings and the Ge–Ge bond is possible although the Ge–C distances are not shorter than those in the germyne complexes in Table 1.

Density functional theoretical studies on isoelectronic models (*e.g.*, $[PhGaGaPh]^{2-}$ and $[2,6\text{-}Ph_2H_3C_6GaGaC_6H_3\text{-}2,6\text{-}Ph_2]^{2-}$) for the electronically related $[Ar^*GaGaAr^*]^{2-}$ have provided a very similar DFT orbital plot to the b_u canonical molecular orbital illustration in Fig. 10 which is consistent with non-bonding character.[47] Later, more detailed DFT calculations on the same model species using natural molecular orbitals afforded a b_u type orbital which was interpreted to be π-bonding on the basis of its contour values.[48] However, the contour map for this orbital (in which there is also a strong correlation with the Ga–C bond) also bears a strong resemblance to the contour diagram given in Fig. 10 and has little Ga–Ga bonding character. The authors concluded that there exists “a weak triple bond—or perhaps a bond between triple and double” for the gallium compound. Furthermore, an NLMO/NPA bond order of 2.794 was calculated although a significantly lower Wiberg bond index value of 2.019 was also obtained for this homonuclear system.[48]

Further calculations on group 13 and group 14 homonuclear alkyne analogues using hybrid density functional theory methods afforded structural parameters for RMMR species (M = Si–Pb; R = H, Me, Ph).[11] It was shown that *trans*-bending of the core leads to a lengthening of the M–M bond and a corresponding decrease in the bond orders. Some of the calculated structural data and bond orders for these compounds are provided in Table 4. It can be seen that the calculated M–M distances vary slightly with the R substituent with marginally longer distances being calculated for the phenyl substituted compounds (also accompanied by narrower M–M–C angles for the Ge, Sn and Pb species). For the germanium and tin compounds the bond orders are in the ranges 2.32–1.74(Ge) and 1.87–1.73(Sn).[11] Some multiple character was also calculated for the lead species and this may be contrasted to the Pb–Pb single bonding when almost 90° angles are seen with large groups as in Ar*PbPbAr*. Higher bond orders (2.20–2.37) were calculated for the silicon species, however. In addition, calculations by Nagase have shown that with use of silyl substituents instead of H or Me the energy difference between the *trans*-bent and linear forms can be reduced to a low value, *ca.* 6 kcal mol^{-1}.[12] Higher bond orders, perhaps approaching three, may be anticipated for these species.

The bonding in multiply bonded alkene analogues $[R_2MMR_2]$ (M = C–Pb) and $[RGaGaR]^{2-}$ and related species has also been studied with use of electron localization function (ELF) to resolve the bond order question.[49] On the basis of these functions topographical comparisons between classical (as in carbon compounds) and non-classical (as in heavier main group 13 and 14 element compounds) could be made. From these the multiply bonded species were divided into compounds that had slipped (non-classical) and unslipped (classical) π-bonds. Studies of the ELF functions of the alkene analogue series H_2MMH_2 (M = C–Pb) and $[HGaGaH]^{2-}$ were interpreted to support the existence of double and triple bonding, respectively. However, in the gallium case, and presumably in the isoelectronic HGeGeH species, although the slipped π-bonding orbital (which resembles the b_u orbital discussed earlier) has some electron density in the region between the galliums, the electron density is maximized in the areas expected for lone pairs. Moreover, these maxima lie outside the internuclear region defined by lines perpendicular to the Ga–Ga bond. Thus the major portion of the electron density of this orbital is outside the internuclear region. Its bonding character is derived from the very small amount of electron density between the galliums. On this basis the bond was regarded as a triple one.

A more recent ELF and AIM study[50] of RMMR and R_2MMR_2 (E = Si, Ge, Sn; R = H or CH_3) compounds also led to non-linear or non-planar geometries but to different conclusions about the bonding. The ELF studies did not yield quantitative values for the M–M bond orders owing to difficulties in assigning bonding or non-bonding character to the electron density. Nonetheless the ELF results showed that the bond orders were less than three for RMMR species and less than two for R_2MMR_2 species, due to the fact that there were less than six or four electrons, respectively, in the bonding region. Upon descending the group the amount of non-bonding electron density increases and it is the presence of this non-bonding density that causes the non-planarity or non-linearity of the molecules. The increase in the non-bonding electron density comes at the expense of electron density in the bonding region between the tetrels which results in a weakening and lengthen-

Table 4 Density functional theory calculated structural parameters[a] and bond orders for RMMR (M = Si–Pb; R = H, Me or Ph)[11]

H				Me			Ph		
M	M–M	M–M–R	B.O.[b]	M–M	M–M–R	B.O.[b]	M–M	M–M–R	B.O.[b]
Si	2.10	124	2.37	2.12	129	2.30	2.12	130	2.20
Ge	2.22	124	2.32	2.24	127	2.10	2.25	118	1.74
Sn	2.65	122	1.87	2.66	124	1.84	2.67	119	1.73
Pb	2.74	124	1.65	2.77	126	1.62	2.77	119	1.51

[a] Distances in Å, angles in (°). [b] B.O. = bond order.

ing of the M–M bond. These trends result from the fact that in the heavier congeners the valence electrons are less attracted into the M–M bonding region and the electrons are less localized into localized pairs than in the carbon molecules due to the lower EN values of the heavier elements. Accordingly, it becomes increasingly difficult to distinguish between the bonding and non-bonding electron density. Nonetheless, calculations for the model species MeGeGeMe and MeSnSnMe (at the cc-pVD2 level) yielded bond lengths of 2.25 and 2.66 Å in good agreement with those experimentally found. Furthermore, topological bond orders of 2.0 and 1.9 were calculated for these molecules.

To summarize, arguments about bond order in RMMR species (M = Si–Pb) or their related group 13 element dianions $[RM'M'R]^{2-}$ (M = Al–Tl) have been based to a large extent on theoretical models (involving LMO's and CMO′s) that lead to apparently different conclusions. It is worrisome that these bonding models, whose orbitals are related in principle by a unitary transformation, lead to very different views about bond orders in the heavier main group elements. Quite simply, the models, which have provided a clear and relatively consistent picture of the bonding in multiply bonded compounds of the lighter main group elements, become confusingly inconsistent when applied to their heavier counterparts. Furthermore, bond orders calculated by several currently available approaches do not resolve the issue since they can afford bond indices that vary considerably. But such inconsistency cannot obscure the essential truth that the double and triple bonds in archetypal lighter element compounds such as ethylene and acetylene (and isoelectronic species) transform to two lone pairs or two lone pairs and a single bond upon descending a group to the heaviest derivative. The extent to which the four or six valence electrons originally associated with double or triple bonding between light elements become non-bonding in their heavier congeners has not been yet calculated in a widely accepted and consistent manner. Nonetheless, the bond distances and angles in the germanium and tin alkyne analogues strongly suggest that bond orders near two are present in these compounds.

7 Why do the transition metal–group 14 metallynes have essentially linear geometry whereas the alkyne analogues have a *trans*-bent configuration?

The formation of RMMR species from two group 14 RM moieties may be viewed as a stepwise process that is illustrated schematically in Fig. 11. The R–M moieties exist as doublets in the ground state and an energy input of ΔE_{D-Q} is required to convert each doublet state to a quartet state; *i.e.*, $2\Delta E_{D-Q}$ for the whole molecule. The doublet fragments can be coupled to give a *trans*-bent (by *ca*. 90°) $R\ddot{M}\ddot{M}R$ species that has a single M–M bond (E_σ). The quartet fragments can be coupled to give a linear RM≡MR species that has a triple bond, the energy of which is $E_{\sigma+2\pi}$. The difference between the linear and *trans*-bent molecules is $E_{2\pi}$. This statement is an approximation since it does not take into account the changes in the σ-bond strength or steric effects. However, if this approximation is accepted it can be predicted that if the magnitude of $E_{2\pi}$ exceeds $2\Delta E_{D-Q}$, a linear structure should be observed. On the other hand if $E_{2\pi}$ is less than $2\Delta E_{D-Q}$ a *trans*-bent structure is predicted. It is possible to calculate the ΔE_{D-Q} energy separation for MH (M = C, Si or Ge) fragments. Approximate values for the strength of the C–C, Si–Si and Ge–Ge π-bonds are also known. These are given in Table 5.

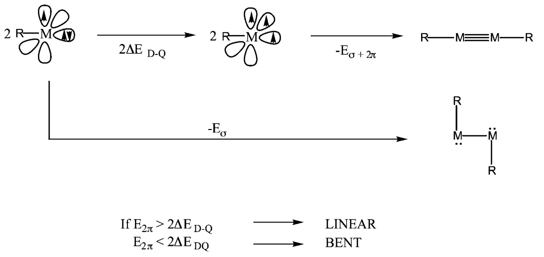


Fig. 11 Stepwise formation of singly and triply bonded group 14 RMMR species

Table 5 ΔE_{D-Q} approximate π-bond energies (kcal mol^{-1}) and predicted geometries for HMMH (M = C, Si, Ge) model species

Compound	H–C≡C–H	H–Si≡Si–H	H–Ge≡Ge–H
$2\Delta E_{D-Q}$	28.9[a]	76.0[a]	82.4[a]
$E_{2\pi}$	120–130[b]	46–62[c]	44–50[c]
	$E_{2\pi} > 2\Delta E_{D-Q}$	$E_{2\pi} < 2\Delta E_{D-Q}$	$E_{2\pi} < 2\Delta E_{D-Q}$
Geometry	Linear	*trans*-Bent	*trans*-Bent

[a] Ref. 51. [b] Ref. 52. [c] Ref. 53.

It is clear that the linear geometry is strongly favored for acetylene whereas *trans*-bent geometries are favored for silicon (by 14–30 kcal mol^{-1}) and germanium (by 32–38 kcal mol^{-1}).

A similar model can be used for the formation of species $(\eta^5\text{-}C_5H_5)(CO)_2M{=}Ge{-}R$ (M = Cr, Mo or W; see Fig. 3). The most important point to note in such cases is that their formation requires just one input of ΔE_{D-Q} (*i.e.*, 38 kcal mol^{-1}) energy for the GeR moiety since the 15-electron $(\eta^5\text{-}C_5H_5)(CO)_2M$ fragment already exists in the quartet configuration. Accordingly, it is reasonable to conclude that the two M–Ge "π-bonds" are together worth at least 45 kcal mol^{-1} and it is not unreasonable to predict that the corresponding tin and lead compounds would also possess wide, and possibly near linear angles at the group 14 element. This conclusion supports the existence of π-bonding for the M–R ligands.

8 Future developments

The silicon analogues of alkynes RSiSiR are the most obvious and immediate synthetic objective in the title area.[54] They remain unknown as well characterized, stable species in spite of several attempts to synthesize them.[15–17] The most recent synthetic approach[17] (see also ref. [15]) has involved the reduction of the disilene $(R^*_2MeSi)(Cl)Si{=}Si(Cl)(SiMeR^*_2)$ (R* = $SiBu^t_3$) with lithium naphthalenide in tetrahydrofuran with formation of a reaction mixture containing a chlorine free product that gives a low field ^{29}Si NMR signal at δ = 91.5 that may be consistent with the presence of $(R^*_2MeSi)Si{\equiv}Si(SiMeR^*_2)$. This species reacts with oxygen to give a product whose formula corresponds to $(R^*MeSi)SiSi(SiMeR^*_2)$ plus two oxygen atoms.[17] Calculations have predicted that the disilyne $(R^*_2MeSi)Si{\equiv}Si(SiMeR^*_2)$ should be stable enough to isolate, and should have a short Si–Si bond length of 2.072 Å and a wide Si–Si≡Si bond angle of 148° consistent with substantial triple bonding.[13] These experiments and others indicate that a disilyne that is stable at room temperature will be isolated in the near future, thereby completing the heavier group 14 element alkyne analogue series.

Another class of compounds that is closely related to the RMMR (M=Si–Pb) compounds are derivatives where only one of the carbons in an alkyne is replaced by a heavier tetrel. No stable compounds of this type have been characterized, although calculations have been performed on various model species.[8] Like their heavier ditetrel model counterparts the model hydrogen substituted derivatives differ from those with bulkier ligands. For example, calculations on CH_2Si indicate that the 1-silavinylidene *(i.e.* $H_2C{=}Si$) form is more than 30 kcal mol^{-1} more stable than the HCSiH isomer which exists in the *trans*-bent form (HSiC = *ca*. 130°; HCSi = *ca*. 150°; C–Si = 1.632 Å). Although the formation of transient species such as $HC{\equiv}SiCH_3$, $HC{\equiv}SiCl$ and $MeSi{\equiv}SiMe$ has been suggested by various experiments, it was not until 1999 that the first examples were detected spectroscopically.[55] These experiments on a silicon carbon system were performed on the basis of calculations that showed the use of halogen substituents at silicon conferred much larger barriers to rearrangement and a higher stability of the *trans*-bent isomer (by *ca*. 10.4 kcal mol^{-1}) $HC{\equiv}SiF$ *versus* the vinylidene $H(F)C{=}Si$. It was suggested that the use of very large carbon substituents (*e.g.* C_6H_2-2,4,6-$\{CH(SiMe_3)_2\}_3$) might allow the isolation of a stable RCSiX (X = halogen or alkoxide) compound. Recent experimental work involving the photolysis of the diazo derivative $ArGeC(N)_2SiMe_3$ (Ar = C_6H_3-2,6-$(NMe_2)_2$) in the presence of alcohols has shown that $ArGe(OR)_2CH_2SiMe_3$ could be obtained.[18] These results supported the view that the germyne species $ArGeCSiMe_3$ was probably generated as an intermediate that is trapped upon reaction with the alcohol. Stable germyne compounds related to this intermediate cannot be far in the future.

The reactions that the heavier alkyne analogues undergo will play a very important role in defining the nature of their multiple bonds. To date only a few such reactions have been described. The first of these involves the reduction of the neutral compounds which occurs relatively easily at *ca*. −1.4 and 1.2 V (*versus* SCE) in case of the Ar′GeGeAr′ and Ar′SnSnAr′ compounds in Table 3.[40,41] Their facile reduction to give a stable radical is consistent with the existence of a low lying empty orbital associated with the M–M interaction. EPR studies of the radical anion $[Ar^*SnSnAr^*]^{\cdot-}$ suggest that the added electron is in an orbital of p-character associated with the tins, although this is not known with certainty.[21] A second electron can also be added to generate species containing digermanium and ditin dianions $[Ar^*MMAr^*]^{2-}$ (M = Ge or Sn) that are isoelectronic to the corresponding neutral diarsenes and distibenes.[29] This behavior may be contrasted with that of less bulky alkynes where reduction of Ph–C ≡C–Ph by lithium affords a radical that couples to give a tetraphenyl butadienide as a dilithium salt. The only other reaction concerns the cycloaddition outlined in Scheme 3 in which 2,3-dimethyl-1,3-butadiene reacts in a unique way with Ar*GeGeAr*. This reaction suggested the presence of substantial lone-pair character at the germanium centers. A wide range of such addition reactions seems likely with various unsaturated molecules, cumulenes and heterocumulenes.

Since the *trans*-bending of the CMMC arrays indicates lone pair character at the M atoms, these centers should show Lewis base behavior and function as ligands to transition and main group metal centers. Likewise, the ready reduction of the molecules indicate low-lying orbitals that are mainly located at with the group 14 elements. Accordingly, Lewis acidic properties at the M centers should also be apparent and this expectations could be tested with a variety of Lewis bases.

9 Conclusions

Germanium, tin and lead compounds that are formal analogues of acetylene have been isolated and structurally characterized. They were stabilized with the use of versatile terphenyl substituents.[56] They possess *trans*-bent, planar structures due to non-bonding electron density at the tetrel atoms. The strength of the M–M is diminished by the removal of electron density from the region between the atoms. The M–M bonds are no longer triple but are approximately double in character for the germanium and tin compounds and essentially single for the lead species. For the, as yet unisolated, silicon species a bond order of between two and three (depending on the substituent) can be expected.

Note added in proof: Two recent publications have extended the range of heavier group 14 alkyne-like species. These involve triple bonding between tin and tungsten in *trans*-$[Cl(PMe_3)_4W{\equiv}Sn\text{-}C_6H_3\text{-}2,6\text{-}Mes_2]$[57] and possible triple bonding between silicon and molybdenum in $[Cp^*(dmpe)(H)Mo\text{-}SiMes][B(C_6F_5)_4]$.[58]

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Notes and References

1 W. Kutzelnigg, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 272.
2 J. P. Desclaux, *At. Data Nucl. Data Tables*, 1973, **12**, 31.
3 (*a*) P. J. Davidson and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1973, 261; (*b*) P. J. Davidson, D. H. Harris and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2268.
4 R. West, M. J. Fink and J. Michl, *Science*, 1981, **214**, 1343.
5 A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst and R. K. M. R. Kallury, *J. Chem. Soc., Chem. Commun.*, 1981, 191.
6 M. Weidenbruch, *J. Organomet. Chem.*, 2002, **646**, 39; J. Escudie and H. Ranaivonjatovo, *Adv. Organomet. Chem.*, 1999, **44**, 114; M. F. Lappert, *Main Group Met. Chem.*, 1994, **17**, 183; P. P. Power, *Chem. Rev.*, 1999, **99**, 3463.
7 R. West, J. D. Cavalieri, J. J. Buffy, C. Fry, K. W. Zilm, J. C. Duchamp, M. Kira, T. Iwamoto, T. Müller and Y. Apeloig, *J. Am. Chem. Soc.*, 1997, **119**, 4972.
8 R. S. Grev, *Adv. Organomet. Chem.*, 1991, **33**, 125.
9 S. Nagase, K. Kobayashi and N. Takagi, *J. Organomet. Chem.*, 2000, **611**, 264.
10 M. Cordonnier, M. Bogey, C. Demuynck and J.-L. Destombes, *J. Chem. Phys.*, 1992, **97**, 7984; M. Bogey, H. Bolvin, C. Demuynck and J. L. Destombes, *Phys. Rev. Lett.*, 1991, **66**, 413.
11 A. J. Bridgeman and L. R. Ireland, *Polyhedron*, 2001, **20**, 2841.
12 K. Kobayashi and S. Nagase, *Organometallics*, 1997, **16**, 2489; N. Takagi and S. Nagase, *Chem. Lett.*, 2001, 966; N. Takagi and S. Nagase, *Eur. J. Inorg. Chem.*, 2002, 2775.
13 N. Takagi and S. Nagase, *Eur. J. Inorg. Chem.*, 2002, 2775.
14 A. Sekiguchi, S. S. Zigler and R. West, *J. Am. Chem. Soc.*, 1986, **108**, 4241.
15 R. Pietschnig, R. West and D. R. Powell, *Organometallics*, 2000, **19**, 2724.
16 N. Wiberg, C. M. M. Finger and K. Polborn, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1054.
17 N. Wiberg, W. Neidermeyer, G. Fischer, H. Nöth and M. Suter, *Eur. J. Inorg. Chem.*, 2002, 1066.
18 C. Bibal, S. Mazieres, C. Gornitzka and C. Couret, *Angew. Chem., Int. Ed.*, 2001, **40**, 952.
19 R. S. Simons and P. P. Power, *J. Am. Chem. Soc.*, 1996, **118**, 11966.
20 L. Pu, B. Twamley, S. T. Haubrich, M. M. Olmstead, B. V. Mork, R. S. Simons and P. P. Power, *J. Am. Chem. Soc.*, 2000, **122**, 650.
21 A. C. Filippou, A. Phillippopoulos, I. Athanassios, P. Portius and D. U. Neumann, *Angew. Chem., Int. Ed.*, 2000, **39**, 2778.
22 A. C. Filippou, P. Portius, A. Phillippopoulos and I. Athanassios, *Organometallics*, 2000, **21** , 653.
23 S. J. Dossett, A. F. Hill, J. C. Jeffrey, F. Martien, P. Sherwood and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1988, 2453.
24 M. M. Olmstead, R. S. Simons and P. P. Power, *J. Am. Chem. Soc.*, 1997, **119**, 11705.
25 L. Pu, S. T. Haubrich and P. P. Power, *J. Organomet. Chem.*, 1999, **582**, 100.
26 C. Eaborn, P. B. Hitchcock, J. D. Smith and S. E. Sözerli, *Organometallics*, 1997, **16**, 5653.

27 B. E. Eichler, L. Pu, M. Stender and P. P. Power, *Polyhedron*, 2001, **20**, 551.
28 L. Pu, B. Twamley and P. P. Power, *Organometallics*, 2000, **19**, 2874.
29 L. Pu, M. O. Senge, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 1998, **120**, 12682.
30 A. F. Wells, *Structural Inorganic Chemistry*, 5th edn.,Clarendon, Oxford, 1984, Chapter 26.
31 B. Twamley, C. D. Sofield, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 1999, **121**, 3357.
32 M. Stender, A. D. Phillips and P. P. Power, *Chem. Commun.*, 2002, 1312.
33 L. Pu, B. Twamley and P. P. Power, *J. Am. Chem. Soc.*, 2000, **122**, 3524.
34 B. E. Eichler and P. P. Power, *J. Am. Chem. Soc.*, 2000, **122**, 8785.
35 Y. Chen, M. Hartmann, M. Diedenhofen and G. Frenking, *Angew. Chem., Int. Ed.*, 2001, **40**, 2052.
36 B. T. Colegrove and H. F. Schaefer, *J. Am. Chem. Soc.*, 1991, **113**, 1557.
37 T. L. Allen, W. H. Fink and P. P. Power, *J. Chem. Soc., Dalton Trans.*, 2000, 407.
38 D. Danovich, F. Ogliano, M. Karni, Y. Apeloig, D. L. Cooper and S. Shaik, *Angew. Chem., Int. Ed.*, 2001, **40**, 4023.
39 B. Schiemenz and P. P. Power, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2150.
40 M. Stender, A. D. Phillips, R. J. Wright and P. P. Power, *Angew. Chem., Int. Ed.*, 2002, **41**, 1785.
41 A. D. Phillips, R. J. Wright, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 2002, **124**, 5930.
42 N. Takagi and S. Nagase, *Organometallics*, 2001, **20**, 5498.
43 (*a*) G. H. Robinson, *Chem. Commun.*, 2002, 2175; (*b*) Y. Xie, R. S. Grev, J. Gu, H. F. Schaefer, P. v. R. Schleyer, J. Su, X.-W. Li and G. H. Robinson, *J. Am. Chem. Soc.*, 1998, **120**, 3773.
44 P. P. Power, *Struct. Bonding*, 2002, **103**, 57.
45 R. S. Grev, B. J. Deleeuw and H. F. Schaefer, *Chem. Phys. Lett.*, 1990, **165**, 257.
46 L. Pauling, *Proc. Natl. Acad. Sci. USA*, 1983, **80**, 3871.
47 F. A. Cotton, A. H. Cowley and X. Feng, *J. Am. Chem. Soc.*, 1997, **119**, 11705.
48 Y. Xie, H. F. Schaefer and G. H. Robinson, *Chem. Phys. Lett.*, 2000, **317**, 174.
49 H. Grützmacher and T. F. Fässler, *Chem. Eur. J.*, 2000, **6**, 2317.
50 N. O. J. Malcolm, R. J. Gillespie and P. L. A. Popelier, *Dalton Trans.*, 2002, 3333.
51 A. D. Phillips and P. P. Power, unpublished calculations.
52 M. B. Smith and J. March, *March's Advanced Organic Chemistry*, 5th edn., Wiley, New York, 2001, p. 24.
53 T. Tsumaraya, S. A. Batcheller and S. Masamune, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 902.
54 P. Jutzi, *Angew. Chem., Int. Ed.*, 2000, **39**, 3797.
55 M. Karni, Y. Apeloig, D. Schröder, W. Zummack, R. Rabezanna and H. Schwarz, *Angew. Chem., Int. Ed.*, 1999, **38**, 332.
56 J. A. C. Clyburne and N. McMullen, *Coord. Chem. Rev.*, 2000, **210**, 73; B. Twamley, S. T. Haubrich and P. P. Power, *Adv. Organomet. Chem.*, 1999, **44**, 1.
57 A. C. Filippou, P. Portius, A. I. Philippopoulos and H. Rohde, *Angew. Chem., Int. Ed.*, 2003, **42**, 445.
58 B. V Mork and T. D. Tilley, *Angew. Chem., Int. Ed.*, 2003, **42**, 357.