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PERSPECTIVE

Homonuclear multiple bonding in heavier main group elements

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Recent developments in multiple bonding between heavier main group atoms are the focus of this review. Emphasis is placed on compounds with homonuclear bonds. It is clear that the Group 15 derivatives REER (E = P, As, Sb or Bi; R = alkyl or aryl ligand) display double bonding throughout the group. For the Group 14 species R_2EER_2 (E = Si, Ge, Sn or Pb, R = organo or related group), it is argued that, at present, only the silicon and certain germanium derivatives merit designation as 'dimetallenes'. Data for multiply bonded heavier Group 13 compounds are currently very scarce. Nonetheless, the available structures of compounds such as $(MR)_n$ (M = Al, Ga, In or Tl; R = alkyl or aryl group; n = 1–6) indicate weakness of the M–M interaction especially for the gallium, indium and thallium compounds where monomeric species are obtained readily. The M–M bond order in the dimers RMMR is apparently less than 1 but can be increased by reduction to give $[RMMR]^{2-}$ but it is probable that the overall M–M bond order remains less than 2.

1 Introduction

The stabilization of heavier main group element compounds having multiple bonding has been a central research theme in organometallic chemistry for almost 30 years. Much of this work has focused on compounds of Groups 14[1] and 15,[2] although heavier Group 13 element derivatives have attracted increasing attention within the past decade.[3] It was recognized from the early work, particularly in Group 14, that the multiple bonding of the heavier elements differs from that seen for the lightest group members. This difference was first illustrated experimentally by Lappert and co-workers through the synthesis[4] and structure[5] of the landmark compound $[Sn\{CH(SiMe_3)_2\}_2]_2$. This was the first isolable species in which there was a possibility of multiple bonding between two heavier main group elements. In the solid state (Fig. 1) it has a *trans*-bent dimeric structure, with a pyramidal metal geometry and an out-of-plane angle (δ, see below) of 41°. The Sn–Sn distance, 2.768(1) Å[5b] is *ca.* 0.03 Å shorter than the 2.80 Å in elemental tin[6] and is very similar to the 2.764(2) Å in $(SnPh_3)_2$.[7] Nonetheless, the compound is dissociated[4,5] in solution [ΔH = 12.8 kcal mol^{-1}, ΔS = 33 cal K^{-1} mol^{-1} (cal = 4.184 J)][8] into stannanediyl monomers which exist in the singlet form and its chemistry is consistent with a monomeric structure.[9] The germanium analog $[Ge\{CH(SiMe_3)_2\}_2]_2$[5b,10] also is monomeric in solution and dimeric in the solid with a Ge–Ge bond length of 2.347(2) Å which is *ca.* 0.09 Å less than a Ge–Ge single bond.[6] The out-of-plane angle at germanium is 32° (*cf.* 41° for tin). Evidently, the Ge–Ge interaction is stronger than the corresponding one in its tin congener.

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In addition to these early results there were also extremely important achievements in heavier Main Group 15 chemistry that provided a foretaste of developments to come. The first stable phosphabenzene was reported as early as 1966.[11] In the 1970s the isolation and characterization of stable phosphaimines,[12] phosphaalkenes[13] and phosphaalkynes[14] were published. (It should be borne in mind, however, that related compounds involving multiple bonding between sulfur and carbon or nitrogen or oxygen had been already well established, in some cases, for many decades.) These discoveries heralded the explosive growth in the 1980s when a large variety of stable molecular compounds with multiple bonding between two heavier main group elements or between a heavier and lighter main group element were reported. Examples include Si=C,[15] Si=Si,[16] Ge=C,[17] Ge=Ge,[10,18] Si=N,[19] Ge=N,[20] Sn=C,[21] Si=P,[22] Ge=P,[23] Sn=P,[24] P=P,[25] P=As,[26] As=As,[27] P=B,[28,29] As=B[30] and As≡C bonds.[31]

Recent work in the 1990s has afforded more examples of dimeric tin species[32–35] related to Lappert's original $[Sn\{CH(SiMe_3)_2\}_2]_2$ compound. These and related germanium[18,35–40] and lead[33] analogues are listed in Table 1.[5b,10,18,35–40] Structural details of the anion $[\{Sn(C_6H_3Trip_2\text{-}2,6)\}_2]^-$[41] (Trip = $C_6H_2Pr^i_3$-2,4,6), a singly reduced valence isomer of a 'distannyne', are also given in Table 1. It has a formal bond order of 1.5 and a Sn–Sn bond length of *ca.* 2.81 Å. The trigermanium ring compounds $[\{Ge(SiBu^t_3)_2\}_2Ge(SiBu^t_3)_2]$[42a] $[\{Ge(SiBu^t_3)\}_3][BPh_4]$[42b] and $[Ge(C_6H_3Mes_2\text{-}2,6)]_3^{\bullet}$ (Mes = $C_6H_2Me_3$-2,4,6)[42c] are also included. In addition, the first structural details for a $(PbR_2)_2$ compound, $[Pb\{Si(SiMe_3)_3\}\{C_6H_2(CF_3)_3\text{-}2,4,6\}]_2$,[33] with a Pb–Pb interaction, are listed.

Besides these compounds, heteronuclear heavier Group 14 derivatives with Si=S,[43] Ge=O,[44a] Ge=S,[44b,45,46] Ge=Se,[44c,46]

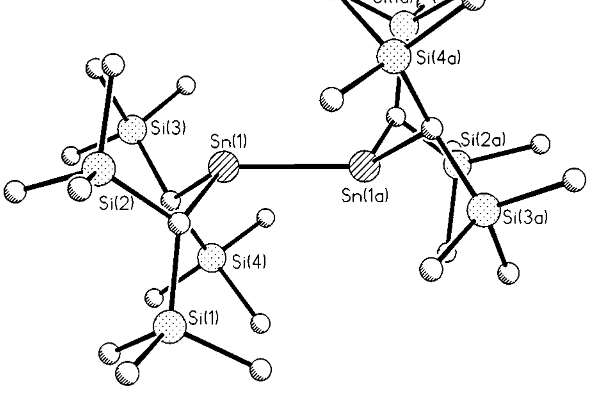

Fig. 1 A drawing of the structure of $[Sn\{CH(SiMe_3)_2\}_2]_2$ illustrating its *trans*-bent configuration (ref. 5*b*)

Table 1 Selected structural data for diorgano-germanium(II), -tin(II) and -lead(II) dimers and related species

Compound	M–M/Å	δ*/°	γ*/°	Ref.
$[Ge(C_6H_3Et_2\text{-}2,6)_2]_2$	2.213(2)	12	10	18
$[Ge(C_6HMe_3\text{-}2,3,4\text{-}Bu^t\text{-}6)_2]_2$	2.2521(8)	0	20.4	36
$[Ge(SiMePr^i{}_2)_2]_2$	2.267(1)	0	6.5	37
$[Ge(SiPr^i{}_3)_2]_2$	2.298(1)	0	16.4	37
$[Ge(Mes)(C_6H_3Pr^i{}_2\text{-}2,6)]_2$	2.301(1)	36	7	38
$[Ge\{CH(SiMe_3)_2\}_2]_2$	2.347(2)	32	0	5*b*, 10
$[GeCl(C_6H_3Mes_2\text{-}2,6)]_2$	2.443(2)	39	0	39
$\{GeN(Bu^t)(CH_2)_3N(Bu^t)SiN(Bu^t)(CH_2)_2N(Bu^t)\}_2$	2.451(2)	41.3	42.3	40
$[\{Ge(SiBu^t{}_3)_2\}_2Ge(SiBu^t{}_3)_2]$	2.239(4)	—	—	42*a*
$[\{Ge(SiBu^t{}_3)\}_3][BPh_4]$	2.226(4)	—	—	42*b*
$[Ge(C_6H_3Mes_2\text{-}2,6)]_3^{\bullet}$	2.35(7)	—	—	42*c*
$K[\{Ge(C_6H_3Mes_2\text{-}2,6)\}_3]$	2.422(2)	—	—	42*c*
$[Sn\{CH(SiMe_3)_2\}_2]_2$	2.768(1)	41	0	5*b*
$[Sn\{Si(SiMe_3)_3\}_2]_2$	2.8247(6)	28.6	63.2	32
$[Sn\{C_6H_2(CF_3)_3\text{-}2,4,6\}\{Si(SiMe_3)_3\}]_2$	2.833(1)	41.5	0	33
$[Sn(C_6HMe_3\text{-}2,3,4\text{-}Bu^t\text{-}6)_2]_2$	2.910(1)	21.4, 64.4	—	34
$[Sn\{C_6H_2(CF_3)_3\text{-}2,4,6\}_2]_2$	3.639(1)	46	0	35
$[K(THF)_6][\{SnC_6H_3Trip_2\text{-}2,6\}_2]$	2.8123(9)	95.20	0	41
$[Pb\{C_6H_2(CF_3)_3\text{-}2,4,6\}\{Si(SiMe_3)_3\}]_2$	3.537(1)	40.8	0	33

* The angles δ and γ are represented below:

Table 2 Selected structural parameters for organo-arsenic, -antimony and -bismuth double bonded compounds

Compound	E–E/Å	E–E–C*/°	Ref.
$[Mes^*PAs\{CH(SiMe_3)_2\}]$	2.124(2)	101.2(2), 96.4(2)	26
$[MesPAs(C_6H_3Trip_2\text{-}2,6)]$	2.134(2)	96.7(2), 101.5(2)	53
$[Mes^*AsAs\{CH(SiMe_3)_2\}]$	2.224(2)	93.6(3), 99.9(3)	27
$[AsC(SiMe_3)_3]_2$	2.244(1)	106.3(2)	54
$[As(C_6H_3Trip_2\text{-}2,6)]_2$	2.285(3)	96.40(22)	53
$[MesPSb(C_6H_3Trip_2\text{-}2,6)]$	2.335(2)	95.7(3), 100.9(2)	53
$[Sb\{C_6H_2[CH(SiMe_3)_2]_3\text{-}2,4,6\}]_2$	2.642(1)	101.4(1)	51
$[Sb(C_6H_2Trip_2\text{-}2,6)]_2$	2.664(2)	98.58(32)	53
$[Bi\{C_6H_2[CH(SiMe_3)_2]_3\text{-}2,4,6\}]_2$	2.8206(8)	100.5(2)	52

* Where two angles are given they are listed in the order in which the atoms appear in the formula.

Ge=Te,[44d,46] Sn=S,[47,48] Sn=Se[47–49] and Sn=Te[49] multiple bonds have been characterized. The compound $(\eta^5\text{-}C_6H_5)(CO)_2MoGeC_6H_3Mes_2\text{-}2,6$, in which there is a Mo–Ge triple bond, has also been reported.[50] The characterization of the first stable Sb=Sb[51] and Bi=Bi[52] bonds has been described and structural information for these and their arsenic and mixed Group 15 congeners[26,27,51–54] is in Table 2. Triply bonded phosphorus–transition-metal compounds have also been characterized.[55]

Another development of the 1990s has been the expansion of the range of multiple bonds to aluminum and gallium.[3a] Some structural parameters for homonuclear Group 13 multiple bonded compounds are included in Table 3.[56–74] In addition, stable complexes featuring heteronuclear Ga=Se,[75] Ga=Te[75] and In=Se[76] double bonds have been synthesized. Table 3 includes structural data for the radical species $[R_2MMR_2]^-$ [M = Al or Ga; R = $CH(SiMe_3)_2$ or Trip] which have a formal M–M bond order of 1.5 and the ring compound $[\{Ga(C_6H_3Mes_2\text{-}2,6)\}_3]^{2-}$ which has a 2 π-electron, three-membered ring with a formal Ga–Ga bond order of 1.33. It is related to the above-mentioned, isoelectronic cyclotrigermanium cation $[\{Ge(SiBu^t{}_3)_3\}_3]^+$.[42b] The radical $[(Bu^t{}_3Si)GaGa(SiBu^t{}_3)_2]^{\bullet}$[63] with a formal Ga–Ga bond order of 1.5 and the dimer $Na_2[\{Ga(C_6H_3Trip_2\text{-}2,6)\}_2]$,[74] which was stated to have a Ga–Ga triple bond, are also listed. More recently, it was reported that the related species $(OC)_4FeGa(C_6H_3Trip_2\text{-}2,6)$[77] also had a Ga–Fe triple bond.

The bonding description of the last two compounds, in particular, has generated considerable discussion. Some say that the Ga–Ga bond is a double one on the basis of its bond length or its *trans*-bent geometry, DFT[78] and *ab initio* calculations.[79a] The possibility of single bonding has also been suggested.[79b] In contrast, others have supported triple bonding on theoretical grounds.[80,81] The claim for Fe–Ga triple bonding has also been questioned[82] on the basis of DFT calculations and a comparison of IR data with related aluminum[83] and indium[84] compounds which imply essentially negligible π-bonding between the Group 13 element and the transition metal.

The bonding of the Group 14 compounds[1] in Table 1 has also been the subject of considerable discussion (see below). This is based on the fact that none of the tin or lead compounds has a distance much shorter than a single bond and all are dissociated to monomers in solution. They deviate from the planar geometries expected in ethylene analogs and have large out-of-plane angles at the metals. Three of the eight germanium dimers have similar characteristics. As a result of this behavior (which is at such variance to that normally seen in alkenes) several interesting questions arise. For example, is it justified to refer to the tin compounds in Table 1 as distannenes, thereby suggesting a behavior normally associated with corresponding alkenes? Is it expedient to refer to $Na_2[\{Ga(C_6H_3Trip_2\text{-}2,6)\}_2]$ as a (triply-bonded) digallyne when it has a Ga–Ga distance similar to some Ga–Ga single bonds[61,62] as well as a non-linear structure? The object of the rest of this perspective is to examine some current views of these questions. The discussion is focused primarily on homonuclear bonds to avoid the complicating effect of ionic factors associated with heteronuclear species. Furthermore, emphasis is given to recent developments in compounds of the third, fourth and fifth rows where deviations in the structural and chemical properties from compounds of the first row are the most marked.

2 Phosphorus, Arsenic, Antimony and Bismuth Multiple Bonding

It is, perhaps, easiest to begin with the least controversial of the heavier main group multiply bonded compounds, the Group 15 derivatives of formula REER (E = P, As, Sb or Bi; R = alkyl or aryl group).[2] Currently, there are structural data for about 20 diphosphenes (which generally have *trans*-planar structures) as well as several η^1-diphosphene transition-metal complexes in

Table 3 Metal–metal bond lengths and torsion angles in structurally characterized Group 13 tetraorganodimetallanes and related species and their reduced analogs

Compound	M–M/Å	M–C/Å	$\delta^{a}/^{\circ}$	Ref.
$[\mathrm{Al\{CH(SiMe_3)_2\}_2}]_2$	2.660(1)	1.982(3)	≈0	56
$(\mathrm{AlTrip_2})_2$	2.647(3)	1.996(3)	44.8	57
$[\mathrm{Ga\{CH(SiMe_3)_2\}_2}]_2$	2.541(1)	1.995(5)	≈0	58*a*
$(\mathrm{GaTrip_2})_2$	2.515(3)	2.008(7)	43.8	59
$[\mathrm{GaCl\{Si(SiMe_3)_3\}_2}]_2$	2.505(4)	2.395(5)[b]	—	60*a*
$[\mathrm{Ga\{CH(SiMe_3)_2\}DPPD}]_2$[c]	2.44(1)	1.995(5)	—	58*b*
$[\mathrm{Ga\{CH(SiMe_3)_2\}N_3Ph}]_2$	2.457(9)	1.977(2)	—	58*c*
$[\mathrm{Ga(TMP)_2}]_2$[d]	2.525(1)	1.901(4)[e]	31	60
$[\mathrm{GaB_4H_4(CSiMe_3)_2}]_2$	2.340(2)	—	—	61
$[\mathrm{Ga}\overline{\mathrm{N(Bu^t)CHCHN}}\mathrm{(Bu^t)}]_2$	2.333(1)	1.836(4)[e]	90	62
$[\mathrm{GaI(C_6H_3Trip_2\text{-}2,6)}]_2$	2.511(3)	1.994(9)	0	64
$[\mathrm{(Bu^t{}_3Si)GaGa(SiBu^t)_3)_2}]$	2.420(1)	—	—	63
$[\mathrm{In\{CH(SiMe_3)_2\}_2}]_2$	2.828(1)	2.194(5)	≈0	65
$(\mathrm{InTrip_2})_2$	2.775(2)	2.184(7)	47.8	66
$[\mathrm{In\{C_6H_2(CF_3)_3\text{-}2,4,6\}_2}]_2$	2.744(2)	2.21(1)	85.9(5)	67
$[\mathrm{In\{N(Bu^t)SiMe_2\}_2N(Bu^t)}]_2$	2.768(1)	2.12(1)–2.29(8)[e]	—	68
$[\mathrm{In(SiBu^t{}_3)_2}]_2$	2.922(1)	2.778(4)[b]	90	69
$[\mathrm{Tl\{Si(SiMe_3)_3\}_2}]_2$	2.914(5)	2.675(2)[b]	78.1	70
$[\mathrm{Tl(SiBu^t{}_3)_2}]_2$	2.966(2)	2.789(12)[b]	90	69
$[\{\mathrm{Al\{CH(SiMe_3)_2\}_2}\}_2]^-$	2.53(1)	2.040(5)	0	72
$[\{\mathrm{Ga\{CH(SiMe_3)_2\}_2}\}_2]^-$	2.401(1)	2.059(4)	0	71
$[\{\mathrm{AlTrip_2}\}_2]^-$	2.470(2)	2.021(1)	1.4	57
$[\{\mathrm{GaTrip_2}\}_2]^-$	2.343(2)	2.038(10)	15.5	59
$\mathrm{Na_2}[\{\mathrm{Ga(C_6H_3Mes_2\text{-}2,6)}\}_3]$	2.441(1)	2.037(3)	—	73
$\mathrm{Na_2}[\{\mathrm{Ga(C_6H_3Trip_2\text{-}2,6)}\}_2]$	2.319(3)	2.044(20)	—	74

[a] Angle between the perpendiculars to the M–C_2 co-ordination planes. [b] M–Si distances. [c] DPPD = 1,3-Diphenylpropane-1,3-dionate. [d] TMP = 2,2,6,6-Tetramethylpiperidine. [e] M–N distances.

Table 4 Relative energies (kcal $\mathrm{mol^{-1}}$) of σ and π bonds in homonuclear main group diatomic species[a]

B–B	70[b]	C–C	81/62[a]	N–N	38/94[a]
Al–Al	36[b]	Si–Si	47/28[a]	P–P	48/34[a]
Ga–Ga	32[b]	Ge–Ge	39/26[a]	As–As	35/28[a]
In–In	23[b]	Sn–Sn	35/11[c]	Sb–Sb	31/20[c]
Tl–Tl	2[b]	Pb–Pb	23(33)/—[c,d]	Bi–Bi	21/10[c,e]

[a] These values are generated by using methods in ref. 88 which are in part abstracted from spectroscopic data in ref. 89(*a*). [b] These values were obtained from ref. 89(*a*) and they represent single bonds. [c] These data were abstracted from ref. 89(*a*) and from single bond values in ref. 89(*b*). [d] The Pb–Pb single bond value (in parentheses) is from ref. 89(*b*); the first value is from 89(*a*) and corresponds to a 'double' bond. [e] These values were estimated from the 41 kcal $\mathrm{mol^{-1}}$ value for the diatomic Bi_2 [see ref. 89(*a*)] and by assuming an approximate 2:1 ratio for the strengths of the σ and π bonds.

which the P–P double bond is conserved.[2d,e] There are also many metallodiphosphenes in which the phosphorus organic substituent is replaced by a transition-metal fragment.[2d] The range of P–P distances in organodiphosphenes lies between 1.985(2)[85] and 2.034(1) Å.[25] This may be compared to the approximate single P–P bond distance of 2.22 Å.[86a] Thus, the percentage difference between singly and doubly bonded P–P moieties lies between *ca.* 7.5 and 9.8%. This impressive margin probably reflects not only P–P π-bond formation, but also a change in σ hybridization at phosphorus which is thought to account for up to half the observed contraction.[87] The shortening is *ca.* 50–60% of the 15.2% difference observed between hydrazine N_2H_4 (N–N 1.45 Å)[86b] and the diimine N_2H_2 (N–N 1.23 Å).[86c] It seems probable that this margin is enhanced in view of the long single N–N σ bond which is thought to be caused by interelectronic repulsion. Nonetheless, there seems to be little doubt that the P–P π bond is much weaker than an N–N π bond and this view is supported by spectroscopic and thermochemical data in Table 4[88] which features a comparison of the σ- and π-bond strengths of some homonuclear main-group element–element bonds.[88,89a] It can be seen that there is more than 50% decrease in π-bond strength between the first and second row. It is also notable that the π-bond strengths are greater in Group 15 than in Group 14, possibly as a result of their smaller size. By using bond dissociation energies for the diatomic triply bonded Group 15 molecules[89a] and single bond strengths, it is possible to distinguish the σ and π components of the bonding within this group. For phosphorus, although the P–P π bond is much weaker than the N–N π bond, the σ:π bond strength ratio (48:34) in a P–P double bond is comparable to the ratio (81:62) in carbon. From this perspective, the P–P double bond is correctly regarded a full-fledged double bond. The P–P π-bond strength, which may be represented by the rotational barrier for the *E*–*Z* isomerization, was calculated[90] to be *ca.* 33.5 kcal $\mathrm{mol^{-1}}$. This value is in good agreement with the 34 kcal $\mathrm{mol^{-1}}$ estimated in Table 4. Laser irradiation studies of the *E*–*Z* isomerization in $(\mathrm{PMes^*})_2$ ($\mathrm{Mes^*} = \mathrm{C_6H_2Bu^t{}_3\text{-}2,4,6}$) afforded a lower energy barrier, *ca.* 20 kcal $\mathrm{mol^{-1}}$.[91]

The σ:π bond strength in arsenic is 35:28. As expected, both bonds are weaker than their phosphorus counterparts, nevertheless, the relative π-bond strength is slightly higher for arsenic. The bond lengths in diarsenes are in the range 2.224(2)[27]–2.285(3) Å.[53] With 2.44 Å as the As–As single bond distance,[86d] this represents a shortening of 6.3–8.0%. This margin is slightly less than that observed in the diphosphenes. Nonetheless, it is fully consistent with the presence of As=As double bonds.

The currently known range of structurally characterized distibenes and dibismuthenes is limited to two of the former[51,53] and just one of the latter.[52] The Sb–Sb distances in the two distibenes are 2.642(1)[51] and 2.664(2)[53] Å which represent shortenings of 6.94 and 6.16% respectively.[86e] It may be noted that both σ and π bonds of the Sb–Sb double bond are weaker than in the arsenic case but the weakening is greater in the case of the π bond. A similar trend is observed for the dibismuthene.[52] In this case the Bi–Bi π-bond strength is estimated to be only about half that of the Sb–Sb π bond. In the dibismuthene the amount of shortening is 5.7%.[86f] Clearly, the percentage shortening diminishes in these heavier metals. This is consistent with the lower π-bond energies in Table 4.

3 Silicon, Germanium, Tin and Lead Multiple Bonding

Moving now to the Group 14 elements, it can be seen that the estimated π-bond strengths are less than those in Group 15. In contrast, the σ-bond strengths for the Group 14 elements are generally higher (the P–P and Si–Si bonds have about equal strength) than in the Group 15 elements. The stronger π bonds in the pnictides may be explained primarily on the basis of the smaller size of these elements, whereas the weakness of the Group 15 σ bonds has often been thought to be due to interelectronic repulsions between the lone pairs which is most pronounced in the case of the very weak N–N single bond. In Group 14 homonuclear double bonding primarily concerns the species R_2MMR_2 (M = Si–Pb; R = alkyl or aryl group). For silicon about a dozen compounds have been structurally characterized.[1i] The Si–Si distances vary from 2.251(1)[92a] to 2.138(1) Å[92b] which represents a shortening in the range 7.3–8.6%. As with the Lappert ditin compound some disilenes adopt *trans*-bent structures but the out-of-plane bending is very much less (maximum published value 18°)[93] and many have essentially planar geometry like most alkenes.[94] The activation enthalpy for *cis–trans* isomerization, which is considered to be a measure of Si–Si π-bond strength, ranges from 25.4 to 30.3 kcal mol^{-1}.[95,1j] This is *ca.* 50% of the π-bond strength in alkenes and in good agreement with the value in Table 4. In one case, the compound $[Si(Mes)C_6H_2\{CH(SiMe_3)_2\}_3\text{-}2,4,6]_2$,[96a,b] there is dissociation to monomers under relatively mild conditions. The ΔH_{diss} is *ca.* 26 kcal mol^{-1}. The dimer has a lengthened Si–Si doubly bonded distance of 2.228(1) Å with out-of-plane angles in the case of the *Z* isomer of 9.4(3) and 14.6(3)°.

The structures of eight $(GeR_2)_2$ compounds are known (Table 1). The Ge–Ge distances and out-of-plane angles range from 2.213(2)[18] to 2.451(2) Å[40] and from 0[36,37] to 42.3°.[40] Thus, the Ge–Ge bond shortenings range between 9.3 and 0%. Two of the three compounds having the longest Ge–Ge bonds are dissociated to monomers in solution, which underlines the weakness of their association. Another feature of the germanium compounds is that the majority (five out of eight) show substantial out-of-plane angles and all display either a substantial out-of-plane or twist angle. The geometrical distortion therefore is greater than in the silicon compounds. The data in Table 4 indicate a π-bond strength of *ca.* 26 kcal mol^{-1} which is close to that predicted theoretically[97] but higher than the enthalpy of activation (*ca.* 22 kcal mol^{-1}) of the interconversion of the *E–Z* isomers of $[Ge(Mes)(C_6H_3Pr^i_2\text{-}2,6)]_2$.[38] The lower value of this compound is in harmony with the elongation [Ge–Ge = 2.301(1) Å] and high out-of-plane angle of 36° which are probably caused by steric crowding. Furthermore, the 22 kcal mol^{-1} barrier is less than the *ca.* 26 kcal mol^{-1} in its silicon analog $[Si(Mes)(C_6H_3Pr^i_2\text{-}2,6)]_2$.[38] A recent variable temperature UV/VIS spectroscopic study[96c] of $[Ge(MeS)(C_6H_2\{CH(SiMe_3)_2\}_3)]_2$ (crystal structure currently unknown) yielded an enthalpy of dissociation of 14.7 kcal mol^{-1}, about half that of the silicon analog.[96a,b] Considerable Ge–Ge multiple bond character is also seen in the cyclotrigermanium cation $[\{Ge(SiBu^t)_3\}_3]^+$ which has an average Ge–Ge distance of 2.226(4) Å.[42b] Short Ge–Ge distances, average 2.35(7) Å, are also observed in the cyclotrigermanium radical $[\{Ge(C_6H_3Mes_2\text{-}2,6)\}_3]^{\bullet}$.[42c]

A sharp decrease in the π-bond energy is predicted in Table 4 upon descending the Group 14 elements from germanium to tin. The Sn–Sn π-bond strength is estimated to be just 11 kcal mol^{-1} (*cf.* Ge–Ge π-bond strength = 26 kcal mol^{-1}) whereas the strength of an Sn–Sn σ bond is marginally less than that of its Ge–Ge counterpart (35 *vs.* 39 kcal mol^{-1}). The decrease in π-bond strength is more abrupt than that in the corresponding Group 15 elements between arsenic and antimony. It is difficult to explain this difference on the basis of sizes since antimony and tin have similar radii as do arsenic and germanium. The weakness of the Sn–Sn bonding in the five $(SnR_2)_2$ structures in Table 1 is supported by the fact that all compounds are dissociated in solution and the shortest tin–tin distances are similar to that of a single bond.[5b,32,33] The longest Sn–Sn interaction is in $[Sn\{C_6H_2(CF_3)_3\text{-}2,4,6\}_2]_2$,[35] Sn–Sn = 3.639(1) Å, which is *ca.* 0.8 Å longer than a single bond. The *trans*-bent structure is observed in all compounds but there is no correlation between the out-of-plane angle and Sn–Sn bond length in the compounds seen here.

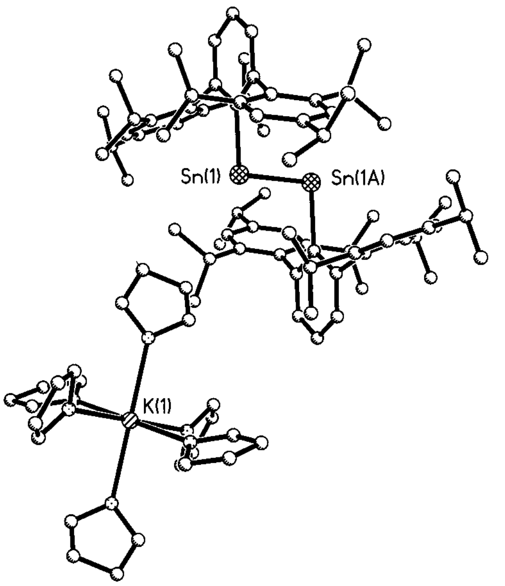

Fig. 2 Schematic drawing of $[K(THF)_6][\{Sn(C_6H_3Trip_2\text{-}2,6)\}_2]^-$ (ref. 41)

The structure of one dimeric $(PbR_2)_2$ species with a Pb–Pb interaction is currently available.[33] In that compound, $[Pb\{C_6H_2(CF_3)_3\text{-}2,4,6\}\{Si(SiMe_3)_3\}]_2$, the Pb–Pb distance is 3.537(1) Å and the out-of-plane angle is 40.8°. This distance is much longer than the single Pb–Pb bond in $(PbMe_3)_2$ [2.88(3) Å][98] which indicates that the Pb–Pb interaction is very weak. This is in agreement with the data in Table 4, which predict a Pb–Pb bond energy of 23 kcal mol^{-1}[89a] in the dimer Pb_2 (putatively a Pb–Pb double bond) much less than the corresponding value (35 kcal mol^{-1}) for its tin analog. A problem arises, however, when this value (23 kcal mol^{-1}) is compared to that for a single Pb–Pb bond in $(PbMe_3)_2$ (33 kcal mol^{-1}).[89b,98] This implies that a single Pb–Pb bond is stronger than a multiple one. This apparently absurd result is consistent with the observation that the 'multiple' Pb–Pb bond in $[Pb\{C_6H_2(CF_3)_3\text{-}2,4,6\}\{Si(SiMe_3)_3\}]_2$[33] is much longer than a single bond whereas the analogous tin species $[Sn\{C_6H_2(CF_3)_3\text{-}2,4,6\}\{Si(SiMe_3)_3\}]_2$ has a bond length similar to a single Sn–Sn bond.[33]

One other class of homonuclear multiply bonded heavier Main Group 14 species needs to be considered. These are compounds of formula RMMR (M = Si, Ge, Sn or Pb; R = organo group), which are heavier analogues of the alkynes. Unfortunately, experimental details of only one related compound currently exist. The radical ion $[\{Sn(C_6H_3Trip_2\text{-}2,6)\}_2]^-$, which is a singly reduced analogue of a neutral tin species of the formula $(SnR)_2$, has a Sn–Sn distance near 2.80 Å and an Sn–Sn–C angle of *ca.* 95° (Fig. 2).[41] This structure suggests that there is a lone pair at each tin occupying orbitals high in s character with p orbitals being used for Sn–Sn and Sn–C σ bonding. The remaining p orbitals, one at each tin, may overlap to form a π orbital occupied by a single electron. Formally, the bond order is 1.5 but the Sn–Sn distance is the same as a single bond. Removal of the π electron should result in a slightly longer Sn–Sn bond but the *trans*-bent structure with lone pairs at each tin should be preserved.

4 Boron, Aluminum, Gallium, Indium and Thallium Multiple Bonding

Homonuclear multiple bonding between the Group 13 elements is a relatively recent development.[3a] Historically, such compounds were more noted for their electron deficiency and consequent absence of sufficient numbers of electrons to form multiple bonds. This was particularly true for derivatives of boron. Nonetheless, there were a number of reports that indicated that the problem of electron deficiency could be remedied. For example, multiply bonded B–B moieties were generated in various metal complexes of reduced six-membered quasi-aromatic rings.[99] In addition, the structures of a number of three-membered delocalized ring compounds containing B–B units have been synthesized.[100] In these, the stabilized ring π orbitals provide the impetus for the delocalization incorporating the B–B unit. Boron–boron bonds as short as 1.58 Å (*cf.* single B–B bond *ca.* 1.71 Å) have been reported.[101] Short B–B distances (*ca.* 1.6 Å) have also been observed in the structures of several transition-metal borides which contain one-dimensional polyacene-type boron chains as part of a three-dimensional metallic lattice.[102] The common feature of these compounds is that B–B units with adjacent empty p orbitals as part of rings or chains are reduced to form multiple bonds between the boron atoms.

The reduction of acyclic, molecular B–B bonded species had to await the synthesis of suitable compounds for reduction. The simplest are the species $(BR_2)_2$ (R = alkyl or aryl groups) which are only stable if the substituents are large. They were first reported in 1980[103] and it was shown that they could undergo a 1-electron reduction to the species $[(BR_2)_2]^-$.[104] Solution EPR data showed that the unpaired electron occupied a π orbital formed by overlap of two adjacent boron p orbitals for a formal B–B bond order of 1.5. However, further reduction of tetraalkyl diboron species was not achieved. Tetraaryl diboron compounds permitted double reduction as seen in the dianion $[Mes_2BB(Ph)Mes]^{2-}$.[105a] It has a shortened B–B bond of 1.636(11) Å and an almost planar $B_2\{C_{ipso}\}_4$ array consistent with the presence of a formal B–B double bond. The dianion $[\{B(NMe_2)Ph\}_2]^{2-}$ has a similar B–B distance of 1.631(9) Å as well as a planar core.[105b] The B–B bonds are *ca.* 0.07–0.08 Å shorter than in their neutral precursors. The shortening is not as great as that in corresponding ethylene species possibly as a result of coulombic repulsion. A comparison with $[\{B[C(SiMe_3)_2]Mes\}_2]^{2-}$, which has a much longer single bond [B–B 1.859(6) Å] between two negatively charged borons, seems to bear out this view.[106] Theoretical data for diborane(4) dianions are scant but one paper suggests that the B–B π bond may be quite strong.[107a]

Extension of these methods to aluminum and gallium has resulted in the synthesis of several monoreduced anions (Table 3) of tetraorganodimetallanes similar to the corresponding boron species.[57,59,71,72] Stable multiply bonded dianion products from further reduction have not yet been obtained. The monoreduced species have a formal M–M (M = Al or Ga) bond order of 1.5. The M–M bond shortening is in the range 0.13–0.18 Å (*ca.* 7–8%) and the torsion angle between the metal coordination planes is decreased. The multiple bonding is not complicated by the presence of associated alkali-metal counter cations which are separated from the anion by solvent coordination. The solution EPR spectra of the monoanions show that the unpaired electron is equally coupled to two metal nuclei and that the magnitude of the couplings is consistent with the location of the electron in a π orbital. For the aluminum compounds there is good agreement with theoretical data[107b] which predict an Al–Al distance of 2.478 Å and a torsion angle of 6.3° in the hypothetical compound $[(AlPh_2)_2]^-$; *cf.* Al–Al 2.470(2) Å and torsion angle 1.4° in $[(AlTrip_2)_2]^-$.

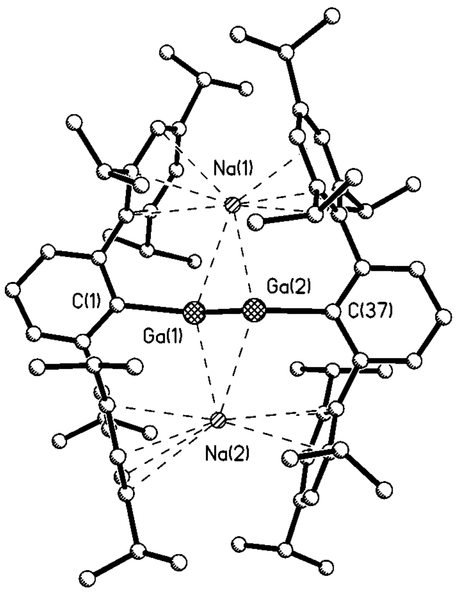

Fig. 3 Schematic drawing of $Na_2[\{Ga(C_6H_3Trip_2\text{-}2,6)\}_2]$ (ref. 74)

Reduction of the substituted *m*-terphenyl gallium dihalides $GaCl_2(C_6H_3Mes_2\text{-}2,6)$ or $GaCl_2(C_6H_3Trip_2\text{-}2,6)$ gave $Na_2[\{GaC_6H_3Mes_2\text{-}2,6\}_3]$[73] or $Na_2[\{GaC_6H_3Trip_2\text{-}2,6\}_2]$,[74] which were the first examples of two new compound classes. The former species has a core composed of a Ga_3 ring with equal Ga–Ga distances near 2.44 Å. It may be regarded as a delocalized 2 π-electron system that conforms to the Hückel rule. It has a formal Ga–Ga bond order of 1.33. This conclusion is supported by calculations,[73b] although the Ga–Ga distances (*ca.* 2.5 Å) in hypothetical species such as $Na_2[(GaH)_3]$ or $K_2[(GaH)_3]$ are significantly longer than those measured experimentally.[73b] This may indicate that Na^+–aromatic ring interactions could play a role in shortening the Ga–Ga bonds. The digallium compound $Na_2[\{GaC_6H_3Trip_2\text{-}2,6\}_2]$ also has no precedent in heavier main group element chemistry.[74] It crystallizes as an ion triple with interactions between the Na^+ ions and the *ortho*-aryl substituents (Fig. 3). The dianion is isoelectronic to the corresponding, unknown, neutral germanium compound and it was stated to have a Ga–Ga triple bond. However, its geometry is not linear and Ga–Ga–C angles of *ca.* 131° are observed. The Ga–Ga bond, 2.319(3) Å, is the shortest reported to date, but it can be seen from Table 3 that this distance is similar to the 2.343(2) Å[59] in the anion $[(GaTrip_2)_2]^-$ (Ga–Ga bond order 1.5) or the 2.340(2) Å in the less crowded species $[GaB_4H_4(CSiMe_3)_2]_2$[61] (Ga–Ga bond order 1) or the 2.333(1) Å in $[Ga\overline{N(Bu^t)CHCHN}(Bu^t)]_2$[62] (Ga–Ga bond order 1). Unfortunately, no stable dimeric, neutral compounds of the type RMMR (M = Al or Ga; R = alkyl or aryl) solvent or separated ion pairs of the type $[M'L_n]_2[RMMR]$ (M′ = alkali metal; L = Lewis base donor) are known at present. Structural data for these would be of interest since the Ga–Ga bond in the dianion $[\{GaC_6H_3Trip_2\text{-}2,6\}_2]^{2-}$ would be illuminated by the synthesis of the corresponding unreduced species, the putative dimer $[Ga(C_6H_3Trip_2\text{-}2,6)]_2$ and the influence (if any) of the metal counter cations on the Ga–Ga bond distance could also be determined. The M–M bonds in compounds of the general formula $(MR)_n$ (M = Al or Ga; R = alkyl or aryl; n = 4–6) are usually weaker than single bonds. Evidence for this comes from structural studies[108–117] of species such as $[Al(\eta^5\text{-}C_5Me_5)]_4$,[108] $[Ga\{C(SiMe_3)_3\}]_4$,[109a,b] $[Ga(\eta^5\text{-}C_5Me_5)]_6$[110] and monomeric $GaTp^{Bu^t_2}$ [$Tp^{Bu^t_2}$ = tris(3,5-di-*tert*-butylpyrazolyl)hydroborate][111] (Table 5). The tetramers, which have electron deficient M_4 frameworks, display somewhat lengthened Al–Al and Ga–Ga bonds of *ca.* 2.77 and 2.69 Å and $[Al(\eta^5\text{-}C_5Me_5)]_4$,[108a] $[Ga\{C(SiMe_3)_3\}]_4$ and $[Ga\{C(SiMe_2Et)\}]_4$[109c] dissociate to monomers in dilute benzene solution[109] and in the vapor phase. However, the recently synthesized tetramer $[Al(SiBu^t_3)]_4$[108b] has a shorter average Al–Al distance of 2.604(4) Å which demon-

Table 5 Selected structural data for some metal–metal bonded and related compounds of the formula $(MR)_n$ (M = Al, Ga, In or Tl; R = alkyl or aryl group; n = 1–6)

Compound	Structure type	M–M/Å	Ref.
$[Al(\eta^5\text{-}C_5Me_5)]_4$ (solid)	Tetrahedral Al_4	2.769(4)	108*a*
$[Al(\eta^5\text{-}C_5Me_5)]$ (vapor)	Monomer	—	117*a*
$[Al(SiBu^t_3)]_4$ (solid)	Tetrahedral Al_4	2.604(4)	108*b*
$[Ga(\eta^5\text{-}C_5Me_5)]_6$ (solid)	Distorted octahedral Ga_6	4.073(2), 4.173(3)	110
$[Ga(\eta^5\text{-}C_5Me_5)]$ (vapor)	Monomer	—	117*b*
$[Ga\{C(SiMe_3)_3\}]_4$ (solid)	Tetrahedral Ga_4	2.688(6)	109*a*
$[Ga\{C(SiMe_3)_3\}]$ (vapor)	Monomer	—	109*b*
$GaTp^{Bu^t_2}$ (solid)	Monomer	—	111
$[In(\eta^5\text{-}C_5Me_5)]_6$ (solid)	Octahedral In_6	3.942(1)–3.963(1)	112
$[In(\eta^5\text{-}C_5Me_5)]$ (vapor)	Monomer	—	117*c*
$[In\{C(SiMe_3)_3\}]_4$ (solid)	Tetrahedral In_4	3.002(1)	113*b*
$[In\{\eta^5\text{-}C_5(CH_2Ph)_5\}]_2$ (solid)	In–In *trans*-bent	3.631(2)	114*a*
$[In(C_6H_3Trip_2\text{-}2,6)]$ (solid)	Monomer	—	116*a*
$[Tl\{C(SiMe_3)_3\}]_4$ (solid)	Tetrahedral Tl_4	3.322(1)–3.638(1)	113*c*
$[Tl\{\eta^5\text{-}C_5(CH_5Ph)_5\}]_2$ (solid)	Tl–Tl *trans*-bent	3.632(1)	114*b*
$[Tl(\eta^5\text{-}C_5Me_5)]$ (vapor)	Monomer	—	117*d*
$[Tl(C_6H_3Trip_2\text{-}2,6)]$ (solid)	Monomer	—	116*b*
$[Tl\{N(SiMe_3)C_6H_3Pr^i_2\text{-}2,6\}]$ (solid)	Tetramer, planar Tl_4	4.06	117*e*

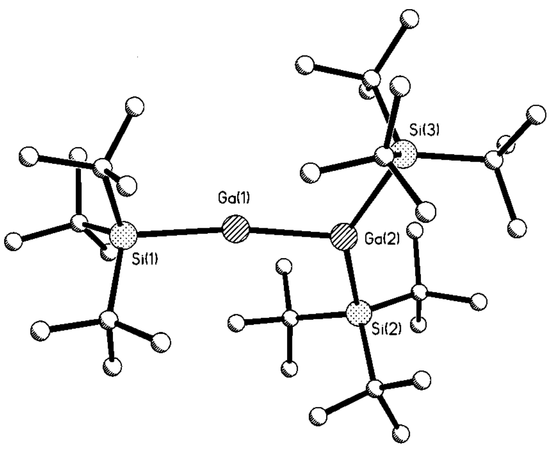

Fig. 4 Schematic drawing of $[(Bu^t_3Si)GaGa(SiBu^t_3)_2]$ (ref. 63)

strates the very important role of the electronic and steric properties of the ligand in determining bond strengths. The hexamer $[Ga(\eta^5\text{-}C_5Me_5)]_6$ has much longer Ga–Ga distances of 4.073(2) and 4.173(3) Å.[110] An unusual gallium species, $[(Bu^t_3Si)GaGa(SiBu^t_3)_2]$ (Fig. 4), which features a relatively short Ga–Ga bond of 2.420(1) Å, has also been reported.[63] The formal Ga–Ga bond order is 1.5. The Ga–Ga bond is composed of a 2-electron σ bond and the unpaired electron occupies a π orbital with coupling to two different galliums.

A number of indium(I) and thallium(I) compounds with metal–metal interactions are known. The metal–metal bonding appears to be very weak in all currently known cases (Table 5). This is exemplified by the indium structures of the hexameric $[In(\eta^5\text{-}C_5Me_5)]_6$[112] (In–In *ca.* 3.95 Å), tetrameric $[In\{C(SiMe_3)_3\}]_4$[113] [In–In 3.002(1) Å], and the dimers $[M\{\eta^5\text{-}C_5(CH_2Ph)_5\}]_2$[114] (M = In or Tl; In–In and Tl–Tl 3.63 Å) which have In–In interactions that are much longer than the distances in the In–In singly bonded compounds $(InR_2)_2$ [2.768(1)–2.828(1) Å]. Indeed, it has been possible to crystallize monomeric species such as $MTp^{Bu^t_2}$ (M = In[115a] or Tl[115b]) and one-co-ordinate metal species of formula $[M(C_6H_3Trip_2\text{-}2,6)]$ (M = In[116a] or Tl[116b]). It is also notable that all the $[M(\eta^5\text{-}C_5Me_5)]$ (M = Al, Ga, In or Tl) derivatives are monomeric in the vapor phase.[112,117]

Unfortunately, no estimates of Group 13 π-bond strengths are available. However, it is probable that they are less than values given for the π bonds in Group 14 or 15 compounds owing to the larger Group 13 element sizes. If it is assumed that there is optimized orbital overlap in the Group 13 species, values for π bonds that are *ca.* half to two thirds those of σ bonds seem warranted by extrapolation of the Group 14 and 15 data.

5 Bonding and Bond Order

Bonding

It is already clear that the bonding in the heavier main group element compounds differs fundamentally from that in the lighter members of the group. Perhaps only in the heavier Group 15 derivatives are the simple bonding models used for the lighter nitrogen congeners usefully applicable. In the Group 13 and 14 compounds, however, there are major distinctions in the molecular architecture between the heaviest and lightest element derivatives. These geometrical changes, which mirror a changed electronic structure, have necessitated a different bonding description of the compounds. It is these bonding models, or, more accurately, the interpretation of them, that give rise to controversy. Prior to discussing these it is perhaps worth quoting a definition for a chemical bond provided by Pauling who said that:[118] 'there is a chemical bond between two atoms or groups of atoms in case that the forces acting between them are such as to lead to an aggregate of sufficient stability to make it convenient for the chemist to consider it as an independent molecular species'. The advantage of this definition is that it does not assume any theory, not even the existence of electrons or orbitals. In essence, chemical bonding is assumed to exist when it is justified by the physical and chemical behavior of the species in question.

If the Pauling criterion is applied to the Group 15 molecules in Table 2, it is clear, beyond doubt, that they are stable molecular entities of the formula REER (E = P, As, Sb or Bi). There is no dissociation to monomeric units of formula ER either in solution or in the vapor phase. In addition, the E–E bonds are *ca.* 6–10% shorter than corresponding single bonds, and there are substantial barriers to *cis–trans* isomerization.[2] There is good agreement between calculations[2,78,119] and experimental findings and electron density measurements on a diphosphene have confirmed the existence of strong σ and π bonds.[120] Apart from these data there is an extensive chemistry of compounds related to those in Table 2 which show that E–E bonding is retained in many different reactions.[2]

When the simple bonding definition is applied to the heavier diorgano–Group 14 element species (Table 1) a more complex picture emerges.[121] Clearly, the disilenes are stable chemical species and chemical[1] and NMR data[122] support their double bonding. Even where one of them has been shown to dissoci-

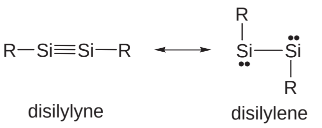

Fig. 5 Disilylyne and disilylene forms of a compound of the general formula $(SiR)_2$

ate,[96] the enthalpy of dissociation is sufficiently high that the molecule remains mostly dimeric in solution at room temperature. With germanium, however, two[39,40] of the eight $(GeR_2)_2$ species have Ge–Ge bond lengths similar to a Ge–Ge single bond and two[5b,10,40] are monomers in solution. Five compounds[18,36–38] do not dissociate readily, have short Ge–Ge bonds with significant rotation barriers, undergo reactions that retain the Ge–Ge moiety,[1h,k,121] and are, essentially, germanium analogs of alkenes.

The structures of the five $(SnR_2)_2$ compounds show that three compounds[5b,32,33] have an Sn–Sn distance comparable to the Sn–Sn single bond (2.80 Å) in elemental tin. In the other two, the Sn–Sn distances are significantly longer.[34,35] More importantly, all the compounds are dissociated to monomers in solution at room temperature. Since the enthalpy of association of $[Sn\{CH(SiMe_3)_2\}_2]_2$ is 12.8 kcal mol^{-1}, and this compound[8] has the shortest Sn–Sn bond in the $(SnR_2)_2$ series, it may be assumed that the other four compounds have enthalpies of dissociation of the order of *ca.* 10 kcal mol^{-1} which is somewhat greater in strength than an average hydrogen bond but is considerably less than the 35 kcal mol^{-1} predicted for a single bond in Table 4.[123] It is also noteworthy that the chemistry of the tin compounds is usually consistent with a monomeric stannanediyl formulation seen in compounds that are monomeric in the solid, *e.g.* $[\overline{Sn\{C(SiMe_3)_2(CH_2)_2C}(SiMe_3)_2\}]$[124a] or $[Sn(C_6H_2Bu^t_3\text{-}2,4,6)_2]$.[124b] Products with Sn–Sn bonds are rarely obtained from such reactions. Exceptions are the reaction of $[Sn\{CH(SiMe_3)_2\}_2]_2$ with HCCPh,[125a] the reaction of $[Sn\{C_6H_2(CF_3)_3\text{-}2,4,6\}_2]$ with $MesN_3$,[125b] and the reaction of $(SnTrip_2)_2$ with tellurium.[125c] The latter diaryl is unusual in that it is the only diorganotin(II) species that exists as a dimer in solution.[126] It is stable only at low temperature (*ca.* −70 °C) however, and it readily converts to the cyclic trimer $(SnTrip_2)_3$ above 0 °C. The structure of the dimer would be of great interest since it may display a short Sn–Sn bond and a less pyramidal metal geometry. The sole dilead compound, $[Pb\{C_6H_2(CF_3)_3\text{-}2,4,6\}\{Si(SiMe_3)_3\}]_2$, has a Pb–Pb distance that is *ca.* 0.65 Å longer than that predicted for a single bond.[98] Clearly, the Pb–Pb interaction is very weak even in the solid state. The compound, not surprisingly, is monomeric in solution.

It is clear from their physical properties, structures and chemical behavior that the weakly associated germanium, tin or lead species bear little resemblance to alkenes. As a result the terms digermenes, distannenes, or diplumbenes hardly seem justified. These names often appear to be used for convenience[127] rather than accuracy. Since they behave as simple monomeric dialkyl or diaryl metal compounds in solution, the IUPAC terms germane-, stannane- or plumbane-diyls are obviously more descriptive. If they are weakly associated in the solid state, the terms bis-(germane-, stannane- or plumbane-diyls), which have been used in some of the recent literature, seem apt.[33,35] The terms digermylene, distannylene and diplumbylene are, apparently, inappropriate. Such nomenclature is used[128] to describe the putatively singly bonded valence isomer of the corresponding dimetallyne (Fig. 5). The term distannylene may be an appropriate description of the (as yet unisolated) neutral analog of the anion $[Sn(C_6H_3Trip_2\text{-}2,6)_2]^-$[41] that has a lone pair at each of the tin atoms which appear to be connected by a single bond.

The Pauling definition may also be applied to the lower valent Group 13 compounds. It has already been seen that the

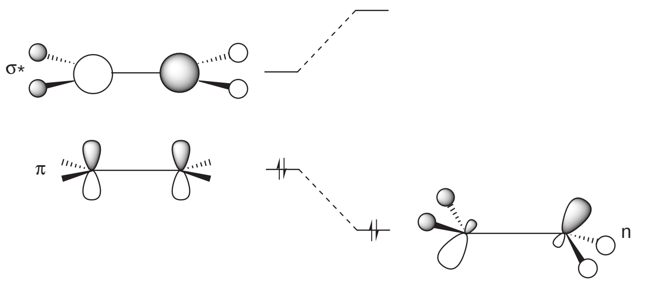

Fig. 6 Schematic drawing of the mixing of the π and σ* molecular orbitals in a heavier group 14 species

currently known (Table 5) neutral, lower valent organic derivatives of the Group 13 metals are usually weakly associated, often becoming monomers in the vapor phase or in solution. By analogy with the lower valent Group 14 species the terms digallene, diindene or dithallene for dissociating RMMR species are not indicative of their structures. For the monomeric species, the IUPAC name gallanediyl, indanediyl, *etc.* seems sufficiently descriptive, and for the dimeric species bis(metallanediyl) is more representative of their structures than the term dimetallene.

Bonding models

The various bonding models for the heavier Group 14 and Group 15 compounds have been described in a recent review.[121] Accordingly, these models are only briefly discussed here. As expected, the bonding in the Group 15 species is the most straightforward. In simplistic terms, the π bond is formed from parallel overlap of p orbitals and the σ bond results in the nitrogen case from overlap of two orbitals with approximate sp^2 hybridization. As the group is descended the s character in the σ bond decreases and that in the lone pair increases so that in the heaviest antimony and bismuth compounds, the lone pair is predominantly s in character.[78]

In the Group 14 compounds a molecular orbital (MO) view[128a,b] of the M–M bonding in R_2MMR_2 dimers (M = Si, Ge, Sn or Pb) is that upon descending the group there is increased mixing (Fig. 6) of an antibonding M–M σ* orbital and a π orbital due to the lowering of the π–σ* energy gap. This is closely related to the critical orbital interactions in the pyramidalization[129] (which is a second-order Jahn–Teller effect[130]) of AH_3 systems such as NH_3, CH_3^- or PH_3 and the bending of AH_2 molecules such as H_2O or H_2S. The mixing is particularly marked in the case of tin and lead dimers and to a lesser extent in the silicon and germanium analogues. The increased mixing of the σ* orbital results in stabilization of the original π orbital but weakens that π bond by increasing its lone pair character. In effect, it comes to resemble an n lone pair orbital more than a π bond (n = non-bonding, lone pair orbital). The σ bond is also weakened since the orbital orientations are not as favorable in the pyramidalized species as in the planar one. In effect, bonding electron density is lowered between the two Group 14 atoms. In the tin and lead compounds in Table 1, the bonding interaction is weakened to such an extent that the compounds are dissociated to monomers in solution at room temperature. An appealing aspect of the MO bonding model is that it readily explains why the use of more electronegative (EN) substituents usually results in dissociation to monomers. Increasing the EN of the substituent (*e.g.* by using amide[131] instead of alkyl or aryl groups) or decreasing the EN of the central (Group 14) atom reduces the π–σ* energy gap and gives σ-bonding orbitals that are more located on the substituent atom while the σ* orbitals are biased toward the central atom. This gives a greater interaction between the π and σ* orbitals which increases the stabilization of the lone pair relative to the π orbital and increases the likelihood of a monomeric structure. On the other hand, more electropositive substituents, *e.g.* silyl groups,[32,33,37] decrease the

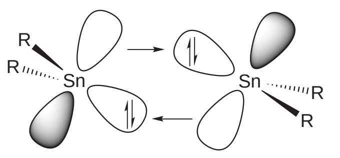

Fig. 7 Donor–acceptor bonding model for $[Sn\{CH(SiMe_3)_2\}_2]_2$

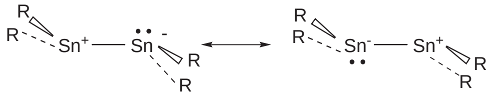

Fig. 8 Schematic drawing of the unshared electron-pair resonance in $(SnR_2)_2$ (ref. 138)

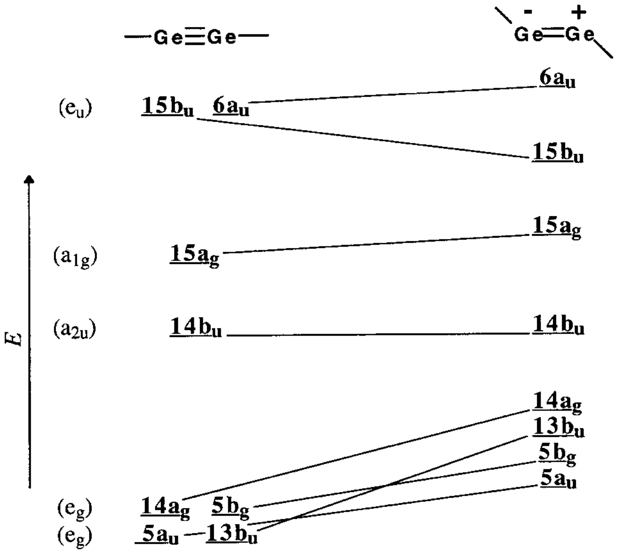

Fig. 9 Calculated MO energy and correlation diagram for $(GeMe)_2$ (ref. 79)

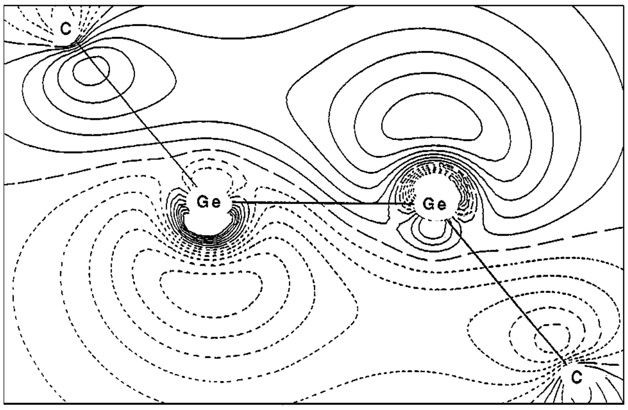

Fig. 10 Contour diagram of the $15b_u$ lone pair MO in *trans*-$(GeMe)_2$ obtained with a 6–31G* basis set [ref. 79(*a*)]

stability of the lone pair form and favor a π-bonded dimeric structure.

The *trans*-bending in the heavier element compounds has also been considered[132] in light of the splittings of the singlet–triplet states (ΔE_{ST}) based on calculations on the hydrogen derivatives $(MH_2)_2$ (M = Si, Ge or Sn). According to this criterion the double bonds will be unstable with respect to the *trans*-bent distortion if the sum of the ΔE_{ST} values of the fragments is more than one half the total bend energy. It can be seen from Table 4 that the total bond energy drops rapidly descending the group. Moreover, the singlet–triplet (ST) splitting increases[132] so that the *trans*-bent structure is normally observed. The type of bonding occurring in such compounds has also been described as two weak semipolar dative bonds between two singlet metallanediyls, the so-called ‘pawpaw’ bond.[133] This approach emphasizes the important role of ST separation in the bending; the larger the ST splitting the more *trans*-bent the structure becomes.

This view of the M–M interaction is similar to the donor–acceptor model (Fig. 7) proposed originally by Lappert and co-workers.[134] In effect, the metals are held together by weak (*cf.* 6.4 kcal mol^{-1})[8] polarized dative bonds in which electron density is distributed asymmetrically. *Ab initio* MO calculations[5*b*,135] on the $(MH_2)_2$ (M = Ge or Sn) model compounds have afforded an M–M dissociation energy of *ca.* 31.0 kcal mol^{-1} for the Ge species and 21.5 kcal mol^{-1} for the tin analog. These values are much less than the experimental M–M single bond dissociation energies of compounds such as $(MH_3)_2$ and $(MMe_3)_2$ (M = Ge or Sn) which are in the range of *ca.* 50 to 70 kcal mol^{-1}.[136] However, the calculated value for $(SnH_2)_2$[137] is almost double the enthalpy of dissociation for the sterically hindered compound $[Sn\{CH(SiMe_3)_2\}_2]_2$. Apparently, steric effects are very important in determining the strength of the M–M bond. Density functional theoretical (DFT) studies[137] have indicated a significant influence of intra- and inter-atomic Pauli repulsion on *trans*-bending and π-bond strength in the heavier $(MH_2)_2$ species (M = Si, Ge, Sn or Pb). Moreover, quite high intrinsic π-bond strengths were calculated, 38 kcal mol^{-1} (Ge), and 32 kcal mol^{-1} (Sn). This study also showed that in the heavier elements the dissociation energy is less for double than for single bonds but that this was due to the fact that preparation energy for the singlet fragments and the interatomic Pauli repulsion was higher for the heavier elements. Pauling[138] also proposed that the Sn–Sn single bond distance in $[Sn\{CH(SiMe_3)_2\}_2]_2$ can be explained by assuming that an unshared electron pair resonates between two tin atoms that are connected by a single bond (Fig. 8). A theoretical study of fractional bond orders in $(MH_2)_2$ (M = Si, Ge or Sn) molecules[139] revealed bond orders that were less than two but greater than one, and were in reasonable agreement with the bond order formula of Pauling.[140]

The MO explanation of the bonding in heavier Main Group 14 analogues of alkynes is similar to that for alkenes. The bending from the linear geometry and the lengthening of the element–element bonds occurs for the same reason it occurs in the alkene analogues. As the energies of the π and σ* levels become closer going down the group the two levels interact and there is increased mixing of a σ* antibonding orbital into one of the π orbitals which causes it to become more stable and assume non-bonding n character. Calculations[79] on the hypothetical species $(GeMe)_2$ show that the *trans*-bent form is more stable than the linear form by *ca.* 15 kcal mol^{-1}. In the higher energy linear form the two π orbitals are degenerate (e_u symmetry) and the σ bond (a_g symmetry) is lower in energy (Fig. 9). As long as the geometry remains linear the σ* orbital cannot mix with the π levels as they are mutually orthogonal. With bending, this restriction is removed, and one of the original π orbitals ($15b_u$) becomes progressively more stable as the amount of mixing increases. The mainly non-bonding, lone-pair character of this orbital is indicated by the contour (Fig. 10) which shows regions of electron density opposite the methyl groups. In contrast, the energies of the remaining π orbital ($6a_u$) and the σ orbital ($15a_g$) are increased, indicating that these bonds are also weakened by the bending process. If this MO view of the bonding is accepted then it is clear that in the linear configuration the bond order is 3 since there are three bonding MOs each occupied by an electron pair. However, distortion of the geometry toward *trans*-bent and mixing of antibonding character from the σ* level reduces the bond order below 3 by converting one of the three bonding orbitals originally associated with the Ge–Ge bond to an essentially non-bonding one. In effect, the formal bond order is reduced from 3 to 2, or less than 2 if the weakening of the remaining σ and π bonds is taken

Table 6 Selected calculated structural parameters for some low-valent derivatives of aluminum and gallium

Compound	Structure	M–M/Å	M–M–C/°	Ref.
$(AlH)_2$	Linear	2.298	180	143
	trans-bent	2.613	120	143
$(GaH)_2$	Linear	2.2512	180	144
	trans-bent	2.656	120.4	144
$[(GaH)_2]^{2-}$	Linear	2.214	180	81
	trans-bent	2.4568	125.2	81
$[(GaMe)_2]^{2-}$	*trans*-bent	2.5221	123.8	81
$Na_2[(GaMe)_2]$	*trans*-bent	2.5082	126.0	81
$Li_2[(GaMe)_2]$	Linear	2.161	180	79
	trans-bent	2.388	132.5	79
$Na_2[(GaPh)_2]$	*trans*-bent	2.461	126.1	78
$Na_2[\{Ga(C_6H_3Ph_2\text{-}2,6)\}_2]$	*trans*-bent	2.362	124.3	78

into account. Accordingly, the Ge–Ge bond (2.167 Å) in the lowest energy *trans*-bent configuration is considerably longer than that calculated (2.014 Å) for the triply bonded linear form. Interestingly, if this distance is compared to 2.417 Å calculated (with the same basis set) for the single Ge–Ge bond in $(GeH_3)_2$ and a line is drawn between the two points on a semilog plot based on the Pauling relationship between bond length and bond order,[140] then the bond length for the *trans*-structure, 2.167 Å, affords a bond order of 1.98. Calculations on $(SnMe)_2$[141] show a similar pattern. In the linear distannyne the Sn–Sn distance is 2.432 Å whereas the lower (by 34 kcal mol^{-1}) energy configuration has a *trans*-bent structure (Sn–Sn–C 125°) and an Sn–Sn distance of 2.673 Å. This gives a Sn–Sn bond order of 1.46. However, it is clear that steric effects can play a large role in determining the Sn–Sn bond length and longer Sn–Sn distances are seen in practice. The hypothetical compound $(SiMe)_2$[142] (Si–Si *ca.* 2.07 Å) also has a bent geometry and is 14.4 kcal mol^{-1} more stable than the linear form. The calculated bond order is 2.17.

Several theoretical studies have been made on aluminum and gallium Main Group 13 species that have possible multiple M–M interactions.[121] Some data are given in Table 6.[78,79,81,143,144] In addition, the influence of the ligand geometry on In^{I}–In^{I} and Tl^{I}–Tl^{I} bonding has been investigated[145,146] *via* extended Hückel theory. The latter studies[146] showed that the weak M–M interaction occurs between empty p levels and the occupied s orbitals. Variation of the angle in the *trans*-bent structures such as $(TlH)_2$ or $[Tl(\eta^5\text{-}C_5H_5)]_2$ indicated that interaction is almost non-bonding (or repulsive) in the linear arrangement but that upon *trans*-bending to a Tl–Tl–ligand angle of *ca.* 120° there is a significant increase in the overlap population.[145] Attention has been drawn to the similarity between the Group 14 and 15 metallanediyl fragments, *e.g.* $:SnR_2$ and $:InR$, which only differ in the number of acceptor orbitals.[146] Thus, the *trans*-bending in dimers $(MR)_2$ (M = In or Tl) corresponds to mixing of the π-acceptor orbitals into the in-phase and out-of-plane lone pair orbitals. In MO terms there is mixing of the antibonding σ* level into a π level very similar to that already described for the Group 14 compounds. The valence bond description involves a polarized donor–acceptor bonding model like that proposed for the tin(II) dialkyl. The In···In[146] or Tl···Tl[146,147] interactions are quite weak and are weaker than the Sn···Sn interaction in $[Sn\{CH(SiMe_3)_2\}_2]_2$.[8] This weakness is exemplified by the M–M distances (*ca.* 3.63 Å) in the dimers $[M\{\eta^5\text{-}C_5(CH_2Ph)_5\}]_2$ (M = In or Tl) which are much longer than normal In–In (*ca.* 2.8 Å) or Tl–Tl (*ca.* 3.0 Å) single bonds (*cf.* Table 3). In the lighter species $(AlH)_2$ and $(GaH)_2$ the *trans*-bent form is also calculated to be lower in energy than the linear forms.[143,144] The Ga–Ga distance, 2.656 Å is *ca.* 0.14 Å longer than the normal Ga–Ga single bonds given in Table 3, whereas the calculated Al–Al bond length is very similar to that of a single bond.

A number of calculations have been carried out on the doubly reduced gallium analogues of these compounds since the structure of $Na_2[\{Ga(C_6H_3Trip_2\text{-}2,6)\}_2]$ was published.[74] Calculations using density functional quantum mechanical methods on $Na_2[(GaMe)_2]$ or $[(GaMe)_2]^{2-}$ afford a *trans*-bent structure with long Ga–Ga distances of 2.508 and 2.522 Å. It was concluded[81] that there was no Ga–Ga bond length–bond order relationship and that the bonding in the experimental molecule[74] was between triple and double in character despite the relatively long bond length. The bond order was adduced on the basis of localized rather than canonical MOs. It may be noted, however, that extended Hückel MO calculations (see below)[79a] show that the three canonical MOs associated with the Ga–Ga bonds (of which one is essentially non-bonding) are already mainly localized[79] on the digallium moiety. The calculated distances are considerably longer than those experimentally observed in $Na_2[\{Ga(C_6H_3Trip_2\text{-}2,6)\}_2]$. A possible explanation for this discrepancy comes from DFT calculations on the hypothetical compound $Na_2[\{Ga(C_6H_3Ph_2\text{-}2,6)\}_2]$ which suggest that the alkali metals may play a significant role in shortening the Ga–Ga bond since the potential energy curve as a function Ga–Ga distance is relatively flat in this region.[78] Thus, the Ga–Ga distance in $Na_2[(GaPh)_2]$ is 2.46 Å whereas the Ga–Ga distance in $Na_2[\{Ga(C_6H_3Ph_2\text{-}2,6)\}_2]$, which has non-covalent $Na^+\cdots o$-Ph interactions, is only 2.36 Å, *i.e.* 0.1 Å shorter. The relatively shallow potential energy curve for the Ga–Ga bond is also suggestive of overall bond weakness. The DFT calculations also led to the conclusion that the Ga–Ga bond is a double one.[78] Extended Hückel MO calculations[79] on $Li_2[(GaMe)_2]$, in which the $[(GaMe)_2]^{2-}$ ion is isoelectronic to the $(GeMe)_2$ compound discussed above, reveal a similar pattern and Ga–Ga bond order of 2 or less. In this case [*cf.* $(GeMe)_2$, Fig. 10] the HOMO ($15b_u$) is the lone pair orbital (*i.e.* the n_- combination) and the HOMO-1 ($7a_u$) is the π orbital which is believed to have been stabilized by the Li^+ ions. The Ga–Ga bond length in the lowest energy *trans*-bent form was calculated to be 2.388 Å and the Ga–Ga–C angle is 132.5°. The linear, triply bonded valence isomer lies *ca.* 7.5 kcal mol^{-1} higher in energy and has a much shorter Ga–Ga bond of 2.161 Å. The calculated angle is similar to that observed experimentally (*ca.* 131°) although the Ga–Ga distance is about 0.06 Å longer than the experimental one. The calculations also indicated that the bending of the $(GaMe)_2$ array in $Li_2[(GaMe)_2]$ results in a weakening of the remaining π and σ bonds. A recent paper, however, reported[80] that a natural bond order analysis of the anion $[(GaH)_2]^{2-}$ led to the conclusion that, although one of the π bonds is 'slipped', 'three bonds are . . . obtained'. The contour diagram for the 'slipped' π bond, however, can also be interpreted mainly in terms of an n lone pair orbital where the maxima of electron density are not located in the region between the gallium nuclei.[79a]

6 Summary and Conclusions

Differing interpretations of the structural, spectroscopic and theoretical data have given rise to the current debate. One interpretation says that the weak interactions frequently observed or calculated for heavier Main Group 13 or 14 analogs of compounds such as alkenes or alkynes fully merit designation as multiple bonds, with a nomenclature that emphasizes their relationship to their lighter analogs. Another holds that the bond lengths observed for these compounds can, in many cases, be greater than the lengths of normal single bonds and the interactions are frequently so weak that the 'multiple' bonds effectively do not exist in solution. In short, the relationship between bond order and bond strength and length becomes increasingly meaningless if any interaction, no matter how weak, can be qualified as a 'bond'. Not surprisingly, each side can cite theoretical data that support their position. However, the theoretical data have proved their usefulness in the sense that they demonstrate that pyramidalization or bending of the geometries at the heavier elements usually leads to a significantly weakened element–element bond in comparison to the idealized planar or linear configuration. Thus the theoretical data provide bond lengths for the idealized linear or planar species against which the significantly longer bonds in the real molecules can be compared. It is, therefore, to be hoped that further experimental investigation will provide deeper insight on the factors that influence the strength of these bonds. In the long run, it is probable that the actual physical behavior and chemical properties of these compounds will determine the bonding model that is most practical for chemists to use. More specific observations and comments as well as suggestions for further experiments are given below.

Group 14 and 15 compounds

At present, it seems clear that in the Group 15 element compounds there can be relatively strong double bonding for all elements of this group. In such compounds the physical and chemical characteristics of double bonding are maintained in the solution and solid states. In Group 14, however, no currently known compounds of formula $(SnR_2)_2$ or $(PbR_2)_2$ remain dimerized in solution at room temperature. Some germanium species also have this characteristic. The M–M bonding in these weakly associated compounds is much weaker than single bonding and their chemistry is more consistent with their formulation as monomers. The terms digermenes, distannenes or diplumbenes provide an inadequate description of the metal–metal bond. Similarly, the term dimetallyne seems inappropriate for neutral molecules of the type RMMR where the MM distances are close to that of a single bond and there is a strongly bent M–M–C angle {*cf.* the highly bent structure of the anion $[\{Sn(C_6H_3Trip_2\text{-}2,6)\}_2]^-$}.[41] It has been correctly said that amongst Group 14 elements the carbon species are in reality the 'exotic' compounds[121] in the type of bonds they form and that it is the *trans*-bent structures of the dimers $(MR_2)_2$ or $(MR)_2$ (M = Si, Ge, Sn or Pb) that are normal. The multiple bonding model (*i.e.* distinct σ and π bonds) used for alkenes and alkynes is so ingrained in the chemical consciousness that it is difficult to think of their heavier analogues without citing it. However, the continuing emphasis of bonding models and terminologies appropriate for elements of the first row has tended to obscure the uniqueness of the bonding in the heavier element compounds. In short, the bonding in these elements is inherently interesting and distinct, and does not require an often misleading analogy with lighter congeners to emphasize its importance.

Group 13 compounds

In the Group 13 elements a similar pattern to that seen in the Group 14 elements (albeit with weaker bonding) is rapidly emerging, although data are scant. Stable $(BR)_2$ and $[(BR)_2]^{2-}$ compounds are currently unknown but calculations[148] indicate that only $(BH)_2$ has a double bond with a triplet ground state. In contrast, the association of species of formula $(MR)_2$ (M = Al, Ga, In or Tl) appears to be relatively weak and, except in the hypothetical aluminum compound $(AlH)_2$, which has a singly bonded Al–Al distance, the M–M bonds are longer than normal single bonds. The long bonds and *trans*-bent geometry observed[114] for the organo-indium and -thallium dimers imply ever weaker bonding than that seen in related Group 14 species. In no sense do they resemble doubly bonded 'dimetallenes' either in their physical properties or their chemistry. Recent calculations[79a] on the dimeric organogallium species $(GaMe)_2$ also indicate a *trans*-bent structure and a long Ga–Ga distance of 2.676 Å which is *ca.* 0.16 Å longer than a single bond and incompatible with a bond order of 2. Irrespective of how the bonding in the RMMR (M = Al, Ga, In or Tl) dimer is seen, *i.e.* whether it involves the bending of the geometry and mixing of a σ* orbital into a π level or that it is composed of weak donor–acceptor bonds that may be similar in strength to hydrogen bonds, there is little doubt that the bond order is much less than 2 (less than 1 in the case of the indium and thallium derivatives) and the generation of a further bond by double reduction to give the $[RMMR]^{2-}$ ion may be insufficient to generate a bond order of 3. In this sense, the terms dimetallene and 'dimetallyne' are unrepresentative of their bonding.

s Electron participation

The most striking aspect of the currently available experimental and theoretical data for the heavier Group 13, 14 and 15 compounds is how profoundly the lower tendency of the s electrons to participate in bonding affects the molecular configurations in homonuclear species.[147b] In the Group 15 elements it seems possible to form double bonds with p orbitals in compounds of formula REER (E = P, As, Sb or Bi) with little s electron participation (they remain primarily lone pair in character)[78] so that double bonding is observed even for the heavier elements antimony and bismuth. In Group 14 elements, however, full-fledged doubly bonded molecules that are formally analogous to ethylene would require substantial s orbital participation in the double bonding which becomes less energetically favored upon descending the group. In effect, the s electrons display an increasing preference to remain in essentially non-bonded, lone pair orbitals which is, of course, just another manifestation of the so-called inert pair effect. In Group 13 this behavior is seen in the increasing stability of the bent form of the $[RMMR]^{2-}$ ions, or weak association in the neutral molecules RMMR (M = Al, Ga, In or Tl).

7 Future Work

Multiple bonding that is stable to dissociation in solution at room temperature has yet to be observed for In–In, Tl–Tl, Sn–Sn or Pb–Pb compounds. The synthesis of homonuclear derivatives of these elements with stable multiple bonds remains, therefore, an exciting synthetic challenge. As has also been seen, no stable dimeric compounds of formula RMMR (M = Al or Ga) are known currently. The synthesis of these would be of particular interest since they would help resolve the nature of the bond in their reduced $M'_2[RMMR]$ (M′ = alkali metal) analogues. Furthermore, the synthesis of solvent separated ion pairs of the type $[ML_n]_2[RMMR]$ will also illuminate the role played by ligand–alkali metal π interactions in determining M–M bond lengths which has been suggested theoretically,[78] but which remains undefined experimentally. Apart from one tentative estimate,[3a] there are no experimental data for π-bond strengths for homonuclear multiple bonding in the heavier Group 13 elements. Other families of compounds also beckon. There is a scarcity of stable compounds with heteronuclear multiple bonding, for instance heavier Group 13–15 compounds with valence multiple bonds. Stable, neutral homonuclear heavier Group 14 alkyne analogues and their doubly reduced derivatives (isoelectronic to neutral Group 15 species) also remain unknown. Data on these may throw light on the tendency to isolate the singly reduced anion $[\{Sn(C_6H_3Trip_2\text{-}2,6)\}_2]^-$ in preference to the neutral analogue.[41] This tendency implies the presence of a low-lying unoccupied orbital in the neutral species and, possibly, a weak Sn–Sn bond order of 1 or less. The increasing use of electropositive substituents such as silyl groups[32,42,63,108b] to enhance M–M bond strengths may also be expected in future experiments.

Bond lengths

Inevitably, future investigations will rely on various spectroscopies and X-ray diffraction data. The latter technique, in particular, has proved of key importance but it can lead to erroneous conclusions if used in isolation. The observation of short bond lengths and deviations from idealized geometries often provides reliable information on the nature and strength of the bonds involved. Nonetheless, in some cases the unusual geometries and unsuitable orbital orientations or energies can allow a fairly close approach of atoms without affording a bond of the expected strength, as in $[Sn\{CH(SiMe_3)_2\}_2]_2$.[5] Also, some bond distances in relatively weak bonds may be easily shortened by other interactions, owing to a relatively flat potential curve in certain ranges, *cf.* calculations on $Na_2[\{Ga(C_6H_3Ph_2\text{-}2,6)\}_2]$[78] which suggest that the interactions of the Na^+ with aryl rings may have shortened the Ga–Ga distance by as much as 0.1 Å. In essence, such effects tend to shorten the intermetallic distance and increase the apparent bond order rather than the opposite. Thus, the Sn–Sn distance in $[Sn\{CH(SiMe_3)_2\}_2]_2$ suggests single bonding, yet the enthalpy of association indicates the bond strength is a fraction of the strength of a single bond. With the synthesis of further heavier main group compounds such effects may be more accurately gauged and taken into consideration in subsequent discussions.

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9 References

1 (*a*) R. West, *Science*, 1984, **225**, 1109; (*b*) G. Raabe and J. Michl, *Chem. Rev.*, 1985, **85**, 419; (*c*) A. G. Brook and K. M. Baines, *Adv. Organomet. Chem.*, 1986, **25**, 1; (*d*) R. West, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1201; (*e*) *The Chemistry of Organic Silicon Compounds*, eds. S. Patai and Z. Rappaport, Wiley, New York, 1989; (*f*) J. Barrau, J. Escudié and J. Satgé, *Chem. Rev.*, 1990, **90**, 283; (*g*) A. G. Brook and M. A. Brook, *Adv. Organomet. Chem.*, 1996, **39**, 71; (*h*) T. Tsumuraya, S. A. Batcheller and S. Masamune, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 902; (*i*) J. Escudié, C. Couret, H. Ranaivonjatovo and J. Satgé, *Coord. Chem. Rev.*, 1994, **130**, 427; (*j*) R. Okazaki and R. West, *Adv. Organomet. Chem.*, 1996, **39**, 232; (*k*) K. M. Baines and W. G. Stibbs, *Adv. Organomet. Chem.*, 1996, **39**, 275.

2 (*a*) A. H. Cowley, *Polyhedron*, 1984, **3**, 389; (*b*) A. H. Cowley and N. C. Norman, *Prog. Inorg. Chem.*, 1986, **34**, 1; (*c*) M. Yoshifuji, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, eds. M. Regitz and O. J. Scherer, Georg Thieme Verlag, Stuttgart, 1990; (*d*) L. Weber, *Chem. Rev.*, 1992, **92**, 1839; (*e*) N. C. Norman, *Polyhedron*, 1993, **12**, 2431.

3 (*a*) P. J. Brothers and P. P. Power, *Adv. Organomet. Chem.*, 1996, **39**, 1; for reviews of species with heavier Group 13 element–element single bonds, see, (*b*) W. Uhl, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1386; (*c*) C. Dohmeier, D. Loos and H. Schnöckel, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 124.

4 P. J. Davidson and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1973, 317.

5 (*a*) D. E. Goldberg, D. H. Harris, M. F. Lappert and K. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1976, 261; (*b*) D. E. Goldberg, P. B. Hitchcock, M. F. Lappert, K. M. Thomas, A. J. Thorne, T. Fjelberg, A. Haaland and B. E. R. Schilling, *J. Chem. Soc., Dalton Trans.*, 1986, 2387.

6 A. F. Wells, *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 5th edn., 1984, p. 1279.

7 H. J. Haupt, F. Huber and H. Pruet, *Z. Anorg. Allg. Chem.*, 1973, **396**, 81.

8 K. W. Zilm, G. A. Lawless, R. M. Merrill, J. M. Millar and G. G. Webb, *J. Am. Chem. Soc.*, 1987, **109**, 7236.

9 J. D. Cotton, P. J. Davidson and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2275; M. F. Lappert, *Main Group Met. Chem.*, 1994, **117**, 183.

10 P. B. Hitchcock, M. F. Lappert, S. J. Miles and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1984, 480.

11 G. Märkl, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 846; for related arsenic and antimony derivatives, see, A. J. Ashe, III, *J. Am. Chem. Soc.*, 1971, **93**, 3293.

12 E. Niecke and W. Flick, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 585.

13 G. Becker, *Z. Anorg. Allg. Chem.*, 1976, **423**, 242.

14 G. Becker, G. Gresser and W. Uhl, *Z. Naturforsch., Teil B*, 1981, **36**, 16; R. Appel and A. Westerhaus, *Tetrahedron Lett.*, 1981, **22**, 2159.

15 A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst and R. K. Kallury, *J. Chem. Soc., Chem. Commun.*, 1981, 191.

16 R. West, M. J. Fink and J. Michl, *Science*, 1981, **214**, 1343.

17 H. Meyer, G. Baum, W. Massa and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 798; M. Lazraq, J. Escudié, J. Couret, J. Satgé, M. Dräger and R. Dammel, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 828.

18 J. T. Snow, S. Murukami, S. Masamune and D. J. Williams, *Tetrahedron Lett.*, 1984, **25**, 4191.

19 N. Wiberg, K. Schurz and G. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 1053; R. Boese and U. Klingebiel, *J. Organomet. Chem.*, 1986, **315**, C17.

20 M. Veith, S. Becker and V. Huch, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 216.

21 H. Meyer, G. Baum, W. Massa, S. Berger and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 546.

22 C. N. Smit, F. M. Look and F. Bickelhaupt, *Tetrahedron Lett.*, 1984, **25**, 3011.

23 M. Dräger, J. Escudié, C. Couret, H. Ranaivonjatovo and J. Satgé, *Organometallics*, 1988, **7**, 1010.

24 C. Couret, J. Escudié, J. Satgé, A. Rahaarinirina and J. D. Andriamizaka, *J. Am. Chem. Soc.*, 1985, **107**, 8230.

25 M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Am. Chem. Soc.*, 1981, **103**, 4587.

26 A. H. Cowley, J. G. Lasch, N. C. Norman, M. Pakulski and B. R. Whittlesey, *J. Chem. Soc., Chem. Commun.*, 1983, 881.

27 A. H. Cowley, J. G. Lasch, N. C. Norman and M. Pakulski, *J. Am. Chem. Soc.*, 1983, **103**, 5506.

28 R. A. Bartlett, X. Feng and P. P. Power, *J. Am. Chem. Soc.*, 1986, **108**, 6817.

29 G. Linti, H. Nöth, K. Polborn and R. T. Paine, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 622.

30 M. A. Petrie, S. C. Shoner, H. V. R. Dias and P. P. Power, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1033.

31 G. Märkl and H. Sejpka, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 264.

32 K. W. Klinkhammer and W. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1334.

33 K. W. Klinkhammer, T. F. Fässler and H. Grützmacher, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 124.

34 M. Weidenbruch, H. Kilian, K. Peters, H. G. v. Schnering and H. Marsmann, *Chem. Ber.*, 1995, **128**, 983.

35 U. Layh, H. Pritzkow and H. Grützmacher, *J. Chem. Soc., Chem. Commun.*, 1992, 260.

36 M. Weidenbruch, M. Stürmann, H. Kilian, S. Pohl and W. Saak, *Chem. Ber./Recl.*, 1997, **130**, 735.

37 M. Kira, T. Iwamoto, T. Maruyama, C. Kabuto and H. Sakurai, *Organometallics*, 1996, **15**, 3767.

38 S. A. Batcheller, T. Tsumuraya, O. Tempkin, W. M. Davis and S. Masamune, *J. Am. Chem. Soc.*, 1990, **112**, 9394.

39 R. S. Simons, L. Pu, M. M. Olmstead and P. P. Power, *Organometallics*, 1997, **16**, 1920.

40 A. Schäfer, W. Saak, M. Weidenbruch, H. Marsmann and G. Henkel, *Chem. Ber./Recl.*, 1997, **130**, 1733.

41 M. M. Olmstead, R. S. Simons and P. P. Power, *J. Am. Chem. Soc.*, 1997, **119**, 11 705.

42 (*a*) A. Sekiguchi, H. Yamazaki, C. Kabuto and H. Sakurai, *J. Am. Chem. Soc.*, 1995, **117**, 8025; (*b*) A. Sekiguchi, M. Tsukamoto and M. Ichinohe, *Science*, 1997, **275**, 60; (*c*) M. M. Olmstead, L. Pu, R. S. Simons and P. P. Power, *Chem. Commun.*, 1997, 1595.

43 P. Arya, J. Boyer, F. Carré, R. Corriu, G. Lanneau, J. Lapasset, M. Pernot and C. Priou, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1010; H. Suzuki, N. Tokitoh, S. Nagase and R. Okazaki, *J. Am. Chem. Soc.*, 1994, **116**, 11 578.

44 (*a*) N. Tokitoh, T. Matsumoto and R. Okazaki, *Chem. Lett.*, 1995, 1087; (*b*) N. Tokitoh, T. Matsumoto, K. Manmaru, R. Okazaki, *J. Am. Chem. Soc.*, 1993, **115**, 8855; (*c*) T. Matsumoto, N. Tokitoh and R. Okazaki, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2316; (*d*) N. Tokitoh, T. Matsumoto and R. Okazaki, *J. Am. Chem. Soc.*, 1997, **119**, 2337.

45 M. Veith, S. Becker and V. Huch, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1237.

46 M. C. Kuchta and G. Parkin, *J. Chem. Soc., Chem. Commun.*, 1994, 1351.

47 M. C. Kuchta and G. Parkin, *J. Am. Chem. Soc.*, 1994, **116**, 8372.

48 W.-P. Leung, W.-H. Kwok, L. T. C. Low, Z.-Y. Zhou and T. C. W. Mak, *Chem. Commun.*, 1996, 505.

49 N. Tokitoh, M. Saito and R. Okazaki, *J. Am. Chem. Soc.*, 1993, **115**, 2065; M. Saito, N. Tokitoh and R. Okazaki, *J. Am. Chem. Soc.*, 1997, **119**, 11 124.

50 R. S. Simons and P. P. Power, *J. Am. Chem. Soc.*, 1996, **118**, 11 966.

51 N. Tokitoh, Y. Arai, T. S. Sasamori, R. Okazaki, S. Nagase, H. Uekusa and Y. Ohashi, *J. Am. Chem. Soc.*, 1998, **120**, 433.

52 N. Tokitoh, Y. Arai, R. Okazaki and S. Nagase, *Science*, 1997, **277**, 78.

53 B. Twamley and P. P. Power, unpublished work.

54 A. H. Cowley, N. C. Norman and M. Pakulski, *J. Chem. Soc., Dalton Trans.*, 1985, 383.

55 C. E. Laplaza, W. M. Davis and C. C. Cummins, *J. Am. Chem. Soc.*, 1995, **34**, 2044; N. C. Zanetti, R. R. Schrock and W. M. Davis, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2044.

56 W. Uhl, *Z. Naturforsch., B: Chem. Sci.*, 1988, **43**, 11 213.

57 R. J. Wehmschulte, K. Ruhlandt-Senge, M. M. Olmstead, H. Hope, B. E. Sturgeon and P. P. Power, *Inorg. Chem.*, 1993, **32**, 2983.

58 (*a*) W. Uhl, M. Layh and T. Hildenbrand, *J. Organomet. Chem.*, 1989, **364**, 289; (*b*) W. Uhl, R. Graupner, I. Hahn, T. Spies and W. Frank, *Eur. J. Inorg. Chem.*, 1998, 355; (*c*) W. Uhl, I. Hahn and R. Wartschow, *Chem. Ber.*, 1997, **130**, 417.

59 X. He, R. A. Bartlett, M. M. Olmstead, K. Ruhlandt-Senge, B. E. Sturgeon and P. P. Power, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 717.

60 (*a*) G. Linti, R. Frey and M. Schmidt, *Z. Naturforsch., B: Chem. Sci.*, 1994, **49**, 958; (*b*) G. Linti and W. Köstler, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 550.

61 A. K. Saxena, M. Zhang, J. A. Maguire, N. S. Hosmane and A. H. Cowley, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 332.

62 D. S. Brown, A. Decken and A. H. Cowley, *J. Am. Chem. Soc.*, 1995, **117**, 7578.

63 N. Wiberg, K. Amelunxen, H. Nöth, H. Schwenk, W. Kaim, A. Klein and T. Scheiring, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1213.

64 S. Haubrich and P. P. Power, unpublished work.

65 W. Uhl, M. Layh and W. Hiller, *J. Organomet. Chem.*, 1989, **368**, 139.

66 P. J. Brothers, M. M. Olmstead and P. P. Power, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2355.

67 R. D. Schluter, A. H. Cowley, D. A. Atwood, R. A. Jones, M. R. Bond and C. J. Carrano, *J. Am. Chem. Soc.*, 1993, **115**, 2070.

68 M. Veith, F. Goffing, S. Becker and V. Huch, *J. Organomet. Chem.*, 1991, **40**, 105.

69 N. Wiberg, K. Amelunxen, H. Nöth, H. Schmidt and H. Schwenk, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 65.

70 S. Henkel, K. W. Klinkhammer and W. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 681.

71 W. Uhl, U. Schutz, W. Kaim and E. Waldhör, *J. Organomet. Chem.*, 1995, **501**, 79.

72 C. Pluta, K.-R. Pörschke, C. Krüger and K. Hildebrand, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 388.

73 (*a*) X.-W. Li, W. T. Pennington and G. H. Robinson, *J. Am. Chem. Soc.*, 1995, **117**, 7578; (*b*) X.-W. Li, Y. Xie, K. D. Gripper, R. C. Crittendon, C. F. Campana, H. F. Schaefer III and G. H. Robinson, *Organometallics*, 1996, **15**, 3798.

74 J. Su, X.-W. Li, R. C. Crittendon and G. H. Robinson, *J. Am. Chem. Soc.*, 1997, **119**, 5471.

75 M. C. Kuchta and G. Parkin, *Inorg. Chem.*, 1997, **36**, 2492.

76 M. C. Kuchta and G. Parkin, *J. Am. Chem. Soc.*, 1995, **117**, 12 651.

77 J. Su, X.-W. Li, R. C. Crittendon, C. F. Campana and G. H. Robinson, *Organometallics*, 1997, **16**, 4511.

78 F. A. Cotton, A. H. Cowley and X. Feng, *J. Am. Chem. Soc.*, 1998, **120**, 1795.

79 (*a*) T. L. Allen, W. H. Fink and P. P. Power, unpublished work; (*b*) *Chem. Eng. News*, 1997, June 16th, 9.

80 K. W. Klinkhammer, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2320.

81 Y. Xie, R. S. Grev, J. Gu, H. F. Schaefer, III, P. v. R. Schleyer, J. Su, X.-W. Li and G. H. Robinson, *J. Am. Chem. Soc.*, 1998, **120**, 3773.

82 F. A. Cotton and X. Feng, *Organometallics*, 1998, **17**, 128.

83 J. Weiss, D. Stelzkauf, B. Huber, R. A. Fischer, C. Bochine and G. Frenking, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 70.

84 D. L. Reger, S. S. Mason, A. L. Rheingold, B. S. Haggerty and F. P. Arnold, *Organometallics*, 1994, **13**, 5049.

85 E. Urnézius and J. D. Protasiewicz, *Main Group Chem.*, 1996, **1**, 369.

86 Ref. 6; (*a*) p. 839; (*b*) p. 803; (*c*) p. 804; (*d*) p. 876; (*e*) *cf.* Sb–Sb single bond of 2.837 Å for $(SbPh_2)_2$ in: H. Bürger and R. Eujen, *J. Mol. Struct.*, 1983, **98**, 265; (*f*) *cf.* Bi–Bi single bond of 2.990(2) in $(BiPh_2)_2$ in: F. Calderazzo, R. Poli and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1984, 2365.

87 D. C. Pestana and P. P. Power, *J. Am. Chem. Soc.*, 1989, **111**, 6887; D. C. Pestana and P. P. Power, *Inorg. Chem.*, 1991, **30**, 528.

88 W. Kutzelnigg, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 272.

89 (*a*) K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structures IV. Constants of Diatomic Molecules*, Van Nostrand, New York, 1979; (*b*) Sn–Sn in Sn_2Me_6, J. V. Davies, A. E. Pope and H. A. Skinner, *Trans. Faraday Soc.*, 1963, **59**, 2233; Pb–Pb in Pb_2Me_6, M. F. Lappert, J. B. Pedley, J. Simpson and T. R. Spalding, *J. Organomet. Chem.*, 1971, **29**, 195; Sb–Sb in Sb_2H_4, F. E. Saalfield and H. J. Svec, *Inorg. Chem.*, 1963, **2**, 50; S. R. Gunn, *Inorg. Chem.*, 1972, **11**, 786.

90 T. L. Allen, A. C. Scheiner, Y. Yamaguchi and H. F. Schaefer, III, *J. Am. Chem. Soc.*, 1986, **108**, 7579.

91 A.-M. Caminade, M. Verrier, C. Ades, N. Paillous and M. Koenig, *J. Chem. Soc., Chem. Commun.*, 1984, 875.

92 (*a*) M. Kira, T. Maruyama, C. Kabuto, K. Ebata and H. Sakurai, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1489; (*b*) B. D. Shepherd, D. R. Powell and R. West, *Organometallics*, 1989, **8**, 2664.

93 M. J. Fink, M. J. Michalczyk, K. J. Haller and R. West, *Organometallics*, 1984, **2**, 793.

94 Unassociated divalent organosilicon compounds have been described in: (*a*) P. Julzi, D. Kanne and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 164; (*b*) R. West and M. Denk, *Pure Appl. Chem.*, 1996, **68**, 785.

95 M. J. Michalczyk, R. West and J. Michl, *Organometallics*, 1985, **4**, 826; Si–Si π-bond strengths in the range 24.2–26.0 kcal mol^{-1} have been calculated in: G. Olbrich, P. Potzinger, B. Riemann and R. Walsh, *Organometallics*, 1984, **3**, 1267; M. W. Schmidt, P. N. Truong and M. S. Gordon, *J. Am. Chem. Soc.*, 1987, **109**, 5217; P. v. R. Schleyer and D. Kost, *J. Am. Chem. Soc.*, 1988, **110**, 2105.

96 (*a*) N. Tokitoh, H. Suzuki, R. Okazaki and K. Ogawa, *J. Am. Chem. Soc.*, 1993, **115**, 10 428; (*b*) H. Suzuki, N. Tokitoh and R. Okazaki, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2471; (*c*) K. Kishikawa, N. Tokitoh and R. Okazaki, *Chem. Lett.*, 1998, 239.

97 A π-bond strength of 25 kcal mol^{-1} was calculated for a Ge–Ge π bond in: R. S. Grev, H. F. Schaefer, III and K. M. Baines, *J. Am. Chem. Soc.*, 1990, **112**, 9458.

98 H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, 1940, **36**, 1209.

99 W. T. Robinson and R. N. Grimes, *Inorg. Chem.*, 1975, **14**, 3056; G. E. Herberich, B. Hessner and M. Hostalek, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 642; G. E. Herberich, B. Hessner and M. Hostalek, *J. Organomet. Chem.*, 1988, **355**, 473; J. H. Davis, E. Sinn and R. M. Grimes, *J. Am. Chem. Soc.*, 1989, **111**, 4784; G. E. Herberich, C. Ganter, L. Weseman and R. Boese, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 912.

100 J. J. Eisch, *Adv. Organomet. Chem.*, 1996, **39**, 355.

101 H. Meyer, G. Schmidt-Lukasch, G. Baum, W. Massa and A. Berndt, *Z. Naturforsch., Teil B*, 1988, **43**, 801.

102 Ref. 6, p. 1052; R. M. Minyaev and R. Hoffmann, *Chem. Mater.*, 1991, **3**, 547.

103 W. Biffar, H. Nöth and H. Pommerening, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 56; K. Schlüter and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 57.

104 H. Klusik and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 870; H. Klusik and A. Berndt, *J. Organomet. Chem.*, 1981, **222**, C25.

105 (*a*) A. Moezzi, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 1992, **114**, 2715; (*b*) A. Moezzi, R. A. Bartlett and P. P. Power, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1082.

106 M. Pilz, J. Allwohn, P. Willershausen, W. Massa and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1030.

107 (*a*) E. Kaufman and P. v. R. Schleyer, *Inorg. Chem.*, 1980, **27**, 3987; (*b*) E. L. Hamilton, J. G. Pruis, R. L. DeKock and K. J. Jalkanen, *Main Group Chem.*, in the press.

108 (*a*) C. Dohmeier, C. Robl, M. Tacke and H. Schnöckel, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 564; (*b*) A. Purath, C. Dohmeier, A. Ecker and H. Schnöckel, *Organometallics*, 1998, **17**, 1894.

109 (*a*) W. Uhl, W. Miler, M. Layh and W. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1364; (*b*) A. Haaland,K.-G. Martinsen, H. V. Volden, W. Kaim, E. Waldhör, W. Uhl and U. Schutz, *Organometallics*, 1996, **15**, 1146.

110 D. Loos, E. Baum, A. Ecker, H. Schnöckel and A. J. Downs, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 860.

111 M. C. Kuchta, J. B. Bonanno and G. Parkin, *J. Am. Chem. Soc.*, 1996, **118**, 10 914.

112 O. T. Beachley, jun., R. Blom, M. R. Churchill, J. Fettinger, J. C. Pazik and L. Victoriano, *J. Am. Chem. Soc.*, 1986, **108**, 4666.

113 (*a*) R. D. Schluter, A. H. Cowley, D. A. Atwood, R. J. Jones and J. L. Atwood, *J. Coord. Chem.*, 1993, **30**, 215; (*b*) W. Uhl, R. Graupner, M. Layh and U. Schutz, *J. Organomet. Chem.*, 1995, **493**, C1; (*c*) W. Uhl, S. U. Keimling, K. W. Klinkhammer and W. Schwartz, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 64.

114 (*a*) H. Schumann, C. Janiak, F. Görlitz, J. Loebel and A. Dietrich, *J. Organomet. Chem.*, 1989, **363**, 243; (*b*) H. Schumann, C. Janiak, J. Pickhardt and U. Börner, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 789.

115 (*a*) M. C. Kuchta, H. V. R. Dias, S. G. Bott and G. Parkin, *Inorg. Chem.*, 1996, **35**, 943; (*b*) G. Parkin, *Adv. Inorg. Chem.*, 1995, **42**, 291.

116 (*a*) S. T. Haubrich and P. P. Power, *J. Am. Chem. Soc.*, 1998, **120**, 2202; (*b*) M. Niemeyer and P. P. Power, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1277.

117 (*a*) A. Haaland, K.-G. Martinsen, S. A. Shlykov, H. V. Volden, C. Dohmeier and H. Schnöckel, *Organometallics*, 1995, **14**, 3116; (*b*) A. Haaland, K.-G. Martinsen, H. V. Volden, D. Loos and H. Schnöckel, *Acta Chem. Scand.*, 1994, **48**, 172; (*c*) O. T. Beachley, jun., R. Blom, M. R. Churchill, K. Faeger, J. C. Fettinger, J. C. Pazik and L. Victoriano, *Organometallics*, 1989, **8**, 346; (*d*) R. Blom, H. Werner and J. Wolf, *J. Organomet. Chem.*, 1988, **354**, 293; (*e*) S. O. Waezsada, T. Belgardt, M. Noltemeyer and H. W. Roesky, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 1351.

118 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 3rd edn., 1960, p. 6.

119 S. Nagase, S. Suzuki and T. Kurakake, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 1724.

120 A. H. Cowley, A. Decken, N. C. Norman, C. Kruger, F. Lutz, H. Jacobsen and T. Ziegler, *J. Am. Chem. Soc.*, 1997, **119**, 3389.

121 M. Driess and H. Grützmacher, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 828.

122 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.

123 M. D. Joesten and L. J. Schaad, *Hydrogen Bonding*, Marcel Dekker, New York, 1974.

124 (*a*) M. Weidenbruch, J. Schlaefke, A. Schäfer, K. Peters, H. G. v. Schnering and H. Marsmann, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 1846; (*b*) M. Kira, R. Yauchibara, R. Hirano, C. Kabuto and H. Sakurai, *J. Am. Chem. Soc.*, 1991, **113**, 7783.

125 (*a*) M. Weidenbruch, A. Schädwe, H. Kilian, S. Pohl, W. Saak and H. Marsmann, *Chem. Ber.*, 1992, **125**, 563; (*b*) H. Grützmacher and H. Pritzkow, *Angew. Chem.*, *Int. Ed. Engl.*, 1991, **30**, 1017; (*c*) A. Schäfer, M. Weidenbruch, W. Saak, S. Pohl and H. Marsmann, *Angew. Chem.*, *Int. Ed. Engl.*, 1991, **30**, 834.

126 S. Masamune and L. R. Sita, *J. Am. Chem. Soc.*, 1985, **107**, 6390.

127 In this regard it is interesting to note that in the original investigations[4,5a,9,10] of the compounds $[M\{CH(SiMe_3)_2\}_2]_2$ (M = Ge, Sn or Pb) they are generally referred to as Ge^{II}, Sn^{II} and Pb^{II} dialkyls and the terms double bond and dimetallene were used with quotation marks.

128 For further explanation of this phenomenon in some Group 14 and 15 species, see (*a*) T. A. Albright, J. K. Burdett and M. H. Whangbo, *Orbital Interactions in Chemistry*, John Wiley, New York, 1985, p. 127; (*b*) R. S. Grev, *Adv. Organomet. Chem.*, 1991, **33**, 125; (*c*) D. G. Gilheany, *Chem. Rev.*, 1994, **94**, 1339.

129 C. C. Levin, *J. Am. Chem. Soc.*, 1975, **97**, 5649.

130 R. F. W. Bader, *Can. J. Chem.*, 1962, **40**, 1164; R. G. Pearson, *J. Am. Chem. Soc.*, 1969, **91**, 4947.

131 D. H. Harris and M. F. Lappert, *J. Chem. Soc.*, *Chem. Commun.*, 1974, 895; C. D. Schaeffer and J. J. Zuckerman, *J. Am. Chem. Soc.*, 1974, **96**, 7160; T. Fjelberg, H. Hope, M. F. Lappert, P. P. Power and A. J. Thorne, *J. Chem. Soc.*, *Chem. Commun.*, 1983, 639.

132 G. Trinquier and J.-P. Malrieu, *J. Am. Chem. Soc.*, 1987, **109**, 5303; *J. Am. Chem. Soc.*, 1989, **11**, 5916; *J. Am. Chem. Soc.*, 1991, **113**, 144.

133 G. Trinquier, J.-P. Malrieu and P. Riviere, *J. Am. Chem. Soc.*, 1982, **104**, 4529.

134 P. J. Davidson, D. H. Harris and M. F. Lappert, *J. Chem. Soc.*, *Dalton Trans.*, 1976, 2268.

135 T. Fjelberg, A. Haaland, M. F. Lappert, B. E. R. Schilling, R. Seip and A. J. Thorne, *J. Chem. Soc.*, *Chem. Commun.*, 1982, 1407; T. Fjelberg, A. Haaland, B. E. R. Schilling, H. V. Volden, M. F. Lappert and A. J. Thorne, *J. Organomet. Chem.*, 1984, **254**, C1.

136 J. B. Pedley and J. Rylance, *Sussex NPL Computer Analysed Thermochemical Data: Organic and Organometallic Compounds*, University of Sussex, 1977.

137 J. Jacobsen and T. Ziegler, *J. Am. Chem. Soc.*, 1994, **116**, 3667.

138 L. Pauling, *Proc. Natl. Acad. Sci. USA*, 1983, 3871.

139 G. Lendvay, *Chem. Phys. Lett.*, 1991, **181**, 88.

140 Ref. 118, p. 239.

141 T. L. Allen, unpublished work.

142 K. Kobayashi and S. Nagase, *Organometallics*, 1997, **16**, 2489.

143 Z. Palágyi, R. S. Grev and H. F. Schaefer, III, *J. Am. Chem. Soc.*, 1993, **115**, 1936.

144 Z. Palágyi and H. F. Schaefer, III, *Chem. Phys. Lett.*, 1993, **203**, 195; G. Treboux and J.-C. Barthelat, *J. Am. Chem. Soc.*, 1993, **115**, 4870.

145 C. Janiak and R. Hoffmann, *Angew. Chem.*, *Int. Ed. Engl.*, 1989, **28**, 1688; C. Janiak and R. Hoffmann, *J. Am. Chem. Soc.*, 1990, **112**, 5924.

146 P. H. M. Budzelaar and J. Boersma, *Recl. Trav. Chim. Pays-Bas*, 1990, **109**, 187.

147 (*a*) P. Schwerdtfeger, *Inorg. Chem.*, 1991, **30**, 1660; (*b*) P. Schwerdtfeger, G. A. Heath, M. Dolg and M. A. Bennett, *J. Am. Chem. Soc.*, 1992, **114**, 7518.

148 C. Jouany, J. C. Barthelat and J. P. Dandey, *Chem. Phys. Lett.*, 1987, **36**, 52; D. R. Armstrong, *Theor. Chim. Acta*, 1981, **60**, 159; J. D. Dill, P. v. R. Schleyer and J. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 3402.

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