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π-Bonding and the Lone Pair Effect in Multiple Bonds Involving Heavier Main Group Elements: Developments in the New Millennium

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Contents

1. Introduction

This review is essentially an update of one entitled "π-Bonding and The Lone Pair Effect in Multiple Bonds Between Heavier Main Group Elements" which was published more than 10 years ago in this journal.[1] The coverage of that survey was focused on the synthesis, structure, and bonding of stable compounds[2] of heavier main group elements that correspond to the skeletal drawings reproduced in Tables 1 and 2. A row of numbers is listed at the bottom of each column in these tables. This refers to the number of stable complexes from each class that are currently known. The numbers in parentheses refer to the number of stable species that were known at the time of the previous review. Clearly, many of the compound classes listed have undergone considerable expansion although some remain stubbornly rare. The most significant developments for each class will be discussed in detail under the respective sections. As will be seen, there are also a limited number of multiple bonded heavier main group species that do not fit neatly in the classifications in Tables 1 and 2. However, to keep the review to a manageable length, the limits and exclusions, which parallel those used earlier, are summarized as follows: (i) discussion is mainly confined to compounds where experimental data on stable, isolated species have been obtained, (ii) stable compounds having multiple bonding between heavier main group elements and transition metals are not generally discussed, (iii) compounds in which a multiple bonded heavier main group element is incorporated within a ring are generally not covered, and (iv) hypervalent main group compounds that may incorporate faux multiple bonding are generally excluded. Such compounds are distinguished from those in Tables 1 and 2 in that they apparently require the use of more than four valence bonding orbitals at one or more of the bonded atoms. The remainder of this review is organized in a similar manner to that of the previous one wherein the compounds to be discussed are classified according to those summarized in Tables 1 and 2. The key unifying feature of almost all molecules discussed in this review is that they are generally stabilized by the use of bulky substituents which block associative or various decomposition pathways.[3] Since the previous review was published in 1999, several review articles that cover parts of the subject matter have appeared.[4]

2. Bonding

Molecules incorporating multiple bonding between two heavier main group elements are often characterized by "strained" geometries that are pyramidalized or bent in

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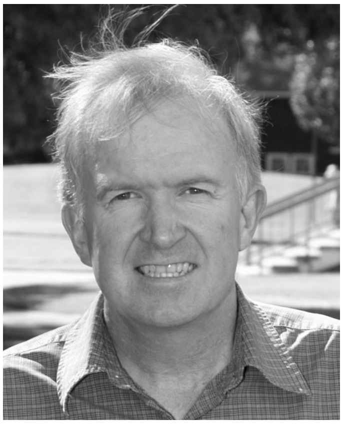
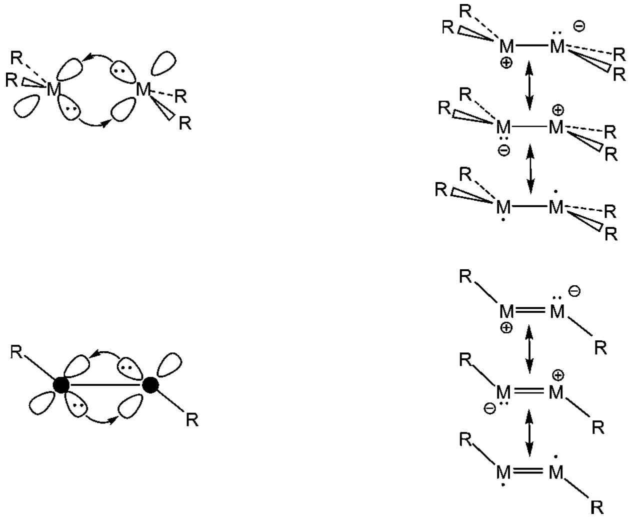
Roland C. Fischer, born in 1976, received a Ph.D. degree from Graz University of Technology, Austria, in 2003 under the supervision of Christoph Marschner. In 2005/2006 he was a postdoctoral fellow in the research group of Philip P. Power at UC Davis. He is currently assistant professor at the Institute for Inorganic Chemistry at Graz University of Technology. His research interests cover the synthesis of main group element derivatives in unusual bonding situations, the chemistry of heavier group 14 anions, the synthesis of cages and clusters, and heteronuclear NMR spectroscopy.



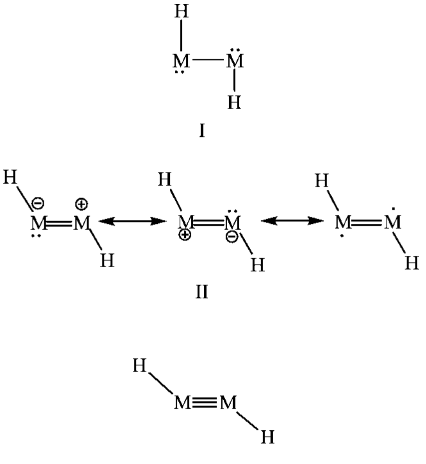
Philip Power received a B.A. from Trinity College Dublin in 1974 and a D. Phil. under M. F. Lappert from the University of Sussex in 1977. After postdoctoral studies with R. H. Holm at Stanford University, he joined the faculty at the Department of Chemistry at the University of California at Davis in 1981, where he is a Distinguished Professor of Chemistry. His main interests lie in the exploratory synthesis of new main-group and transition-metal complexes. A major theme of his work has been the use of sterically crowded ligands to stabilize main group and transition metal species with new type of bonding, low coordination numbers, and high reactivity toward small molecules such as dihydrogen, ethylene, or carbon monoxide relevant to their potential use as catalysts. He has been the recipient of several awards including the A. P. Sloan Foundation Fellow (1985), Alexander von Humboldt Fellowship for Senior U.S. Scientists (1992), Ludwig Mond Medal of the Royal Society of Chemistry (2005), F. A. Cotton Award in Synthetic Inorganic Chemistry of the American Chemical Society (2005), and was elected Fellow of the Royal Society of London (2005).

Scheme 1. Pictorial Representations of Simple Bonding Models for Moderately Strained Heavier Main Group Element Alkene (Upper) and Alkyne (Lower) Analogues (M = Si, Ge, Sn, or Pb)[a]



[a] Those on the left-hand side represent double and triple bonding, whereas those on the right represent single and double bonding, respectively.

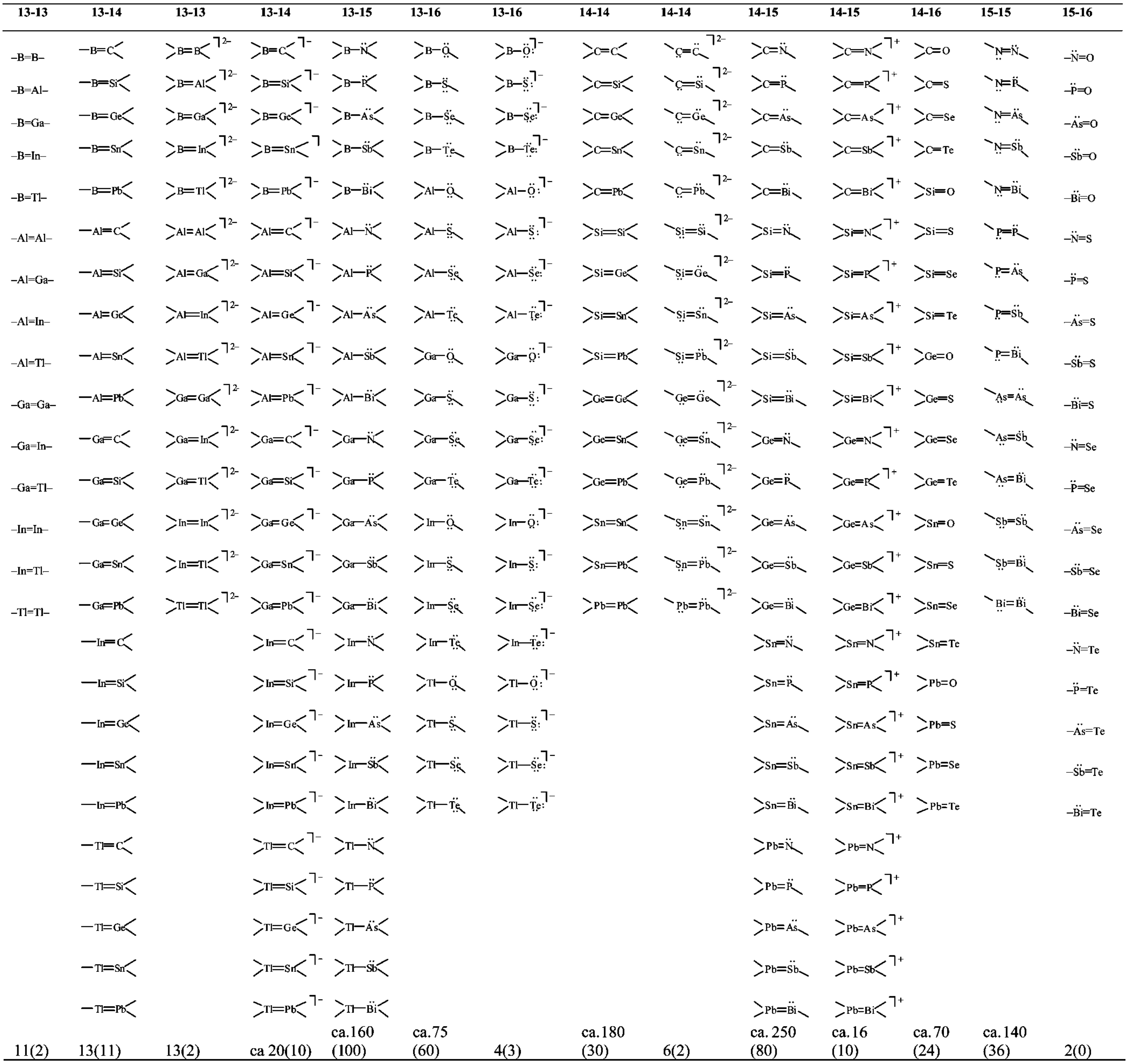
Scheme 2. Lewis-Like Structures of the Non-H-Bridged Structures of HMMH (M = C, Si, Ge, Sn, Pb)[a,14]



[a] Their NRT-computed M−M bond orders and the contributions of the leading resonance structures are shown in Table 3.

comparison to the idealized planar or linear structures in their lighter element congeners. These deformations are consistent with increased nonbonded electron pair character at the heavier main group element and weakened multiple bonding. The description and interpretation of such bonding has continued to be controversial, and there has been frequent discussion of various bonding models accompanied by numerous computational studies.[5] The various approaches to the bonding differences that exist between these compounds and their lighter congeners were summarized not only in the previous review and also in many others so that only the main points are updated in the context of more recent experimental results.[6] As before, the most controversial issues continue to be the multiplicity and the bond order of the multiple bonds. However, these points are often difficult to resolve because they are essentially subjective interpretations of several observable parameters. In principle, the question of the number of bonds should be a simple one. A bond has been defined by Cotton as "how many electron pairs... play a significant role in holding atoms together."[7] In practice, it is not so straightforward because there is often considerable difficulty in deciding if particular electron pairs (or electron density) located at or near the bonding region are indeed involved in holding the atoms together. This is especially true for many of the heavier element multiple bonded species.[8,9] In addition, SCF or DFT theory produce delocalized canonical or Kohn−Sham molecular orbitals (CMOs directly),[10,11] whereas natural bond orbital and natural resonance theory (NRT)[12] methods provide localized rather

Table 1. Selected Element Combinations Related to Alkenes from Groups 13−16 that May Feature Double Bonding



than delocalized MO bonding depictions of the bonding region. Despite the fact that the conversion of the CMOs to localized or natural molecular orbitals is achieved by unitary transformations which are independent of the basis sets used,[13] each of the two descriptions can result in different numbers of bonds as shown by the schematic illustrations of bonding in the heavier elements alkene and alkyne analogues in Scheme 1.

The two different pictorial methods of representation, which are loosely based on natural localized molecular orbitals (left) and delocalized canonical molecular orbitals (right), give different numbers of bonds. Neither representation is without drawbacks. For instance, the triple bond in the alkyne analogue structure on the bottom left of Scheme 1 consists of two donor−acceptor (polarized σ or paw−paw) bonds and a π-bond (represented in an end-on fashion by black circles). However, if the bending angle is increased to 90°, the donor−acceptor bonds are broken to leave the elements connected by a π-bond rather than a single σ-bond contrary to experimental or computational findings. The models on the right-hand side are useful only for moderate degrees of pyramidalization, and in more strongly pyramidalized or bent structures, for which a more complicated correlation diagram is required, the bonding is weakened further until either complete dissociation of the alkene analogue, or single bonding in the alkyne analogue, is obtained.

Another illustration of the bonding dilemma is furnished by recent NRT work by Landis and Weinhold[14] on the hypothetical HMMH (M = C, Si, Ge, Sn, Pb) molecules which, in their non-hydrogen bridged[15] structures, can be written in the canonical forms in Scheme 2 and Table 3.

The calculations and bond orders indicate that the structure may be regarded as a composite of two or more of Lewis-like representations. Moreover, the multiple bonding is computed to be significant even in the heaviest sixth period "diplumbyne", where the bond order only decreases to about two. However, experimental data for the stable derivative

Table 2. Selected Element Combinations from Groups 13−16 that May Feature Triple Bonding

13-13	13-14	13-15	13-16	14-14	14-15
$-\mathrm{B}\equiv\mathrm{B}-\rceil^{2-}$	$-\mathrm{B}\equiv\mathrm{C}-\rceil^{-}$	$-\mathrm{B}=\ddot{\mathrm{N}}-$	$-\mathrm{B}=\ddot{\mathrm{O}}:$	$-\mathrm{C}\equiv\mathrm{C}-$	$-\mathrm{C}\equiv\mathrm{N}$
$-\mathrm{B}\equiv\mathrm{Al}-\rceil^{2-}$	$-\mathrm{B}\equiv\mathrm{Si}-\rceil^{-}$	$-\mathrm{B}=\ddot{\mathrm{P}}-$	$-\mathrm{B}=\ddot{\mathrm{S}}:$	$-\mathrm{C}\equiv\mathrm{Si}-$	$-\mathrm{C}\equiv\mathrm{P}$
$-\mathrm{B}\equiv\mathrm{Ga}-\rceil^{2-}$	$-\mathrm{B}\equiv\mathrm{Ge}-\rceil^{-}$	$-\mathrm{B}=\ddot{\mathrm{As}}-$	$-\mathrm{B}=\ddot{\mathrm{Se}}:$	$-\mathrm{C}\equiv\mathrm{Ge}-$	$-\mathrm{C}\equiv\mathrm{As}$
$-\mathrm{B}\equiv\mathrm{In}-\rceil^{2-}$	$-\mathrm{B}\equiv\mathrm{Sn}-\rceil^{-}$	$-\mathrm{B}=\ddot{\mathrm{Sb}}-$	$-\mathrm{B}=\ddot{\mathrm{Te}}:$	$-\mathrm{C}\equiv\mathrm{Sn}-$	$-\mathrm{C}\equiv\mathrm{Sb}$
$-\mathrm{B}\equiv\mathrm{Tl}-\rceil^{2-}$	$-\mathrm{B}\equiv\mathrm{Pb}-\rceil^{-}$	$-\mathrm{B}=\ddot{\mathrm{Bi}}-$	$-\mathrm{Al}=\ddot{\mathrm{O}}:$	$-\mathrm{C}\equiv\mathrm{Pb}-$	$-\mathrm{C}\equiv\mathrm{Bi}$
$-\mathrm{Al}\equiv\mathrm{Al}-\rceil^{2-}$	$-\mathrm{Al}\equiv\mathrm{C}-\rceil^{-}$	$-\mathrm{Al}=\ddot{\mathrm{N}}-$	$-\mathrm{Al}=\ddot{\mathrm{S}}:$	$-\mathrm{Si}\equiv\mathrm{Si}-$	$-\mathrm{Si}\equiv\mathrm{N}$
$-\mathrm{Al}\equiv\mathrm{Ga}-\rceil^{2-}$	$-\mathrm{Al}\equiv\mathrm{Si}-\rceil^{-}$	$-\mathrm{Al}=\ddot{\mathrm{P}}-$	$-\mathrm{Al}=\ddot{\mathrm{Se}}:$	$-\mathrm{Si}\equiv\mathrm{Ge}-$	$-\mathrm{Si}\equiv\mathrm{P}$
$-\mathrm{Al}\equiv\mathrm{In}-\rceil^{2-}$	$-\mathrm{Al}\equiv\mathrm{Ge}-\rceil^{-}$	$-\mathrm{Al}=\ddot{\mathrm{As}}-$	$-\mathrm{Al}=\ddot{\mathrm{Te}}:$	$-\mathrm{Si}\equiv\mathrm{Sn}-$	$-\mathrm{Si}\equiv\mathrm{As}$
$-\mathrm{Al}\equiv\mathrm{Tl}-\rceil^{2-}$	$-\mathrm{Al}\equiv\mathrm{Sn}-\rceil^{-}$	$-\mathrm{Al}=\ddot{\mathrm{Sb}}-$	$-\mathrm{Ga}=\ddot{\mathrm{O}}:$	$-\mathrm{Si}\equiv\mathrm{Pb}-$	$-\mathrm{Si}\equiv\mathrm{Sb}$
$-\mathrm{Ga}\equiv\mathrm{Ga}-\rceil^{2-}$	$-\mathrm{Al}\equiv\mathrm{Pb}-\rceil^{-}$	$-\mathrm{Al}=\ddot{\mathrm{Bi}}-$	$-\mathrm{Ga}=\ddot{\mathrm{S}}:$	$-\mathrm{Ge}\equiv\mathrm{Ge}-$	$-\mathrm{Si}\equiv\mathrm{Bi}$
$-\mathrm{Ga}\equiv\mathrm{In}-\rceil^{2-}$	$-\mathrm{Ga}\equiv\mathrm{C}-\rceil^{-}$	$-\mathrm{Ga}=\ddot{\mathrm{N}}-$	$-\mathrm{Ga}=\ddot{\mathrm{Se}}:$	$-\mathrm{Ge}\equiv\mathrm{Sn}-$	$-\mathrm{Ge}\equiv\mathrm{N}$
$-\mathrm{Ga}\equiv\mathrm{Tl}-\rceil^{2-}$	$-\mathrm{Ga}\equiv\mathrm{Si}-\rceil^{-}$	$-\mathrm{Ga}=\ddot{\mathrm{P}}-$	$-\mathrm{Ga}=\ddot{\mathrm{Te}}:$	$-\mathrm{Ge}\equiv\mathrm{Pb}-$	$-\mathrm{Ge}\equiv\mathrm{P}$
$-\mathrm{In}\equiv\mathrm{In}-\rceil^{2-}$	$-\mathrm{Ga}\equiv\mathrm{Ge}-\rceil^{-}$	$-\mathrm{Ga}=\ddot{\mathrm{As}}-$	$-\mathrm{In}=\ddot{\mathrm{O}}:$	$-\mathrm{Sn}\equiv\mathrm{Sn}-$	$-\mathrm{Ge}\equiv\mathrm{As}$
$-\mathrm{In}\equiv\mathrm{Tl}-\rceil^{2-}$	$-\mathrm{Ga}\equiv\mathrm{Sn}-\rceil^{-}$	$-\mathrm{Ga}=\ddot{\mathrm{Sb}}-$	$-\mathrm{In}=\ddot{\mathrm{S}}:$	$-\mathrm{Sn}\equiv\mathrm{Pb}-$	$-\mathrm{Ge}\equiv\mathrm{Sb}$
$-\mathrm{Tl}\equiv\mathrm{Tl}-\rceil^{2-}$	$-\mathrm{Ga}\equiv\mathrm{Pb}-\rceil^{-}$	$-\mathrm{Ga}=\ddot{\mathrm{Bi}}-$	$-\mathrm{In}=\ddot{\mathrm{Se}}:$	$-\mathrm{Pb}\equiv\mathrm{Pb}-$	$-\mathrm{Ge}\equiv\mathrm{Bi}$
	$-\mathrm{In}\equiv\mathrm{C}-\rceil^{-}$	$-\mathrm{In}=\ddot{\mathrm{N}}-$	$-\mathrm{In}=\ddot{\mathrm{Te}}:$		$-\mathrm{Sn}\equiv\mathrm{N}$
	$-\mathrm{In}\equiv\mathrm{Si}-\rceil^{-}$	$-\mathrm{In}=\ddot{\mathrm{P}}-$	$-\mathrm{Tl}=\ddot{\mathrm{O}}:$		$-\mathrm{Sn}\equiv\mathrm{P}$
	$-\mathrm{In}\equiv\mathrm{Ge}-\rceil^{-}$	$-\mathrm{In}=\ddot{\mathrm{As}}-$	$-\mathrm{Tl}=\ddot{\mathrm{S}}:$		$-\mathrm{Sn}\equiv\mathrm{As}$
	$-\mathrm{In}\equiv\mathrm{Sn}-\rceil^{-}$	$-\mathrm{In}=\ddot{\mathrm{Sb}}-$	$-\mathrm{Tl}=\ddot{\mathrm{Se}}:$		$-\mathrm{Sn}\equiv\mathrm{Sb}$
	$-\mathrm{In}\equiv\mathrm{Pb}-\rceil^{-}$	$-\mathrm{In}=\ddot{\mathrm{Bi}}-$	$-\mathrm{Tl}=\ddot{\mathrm{Te}}:$		$-\mathrm{Sn}\equiv\mathrm{Bi}$
	$-\mathrm{Tl}\equiv\mathrm{C}-\rceil^{-}$	$-\mathrm{Tl}=\ddot{\mathrm{N}}-$			$-\mathrm{Pb}\equiv\mathrm{N}$
	$-\mathrm{Tl}\equiv\mathrm{Si}-\rceil^{-}$	$-\mathrm{Tl}=\ddot{\mathrm{P}}-$			$-\mathrm{Pb}\equiv\mathrm{P}$
	$-\mathrm{Tl}\equiv\mathrm{Ge}-\rceil^{-}$	$-\mathrm{Tl}=\ddot{\mathrm{As}}-$			$-\mathrm{Pb}\equiv\mathrm{As}$
	$-\mathrm{Tl}\equiv\mathrm{Sn}-\rceil^{-}$	$-\mathrm{Tl}=\ddot{\mathrm{Sb}}-$			$-\mathrm{Pb}\equiv\mathrm{Sb}$
	$-\mathrm{Tl}\equiv\mathrm{Pb}-\rceil^{-}$	$-\mathrm{Tl}=\ddot{\mathrm{Bi}}-$			$-\mathrm{Pb}\equiv\mathrm{Bi}$
3(1)	0(0)	4(0)	7(4)	22(0)	20(15)

Ar*PbPbAr* (Ar* = C_6H_3-2,6-C_6H_2-2,4,6-$^iPr_3)_2$ show a Pb−Pb−C bending angle of ca. 94° and a long Pb−Pb bond of ca. 3.2 Å, which strongly suggest single bonding for this derivative.[16] Furthermore, structural data for Ar′SnSnAr′ (Ar′ = C_6H_2-2,6-C_6H_2-2,4,6-$^iPr_2)_2)$[17] show that it has a shortened Sn−Sn bond (ca. 2.67 Å, cf. 2.8 Å for a single bond) and a much wider Sn−Sn−C bending angle near 125° (i.e., a structure indicative of some multiple bonding). Yet, a change of a *para*-substituent in this ligand to give the complex Me_3Si-4-Ar′SnSnAr′-4-$SiMe_3$ (Ar′-4-$SiMe_3$ = C_6H_2-2,6(C_6H_3-2,6-$^iPr_2)_2$-4-$SiMe_3$) produces a much longer Sn−Sn distance (3.07 Å) and a narrower bonding angle of ca. 99°, which

Table 3. Selected Structural Parameters and NRT-Computed M−M Bond Orders for Planar *trans*-Bent Models of HMMH (M = C, Si, Ge, Sn, Pb)[14]

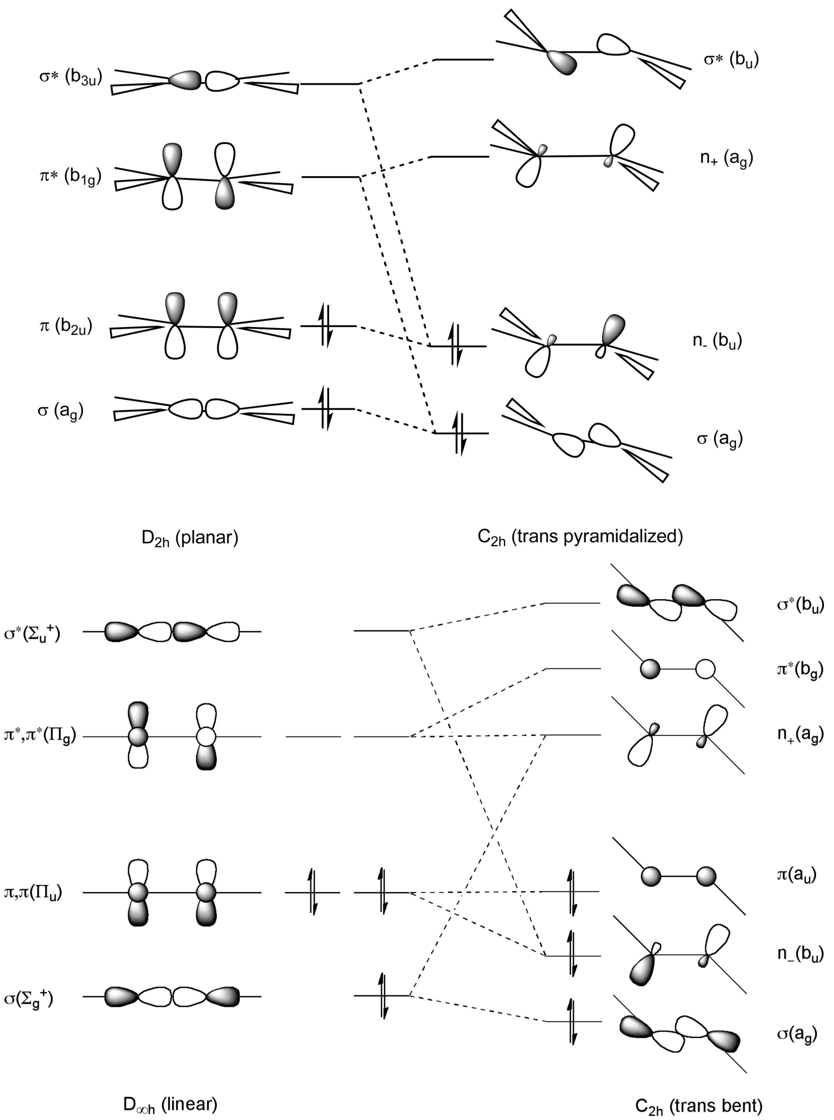
M	M−M(Å)	bending (deg)	BO[a]	III (%)	II (%)	I (%)	other (%)[b]
C	1.2	180	2.82	51	18		30, $H^+C{\equiv}CH^-$
Si[a]	2.10	125	2.79	76	6		5, $H^+Si{\equiv}SiH^-$
Ge[a]	2.26	124	2.51	48	34		3, $H^+Ge{\equiv}GeH^-$
Sn[a]	2.63	122	2.38	35	44		5, $H^+Sn{\equiv}SnH^-$
Pb[a]	2.74	123	1.97	25	26	26	20, $H^+Pb{\equiv}PbH^-$

[a] BO = bond order. [b] Several other low-population resonance forms are also found.

are indicative of a Sn−Sn single bond.[18] Consistent with the experimental data, calculations by Frenking, Nagase, Head-Gordon, and co-workers[19−22] have shown that there are only small energy differences (generally less than 5 kcal mol^{-1}) between the single and multiple bonded forms of the tin and lead alkyne analogues although the Sn−Sn and Pb−Pb bond lengths change by ca. 0.4−0.5 Å. Apparently, even crystal packing effects are sufficient to induce the large structural changes and different bond orders in these compounds. The bond order (ca. 2.5) in Sekiguchi's stable disilyne[23] $\{(Me_3Si)_2CH\}_2{}^iPrSiSiSiSi^iPr\{CH(SiMe_3)_2\}_2$, which has a Si−Si distance (2.0622(9) Å) that is significantly shorter than a double bond, has also been questioned[24,25] although the spectroscopic and structural data clearly indicate that Si−Si bond approaches triple character.[23,26]

Multiple bonding in related group 13 element derivatives has also been a continued subject of debate.[27−38] In particular, attention has been focused on the bonding in the much discussed $Na_2Ar^*GaGaAr^*$[39] ($Ar^* = C_6H_3$-2,6(C_6H_2-2,4,6-$^iPr_3)_2$), which contains the dianion $[Ar^*GaGaAr^*]^{2-}$ as part of an alkali metal stabilized ion triple, has a planar *trans*-bent structure similar to the corresponding neutral Ar*GeGeAr* species. It has been argued, with computational support,[27,37] that it is triple bonded (see below). Yet oxidation of two electrons from the HOMO π orbital of the dianion affords a neutral, putatively double-bonded Ar*GaGaAr* species which has low association energies that average only ca. 5 kcal mol^{-1} and which readily disassociates to monomeric :GaAr* units in solution.[40] Other studies based on computations of

Scheme 3. Schematic Double and Triple Bonded Models for Moderately *trans*-Bent, Heavier Main Group Alkene and Alkyne Analogues[a]



[a] Second-order Jahn−Teller mixing of σ^* and π as well as σ and π^* levels (n_+ and n_- signify non-bonding orbital which is symmetric or unsymmetric with respect to inversion) leads to non-bonded electron pair character (as in the b_u (n_-) orbital, right) at the heavier group 14 elements.

compliance matrices[29−31] of the heat of hydrogenation[34,36] support the weakness of such bonds.

In short, the conflicting views of the various theoretical approaches, although they have provided much information on fundamental bonding questions, have not led to agreement on the bond number/order issue. However, it could be argued that the bond number/order idea with its emphasis on assigning numbers (preferably whole integers) to the number of bonds and the bond orders is appropriate only for compounds of the lighter p-block elements B, C, N, or O. The more complex bonding in their heavier element congeners requires a more flexible approach, especially since the bonding changes considerably (usually manifested in increasing nonbonded electron pair character) upon descending each group. One model, which incorporates at once an explanation for the geometrical distortions and a representation of different degrees of mixing of the molecular energy levels upon descending each group is derived from the assumption of second order Jahn−Teller mixing (SOJT) in the heavier elements species as exemplified in Scheme 3.

The multiple bonding in the group 14 element alkene and alkyne analogues, which are of central importance to the field of multiple bonding, has been chosen for illustration. In these species, mixing occurs in the heavier element compounds because the energy levels, which have different symmetries in the undistorted structures and the same symmetry in the pyramidalized and bent structures, are sufficiently close to each other because of weaker bonding in the heavier elements. The illustrations given in Scheme 3 are very simplified ones (for example, only three of the four valence orbitals at each element or shown) but it provides a rough picture of frontier energy levels that is consistent with computations as well as spectroscopic and reactivity studies. Whether the $b_u(n_-)$ is regarded as a “slipped π-bond” or an out-of-phase lone pair molecular orbital seems a less important question than the fact that the model accommodates the view that extent of the SOJT interactions are variable and generally increase upon descending each group consistent with weakening bonds. Note that the original σ bonds (a_g) are also weakened by the distortions. With further bending, as in the sixth period, the alkene analogues become dissociated to monomers. For the alkyne congeners, the original $\sigma+2\pi$ triple bond in carbon-based alkynes ultimately changes to two lone pair orbitals that are mostly 6s in character as well as a σ-bond in its strongly bent lead congeners.

3. Doubly Bonded Compounds

3.1. Compounds of Formula RE=ER (E = Group 13 Element)

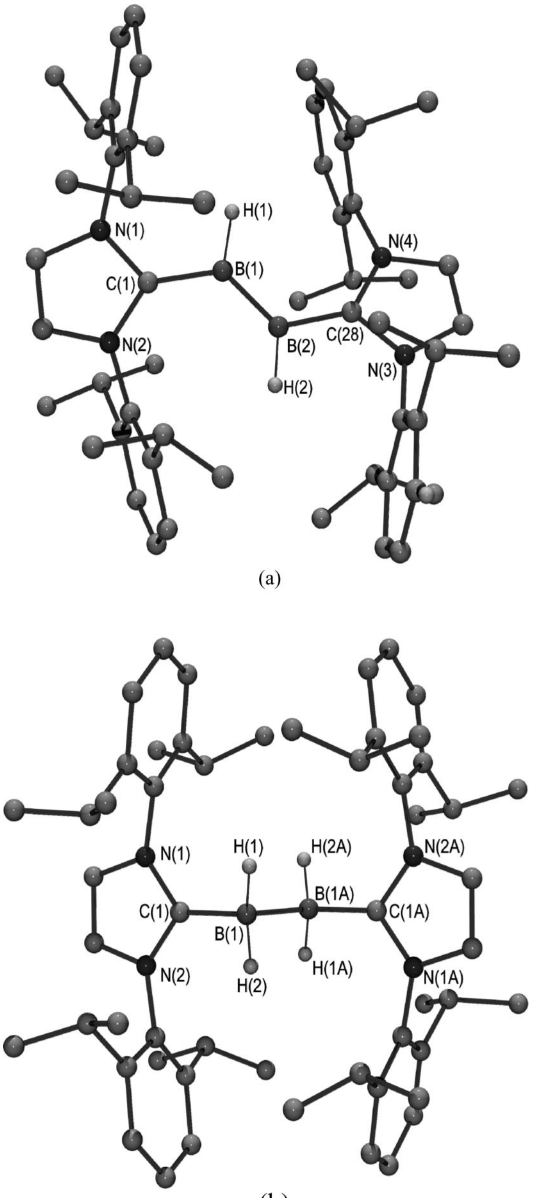
In the earlier review, structurally characterized stable compounds of the formula REER (E = B, Al, Ga, In, or Tl) were restricted to the indium and thallium derivatives $[M\{\eta^5\text{-}C_5(CH_2Ph)_5\}]_2$ (M = In or Tl),[41,42] $Tl_2(\eta^5{:}\eta^5\text{-t-}Bu_4C_{10}H_4)$,[43] or $Tl_2B_9H_9C_2Me_2$,[44] which featured weak M---M interactions (3.6−3.76 Å) that were ca. 0.6−0.8 Å longer than single bonds.[45] These distances are indicative of weak bonding and are characteristic of closed shell interactions.[46] Since then several “dimetallenes” in which the ligand is bound only through one atom to the group 13 metal have been synthesized and characterized. Their most important structural parameters and those of related species[40,47−54] are listed in Table 4.

Data for the base stabilized parent diborene complexes (L)HBBH(L)[47] (Figure 1) and (L′)HBBH(L′)[48] are also included also in Table 4. These species were obtained by Robinson and co-workers by reduction of the carbene−boron bromide adducts $LBBr_3$ L = $:CN(C_6H_3\text{-}2,6\text{-}{}^iPr_2)(CH)_2NC_6H_3\text{-}2,6\text{-}{}^iPr_2$ or $L'BBr_3$ L′ = $:CN(C_6H_3\text{-}2,4,6\text{-}Me_3)(CH)_2NC_6H_3\text{-}2,4,6\text{-}Me_3$ with KC_8 in diethyl ether. Prior calculations[55] had shown that the ground state for neutral HBBH is a triplet diradical in which the boron atoms are linked by a σ and two singly occupied π-bonds (B−B = 1.553 Å). As a result of their triplet diradical character, diborenes are predicted to be quite reactive and no stable derivatives of this molecule had been isolated. However, complexation of each boron atom by a carbene ligand induces stability and the borons are then linked by a σ and a doubly occupied π-bond. The experimentally measured B−B bond distances, which are in the range 1.56(2)−1.679(9) Å, are much shorter than the single bond (B−B = 1.828(4) Å) in $(L)H_2BBH_2(L)$ (which was obtained from the same preparation) and are slightly shorter than the double bonds in the anionic $[R_2BBR_2]^{2-}$ species (see below Table 5). They are similar in length to the computed double bond of 1.590 Å in (OC)HBBH(CO).[56] The complexes are also characterized by ^{11}B NMR chemical shifts of δ +23.50 for ((L)HBBH(L)) and +23.45 for ((L′)HBBH(L′)) and an absorption at 574 nm in the electronic spectrum for (L′)HBBH(L′), which was proposed to correspond to the B−B $\pi-\pi^*$ transition. In addition, DFT calculations confirm the presence of the BB double bond in both complexes. As is apparent from Table 4, compound (L′)HBBH(L′) can exist in at least three conformations in

Table 4. Selected Structural Data for Group 13 Element Dimetallenes

compd	M−M(Å)	bending angle (deg)	ref
(L)HBBH(L)[a]	1.56(2)	126(4)	47
(L′)HBBH(L′)[b]	1.602(5)	125.6(16)	48
	1.582(4)	126(2)	
	1.679(9)	118(2)	
Ar′GaGaAr′[c]	2.6268(7)	123.16(7)	49, 50
4-^{t}BuAr*GaGaAr*^{t}Bu-4[d]	2.55(3) av	117.4 av	40
4-CF_3Ar*GaGaAr*CF_3-4	2.59(3) av	121.68(5), 128.53(5)	40
Ar′InInAr′	2.9786(5)	121.26(6)	51
Ar′TlTlAr′	3.0936(8)	122.9(4)	52
HC{C(Me)N(Mes)}InIn{(Mes)NC(Me)}$_2$CH[e]	3.1967(4)		53
HC{C(Me)N(Dmp)}InIn{(Dmp)N(CMe)}$_2$CH[f]	3.3400(5)	113.02	54

[a] L = $:CN(C_6H_3\text{-}2,6\text{-}{}^iPr_2)(CH)_2NC_6H_3\text{-}2,6\text{-}{}^iPr_2$. [b] L′ = $:CN(C_6H_3\text{-}2,4,6\text{-}Me_3)(CH)_2NC_6H_3\text{-}2,4,6\text{-}Me_3$. [c] Ar′ = $C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}iPr_2)_2$. [d] Ar*-4-X = $C_6H_2\text{-}2,6(C_6H_2\text{-}2,4,6\text{-}iPr_3)_2\text{-}4\text{-}X$ (X = H(Ar$_2$), tBu or CF_3). [e] Mes = $C_6H_2\text{-}2,4,6\text{-}Me_3$. [f] Dmp = $C_6H_3\text{-}2,6\text{-}Me_2$.



(a)

(b)

Figure 1. Molecular structure of (L)HB=BH(L) (a) and $(L)H_2BBH_2(L)$ (b). Selected bond distances (Å) and angles (deg) for (L)HB=BH(L) (a): B(1)−B(2) 1.56(2), B(1)−C(1) 1.54(2), B(2)−C(28) 1.53(2), B(1)−H(1) 1.14(3), B(2)−H(2) 1.13(3); B(2)−B(1)−C(1) 126(1), B(1)−B(2)−C(28) 128(1). $(L)H_2BBH_2(L)$ (b): B(1)−B(1A) 1.828(4), B(1)−C(1) 1.577(2), B(1)−H(1) 1.155(18), B(1)−H(2) 1.147(19); B(1A)−B(1)−C(1) 107.45(16), B(1A)−B(1)−H(1) 110.7(9), B(1A)−B(1)−H(2) 110.3(9), C(1)−B(1)−H(1) 108.9(9), C(1)−B(1)−H(2) 108.1(10), H(1)−B(1)−H(2) 111.3(13).[47]

the crystal phase in which the B−B distance can vary by up to ca. 0.1 Å.[48] This is believed to be due to the relatively shallow potential energy surface for B−B bond stretching. In addition, packing effects may influence the BB bond length. The use of stable carbene ligands in the isolation of diborenes and other new multiple bonded main group species has been reviewed.[4w]

Stable uncomplexed dimetallene derivatives are currently known only for the heavier elements Ga, In, and Tl as listed in Table 4. It is believed that the red aluminum derivative Ar′AlAlAr′ is generated in solution via the reduction of $Ar'AlI_2$ with KC_8.[57] However, this highly reactive molecule undergoes rapid cyclization in toluene in which the dialuminene unit is added in a 1,4-manner across the toluene ring to give a bicyclic species with an Al−Al single bond (2.5828(7) Å). The corresponding Ar′MMAr′ (M = Ga, In, or Tl) species can be readily isolated and are stable at room temperature.[40,49−52] They possess planar *trans*-bent geometry consistent with increasing nonbonded electron density with increasing atomic number. They are highly colored, and electronic spectroscopy indicates that they are dissociated to monomeric :MAr′ units in solution whose spectra display two absorptions that have been shown to be due to n→p (in plane) higher energy and n→p (out of plane) lower energy transitions. The use of larger substituents readily afforded monomeric structures, for example :GaAr′-3,5-$^iPr_2$[40] (Ar′-3,5-$^iPr_2$ = C_6H-2,6(C_6H_3-2,6-$^iPr_2$)$_2$-3,5-$^iPr_2$) and :MAr* (M = In,[58] Tl;[59] Ar* = C_6H_2-2,6(C_6H_2-2,4,6-$^iPr_3$)$_2$ in the solid state. The weakness of the M−M bonds in all the ArMMAr (M = Ga, In, or Tl) derivatives is consistent with the measured M−M bond distances which exceed the predicted double bond distances (Ga = 2.34 Å, In = 2.72 Å, Tl = 2.84 Å) calculated from double bond covalent radii[60] by at least 0.25 Å. The planar *trans*-bent structures with their weakened bonds can be accounted for by the two models given in Scheme 4 in which the bonding is represented by two weak donor−acceptor bonds (left) or as a weakened single bond (right). Note that in the donor−acceptor model the out-of-plane p-orbitals, represented by an open circle, are empty. The *trans*-bent structures of the stable aryl indium and thallium derivatives are consistent with those calculated for the parent HMMH (M = In or Tl) molecules that were generated at low temperature trapped in frozen matrices and spectroscopically characterized.[61]

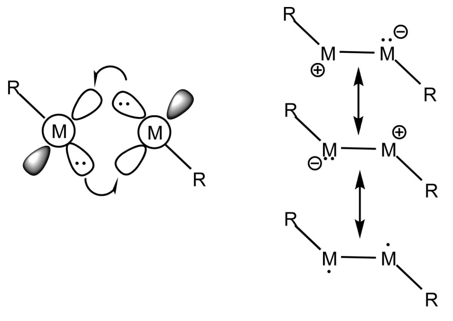
The list of compounds in Table 4 also includes the *β*-diketiminate derivatives HC{C(Me)N(R)}$_2$InIn{N(R)C(Me)}$_2$CH (R = C_6H_2-2,4,6-Me_3 or C_6H_3-2,6-Me_2).[53,54] Strictly speaking, these compounds fall outside the scope of the review because the indium is incorporated in a ring but they are included here because of the low coordination of

Table 5. Selected Structural Data for $[R_2E{=}ER_2]^{2-}$ Dianionic and Related Species (E = B-Tl)[a]

compd	E−E (Å)	torsion angle (deg)	ref
$\{Et_2OLi\}_2\{Mes_2BB(Ph)Mes\}$	1.714(4)	7.3	72
$\{Et_2OLi\}_2\{Ph(Me_2N)BBNMe_2Ph\}$	1.627(4) (av)	0	73
$\{Et_2OLi\}_2\{(Me_2N)(CH_2)_4NBBN(CH_2)_4(NMe_2)\}$	1.59(1)	0	74
$\{Et_2OLi\}_2\{(Me_2N)$(indolyl)BB(indolyl)$(NMe_2)\}$	1.584 (4)	0	74
$\{Et_2OLi\}(Me_2N)$(carbazolyl)BB(carbazolyl)$(NMe_2)\}$	1.566(9)−1.578(9)	0−3	74
$\{Et_2OLi\}$(MeO)(Mes)BB(Mes)OMe}	1.636(7)	25	75
[K(THF)(18-crown-6)]$[Mes_2BB(Ph)Mes]$	1.649(11)	6.9	76
$[R_2AlAlR_2]^-$	2.53(1)	0	77
$[Ar_2AlAlAr_2]^-$	2.470(2)	1.4	78
$[R_2GaGaR_2]^-$	2.401(1)	0	79
$[Ar_2GaGaAr_2]^-$	2.343(2)	15.5	80

[a] Mes = C_6H_2-2,4,6-Me_3, R = $CH(SiMe_3)_2$, Ar = C_6H_2-2,4,6-Pr^i_3.

Scheme 4. Pictorial Representation of the Bonding in the Group 13 Dimetallenes: Double Bond (Left) or a Single Bond (Right)[a]



[a] Open circles represent an end-on view of the metal p-orbitals perpendicular to the molecular plane.

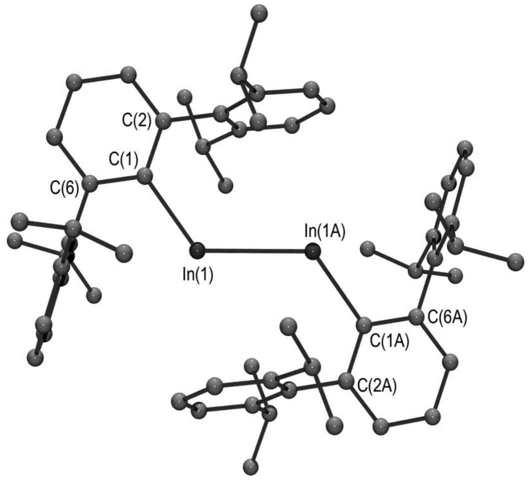


Figure 2. Selected bond lengths (Å) and angles (deg) for Ar′InInAr′. H atoms are not shown. In(1)−In(1A) 2.9786(5), In(1)−C(1) 2.256(2), C(1)−C(2) 1.406(3), C(1)−C(6) 1.405(3); In(1)−In(1A)−C(1A) 121.23(6), C(2)−C(1)−C(6) 118.6(2), In(1)−C(1)−C(2) 119.95(15), In(1)−C(1)−C(6) 120.47(16)°.[58]

the metal and the metal−metal interaction). In these compounds, the indiums are coordinated by two nitrogen atoms of the β-diketiminate ligand and the InN_2 coordination planes are disposed in an *anti* fashion across the InIn bond to give an analogous core arrangement to those observed for the monodentate aryls. The In−In distances, 3.1967(4) and 3.3400(5) Å, are lengthened considerably in comparison to those of the aryls and the compounds are dissociated to monomeric units in solution (Figure 2).

Multiple bonded character is also present in the unique radical species $(^tBu_3Si)\dot{M}M(Si^tBu_3)_2$ (M = Al[62] or Ga[63]) in which the unpaired electron was shown to be delocalized over the two metals in a π-orbital by EPR spectroscopy. The crystal structure of the gallium derivative was determined earlier[64] and displayed a short Ga−Ga distance of 2.420(1) Å and a wide GaGaSi angle of 170.34(6)°. The structure of the aluminum analogue could not be determined crystallographically, but DFT calculations afforded an Al−Al distance of 2.537 Å with an AlAlSi angle of 174.9°. EPR spectroscopy confirmed the delocalization of the unpaired electron over the two aluminums. The reduced salt $(THF)_3Na(^tBu_3Si)GaGa(Si^tBu_3)$[63] has a shorter Ga−Ga distance (2.3797(6) Å) than the neutral radical. The core Si_2GaGa array is almost planar, and the electron pair at the anionic gallium is available for π-bonding. Its delocalization is also reflected in the wide Si−Ga(anion)−Ga angle of 142.41(4)°.

3.2. Compounds of Formula RE=E′R₂ (E Group 13, E′ = Group 14 Element) and Related Species

At the time of the previous review, the only stable compounds known in this class were methyleneborane derivatives for which about a dozen examples have been structurally characterized and which had B−C double bond lengths in the range, 1.31−1.42 Å. One further example of a stable molecule from this class, $DurB{=}C(SiMe_3)\{B(Dur)(CHCHSiMe_3)\}$ (Dur = durene, C_6H-2,3,5,6-Me_4; B=C = 1.379(3) Å), has been structurally characterized[65] and some methyleneborane reactions have also been investigated.[66] In a notable advance, the first stable neutral species containing a multiple bond between boron a heavier group 14 element $(^tBu_2MeSi)_2Si{=}B(Tmp)$ (Tmp = 2,2,6,6-tetramethylpiperidinyl) was described.[67] It was obtained by the reaction of $Li_2Si(SiMe^tBu_2)_2$ with Cl_2BTmp and features an almost linear SiBN angle of 176.87(13)° and short SiB and BN distances of 1.8379(17) and 1.3695(19) Å together with high upfield (δ −128.1) and downfield (δ 87.7) shifts of the ^{29}Si and ^{11}B NMR signals, which were in harmony with computational work. Consistent with its double bond character, the Si−B distance is shorter than the 1.85 Å predicted from the sum of the double bond radii.[60] Similar reactions involving $Li_2E(SiMe^tBu_2)_2$ (E = Si or Ge) and $MesBCl_2$ resulted in the insertion reaction of the sila or germaborene into solvent THF to yield the cyclic product $(^tBu_2MeSi)_2E(CH_2)_4OBMes$ with Si−B (2.1249(18) Å) or Ge−B (2.1647(17) Å) single bonds.[68]

3.3. Dianions of Formula [R₂E=ER₂]²⁻ (E = Group 13 Element)

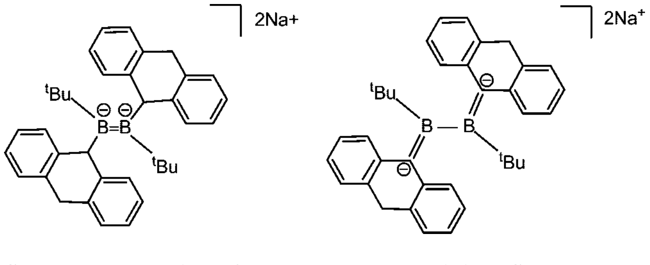
These compounds are isoelectronic to their neutral group 14 alkene analogues and possess a double negative charge which introduces a degree of Coulombic repulsion and consequent instability across the double bond. Calculations on $Li_2M_2R_4$ derivatives suggest that formation of the doubly reduced complexes is disfavored for this reason, particularly in the heavier elements where *trans*-pyramidalization of the geometry was calculated to become more pronounced with increasing atomic number.[69] Strong solvation was predicted to be the key to the isolation of such compounds. There have been limited changes in this area over the past 10 years. The only stable dianionic species to have been characterized are all derivatives of boron. Without exception, all of the isolated compounds are contact ion triples in which the lithium counter cations are strongly associated with the diboron dianion. Selected structural data for the known complexes as well as a related mono reduced species containing half a π-bond are given in Table 5.[70−80]

All the complexes have planar boron geometries and zero or small torsion angles between the boron coordination planes. Despite their dianionic character the B−B distances are in the range 1.566(9)−1.714(4) Å, the lower end of which is similar to that in the base stabilized diborenes[47,48] in Table 4. The B−B distances in the dianions are up to ca. 0.3 Å shorter than the 1.859(2) Å observed for a B−B single bond distance between two anionic boron atoms.[81] The ^{11}B NMR chemical shifts are in the range δ +24.7 to +33.0,[72−74] which is close to that observed for the diborene adducts in Table 4. Thus far in the heavier group 13 elements, it has proven possible to synthesize only mono reduced species which have formal bond orders of 1.5. These compounds were obtained by one electron reduction of the neutral tetraorgano precursors. One of the gallium mono anions has a Ga−Ga distance of 2.343(2) Å that is similar to that predicted (2.34 Å) for a Ga−Ga double bond[60] and is also similar to the putative Ga−Ga triple bond distances in the “digallynes” in Table 29. Attempts at further reduction of the gallium aryl led to rearrangement and ligand stripping of aryl groups.[82]

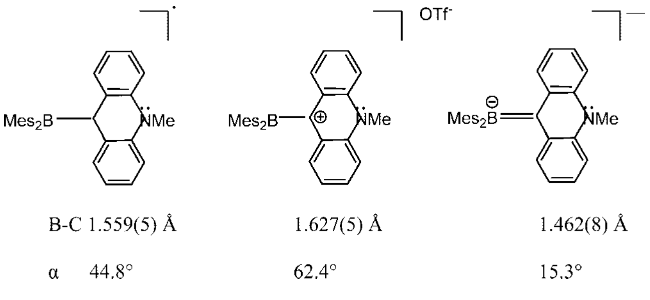
3.4. Monoanions of Formula $[R_2E{=}E'R'_2]^-$ (E = Group 13, E' = Group 14 Element)

The simplest compounds of this type are the boron−carbon species of formula $[R_2B{=}CR_2]^-$, which can be regarded as boron stabilized carbanions which have found application in organic synthesis as boron ylids. Approximately 10 structures of this type had been characterized at the time of the previous review and they were found to have B−C bond lengths in the approximate range 1.44−1.52 Å. In the ensuing years, a number of molecules containing formally double or partial multiple B−C bonds have been structurally characterized. For example, the dimeric difluorenyldiborate species shown in Scheme 5 was obtained by deprotonation of the neutral diborane has B−C multiple bond character as evidenced by shortened B−C bond lengths of ca.1.53 Å which lie near the upper end of the previously known scale.[83] Similarly, the series of 9-borylated acridinyl derivatives shown in Scheme 6 illustrates the structural effects of having 0, 1, or 2 electrons in the B−C π-bond. It can be seen that the addition of 1 and 2 electrons shortens the B−C bond sequentially from 1.627(5) to 1.559(5) to 1.462(8) Å (at the lower end of the previously known range) and effects closure of the torsion angle between the boron and carbon coordination planes. Boron carbon double bonds have also been incorporated into various cyclic species but discussion of these lies beyond our scope.[85,86]

Scheme 5. Schematic Drawing of the Resonance Forms of a Difluorenyldiborate Salt B−C = 1.529(8) and 1.533(9) Å, B−B = 1.744(9) Å (Both Borons Have Planar Coordination)[83]



Scheme 6. Drawing of the 9-Borylatedacridinyl System: Structural Changes That Occur upon Stepwise Population of the Boron−Carbon π-Bond[84] (Mes = C_6H_2-2,4,6-Me_3, α = Torsion Angle between B and C Coordination Planes)[84]



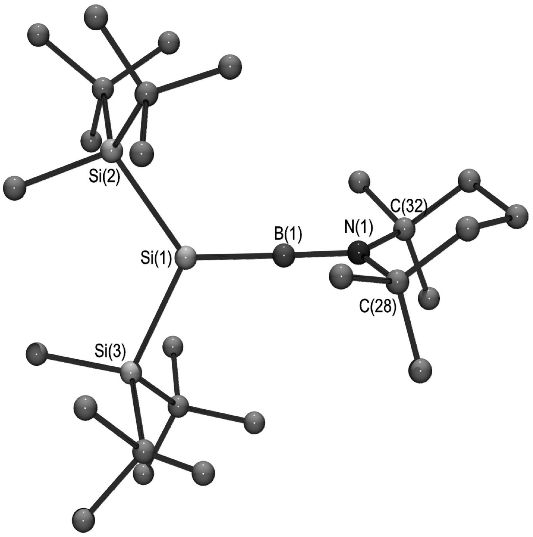
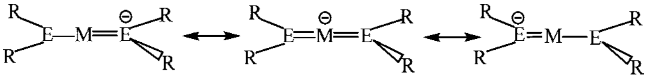


Figure 3. Drawing of the silaborene $(^tBu_2Me)_2SiB(Tmp)$. Hydrogen atoms are not shown. Selected bond lengths (Å) and angles (deg): Si(1)−B(1) 1.8379(17), N(1)−B(1) 1.3695(19), Si(1)−Si(2) 2.3413(6), Si(1)−Si(3) 2.3419(6), N(1)−C(28) 1.5175(18), N(1)−C(32) 1.5212(18); bond angles (deg): Si(1)−B(1)−N(1) 176.87(13), B(1)−Si(1)−Si(2) 119.45(5), B(1)−Si(1)−Si(3) 119.91(6), Si(2)−Si(1)−Si(3) 118.93(3), B(1)−N(1)−C28 120.01(12), B(1)−N(1)−C(32) 120.46(12), C(28)−N(1)−C(32) 119.27(11).[67]

Scheme 7. Resonance Forms of the Alkene Like Dianion $[E(SiR_2)_2]^-$ (M = Ga or In; E = Si or Ge; R = $SiMe^tBu_2$)[87,88]



The addition of $LiC{\equiv}CSiMe_3$ in the presence of 1,2-dimethoxyethane (Dme) to the double bonded $(Bu^t_2MeSi)_2Si{=}BTmp$ species discussed earlier (Figure 3) yielded the salt $[Li(Dme)_3][^tBuMeSi]_2Si{=}B(CCSiMe_3)Tmp]$, which has a Si−B double bond distance of 1.933 (3) Å and a B−N distance of 1.527(3) Å, cf. 1.8397(17) and 1.3695(19) Å in the neutral precursor. The longer B−Si distance is presumably due to the increased coordination number at boron and the B−N distance increases because the B−N π-bond is broken by the addition of the acetylide moiety, which is also reflected in the pyramidal coordination at the nitrogen.

The addition of $Li_2E(SiMeBu^t_2)_2$ (E = Si or Ge) to MCl_3 (M = Ga or In) afforded complexes of formula $[Li(THF)_4][(^tBu_2MeSi)_2E\overset{..}{-}M\overset{..}{-}E(SiMe^tBu_2)_2]$.[87,88] It is possible to write the anions in the resonance forms shown in Scheme 7.

For M = Ga or In and E = Si, the Ga−Si distances are 2.2828(9) and 2.2775(9) Å and the In−Si distances are 2.4849(9) and 2.4792(9) Å with SiMSi angles of 161.61(3)° (Ga) and 161.35(3)° (In). The silicons bound to the metals have pyramidal coordination with Σ°Si = ca. 342° for Ga and ca. 326° for In. The Ga−Si and In−Si bond lengths are slightly longer than the predicted double bond distances of 2.24 and 2.43 Å.[60] The orientation of the $Si(SiBu^t_2Me)_2$ units with respect to each other is consistent with an allene-like bonding scheme. The corresponding $[Li(THF)_4][In\{Ge(SiMe^tBu)_2\}_2]$ species has a similar structure and Ge−In bonds of 2.5453(4) and 2.5387(4) Å.[88]

Other potentially multiple bonded heavier group 13/14 species have been obtained from the reaction of potassium salts in the anionic gallium(1) N-heterocyclic carbene (NHC) analogue $K[Ga\{N(Ar)C(H)\}_2]$ (Ar = C_6H_3-2,6-$^iPr_2$) with digermenes[89] and distannenes, which afford products of the formula $K\{(H)CN(Ar)\}_2GaER_2$ (E = Ge, R = Mes, $CH(SiMe_3)_2$; E =

Ge or Sn, R = $CH(SiMe_3)_2$).[90] However, the group 14 atoms have strongly pyramidal coordination and are also bound to the K^+ countercation. For the E = Ge, R = Mes derivative, the Ga−Ge distance is 2.4600(8) Å (cf. predicted Ga−Ge double bond = 2.28 Å)[60] and is consistent with a single rather than a double bond. The addition of Me_3SiCl affords $\{HCN(Ar)\}_2GaGe(SiMe_3)Mes_2$, which has four coordinate Ge and features a Ga−Ge single bond distance of 2.4311(10) Å. For R = $CH(SiMe_3)_2$, the Ga−Sn bond length was found to be 2.7186(6) Å and is consistent with single bonding. It also proved possible to obtain a 2:1 complex Ga:Sn of formula $[K(TMEDA)_2][(\{HCN(Ar))_2Ga\}_2Sn\{CH(SiMe_3)_2]_2$, which has Sn−Ga = 2.6610(6) and 2.6361(5) Å, which are also consistent with single bonding. In addition, the related guanidinate complexes $\{HCN(Ar)\}_2GaGe\{(NAr)_2CH\}$ (E = Ge or Sn) were synthesized. They had Ga−E = 2.5157(7) Å (Ge) and 2.6888(6) Å (Sn).

3.5. Compounds of Formula $R_2E{-}\ddot{E}'R_2$ (E = Group 13, E′ = Group 15 Element) and Related Species

The earlier review[1] provided a discussion of the bonding in these compounds where the degree of multiple character derived from the extent of the electron density transfer from the pair of electrons on the group 15 element to an empty orbital on the group 13 element. The new examples of these compounds (as in the previous review, amido borane derivatives are not covered) are listed in Tables 6 and 7. For the amido derivatives of Al, Ga, In, and Tl and the related species, the nitrogen atoms are planar coordinated and the experimental M−N bond lengths can be as much as 0.2 Å shorter than that of the sum of the metal and nitrogen covalent radii (cf Al−N = 1.97 Å, Ga−N = 1.95 Å, In−N = 2.13 Å, Tl−N = 2.15 Å),[91] consistent with structural data from the previous review. The apparent shortening is misleading, however, and currently there is general acceptance that in amido alanes, gallanes, indanes, and thallanes ionic resonance effects are the major cause of shortening of the M−N bonds. M−N π-bonding as a result of electron donation via p−p orbital overlap is relatively less important and has a maximum value of ca. 10 kcal mol^{-1}. This view receives support from empirically predicted bond distances, corrected for ionic effects,[92,93] and the more recent experimental data which confirm the earlier conclusions.

Several reviews dealing with various aspects of the group 13−15 species, either fully or in part, have appeared. These include a review of amido derivatives of gallium and indium,[94] a wide ranging review of low valent indium compounds,[95] a review of low-valent thallium amides,[96] a review of group 13 imido metallanes and their heavier

Table 6. Group 13 Metal−Nitrogen Bond Lengths and Torsion Angles between the Metal and Nitrogen Coordination Planes (Where Published) for Two- and Three-Coordinate Aluminum, Gallium, Indium, and Thallium Amides (1999−2009, See ref 1 for Earlier Listings)[a]

compd	M−N (Å)	torsion angle (deg)	ref
$R_2AlN(C_6H_4\text{-}2\text{-}Ph)_2$, R = Cl	1.814(3)	~0	104
R = Me	1.845(3)	~0	104
R = Et	1.824(3)	~0	104
R = C_6F_5	1.815(3)	~0	104
$(\eta^1\text{-}C_5Me_5)Al(\mu\text{-}NSi^tBu_3)_2Al(\eta^1\text{-}C_5Me_5)$	1.840(1) av	~0	105
$MeAlN(Dipp)(CH_2)_3N(Dipp)$	1.763(3) av	~0	106
$H_2C\{Al(Tmp)_2\}_2$	1.835(3) av	50−75	107
$H_2C[Al\{N(SiMe_3)_2\}_2]_2$	1.815 av	50−75	107
$(Me_3Si)_2PAl(Tmp)_2$	1.847(2) av		108
$(Me_3Sn)_2PAl(Tmp)_2$	1.825(7) av		108
$\{(Tmp)_2Al\}_2PPh$	1.821(5) av		108
$Tmp_2AlN(BMe)NH(BMe)NH(BMe)$	1.821(2) (Tmp)		109
	1.844(3) (Bzn)		109
$[\{^tBuAlN(SiMe_3)\}_2]_2$	1.866(4)	0	110
$:Ga\{N(SiMe_3)Ar^\#\}$	1.980(2)		111
$Ar^\#NGa\{N(SiMe_3)Ar^\#\}$	1.862(5)		111
$TmpGaCr(CO)_5$	1.842(3)		112
$(OC)_3Cr(\mu\text{-}GaTmp)_3Cr(CO)_3$	1.828(3) av		112
$(CO)_3Co(\mu\text{-}GaTmp)_2Co(CO)_3$	1.838(5)		112
$(TmpGa)_2Ni(\mu\text{-}GaTmp)_3Ni(GaTmp)_2$	term 1.863(6) av bridg. 1.900(7) av		112
$(carbazole)GaCl_2$	1.852(2)	~0	113
$(Tmp)_2GaCl$	1.843(3) av	41, 70	114
$Fe\{\eta^5\text{-}C_5H_4Ga(Tmp)_2\}_2$	1.876(4) av	40, 71	114
$Ar'GaN(Ph)N(Ph)GaAr'$	1.909(2) av		111
$Ar'Ga(\mu\text{-}NNCPh)_2GaAr'$	1.882(15) av		111
$Ga(NCy_2)_3$	1.836(6) av		115
$\{GaN(SiMe_3)CH_2CH_2N(SiMe_3)\}_2$	1.831(4) av	~0	116
$[Li(THF)]\{Ga_6IO\{N(SiMe_3)_2\}_2\}$	term 1.900(3) av	~45	117
$[Ga_8\{N(H)Dipp\}\{N(SiMe_3)Dipp\}\{NDipp\}OLi[Li(Et_2O)_8]$	1.86−2.00		118
$(Me_3Si)_2NIn\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}$	2.123(3)	78.6	119
$\{(Me_2Si)_2N\}InMo(\eta^5\text{-}C_5H_5)(CO)_3$	2.106(10) av	42.2, 83.9	119
$In(NCy_2)_3$	2.019(6)	47	120
	2.042(5)	50	
	2.044(5)	59	121
$In\{N(SiMe_3)NMe_2\}_3$	2.075(2)-2.081(2)	51.5−59.9	121
$TlN(SiMe_3)_2$(ged)	2.164(13)		122
$TlN(Me)Ar^\#$	2.364(3) av		123

[a] $Ar^\#$ = $C_6H_3\text{-}2,6(C_6H_2\text{-}2,4,6\text{-}Mes)_2$, Dipp = $C_6H_3\text{-}2,6\text{-}^iPr_2$, Tmp = 2,2,6,6=tetramethylpiperdinyl, Cy = cyclohexyl.

Table 7. Selected Structural Data for Some Group 13-Heavier Group 15 (E) Element Compounds with Varying Degrees of Multiple Bonding (1999−2009, See ref 1 for Earlier Listings)[a]

compd	B−E (Å)			Σ E° (deg)	ref
$(F_5C_6)_2BP^tBu_2$	1.786(4)			359.07	125
$(Tmp)BP^tBu(AlBr_3)$	1.787(4)			304.4	126
$(Tmp)(Dmap)BPAr*$	1.809(2)				127, 128
$(Tmp)(Br)BP(H)Ar*$	1.954(3)			296	128
$\{(Me_3Si)_3Si\}(Pr^i_2N)BPPh_2$	1.982(5)			318.5	129
$(\eta^5\text{-}C_5H_5)_2Zr\{P(H)B(N^iPr_2)N(SiMe_3)_2\}_2$	1.916(7)			346.6	130
	1.926(6)			341.3	130
$PhP(BCy_2)_2$	1.872(6)			359.5	131
	1.866(6)				
$^tBuP\{B(cat)\}B(Cl)(Tmp)$	1.884 (B(cat))			319.7	132
	1.933 (B(Cl)Tmp)				
$Ph_2P(Dur)BB(Dur)PPh_2$	1.835(2)			350.6	133
$Ph_2P(Dur)BBCl(Dur)$	1.845(2)			343.1	133
$Ph_2P^1B^1(Dur)P^2(Ph)B^2(Dur)Ph(Dur)$	1.911(8) B^1P^1			317.0 P^1	133
	1.866(7) B^1P^2			359.9 P^2	
	1.883(7) B^2P^2				
		R	R′		
$\{R_2'B\}(R)PP(R)BR_2'$	1.886(2)	^tBu	Cy	341.3	131
	1.898(2)	Ph	^tBu	335.2	
	1.925(2)	^tBu	Ph	328.3	
$Bu^tCH_2\overline{CB(Cl)P(SiMe_3)_2B}{-}P(SiMe_3)_2$	1.924(3)		85	315.9	
$Tmp(Dmap)BAsAr*$	1.914(6)				127, 128
$Tmp_2AlP(SiMe_3)_2$	2.361(2)			335.5	108
$Tmp_2AlP(SiMe_3)_2$	2.34(2)			326.3	108
$PhP(AlTmp_2)_2$	2.287(3), 2.292(3)			359.9	108
$^tBu_3Si(H)PGa(\mu\text{-}PSi^tBu_3)_2GaP(H)P(H)SiBu^t_3$	2.307(2)			301(2) av	134
	2.258(6) ring			360.0(2)	
	233.6(2) ring			298.4(2)	
$Mes_2*GaP(H)Si^iPr_3$	235.3(3)				135
$(Me_3Si)_3CGa(\mu\text{-}P^tBu)_2P^tBu$	2.3577(7)			301 (av)	136
	2.3700(7)			302 (av)	
$(THF)_3Li(^tBu_3Si)AsGa(\mu\text{-}AsSiPr^i_3)_2Ga(Si^tBu_3)Li(THF)_3$	2.318(1)			343.2(3)	137
	2.436(1) ring			295.43(3)	
	2.473(1) ring			295.43(3)	
$Mes*In(\mu\text{-}PSi^iPr_3)_2InMes*$	2.493(2)-2.515(2)			341.09	135

[a] Tmp = 2,2,6,6-tetramethylpiperidinyl, Dmap = 4-dimethylaminopyridine, Cy = cyclohexyl, Dur = durene.

analogues,[97] and a chapter dealing with amido group 13 metal derivatives in a book on metal amide chemistry.[98]

The parent metal amides H_2MNH_2 (M = Al, Ga, or In) and related derivatives have been prepared by photolysis of Al, Ga, or In atoms and isolated in NH_3-doped frozen argon matrixes.[99−103] Although the species are unstable with respect to further reaction at higher temperatures, vibrational spectroscopy and DFT calculations provide benchmark stretching frequencies, bond lengths, and M−N rotational barriers because the data concern molecules that are essentially free of the potential structural distortions produced by bulky groups. The calculated structures afford planar molecules with M−N bond lengths of 1.7790 (Al), 1.8211 (Ga), and 1.9703 (Å, In) as well as M−N rotational barriers of 12.09, 15.7, and 12.3 kcal mol^{-1}.[99] These distances are marginally longer than the double bond lengths, 1.73, 1.77, and 1.96 Å, calculated from double bond radii.[60] It is noteworthy that the calculated rotational barrier for H_2GaNH_2 is highest, perhaps because the lower EN difference of this pair of atoms promotes better electron sharing and stronger π-bonding. A VT ^1H NMR study of $Me_2Ga\{N(Me)Mes*\}$, which afforded a rotation barrier of ca. 17 kcal mol^{-1}, tends to bear out this view.[124] Calculations on parent mono-, di-, and triamidoborane, alane, gallane, and indane and their silyl substituted congeners provided similar M−N bond lengths and showed that, although π-bonding plays a significant role in the structures of amido boranes, it is weak in the heavier group 13 congeners. The calculations also showed that negative hyperconjugative interactions are significant when the amido groups are rotated out of the metal coordination plane.[103]

Inspection of the structural data in Table 6 show that the bond lengths for the aluminum amido compound span the range 1.763(3)[106]−1.866 (4)Å,[110] which is very close to, but slightly expands, the 1.782(6)−1.847(4) Å limits previously known.[1] As before, the Ga−N bond lengths are generally slightly longer than those of the aluminum species.[98] A noteworthy feature of the gallium amide data is the first appearance of well-characterized low-coordinate Ga(I) amides where Ga−N π-interactions are a possibility.[111,112] Their Ga−N bond lengths are significantly longer than those of their Ga(III) counterparts, presumably because of the smaller ionic resonance contribution and the larger size of Ga^+ versus Ga^{3+}. The new indium amides listed in Table 6 feature In−N distances that are all in excess of 2.0 Å like the previously known indium amides.[1] The monomeric Tl(I) amide $TlN(Me)Ar^\#$, with a Tl−N distance of 2.364(3) Å, is also noteworthy. Its structure may be compared with the behavior of $TlN(SiMe_3)_2$, which has a dimeric structure in which two Tl^+ ions symmetrically bridge two $N(SiMe_3)_2$ ligands in the solid state but was shown by gas electron diffraction (ged) to have a monomeric structure in the vapor phase.[124]

The corresponding structurally characterized group 13 element derivatives of the heavier pnictogens are given in Table 7.[108,125−137] Most derivatives involve bonding to phosphorus. As in the previous review, the coordination geometry at the pnictogen in most instances is pyramidal owing to its larger inversion barrier which hinders conjugation of the lone pair. However, this barrier can be overcome by more extended delocalization or by electronic and steric effects. The latter are illustrated by the structure of

$^tBu_2PB(C_6F_5)_2$, which has a planar core structure and the shortest B−P bond (1.786(4) Å) recorded in a molecular species.[125] The planar geometry can be attributed to both the large ^{t}Bu substituents at phosphorus as well as the electron withdrawing C_6F_5 substituents on boron. The molecule also displays unusual reactivity in that it reacts directly with hydrogen under ambient conditions. Short B−P bonding is also observed in the formally doubly bonded (Tmp)BP^{t}Bu($AlBr_3$)[126] in which association is prevented by the coordination of the phosphorus lone pair to $AlBr_3$ and in (Tmp)(Dmap)BPAr*,[127] where association is blocked by coordination of Dmap to one of the boron p-orbitals. A short B−As distance 1.914(6) Å is also observed in the arsenic analogue of the latter (Tmp)(Dmap)BPAr*.[127] Planar coordination at phosphorus or arsenic is usually observed when these atoms are substituted by two BR_2[131] or AlR_2[108] groups whose delocalized backbone and orbital occupancy resembles those found in the allyl anion.

3.6. Compounds of Formula $R_2E{-}E'R$ and $[R_2E{-}E']^-$ (E = Group 13, E′ = Group 16 Element)

As is apparent from Table 8, relatively few structures of this class have published been since 1999.[138−146] The relative paucity of the recent structural data is borne out by a comprehensive review of gallium(III) and indium(III) alkoxides and aryloxides published in 2006.[147] As before, derivatives with bonding between the two light atoms boron and oxygen are not considered. However, the β-diketiminate complex $HC\{C(Me)N(C_6F_5)\}_2BO{\cdot}AlCl_3$, which features a very short, formally double, B−O bond length of 1.304(2) Å, is noteworthy.[148] The reported B−S distances for (η^5-C_5H_5)$(CO)_2$FeB(OMes)SPh, 1.848(4) Å,[138] and ($^tBu_2MeSi$)$_2$Si(μ−S)B(Tmp), 1.816(3) Å, lie above (the latter only technically) the previously known limit of 1.81(2) Å probably because of competitive π-bonding to the boron p-orbital in both molecules.[139] All the other B−E (E = S, Si, or Te) molecular structures published since 1999 involve boron as part of the delocalized ring and are thus beyond our scope.

The bond distances to the heavier group 13 metals lie within the previously known ranges. The data for indium aryloxides[145,146] had no precedent in the previous review, but the $O(M\{CH(SiMe_3)_2\}_2)_2$ (M = Ga or In)[145] data show that In−O distance is ca. 0.2 Å longer than that of Ga−O and is consistent with the difference in the radii of these atoms. The synthesis and crystal structure of $HC\{C(Me)N(CH_2CH_2NEt_2)\}_2AlO{\cdot}B(C_6F_5)_3$ is also noteworthy in that it is a base stabilized monoalumoxane that features four coordinate aluminums bound to three ligand nitrogens and oxygen.[149] The shortness of the Al−O bond (1.659(3) Å) is exceeded only by the average 1.648(7) Å seen in Al(OC_6H_2-2,6-^{t}Bu-4-Me)$_3$.[150]

3.7. Compounds of Formula $R_2E{=}ER_2$, $[L{:}\ddot{E}{=}\ddot{E}{:}L]$ and $[R\ddot{E}{=}\ddot{E}R]^{2-}$ (E = Group 14 Element)

Ever since the first experimental data on silenes (compounds having a silicon−carbon double bond) were published some 40 years ago, transient and stable species have been studied in great detail by both synthetic and computational methods. This very active area has been regularly reviewed in recent years.[3]

The first experimental evidence for a transiently formed silicon−carbon double bond was published by Gusel'nikov and Flowers in 1967.[151] Pyrolysis of 1,1-dimethyl-l-silacyclobutane resulted in the formation of 1,1-dimethylsilene as a transient intermediate. In 1981, Brook and co-workers succeeded in isolating $(Me_3Si)_2Si{=}C(OSiMe_3)$ (l-Ad), the first example of a silene that was stable at room temperature,[152] which was also characterized by X-ray crystallography.[153,154] $(Me_3Si)_2Si{=}C(OSiMe_3)$(l-Ad) had a Si=C bond distance of 1.764(4) Å and angular sums at silicon and carbon of 359.9 and 359.8°, indicating an essentially planar arrangements of the substituents of the double bond. The parent silene, $H_2C{=}SiH_2$, was isolated at 10 K in an Ar matrix.[155] Its structure was determined by Bailleux et al. by means of millimeter and submillimeter wave spectroscopy. The molecule had a planar geometry with C_{2v} symmetry and a bond distance of ca. 1.7039 Å was deduced from the spectra.[156,157] The Si=C bond stretching frequency was assigned to an absorption at 985 cm^{-1}, indicating a weaker bond than found for typical C=C systems. In silico methods revealed a π-bond strength for $H_2C{=}SiH_2$ of 37−54 kcal/mol, which compares to 65 kcal/mol found in ethylene[158] and thus is 43−17% weaker.[159−161] The $\pi{-}\pi^*$ transition observed at 258 nm in the UV spectrum[155] is bathochromically shifted by ca. 100 nm compared to ethylene,[162] indicating a smaller HOMO−LUMO gap. Moreover, the first ionization potential was determined at 8.9 eV,[163] which is significantly lower than the 10.5 eV for $H_2C{=}CH_2$.[164−166] On the basis of CCSD(T)/ccpV(Q,T)Z level calculations, a dipole moment of 0.693 D[167] with $H_2C^{\delta-}{=}SiH_2^{\delta+}$ polarization was estimated, a result which is in fair agreement with expectations based on electronegativities of silicon and carbon.

In comparison to $H_2Si{=}CH_2$, the Si=C bond length in 1,1-dimethyldisilene (1.6921 Å)[168] is shortened by ca. 0.012 Å, which can be rationalized on the basis of the higher

Table 8. Structural Data for Compounds of Formula $R_2E{-}E'R$ (E = Group 13, E′ = Group 16 Element) and Related Species (1999−2009, See ref 1 for earlier listings)

compd	M−E	M−E−C (deg)	ref
(η^5-C_3H_5)$(CO)_2$FeB(OMes)SPh	1.848(4)	107.8(2)	138
($^tBu_2MeSi$)$_2$Si(μ-S)B(Tmp)	1.816(3)		139
($^tBu_2MeSi$)$_2$Si(μ-Se)B(Tmp)	1.963(3)		139
MeAl{OC_6H_3-2,6(C_6H_3-2-^{i}Pr-5-Me)$_2$}$_2$	1.708(1), 1.716(1)	131.0(11), 132(1)	140
diphenylether-2,2′-bis(fencholato)-0,0′methyaluminum	1.70, 1.71		141
Mes_2*GaOH	1.783(2)	109.5	142
$\{(Me_3Si)_2CH\}_2GaOC_6F_5$	1.844(2)	130.8(2)	143
$(Me_3Si)_3$CGa(μ^2: $\eta^2O_2CC_6H_3$-3,5-Me_2)Ga(I)C$(SiMe_3)_2$	1.983(3)		144
$\{(Me_2Si)_2CH\}GaOGa\{CH(SiMe_3)_2\}_2$	1.785(5) av	142.7 (av)	145
(η^5-C_5Me_5(CO)$_2$FeIn(Mes*)OC_6H_4-4-^{t}Bu	2.091(4)	131.97(4)	146
$\{(Me_2Si)_2CH\}_2InOIn\{CH(SiMe_3)_2\}_2$	1.985(4) av	138.6(1)	145

electronegativity of the methyl carbon versus hydrogen. Electron withdrawing groups located at silicon result in an increase in bond polarity, which shortens the (polar) Si═C bond by increasing its ionic character.[169−173] Electronegative substituents on carbon, however, cause the opposite effect. Nevertheless, in accordance with the CGMT model for double bonded alkene-like compounds, an increase in the electronegativity of the silicon substituents should lead to greater pyramidalization at silicon to afford a *trans*-bent rather than planar geometry.[174] In the CGMT (Carter, Goddard, Malrieu and Trinquier) approach, multiple bond formation is rationalized on the basis of singlet−triplet energy gaps ΔE_{S-T} (doublet-quartet energy gap ΔE_{D-Q} for triple bonds) of the multiple bond fragments which control the extent of the interaction and the degree of *trans*-bending in the multiple bond. When the sum of σ- and π-bond energies, $E_{\sigma-\pi}$, exceeds $2\cdot\Delta E_{S-T}$, a planar structure is formed, whereas $E_{\sigma-\pi} < 2\cdot\Delta E_{S-T}$ results in the onset of *trans*-bending, but when $E_{\sigma-\pi} < \Delta E_{S-T}$, the fragments remain monomers. More detailed accounts of the CGMT bonding model are given in the earlier review[1] and in several others.[174−179] The singlet states of the multiple bond fragments (a carbene and silylene) are stabilized by π-donating and electronegative substituents stabilize the singlet states and *trans*-pyramidalization effects will dominate in these compounds. In contrast π-acceptor, electropositive, or bulky substituents tend to favor planar geometries in silenes.

The structures of at least 21 stable silenes have now been reported (Table 9). As mentioned above, the first example, $(Me_3Si)_2Si{=}C(OSiMe_3)(1\text{-}Ad)$, featured a long (1.764(4) Å) Si═C bond, with essentially planar geometries at the silicon and carbon atoms. There is also a torsion angle of 14.6° between the silicon and carbon coordination planes.[152,154] In this species, electron donating silyl groups coordinate the silicon atom of the double bond and more electronegative groups (oxygen and carbon) ligate the low valent carbon center. In addition, the Me_3SiO^- group acts as a π-donor. The related species, $Me_2Si{=}C(SiMe_3)(SiMe^tBu_2)$, also has essentially planar coordination geometry but exhibits a much shorter Si═C distance of 1.703(5) Å, owing to the fact that the alkyl substituents replace the Me_3Si groups at silicon and there is no π-donor ligand at carbon. The torsion angle along the silicon−carbon bond is only 1.6°.[180] A longer Si═C distance (1.741(2) Å) and small torsion angle (4.6°) was observed for $(Me_3Si)(^tBuMe_2Si)Si{=}(2\text{-}Ad)$. Quantum chemical calculations suggest that the elongation of the Si═C distance in $(Me_3Si)(^tBuMe_2Si)Si{=}(2\text{-}Ad)$ with respect to $Me_2Si{=}C(SiMe_3)(SiMe^tBu_2)$ was due to electronic effects rather than the consequences of larger steric congestion.[184]

An alternative to the stabilization of silenes by steric effects is provided via transfer of electron density from donor groups to silicon, which partially offsets the $Si^{\delta+}{=}C^{\delta-}$ polarization. The use of both intermolecular[196,197] and intramolecular donor ligands have led to isolable species.[198] In these, the Lewis-donor groups generally have little influence on the silicon carbon double bond distance, but both strong deviations from planar coordination at the silicon center and the onset of twisting along the central bond become apparent.

The structures of two cyclic silenes, a 1,2-disilacyclobut-2-ene and a 4-oxa-1,2- disilacyclobut-2-ene, have been reported. The Si═C bond length was 1.745(2) Å in the former species,[199] whereas the Si═C bond distance in the oxygen containing ring was lengthened to 1.775(2) Å.[190] The 1,2-disilacyclobut-2-ene exhibits moderate pyramidalization at the silicon (sum of angles 356.24°), in contrast to the oxygen containing homologue, which displays greater deviation from planarity with a sum of angles of 342.2°.

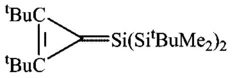
A higher degree of pyramidalization, i.e. *trans*-bending, was observed in several silenolates. In agreement with theoretical investigations,[200] the bond elongating π-donor effect of the oxygen substituent at carbon resulted in a Si−C bond distance of 1.926 Å in $(Me_3Si)_2Si{=}C^tBu(OK)$.[201] This is somewhat longer than the average Si−C single bond distance which falls in the range 1.87−1.91 Å. The sum of angles at silicon in $(Me_3Si)_2Si{=}C^tBu(OK)$ is 317.8°. The X-ray crystal structure analysis revealed the potassium to be in a bridging position between the oxygen (d K−O: 2.846 Å) and silicon (Si−K = 3.714 Å) atoms. As a consequence, this species can also be described as an acyl substituted silyl anion, $(Me_3Si)_2KSi\text{-}C({=}O)^tBu$.[201] The related lithium derivatives $(^tBuMe_2Si)_2Si{=}C(1\text{-}Ad)(OLi)$ and $(^tBu_2MeSi)_2Si{=}C(1\text{-}Ad)(OLi)$, which display different degrees of aggregation in the solid state, had shorter Si═C distances (1.822(7) Å and 1.81(2), respectively) and planar coordination around silicon and carbon and are thus rather enol- than keto-like.[192] A silene bearing a silyl anion attached to the double bonded silicon, $[(^tBu_2MeSi)_2LiSi](^tBu_2MeSiO)Si{=}(2\text{-}Ad)$, was reported by Sekiguchi and co-workers. The coordination geometries are essentially planar with a Si═C distance of 1.743(2) Å.[188]

Species that can be formally regarded as silenes can also be obtained by the reaction of stable silylenes with carbenes. For example, reaction of a benzannulated N-heterocyclic carbene and benzannulated N-heterocyclic silylene afforded a weakly associated donor−acceptor complex $C_6H_4\text{-}1,2\text{-}\{N(CH_2{}^tBu)_2\}Si{=}C\{N(CH_2{}^tBu)_2\}\text{-}1,2\text{-}C_6H_4$,[190] which had a long bond distance (2.162(5) Å) and a high degree of pyramidalization at the silicon atom (sum of angles 291.4°) and more planar coordination around the carbon center with a sum of angles of 351.4°. The structure is also highly twisted, hence the formation of a π-bond can be ruled out. Moreover, at elevated temperatures, NMR spectroscopy indicated dissociation to the free carbene and silylene.[202] A mercury substituted bis(silene) was obtained from the reaction of a dilithiated bis(silyl)mercury species with adamantoyl chloride via 2-fold Brook rearrangement. $(1\text{-}Ad)(^iPr_3Si)C{=}Si(^iPr_3Si)HgSi(^iPr_3Si){=}C(^iPr_3Si)(1\text{-}Ad)$ is both the only silene which is metal-substituted at one of the low coordinate centers and the only bis(silene) structurally characterized to date. The coordination of the doubly bonded silicons was essentially planar, with Si═C bond distances of 1.770(8) and 1.758(8) Å.[203]

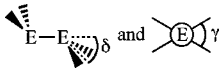
The first structural characterization of a silaallene was reported in 1993 by West and co-workers.[194] In the solid state, a short Si═C distance of 1.704(4) Å and C═C distance of 1.324(5) Å were observed. The Si═C═C array has an almost linear geometry with an Si═C═C angle of 173.5°, the geometry at silicon is almost planar. Three additional examples of silaallenes were reported by the same group. Among these, $Trip_2Si{=}C{=}CPh(^tBu)$ showed the shortest Si═C bond (1.693(4) Å),[193] hence being even shorter than the distance in $Me_2Si{=}C(SiMe_3)(Si^tBu_2Me)$. The shortening of the Si═C bond was attributed to bonding of sp^2-hybridized silicon orbital with a sp-orbital of the central carbon.

After initial reports on isolable silaketenimines,[204,205] X-ray crystallographic data for two further silaketenimines, $1,1,4,4\text{-}(Me_3Si)_4\text{-}1,4\text{-}[C(CH_2)_2C]Si{=}C{=}NR$ (R = Dipp, 1-Ad) (Fig-

Table 9. Selected Structural Data for Silenes $R_2Si{=}CR'_2$[a]

Compound	C-Si (Å)	δ (deg)	γ (deg)	Ref
Silenes				
$Me_2Si{=}C(SiMe_3)(Si^tBu_2Me)$	1.703(5)	1.3/1.0	1.6	180
$(Me_3Si)_2Si{=}C(1\text{-}Ad)(OSiMe_3)$	1.764(4)	3.7/5.2	14.4	154,181
$Me_2EtN{\cdot}Me_2Si{=}C(SiMe_2Ph)_2$	1.758(4)	38.7/8.8	31.0	182
$Ph(2,6\text{-}Et_2NCH_2\text{-}C_6H_3)Si{=}C(SiMe_3)_2$	1.743(3)	30.1/7.5	19.8	183
$(Me_3Si)(2,6\text{-}Et_2NCH_2\text{-}C_6H_3)Si{=}C(SiMe_3)_2$	1.764(2)	33.1/6.8	27.9	183
$(^tBuMe_2Si)(Me_3Si)Si{=}C(2\text{-}Ad)$	1.741(2)	5.4/2.6	1.7	184
$(Me_3Si)(8\text{-}Me_2N\text{-}Np)Si{=}C(SiMe_3)_2$	1.751(3)	32.8/10.5	30.8	185
$(Me_3Si)(2\text{-}Me_2N\text{-}C_6H_4)Si{=}C(SiMe_3)_2$	1.748(3)	35.8/8.0	30.2	186
$(Me_3Si)\{2,6\text{-}(Me_2N)_2\text{-}C_6H_4\}Si{=}C(SiMe_3)_2$	1.759(4)	39.9/1.2	22.1	187
$\{(1\text{-}Ad)(^iPr_3Si\}C{=}Si(Si^iPr_3)\}Hg$	1.76(1)	9.1/3.7	22.1	203
$(Me_3Si)_2Si{=}C^tBu(OK)$	1.926(3)	62.8/7.3	24.3	201
$R_2LiSi(RO)Si{=}(2\text{-}Ad)$, $R{=}^tBu_2MeSi$	1.743(2)	15.4/4.5	3.7	188
$(^tBu_3Si)\overline{Si{=}C(1\text{-}Ad)Si}(Si^tBu_3)_2$	1.745(2)			189
$\overline{TripSi{=}C(1\text{-}Ad)OSi}Trip_2$	1.775(2)			189
$C_6H_4\text{-}1,2\text{-}\{N(CH_2{}^tBu)_2\}Si{=}C\{N(CH_2{}^tBu)_2\}\text{-}1$	2.162(5)	51.9	71/28	190
	1.755(2)	6.5/2.6	1.6	191
$(^tBuMe_2Si)_2Si{=}C(1\text{-}Ad)(OLi)$	1.822(7)			192
$(^tBu_2MeSi)_2Si{=}C(1\text{-}Ad)(OLi)$	1.81(2)			192
Silaallenes	C-Si [Å]	δ (deg)	Si=C=C (deg)	
$Trip_2Si{=}C{=}CPh(^tBu)$	1.693(4)	17.1	172.0	193
$(1\text{-}Ad)Mes^*Si{=}C{=}fluorenyl\text{-}\{3,5,10,12\text{-}^iPr\text{-}4,11\text{-}(MeO)_2\}$	1.704(4)	1.3	174.5	194
Silaketenimines	Si-C [Å]	δ (deg)	Si=C=N (deg)	
$(Me_3Si)_2\overline{CCH_2CH_2C(SiMe_3)_2Si}{=}C{=}N\text{-}Dipp$	1.794(3)	49.5	164.8	195
$(Me_3Si)_2\overline{CCH_2CH_2C(SiMe_3)_2Si}{=}C{=}N\text{-}(1\text{-}Ad)$	1.782(2)	48.3	163.1	195

[a] The angles δ and γ are represented as



ure 4), have been published during the past decade by Kira and co-workers. In contrast to silaallenes, these compounds are characterized by long Si=C distances of 1.794(3) and 1.782(2) Å, respectively. The silicon geometries are highly pyramidalized with a sum of angles of ca. 331° in both cases, suggesting donor−acceptor complex rather than conventional multiple bonding.[195] Currently, silaketenes, $R_2Si{=}C{=}O$, have only been investigated by means of matrix isolation spectroscopy in combination with computational methods.[206−208] Experimental and calculated data suggest a sum of angles around silicon as small as ca. 277°, indicating a highly pyramidalized silicon geometry.[206]

The structural chemistry of the heavier homologues of silenes, i.e. compounds with Ge=C, Sn=C, or Pb=C bonds, remains much less developed. In 1997, bis(dialkylamino)cyclopropylidene adducts of germanium, tin, and lead bis(bis(trimethylsilyl)amides), i.e. compounds with a formal C−E (E = Ge, Sn, Pb) double bond, were reported by Schumann, Hahn, and co-workers.[209] These exhibited *trans*-bent structures consistent with donor−acceptor bonding, with increas-

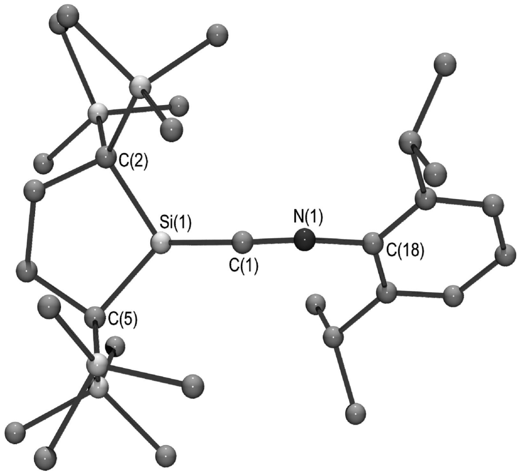


Figure 4. Molecular structure of 1,1,4,4-$(Me_3Si)_4$-1,4-$[C(CH_2)_2C]$-$Si{=}C{=}NC_6H_3$-2,6-$^iPr_2$ (hydrogen atoms are not shown). Selected bond distances (Å) and angles (deg): Si(1)−C(1) 1.794(3), C(1)−N(1) 1.203(4), N(1)−C(18) 1.406(4), Si(1)−C(2) 1.911(3), Si(1)−C(5) 1.915(3); Si(1)−C(1)−N(1) 164.8(2), C(1)−N(1)−C(18) 146.3(3), C(1)−Si(1)−C(2) 113.4(1), C(1)−Si(1)−C(5) 116.9(1), C(2)−Si(1)−C(5) 100.3 (1).[195]

ing pyramidalization of the heavier group 14 center upon descending the group (Table 10). All of them exhibit long C═E bond distances (E−Ge, 2.085(3) Å; E−Sn, 2.303(9) Å; E−Pb, 2.423(8) Å) that exceed those of the respective element−carbon single bonds and a torsion angle of ca. 90° around the C−E bond.[209] Comparable bonding was observed for N-heterocyclic carbene complexes of GeI_2[210] and SnR_2.[211,212]

Ever since the groundbreaking synthesis of the first stable, doubly bonded silicon−silicon compound, $Mes_2SiSiMes_2$, in 1981 by West and co-workers, the chemistry of disilenes has remained at the center of attention in heavier main group element chemistry. Currently, the crystal structures of at least 73 stable disilenes have been reported, with bond distances ranging from 2.132(2) Å for $RSi{=}SiRSiRSiR_3$, R = $^tBuMe_2Si$, to as long as 2.360(2) Å for $RSi{=}SiRSiHRSiHR$, R = $^tBu_3Si$. In general, the Si−Si distances in silenes are considerably shorter than silicon−silicon single bonds, which are typically ca. 2.34 Å. In comparison to carbenes, which usually feature a triplet ground state, almost all the silylenes, which are the constituents of disilenes, have a singlet ground state associated with a large singlet−triplet energy difference.

Table 10. Selected Structural Data for Heavy Alkenes $R_2E{=}CR'_2$ (E = Ge, Sn, Pb) and Related Species[a]

compd	E═C (Å)	δ (deg)	γ (deg)	ref
Germenes				
$\{(Me_3Si)_2N\}_2Ge{=}CB^tBuC(SiMe_3)_2B^tBu$	1.826(5)	1.9/4.9	39.6/31.7	213
$Mes_2Ge{=}$(9-fluorene)	1.806(3)	3.3/1.5	4.5/8.9	214
$Ar_2Ge{=}C(^nBu)C{\equiv}CC(^nBu){=}GeAr_2$ Ar=2-^{t}Bu-4,5,6-Me_3-C_6H	1.818(2)	3.0/2.5	2.8	215
$Ar_2Ge{=}C(Ph)CCC(Ph){=}GeAr_2$ Ar=2-^{t}Bu-4,5,6-Me_3-C_6H	1.841(4)	1.3/3.2	2.4	216
$\{(Me_3Si)_2N\}_2Ge{=}CC(N^iPr_2){=}C(N^iPr_2)$	2.085(3)	75.6/11.6	64.6/25.1	209
$Ar_2Ge{=}CB^tBuC(SiMe_3)_2B^tBu$ Ar=2-^{t}Bu-4,5,6-Me_3-C_6H	1.85(1)	0/0	23.0	217
$Ar_2Ge{=}C(Me)CCC(Me){=}GeAr_2$ Ar=2-^{t}Bu-4,5,6-Me_3-C_6H	1.819(6)	1.0/4.5	0.6	218
$Ar_2Ge{=}C^tBuPP{=}C(^tBu)GeAr_2$ Ar=2-^{t}Bu-4,5,6-Me_3-C_6H	1.832(3)	4/16.2	13.2/26.4	219
TbtTrip Ge═CSGeTbtTripS	1.77(2)	9.5/7.3	2.7	220
Germaallene				
$Trip_2Ge{=}C{=}CPh^tBu$	1.783(2)	23.4	159.2(1)	221
Stannenes				
$\{(Me_3Si)_2CH\}_2Sn{=}CB^tBuC(SiMe_3)_2B^tBu$	2.025(3)	5.4/15.7	47.9/73.8	222
$Ar_2Sn{=}CB^tBuC(SiMe_3)_2B^tBu$ Ar=2-^{t}Bu-4,5,6-Me_3-C_6H	2.031(5)	4.8/4.5	43.8/29.2	223
$Ar\{(Me_3Si)_3Si\}Sn{=}CB^tBuC(SiMe_3)_2B^tBu$ Ar=2-^{t}Bu-4,5,6-Me_3-C_6H	2.032(2)	32.2/9.7	10.7/12.9	217
TbtMesSn═(9-fluorene)	2.015(5)	8.8/3.0	29.3	224
$\{(Me_3Si)_2N\}_2Sn{=}CC(N^iPr_2){=}C(N^iPr_2)$	2.303(9)	81.3/13.2	55.0/25.7	209
$Trip_2Sn{=}CC(N^iPr_2){=}C(N^iPr_2)$	2.379(4)	71.6/14.7	44.7/83.9	211
$Trip_2Sn{=}$(2,7-$^tBu_2$-9-fluorene)	2.003(5)	1.9/1.4	10.0	225
Stannaketenimines				
$\{C_6H_2$-2,4,6-$(CF_3)_3\}_2Sn{=}C{=}N$-Mes	2.397(3)	83.5	153.9(2)	226
Plumbenes				
$\{(Me_3Si)_2N\}_2Pb{=}CC(N^iPr_2){=}C(N^iPr_2)$	2.423(8)	83.9/7.3	81.5/12.9	209
$Trip_2Pb{=}CC(N^iPr_2){=}C(N^iPr_2)$	2.540(5)			227

[a] The angles δ and γ are represented as

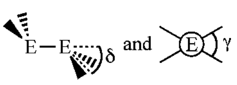
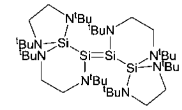
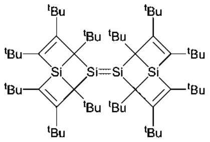
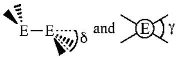


Table 11. Selected Structural Data for Disilenes $R_2Si{=}SiR_2$ and Some Related Si=Si Double-Bonded Species[a]

Compound	Si-Si (Å)	δ (deg)	γ (deg)	Ref
{Si(Mes)$_2$}$_2$	2.1433(2)	12	3	233
{Si(Mes)$_2$}$_2$	2.147(3)	0	13	234
{Si(Mes)$_2$}$_2$	2.169(1)	20.8	6.5	235
{Si(Trip)$_2$}$_2$	2.145(6)	2.0	1.6	236
Trip$_2$Si=SiTripPh	2.174(1) av	23.0/ 23.2 avg.	1.0 avg.	237
1,4-{Trip$_2$Si=SiTrip}$_2$C$_6$H$_4$	2.1673(9)	22.6/ 19.7	0.7	237
Trip$_2$Si=SiTripLi·2DME	2.1919(6)	18.9/26.9	7.4	238
(*E*)-[{(Me$_3$Si)$_2$N}Cp*Si]$_2$	2.1683(4)	8.5	4.4	239
{Dep$_2$Si}$_2$	2.1403(3)	4.0	10.6	240
(*E*)-{^{t}BuMesSi}	2.1432(5)	0	0	235
[{^{t}Bu$_2$MeSi}$_2$Si=SiMes]$_2$	2.199(1) av	2.3/8.6	11.5	241
{^{t}Bu$_2$MeSi}$_2$Si=SiMesLi·3THF	2.2092(6)	6.8/6.2	7.0	241
{^{t}Bu$_2$MeSi}$_2$Si=Si{^{i}Pr$_2$MeSi}$_2$	2.196(1) av	0	10.3	242
{^{t}BuMe$_2$Si}$_2$Si=Si{iPr$_3$Si}$_2$	2.201(1)	0	28.0	242
(*E*)-{TbtTripSi}$_2$	2.229(3)	13.5	8.8	243
(*E*)-{(1-Ad)MesSi}$_2$	2.138(2)	2.9	0	244
(*E*)-{Trip(Me$_3$Si)Si}$_2$	2.153(2)	2.2	0	245
(*E*)-{Trip(^{t}Bu)Si}$_2$	2.156(2)	2.5	0	245
{^{t}Bu$_2$MeSi}$_2$Si=SiTripK·DME	2.211(1)	7.0/9.0	9.4	246
(E)-[{(^{t}Bu$_3$Si)$_2$MeSi}$_2$ClSi]$_2$	2.163(3)	7.4	0	247
(*E*)-{(^{t}Bu$_3$Si)PhSi}$_2$	2.181(1)	8.2	0	248
{Trip$_2$Si=SiTrip}$_2$	2.175(2)	8.2/1.8	19.2	249
RMeSi=SiRSiMeR$_2$ R=^{t}BuMe$_2$Si	2.1984(5)	6.6/5.0	31.22	250
(*E*)-{(^{t}BuMe$_2$Si)(^{i}Pr$_2$MeSi)Si}$_2$	2.196(1)	0.8	0	251
{(^{t}Bu$_2$MeSi)$_2$Si}$_2$	2.260(2)	7.2	55.8	252
R$_2$^{i}PrSiSi(H)=Si(Li)SiR$_2$^{i}Pr R=(Me$_3$Si)$_2$CH	2.203(1)	0	2.1	253
{EindPhSi}$_2$ *	2.159(1)	3.1	0	254
1,4-{EindPhSiSiEind}$_2$C$_6$H$_4$ *	2.156(2)	3.0/0.9	2.2	254
{(^{i}Pr$_2$MeSi)$_2$Si}$_2$	2.226(4)	6.6	0	255
{(^{t}BuMe$_2$Si)$_2$Si}$_2$	2.2006(4)	0	8.9	255
{(^{i}Pr$_3$Si)$_2$Si}$_2$	2.252(2)	12.8	0	255
Trip$_2$Si=SiTripCp$_2$ZrCl	2.2144(8)	5.8/8.6	20.2	256
(^{t}BuMe$_2$Si)$_2$Si=Si(^{t}BuMe$_2$Si)Li·2THF	2.198(2)	0	0	257
{(Trip$_2$ClSi)TripSi}$_2$	2.215(1)	0.4	23.6	258
(*Z*)-{TbtMesSi}$_2$	2.196(4)	9.2	14.4	259
Trip$_2$Si=SiTrip(SiPh$_2$Cl)	2.180(1) av	4.8-20.8	8.7-14.1	260
Trip$_2$BrSiSi(Trip)=Si(Trip)SiTrip$_2$H	2.209(1)	0.6/0.8	26.8	258
RSi=SiGeMeRGeMeR R=Si^{t}Bu$_2$Me	2.191(2) av			261
RSi=SiCH$_2$CH$_2$ R=(^{t}Bu$_3$Si)$_2$MeSi	2.175(1)			262
R$_2$CCH$_2$CH$_2$CRCSiMe$_2$Si=SiCRSiMe$_2$CH$_2$CH$_2$CR$_2$ R=SiMe$_3$	2.2689(8)			263
cis-R$_2$C(CH$_2$)$_2$CRCSiMe$_2$Si=SiCRSiMe$_2$(CH$_2$)$_2$CR$_2$ R=SiMe$_3$	2.1768(7)			263
trans-R$_2$C(CH$_2$)$_2$CRCSiMe$_2$Si=SiCRSiMe$_2$(CH$_2$)$_2$CR$_2$ R=SiMe$_3$	2.208(1)			264
R$_2$CCH$_2$CH$_2$CR$_2$SiSiSiR=SiR R=SiMe$_3$	2.1428(5)			264
RSi=SiRSiR$_2$ R=^{t}Bu$_2$MeSi	2.138(3)			265
RSi=SiRSiRISiRI R=^{t}Bu$_3$Si	2.257(2)			266
RSi=SiRSiRSiR$_3$ R=^{t}BuMe$_2$Si	2.132(2)			267
RSi=SiRSiR'$_2$ R=^{t}Bu$_3$Si, R'=^{t}Bu$_2$MeSi	2.161(1)			268
RSi=SiRCHMeCHMe R={(Me$_3$Si)$_2$CH}$_2$^{i}PrSi	2.163(1)			269
TripSi=SiTripSiTrip$_2$Mg·2THF	2.1975(8)			270
RSi=SiR^{t}Bu$_2$SiRLi R=^{t}Bu$_2$MeSi	2.2244(6)			271
	2.360(2)			272
TripSi=SiTripSiTrip$_2$SiTrip$_2$S	2.173/1)			273
TripSi=SiTripSiTrip$_2$SiTrip$_2$Se	2.181(1)			273
TripSi=SiTripSiTrip$_2$SiTrip$_2$Te	2.198(2)			273
RSi=SiRSiSi=SiR R=(^{t}Bu$_2$MeSi)$_2$Si	2.186(3)			274
R$_2$SiSiMe$_2$SiR$_2$Si=SiSiR$_2$SiMe$_2$SiR$_2$ R=SiMe$_3$	2.180(2)			275
RSi=SiRSiR$_2$SiR$_2$ R=^{t}Bu$_2$MeSi	2.174(3)			276
RSi=SiRGeR$_2$ R=^{t}Bu$_2$MeSi	2.146(2)			277
RSi=SiRSiR$_2$Se R=^{t}Bu$_2$MeSi	2.171(1)			278
	2.289(1)			279
	2.2621(9)			280
Sila-allene				
R$_2$CCH$_2$CH$_2$CR$_2$Si=Si=SiCR$_2$CH$_2$CH$_2$CR$_2$ R=SiMe$_3$	2.166(2)			281

[a] The angles δ and γ are represented as



*Eind = 1,1,3,3,5,5,7,7-Et$_8$-s-hydrindacen-4-yl.

This frequently induces a *trans*-pyramidal structure in the disilene. The trend in singlet−triplet energy gaps ($\Delta E_{S-T} = E_{triplet} - E_{singlet}$) for the series H_2E: (E = C, Si, Ge, Sn, Pb) was investigated by Trinquier and co-workers on the basis of ab initio calculations. A negative ΔE_{S-T} of −14 kcal/mol was calculated only for carbene, H_2C:, but for all other tetrylenes increasingly positive values were obtained, indicating singlet ground states for all heavier carbene homologues, i.e. 16.7 kcal/mol (E = Si), 21.8 kcal/mol (E = Ge), 24.8 kcal/mol (E = Sn), and 34.8 kcal/mol for E = Pb.[228] Recently, the bis(triorganosilyl)silylenes, (R = $\mathrm{Si^iP_{R_3}}$ or $\mathrm{Si^tBu_3}$), the first examples of silylenes with triplet ground states were reported.[229−232]

Singlet tetrylene fragments become increasingly stable upon descending the group with respect to the dimeric forms [$R_2E{=}ER_2$], due to progressively weaker bonding in the respective dimers (Table 11). According to CGMT theory,[174−179] this often makes *trans*-pyramidal geometries for disilenes energetically more likely than the planar arrangements typically found for their carbon congeners. Nevertheless, of all of the homonuclear heavier congeners of alkenes, disilenes exhibit the smallest degrees of *trans*-bending and torsion angles, which is indicative of relatively strong double bonding.

In addition to derivatives with the $R_2Si{=}SiR_2$ formulation, trisilacyclopropenes,[265,268,269] tetrasilacyclobutenes,[267,272,273,277] a trisilaallene,[281] and a pentasilaspiropentadiene[274] have been isolated and characterized by X- ray crystallography.[4y,282−284]

The trisila-allene in Figure 5 is characterized by short Si−Si distances of 2.179(3) and 2.206(3) Å and, in contrast to the lighter homologues which display a strictly linear arrangement of the C=C=C array, a bent trisila array (Si=Si=Si 137.2(1)°). The substituents at the outer silicons adopt an almost perpendicular orientation with respect to each other.[281] In addition to the trisila-allene, structurally related 1,3-disila-2-germa-, 1,3-digerma-2-sila-, and trigerma-allenes were prepared.[285,286,320] Among these, the two isomers with a silicon atom in the central position display temperature dependent dynamic disorder as indicated in Figure 5. From the temperature dependent data, the relative energies of the four isomers were calculated to be separated by about 1.4 kcal/mol.[287] The description of the bonding in these com-

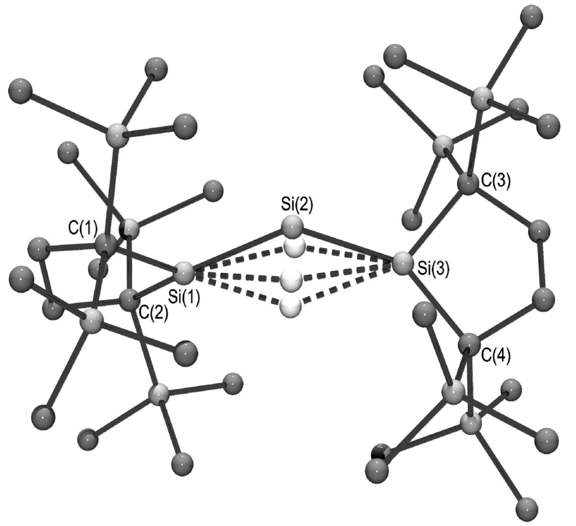


Figure 5. Molecular structure of a trisila-allene. Si(2) was found to be disordered over four positions in the solid state (see text); (hydrogen atoms are not shown). Selected bond distances (Å) and angles (deg): Si(1)−Si(2) 2.179(3), Si(2)−Si(3) 2.206(3), C(1)−Si(1) 1.898(4), C(2)−Si(1) 1.895(4), C(3)−Si(3) 1.896(3), C4−Si(3) 1.900(4); Si(1)−Si(2)−Si(3) 137.2(1), C(1)−Si(1)−C(2) 100.1(2), C(1)−Si(1)−Si(2) 116.1(4), C(2)−Si(1)−Si(2) 138.6(1), C(3)−Si(3)−Si(2) 111.4(3), C(3)−Si(3)−C(4) 99.9(2), C(4)−Si(3)−Si(2) 142.9(3).[281]

pounds either as bent and twisted, heavy allenes or as tetrylene substituted, divalent central E(0) species is a matter of considerable debate.[288−291]

Tetrasilacyclobutenes have a typical Si−Si double bond distance of about 2.17 Å with planar coordination at the low coordinate silicon centers. Because of their intrinsic strain, they have a tendency to undergo photochemically induced rearrangements to yield bicyclo[1.1.0]butane derivatives. Similar rearrangements have also been observed for trisilacyclopropenes. On the other hand, the retrocyclization, i.e. the thermal conversion of bicyclo[1.1.0]butanes into unsaturated three-[292,277] and four-membered[276,293] silicon rings, has also been described. More recently, these rearrangement reactions were extended to chalcogen containing systems.[280]

The pentaspiropentadiene RSi═SiRSiSi═SiR, R = (^{t}Bu$_2$MeSi)$_2$Si, is also noteworthy because of the possible spiro conjugation of the parent carbon compound, spiropentadiene. The carbon homologues have only been studied in solution, however. In the pentasilaspiropentadiene, the trisilacyclopropene rings are not exactly perpendicular to each other but enclose an angle of 78.3°. Moreover, the exocyclic substituents adopt a *trans*-conformation with respect to each other, giving raise to a local D_2 rather than D_{2d} symmetry. As a consequence, two degenerate π(e) orbitals in D_{2d} symmetry are split into π(b$_2$) and π(b$_2$) orbitals. The observation of four $\pi-\pi^*$ transitions in UV−vis spectra support this interpretation.[275]

The chemistry of disilenides, i.e. the heavier congeners of vinyl anions, stems from the discovery by Weidenbruch and co-workers that treatment of Trip$_2$Si═SiTrip$_2$[236] with lithium in Dme results in the reductive cleavage of a silicon−aryl bond under formation of Trip$_2$Si═SiTripLi.[249] More recently, considerable progress has been made in the chemistry of this class of compounds. A convenient access to Trip$_2$Si═SiTripLi and its solid state structure were recently reported.[238] In this, the Si═Si distance was 2.1919(6) Å, about 0.048 Å longer than that in the parent Trip$_2$Si═SiTrip$_2$ (2.145(6) Å) (Figure 6). Other examples of alkali metal substituted disilenes are (^{t}Bu$_2$MeSi)$_2$Si═SiMesLi (Si═Si = 2.2092(6) Å),[241] (^{t}Bu$_2$MeSi)$_2$Si═Si(^{t}Bu$_2$MeSi)M (M = Li, Na,K)(dSi═Si:2.198(2)ÅforM═Li),[257]orthe[Me$_2$^{i}PrSi]HSi═Si[{(Me$_3$Si)$_2$CH}$_2$^{i}PrSi]$_2$Li (d Si═Si: 2.2034 Å).[253] The cyclic magnesium salt of a 1,3-trisilene-diide, [Trip$_2$Si-TripSi═SiTrip$_2$]$^{2-}$ displayed Si−Si distances of 2.198 Å (Si═Si) and 2.362 Å (Si−Si), respectively, indicating a strong localization of the negative charges on both terminal silicons rather than delocalization over Si$_3$ framework.[271] In the related zirconocene derivative Trip$_2$Si═SiTripZrCp$_2$Cl, the silicon−silicon bond lengthens to 2.2144(8) Å. Although the geometries around the silicon atoms are almost planar, there is a large torsion angle (20.2°) such that the π-bond is weakened and is thus more likely to undergo further reactions due to twisting. As a consequence, Trip$_2$Si═SiTripZrCp$_2$Cl undergoes C−H activation by insertion of the disilene unit into a ligand *iso*-propyl group.[256] In contrast, alkali metal substituted disilenides display somewhat longer Si═Si distances but have planar structures with little or no *trans*-bending and twisting. Similaraly, alkali metal fluoride adducts of disilenes and digermenes displayed elongated E−E distances.[294,295] Dialkoxy-boryl substituted disilenes exhibited no delocalization of π-electron density into the empty boron orbital as evidenced by a perpendicular arrangement of the disilene and boryl units in the solid state and, additionally, from UV−vis spectra.[296]

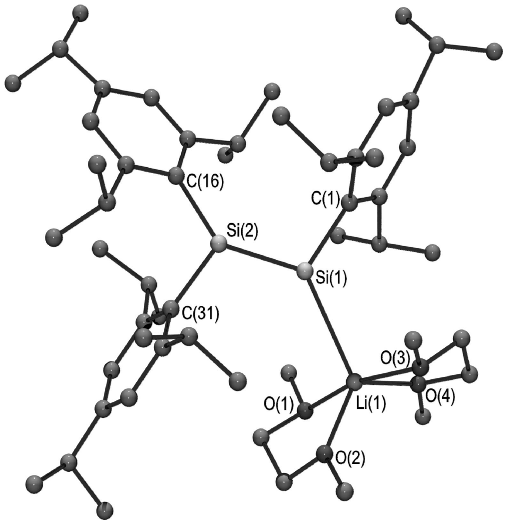


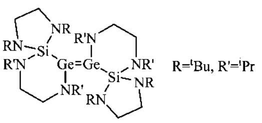
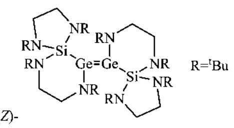
Figure 6. Molecular structure of Trip$_2$Si═SiTripLi·Dme$_2$ (hydrogen atoms are not shown). Selected bond distances (Å) and angles (deg): Si(1)−Si(2) 2.1919(6), Si(1)−Li(1) 2.853(3), Si(1)−C(1) 1.931(2), Si(2)−C(16) 1.915(2), Si(2)−C(31) 1.905(2); C(1)−Si(1)−Si(2) 107.58(5), Li(1)−Si(1)−Si(2) 131.73(6), C(1)−Si(1)−Li(1) 118.97(7), Si(1)−Si(2)−C(16) 140.33(5), Si(1)−Si(2)−C(31) 111.03(4), C16−Si(2)-C(31) 108.20(6).[238]

The discovery of disilenides provided useful synthons for the generation of a rich variety of compounds with silicon−silicon and silicon−carbon double bonds. This active field of research has recently been reviewed.[4d,j] As initially shown by Weidenbruch and co-workers, reaction of Trip$_2$Si═SiTripLi with mesityl bromide provided the first example of a tetrasila-1,3-butadiene, {Trip$_2$Si═SiTrip}$_2$.[249] In this, the Si═Si double bond distance was 2.175(2) Å, longer compared to the 2.145(6) Å in Trip$_2$Si═SiTrip$_2$[236] but shorter than that in Trip$_2$Si═SiTripLi (2.1919(6) Å).[238] The short Si−Si single bond distance (2.321(1) Å) and a bathochromically shifted UV−vis maximum at $\lambda_{\max} = 518$ nm (Trip$_2$Si═SiTrip$_2$ $\lambda_{\max} = 432$ nm) suggest electronic delocalization, a finding which was further corroborated by theoretical investigations.[297−299] A second example of a tetrasilabutadiene is given by $\{(^tBu_2Me_2)_2Si{=}SiMes\}_2$, which also featured long (2.198(2)) and 2.200(1) Å) double bond distances and a shorter (2.338(1) Å) single bond,[241] thus supports a degree of electron delocalization in tetrasilabutadienes. $Trip_2Si{=}SiTripLi$ was also the starting point for the synthesis of an isomer of hexasilabenzene, $Trip_2SiSiTripSiSiTrip_2SiTripSi$.[300]

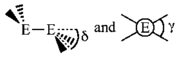
The first X-ray crystallographic data on digermenes were published in 1984 by the groups of Lappert and Masamune.[301,302] Similar to the iconic distannene (see below), Lappert's germanium analogue $[\{(Me_3Si)_2CH\}_2Ge]_2$ has a *trans*-bent structure ($\delta = 32°$) but has no twisting along the Ge−Ge axis. The tetrel atoms were separated by a bond distance of 2.3458(7) Å. In Masamune's $[Dep_2Ge]_2$, the Ge−Ge distance was a short 2.212(3) Å, and there were modest *trans*-bending angle of 12.4° and a 10.8° torsion angle along the central bond. Nevertheless, both Ge−Ge distances are shorter than the sum covalent radii for germanium (ca. 2.44 Å). In contrast to disilenes, where planar or almost planar structures prevail, digermenes tend to show larger *trans*-bending angles in full agreement with a higher energy gap between s- and p-orbitals and lower tendency to hybridize. In sharp contrast to disilenes, in which the Si−Si bond generally remains intact in solution, most digermenes dissociate in solution or show a monomer/dimer equilibrium upon dissolution. Digermenes for which 1,2-addition reactions afforded Ge−Ge bonded products, e.g. $[Dep_2Ge]_2$,[302,307] $[Trip_2Ge]_2$,[307] or $[Mes_2Ge]_2$,[305] suggest retention of a dimeric structure in solution. The structure of the lithium substituted digermene $\{(1,4\text{-dioxane})Et_2OLi_2Ar^\#GeGeAr^\#\}_n$ ($Ar^\# = C_6H_3$-2,6-(C_6H_2-2,4,6-$Me_3)_2$) is unique in that in has a planar $Li_2Ge_2\{C_{ipso}\}_2$ core.[315]

Further weakening to the tetrel−tetrel multiple bond is apparent in the properties of distannenes. Almost all compounds with a formal tin−tin double bond in the solid state dissociate in solution. An important exception is $[(^tBu_2MeSi)_2Sn]_2$. It displayed almost planar coordination at the tins but had a high torsion angle between the tin coordination planes in the solid state. It also featured, with

Table 12. Selected Structural Data for Symmetric and Unsymmetric Heavier Main Group 14 Element Alkene Congeners $R_2E{=}E'R_2$ (E = Ge, Sn, Pb) and Related Species[a]

Compound	Ge-Ge (Å)	δ (deg)	γ (deg)	Ref
Digermenes				
$[\{(Me_3Si)_2CH\}Ge]_2$	2.3458(7)	32.7	0	301
$[GeDep_2]_2$	2.212(3)	12.4	10.8	302
$[GeAr'H]_2$	2.3025(8)	45.0	0	303
$[GeAr^*H]_2$	2.3724(9)	20.5	0	304
$[GeMes_2]_2$	2.2855(7)	23.4	10.2	305
(*Z*)-$[GeMesDipp]_2$	2.3011(9)	36.3	3.4	306
$[GeTrip_2]_2$	2.2130(9)	20.7	1.6	307,308
$[GeAr^*Me]_2$	2.316(2)	39.7	0	309
$[GeAr^*Et]_2$	2.347(2)	37.9	0	309
$[GeAr^*Ph]_2$	2.318(3)	33.6	0	309
$[GeAr^*Cl]_2$	2.363(2)	38.9	0	309
$[GeBbtBr]_2$	2.5088(6)	49.5	0	310
$[Ge(C_6H\text{-}2\text{-}^tBu\text{-}4,5,6\text{-}Me_3)_2]_2$	2.2521(8)	21.2	0.6	311
$[Ge(C_6H_3\text{-}2,5\text{-}^tBu_2\text{-})_2]_2$	2.3644(5)	47.7	10.9	218
$[Ge(^iPr_2MeSi)_2]_2$	2.269(2)	6.3	0	312
$[Ge(^iPr_3Si)_2]_2$	2.2957(2)	17.1	0	312
$[GeAr'Cl]_2$	2.4626(4)	53.2	0	313
(*E*)-$[GeTbtMes]_2$	2.416(3)	21.4	9.0	314
$\{(1,4\text{-dioxane})Et_2OLi_2Ar^\#GeGeAr^\#\}_n$	2.3278(7)	0	0	315
$[GeTrip_2]_2$	2.3438(5)	35.7/32.7	8.1	316
$RGe{=}GeRSiRClSiRCl$ $R{=}^tBu_2MeSi$	2.291(6)			317
$Ar'Ge{=}GeAr'CPh{=}CPh$	2.4710(8)			318
$RGe{=}GeRGeRCl$ $R{=}^tBu_3Si$	2.2723(9)			319
$RGe{=}GeRGeRBr$ $R{=}^tBu_3Si$	2.2742(9)			319
$RGe{=}GeRGeRI$ $R{=}^tBu_3Si$	2.2720(6)			319
$R_2CCH_2CH_2CR_2Ge{=}Ge{=}GeCR_2CH_2CH_2CR_2$ $R{=}SiMe_3$	2.326(2) avg.	Ge=Ge=Ge 122.6		320
$RGe{=}GeRGeRSi(SiMe_3)_3$ $R{=}^tBu_3Si$	2.264(1)			321
(*E*)- 	2.4570(8) avg.			322
 (*Z*)-	2.454(1) avg.			323
Digermenes				
$RGe{=}GeRGeR_2$ $R{=}^tBu_2MeSi$	2.2429(5)			324
$RGe{=}GeRGeR_2$ $R{=}^tBu_3Si$	2.241(3)			325
$RGe{=}GeRGeR_2$ $R{=}^tBu_3Ge$	2.240(3)			325
$TripGe{=}GeTripGeTrip_2GeTrip_2O$	2.4542(4)			308,326
$TripGe{=}GeTripGeTrip_2GeTrip_2S$	2.2842(5)			243
$TripGe{=}GeTripGeTrip_2GeTrip_2Se$	2.2975(5)			308
$TripGe{=}GeTripGeTrip_2GeTrip_2Te$	2.2842(5)			326
Distannenes				
(*E*)-$[Sn\{Si(Me_3Si)_3\}(C_6H\text{-}2\text{-}^tBu\text{-}4,5,6\text{-}Me_3)]_2$	2.7914(4)	45.0	0	327
$[Sn(Si^tBu_2Me)]_2$	2.6682(7)	1.6	42.8	328
$[Sn\{CH(SiMe_3\}_2]_2$	2.7683(7)	41.6	0	329,330
(*E*)-$[Sn\{Si(Me_3Si)_3\}\{C_6H_2\text{-}2,4,6\text{-}(CF_3)_3\}]_2$	2.8325(5)	42.2	0	331
(*E*)-$[Sn\{Si(Me_3Si)_3\}Mes_2]_2$	2.7022(8)	39.4	0	332
$[Sn\{Si(Me_3Si)_3\}_2]_2$	2.8247(6)	28.6	63.2	333
$[Sn\{C_6H_2\text{-}2,4,6\text{-}(CF_3)_3\}_2]_2$	2.693(1)	46.1	0	334
$[(Me_3Si)(C_9H_5N)CH]_2SnSnCl_2$	2.961(1)			335
$Ar'(4\text{-}^tBu\text{-}C_6H_4CH_2)SnSn(CH_2C_6H_4\text{-}4\text{-}^tBu)Ar'$	2.7705(8)	50.0	0	336
$[\{C_6H_3\text{-}2,6\text{-}(NMe_2)_2\}_2]_2Sn{=}$ $={}Sn[1,8\text{-}(^tBuCH_2N)_2C_{10}H_6]$	3.087(2)			337
$(^tBu_3Si)_2Sn{=}Sn{=}Sn(Si^tBu_3)_2$	2.679(1) avg.	Sn=Sn=Sn 155.9		338
$RSn{=}SnRSnR_2$ $R{=}^tBu_3Si$	2.601(1)			338
Diplumbenes				
$[PbTrip_2]_2$	3.0515(3)	43.9/51.2	21.7	339
$[Pb\{Si(SiMe_3)_3\}Trip\}]_2$	2.9900(5)	42.7	0	340
$[PbMes_2]_2{\cdot}(MgBr_2{\cdot}4THF)$	3.3549(6)	71	0	341
(*E*)-$[Pb\{Si(Me_3Si)_3\}(C_6H\text{-}2\text{-}^tBu\text{-}4,5,6\text{-}Me_3)]_2$	3.3695(2)	46.5	0	339
(*E*)-$[Pb\{Si(Me_3Si)_3\}\{C_6H_2\text{-}2,4,6\text{-}(CF_3)_3\}]_2$	3.537(1)	40.8	0	331
$[Pb\{Si(SiMe_3)_3\}Mes\}]_2$	2.9033(9)			332
$[Pb\{CH(SiMe_3\}_2]_2$	4.129	34.2		340
$[PbAr^\#Me]_2$	3.1606(5)	52.10	0	342
Heteroelement Heavier Alkene Homologues				
$Trip_2Ge{=}SnTrip_2$	2.5066(5)	30.4/43.8	8.3/7.5	343
$Trip_2Ge{=}Si(Si^tBu_2Me)_2$	2.419(1)	9.7/26.3	28.6/32.2	285
$R_2CCH_2CH_2CR_2Ge{=}Si{=}GeCR_2CH_2CH_2CR_2$ $R{=}SiMe_3$	2.2694(7)	Ge=Si=Ge 125.7		320
$R_2CCH_2CH_2CR_2Si{=}Ge{=}SiCR_2CH_2CH_2CR_2$ $R{=}SiMe_3$	2.229(2)	Si=Ge=Si 135.8		344
$RGe{=}SiRSiR_2CH_2{=}CPh$ $R{=}^tBu_2MeSi$	2.250(1)			345

[a] The angles δ and γ are represented as



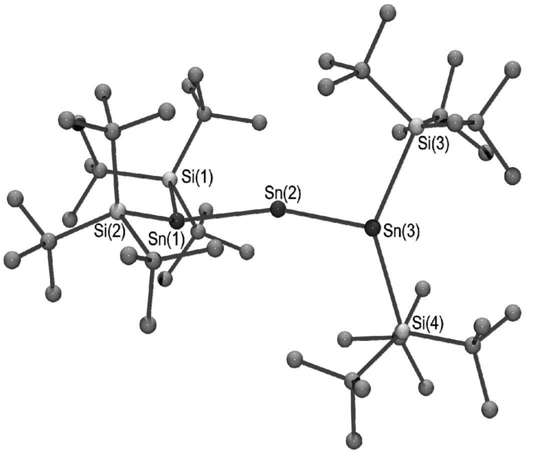


Figure 7. Molecular structure of tristanna allene $(^tBu_3Si)_2Sn{=}Sn{=}Sn(Si^tBu_3)_2$ (hydrogen atoms are not shown). Selected bond distances (Å) and angles (deg): Sn(1)−Sn(2) 2.684(1), Sn(2)−Sn(3) 2.674(1), Si(1)−Sn(1) 2.693(4), Si(2)−Sn(1) 2.688(4), Si(3)−Sn(3) 2.679(4), Si(4)−Sn(3) 2.696(4); Sn(1)−Sn(2)−Sn(3) 156.04(4), Si(1)−Sn(1)−Sn(2) 100.61(9), Si(2)−Sn(1)−Sn(2) 109.40(9), Si(1)−Sn(1)−Si(2) 134.30(10), Si(3)−Sn(3)−Sn(2) 100.50(8), Si(4)−Sn(3)−Sn(2) 112.84(9), Si(3)−Sn(3)−Si(4) 133.60(10).[338]

the excaption of a unique cyclotristannene in which the Sn−Sn also remains intact in solution, the shortest tin−tin distance of 2.6682(7) Å reported for a distannene.[328] The unique properties of $[(^tBu_2MeSi)_2Sn]_2$ are readily explainable on the basis of the CGMT model[174−179] as silyl substituents strongly tend to decrease the singlet−triplet gap, thus making a planar geometry and short tin−tin distances more favorable over the usually encountered *trans*-bent structures. In this case, a ΔE_{S-T} of only 8.5 kcal/mol was calculated.[346] The influence of subtituents on tin−tin distances becomes evident upon inspection of Table 12, where tetra-aryl ligated distannanes all exhibit relatively long, but nontwisted structures and *trans*-bending angles of around 40°. In contrast, the tetrasilyl substituted species have short tin−tin distances, and both noncyclic derivatives display lower degrees of *trans*-bending and a distinctly twisted arrangements around the Sn−Sn bond. The heterosubstituted species *trans*-$[\{(Me_3Si)_3Si\}(2\text{-}^tBu\text{-}4,5,6\text{-}Me_3C_6H)Sn]_2$*trans*-$[\{(Me_3Si)_3Si\}\{2,4,6\text{-}(CF_3)_3\text{-}C_6H_2\}Sn]_2$, and *trans*-$[\{(Me_3Si)_3Si\}MesSn]_2$ were obtained from the reactions of equimolar amounts of the respective homosubstituted stannylenes, $Ar_2Sn + \{(Me_3Si)_3Si\}_2Sn$. The reaction most likely proceeds via a transition state with ligands bridging the tin atoms.

In comparison with its lighter congeners, the structure of the tristanna-allene more closely resembles that of the parent all-carbon allenes as evidenced by the wide bending angle of the tin array (Sn(1)−Sn(2)−Sn(3) 156.04(4)°) and a largely perpendicular arrangement of the silyl groups (Figure 7). Moreover, the planar coordination and significantly elonganted Si−Sn distances are indicative of the donor character of the terminal tin atoms.[338]

The series of structurally authenticated, homonuclear heavier group 14 dimetallenes was completed only in 1998, when the structure of the first diplumbene was published.[331] Typically, the Pb−Pb distances in these compounds exceed Pb−Pb single bond lengths. e.g., 2.847(6) Å, in Ph_6Pb_2.[347] The shortest Pb−Pb distance (2.9033(9) Å) was found in the silyl-substituted species *trans*-$[\{(Me_3Si)_3Si\}MesPb]_2$. Mixed aryl/silyl substituted derivatives were accessed via ligand exchange routes similar to those discussed for the tin case. The longest Pb−Pb bond reported for this class of compounds was found in $[\{(Me_3Si)_2CH\}_2Pb]_2$, 4.129 Å.[340] To a greater degree than distannenes, diplumbenes are best represented as two relatively weakly associated plumbylenes. In the magnesium bromide adduct of $[Mes_2Pb]_2$, the bromide acts as a Lewis base, hence is donating electron density into the empty orbital of the low coordinate Pb center. As a consequence, the *trans*-bent angle observed in $[Mes_2Pb]_2{\cdot}2(MgBr_2{\cdot}4THF)$ is very large at ca. 71°.

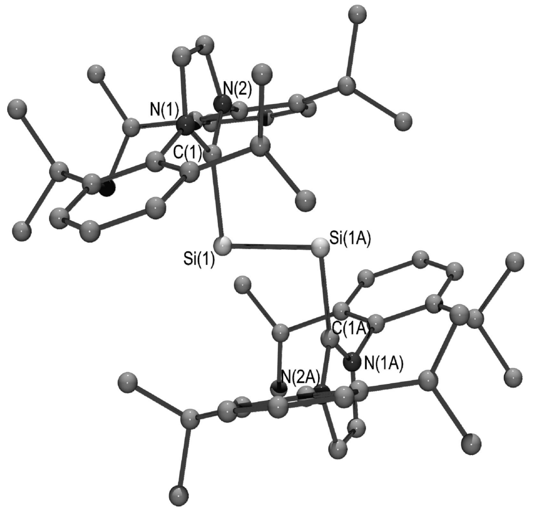


Figure 8. Molecular structure of L:Si═Si:L. (L = :C(NDippCH)$_2$); (hydrogen atoms are not shown). Selected bond distances (Å) and angles (deg): Si(1)−Si(1A) 2.2295(8), Si(1)−C(1) 1.927(1); C(1)−Si(1)−Si(1A) 93.37(5).[346]

Following initial reports for a silagermene[348,349] and a silastannene,[350] structural data for several heteronuclear heavier alkenes have been reported (cf. Table 12) and, in addition, 1,3-digerma-2-silaallene and 1,3-disila-2-germaallene derivatives are known. The latter display a bent coordination of 125.7° (Ge−Si−Ge) and 135.8° (Si−Ge−Si), respectively, at the tetrel atoms. As Frenking and co-workers have pointed out recently that these compounds are better described as bis-tetrylene complexes of a zerovalent central atom rather than classical allenes.

Recently, Robinson and co-workers extended the family of doubly bonded silicon species to a completely new class of compounds described by the formula L:Si═Si:L where L is a N-heterocyclic carbene, :C(NDippCH)$_2$ (Figure 8). This compound, along with the chloro derivative L(Cl)SiSi(Cl)L, was obtained by reduction of the adduct $LSiCl_4$ with KC_8 in THF and hexane. In L:Si═Si:L, two two-electron donor ligands stabilize the low valent Si−Si core in which silicon has the oxidation state zero. The Si−Si distance is 2.2295(8) Å. The ^{29}Si NMR ($\delta = 224.5$ ppm in C_6D_6) and UV−vis ($\lambda_{max} = 466$ nm) spectroscopic data further supported the interpretation of the bonding in L:Si═Si:L as a bis-carbene stabilized disilicon moiety. The L−Si═Si angles of 93.4° suggest high p-character for the molecular orbitals involved in the ligand−core bonding interactions. As evidenced by ab initio methods, in this species, the HOMO is equivalent to a Si−Si π-bond, the HOMO-1 corresponds to a Si−Si σ-bond, but the HOMO-2 orbital has lone pair character with prevailing s-character and is mostly located at the silicons.[346] In the germanium homologue L:Ge═Ge:L, the Ge−Ge distance was 2.3490(8) Å, the L:Ge═Ge angle was 89.87(8)°.[351]

Dianionic compounds with general formula $[RE{=}ER]_2^{2-}$ (E = Ge, Sn), which are isoelectronic to the corresponding neutral group 15 derivatives, have formal double bonds

Table 13. Selected Structural Data for Dianionic Heavy Alkenes Analogues [RE=ER]M$_2$ (E = Ge, Sn, Pb)

compd	E=E (Å)	C−E−E (deg)	ref
Li_2[Ar′GeGeAr′]	2.455(9)	102.97(9)	313
Na_2[Ar*GeGeAr*]	2.394(1)	102.37(8)	352
K_2[Ar*GeGeAr*]	2.3912(6)	112.14(7)	313
Na_2[Ar*SnSnAr*]	2.789(1)	104.8(2)	313
K_2[Ar′SnSnAr′]	2.7754(3)	106.02(5)	313
K_2[Ar*SnSnAr*]	2.7763(9)	107.5(1)	352

between two tetrel elements and were first reported in 1998 (Table 13). Na_2Ar*GeGeAr* and K_2Ar*SnSnAr* were both synthesized by alkali metal reduction of the aryl element chloride {Ar*E(Cl)}$_2$.[352] Subsequently, further derivatives were obtained.[313] The alkali metal cations are complexed by flanking aryl groups of the terphenyl ligands. They exhibit strictly *trans*-bent structures with narrow angles Ar−E=E. Ge−Ge bond distances lie between 2.3912(6) Å in K_2Ar*GeGeAr* and 2.455(9) Å in Li_2Ar′GeGeAr′, C−Ge=Ge angles of 102.37(8)° for Na_2Ar*GeGeAr* and 112.14(7)° for K_2Ar*GeGeAr* were found.[313]

In the respective tin analogues, the Sn−Sn distances were between 2.7754(3) Å for K_2Ar′SnSnAr′ and 2.789(1) Å for Na_2Ar*SnSnAr* with C−Sn=Sn angles of ca. 106°.[313] The average bond distances in these formally double bonded dianionic species are only slightly shorter than normal single bonds, probably as a result of Coulombic interactions.

3.8. Compounds of Formula $R_2E{=}\ddot{E}'R$ (E = Group 14, E′ = Group 15 Element)

The chemistry of heavier element analogues of imines has been a very active field of research over the past decade. Because the large number of publications, especially in the case of phosphenes, $R_2C{=}PR'$, a comprehensive discussion is beyond the scope of this text. In comparison to imines, the bond polarity in phosphaalkenes is lower due to the lower electronegativity of phosphorus relative to nitrogen. As a consequence, the chemical reactivity of phosphaalkenes is more related to alkenes than imines, rendering them interesting as potentially conjugated polymeric materials.

A compilation of acyclic, uncomplexed phosphenes for which X-ray crystallographic data are available is given in Table 14. The average carbon−phosphorus bond distance in phosphenes is about 1.67 Å, with extremes close to 1.63 Å for the shortest and 1.80 Å for the longest distances. The typical R−P=C angle in uncomplexed, acyclic phosphenes is about 103°. The substitution pattern in carbon phosphorus double bonded species at the short end of the distance range consists of hydrogen or silyl subtituents at carbon and σ-electron withdrawing, π-donor ligands at phosphorus such as halogens or amides. In these, the R−P=C angles frequently exceed 110°. Representative examples in this context are IP=C(SiMe$_3$)$_2$[381] (C=P 1.641(4) Å, I−P=C 111.7(2)°), ^{i}Pr$_2$NP=CPh(SiMe$_3$)[390] (C=P 1.641(6) Å, N−P=C 115.4(3)° av), ClP=C(SiMe$_3$)$_2$[446] (C=P 1.637(3) Å, Cl−P=C 108.4(1)°), or BrP=C(SiMe$_3$)$_2$[446] (C=P 1.644(3) Å, Br−P=C 109.7(1)°).

Exceptionally long C=P distances are encountered in phosphenes which carry electronegative substituents at carbon and electron releasing groups at phosphorus. For example, (Me$_3$Si)P=C(NMe$_2$)NEt$_2$ features a C=P distance of 1.759(3) Å.[372] Even longer carbon phosphorus bonds are found in the tetrakis dimethylamino-2-phospha-allyl perchlorate (Me$_2$N)$_2$HCP=(NMe$_2$)$_2$[ClO$_4$] (1.796 Å av)[379] or in ^{t}BuC(OH)P(C=O)^{t}Bu (1.801(3) Å)[384] and the related (1-Ad)C(OH)P(C=O)(1-Ad) (1.794 av).[412] In the last two examples, the long C=P separation is caused by tautomerism of the C(OH) and (C=O) units. A particularly instructive example in the context of the interplay between substitution pattern and bonding is furnished by {(Et$_2$N)$_2$N}C=P−P=C(SiMe$_3$)$_2$, a molecule in which both polarization patterns are present. In this, a C=P distance of 1.778(2) Å at the nitrogen substituted half of the molecule and of 1.683(2) Å at the bis-silylated side are found. Consequently, the smaller angle of 95.59(5)° for the nitrogen substituted phosphene is opposed by 110.66(4)° for the angle at phosphorus in the P=C(SiMe$_3$)$_2$ unit.[402]

The reaction of white phosphorus with N-heterocyclic carbene :CNDippC(Me$_2$)CH$_2$CC^{i}PrH(CH$_2$)$_2$CHMeC yielded the first example of a 2,3,4,5-tetraphosphatriene (Figure 9),[409] a molecule with a diphosphene and two phosphaalkene units. In this, the phosphaalkene distances are 1.77(1) and 1.75(1) Å and the P−P distance of the diphosphene unit is 2.080(4) Å. The tetraphosphatriene unit has an all-*trans* conformation with narrow angles at phosphorus, all only slightly over 90°. Among the three double bonded units present in the molecule, the diphosphene moiety is the most reactive and readily undergoes 2 + 4 cycloaddition reactions with, e.g., 2,3-dimethylbutadiene.[409]

Compared to phosphaalkenes, less progress has been made in the field of arsa- and stiba-alkenes. The arsa alkenes currently known feature C=As double bond distances between 1.790(3)[504] and 1.902(7) Å[455] with an average value of about 1.85 Å (Table 15).

Similar to the phosphorus congeners, the shortest C=As distances are found in species where a silyl substituent at carbon is present (hydrogen substituted derivatives are currently unknown). In contrast, the longest distances are encountered in the 1,3-imidazol-2-ylidene complexes of the Ph- and C$_6$F$_5$-substituted arsenidenes PhAs=CNMesCHCHNMes and C$_6$F$_5$As=CNMesCHCHNMes.[455] In these, the carbon and arsenic atoms are separated by 1.899(3) for Ph and 1.902(7) Å for C$_6$F$_5$, respectively. Moreover, Ar−As−C angles are well below 100° and substituents at arsenic and carbon adopt a considerably twisted conformation with respect to each other. The bonding in these is better described by a polar canonical form NHC$^+$-As$^-$Ar or as a donor−acceptor complex NHC:→AsAr rather than a conventional double bond.[455] At present, the crystal structures of only three stiba-alkenes have been reported. In these, C=Sb distances fall between 2.06(1) for Mes*(Me$_3$SiO)C=Sb−Sb=C(OSiMe$_3$)-Mes*[506] and 2.078(3) Å for Mes*C(=O)-Sb=C(OH)-Mes*.[505] The bending angles at antimony are in all cases only slightly wider than 90°.

In addition to double bonds between carbon and heavier group 15 elements, a series of nitrogen-heavier group 14 element double bonded species has been structurally characterized. The silaimines are the best studied, and these have silicon nitrogen distances between 1.568(3)[509,510] and 1.678(2) Å.[516] The shortest Si=N bond length was observed in ^{t}Bu$_2$Si=N−Si^{t}Bu$_3$, the first stable silaimine, which was reported by Wiberg and co-workers in 1986.[506] It has an angle at nitrogen of 177.8(2)°. Similar geometric parameters describe the related ^{t}Bu$_2$Si=N-SiPh^{t}Bu$_2$ (1.573(2) Å, 173.0(2)° Si=N−Si).[510] The linear geometry at nitrogen in the uncomplexed silaimines ^{t}Bu$_2$Si=N−Si^{t}Bu$_3$ and ^{t}Bu$_2$Si=N-SiPh^{t}Bu$_2$ is a consequence of electronic effects rather than

Table 14. Selected Structural Data for Phosphenes R$_2$C=PR′

compd	P=C (Å)	R−P−C [deg]	ref
Mes*P=C(^{t}Bu)[2-{6-C(OH)^{t}BuCH$_2$CN}pyridine]	1.674(7)	103.4(2)	353
2,6-(Mes*P=C)$_2$-pyridine	1.674(3)	103.0(2)	353
Mes*P=C-C-(CH$_2$)$_5$-C-C=PMes*	1.661(6)/1.673(5)	100.4(2)/99.6(3)	354
Mes*P=CCH$_2$C=PMes*CH$_2$	1.68(1)	94.8(6)	355
(Mes*P=CCH=)$_2$	1.698(3)	97.5(1)	356
ArP=CCPArPArCH=CHPAr Ar=C$_6$H$_2$-2,4-^{t}Bu$_2$-6-Me	1.671(4)	106.0(4)	356
Php=CPPhCPh(OSiMe$_3$)N(SiMe$_3$)	1.7054(4)	101.16(5)	357
[PhP=C{NPh(SiMe$_3$)}PPh]$_2$	1.6766(8)	108.38(9)	358
MesP=C^{t}BuPHMes	1.690(2)	108.60(7)	359
HP=C(N^{i}Pr$_2$)P(N^{i}Pr$_2$)$_2$	1.713(3)	104(2)	360
PhP=C{N(SiMe$_3$)(C$_6$H$_4$-4-F)}P(SiMe$_3$)Ph	1.6694(4)	107.87(6)	361
[P=C^{t}Bu(OSiMe$_3$)]$_2$	1.6842(4)	100.29(5)	362
Mes*P=CCBr=CBrC=PMes*PS	1.7009(5)−1.713(2)	98.1(3)−101.24(16)	363
MesP=CPh$_2$	1.691(1)	107.46(9)	364, 365
Mes*P=C(SiMe$_3$)CH=PMes*	1.685(2)/1.696(2)	100.00(8)/108.00(8)	366
PhP=C(SSiMe$_3$)$_2$	1.700(2)	106.75(9)	367
Mes*P=C(SiMe$_3$)$_2$	1.659(5)	110.7(2)	368
Mes*P=CSC(=S)PMes*	1.673(8)	99.2(3)	369
Mes*P=C(SH)PHMes*	1.681(3)	102.0(2)	369
Mes*P=CClLi·2DME	1.677(2)	115.3(1)	370
Mes*P=CH$_2$	1.643(3)	104.0(1)	371
(Me$_3$Si)P=C(NMe$_2$)NEt$_2$	1.759(3)	106.24(9)	372
Mes*P=(9-fluorenyl)	1.701(4)	105.0(4)	373
(C$_6$H$_2$-2,6-^{t}Bu$_2$-4-MeO)P=(9-fluorenyl)	1.692(6)	104.6(2)	373
(C$_6$H$_2$-2,6-^{t}Bu$_2$-4-Me$_2$N)P=(9-fluorenyl)	1.695(5)	104.0(2)	373
4,6-(Mes*P=C)$_2$dibenzofuran	1.674(1)	98.72(7)	374
Mes*P=C(Me)P(=O)(C$_6$H$_4$−OMe)	1.673(3)	99.8(1)	375
(C$_6$H$_4$-4-^{t}Bu)P=CPh(SiMe$_3$)	1.651(7)/1.682(8)	109.2(4)/111.1(4)	376
[(Me$_2$N)$_2$C=P=C(NMe$_2$)$_2$][ClO$_4$]	1.791(4)/1.801(4)	103.6(2)	377
(*Z*)-Mes*P=CHPh	1.672(2)	105.82(9)	378, 379
(*E*)-Mes*P=CHPh	1.674(7)	100.9(3)	379, 380
IP=C(SiMe$_3$)$_2$	1.641(4)	111.7(2)	381
(Me$_3$Si)$_2$CHP=C(SiMe$_3$)SiMe$_2$CH$_2$P{CH(SiMe$_3$)$_2$}$_2$	1.664(5)	113.3(2)	382
Mes*P=C(OSiMe$_3$)P=C^{t}Bu(OSiMe$_3$)	1.695(4)/1.696(4)	104.6(2)/110.3(2)	383
^{t}BuC(OH)=PC(=O)^{t}Bu	1.801(3)	97.8(3)	384
(Me$_3$SiCC)$_2$PC(SiMe$_3$)$_2$P=C(SiMe$_3$)$_2$	1.662(5)	121.7(2)	385
Mes*P=CPh(OSi^{t}BuMe$_2$)	1.686(5)	103.9(2)	386
[Mes*P=C(OSiMe$_3$)PPh]$_2$	1.672(4)	101.5(2)	387
Mes*P=CCH^{cy}Pr	1.666(4)	103.2(1)	388
^{i}Pr$_2$NP=CMes*P(=O)MeCHMes*	1.670(5)	115.2(2)	389
^{i}Pr$_2$NP=CPhSiMe$_3$	1.641(6)	114.1(3)/116.7(3)	390
^{t}Bu$_2$PP=CPh(SiMe$_3$)	1.669(5)	105.1(2)	390
Mes*P=PC(OSiMe$_3$)=PMes*	1.700(5)	100.7(2)	391
Cp*P=C(SiMe$_3$)$_2$	1.665(4)	118.7(2)	392
[Mes*P=CCPh]$_2$	1.679(6)/1.690(8)	104.7(3)/105.5(3)	393
[Mes*P=CHCHPh]$_2$	1.634(5)/1.649(5)	103.3(2)/101.1(2)	393
Mes*P=CHPMes*CH(Me)(CH=CH$_2$)	1.667(7)	101.8(3)	394
Mes*P=CHPMes*(2-butenyl)	1.682(6)	100.9(4)	394
HP=C(NMe$_2$)$_2$	1.740(1)	103(1)	395
[Mes*P=CC(=PMes*)CH^{t}BuCH]$_2$	1.683(7)−1.707(9)	104.0(3)−109.5(4)	396
MesP=CPh(C$_6$H$_4$-2-^{i}Pr)	1.682(2)	106.20(8)	397
[Mes*P=C(OSiMe$_3$)]$_2$P^{t}Bu	1.672(8)−1.690(10)	104.3(4)−106.6(4)	398
[Mes*P=C(OSiMe$_3$)]$_2$PCl	1.645(5)−1.667(5)	103.0(2)−106.0(3)	398
[Mes*P=C(OSiMe$_3$)]P^{t}BuC[N(SiMe$_3$)(C$_6$H$_4$-4-CF$_3$)]=P^{t}Bu	1.670(7)−1.690(7)	107.2(4)−115.0(4)	398
F$_3$CP=CF(NMe$_2$)	1.743(2)	97.06(8)	399
(Me$_3$SiS)C(=S)P=C(NMe$_2$)$_2$	1.827(2)	101.86(9)	400
[CyP=C^{t}Bu$_2$]$_2$GaI	1.671(2)/1.673(2)	106.2(1)/105.9(1)	401
phthalimidoP=C^{t}BuSePh	1.686(4)	105.9(2)	401
{(Et$_2$N)$_2$N}$_2$C=P−P=C(SiMe$_3$)$_2$	1.778(2)/1.683(2)	95.59(5)/110.66(4)	402
Mes*P=CClC(=O)^{t}Bu	1.658(4)	102.4(2)	403
Mes*P=CClC(=O)Ph	1.679(2)	103.6(1)	403
Mes*P=[(5*H*)dibenzo(*c*,*f*)cyclohepten-5-yliden]	1.678(3)	104.6(2)	404
Mes*P=C^{t}BuPBrMes*	1.694(2)	109.19(9)	405
MesP=C^{t}BuPMesLi·3THF	1.736(2)	107.0(1)	405
DippP=C(C$_6$H$_4$-4-^{t}Bu)NHDipp	1.709(2)	101.9(1)	406
DippP=C(C$_6$H$_4$-4-^{t}Bu)Li·3THF	1.765(2)	103.1(1)	406
Mes*P=CSiTripPhC(=PMes*)SiTripPh	1.650(7)/1.656(8)	115.5(4)/112.4(4)	407
Mes*P=CClPClMes*	1.66(1)	104.7(5)	408
NHC=P−P=P−P=NHC^a	1.75(1)/1.77(1)	110.7(4)/109.5(4)	409
NHC=P-P(CH$_2$CMe=CMeCH$_2$P)-P=NHC^a	1.720(8)−1.745(7)	110.0(3)−114.3(2)	409

Table 14. Continued

compd	P=C (Å)	R−P−C [deg]	ref
NHC=P-P-PCH$_2$CMe=CMeCH$_2$P	1.735(4)	109.7(1)	409
trans-Mes*P=C^{t}Bu$_2$GeC=PMes*Ge^{t}Bu$_2$	1.672(2)	111.6(1)	410
cis-Mes*P=C^{t}Bu$_2$GeC=PMes*Ge^{t}Bu$_2$	1.665(3)	109.7(1)	410
Trip(Me$_3$Si)NP=C(SiMe$_3$)$_2$	1.651(2)	121.38(8)	411
(1-Ad)C(OH)=P−C(=O)(1-Ad)	1.789(6)/1.799(6)	99.1(3)	412
Mes*P=CCH^{t}BuC(=O)C^{t}BuCH	1.705(2)	101.59(7)	413
Mes*P=CH(2-pyridinyl)	1.66(1)	99.1(5)	414, 415
(9-fluorenyl)P=C(SiMe$_3$)$_2$	1.667(3)	109.8(1)	416
Mes*P=CH(C$_6$H$_4$-4-NMe$_2$)	1.674(2)	105.4(1)	417
Mes*P=CI$_2$	1.70(3)	101(1)	418
Mes*P=CHCN	1.66(1)	103.4(4)	419
Mes*P=CHNDippLi·3THF	1.736(9)	101.0(3)	420
[Mes*P=CSPh]$_2$	1.70(2)/1.72(2)	103.2(6)/103.4(6)	421
(Me$_3$Si)$_2$C=P−P=CC^{t}BuC^{t}Bu	1.678(4)	111.6(4)	422
	1.732(5)	93.9(3)	
TmpP=C(SiMe$_3$)Sn(NMe$_2$){N(SiMe$_3$)$_2$}$_2$	1.676(5)	113.5(2)	423
Mes*P=CC(SiMe$_3$)=C(SiMe$_3$)C=PMes*	1.676(6)/1.679(7)	108.0(3)/110.7(3)	424
Mes*P=CN(CF$_3$){C=N(CF$_3$)$_2$}PMes*	1.683(5)	112.9(2)	425
[CyP=C^{t}BuMgCl]$_2$	1.668(3)/1.669(3)	107.1(2)/107.3(1)	426
[^{cy}PentP=C^{t}BuMgCl]$_2$	1.672(2)	106.49(7)	426
(Me$_3$Si)$_2$C=PSeP=C(SiMe$_3$)$_2$	1.664(3)/1.667(3)	109.6(1)/109.7(1)	427
Mes*P=C(PMes*)N(Si^{t}BuMe$_2$)(C$_6$H$_4$-4-Cl)	1.700(5)	104.8(2)	428
Mes*P=C[C-{3-(5-Me-thiopheny1)}]$_2$C=PMes*	1.673(3)/1.675(3)	105.5(2)/106.8(2)	429
1,2-(Mes*P=CC1)$_2$-GeMes (fluorenylidene)$_2$GeMes	1.657(4)/1.668(4)	104.2(2)/106.2(2)	430
Mes*P=C(SiMe$_3$)PPh$_2$	1.672(3)	107.6(1)	431
Mes*P=C(SiMe$_3$)P(=S)Ph$_2$	1.681(7)/1.690(7)	106.6(3)/108.4(3)	431
MesP=C(C$_6$H$_4$-4-F)$_2$	1.687(2)/1.690(1)	108.15(8)/107.13(8)	432
MesP=CPh(C$_6$H$_4$-4-OMe)	1.708(1)	106.52(6)	432
MesP=CPh(2-pyridinyl)	1.704(2)	107.79(8)	432
(CF$_3$)$_3$GeP=CCF(NEt$_2$)	1.749(3)	95.4(1)	433
Mes*P=CClP(=S)Ph$_2$	1.675(3)	101.6(2)	434
Mes*P=CClP(=SI$_2$)Ph$_2$	1.678(1)	100.1(4)	434
Mes*P=CMeP=C(CH$_2$Ph)Mes*	1.687(8)/1.694(8)	106.9(3)/110.2(3)	435
Mes*P=CCH$_2$(2-furyl)	1.70(2)	97.7(6)	436, 437
Mes*P=CClPPh$_2$	1.67(1)	104.8(6)/104.6(6)	438
1,4-{(Me$_3$Si)P=C(OSiMe$_3$)}$_2$-bicyclo[2.2.2]octane	1.701(2)/1.705(2)	105.97(6)/102.73(6)	439
CyP=C^{t}BuC(=O)Ph	1.681(3)/1.682(3)	108.8(2)/108.7(2)	440
Mes*P=CClSiCl$_2${9-(9-Me-fluorenyl)}	1.669(2)	104.4(1)	441
Mes*P=CH-2-(6-^{i}Pr-azulenyl)	1.666(4)	102.9(2)	442
Mes*P=CC(=CHPh)C=PMes*C(=CHPh)	1.669(5)/1.684(5)	102.1(2)/101.2(2)	443
MesP=CC(*N*-morpholino){CH=C(^{t}Bu)CC^{t}Bu}	1.711(8)	100.3(4)	444
(Me$_3$Si)$_2$NP=CCl$_2$	1.685(2)	105.3(1)	445, 446
ClP=C(SiMe$_3$)$_2$	1.637(3)	108.4(1)	446
BrP=C(SiMe$_3$)$_2$	1.644(3)	109.7(1)	446
(^{t}Bu$_2$N)P=CCl$_2$	1.684(3)	104.41(8)	446
(2,6-^{t}Bu$_2$-4-Me-C$_6$H$_2$O)P=CCl$_2$	1.669(2)	100.01(6)	446
(Me$_2$N)PhC=NP=C(SiMe$_3$)$_2$	1.667(2)	106.96(8)	447
Mes*P=CCH=CHC=(C-*p*-toly1$_2$)S	1.704(2)	98.48(6)	448
Mes*P=C(H)SPh	1.656(5)	102.0(2)	449
[Mes*P=C(S-*p*-tolyl)$_2$]$_2$	1.71(2)/1.75(2)	105.6(8)/101.6(8)	449
Mes*N=P−P=C(NMe$_2$)$_2$	1.807(7)	94.1(2)	450
(CyP=C^{t}Bu)$_2$In^{cy}Hex	1.677(4)/1.664(4)	105.7(2)/104.4(2)	451
(^{i}Pr$_3$SiO)^{t}BuC=C(SiMe$_3$)P=C^{t}Bu(OSiMe$_3$)	1.702(3)	109.6(1)	452
Mes*P=CNPhC(=NPh)PMes*	1.673(8)	109.0(2)	453
PhP=CNMe(CMe)$_2$NMe	1.794(3)	102.3(1)	454
PhP=CNMes(CH)$_2$NMes	1.763(6)	99.9(3)	455
F$_3$CP=CNMes(CH)$_2$NMes	1.784(2)	101.6(1)	455
PhP=CNMes(CH$_2$)$_2$NMes	1.745(4)	100.5(2)	455
Mes*P=C{9-(2,7-^{t}Bu$_2$-fluorenylidene)}	1.677(5)/1.687(5)	106.7(2)/107.3(2)	456
(1,2-Mes*P=)$_2$cyclobuta(l)phenanthrene	1.669(2)	105.45(8)	457
Mes*P=CClPClC(SiMe$_3$)$_3$	1.666(8)	105.0(4)	458
[^{i}Pr$_2$NP=CPPh$_3$]$^+$BF$_4^-$	1.68(1)	105.3(7)	459
Mes*P=CBrCH(OMe)^{cy}Pr	1.671(4)	105.0(1)	460
Mes*P=C(C^{cy}Pr)$_2$C=PMes*	1.673(5)/1.682(5)	100.5(3)/100.0(3)	460
(*E*)-4-Br-2,6-MesC$_6$H$_2$P=CH(C$_6$H$_4$-4-Br)	1.683(3)	101.6(1)	461
(*Z*)-4-Br-2,6-MesC$_6$H$_2$P=CH(C$_6$H$_4$-4-Br)	1.666(4)	107.3(1)	461

Table 14. Continued

compd	P=C (Å)	R−P−C [deg]	ref
Mes*P=CBr$_2$	1.703(9)	103.3(4)	462
Mes*P=CCl$_2$	1.643(6)	102.6(3)	462
Mes*P=CH(CH$_2$)$_2$PMes*R^b	1.649(3)	100.4(1)	463
Mes*P=CH(CH$_2$)$_2$PMes*R·HO$_3$SCF$_3$^{b}	1.623(8)	102.2(4)	463
Mes*P=CH(CH$_2$)$_2$PMes*R·HBr^b	1.658(3)	103.2(1)	463
Mes*P=CPhCMe$_2$C(=O)CH$_2$CH^{i}PrN	1.679(2)	105.3(1)	464
Mes*P=C(CCSi^{i}Pr$_3$)$_2$	1.676(7)	104.6(3)	465
Mes*P=CPh(CC)$_4$CPh=PMes*	1.688(4)/1.692(4)	103.2(2)/102.7(2)	465
Mes*P=CClPCl(=S)^{t}Bu	1.681(2)	100.11(8)	466
TmpP=CCl$_2$	1.670(6)	103.4(3)	418
{^{t}Bu(Me$_3$SiO)C=P}$_2$CH$_2$	1.694(1)/1.695(1)	103.5(1)/103.4(1)	467
(F$_3$C)PP=CFNEt$_2$	1.760(2)	94.84(6)	468
Mes*P=CPh$_2$	1.690(2)	106.2(1)	469
Mes*NHP=(9-fluorenyidene)	1.655(8)	109.2(4)	470
[(Me$_3$Si){2-(6-Me-py)}P=C^{t}Bu(SiMe$_3$)]$^-$Li$^+$·tmeda	1.710(2)	124.03(9)	471
{C$_6$H$_3$-2,6-(C$_6$H$_3$-2,6-Cl$_2$)}P=C(H)Ph	1.634(3)	102.9(1)	472
Mes*P=CBr(SMe)	1.70(1)	103.7(6)	473
[Mes*P=C(SMe)]$_2$	1.693(6)/1.702(5)	104.3(3)/105.0(2)	473
Mes*P=CClP(=S)(N^{i}Pr$_2$)	1.68(1)/1.70(1)	101.4(3)/101.7(6)	474
1,4-[(Me$_3$SiO)PhC=P]$_2$C$_6$H$_4$	1.702(2)	102.95(9)	475
Mes*P=CPh(OSiMe$_3$)	1.708(1)	104.20(6)	475
1,4-[MesP=C(OSiMe$_3$)]$_2$C$_6$H$_4$	1.700(2)/1.696(2)	104.2(1)/106.3(1)	475
Mes*P=C{C(SiMe$_3$)$_2$}$_2$C=PMes*	1.669(4)/1.669(5)	102.5(2)/108.8(2)	476, 477
Mes*P=C(SiMe$_3$)CH(SiMe$_3$)PHMes*	1.684(3)	109.7(4)	478
[(^{i}Pr$_3$Si)P=CSiTrip$_2$CN(CH$_2$)$_6$]$_2$	1.699(4)	115.9(2)	479
Mes*P=CHP(=O)(OH)Mes*	1.650(5)	106.6(2)	480
[Mes*P=CCMe]$_2$	1.699(2)/1.703(2)	103.27(9)/103.29(9)	481
CyP=C^{t}BuPPh$_2$	1.677(3)	111.2(1)	482
Mes*P=CMeC(Ph)=NDipp	1.684(2)	104.37(9)	483
1,4-(PhCH=P)$_2$-(C$_6$-2,3,5,6-Ar) Ar=C$_6$H$_4$-4-^{t}Bu	1.676(5)	101.4(2)	484
[Mes*P=CBrSiMe$_2$]$_2$O	1.659(9)	107.1(4)	485
Mes*P=CSiMe$_2$OSiMe$_2$C=PMes*SiMe$_2$OSiMe$_2$	1.667(5)	108.8(2)	485
TmpP=C(SiMe$_3$)PF(NMe$_2$)=NDipp	1.676(2)	110.03(8)	486
(*E*,*E*)-1,3-(Mes*P=C)$_2$C$_6$H$_4$	1.656(9)/1.660(10)	100.3(5)/101.1(6)	487
(*Z*,*Z*)-1,3-(Mes*P=C)$_2$C$_6$H$_4$	1.67(1)/1.66(1)	107.1(6)/107.0(6)	487
1,4-{(Me$_3$SiO)^{t}BuC=P}$_2$-C$_6$H$_4$	1.683(4)	104.6(2)	488
Mes*P=C(NH$_2$)Ph	1.704(2)	101.8(1)	489
1,2-(Mes*P=C)$_2$C$_6$H$_4$	1.670(4)/1.665(4)	98.6(2)/101.6(2)	490, 491
Mes*P=CC(=O)NPhC(=O)NPh	1.693(7)	109.1(4)	492

[a] NHC = :CNDippC(Me$_2$)CH$_2$CC^{i}PrH(CH$_2$)$_2$CHMeC. [b] R = 2,3,4,6,7,8-hexahydropyrrolo(1,2-*a*)pyrimidine.

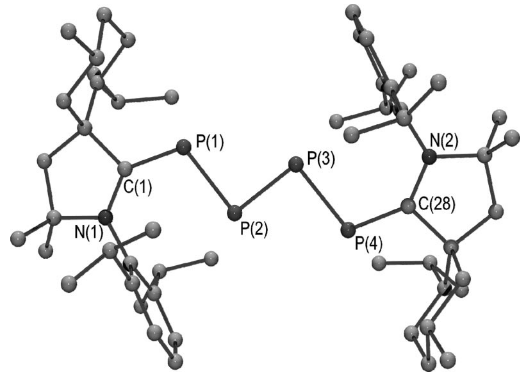


Figure 9. Molecular structure of NHC=P-P=P-P=NHC (NHC: =:CNDippC(Me$_2$)CH$_2$CC^{i}PrH(CH$_2$)$_2$CHMeC). Hydrogen atoms are not shown. Selected bond lengths (Å) and angles (deg): P(1)−C(1) 1.77(1), P(1)−P(2) 2.191(4), P(2)−P(3) 2.080(4), P(3)−P(4) 2.193(4), P(4)−C(28) 1.75(1), C(1)−N(1) 1.38(1), C(28)−N(2) 1.38(1); C(1)−P(1)−P(2) 110.7(4), P(1)−P(2)−P(3) 92.8(2), P(2)−P(3)−P(4) 93.4(2), P(3)−P(4)−C(28) 109.5(4), C(1)−P(1)−P(2)-P(3) 169.6(4), P(1)−P(2)−P(3)-P(4) −177.4(2), P(2)−P(3)−P(4)-C(28) 171.6(4).[409]

steric interaction of the substituents. In sila imines, the rotation barrier along the Si=N axis has values of about 38 kcal mol^{-1}. Nevertheless, isomerization through a linear transition state is facile, with a barrier of only 5.6 kcal mol^{-1}.[507,508]

A linear geometry at nitrogen is also seen in a series of donor−acceptor complexes of the silicon center in silaimines which readily complexes with oxygen or nitrogen donors. This is due of the high electronegativity of nitrogen, which leaves the silicon center electron poor and susceptible to complexation by Lewis bases. In these, the Si−N distances are slightly elongated by about 0.02−0.05 Å relative to the uncomplexed species but coordination around nitrogen remains largely linear. Much larger structural changes are seen when lithium fluoride acts as a donor via F$^-$. The dimeric [^{t}Bu$_2$Si=N^{t}Bu]$_2$(LiF)$_2$Et$_2$O features very long Si−N distances of 1.640(2) and 1.678(2)°, accompanied by narrow Si−N−tBu angles of 137.9(2) and 132.7(2)°.[516] Stronger deviations from linearity (Si=N−C (131.3(3)°) and also somewhat longer Si−N distances (1.559(4) Å) characterize the THF adduct of (THF)^{t}BuNCH$_2$CH$_2$N^{t}BuSi=NCPh$_3$.[518] The bent structural motif in (THF)^{t}BuNCH$_2$CH$_2$N^{t}BuSi=NCPh$_3$ is related to the increased stability of the silylene fragment ^{t}BuNCH$_2$CH$_2$N^{t}BuSi. Like the above-mentioned N-heterocyclic carbene adducts of phosphinidenes of arsenidenes, the

Table 15. Selected Structural Data for Arsa- and Stibaalkenes

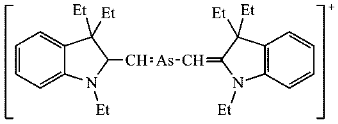
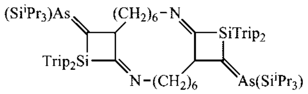
Compound	E=C (Å)	R-E-C [deg]	Ref
Arsaalkenes			
$FpAs{=}C^tBu(OSiMe_3)$	1.822(3)	111.4(1)	493,494
$[tpz\{W(CO)_2\}]C\text{-}As{=}C(NMe_2)_2$	1.898(9)	101.6(3)	495
$Fp^*As{=}CPhNMe_2$	1.849(7)	116.0(1)	496
$PhAs{=}CNMesCHCHNMes$	1.899(3)	97.3(2)	455
$C_6F_5As{=}CNMesCHCHNMes$	1.902(7)	99.8(3)	455
$Mes^*As{=}Fluorenyl\text{-}2,7\text{-}^tBu$	1.807(3)	105.5(1)	497
$Mes^*C({=}O)\text{-}As{=}C(OH)Mes^*$	1.857(3)	97.2(2)	498
$CyNC{=}N^{cy}HexSiTrip_2C{=}AsSi^iPr_3$	1.827(3)	115.48(9)	499
$Mes^*As{=}CBr(SiMe_3)$	1.790(3)	101.0(1)	500
$CF_3As{=}CFNEt_2$	1.867(8)	94.3(4)	501
$Et_5CpFe(CO)_2As{=}C(NMe_2)_2$	1.877(8)	116.2(3)	502
	1.831(1)	101.5(3)	503
	1.790(3)/ 1.816(6)	101.0(1)/ 113.4(2)	504
Stibaalkenes			
$Mes(Me_3SiO)C{=}Sb\text{-}Sb{=}C(OSiMe_3)Mes$	2.066(4)	93.0(1)	505
$Mes^*(Me_3SiO)C{=}Sb\text{-}Sb{=}C(OSiMe_3)Mes^*$	2.06(1)	94.7(3)	506
$Mes^*C({=}O)\text{-}Sb{=}C(OH)Mes^*$	2.078(3)	91.3(1)	505

Table 16. Selected Structural Data for Heavier Main Group Element Imine Analogues $R_2E{=}NR'$ (E = Si, Ge, Sn)

compd	E=C (Å)	R−E−C [deg]	ref
Silaimines			
$^tBu_2Si{=}NSi^tBu_3$	1.568(3)	177.8(2)	509, 510
$(THF)^tBu_2Si{=}NSi^tBu_3$	1.589(6)	161.5(5)	509, 510
$(Ph_2C{=}O)^tBu_2Si{=}NSi^tBu_3$	1.601(3)	169.4(2)	511, 510
$(THF)^tBu_2Si{=}NSi^tBu_2Me$	1.597(3)	174.2(2)	512
$(EtMe_2N)^tBu_2Si{=}NSi^tBu_3$	1.603(2)	156.5(1)	513
$[(THF_3Li)^+F^-]^tBuMeSi{=}NMes^*$	1.605(4)	161.2(3)	514
$[(THF_3Li)^+F^-]^tBu_2Si{=}NSi^tBu_2Ph$	1.609(3)	176.3(2)	515
$[^tBu_2Si{=}N^tBu]_2(LiF)_2Et_2O$	1.640(2)/ 1.678(2)	137.9(2)/ 132.7(2)	516
$^tBu_2Si{=}NSi^tBu_2Ph$	1.573(3)	173.0(2)	517
$(THF)^tBu_2Si{=}NSi^tBu_2{}^iPr$	1.599(3)	168.9(1)	517
$(pyridine)^tBu_2Si{=}NSi^tBu_2Ph$	1.611(3)	172.5(1)	517
$(pyridine)^tBu_2Si{=}NSi^iPr_2{}^tBu$	1.606(2)	176.0(1)	517
$(THF)^tBuNCH_2CH_2N^tBuSi{=}NCph_3$	1.599(4)	131.3(3)	518
Germaimines			
$\{(Dipp(Me_3Si)N\}_2Ge{=}NDipp$	1.703(2)	134.2(2)	519
$\{(Mes(Me_3Si)N\}_2Ge{=}NDipp$	1.690(4)	139.0(2)	519
$\{(Me_3Si)_2N\}_2Ge{=}N\text{-}(1\text{-}Ad)$	1.701(2)	130.1(1)	520
$\{(Me_3Si)_2N\}_2Ge{=}N\text{-}Si^tBu_2N_3$	1.703(5)	136.0(4)	521, 522
$[\{(Me_3Si)_2CH\}_2Ge{=}N]_2SiMes_2$	1.682(8)	137.3(5)	521
Stannaimines			
$\{(Me_3Si)_2N\}_2Sn{=}NDipp$	1.921(3)	120.5(2)	523
$\{(Me_3Si)_2N\}_2Sn{=}N\text{-}Si^tBu_2N_3$	1.905(5)	130.6(3)	522

stability of the silylene unit is responsible for the weaker bonding in $(THF)^tBuNCH_2CH_2N^tBuSi{=}NCPh_3$.

Several germa- and stanna-imines have been structurally characterized. In these, the E−N distances are close to 1.70 Å for E = Ge and 1.91 Å for E = Sn (cf. Table 16). The bending angle at nitrogen progressively narrows upon descending the group from values close to 180° for silicon to about 135° for germanium and 120−130° for tin. No lead-imine has been structurally characterized to date.

Examples of double bonds between two heavier elements of group 14 and 15 are scarce, but several have been reported during the past decade. For example, the silicon and phosphorus atoms in $HP{=}Si(Si^tBu_3)Trip$[524] are separated by 2.094(5) Å and coordination around the low valent silicon center is planar with a sum of angles of 359.9°. Metalation with dimethyl zinc afforded $MeZnP{=}Si(Si^tBu_3)Trip$, the first example of a silaphosphene metalated at phosphorus. In this species, Si−P distance of 2.064(1) Å is somewhat shorter than in the parent $HP{=}Si(Si^tBu_3)Trip$.[524] The silicon atom features planar coordination, and the bending angle at phosphorus is 103.20(5)°. Reaction of $HP{=}Si(Si^tBu_3)Trip$ with a bis(trimethylsilyl)amido β-diketimidinato Pb(II) species resulted in a lead(II) substituted phosphasilene (Figure 10). In this species, the silicon−phosphorus double bond distance is 2.085(1) Å, the angle at phosphorus is 97.10(5), and the $Si_2Si{=}PPb$ entity is strictly planar.[526] The phosphasilene $(^tBu_2MeSi)_2Si{=}PMes^*$ and phosphagermene $(^tBu_2MeSi)_2Ge{=}PMes^*$ were isolated from the reaction of $(^tBu_2MeSi)_2ELi_2$ (E = Si, Ge) with Mes^*PCl_2.[529] Both compounds feature a planar arrangement of the double bond and the attached substituents. The Si=P and Ge=P distances are 2.1114(7) and 2.1748(14) Å, respectively, values which are slightly longer than for the carbon substituted examples given in Table 17. The angles are similar in both cases and are 110.66(7) for Si and 109.90(6) for Ge.

3.9. Compounds of Formula $[R_2E{=}\ddot{E}'R_2]^+$ (E = Group 14, E′ = Group 15 Element)

Methylene phosphonium ions, $[R_2C{=}PR_2]^+$, have C=P bond distances similar to those in phosphenes with an average value near 1.68 Å and mostly planar geometries at both carbon and phosphorus. However, nonplanar structures are observed for derivatives in which the carbene fragment is bis amino substituted like $[Ph_2P{=}CN^iPrCMeCMeN^iPr][GaCl_4]$[533] or $[Ph_2P{=}CN^iPrCMeCMeN^iPr][AlCl_4]$.[534] In these, long C−P distances of over 1.81 Å are accompanied by drastic

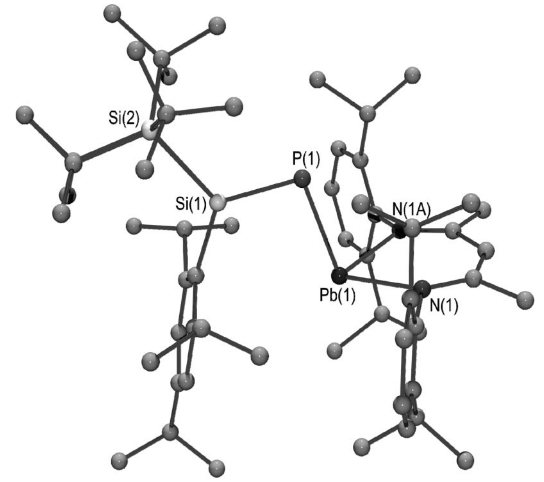


Figure 10. Molecular structure of $Trip(^tBu_3Si)Si{=}P\text{-}PbNDippC(CH_3)CHC(CH_3)NDipp$. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (deg): P(1)−Si(1) 2.085(1), P(1)−Pb(1) 2.671(1), Si(1)−Si(2) 2.414(2), Pb(1)−N(1) 2.368(2); Si(1)−P(1)−Pb(1) 97.10(5), Si(2)−Si(1)−P(1) 117.1(1), P(1)−Pb(1)−N(1) 97.24(7), N(1)−Pb(1)−N(1A) 81.97(9).[526]

Table 17. Selected Structural Data for Sila- and Germaphosphenes and -Arsenes $R_2E{=}E'R'$ ($E = Si, Ge$; $E' = P, As$)

compd	E=C (Å)	R−E−C [deg]	ref
Silaphosphenes			
$HP{=}Si(Si^tBu_3)Trip$	2.094(5)		524
(η^2-tmeda)·$MeZnP{=}Si(Si^tBu_3)Trip$	2.064(1)	103.20(5)	524
2,4-$^iPr_2\overline{C_6H_2CHMeCH_2Si}(^tBu)P{=}Si^tBuTrip$	2.063(2)	108.09(8)	525
$Trip(^tBu_3Si)Si{=}P\text{-}\overline{PbNDippC(CH_3)CHC(CH_3)N}Dipp$	2.085(1)	97.10(5)	526
$Trip^tBuFSiP{=}Si^tBuTrip$	2.053(3)	104.6(1)	527
$Mes^*P{=}Si^tBuPMes^*PPh_2$	2.094(3)	104.2(2)	528
$Mes^*P{=}Si(Si^tBu_2Me)_2$	2.1114(7)	110.66(7)	529
$(^iPr_3Si)P{=}SiTrip^tBu$	2.063(3)	112.81(9)	530
Silaarsene			
$(^iPr_3Si)As{=}SiTrip^tBu$	2.165(3)	110.90(9)	530
Germaphosphenes			
$Mes^*P{=}GeMes_2$	2.137(2)	107.5(2)	531
$Mes^*P{=}GeMes^tBu$	2.143(4)	103.1(4)	532
$Mes^*P{=}Si(Si^tBu_2Me)_2$	2.1748(14)	109.90(16)	529

deviations from planarity at phosphorus and almost perpendicular orientations of the substituent coordination planes at carbon and phosphorus which rules out multiple P−C bonding. Similarly, the phosphorus bis amino substituted compound $[(^iPr_2N)_2P{=}C(SiMe_3)_2][CF_3SO_3]$[537] displays a twist angle around the central C−P bond axis of 56.1°, indicating weak π-bonding. Nevertheless, a very short C−P distance of only 1.620(3) Å is seen which is probably a consequence of electrostatic interactions.

Recently, the synthesis and structural parameters for two gallium(III) halide adducts of phosphaalkenes were reported. In these, direct gallium−phosphorus contacts are observed. The C=P distance is 1.686(3) Å in the case of $Ph_2P{=}CMesGaCl_3$[371] and 1.69(1) Å in $Mes^*P(GaI_3)P{=}CHCH{=}P(GaI_3)Mes^*$ (Table 18).[538] Both examples feature planar geometries at the carbon and phosphorus atoms and a very small degree of twisting along the central bond.

3.10. Compounds of Formula $R_2E{=}\ddot{E}'$ (E = Group 14, E′ = Group 16 Element)

The investigations of heavier group 14 analogues of aldehydes and ketones and their heavier congeners have been a very active field over the past decade although many challenges remain. For example no stable compounds with bonding between a three coordinate tetrel and a terminal oxygen, i.e., a heavier tetrel analogue of a ketone, have been published. However, in the field of silicon group 16 multiple bonded compounds, the isolation and structural characterization of a $B(C_6F_5)_3$ complex of a silaaldehyde, $Dipp\overline{NCMeCHCMeNDippSi}(H){=}O\cdot B(C_6F_5)_3$,[541] and the silanoic ester, $Dipp\overline{NC({=}CH_2)CHCMeNDippSi}O\overline{Si({=}O)NDippCMeCHCMeN}Dipp$,[540] which feature four coordinate silicons, were reported (Figure 11, Table 19). In these, the Si=O distances were 1.552(2) Å for the sila aldehyde and 1.579(3) Å in the case of the

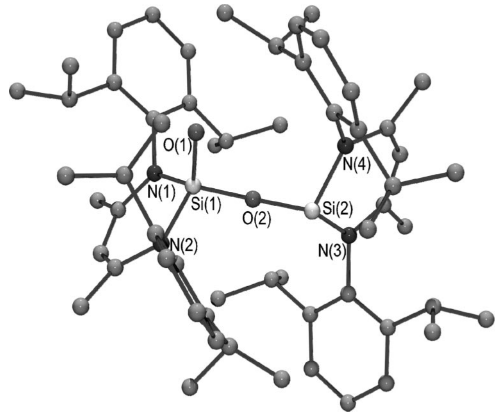
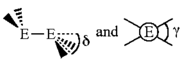


Figure 11. Structure of $Dipp\overline{NCMeCHCMeNDippSi}O\overline{Si({=}O)NDippCMeCHMeN}Dipp$. Hydrogen atoms are not shown. Selected bond lengths (Å) and angles (deg): Si(1)−O(1) 1.579(3), Si(1)−O(2) 1.629(3), Si(2)−O(2) 1.625(2), Si(1)−N(1) 1.768(2), Si(1)−N(2) 1.783(2), Si(2)−N(3) 1.753(2), Si(2)−N(4) 1.746(3); O(1)−Si(1)−O(2) 112.4(1), Si(1)−O(2)−Si(2) 140.5(1), O(1)−Si(1)−N(1) 113.5(1), O(1)−Si(1)−N(2) 112.2(1), N(1)−Si(1)−N(2) 100.4(1), N(3)−Si(2)−N(4) 103.1(1).[540]

Table 18. Selected Structural Data for Compounds of Formula $[R_2E{=}E'R2]^{+a}$

cmpd	C−P (Å)	δ (P) (deg)	δ (C) (deg)	γ (deg)	ref
$Ph_2P{=}CMesGaCl_3$	1.686(3)	16.9	2.8	6.5	371
$[Ph_2P{=}C\overline{N^iPr\ CMeCMeN}^iPr\ ][GaCl_4]$	1.82(2)	68.1	8.5	88.1	533
$[^tBu_2P{=}CPh_2][AlCl_4]$	1.683(11)	3.3	2.5	22.7	534
$[^tBu_2P{=}CPh(o\text{-}Tol][AlCl_4]$	1.680(9)	0.5	1.7	21.9	535
$[Ph_2P{=}C\overline{N^iPr\ CMeCMeN}^iPr\ ][AlCl_4]$	1.813(7)	70.1	6.0	81.4	536
$[(^iPr_2N)_2P{=}C(SiMe_3)_2][CF_3SO_3]$	1.620(3)	0.9	2.5	56.1	537
$Mes^*P(GaI_3){=}CHCH{=}P(GaI_3)Mes^*$	1.69(1)				538
$[^tBu_2P{=}CH(SiMe_3)][AlCl_4]$	1.69(4)				539

[a] The angles δ and γ are represented as



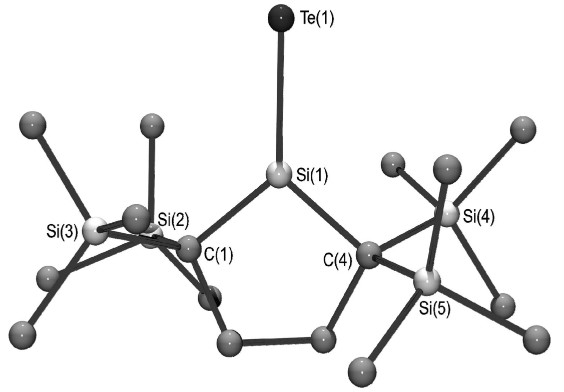


Figure 12. Molecular structure of $(Me_3Si)_2CCH_2CH_2C(SiMe_3)_2Si=Te$. Hydrogen atoms are not shown. Selected bond lengths (Å) and angles (deg): Si(1)−Te(1) 2.3210(7), Si(1)−C(1) 1.863(2), Si(1)−C(4) 1.861(2), C(1)−Si(2) 1.927(2), C(1)−Si(3) 1.915(2), C(4)−Si(4) 1.914(2), C(4)−Si(5) 1.911(2); C(1)−Si(1)−Te(1) 129.51(6), C(4)−Si(1)−Te(1) 128.90(6), C(1)−Si(1)−C(4) 101.59(8).[545]

silanoic ester. Both compounds have a β-diketiminato ligand at silicon as the stabilizing group. These results have been extended to afford a complete series of multiple bonded silicon-heavier group 16 element derivatives. In these, the Si=E distances are 1.980(2) Å for E = S, 2.1173(7) Å for E = Se, and 2.3458(8) for E = Te.[543] Additionally, silathiones, selenones, and tellurones of the general formula $(Me_3Si)_2CCH_2CH_2C(SiMe_3)Si=E$ were described (Figure 12). In these, the silicon is strictly three-coordinate and the Si=E distances are 1.9574(7) Å (E = S), 2.0963(7) (E = Se), and 2.3210(7) Å for E = Te.[545] In ^{t}BuNCPhN^{t}BuSi(=S)S^{t}Bu, the silicon sulfur distance is 1.9843(8) Å.[542] Earlier reports include the isolation of Tbt(Trip)Si=S[546,547] and (1-naphthyl)(1-naphthyl-8-$CHNMe_2$)Si=S.[544] In the latter, the dimethylamino group acts as a donor to the three coordinate silicon center.

A range of germanium compounds with double bonds to a group 16 element heavier than oxygen is known. However, stable and structurally characterized examples mostly feature nitrogen donor ligands, which stabilize the low coordinate germanium center through donation of additional electron density by a nitrogen atom either from a β-diketiminato ligand or an adjacent N-donor functionality. Germanium−sulfur double bond distances are in the range 2.050(4)[551,552] to 2.110(2) Å.[549] Similarly, most of the known germa selenones are stabilized by nitrogen donor groups. In these, Ge=Se double bond distances between 2.1724(9)[552] and 2.248(2)[562] Å are encountered. The number of germa tellurones is currently limited to four examples. Here, a clear difference between compounds with and without donor stabilization becomes apparent. In the donor free Ge=Te compounds, the germanium−tellurium distances are about 0.08 Å shorter and lie between 2.384(2) and 2.398(2) Å,[565] which compares to 2.467(2)[549] and 2.479(1)[562] Å for the donor stabilized complexes.

Stable compounds with double bonds between tin and heavier group 16 elements are also known. In an unusual bis stannylene/pyridinyl complex of SnO (cf. Table 20), the tin is four coordinate and the oxygen is three coordinate and the SnO distance is 2.114(2) Å, which is indicative of little multiple character.[566] Examples of tin−sulfur double bonds are either stabilized through nitrogen donors by sterically demanding ligand like Bbt or a borane fragment. Moreover, several imido stanna cubanes carrying exocyclic Sn=S and Sn=Se bonds are known. The Sn=S distances span a range from 2.221(4)[567] to 2.2958(2)[570] Å. Similarly, a series tin−selenium and tin−tellurium double bonds is known. Sn=S double bond distances are typically slightly shorter than 2.40 Å. Tin−tellurium double bonds which are about 2.60 Å long.

The only structurally characterized example of a lead-group 16 with a putative double bond is provided by the bis stannylene/pyridinyl complex of PbO, analogous to that described above for SnO, in which the lead−oxygen distance of 2.168 Å is observed (Table 21) which indicates little multiple character.[566]

3.11. Compounds of Formula $R\ddot{E}=\ddot{E}R$, (E or E′ = N, P, As, Sb, or Bi)

The original ground-breaking discoveries in this currently very active field of research were the isolation and charac-

Table 19. Bond Distances for Silicon−Chalcogen Multiple-Bonded Molecules

compd	E=C (Å)	ref
Si=O		
DippNC=CH_2CHCMeNDippSiOSi(=O)NDippCMeCHCMeNDipp	1.579(3)	540
DippNCMeCHCMeNDippSi(H)=O·B(C_6F_5)$_3$	1.552(2)	541
Si=S		
^{t}BuNCPhN^{t}BuSi(=S)S^{t}Bu	1.9843(8)	542
DippNC=CH_2CHCMeNDippSiOSi(=S)NDippCMeCHCMeNDipp	1.980(2)	543
(1-naphthyl)(1-naphthyl-8-$CHNMe_2$)Si=S	2.013(3)	544
$(Me_3Si)_2CCH_2CH_2C(SiMe_3)_2Si=S$	1.9574(7)	545
Tbt(Trip)Si=S	1.949(3)/1.952(4)	546, 547
Si=Se		
DippNC=CH_2CHCMeNDippSiOSi(=Se)NDippCMeCHCMeNDipp	2.1173(7)	543
$(Me_3Si)_2CCH_2CH_2C(SiMe_3)_2Si=Se$	2.0963(7)	545
Si=Te		
DippNC=CH_2CHCMeNDippSiOSi(=Te)NDippCMeCHCMeNDipp	2.3458(8)	543
$(Me_3Si)_2CCH_2CH_2C(SiMe_3)_2Si=Te$	2.3210(7)	545

Table 20. Bond Distances for Germanium−Chalcogen Multiple-Bonded Compounds

compd	E=C (Å)	ref
Ge=S		
DippNCMeCHCMeNDippGe(=S)(OH)	2.0770(7)	548
Me$_8$taaGe=S[a]	2.110(2)	549
PhNCMeCHCMeNPhGe(=S)Cl	2.074(1)	550
DippNCMeCHCMeNDippGe(=S)Cl	2.0529(7)	551, 552
DippNCMeCHCMeNDippGe(=S)F	2.050(1)	551, 552
DippNCMeCHCMeNDippGe(=S)Me	2.1043(7)	551, 552
Tbt(Trip)Ge=S	2.050(4)	553, 554
^{t}BuNSiMeN^{t}BuCH$_2$CH$_2$N^{t}BuGe(=S){N(SiMe$_3$)$_2$}NNNNN	2.090(2)	555
^{t}BuNSiMe(N^{t}Bu)$_2$SiMeN^{t}BuGe=S	2.063(3)	556
Me$_3$SiNCPh(SiMe$_3$)-2-py-Ge(=S)Cl	2.056(2)	557
Me$_3$SiNCPhC(SiMe$_3$)-2-py-Ge(=S){C-2-py-CPhN(SiMe$_3$)$_2$}	2.0835(9)	557
DippNCMeCHCMeNDippGe(=S)(SH)	2.0642(4)	558
Ge=Se		
DippNCMeCHCMeNDippGe(=Se)(OH)	2.2058(6)	559
Me$_8$taaGe=Se[a]	2.247(1)	549
DippNCMeCHCMeNDippGe(=Se)Me	2.199(2)	560
PhNCMeCHCMeNPhGe(=Se)Cl	2.2095(8)	550
CyNC^{t}BuN^{cy}HexGe(=Se)N^{cy}HexC^{t}BuN^{cy}Hex	2.195(4)	561
CyNC^{t}BuN^{cy}HexGe(=Se){N(SiMe$_3$)$_2$}	2.2113(3)	561
Tbt{(Me$_3$Si)$_2$CH}Ge=Se	2.173(3)	554
DippNCMeCHCMeNDippGe(=S)Cl	2.1974(6)	552
DippNCMeCHCMeNDippGe(=Se)F	2.1724(9)/2.1762(7)	552
DippNCMeCHCMeNDippGe(=Se)^{n}Bu	2.2185(6)	552
{(Me$_3$Si)$_2$C(2-py)}$_2$Ge=Se	2.248(2)	562
{μ^3-^{t}BuNGe(=Se)}$_3$(μ^3-^{t}BuGe)	2.185(1)−2.187(1)	563
Me$_3$SiNCPhC(SiMe$_3$)-2-py-Ge(=Se)Cl	2.191(1)	557
Me$_3$SiNCPhC(SiMe$_3$)-2-py-Ge(=Se){C-2-py-CPhN(SiMe$_3$)$_2$}	2.2228(9)	557
Tbt(Trip)Ge=Se	2.181(2)	554, 564
Ge=Te		
Me$_8$taaGe=Te[a]	2.467(2)	549
Tbt(Trip)Ge=Te	2.398(2)	565
Tbt{(Me$_3$Si)$_2$CH}Ge=Te	2.384(2)	565
{(Me$_3$Si)$_2$C(2-py)}$_2$Ge=Te	2.479(1)	562

[a] Me$_8$taa = Tetramethyldibenzotetra-aza(14)azulene.

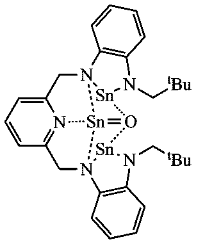
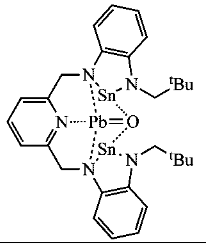
terization iminophosphine (^{t}Bu)N=P−N(SiMe$_3$)(^{t}Bu) in 1973 by Niecke and Flick[580] and the synthesis and characterization of the first stable diphosphene, Mes*P=PMes*, by Yoshifuji and co-workers in 1981.[581]

Synthetic strategies strategies for the generation of iminophosphines R-N=P-R′ largely rely on 1,2 elimination reactions starting firom aminophosphine precursor molecules. In neutral species, the N=P double bond distance falls in the range 1.49(1) Å[611] to 1.629(2) Å[585] and is typically 1.54 Å long (Table 22). Both, *cis*- and *trans*-isomers have been isolated. Among these, the *trans* forms are typically characterized by narrower R−N=P and N=P−R′ angles. With only a few exceptions, the bonding angle at phosphorus are about 15° narrower than those at nitrogen. In the *trans*-isomers, the R−N=P−R′ array deviates only slightly from planarity, but in the *cis* forms higher deviations from idealized geometries are common, which is presumably a result of higher steric congestion in the *cis*-isomer.

The isomerization has been studied by computational methods. According to ab initio calculations on the (hypothetical) parent molecule H−N=P−H, the *trans*-isomer is energetically slightly more favored by about 1.5 kcal/mol. The N=P double bond energy derived from the energy difference between the planar form and a configuration derived from a 90° rotation of the coordination planes at nitrogen and phosphorus is about 40−50 kcal/mol. Nevertheless, an alternative pathway for *cis*−*trans* isomerization is feasible via linearization of one of the pnictogen centers. Among the two possibilities, the barrier to linearization at the nitrogen atom is much lower in energy (by ca. 15 kcal/mol) than that at phosphorus. Structural data for Mes*N=PO-(C$_6$H$_2$-2,6-^{t}Bu$_2$-4-Me) reveal an almost linear arrangement of the P=N−R unit (Mes*-N=P 173.7(1)°) but a bent geometry at phosphorus (O−P=N 109.94(7)°).[614]

The influence of substituents on the N=P bond strengths is complex and has been analyzed in terms of σ- and π-bond effects. More electronegative (σ-acceptor) substituents on phosphorus or less electronegative (σ-donor) substituents on nitrogen, which counteract the natural N−P bond polarization, lead to stronger and shorter σ- and π-bonds. The picture, however, becomes more complex when π-donor/acceptor ligands are present. Introducing π-donor (e.g., NR$_2$ groups)

Table 21. Bond Distances for Heavier Group Element 14 (E)−Chalcogen (E′) Multiple-Bonded Compounds (E = Ge, Sn, Pb)[a]

Compound	E=C (Å)	Ref
Sn=O		
	2.114(2)	566
Sn=S		
Bbt{C_6H_3-2,6-(C_6H_3-2,4-^{i}Pr$_2$)$_2$}Sn=S	2.221(4)	567
Me$_8$taaSn=S$^{1)}$	2.275(2)	568
Me$_3$SiNCPhCHCPhN(SiMe$_3$)Sn(=Se){N(SiMe$_3$)$_2$}	2.255(2)	569
[H$_{11}$B$_{11}$Sn=S]$^{2-}$[HNEt$_3$]$_2^+$	2.2958(5)	570
^{cy}HexNC^{t}BuN^{cy}HexSn(=S)N^{cy}HexC^{t}BuN^{cy}Hex	2.281(4)	571
{μ^3-^{t}BuNSn}$_3${μ^3-^{t}BuNSn(=S)}	2.262(3)	563
Sn=Se		
{μ^3-^{t}BuNSn(=Se)}$_3$Li	2.3861(8)- 2.4040(10)	572
{μ^3-^{t}BuNSn}$_3${μ^3-^{t}BuNSn(=Se)}	2.361(4)	573
Tbt{C_6H_3-2,6-(C_6H_4-2-^{i}Pr)$_2$}Sn=Se	2.373(2)	574,575
Me$_8$taaSn=Se$^{1)}$	2.393(2)	568
[H$_{11}$B$_{11}$Sn=Se]$^{2-}$[NEt$_4$]$_2^+$	2.397(1)	570
{μ^3-^{t}BuNSn}$_2${μ^3-^{t}BuNSn(=Se)}Mg	2.3928(9)	576
{μ^3-^{t}BuNSn}$_2${μ^3-^{t}BuNSn(=Se)}Li$_2$	2.4516(7)	576
{μ^3-^{t}BuNSn}$_2${μ^3-^{t}BuNSn(=Se)}$_2$	2.3633(7)- 2.3713(8)	563
{Ph(Me$_3$Si)C(2-py)}$_2$Sn=Se	2.419(1)	577
{8-(Me$_3$SiCH$_2$)quinoline}$_2$Sn=Se	2.398(1)	578
Sn=Te		
{μ^3-^{t}BuNSn(=Te)}$_3${μ^3-^{t}BuNLi}	2.599(1)- 2.613(1)	572
{μ^3-^{t}BuNSn}$_2${μ^3-^{t}BuNSn(=Te)}$_2$	2.603(1)	573
Bbt{C_6H_3-2,6-(C_6H_3-2,4-^{i}Pr$_2$)$_2$}Sn=Te	2.5706(6)	579
{μ^3-^{t}BuNSn}$_2${μ^3-^{t}BuNSn(=Te)}{μ^3-^{t}BuNMg}	2.6111(7)	576
[{μ^3-^{t}BuNSn}$_2${μ^3-^{t}BuNSn(=Te)}{μ^3-^{t}BuNLi}]Li	2.6394(8)	576
[{μ^3-^{t}BuNSn}{μ^3-^{t}BuNSn(=Te)}$_2${μ^3-^{t}BuNLi}]	2.614(1)	576
{μ^3-^{t}BuNSn}$_3${μ^3-^{t}BuNSn(=Te)}	2.5889(6)	563
{8-(Me$_3$SiCH$_2$)quinoline}$_2$Sn=Te	2.619(2)	578
Pb=O		
	2.158(7)/ 2.177(6)	566

[a] (1) Me$_8$taa = Tetramethyldibenzotetra-aza(14)azulene.

at phosphorus strengthens the σ-bond but at the same time weakens the π-bond via conjugation. In contrast, the presence of a π-donor at nitrogen weakens both. the σ- and the π-bond. Introducing σ-donor (e.g., SiRs groups) subtituents at nitrogen decreases the inversion barrier which leads to more linear structures, whereas σ-acceptor substituents produce the opposite effect. In effect, σ-acceptor (or more electronegative) substituents at nitrogen disfavor linear inversion processes and lead to more bent- geometries. For example, the ^{i}Pr$_3$Si substituted derivative Cp*P=N−Si(^{i}Pr)$_3$ (Cp*= cyclo-C$_5$Me$_5$) exhibits a short N−P distance (1.533(3) Å) in the solid state and a wide P=N−Si angle of 153.3(2)°.[599] In the Mes* substituted analogue, Cp*P=N-Mes*, the N−P distance is 1.551(8) Å and the C$_{Mes*}$−N=P angle is only 125.9(6)°. Even more striking is the difference in the coordination mode of the Cp* group. In Cp*P=N-Mes*, it is bound in a η^1-mode, but in Cp*P=N−Si(^{i}Pr)$_3$ it is η^2-bound, indicating the presence of an intramolecular π-complex between the Cp* anion and the formally triply bonded [N≡P−Si^{i}Pr$_3$]$^+$ moiety. The latter species is isoelectronic with a phosphaalkyne.[599]

The number of arsaimines is quite limited and only *trans*-isomers have been isolated so far. In these, the average N−As is 1.708 Å, which is considerably shorter than the average As−N single bond distance of about 1.88 Å. The shortest As−N distance among the currently known examples was observed in 2,4,6-(CF$_3$)$_3$-C$_6$H$_2$N=As-2,4,6-(CF$_3$)$_3$-C$_6$H$_2$ with 1.707(3) Å. The angle at arsenic approaches 90° (96.3°) and much narrower than the 125.6(2)° bending angle at nitrogen.[623] The corresponding angles in the phosphorus analogue, 2,4,6-(CF$_3$)$_3$-C$_6$H$_2$N=P-2,4,6-(CF$_3$)$_3$-C$_6$H$_2$, are 99.8(1)° (N=P−CAr) and 130.2(2)° (C$_{Ar}$−N=P),[598] demonstrating the higher ability of phosphorus in comparison to arsenic to contribute in π-bonding and the increasing energy gap between s- and p-orbitals upon decending the group. The imino derivative Mes*N(H)-As=N-Mes*, has two similar As−N distances (1.714(7) Å for As=N and 1.745(8) Å for As−N) and a bending angle of 98.76(3)° at arsenic.[586] The compound exhibits slow prototropy in solution, presumably intramolecularly via the *cis*-isomer rather than in an intermolecular exchange process. The phosphorus analogue Mes*N(H)-P=N-Mes* features two more distinct P−N distances, 1.57(1) Å (N=P) and 1.63(1) Å (N−P), and an angle of 103.8(7)° around P.[586,587] No crystallographic data on iminostibines or -bismuthines are currently available.

Dipnictenes in which both group 15 elements are heavy require more sterically encumbering ligands to stabilize the multiple bond and prevent oligomerization. The first stable diphosphene Mes*P=PMes* was reported by Yoshifuji and co-workers in 1981,[581] and a rapidly increasing number of stable compounds featuring P=P double bonds, among which is a large number of donor complexes of transition metal complexes, is now available. A detailed discussion of the latter derivatives, however, is beyond the scope of this text. Nevertheless, species in which transition metal fragments are σ-bound in a covalent rather than dative fashion have been included in Table 23. Almost all uncomplexed diphosphenes feature *trans*-structures. The structures of three *cis*-isomers have been reported. In each of these compounds, at least one of the sterically demanding groups R is bound through nitrogen. The P−P distances in classical diphosphenes fall in the range 1.985[624] to 2.050 Å[648] and are considerably shorter than P−P single bonds for which a distance of about 2.22 Å is expected. R−P=P angles are generally narrow, with typical values near 105° and a range from 89.77°[643] to 114.93° in TbtP=PTbt for *trans*-diphosphenes.[624] Nevertheless, even wider R−P=P angles of up to 126.28°[614] are observed in the *cis*-isomers,[628,639] which is presumably due to the close proximity of the bulky ligands which stretch the P=P bond. A somewhat wider H−P=P angle and a slightly longer P=P distance was also predicted for the *cis*-isomer of HP=PH in recent high level calculations. The heats of formation of the *cis*- and *trans*-isomers differed by about 3.3 kcal/mol with the *trans*-isomer being more energetically favored.[661] Similar results had been

Table 22. Selcted Structural Data for Phosphaimines (RN=PR) and Related Compounds

compd	N−P (Å)	R−N−E [deg]	N−E−R [deg]	ref
Phosphaimines				
$^{t}BuN{=}PMes^*$	1.556(5)	122.7(5)	100.7(3)	582
$^{t}Bu_2P({=}S)N{=}PN(SiMe_3)_2$	1.574(4)/1.575(4)	120.2(2)/120.2(2)	106.3(3)/106.3(6)	583
$(Me_3Si)_2NN{=}P(tmp)$	1.599(5)	107.1(4)	107.7(3)	584
$^{t}BuN{=}P\{C_6H_3\text{-}2,6\text{-}(CF_3)_2\}$	1.537(3)	123.8(2)	99.7(2)	585
$Me_2NN{=}P\{C_6H_3\text{-}2,6\text{-}(CF_3)_2\}$	1.629(2)	121.1(1)	95.31(7)	585
$Mes^*N{=}PN(H)Mes^*$	1.57(1)	126(1)	103.8(1)	586, 587
$^{t}Bu_2PN{=}PN(SiMe_3)P^{t}Bu_2$	1.54(1)	115.6(5)	107.3(4)	588
	1.556(8)	112.4(5)	105.3(4)	
$Mes^*N{=}PCEt_3$	1.566(2)	124.8(2)	104.7(1)	589
$Mes^*N{=}PNMes^*PEt(CH{=}CHPh)$	1.566(8)	122.7(6)	106.5(4)	589
$Mes^*N{=}PN(SiMe_3)_2$	1.563(3)	117.7(1)	109.3(1)	590
$(Z)\text{-}Mes^*N{=}PNMe_2$	1.539(3)	140.7(4)	115.9(2)	591
$Mes^*N{=}PN^{i}Pr_2$	1.555(2)	129.6(2)	105.6(1)	591
$Mes^*N{=}P(OC_6H_4\text{-}2\text{-}Me)$	1.497(2)	164.1(1)	111.81(8)	592
$Mes^*N{=}P(S^{t}Bu)$	1.549(2)	131.3(2)	109.04(9)	593
$Mes^*N{=}PP^{t}Bu_2$	1.568(3)	120.3(2)	105.96(9)	594
$Me_3SiN{=}PC(SiMe_3)P(NMe_2)_3$	1.557(5)	138.8(3)	108.4(3)	595
$(Z)\text{-}Mes^*N{=}PN(H)^{t}Bu$	1.545(6)	128.1(4)	110.3(3)	596
$Mes^*N{=}PN(H)CPh_3$	1.548(5)	127.3(3)	107.4(2)	596
$Mes^*N{=}PN^{t}BuP{=}NMes^*$	1.526(4)	130.3(3)	105.7(2)	596
	1.530(5)	124.5(3)	109.0(2)	
$Mes^*N{=}PNMesP{=}NMes^*$	1.555(6)	122.5(5)	104.7(3)	596
	1.539(7)	121.4(5)	114.6(3)	
$Mes^*N{=}PN(1\text{-}Ad)P{=}NMes^*$	1.510(5)	147.4(4)	116.6(3)	596
	1.544(5)	129.2(3)	109.4(3)	
$^{t}BuN{=}PN^{t}BuSiMe_3$	1.5445(5)	124.41(7)	104.86(6)	597
$ArN{=}PAr\ Ar{=}\{C_6H_2\text{-}2,4,6\text{-}(CF_3)_3\}$	1.561(2)	130.2(2)	99.8(1)	598
$Mes^*N{=}PCp^*$	1.551(7)	126.0(6)	106.0(5)	599
$^{i}Pr_3SiN{=}PCp^*$	1.533(3)	153.3(2)		599
$[Mes^*N{=}P{:}NHC]^+I^{-a}$	1.547(3)	116.2(2)	103.0(2)	600
$Mes^*N{=}PBr{:}NHC^a$	1.578(4)	116.1(3)	101.9(2)	600
$Dipp^*N{=}PCl{:}NHC^a$	1.543(2)	142.9(2)	106.99(9)	600
$Mes^*N{=}P{=}C(NMe_2)_2$	1.583(4)	123.7(4)	111.6(2)	450
$Mes^*N{=}PC(SiMe_3)_3$	1.566(3)	120.2(2)	110.4(1)	601
$Mes^*N{=}P\{OCH(CF_3)_2\}$	1.526(5)	128.9(4)	106.3(2)	602
$Mes^*N{=}P\{N(PPh_2)\}_2NP{=}NMes^*$	1.562(2)	118.6(2)	107.1(1)	603
$Mes^*N{=}PCl$	1.496(6)	154.7(4)	112.5(2)	604−606
$(Me_3Si)_2NN{=}PP^{t}Bu_2$	1.619(2)	124.1(2)	95.77(8)	607
$Mes^*N{=}PN^{t}BuP{=}NMes^*$	1.528(5)	125.7(4)	106.0(2)	608
	1.529(5)	120.4(3)	109.5(2)	
$[^{t}Bu_2MePN{=}PTmp]^+I^-$	1.591(2)	128.3(1)	107.42(9)	609
$Mes^*N{=}PN(CH)_4CH_2$	1.581(2)	129.5(2)	105.0(1)	610
$(Me_3Si)N{=}PN(SiMe_3)_2$	1.5453(6)	129.9(1)	108.4(3)	597
$Mes^*N{=}PSeP({=}Se)^{t}Bu_2$	1.49(1)	169(1)	112.6(5)	611
$Mes^*N{=}PN{=}CH^{t}Bu_2$	1.554(3)	167.5(3)	107.3(2)	612
$Mes^*N{=}PN{=}(9\text{-fluorene})$	1.548(4)	137.2(3)	114.6(2)	612
$Mes^*N{=}P\{OC_6H_2\text{-}2,6\text{-}^{t}Bu_2\text{-}4\text{-}Me\}$	1.498(2)	173.7(1)	109.94(7)	613
$Mes^*N{=}PN(SiMe_3)N(SiMe_3)_2$	1.559(4)	115.4(3)	107.4(2)	614
$Mes^*N{=}PNMes^*PMe\{Si(SiMe_3)_3\}$	1.537(3)	152.3(3)	111.2(2)	615
$Mes^*N{=}PNMes^*P(N{=}CHPh_2)_2$	1.538(6)	135.3(5)	107.4(3)	615
$Mes^*N{=}PBr$	1.498(6)	159.6(5)	113.5(2)	606
$Mes^*N{=}PNMes^*PN{=}CH_2P(N^{i}Pr_2)_2CH_2{=}N$	1.559(3)	128.2(2)	105.3(2)	616
$Mes^*N{=}PCl{:}NHC$	1.585(5)	120.2(3)	101.9(2)	617, 600
$Mes^*N{=}P(OSO_2CF_3){:}NHC$	1.574(4)	116.2(3)		600
$Mes^*N{=}PO^{t}Bu$	1.529(5)	144.7(3)	110.0(2)	618
$Mes^*N{=}PO(\text{-}(-)\text{-menthyl})$	1.504(4)	155.1(4)	113.1(2)	619, 620
Arsaimines				
$Mes^*N{=}AsNHMes^*$	1.714(7)	123.2(6)	98.8(3)	586
$Mes^*N{=}AsN(SiMe_3)N(SiMe_3)_2$	1.708(3)	111.9(2)	104.0(1)	621
$2,4,6\text{-}(F_3C)_3C_6H_2N{=}As(C_6H_2\text{-}2,4,6\text{-}(CF_3)_3)$	1.707(3)	125.6(2)	96.3(1)	622

[a] NHC = $:CN^{i}PrCMe{=}CMeN^{i}Pr$.

obtained earlier.[662] Nonetheless, the preference for *trans*-structure observed in most of the solid structures of diphosphenes is due to steric interaction of the substituents rather than electronic reasons. *cis/trans* Isomerization proceeds via rotation around the P=P bond rather than linearization and rehybridization on one of the phosphorus atoms. Given this finding, the rotation barrier can be assumed to be approximately equal to π-bond strength as there is no π-bonding interaction in the transition state in which both fragments adopt a perpendicular arrangement. Energy barriers of 20.3 kcal/mol for $Mes^*P{=}PMes^*$,[663] 25.5 kcal/mol for $Mes^*P{=}PN(SiMe_3)N(SiMe_3)_2$,[614] and 19.1 kcal/mol at 0° ($\Delta H^{\ddagger} = 29.5 \pm 1.4$ kcal/mol, $\Delta S^{\ddagger} = 38 \pm 6$ cal/(mol K)) in $Mes^*P{=}PTrip$ were experimentally determined.

Table 23. Selected Structural Data for Diphosphenes [RP=PR] and Related Compounds

compd	P=P (Å)	R−P−P (deg)	ref
Mes*P=PMes*	2.03421(7)	102.78	581
Mes*P=PMes*	2.046(2)	103.43	623
TbtP=PTbt	2.050(2)	106.37	624
BbtP=PBbt	2.043(1)	114.93	624
$(Me_3Si)_3CP{=}PC(SiMe_3)_3$	2.009 av	108.6 av	625, 626
$(Me_3Si)_3CP{=}PC(SiMe_3)_3$	2.005 av	108.4 av	627, 628
Mes*P=P(=S)Mes*	2.054(1)	99.87/106.11	629
$(^tBu_2MeSi)_2NP{=}PN(Si^tBu_2Me)_2$	2.0340(5)	102.16	630
$Mes^*P{=}P[Mes^*\{Cr(CO)_3\}]$	2.043(5)	100.56/105.36	631
$[\{Cr(CO)_3\}Mes^*]P{=}P[Mes^*\{Cr(CO)_3\}]$	2.044(2)	102.97	632
$(Me_3Si)_3SiP{=}PSi(SiMe_3)_3$	2.026 av	101.62 av	632
$Mes^*P{=}PC(OSiMe_3){=}PMes^*$	2.035(2)	98.50/96.94	391
TbtP=PFc	2.028(2)	103.17/101.66	633
Mes*P=PFp*	2.027(3)	102.92/109.82	634
Cp*P=PCp*	2.031(3)	103.39	635
Mes*P=P(=S)Fp*	2.042(1)	104.60/114.18	636, 637
$Mes^*P{=}P\{C_6H_3\text{-}2,6\text{-}(CMe_2)(CH_2)_9\}$	2.039(1)	97.91/101.41	638
(*Z*)-$Mes^*P{=}PN(H)^tBu$	2.039(3)	102.2/109.91	639
(*Z*)-Mes*P=PN(H)(1-Ad)	2.043(3)	102.17/109.25	639
BbtP=PFcP=PBbt	2.02(1)	103.25/101.85	640, 641
TbtP=PFcP=PTbt	2.014(4)	98.52/102.08	640, 641
NHC:P−P=P−P:NHC NHC=:CN(Dipp)C(Me)CHC(Me)N(Dipp)	2.076 av	110.1 av	409
$(Me_3Si)_3CP{=}PSiPh_3$	2.006(2)	110.48/98.64	642
$Mes^*P{=}PP(N^iPr_2)_2$	2.019(2)	101.21/92.25	643
$Tmp^*P{=}PP(N^iPr_2)_2$	2.029(2)	114.81/89.35	643
$(^tBu_2MeSi)_2NP{=}PP(N^iPr_2)_2$	2.011(2)	110.56/89.77	643
TbtP=P(9-anthryl)	2.035(2)	100.79/101.86	644
$RP{=}PR\ R{=}\{C(SiMe_3)_2(^iPr_2PCl_2Si)\}$	2.0436(3)	106.05	645
$\{2,4,6\text{-}(CF_3)_3\text{-}C_6H_2\}P{=}P\{C_6H_2\text{-}2,4,6\text{-}(CF_3)_3\}$	2.022(3)	97.8	646
$ArP{=}PAr,\ Ar{=}2,6\text{-}^tBu_2\text{-}4\text{-}MeO\text{-}C_6H_2$	2.043(1)	99.6 av	647
$Aa^{\#}cP{=}PAr^{\#}$	1.985(3)	109.8/97.5	648
$\{(Me_3Si)_3C\}P{=}PFp^*$	2.015(2)	107.41/111.25	649
$ArP{=}PAr\ Ar{=}\{2,6\text{-}(2,6\text{-}Cl_2{-}C_6H_3)_2C_6H_3\}$	2.030 av	98.7 av	650
$Ar^{\#}P{=}PMes^*$	2.024(1)	101.19/98.00	651
$Mes^*P{=}PSn^tBu_3$	2.032(4)	102.14/100.51	652
$Mes^*P{=}PN^iPr_2$	2.049(1)	91.96/108.12	653
Mes*P=PTmp	2.033(2)	89.36/115.21	653
(*E*)-$Mes^*P\text{-}PN(SiMe_3)N(SiMe_3)_2$	2.037(2)	97.65/106.19	614
(*Z*)-$Mes^*P\text{-}PN(SiMe_3)N(SiMe_3)_2$	2.03(9)	121.42/126.28	614
$\{2,6\text{-}(CF_3)_2\text{-}C_6H_3\}P{=}P\{C_6H_3\text{-}2,6\text{-}(CF_3)_2\}$	2.019(2)	98.07	654
$\{2,4,6\text{-}(CF_3)_3\text{-}C_6H_2\}P{=}PN(\text{fluorenyl})Mes$	2.039(3)	90.40/104.51	655
$\{(Cl_3Si)(Me_3Si)_2C\}P{=}P\{C(SiMe_3)_2(SiCl_3)\}$	2.018 av	106.97	656
$\{(Cl_3Ge)(Me_3Si)_2C\}P{=}P\{C(SiMe_3)_2(GeCl_3)\}$	2.019(3)	106.57	656
$1,4\text{-}(Ar^{\#}P{=}P)_2\text{-}Ar\ Ar{=}C_6\text{-}2,3,5,6\text{-}(4\text{-}^tBu\text{-}C_6H_4)_4$	2.009(3)	106.33/97.52	657
$[Mes^*P{=}PPPh_3]^+[BPh_4]^-$	2.025(1)	98.77/96.78	658
$[(Me_3Si)_2N(Me_3Si)N]P{=}P[N(SiMe_3)N(SiMe_3)_2]$	2.038(1)	103.38/103.43	659
(*Z*)-$Ar^{\#}P(Tl)P{=}PP(Tl)Ar^{\#}$	2.141(2)	100.65/101.75	660

The electron density distribution in the archetype Mes*P=PMes* has been investigated experimentally by means of electron deformation density studies. In combination with DFT calculations, the P=P bond clearly comprises σ- and π-contributions. In Mes*P=PMes*, the HOMO-1 is largely formed by the p_z-orbitals of the phosphorus atoms and represents a conventional π-bond. The HOMO, only slightly higher in energy, represents the symmetric P atom lone pair combination n_+.[623] Computational studies on the frontier orbitals of HP=PH afforded a similar picture. In this case, however, the HOMO-1 is the n_+ lone pair combination and, slightly higher in energy, the HOMO represents the π-bond. The LUMO corresponds to the antibonding π* orbital. As a consequence of the inert pair effect, descending the periodic table leads to an increased energy differences between HOMO and HOMO-1 in HE=EH (E = P, As, Sb, Bi) and also leads to progressively more acute angles R−E=E experimentally observed in heavier dipnictenes.[664]

In the recently reported 1,2-bis-*N*-heterocyclic carbene stabilized dicationic diphosphene $[L{:}P{=}P{:}L]^{2+}$ (L=:C-$(NDippCH)_2$), which is isoelectronic to the neutral group 14 derivatives L:E=E:L (E = Si,[346] Ge[351]), the P−P distance in the P_2^{2+} unit was 2.083(1) Å and the angle C−P−P 97.23(8)°. For comparison, in the radical cations $[L{:}P{=}P{:}L]^+$, somewhat longer P−P distances of 2.088(1)−2.094(1) Å were found.[665]

Soon after the discovery of the first diphosphene, the first example of a stable, uncomplexed diarsene, $(Me_3Si)_2CHAsAsCH(SiMe_3)_2$, was synthesized and structurally characterized by Cowley and co-workers.[623,666] The As−As distance of 2.246(2) Å was shortened by about 9% in comparison to a typical As−As single bond distance of about 2.44 Å. The heteroleptic diarsene $Mes^*AsAsCH(SiMe_3)_2$ has an As=As distance of 2.219(3) Å, which is the shortest such distance in a diarsene.[671] The angle at the Mes* substituted As was found to be 6.5° narrower than that at the $CH(SiMe_3)_2$ bearing arsenic atom. The longest As−As separations were observed in the terphenyl substituted derivatives Ar′As=AsAr′ (2.276(2) Å) and Ar*As=AsAr* (2.285(3) Å) (Table 24).[667] In the β-diiminato based complex $(\eta^1\text{-}L)_2As{-}As{=}As\text{-}(\eta^2\text{-}L)$ (L = DippNCHC(Ph)CHN(Dipp)), the As=As double bond dis-

Table 24. Selected Structural Data for Diarsenes [RAs═AsR] and Related Compounds

compd	As═As (Å)	R−As−As (deg)	ref
Mes*As═AsCH(SiMe$_3$)$_2$	2.219(1)	93.5/100.04	626, 666
Mes*As═AsMes*	2.263(1)	97.46	670
Ar$^\#$As═AsAr$^\#$	2.276(2)	98.49	667
Ar*As═AsAr*	2.285(3)	96.39/107.74	667
(Me$_3$Si)$_3$CAs═AsC(SiMe$_3$)$_3$	2.246(2)	106.38	671
DippNCHPhCCHN(Dipp)As═As- As{N(Dipp)CHPhCCHNDipp)}$_2$	2.3328(8)	89.88(3)	668
DippNC(NCy$_2$)NDippAs═AsNDippC(NCy$_2$)NDipp	2.2560(6)	95.07/84.72	672

Table 25. Selected Structural Data for Distibenes [RSb═SbR] and Related Compounds

compd	Sb═Sb (Å)	R−Sb−Sb (deg)	ref
TbtSb═SbTbt	2.642(2)	101.42	673
BbtSb═SbBbt	2.7037(2)	105.38	674
[TbtSb═SbTbt]Li	2.7511(3)	102.30	675
Ar$^\#$Sb═SbAr$^\#$	2.6558(4)	94.12	667
Ar*Sb═SbAr*	2.670(3)	98.92	667

Table 26. Selected Structural Data for Dibismuthenes [RBi═BiR] and Related Compounds

compd	Bi═Bi (Å)	R−Bi−Bi (deg)	ref
TbtBi═BiTbt	2.821(1)	100.56	676
BbtBi═BiBbt	2.8701(5)	104.13	674
Ar$^\#$Bi═BiAr$^\#$	2.833(1)	92.48	667
Ar′Bi═BiAr′	2.8560(2)	105.44	678
{(Ph^{t}Bu$_2$Si)$_2$P}Bi═Bi{P(Si^{t}Bu$_2$Ph)$_2$}	2.8205(9)	89.38	679
[Bi═Bi][K•crypt]$_2$	2.8377(5)		680
[Bi═Bi][Cs˙18-crown-6(NH$_3$)$_2$]$_2$	2.8634(4)		681

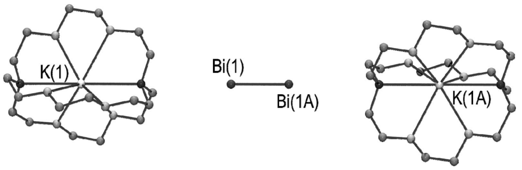


Figure 13. Molecular structure of [Bi═Bi][K•crypt]$_2$. Hydrogen atoms are not shown. Selected bond lengths (Å): Bi(1)−Bi(1A) 2.8377(5), Bi(1)−K(1) 7.388(1).[680]

Table 27. Selected Structural Data for Unsymmetrical Dipnictenes [RE═ER] (E = Pb, As, Sb, Bi ≠ E′= P, As, Sb, Bi)

compd	E═E′ (Å)	R−E−E′ (deg)	E−E′−R (deg)	ref
Mes*P═As{CH(SiMe$_3$)$_2$}	2.124(2)	96.45(8)	101.24(8)	682
MesP═AsAr*	2.134(3)	96.7(3)	101.5(2)	683
Mes*P═AsAr*	2.142(7)	98.6(2)	100.8(4)	670
MesP═SbAr*	2.335(3)	95.7(3)	100.9(2)	683
Mes*P═BiBbt	2.4541(7)	96.41(8)	102.16(6)	684
BbtSb═BiBbt	2.972(5)	101.2(2)	107.4(2)	685

tance was 2.3328(8) Å.[668] Of historical interest in the context of diarsenes is the formulation of Ehrlich's anti-syphilitic drug "Salvarsan", initially considered a diarsene (3-NO$_2$-4-OH-C$_6$H$_3$As)$_2$ but later confirmed to be a mixture of oligomers.[669]

Only a handful of stable distibenes have been synthesized. The first reported structure was that of TbtSb═SbTbt,[673] which was originally prepared by reduction ofTbtSbCl$_2$ with Mg, Li, or LiNp, but due to its surprisingly low solubility could only be characterized when obtained from the deselenation of (TbtSbSe)$_3$ with (Me$_2$N)$_3$P. As evidenced by trapping reactions, its formation proceeds via a stibolene, TbtSb. The Sb−Sb distance and the C−Sb−Sb angle were found to be 2.642(2) Å and 101.42°. A somewhat longer distance and slightly wider angles were observed in BbtSb-SbBbt (Sb═Sb 2.7037(2) Å, C−Sb═Sb 105.380).[674] Shortly after, the terphenyl-based distibenes Ar$^\#$SbSbAr$^\#$ (Sb═Sb 2.6558(4)Å, C−Sb−Sb 94.12°) and Ar*SbSbAr* (Sb═Sb 2.670(3) Å, C−Sb═Sb 98.92°) were synthesized (Table 25).[667] Reduction at BbtSbSbBbt with elemental lithium yielded the singly reduced anion radical [BbtSbSbBbt]Li with formal bond order of 1.5, which featured an elongated Sb−Sb bond (2.7511(3) Å) but almost unchanged C−Sb−Sb angles of 102.30°. According to EPR measurements, the electron is delocalized over the central Sb−Sb bond.[675]

A series of dibismuthenes completes the family of homonuclear, heavier dipnictenes. The Bi−Bi distances are in the range 2.8205(9)[679] to 2.8701(5)[674] Å. The first example, published in 1997, was TbtBi═BiTbt, with Bi−Bi bond length 2.821(1) Å and C−Bi−Bi angle of 100.56°.[262,676] Interestingly, the C−Bi−Bi angle in this species is almost identical to the 101.42° in antimony derivative TbtSb-SbTbt.[673]

Salts containing the ion [Bi$_2$]$^{2-}$[680,681] were, e.g., obtained from ethylene diamine solutions of K$_5$In$_2$Bi$_4$ by treatment with a crown ether or a cryptand. They have short Bi−Bi distances of 2.8377(5) Å in ([Bi═Bi][K•crypt]$_2$) and 2.8634(4) Å in ([Bi═Bi][Cs•18cr6(NH$_3$)$_2$]$_2$) (Table 26). The short distances are particularly noteworthy when the electrostatic repulsion of two adjacent negative centers is taken into account. For comparison, in the 14 electron species [Bi$_2$]$^{4-}$ as observed in Ca$_{11}$Bi$_{10}$, a Bi−Bi distance of 3.15 Å was found.[677] Formally, [Bi$_2$]$^{2-}$ is a 12 valence electron species. It is isoelectronic to dioxygen but is EPR silent in both the solid state and in solution. In the potassium salt, the [Bi$_2$]$^{2-}$ unit is completely separated from the potassium cations which are complexed by a cryptand (Figure 13). In [Bi═Bi][Cs•18-crown-6(NH$_3$)$_2$]$_2$, however, a distance of ca. 3.69 Å between the cesium cations and the center of the Bi−Bi spacing and the somewhat elongated Bi−Bi distance indicate an interaction between the alkali cations and the electron density of the Bi−Bi double bond.

All the heavier dipnictenes are typically intensely colored species in which the E═E double bond is the main chromophore. In accordance with their electronic structures, the symmetry allowed $\pi-\pi^*$ transition at shorter wavelengths and the n−n* transition at longer wavelengths fall in the range of UV−vis excitations. Ignoring ligand effects, both transitions are shifted to longer wavelengths upon descending the group, indicating more closely spaced energy levels and weaker π-bonding, which is corroborated by DFT studies (Table 27).[675]

Several unsymmetrical heavier dipnictenes REE′R′ have been prepared, mostly via base mediated hydrogen chloride or bromide abstraction from REX$_2$, X = Cl, Br, and R′E′H$_2$ precursors. The first phosphorus−arsenic double bonded molecule was reported by Cowley and co-workers in 1983.[682] Later, a second example of a P═As double bond together

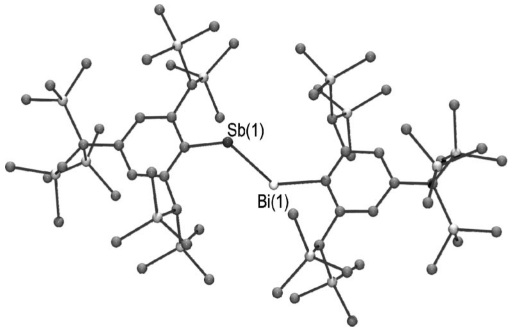


Figure 14. Molecular structure of BbtSb═BiBbt. Hydrogen atoms are not shown. Sb(1)−Bi(1) 2.972(5) Å.[685]

with the first P═Sb double bonded compound were reported.[683] Similarly, the reaction of Mes*PH_2 or BbtSbH_2 with Bbt$BiBr_2$ in the presence of DBU as a proton scavenger resulted in the isolation of a phosphabismuthene[684] and stibabismuthene.[685] Heating benzene solutions of the mixed Bbt-substituted P/Sb or Sb/Bi systems to temperatures higher than 80 °C yielded the respective homonuclear dipnictenes, Mes*PPMes* and BbtSbSbBbt or BbtSbSbBbt and BbtBiBiBbt, respectively.[684,685] Bond distances and spectral data for the mixed derivatives display characteristics intermediate between the homonuclear homologues, but the angles $C_{Ar}{-}E{=}E'$ and $E{=}E'{-}C_{Ar}'$ closely resemble those in the homonuclear derivatives (Figure 14).

Generally speaking, the bond lengths of heavier dipnictenes are shortened on average by about 8.1% for diphosphenes, 7.4% for diarsenes, 5.0% for distibenes, and 4.1% for dibismuthenes. In absolute numbers, this accounts for a shortening of the interpnictene bond by 0.18 Å (P), 0.18 Å (As), 0.14 Å (Sb), and 0.12 Å (Bi). Heteronuclear dipnictenes display a shortening effect which is roughly the average of the two homonuclear shortenings. As a consequence of the increasing energy difference between *n*s and *n*p orbitals, the lone pair adopts a steadily growing s-character and this results in narrower angles around the low coordinate pnictene centers.

3.12. Compounds of Formula $R\ddot{E}{=}E'$ (E = Group 15, E' = Group 16 Element)

If only low coordinate compounds that follow the general formula $RE{=}E'$ (E = heavier group 15 element, E' = heavier group 16 element) are considered, a very limited number of such species has been structurally characterized. In these, one sterically encumbering ligand has to support two low valent centers. An important example in this context, however, is provided by the antimony−tellurium double bond of 2.6620(7) Å in length in C_6H_3-$(CH_2NMe_2)_2$Sb═Te.[687]

Finally, the arsenic−selenium double bond in the sandwich complex (Cp*Fe)(μ^2-η^4,η^4-Se═As−As═Se)(Cp*Fe) is about 2.281 Å long (Table 28).[686]

Table 28. Bond Distances for Compounds of Formula [$R\ddot{E}{=}E'$] (E = As, Sb, E' = Group 16 Element)

compd	E═C (Å)	ref
As═Se		
(Cp*Fe)(μ^2-η^4,η^4-Se═As−As═Se)(Cp*Fe)	2.279(3)/2.283(3)	686
Sb═Te		
$C_6H_3(CH_2NMe_2)$Sb═Te	2.6620(7)	687

4. Triply Bonded Compounds

4.1. Group 13 Derivatives

Compounds with triple bonding or triple bond character involving heavier main group elements remain much scarcer than the doubly bonded species (cf. Tables 1 and 2). As pointed out in the earlier review, a major reason for this is that triple bonding requires the use of three of the four valence orbitals of the main group element which leaves only one orbital available for bonding to a substituent or occupation by a nonbonded pair. Thus, exceptionally crowding ligands are almost always required to prevent association of the triple bonded species. Because of their scarcity in the earlier review, the section dealing with triple bonds included no tables of compounds involving triple bonded heavier main group elements other than one listing the phosphalkynes. In the ensuing period, several compounds with potential triple bonding to heavier group 13 elements together with examples of all the heavier group 14 elements alkyne analogues have been synthesized and characterized.

In the group 13 elements, there have been a number of publications concerning triple bonding between two boron atoms in unstable[2] species. These papers have described spectroscopic and theoretical studies of a matrix isolated OCBBCO at low temperature and of a $B_2(BO)_2^{2-}$ cluster in the vapor phase.[688−690] The calculations afforded BB distances near 1.45 Å in both molecules, which is in good agreement with the 1.46 Å predicted by the sum of the triple bond radii.[691] The currently known stable species with potential triple bonding involving group 13 elements are listed in Table 29.[39,49,50,58−78,111,692−694]

This list includes the well-known Na_2Ar*GaGaAr* species (mentioned in section 2), which was published by Robinson and co-workers in 1997.[39] One further example of a digallium species Na_2Ar′GaGaAr′ has been shown to have a similar planar *trans*-bent CGaGaC core with a slightly longer Ga−Ga bond of 2.347(1) Å but with a similar degree of bending. The corresponding aluminum species has a longer Al−Al bond (Figure 15)[692] length of 2.428(1) Å but a similar bending angle. The longer bond length is consistent with the view that covalent radius of aluminum is larger than that of gallium.[695] However, the predicted triple bond length for Al (2.22 Å) and Ga (2.42 Å) are in sharp disagreement with the experimentally determined values. It is significant that in these multiple bonded species the bonding is complicated by the fact that sodium ions bridge the dialuminum and digallium units and can shorten the bonds by complexation to the flanking aromatic rings of their terphenyl ligands.

Table 29 also lists four species with potential triple bonding between gallium or indium and nitrogen. All the compounds have *trans*-bent structures, suggesting weakened orbital overlap. However, for the gallium species, the bond lengths are in the range 1.701(3)−1.743(5), which are considerably shorter than those listed in Table 6 and are slightly shorter than the 1.75 Å predicted from triple bond radii (Figure 16).[691] The In−N bond, 1.928 (3) Å, is also significantly shorter than 2.00 Å predicted from the sum of the triple bond radii. An interesting sidelight on the triple bonded species of the general formula RMNR (M = group 13 element) is that they are isomeric with the corresponding monovalent amides :MNR_2. Calculations[693,78] have shown that the monovalent amido isomer is energetically preferred

Table 29. Structural Characterized Complexes with Triple Bond Character Involving Heavier Group 13 Elements

compd	M−M(N) Å	M−M−C (deg)	ref
$Na_2Ar'AlAlAr'$	2.428(1)	131.71(7)	692
$Na_2Ar'GaGaAr'$	2.347(1)	130.69(13)	49, 50
$Na_2Ar^*GaGaAr^*$	2.324(1)	125.9(17), 134.03(10)	38
$HC\{C(Me)N(Dipp)\}_2GaNC_6H_3$-2,6($C_6H_2$-2,6-$Me_2$-4-$^tBu$)	1.742(3)	134.6(3)	693
$Ar'GaNC_6H_3$-2,6(C_6H_2-2,6-Me_2-4-^tBu)	1.701(3)	148.2, 141.7	694
$Ar^{\#}(Me_3Si)NGaNAr^{\#}$	1.743(5)		111
$Ar'InNC_6H_3$-2,6(C_6H_2-2,6-Me_2-4-^tBu)	1.928(3)	142.2, 134.9	694

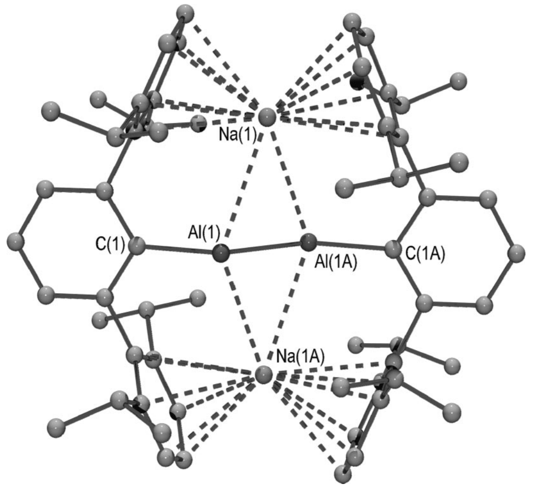


Figure 15. A drawing of $Na_2Ar'AlAlAr'$ without H atoms. Selected bond lengths (Å) and angles (deg): Al(1)−Al(1A) 2.428(1), Al(1)−C(1) 2.043(2), Al(1)−Na(1A) 3.152(1), Na−C_{ring} 2.881(2)−3.084(2) [av 2.991(2)], Dipp(centroid)−Na(1) 2.656(2), Dipp(centroid)−Na(1A) 2.637(2); C(1)−Al(1)−Al(1A) 131.71(7), Na(1)−Al(1)−Na(1A) 134.58(2), Al(1A)−Al(1)−Na(1) 67.65(3), Al(1A)−Al(1)−Na(1A) 66.93(3), C(1)−Al(1)−Na(1) 104.71(6), C(1)−Al(1)−Na(1A) 105.07(6), Al(1)−C(1)−C(2) 121.9(1), Al(1)−C(1)−C(6) 122.2(1), C(1)−C(2)−C(7) 120.7(2), C(1)−C(6)−C(13) 120.8(2). Dipp = C_6H_3-2,6-iPr_2.[692]

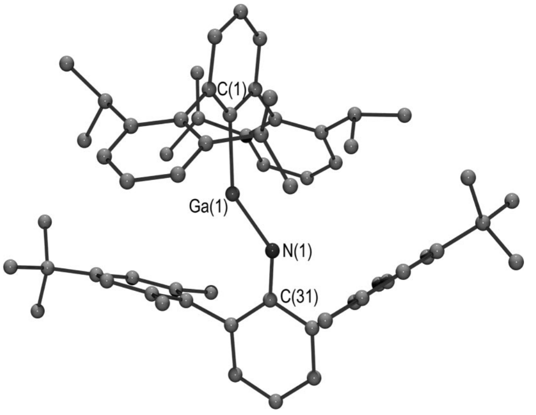


Figure 16. A drawing (without H atoms) of $Ar'GaNC_6H_3$-2,6(C_6H_2-2,6-Me_2-4-^tBu). The structure of its in indium analogue is similar. Selected bond distances (Å) and angles (deg) with those for the indium analogue in braces Ga−N 1.701(3) {1.928(3)}, Ga−C 1.940(3) {2.2127(3)}; N−Ga−C 148.2(2) {142.2(1)}, M−N−C 141.7 {134.9}.[694]

by a considerable margin, which is likely a result of increasing stabilization of the metal nonbonded pair.

Compounds of formula RME (R = monodentate organic ligand; M=Al−Tl; E=O−Te) have the potential for triple bonding between the triel metal and the chalcogen. However, none has been stabilized at room temperature. Very recent work has shown that the oxoboryl platinum complexes $(Cy_3P)_2(PhS)Pt$-BO and $(Cy_3P)_2BrPt$-BO featured B−O distances of 1.210(3) and 1.205(7) Å and an almost linear Pt−B−O array consistent with triple B−O bonding.[696]

4.2. Group 14 Derivatives

The heavier group 14 alkyne analogues are compounds of the general formula REER. Stable examples were unknown at the time of the previous review. In contrast to their carbon analogues, which have a linear structure (unless they are incorporated in a constrained environment), the heavier homologues have *trans*-bent structures which are indicative of nonbonded electron density at the tetrel atoms. To isolate these species, extreme steric protection is required because the low coordinate centers each carry only one ligand. The degree of *trans*-bending increases upon descending the heavier group 14 elements from moderate deviation from linearity for RSiSiR (*trans* bending angles 137.44° for R = $[Si(^iPr)\{CH(SiMe_3)_2\}_2]$[22] and 133.04(3)° for R = Bbt[697]) to 94.26(4)° in $Ar^*PbPbAr^*$, the latter being singly bonded, probably as a result of packing effects, with a Pb−Pb distance of 3.1881(1) Å, which exceeds the lead−lead single bond distance of 2.839(5) Å[347] in $Ph_3PbPbPh_3$ by almost 0.35 Å. As a rule of thumb, the bond order in heavier group 14 alkyne analogues decreases by about 0.5 units with each increase in the period number.

The tetrelyne derivatives have also attracted considerable theoretical interest. The calculations predicted that the bonding in the heavier alkyne analogues would differ dramatically from that observed for acetylenes. For example, those for the hydrogen substituent (hypothetical) series HEEH showed that bridged isomers were favored if E had a principal quantum number >2. Changing the substituent to methyl groups, which are much weaker bridging ligands, leads to vinylidene and *trans*-bent structures as minima on the potential energy surface. A further increase in steric demand disfavors the geminally substituted vinylidene structure and finally renders *trans*-bent isomers into the global minima on a relatively shallow potential energy surface. For the heaviest homologues, an even more bent, singly bonded isomer can be energetically more favored when extremely bulky ligands are introduced. Nevertheless, and most importantly, the linear $D_{\infty h}$ structure is a minimum only for the acetylenes and never a minimum on the potential energy surface of the heavier homologues.

As discussed in the introduction, the *trans*-bending effect may also be rationalized in terms of a second-order Jahn−Teller interaction (SOJT), i.e. a mixing of the in-plane π- and σ^*-orbitals which have the same symmetry in the C_{2h} point group. This results in nonbonding electron density at the tetrel centers in orbitals which have lone pair character. As the extent of the SOJT interaction increases, the bond order decreases from 3 in the linear acetylenes to about 1 in the highly bent lead species in

Table 30. Selected Structural Data for Heavier Group 14 Alkyne Analogues and Related Species

compd	E−E (Å)	R−E−E (deg)	ref
RSiSiR R = [Si^{i}Pr{CH(SiMe$_3$)$_2$}$_2$]	2.0622(9)	137.44(4)	23
BbtSiSiBbt	2.108(4)	133.04(3)	697
^{t}BuNC(Ph)N^{t}BuSiSiN^{t}BuC(Ph)N^{t}Bu	2.413(2)		705
Ar′GeGeAr′	2.2850(6)	128.27(8)	699
3,5-^{i}Pr$_2$−Ar′GeGeAr′−3,5-^{i}Pr$_2$	2.2125(13)	136.13(17)	698
4-Cl−Ar′GeGeAr′−4-Cl	2.3071(3)	124.19(16)	698
4-Me$_3$Si−Ar′GeGeAr′−4-SiMe$_3$	2.2438(8)	128.44(16)	698
BbtGeGeBbt	2.2060(8)−2.2260(8)	123.60(13)−138.66(16)	700
DippNC^{t}BuN(Dipp)GeGeN(Dipp)C^{t}BuNDipp	2.6380(8)		701
DippNCN(^{i}Pr)$_2$N(Dipp)GeGeN(Dipp)C(N^{i}Pr$_2$)NDipp	2.6721(3)		701
^{t}BuNC(N^{i}Pr$_2$)N(^{t}Bu)GeGeN(^{t}Bu)C(N^{i}Pr$_2$)N^{t}Bu	2.569(5)		702
MeC═CHC(Me)N(Dipp)GeGeN(Dipp)CMeCHCMeN(Dipp)	2.549(1)		704
MeC═CHC(Me)N(Dipp)GeSnN(Dipp)CMeCHCMeN(Dipp)	2.7210(4)		704
Ar′SnSnAr′	2.6675(4)	125.24(7)	17
4-Me$_3$Si−Ar′SnSnAr′−4-SiMe$_3$	3.0660(10)	99.25(14)	18
4-Cl−Ar′SnSnAr′−4-Cl	2.672(2)	121.8(4)	698
4-MeO−Ar′SnSnAr′−4-OMe	2.6480(12)	124.2(2)	698
4-^{t}Bu−Ar′SnSnAr′−4-^{t}Bu	2.6461(3)	123.98(5)	698
4-Me$_3$Ge−Ar′SnSnAr′−4-GeMe$_3$	3.077(12)	97.79(17)	698
3,5-^{i}Pr$_2$−Ar′SnSnAr′−3,5-^{i}Pr$_2$	2.7205(12)−2.7360(14)	125.1(2)−127.6(2)	698
{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}SnSn{C$_6$H$_3$-2,6-(Me$_2$NCH$_2$)$_2$}	2.9712(12)	94.3(3)	709
Ar*PbPbAr*	3.1881(1)	94.26(4)	16

which the R−Pb−Pb angle is close to 90°. In the case of silicon, the in plane π-orbital is somewhat slipped but still retains about 50% bonding character to yield a bond order above 2.5 units. With germanium, the slipping is more pronounced and almost complete, converting the initially bonding HOMO orbital into what is now an essentially nonbonding orbital, accounting for a bond order of slightly over 2. With tin, the situation becomes more complex because, depending on the ligands employed, multiple bonding similar to that seen for germanium can be observed. However, a second isomeric form with a much longer tin−tin interatomic distance and a more strongly bent R−E−E structure has been confirmed experimentally (vide infra).[17,698] Calculations[18,20] for the lead molecules have indicated that similar single and multiple bonded isomers were close in energy. However, at present, only the single bonded form has been isolated.

The first structurally characterized example of a stable heavier group 14 dimetallyne, REER, was was obtained during an attempt to synthesize a Pb(II) hydride Ar*PbH. This resulted in the isolation of the first diplumbyne, Ar*PbPbAr*, in moderate yield. Apparently, the decreased stability of element−hydrogen bonds in the sixth period disfavored isolation of the divalent lead hydride. Instead, spontaneous elimination of hydrogen led to the diplumbyne Ar*PbPbAr*, which exhibited a strongly *trans*-bent structure (C$_{ipso}$−Pb−Pb 94.26(4)°) and a long Pb−Pb distance of 3.1881(1) Å.[16]

Alkali metal reductions of aryl substituted germanium(II) and tin(II) halides provided the first of stable digermynes[699] and distannynes.[16] Thus, reduction of Ar′GeCl with potassium in aromatic solvents gave Ar′GeGeAr′. It had a centrosymmetric, *trans*-bent structure, in which the central aromatic rings of the terphenyl ligands and the Ge−Ge core are found to be coplanar. The Ge−Ge distance was 2.2850(6) Å, and is considerably shorter than the Ge−Ge single bond distance of ca. 2.44 Å and the C$_{ipso}$−Ge−Ge angle was 128.27(8)°. The structure is consistent with multiple Ge bonding, and it is noteworthy that the Ge−Ge bond length lists in the lower half of the Ge−Ge double bonded range in digermenes (cf. Table 30).[699] Nevertheless, the high chemical reactivity of Ar′GeGeAr′, as manifested in numerous addition reactions,[4q] suggested the existence of diradicaloid character which was further corroborated by high level imperfect pairing calculations.[22] The Bbt ligand has also been used to stabilize the digermyne BbtGeGeBbt and an average Ge−Ge distance of ca. 2.22 Å and a C−Ge−Ge angle of 131° was found.[700] The slightly shorter Ge−Ge distance in this species was rationalized by a lower Δ_{D-Q} gap of the BbtGe moiety induced by the electron releasing silyl groups of the Bbt ligands. Consequently, and in sharp contrast to the respective terphenyl substituted analogue, the Bbt substituted digermyne did not react with, e.g., triethylsilane, suggesting little diradicaloid character. Three additional examples of related dimeric Ge(I) derivatives were provided through the stabilization with bulky amidinate and guadinate ligands, respectively. The dimers [RC(NDipp)$_2$Ge]$_2$ featured long Ge−Ge bonds (2.6380(8) Å for R═^{t}Bu and 2.6721(3) Å for R═N(^{i}Pr)$_2$),[701] (2.569(5) Å for [PhC{N(^{t}Bu)}$_2$Ge]$_2$)[702] and strongly *trans*-bent geometries which indicated essentially single Ge−Ge bonds (Figure 17). An unsymmetric Ge(I) dimer and the first example of a compound featuring a bond between Ge(I) and Sn(I) recently became available by the reaction of [C(Me)CHC(Me)NDipp]GeK[703] and the β-diketiminato E(II) chlorides, [CH{CMe(NDipp}$_2$]ECl, E = Ge, Sn. In these, the increased Δ_{D-Q} gap of the fragments caused by the electron delocalization onto the ligands afforded weakly bonded products with long E−E distances.[704] The related silicon species ^{t}BuNC(Ph)N^{t}BuSiSiN^{t}BuC(Ph)N^{t}Bu had a long Si−Si bond of 2.413(2) Å and featured a similarly high degree of *trans*-bending.[705]

The digermyne Ar′GeGeAr′ forms an acceptor complex Ar′GeGeAr′(:CN^{t}Bu) with the isonitrile:CN^{t}Bu which binds to the LUMO n$_+$ orbital in the plane of the C$_{ipso}$GeGeC$_{ipso}$ core. Consistent with the mainly nonbonding character of this orbital the Ge−Ge bond length increases slightly to 2.3432(9) Å. In contrast, binding a second isonitrile as in Ar′GeGeAr′(:CNMes)$_2$ results in the dissapearance of mul-

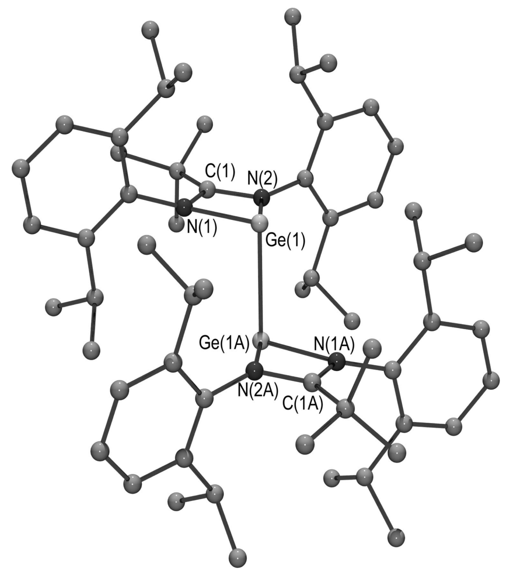


Figure 17. Molecular structure of DippNC^{t}BuN(Dipp)GeGeN-(Dipp)C^{t}BuNDipp. Hydrogen atoms are not shown. Selected bond lengths (Å) and angles (deg): Ge(1)−Ge(1A) 2.6378(6), Ge(1)−N(1) 2.032(2), Ge(1)−N(2) 2.049(2), N(1)−C(1) 1.339(3), N(2)−C(1) 1.339(3); N(1)−Ge(1)−N(2) 63.61(8), N(1)−Ge(1)−Ge(1A) 96.74(6), N(2)−Ge(1)−Ge(1A) 97.79(6), C(1)−Ge(1)−Ge(1A) 100.65.[701]

tiple Ge−Ge bond character as evidenced by a large increase in the Ge−Ge distance to 2.6628(2)Å.[706,707]

The first thermally stable distannyne was also prepared using the Ar′ ligand via reduction of Ar′SnCl with potassium metal to afford Ar′SnSnAr′, which had a planar core structure and a tin−tin bond length of 2.6675(4) Å.[17] This is considerably shorter than the average Sn−Sn single bond distance of about 2.81 Å. The C$_{ipso}$−Sn−Sn angle (125.24(7)°) was narrower than in its germanium analogue. The imperfect pairing calculations of Head-Gordon and co-workers on the MeMMMe model system reproduced the experimentally determined values quite well for Si, Ge, and Pb but favored the single bonded structure for MeSnSnMe.[22] The calculations also revealed a decrease of singlet diradical character in MeEEMe upon descending the group; it was ca. 17% for E = Si, 13% for Ge, and less than 4% for tin and lead. Similarly, DFT calculations for Ar′SnSnAr′ by Nagase and Takagi suggested the existence of multiple and single bonded structures[20,708] separated by only small (ca. 5 kcal mol^{-1}) energy differences with the multiple bonded structure being more favored. The multiple bonded isomer was calculated to have a Sn−Sn distance of ca. 2.667 Å and C−Sn−Sn angle of about 126.5°, a second minimum with a long Sn−Sn distance of 3.10 Å and a narrower C−Sn−Sn angle of 101.7° for the singly bonded isomer of Ar′SnSnAr′ was found. The very small energy difference of only about 4.8 kcal/mol between these isomers suggested that small changes in ligand design could lead to large changes in the structures of distannynes.[20,708] Indeed, the introduction of a trimethylsilyl group in the para-position of the central aryl ring of the Ar′ ligand resulted in an increase of the Sn−Sn distance by almost 0.4 Å to 3.0660(10) Å and a decrease of the C−Sn−Sn angle by some 26° to a value of 99.25(14)°.[18] More recently, in a systematic investigation the strucutures of the modified, terphenyl substituted Ge(I) and Sn(I) dimers, the compounds (4-Cl-Ar′Ge)$_2$, (4-Me$_3$Si−Ar′Ge)$_2$, (3,5-^{i}Pr$_2$−Ar*Ge)$_2$, (4-Cl−Ar′Sn)$_2$, (4-Me$_3$Ge−Ar′Sn)$_2$, (3,5-^{i}Pr$_2$−Ar*Sn)$_2$, (4-MeO−Ar′Sn)$_2$ and (4-^{t}Bu−Ar′Sn)$_2$ (Ar′=C$_6$H$_3$-2,6-(C$_6$H$_3$-2,6-^{i}Pr$_2$)$_2$), Ar*=C$_6$H$_3$-2,6-(C$_6$H$_2$-2,4,6-^{i}Pr$_3$)$_2$) were synthesized and structurally characterized (Figure 18).[698] Of these, only the 4-Me$_3$Ge−Ar′-ligated Sn(I) derivative had a similar long bond distance and narrow Ar′−Sn−Sn angle to those seen in (4-Me$_3$Si−Ar′Sn)$_2$. Surprisingly, the closely related (4-^{t}Bu-Ar′Sn) had the short Sn−Sn distance, the wider bending angle and a coplanar arrangement of the central aryl rings at the Sn−Sn unit, characteristic of a multiple bonded structure. All the digermynes displayed multiple bonded solid state structures with Ge−Ge distances in the range 2.2125(3)−2.3071(3) Å and C$_{ipso}$−Ge−Ge angles from 124.19(1)−136.13(17)°. The latter angle approaches the value found in disilene RSi≡SiR, R=Si^{i}Pr{CH(SiMe$_3$)$_2$}$_2$ (137.44(4)°) (Figure 19).[23] In these derivatives, the shortest Ge−Ge distances are associated with the widest Ge−Ge−C angles, which support the correlation between bond distance/angle and bond order predicted by CGMT theory.[174−179] In effect, electron releasing groups such as silyls or alkyls decrease the Ge−Ge distance and widen the Ge−Ge−C angle, whereas electron withdrawing substituents such as chlorine have the opposite effect. The intramolecularly coordinated distannyne [{2,6-(MeNCH$_2$)$_2$C$_6$H$_3$}Sn]$_2$ featured a long Sn−Sn bond of ca. 2.9712(12) Å and a very narrow C−Sn−Sn angle of 94.3(3)°.[709]

In 2002, Wiberg and co-workers showed that reduction of the disilene R(Cl)Si=Si(Cl)R (R = Si(Me)Si^{t}Bu$_3$)$_2$) afforded the disilyne RSi≡SiR (characterized by ^{29}Si NMR, δ = 91.5) in solution[248,710] but could not obtain a detailed structure. In 2004, Sekiguchi and co-workers succeeded in the isolation and structural characterization of the first stable disilyne, RSi≡SiR, R = Si^{i}Pr[CH(SiMe$_3$)$_2$}$_2$. It featured a *trans*-bent geometry with Si−Si≡Si angle of 137.44(4)° and a very short Si−Si distance of 2.0622(9) Å, which is about 0.07 Å less than the shortest Si−Si bond length in disilenes.[23] A deshielded ^{29}Si NMR resonance was observed for the triply bonded silicon at 89.9 ppm, which is very similar to the 91.5 ppm observed by Wiberg and his group.[23,248,710]

It was also demonstrated that it is possible to add electrons to the heavier alkyne analogues. Addition of two electrons produced the doubly reduced [REER]$^{2-}$ species that were discussed earlier, but it is also possible to add just one electron to give radical anions. Thus, addition of one electron to RSiSiR R = Si^{i}Pr{CH(SiMe$_3$)$_2$}$_2$ led to the corresponding radical anion with an elongated Si−Si distance of 2.1728(14) Å, Si−Si−Si angles around 113.97(16)°, and a formal bond order of 2.5 because the electron occupies the antibonding π*-orbital, which reduces the bond order by 0.5 units. EPR spectroscopy revealed the electron is π-delocalized over the central Si−Si unit.[253] Singly reduced radical anions of general formula M$^+$[ArEEAr]$^-$ (Ar = terphenyl ligand, E = Ge or Sn, M = Na or K) had been observed earlier. In these the planar, *trans*-bent structure observed in the parent ArEEAr species is retained. For germanium, Ge−Ge distances near 2.32 Å were found in the M$^+$[ArGeGeAr]$^-$ derivatives, whereas in the related tin species of general formula M$^+$[ArSnSnAr]$^-$ the Sn centers were separated by about 2.81 Å. However, the change in bond angles is more pronounced, i.e., in the tin species the C−Sn−Sn angles are reduced by some 30° from about 125° in the neutral ArSnSnAr precursor to values between 93.6 and 98.1° after reduction. The effect is less dramatic for germanium

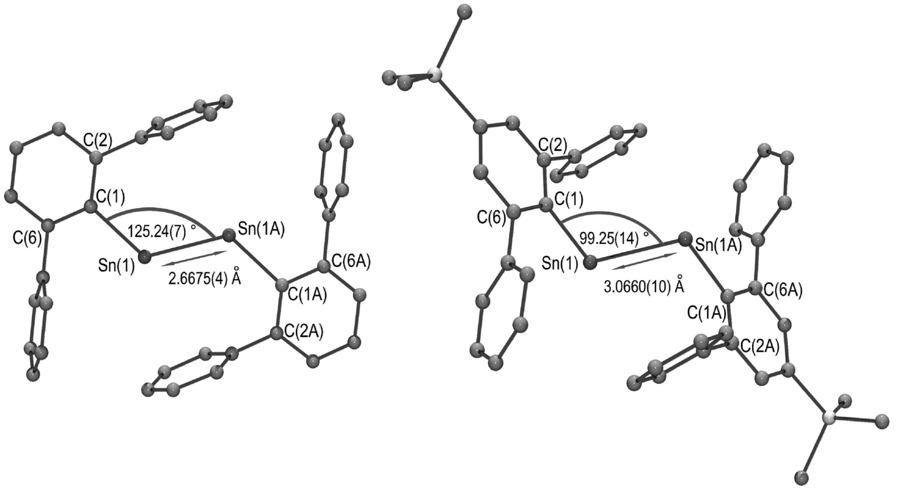


Figure 18. Molecular structures of Ar′SnSnAr′ and 4-(Me_3Si)−Ar′SnSnAr′−4-($SiMe_3$). Hydrogen atoms and iso-propyl groups at the flanking aryls are not shown (Ar′═C_6H_3-2,6-(C_6H_3-2,6-$^iPr_2$)$_2$). Selected bond lengths (Å) and angles (deg): Ar′SnSnAr′: Sn(1)−Sn(1A) 2.6675(4), C(1)−Sn(1) 2.191(4); C(1)−Sn(1)−Sn(1A) 125.24(7), C(2)−C(1)−Sn(1) 124.9(2), C(6)−C(1)−Sn(1) 115.7(2), C(1)−Sn(1)−Sn(1A)-C(1A) 180.0, C(2)−C(1)−Sn(1)-Sn(1A) 3.0(3), C(6)−C(1)−Sn(1)-Sn(1A) −177.0(2). 4-(Me_3Si)−Ar′SnSnAr′−4-($SiMe_3$): Sn(1)−Sn(1A) 3.0660(10), C(1)−Sn(1) 2.208(5), C(1)−Sn(1)−Sn(1A) 99.25(14), C(2)−C(1)−Sn(1) 125.6(4), C(6)−C(1)−Sn(1) 115.1(4), C(1)−Sn(1)−Sn(1A)-C(1A) 180.0, C(2)−C(1)−Sn(1)-Sn(1A) 101.1(5), C(6)−C(1)−Sn(1)-Sn(1A) −91.0(4).[17,18,698]

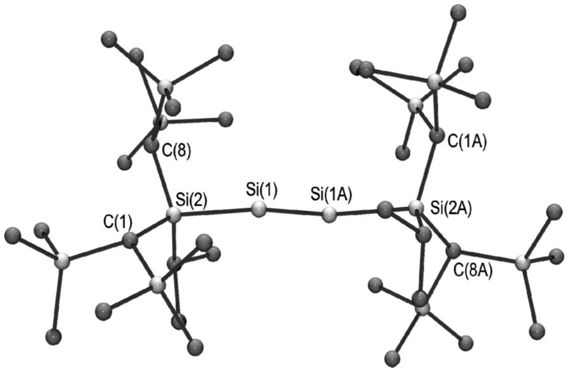


Figure 19. Molecular structure of disilyne RSi≡SiR, R = [Si^{i}Pr{CH($SiMe_3$)$_2$}$_2$]. Hydrogen atoms are not shown. Selected bond lengths (Å) and angles (deg): Si(1)−Si(1A) 2.0620(10), Si(1)−Si(2) 2.3699(7), Si(2)−C(1) 1.912(2), Si(2)−C(8) 1.912(2); Si(2)−Si(1)−Si(1A) 137.44(3), C(1)−Si(2)−C(8) 106.83(7), Si(1)−Si(2)−C(1) 108.97(3), Si(1)−Si(2)−C(8) 108.38(5), Si(2)−Si(1)−Si(1A)-Si(2A) 179.42(3).[23]

where a reduction of about only 15° was observed. The effects of the interaction between the alkali metal cations and the radical anion on the structure are minor because almost identical distances and angles were found in the solvent ion pairs such as [Ar′SnSnAr′]$^-$[K^+(THF)$_6$] and [Ar′SnSnAr′]$^-$[Na^+(THF)$_3$] (Table 31).[28] The experimental data support the view that the addition of a single electron to the ArSnSnAr species is to the π-orbital of the single bonded structure. EPR spectroscopic studies of the terphenyl substituted germanium and tin radical anions indicated that the unpaired electron was located in a π-orbital delocalized over the two tetrels.

4.3. Compounds with Potential Triple Bonding between Group 14 and Group 15 Elements

The first stable phosphalkyne, ^{t}BuC≡P:, was synthesized in 1981 by Becker and co-workers.[712] Formally, these compounds are heavier homologues of nitriles, but their chemistry much more resembles that of the alkynes. This is due to the difference in electronegativity between nitrogen and phosphorus In nitriles, the electron density of the triple bond is biased toward nitrogen, whereas with phosphorus the bond polarity is reversed with a slight negative has toward carbon.

The number of structurally characterized phosphaalkynes has grown considerably over the past decade. They typically exhibit C−P bond distances of about 1.54 Å, a value which remains largely uninfluenced by the substituents present in the molecule; e.g, the bond distances in Mes*-C≡P (1.52(1) Å)[716] and in *para*-dimethyl amino substituted C_6H_2-2,6-$^tBu_2$-4-Me_2N-1-C≡P (1.534(3) Å)[726] are very similar. All R-C≡P angles in the phospha-alkynes that have been structurally characterized so far are very close to 180°, as expected for an sp-hybridized carbon atom and a terminal phosphorus atom in which the lone pair has substantial s-character and points in the opposite direction of the triple bond. Compared with carbon phosphorus single bonds of around 1.82 Å and with the earlier discussed phosphenes, which feature C═P bond distance near 1.67 Å, the carbon−phosphorus bond

Table 31. Selected Structural Parameters for Heavier Group 14 Main Group Element Radical Anions of Formula [REER]M

compd	E−E (Å)	R−E−E (deg)	ref
[RSiSiR]K·4DME, R = [Si{CH($SiMe_3$)$_2$}$_2$^{i}Pr]	2.1728(14)	113.97(16)	253
[Ar*GeGeAr*]Na	2.3089(8)	114.2(1)	313
[Ar′GeGeAr′]K	2.3331(4)	155.55(5)	313
[Ar′SnSnAr′]K·6THF	2.8081(9)	97.91(16)	313
[Ar*SnSnAr*]K·6THF	2.8123(9)	95.20(13)	711
[Ar*SnSnAr*]Na·3THF	2.8107(13)	97.9(3)	313
[Ar*SnSnAr*]K·18cr6·2THF	2.782(1)	95.0(4)	711

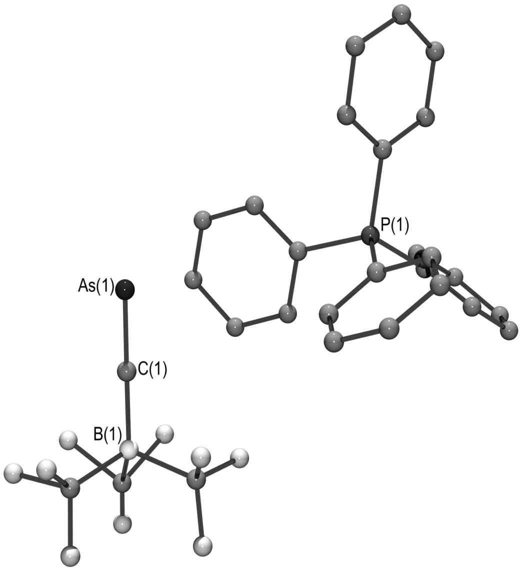


Figure 20. Molecular structure of $[(F_3C)_3B\text{-}C{\equiv}As][PPh_4]$. Hydrogen atoms are not shown. Selected bond lengths (Å) and angles (deg): As(1)−C(1) 1.675(12), C(1)−B(1) 1.59(1); B(1)−C(1)−As(1) 176.4(8).[731]

distances in phospha-alkynes are shortened by about 0.29 and 0.13 Å, respectively.

During the past decade, several novel phospha-alkynes have been reported.[714,715,719,720,725,726] Among these, the calcium derivative $[Ca(Dme)_3][OC{\equiv}P]_2$[720] featured the longest C−P bond (1.574(3) Å) reported for phospha alkynes. Yet, this is only about 0.05 Å longer than the shortest example, given by Mes*C≡P.[716]

The first stable arsa alkyne was reported in 1986, when the synthesis of Mes*C≡As was published.[713] In the meantime, only two other compounds of this kind were reported. From these, the thermally instable Me-C≡As decomposes well below room temperature.[733] More recently, structural and spectroscopic data for $[(F_3C)_3B{-}C{\equiv}As][PPh_4]$[731] together with findings for the lighter congener $[(F_3C)_3B{-}C{\equiv}P][PPh_4]$ were published (Figure 20). Both are quite stable compounds with decomposition temperatures of 290 °C for $[(F_3C)_3B{-}C{\equiv}P][PPh_4]$ and 173 °C for $[(F_3C)_3B{-}C{\equiv}As][PPh_4]$. The latter features a carbon arsenic bond distance of 1.675(12) Å and an almost linear arrangement of the B−C−As entity (Table 32). No structural data for uncomplexed stiba-alkynes have been reported to date.

Table 32. Selected Structural Data for Phospha- and Arsa-Alkynes

compd	C−E (Å)	R−C−E (deg)	ref
Phosphaalkynes			
$C_6H_3\text{-}(C_6H_2\text{-}2,4,6\text{-}Me_3)_2\text{-}C{\equiv}P$	1.539(7)	176.5(5)	714
$^iPr(Me_3Si)N\text{-}C{\equiv}P$	1.558(1)	178.7(1)	715
Mes*-C≡P	1.52(1)	177(1)	716
$^tBu\text{-}C{\equiv}P$	1.5478(8)	179.49(7)	717, 718
$Ph_3C\text{-}C{\equiv}P$	1.538(1)	178.5(2)	719
$[Ca(Dme)_3][O{-}C{\equiv}P]_2$	1.574(3)/ 1.575(3)	179.1(2)/ 179.9(2)	720
$[Li(Dme)_2][O{-}C{\equiv}P]$	1.56(1)	178.5(3)	721
$[Li(Dme)_3][S{-}C{\equiv}P]$	1.555(3)	178.8(7)	722
$^iPr_2NC{\equiv}P$	1.552(2)	179.2(2)	723
TmpC≡P	1.558(3)	178.9(2)	724
trypticene-9,10-(C≡P)$_2$	1.532(2)/ 1.533(2)	177.4(2)/ 179.5(2)	725
$C_6H_2\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}Me_2N\text{-}1\text{-}C{\equiv}P$	1.534(3)	178.6(3)	726
F-C≡P	1.541	180	727
$F_3C{-}C{\equiv}P$	1.542	180	728
H-C≡P	1.542	180	729
Me-C≡P	1.544	180	730
$[(F_3C)_3B{-}C{\equiv}P][PPh_4]$	1.563(10)		731
Arsaalkynes			
Mes*C≡As	1.657(7)	175.9(5)	732
Me-C≡As	1.661(1)	180	733
$[(F_3C)_3B\text{-}C{\equiv}As][PPh_4]$	1.675(12)	177.5(9)	731

4.4. Compounds with Potential Triple Bonding between Group 14 and Group 16 Elements

High vacuum flash pyrolysis of 1,3-dithietan-1,3-dioxide followed by photochemical rearrangement led to H-C≡S-OH, which is currently the only example of a compound with a potential carbon−sulfur triple bond when hypervalent $F_3S\text{-}C{\equiv}SF_3$ and $F_5S\text{-}C{\equiv}SF_3$ are not taken into account.[734] Judging from a combination of matrix isolation IR spectroscopy at 10 K and in silico methods, H−C≡S−OH adopts a *cis*/*cis* conformation with a carbon−sulfur distance of 1.547 Å and an angle of 122.0° around sulfur. The bond distance is in good agreement with the sum of triple bond covalent radii for carbon (0.60 Å) and sulfur (0.95 Å) as suggested by Pyykkö and co-workers[691] and only marginally longer than the distance found in CS (1.535 Å).[735]

4.5. Compounds with Triple Bonding between Group 15 Elements

As mentioned in the earlier review, apart from dinitrogen, the diatomic group 15 compounds are generally unstable but many of these have been identified in the gas phase by various spectroscopic methods.[1] The recently reported N-heterocyclic carbene complexes L:P−P:L (L = :C-{(NDipp)CH}$_2$, L = :C{(NMes)CH}$_2$)[736] are best described as a P_2 unit of two phosphinidene centers linked by a single bond while the carbene donates electron density to the empty orbitals at phosphorus. The long P−P bond distances

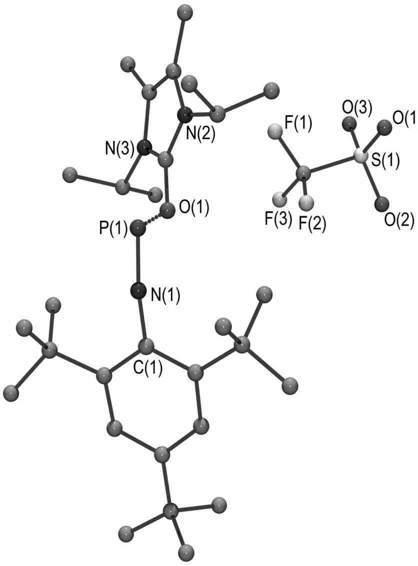


Figure 21. Molecular structure of $[Mes^*N{\equiv}P^+]O{=}\overline{CN(^iPr)CMeN}{}^iPr\text{-}[CF_3SO_3^-]$. Hydrogen atoms are not shown. Selected bond lengths (Å) and angles (deg): N(1)−P(1) 1.493(3), C(1)−N(1) 1.403(6), P(1)−O(1) 1.773(3); O(1)−P(1)−N(1) 107.5(2), C(1)−N(1)−P(1) 159.7(3).[739]

Table 33. N−P Bond Distances in Iminophosphenium Ions

compd	N−P (Å)	ref
$[Mes^{*}N\equiv P^{+}][AlCl_{4}^{-}]$	1.475(8)	737
$[Mes^{*}N\equiv P^{+}][CF_{3}SO_{3}^{-}]$	1.467(4)	604
$[Mes^{*}N\equiv P^{+}]Ph_{3}P[CF_{3}SO_{3}^{-}]$	1.486(4)	738
$[Mes^{*}N\equiv P^{+}]O{=}CN(^{i}Pr)CMeCMeN^{i}Pr[CF_{3}SO_{3}^{-}]$	1.493(3)	739
$[Mes^{*}N\equiv P^{+}]O{=}C(NPhMe)_{2}[CF_{3}SO_{3}^{-}]$	1.486(2)	739
$[Mes^{*}N\equiv P^{+}]S{=}CN(^{i}Pr)CMeCMeN^{i}Pr[CF_{3}SO_{3}^{-}]$	1.498(2)	739
$[Mes^{*}N\equiv P^{+}]Se{=}CN(^{i}Pr)CMeCMeN^{i}Pr[CF_{3}SO_{3}^{-}]$	1.500(2)	739
$[Mes^{*}N\equiv P^{+}]$1-aza-bicyclo[2.2.2]octane$[CF_{3}SO_{3}^{-}]$	1.519(4)	740
$[Mes^{*}N\equiv P^{+}]$2,2′-bipyridine$[CF_{3}SO_{3}^{-}]$	1.498(4)	740
$[Mes^{*}N\equiv P^{+}]Dmap_{2}[CF_{3}SO_{3}^{-}]$	1.559(3)	741
$[Mes^{*}N\equiv P^{+}]_{2}$4,4′-bipyridine$[CF_{3}SO_{3}^{-}]_{2}$	1.488(2)/1.489(2)	741
$[Mes^{*}N\equiv P^{+}]Tmeda[CF_{3}SO_{3}^{-}]$	1.510(2)	742
$[Mes^{*}N\equiv P^{+}]Dppe[CF_{3}SO_{3}^{-}]$	1.489(2)	742
$[Mes^{*}N\equiv P^{+}]Pmdeta[CF_{3}SO_{3}^{-}]$	1.495(2)	742
$[Mes^{*}N\equiv P^{+}]\eta^{6}\text{-}C_{6}H_{6}[GaCl_{4}^{-}]$	1.484(7)	743, 744
$[Mes^{*}N\equiv P^{+}]\eta^{6}$-tol$[GaCl_{4}^{-}]$	1.529(15)	744
$[Mes^{*}N\equiv P^{+}]\eta^{6}\text{-}C_{6}H_{6}[Ga_{2}Cl_{7}^{-}]$	1.463(5)	744
$[Mes^{*}N\equiv P^{+}]\eta^{6}$-tol$[Ga_{2}Cl_{7}^{-}]$	1.464(9)	743
$[Mes^{*}N\equiv P\cdot py]^{+}(OSO_{2}CF_{3})$	1.472(5)	617, 745
$[Mes^{*}N\equiv P^{+}]\eta^{6}$-Mes$[Ga_{2}Cl_{7}^{-}]$	1.471(6)	743

(2.2052(10) Å and 2.1897(11) Å) are well in the range of typical P−P single bond distances of about 2.21 Å.

Yet, examples of stable, heavier element substituted compounds with potential triple bonds between group 15 elements are given by the class of iminophospenium ions $[R\text{-}N\equiv P]^{+}$. Typically, stable examples are based on $[Mes^{*}N\equiv P]^{+}$. The first example, $[Mes^{*}N\equiv P][AlCl_{4}]$ was reported by Niecke and co-workers in 1988.[737] More recently and in contrast to the isoelectronic phospha- and arsa-alkynes, it has been demonstrated that the phosphorus center in $[Mes^{*}N\equiv P]^{+}$ has Lewis-acceptor properties and forms a series of donor−acceptor complexes with Lewis bases.[739−742,744] (Figure 21) Complexation in what are then hypervalent phosphorus compounds results in N−P distances which are slightly elongated by about 0.01−0.08 Å (Table 33).

Nevertheless, the linear conformation of the C−N−P unit remains largely unaltered in the above-mentioned compounds. The Lewis acid properties of the $[Mes^{*}N\equiv P]^{+}$ entity was further exemplified by formation of η^{6}-arene complexes with benzene, toluene, or mesitylene.[743,744]

5. Conclusions

The number of compounds featuring multiple bonding between heavier main group elements has greatly expanded in the past decade. The synthesis of the first stable heavier group 14 element alkyne analogues, group 13 element dimetallenes, and the stabilization of "naked" multiple bonded B_2 and Si_2 by use of carbene donors are arguably the most noteworthy synthetic developments. The structural and spectroscopic data obtained on the new species have underlined the tendency of these molecules to display "strained" geometries with increasing non-bonded electron pair character as the group is descended. Second-order Jahn−Teller effects provide an effective rationale for the "strained" geometries. Although the reaction chemistry of the multiple bonded compounds was not addressed in this review, it is becoming clear that they have a highly interesting chemistry and several of them have already been shown to interact with small molecules such as H_2, CO, or ethylene. Exciting developments in the chemistry of these compounds may be anticipated over the next decade.

6. List of Abbreviations

1-Ad	1-adamantyl
2-Ad	2-adamantyl
$Ar^{\#}$	2,6-dimesitylphenyl $(-C_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}Me_3)_2)$
Ar′	$(-C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}^{i}Pr_2)_2)$
Ar*	$(-C_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}^{i}Pr_3)_2)$
Bbt	4-tris(trimethylsilylmethyl)-2,6-bis(bis-trimethylsilyl)phenyl $(-C_6H_2\text{-}4\text{-}(C(SiMe_3)_3)\text{-}2,6\text{-}\{CH(SiMe_3)_2\}_2)$
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
Dep	2,6-diethylphenyl $(-C_6H_3\text{-}2,6\text{-}Et_2)$
Dipp	2,6-di-*iso*-propylphenyl $(-C_6H_3\text{-}2,6\text{-}^{i}Pr_2)$
Ditp	2,6-bis(4-*tert*-butylphenyl)phenyl $(-C_6H_3\text{-}2,6\text{-}(C_6H_4\text{-}4\text{-}^{t}Bu)_2)$
Dmp	2,6-dimethylpiperidinato
Dme	1,2-dimethoxyethane
Dur	duryl (2,3,5,6-tetramethylphenyl or $-C_6H\text{-}2,3,5,6\text{-}Me_4$)
F_c	ferrocenyl
Fp	$Fe(\eta^5\text{-}C_5H_5)(CO)_2$
Fp^{x}	$Fe(\eta^5\text{-}C_5Ma_5)(CO)_2$
Hyp	hypersilyl $(-Si(SiMe_3)_3)$
Mes	mesityl (2,4,6-trimethylphenyl or $-C_6H_2\text{-}2,4,6\text{-}Me_3$)
Mes*	"supermesityl" (2,4,6-tri-*tert*-butylphenyl or $-C_6H_2\text{-}2,4,6\text{-}^{t}Bu_3$)
Me_8taa	octamethyldibenzatetraaza[14]annulene
Np	naphthyl
py	pyridine
Tbt	2,4,6-tris{bis(trimethylsilyl)}phenyl $(-C_6H_2\text{-}2,4,6\text{-}\{CH(SiMe_3)_2\}_3)$
THF	tetrahydrofuran
Tmp	2,2,6,6-tetramethylpiperidinato
TMEDA	tetramethylethylenediamine
Trip	2,4,6-tri-*iso*-propylphenyl $(-C_6H_2\text{-}2,4,6\text{-}^{i}Pr_3)$
$Tp(^{t}Bu)_2$	tris(di-*tert*-butylpyrazolyl)hydroborato
Xyl	2,6-dimethylphenyl $(-C_6H_3\text{-}2,6\text{-}Me_2)$

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