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π-Bonding and the Lone Pair Effect in Multiple Bonds between Heavier Main Group Elements

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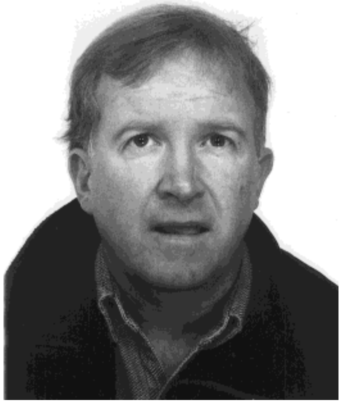

Philip Power received his B.A. degree from Trinity College Dublin in 1974 and his D.Phil. degree, under the supervision of M. F. Lappert, from the University of Sussex in 1977. After postdoctoral studies with R. H. Holm at Stanford, he joined the faculty at the University of California, Davis, where he is currently Professor of Chemistry. His main research interests involve the structural chemistry of organoalkali metal and organocopper compounds, low-coordinate transition metal chemistry, multiple bonding in main group chemistry, and the development of new ligands for the stabilization of low coordination numbers, unusual oxidation states, and multiple bonding in both transition metal and heavier main group compounds. He is a recipient of fellowships from the A. P. Sloan and Alexander von Humboldt foundations. In addition he has been Reilly Lecturer at the University of Notre Dame (1995), Faculty Research Lecturer at the University of Iowa (1993), and the University of Auckland, New Zealand (1993).

I. Introduction

The study of stable[1] compounds with multiple bonds between heavier main group elements (valence electrons of principal quantum number ≥3) is one of the central themes of organometallic and inorganic chemistry. A major reason for the widespread interest in this area is that the frequent new findings continue to challenge widely accepted rules of bonding[2]—especially the so-called double bond rule,[3−5] which relates to the supposed inability of elements of principal quantum number ≥3 to form multiple bonds. The unusual structures and properties of some compounds have stimulated debate on fundamental questions concerning the very definition of chemical bonding.[6,7] In addition to these issues, there is the excitement surrounding the discovery of hitherto unknown types of compounds and the comparison of their physical and chemical properties with corresponding derivatives of the lighter elements. Often, this affords new insights which require the consideration of new bonding models for the heavier element compounds. For example, the fact that the currently known tin and lead ethylene analogues corresponding to the formula R_2EER_2 ($E =$ Sn or Pb; $R =$ bulky alkyl, aryl, or silyl group) dissociate in

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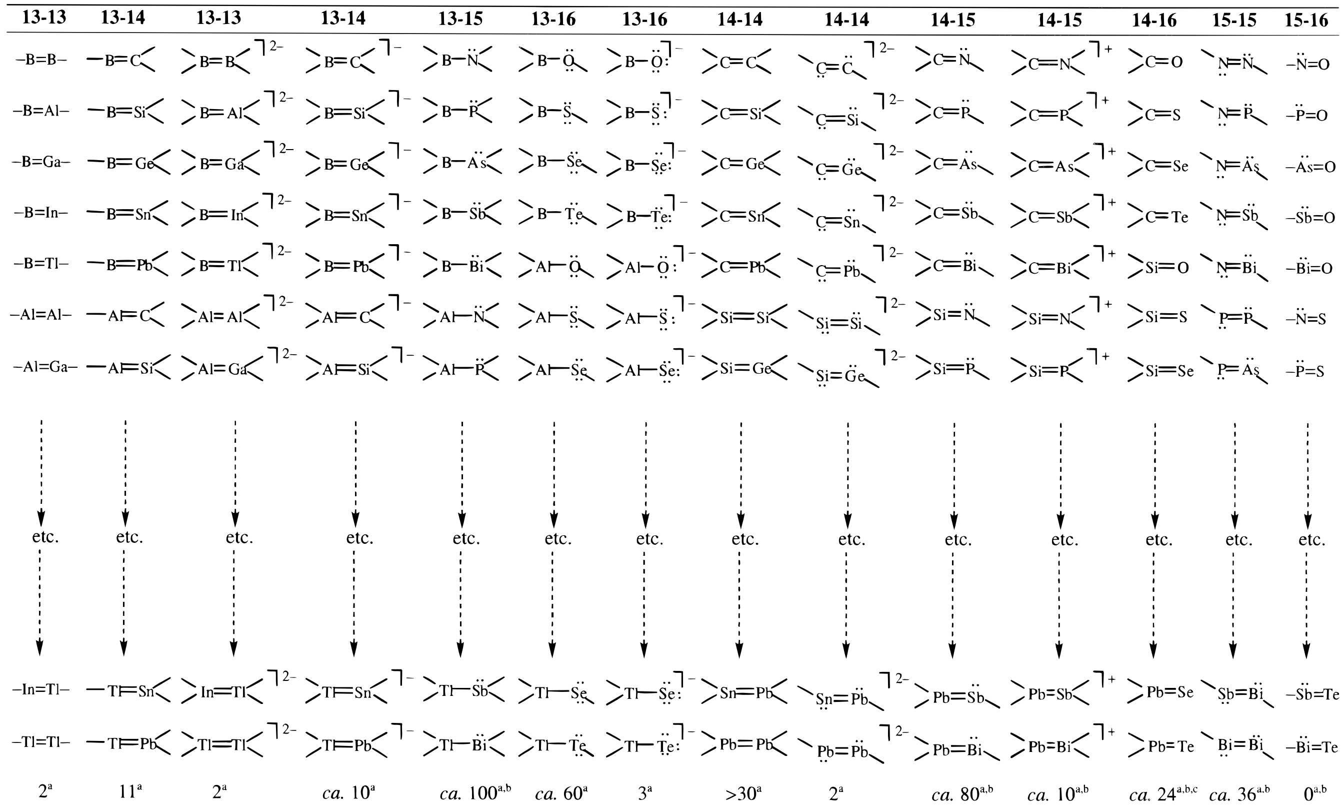
Table 1. Selected Element Combinations Related to Alkenes from Groups 13−16 that may Feature Double Bonding (Discussed in sections IV.A−L)



[a] Number of stable compounds that have been structurally characterized. [b] Examples involving bonding to a heavier main group atom only. [c] Not including carbon compounds.

hydrocarbon solution,[7,8] whereas the electronically related antimony or bismuth analogues, REER (E = Sb or Bi),[9] remain strongly bonded, needs a more sophisticated explanation than the simple valence bonding models normally used for their lighter analogues H_2CCH_2 and HNNH. The major focus of this review is to summarize these bonding models and, in addition, to examine the structure and bonding in a broad range of unsaturated heavier main group element analogues of the simple molecules ethylene and acetylene and their related isoelectronic species.

The scope of the review may be summarized by the various classes of core functional groups given in Tables 1 and 2. These are intended to represent various types of main group double bonds in Table 1, with a similar intention for triple bonds in Table 2. In Table 1 it will be immediately obvious that with the exception of the first two columns, the multiply bonded groups are analogous to ethylene in terms of the numbers of their valence electrons. In Table 2 there is a similar analogy with acetylene. These relationships underline the fact that multiple bonding in organic chemistry, as represented by alkenes and alkynes, remains the major inspiration for the synthesis of multiply bonded species in the heavier s- and p-block elements.

Several other important points should be made with respect to these tables:

(i) For the most part, *discussion has been limited to classes of compounds where significant experimental data have been obtained for at least one member of each class*. In a few cases, e.g., the 13−16 triply bonded species in Table 2, a class of compounds is included since it forms part of an obvious sequence. The group 14−14 compounds are also included in Table 2, even though, at present, only the alkynes are known as stable entities. *No attempt has been made to list compounds that have multiple bonds between heavier main group elements and the transition metals. Similarly, transition metal complexes of molecules with multiple bonds between heavier main group elements will not be discussed.* Odd electron, multiply bonded compounds are also not featured, although several recent stable examples of such compounds have been reported. For example, the radical species $[R_2MMR_2]^{-\bullet}$ (M = Al or Ga),[10,11] R_2GaGaR,[12] and $[RSnSnR]^{-}$ [13] all feature formal multiple bonding and are of considerable significance since they are related to some of the compounds in Tables 1 and 2 by the addition or subtraction of a single electron to the core moiety. Accordingly, they will be discussed briefly at a number of places in the text.

(ii) *Compounds that include multiply bonded heavier main group element as an integral part of a ring structure are not considered*, since there are vast numbers of cyclic species incorporating multiply bonded heavier main group atoms.[14] *Cyclic compounds, many of which contain genuine double bonds, excluded mainly to limit the size of the review.*

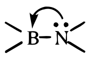
(iii) The core functional groups as they are drawn in Tables 1 and 2 represent species in which there *may* be multiple bonding. In other words, the existence of multiple bonding is not a foregone conclusion

Table 2. Selected Element Combinations from Groups 13−16 that may Feature Triple Bonding (Discussed in sections V.A−E)

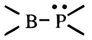
13-13	13-14	13-15	13-16	14-14	14-15
$[-B{\equiv}B-]^{2-}$	$[-B{\equiv}C-]^{-}$	$-B{=}\ddot{N}-$	$-B{=}\ddot{O}:$	$-C{\equiv}C-$	$-C{\equiv}N$
$[-B{\equiv}Al-]^{2-}$	$[-B{\equiv}Si-]^{-}$	$-B{=}\ddot{P}-$	$-B{=}\ddot{S}:$	$-C{\equiv}Si-$	$-C{\equiv}P$
$[-B{\equiv}Ga-]^{2-}$	$[-B{\equiv}Ge-]^{-}$	$-B{=}\ddot{As}-$	$-B{=}\ddot{Se}:$	$-C{\equiv}Ge-$	$-C{\equiv}As$
$[-B{\equiv}In-]^{2-}$	$[-B{\equiv}Sn-]^{-}$	$-B{=}\ddot{Sb}-$	$-B{=}\ddot{Te}:$	$-C{\equiv}Sn-$	$-C{\equiv}Sb$
$[-B{\equiv}Tl-]^{2-}$	$[-B{\equiv}Pb-]^{-}$	$-B{=}\ddot{Bi}-$	$-Al{=}\ddot{O}:$	$-C{\equiv}Pb-$	$-C{\equiv}Bi$
$[-Al{\equiv}Al-]^{2-}$	$[-Al{\equiv}C-]^{-}$	$-Al{=}\ddot{N}-$	$-Al{=}\ddot{S}:$	$-Si{\equiv}Si-$	$-Si{\equiv}N$
$[-Al{\equiv}Ga-]^{2-}$	$[-Al{\equiv}Si-]^{-}$	$-Al{=}\ddot{P}-$	$-Al{=}\ddot{Se}:$	$-Si{\equiv}Ge-$	$-Si{\equiv}P$
↓ etc. ↓	↓ etc. ↓	↓ etc. ↓	↓ etc. ↓	↓ etc. ↓	↓ etc. ↓
$[-In{\equiv}Tl-]^{2-}$	$[-Tl{\equiv}Sn-]^{-}$	$-Tl{=}\ddot{Sb}-$	$-Tl{=}\ddot{Se}:$	$-Sn{\equiv}Pb-$	$-Pb{\equiv}Sb$
$[-Tl{\equiv}Tl-]^{2-}$	$[-Tl{\equiv}Pb-]^{-}$	$-Tl{=}\ddot{Bi}-$	$-Tl{=}\ddot{Te}:$	$-Pb{\equiv}Pb-$	$-Pb{\equiv}Bi$
1[a]	3[a]	0[a,b]	4	0[a,b]	15[a,b]

[a] Number of stable compounds that have been structurally characterized. [b] Examples involving bonding to a heavier main group atom only.

in any particular moiety. For example, dative π bonding in the group 13−15 species, e.g.

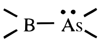


where there is lone pair donation from nitrogen to boron via p orbital overlap, which is usually reflected in a planar core geometry and substantial B−N rotational barriers,[15] is widely acknowledged. In contrast, the corresponding



[16]

and



[17]

species usually have a pyramidal geometry at the pnictogen, with apparently weak π-overlap, although relatively strong B−P or B−As π bonding and planar geometries can be induced by suitable steric and electronic manipulation of the pnictogen substituents. As a result, π-bond strengths comparable to those observed in the nitrogen compounds have been observed.

(iv) Another feature of Tables 1 or 2 is that the listings are confined to groups 13−16. At present no stable molecules are known to have multiple bonds to the s-block elements of groups 1 or 2. However, several group 2 species with formal multiple bonding (e.g., BeE = chalcogenide) have been identified in the gas phase.[18] Nonetheless, it is a possibility that stable molecular compounds will be obtained in the future. For example, molecular magnesium compounds of the type $[(THF)MgNAr]_6$[19a] or $[MgPR]_6$[19b] have already been synthesized, and it is conceivable that related species with lower degrees of aggregation, i.e., dimers, trimers, or even monomers, that may have multiple bond character could be obtained eventually. In addition, dative multiple bonding may be possible in low-coordinate group 2 derivatives where there are empty orbitals in the group 2 element and the substituent atoms have lone pairs available. Thus, short Be−N distances are observed in the vapor phase structure of the compound $Be\{N(SiMe_3)_2\}_2$[20] whose R_2NBeNR_2 framework is analogous to an allene. Also, the crystal structure of the monomer 2,6-$Mes_2H_3C_6BeN(SiMe_3)_2$[21] shows that it has a very short Be−N bond of 1.519(4) Å. No group 17 or 18 derivatives feature in Tables 1 and 2. Multiple bonding involving halogens or the noble gases invariably involves bonding in hypervalent species which are not treated in this review.

(v) *Hypervalent multiply bonded compounds of the heavier main group 13−16 elements also are not listed.* The omission of these important classes of compounds, many of which have extremely interesting multiply bonded structures (e.g., $R_2NP(NR)_2$[22a] Se or $Te(NR)_2$[22b] or $\{Li_2Te(NR)_3\}_2$[22c] or $[S(NR)_n]^{m-}$ [22d] or $(CF_3)_2CSF_4$[22e]) and bonding, is mainly for reasons of space. In addition, the hypervalent compounds, many of which have been known for many decades (e.g.,

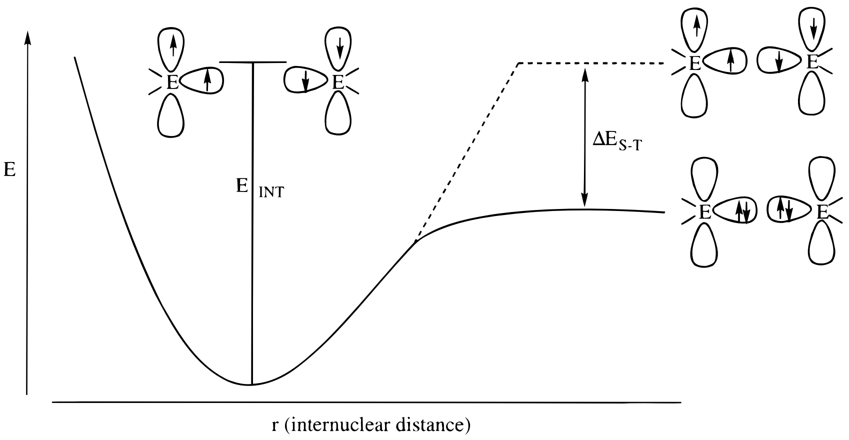


Figure 1. Generalized schematic illustration of the energy of dissociation of an olefinic double bond into two triplet fragments ΔE_{S-T} is the singlet−triplet energy difference which is positive for carbon but negative for Si−Pb. ΔE_{INT} = double bond energy.

the phosphinimines, phosphine oxides and sulfides, sulfur dioxide and trioxide), have often been treated separately on account of their different bonding characteristics.[23]

The following abbreviations will be used: 1-Ad = 1-Adamantanyl; Cp* = pentamethylcyclopentadienyl; Cy = cyclohexyl; Dep = 2,6-diethylphenyl ($-C_6H_3$-2,6-Et$_2$); Dipp = 2,6-diisopropylphenyl ($-C_6H_3$-2,6-i-Pr$_2$); Ditp = 2,6-bis(4-*tert*-butylphenyl)phenyl ($-C_6H_3$-2,6-(C_6H_4-2-t-Bu)$_2$); Dmp = 2,6-dimethylpiperidinato; Dme = 1,2-dimethoxyethane; Dur = duryl (2,3,5,6-tetramethylphenyl or $-C_6H$-2,3,5,6-Me$_4$); Mes = mesityl (2,4,6-trimethylphenyl or $-C_6H_2$-2,4,6-Me$_3$); Mes* = "supermesityl" (2,4,6-tri-*tert*-butylphenyl or $-C_6H_2$-2,4,6-t-Bu$_3$); Me$_8$taa = octamethyldibenzotetraaza[14]-annulene; Np = naphthyl; py = pyridine; Tbt = 2,4,6-tris(bistrimethylsilylmethyl)phenyl ($-C_6H_2$-2,4,6-{CH-(SiMe$_3$)$_2$}$_3$); THF = tetrahydrofuran; Tmp = 2,2,6,6-tetramethylpiperidinato; TMEDA = tetramethylethylenediamine; Trip = 2,4,6-triisopropylphenyl ($-C_6H_2$-2,4,6-i-Pr$_3$); Tp(t-Bu)$_2$ = tris(di-*tert*-butylpyrazolyl)-hydroborato; Xyl = $-C_6H_3$-2,6-Me$_2$.

II. Multiple Bonding Models

Several recent publications have rekindled debate on the question of the nature of multiple bonding.[24,25] Traditionally, the two major bonding theories[26] for molecular compounds—valence bond (VB) and molecular orbital (MO)—were in essential harmony in accounting for double or triple bonding in molecules such as ethylene or acetylene. For example, in VB theory the carbon−carbon double bond in ethylene consists of two electron pairs in orbitals formed by head to head overlap of sp^2 hybrid orbitals (σ bond) and side-on overlap of two p orbitals (π bond). The MO picture was very similar in that the σ and π orbitals comprising the double bond were located primarily on or between the two carbons, although technically they involved molecular orbitals which extended to the four hydrogens also. An alternative approach (very similar to the valence bond picture above) was that the carbon−carbon double bond consisted of a double overlap of two equivalent orbitals from each CH$_2$ unit which resulted in two equivalent banana bonds. It is noteworthy that in all of these approaches the electron density is equally delocalized across each bond (σ, π, or banana) involving the two carbons. Moreover, the C−C bond order provided by each theory (i.e., 2) is the same. Significantly, these three models imply that these double bonds between like atoms consist of two electron pairs, each of which is localized equally on two atoms, i.e., two covalent bonds. This working definition of the homonuclear double bond is consistent with a very similar definition of covalent bonding provided recently.[24c]

In the heavier analogues of ethylene, these three simple bonding models are often no longer adequate. Theoretical data show that the planar forms of the heavier element ethylene analogues do not represent the most stable structures.[27−31] Instead, these molecules assume a trans-bent geometry with pyramidal coordination at the group 14 element. Furthermore, the deviation from planarity becomes more marked with increasing atomic number. One explanation for this change in behavior involves the so-called CGMT[30,31] model which provides a correlation between the singlet−triplet energy separation of molecular fragments with the electronic and structural characteristics of the complete molecule.[32] Thus, if the doubly bonded group 14 species R$_2$EER$_2$ is considered, homolytic cleavage of the double bond leads to two triplet fragments which, for the heavier elements, are significantly less stable than the singlet ground states. This process is illustrated schematically in Figure 1. The double bond energy is thus given by eq 1.

$$E_{\sigma+\pi} = E_{INT} - 2\Delta E_{S-T} \qquad (1)$$

In developing the CGMT model, Trinquier and Malrieu have provided the following general rules regarding the relative values of singlet−triplet energy difference versus the energy of the double bond: if $E_{\sigma+\pi}$ is $>2\Delta E_{S-T}$, a classical planar structure is obtained, if $E_{\sigma+\pi}$ is $<2\Delta E_{S-T}$, a trans-bent structure is observed, whereas if $E_{\sigma+\pi}$ is $<\Delta E_{S-T}$, monomers with no E−E bonding will result. Since, in general, the singlet form of the two EX$_2$ units comprising the

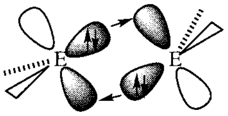


Figure 2. Association of two singlet carbene-like monomers via polar dative bonds.

double bond becomes more stable relative to the triplet form going down the group and since the strength of the E−E bond decreases with increasing atomic number, the energy gained by E−E bond formation is increasingly unable to offset the higher energies required for accessing the triplet state prior to formation of the double bond. Increasingly, the character of the double bond resembles an association of two singlet monomers in which the bonds are of a dative type, as illustrated by Figure 2.

A simpler conceptual approach to rationalizing pyramidal or bent geometries in heavier element compounds begins with the recognition that the singlet form of monomeric moieties such as

(E = Group 14 element)

or

(E = Group 13 element)

becomes more stable relative to the triplet form with increasing atomic number. Bringing these singlet monomers together in order to dimerize them results in considerable repulsion between the lone pairs. This repulsion can be minimized by the assumption of a pyramidal or bent geometry by the main group elements in the incipient dimer, thereby enabling the lone pairs to 'avoid' each other.

It should be noted that this bonding picture is distinct from the banana bonding proposed above for ethylene since in the heavier element analogues the electron pairs are not equally shared between the atoms in each bond. These so-called 'paw-paw' bonds (or polar dative)[31d] represent weak dipolar interactions between atoms of the same electronegativity. Clearly these bonds do not conform to the definition of double bonding provided earlier since the electron pairs remain primarily located on one rather than two atoms. It is important to realize that the changes in bonding that occur going down the group also result in a considerable weakening of the bond even though in many instances the measured bond distances suggest that the bond is stronger. For example, many of the currently known tin and lead derivatives of formula R_2EER_2 (M = Sn or Pb) have Sn−Sn and Pb−Pb bond distances very close to that of single bonds in the solid state (vide infra).[8] Yet they are dissociated to monomers in solution with bond enthalpies that are a small fraction of the corresponding single bond strengths.[7] In many instances the dipolar interactions comprising these bonds are similar in strength to hydrogen bonds.

From the standpoint of molecular orbital theory, the increasing pyramidalization of the R_2EER_2 heavier element ethylene analogues may be compared to the orbital interactions in the inversion process in pyramidal molecules such as ER_3 (E = N, P, As, Sb, or Bi).[33] The larger inversion barriers in the heavier trivalent pnictogen compounds result from increased mixing of a σ^* orbital into the lone pair on the central atom owing to the reduction of the energy separation between these orbitals on descending the group.[33] The energy of the lone pair in the ground state is thus lowered in what is in effect a second-order Jahn−Teller interaction.[34] In a similar manner, the increased mixing of the σ^* and π orbitals in the group 14 ethylene analogues[27b,29b] lowers the energy of (or stabilizes) the π orbital but by the same token gradually changes its character to a nonbonding lone pair orbital (Figure 3). As a result, the original π bond is gradually transformed into the nonbonding n_+ lone pair combination. The σ bond is also weakened, in part owing to less efficient orbital overlap and to a much lesser extent limited mixing (owing to their larger energy separation) of the σ and π^* orbitals. Thus, according to molecular orbital theory, the planar geometry is just a special case of a more general picture which predicts pyramidal or bent geometry in all except the lighter element derivatives This has led to the view that the usual multiple bonding picture for compounds of carbon and its neighboring first-row elements (which entail little interaction between the bonding and antibonding levels owing to their large energy separation) is in reality the exceptional case and it is the heavier congeners which represent the norm.[32,35]

Similar bonding models, in which π bonding is weakened and lone pair character enhanced, can be

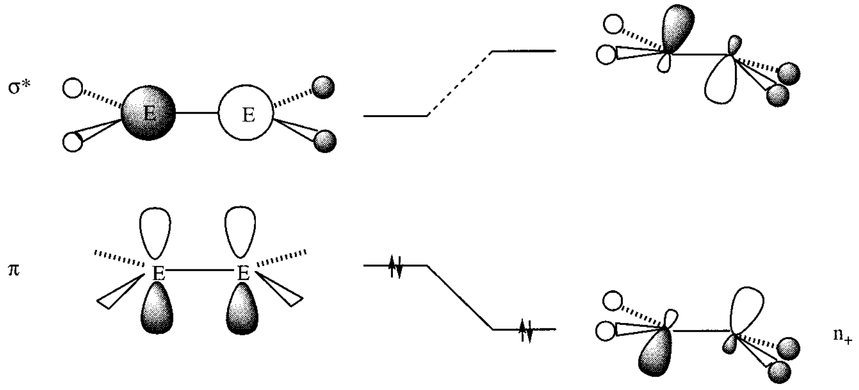


Figure 3. $\pi-\sigma^*$ interaction in heavier element group 14 analogoues of ethylene which produces pyramidialyzed geometries and lowered E−E bond order by introducing lone pair character into the π bond.

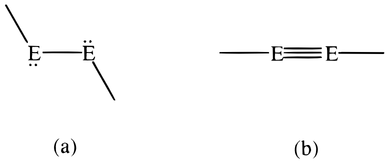


Figure 4. The singly (a) and triply (b) bonded canonical forms of heavier group 14 element (E) alkyne analogues.

developed for the alkyne congeners[29] illustrated in Table 2. For example, the group 14 element alkyne analogues can be written in two canonical forms (Figure 4). The dimethylene form on the right is obtained by converting two π bonds of the dimetalyne form (a). Calculations show that a bent form becomes increasingly favored on descending the group. Although no stable heavier group 14 alkyne analogues have been reported to date, the related singly and doubly reduced $[K(THF)_6][(SnC_6H_3\text{-}2,6\text{-}Trip_2)_2]$,[13] $Na_2(SnC_6H_3\text{-}2,6\text{-}Trip_2)_2$,[36] and $K_2(GeC_6H_3\text{-}2,6\text{-}Trip_2)_2$[36] compounds (obtained by adding one or two electrons to the dimethylene form) display angles of ca. 95−108° at the group 14 element. In addition, the group 13 compound $Na_2(GaC_6H_3\text{-}2,6\text{-}Trip_2)_2$[24a] in which the diaryl digallium dianion is isoelectronic to the corresponding neutral (but currently unknown) germanium dimer $(GeC_6H_3\text{-}2,6\text{-}Trip_2)_2$ has a bent geometry (Ga−Ga−C angles average ca. 130°) at the galliums.

The increasing lone pair character in the heavier group 14 alkene and alkyne analogues and the related heavier group 13 species has led to debate on the description of the bonding in these compounds which can be summarized as follows: taking the substituted tin and lead analogues of ethylene as examples, one opinion is that such compounds are indeed double bonded since they can be written with the tin and lead atoms connected by two dative bonds. Furthermore, the use of names such as distannene and diplumbene (by analogy with ethene) is justified, both for this reason and the fact that the stoichiometries are analogous. An opposing viewpoint is that, in the heavier elements, the mixing of the antibonding and bonding levels lowers the bond order. This is manifested in the appearance of increasingly nonbonding lone pair character at the heavier element and relatively long element−element distances approximately equal to, or greater than, those of single bonds. As a result, the chemistry of the weakly associated dimers bears little resemblance to that of alkenes. Furthermore, the weakness of these bonds underlines the fact that the electron pairs remain, for the most part, undelocalized over two atoms and thus do not meet the definition of covalent bonding given earlier. These arguments may be more than a matter of semantics since if it is accepted that a major justification for having nomenclature systems and bonding models is to describe and represent the typical characteristic physical and chemical properties of a particular class of compounds as accurately as possible, then a term such as "dimetallene" does not provide a good description of their physical behavior and chemical reactivity. Similar arguments can be stated for the heavier main group alkyne analogues.

The dilemma is that the preservation of the idea of formal double or triple bonding in the heavier element alkene and alkyne analogues requires the abandonment of the original definition of covalent multiple bonding. Furthermore, if a very limited degree of delocalization of an electron pair is sufficient to qualify as a bond in a homonuclear system, a strange new bonding realm arises which requires no correspondence between bond energies, bond lengths, and bond orders. This arises from the fact that the heavier element "multiple" bonds are in many instances, a good deal longer and weaker than single ones. This has led to confusion and argument since "multiple" is often correlated with "strength". To avoid this problem, some authors have employed adjectives such as "soft",[32] "non-classical",[32] or "slipped"[24c] to distinguish these "multiple" bonds from the "classical" double or triple ones such as those in ethylene or acetylene.

Efforts to resolve these arguments theoretically and to quantify the heavier element bonding in the future may be focused on such concepts as total charge densities,[37] bond paths, critical points, and force constants. However, it seems probable that experimentalists will have the last word. As the reaction chemistry and spectroscopic properties of the compounds become better explored, the multiple character (or lack thereof) of their bonds will become more accurately defined.

III. Lone Pair Character versus Multiple Bonding

The conflicting views on multiple bonding has tended to obscure a feature which is common to all currently known multiply bonded heavier main group element analogues of ethylene or acetylene; this is the manifestation of lone pair electron density at the multiply bonded element which becomes more pronounced and s-like in character in the heaviest group members. This phenomenon is a direct result of the reluctance of the heavier main group elements to hybridize and it is an inherent characteristic[38,39] of the heavier p-block elements.[40−42] It leads to the gradual exclusion of s electrons from bonding, and this exclusion is often a leading cause of the rapid decrease in multiple bond strength in compounds such as the heavier element analogues of ethylene. For example, it readily accounts for the fact that the currently known, weakly associated "distannenes" and "diplumbenes" are composed of SnR_2 or PbR_2 monomers in which the lone pair resides in what are primarily 5s or 6s orbitals. The low strength of these multiple bonds, however, gives the false impression that π bonding between the heavier elements is inherently weak. In fact π overlap between the 5p or 6p orbitals of the heaviest elements remains quite significant. This can be illustrated by the heavier dipnictenes of formula REER (E = Sb or Bi)[9] which do not dissociate in solution and display planar trans-bent structures with substantial rotation barriers around the EE bond. The contrast between the stability of the double bonding in the dipnictenes and the heavier group 14, R_2EER_2 (E = Sn or Pb), species highlights the obvious message that strong multiple bonding between two heavier main group elements occurs primarily through p orbital overlap which can result in well-defined, classical σ and π bonds while the lone pair combinations become more s-like in character. With the group 14 compounds R_2EER_2 (E = Si, Ge, Sn, or Pb), the classical double bonding model cannot be maintained without incorporation of the s electrons in bonding orbitals and their gradual exclusion from bonding implies that the EE bonds should, in the limit, become completely dissociated. In reality, some characteristics of double bonding are preserved in the weak association of the ER_2 (E = Sn or Pb) fragments in the solid state structures of a number of compounds. This line of reasoning may also be extended to triply bonded species. Here, the limiting case for the complete exclusion of s-electron pairs from bonding is the singly bonded form (a) as already depicted in Figure 4. Currently, REER (E = Si, Ge, Sn, Pb) species are unknown as stable compounds, but calculations show that they adopt trans-bent structures.[29] Experimental support for the increasingly bent geometry and lone pair character at the heavier main group element has come from the structure of the isoelectronic $[RGaGaR]^{2-}$ dianion which has an angle of ca. 130° at the galliums.[24a] The increasing lack of participation of the s electrons in the bonding may, of course, be viewed as a manifestation of the so-called "inert pair effect" in the heavier p-block elements.[43] The validity of the lone pair effect versus π bonding generalization and its extension to other classes of compounds will be further strengthened by many more examples from the various compound classes, which will be discussed in the remainder of this review.

IV. Doubly Bonded Compounds

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

Compounds defined by the dimeric formula R−E=E−R (E = group 13 element) are few in number and at present are confined to species in which the two group 13 elements are the same. For the heavier elements, no stable compounds have been isolated for either aluminum or gallium. The only structurally characterized compounds are the dimeric derivatives of indium and thallium of formula $[M\{\eta^5\text{-}C_5(CH_2Ph)_5\}]_2$ (M = In or Tl)[44a,b] which have trans-bent structures (Figure 5) and almost identical In−In and Tl−Tl distances of 3.631(2) and 3.632(1) Å. Weak Tl−Tl interactions (3.76 and 3.6 Å) have also been observed in the thallium derivative $Tl_2(\eta^5{:}\ \eta^5\text{-}t\text{-}Bu_4C_{10}H_4)$[44c] and $Tl_2B_9H_9C_2Me_2$.[44d] These distances are far longer (by ca. 0.8 and 0.6 Å) than the respective single bonds (ca. 2.8 and 3.0 Å)[45] and indicate that the bonding is extremely weak. The weakness of such bonding is underlined by the fact that monomeric structures can be readily observed with multidentate ligands.[46] In addition, one-coordinate group 13 metals can be observed in the vapor phase, as in $GaC(SiMe_3)_3$,[47a] or in the solid state, as in the structures of $MC_6H_3\text{-}2,6\text{-}Trip_2$ (M = In[47b] or Tl[47c]).

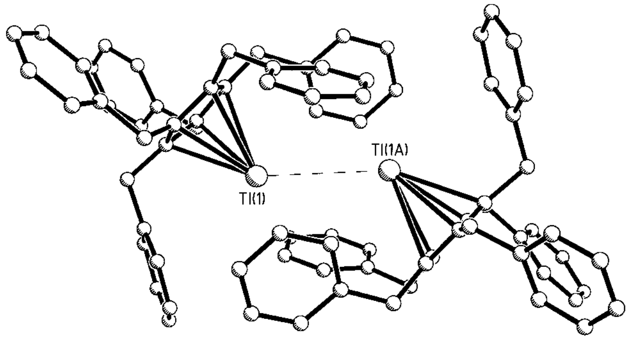


Figure 5. Trans-bent structure of the weakly associated dimer $[Tl\{\eta^5\text{-}C_5(CH_2Ph)_5\}]_2$.[44b]

Calculations on idealized aluminum and gallium derivatives with hydrogen or methyl substituents show that the trans-bent form is more stable than the linear form,[48] although hydrogen-bridged structures are calculated to have the greater stability when hydrogens are the substituents.[48a−c] In addition, the M−M bond lengths in the trans-bent configuration are ca. 0.3−0.4 Å longer than in the linear one.[48d] The latter is predicted to have two unpaired electrons owing to the presence of two degenerate π levels. However, even the more stable, formally double-bonded, trans-bent form of HGaGaH has been calculated to have a Ga−Ga distance of 2.656 Å[48c] which is significantly longer (by ca. 0.1−0.3 Å) than the single bonds (ca. 2.33−2.54 Å) in R_2GaGaR_2 compounds.[7,10,11a,49] The calculated Al−Al distance in HAlAlH is 2.613 Å,[48a] which is very similar to the Al−Al single bond distances in dialanes of formula R_2AlAlR_2.[10,49]

Analogies have been drawn between the trans-bending of Tl_2H_2 and the closely related orbital interactions[33] in the pyramidalization of EH_3 (e.g., NH_3) and the bending of EH_2 (e.g., H_2O).[50] This MO analogy, involving the mixing of σ^* and π levels, is very similar to that made earlier for the heavier main group 14 ethylene congeners. In addition, it has been pointed out that the metallanediyl fragments :ER (E = Al, Ga, In, or Tl) and $E'R_2$ (E′ = Si, Ge, Sn, or Pb), which both have a pair of electrons available, differ only in the number of acceptor orbitals.[51] Thus, the derivatives RMMR may be also considered to be bonded in the valence bond, donor−acceptor fashion (Figure 2). Nonetheless, these bonds have been calculated to be quite weak and are only ca. 3−4 kcal mol^{-1} in strength for the HEEH (M = Ga, In, or Tl)[52] derivatives and ca. 10 kcal mol^{-1} for the aluminum derivative.[52b]

In summary, multiple bonding between the heavier group 13 elements has been calculated to be weak. Moreover, the electrons in the orbitals comprising the E−E bond become increasingly lone pair-like and s in character as the group is descended. In essence, there is less and less electron density available to occupy any bonding molecular orbitals which might result from p orbital overlap. However, as will be seen in section III.B, the addition of electrons to these p orbitals results in a strengthened bond between two galliums in the compound $Na_2\{2,6\text{-}Trip_2H_3C_6Ga\text{-}GaC_6H_3\text{-}2,6\text{-}Trip_2\}$.[24a]

For the boron derivatives RBBR the linear arrangement featuring a triplet ground state is pre-

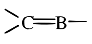
Table 3. Some Important Structural Data for Methyleneboranes

compound	B=C (Å)	–B= (deg)	ref
$(Me_3Si)_2CH{-}B{=}C(SnMe_3)BMes_2$	1.31(1)	173.5(8)	58f
Dur-B=C{C(GeMe$_3$)$_2$}BDur	1.351(9)	168.8(6)	58d
t-Bu-B=C(SiMe$_3$)$_2$	1.361(5)	179.6(3)	57e
Dur(Me)$_2$C–B=C(SiMe$_3$)(SiMe$_2$Dur)	1.363(9)	176.6(7)	58c
Dur-B=C{CH(SiMe$_3$)$_2$}{B(Mes)ODipp}	1.372(9)	176.6(6)	58g
Dur-B=C{B(Dur)}$_2$C(SiMe$_3$)$_2$	1.374(8)	176.7(6)	58b
Dur-B=C{CH(SiMe$_3$)$_2$}{B(OMes)$_2$}	1.382(11)	175.1(8)	58g
(i-Pr)$_2$N–B=C(SiMe$_3$)$_2$	1.391(4)	179.6(1)	57d
Dur-B=C(CH$_2$CMe$_3$)B(Dur)C(CH$_2$CMe$_3$)CC(SiMe$_3$)$_2$	1.391(3)		58e
Dur-B=C(CH(SiMe$_3$)$_2$}{B(Dur)Me}	1.404(9)	179.5(7)	58g
Tmp-B=Fluorenyl	1.424(3)	175.1(2)	57c

dicted to be the most stable structure.[53] The presence of two unpaired electrons suggests extreme reactivity. No examples have been isolated in the pure form to date, although several attempts at reduction of various sterically hindered alkyl-, aryl-,[54] or amido-[55] substituted boron dihalides have led to rearranged products usually without B–B bonding. However, it is possible to obtain the amino-substituted diborenes $(s\text{-}Bu)_2N{-}B{=}B{-}N(s\text{-}Bu)_2$ or (Dmp)B=B(Dmp) via reduction of the appropriate diboroxane $R_2N(Cl)BOB(Cl)NR_2$ or of the 1,2-dihalide derivatives $R_2N(Cl)BB(Cl)NR_2$ with Na/K alloy.[56] The products could not be isolated in pure form, and at present they can only be obtained as part of a mixture from which the diborene was not separated. An absorption band at 1452 cm^{-1} in the Raman spectrum of DmpB=BDmp has been tentatively assigned to the B=B stretching frequency.[56a]

B. Compounds of Formula $RE{=}E'R_2$ (E = Group 13, E′ = Group 14 Element)

The simplest compounds in this group are the boraalkenes or methyleneboranes.[57–60] Since both doubly bonded atoms are light, only a brief summary can be provided here. For this pair of atoms, the s electrons may participate in the bonding through hybridization and no lone pair character is expected at either atom where planar and linear coordination should be observed at carbon and boron, respectively. Calculations[41b] on the hypothetical molecule $HB{=}CH_2$ indicate that the B–C π-bond strength is 53.7 kcal mol^{-1}. Several examples of stable methyleneboranes are known, and a number of these have been structurally characterized (Table 3). They all possess essentially linear geometry at boron and have B=C distances in the range 1.31–1.42 Å which is up to ca. 0.2 Å shorter than a B–C single bond. The methyleneboranes can be categorized into classical and nonclassical types. A number of the classical examples, exemplified by structure **1**, possess an $-NR_2$ substituent at boron which stabilizes the very reactive two-coordinate boron center via delocalization of the nitrogen lone pair.[57] The C–B–N framework is thus isoelectronic to that of allene. However, the presence of the $-NR_2$ substituent is not essential for stability, and several species with alkyl substituents at boron, e.g., t-BuB=C(SiMe$_3$)$_2$[57e] (Figure 6), have been synthesized. The nonclassical species **2** is stabilized by a hyperconjugative interaction with the bond to the carbon substituent X which is often a boryl group.[58,59] The synthesis, characterization, and chemistry of these, as well as the classical boraalkenes, have been reviewed.[60] In addition, several methylene borane complexes of transition metals have been isolated and characterized.[61] No stable compounds featuring double bonds between boron and a heavier group 14 element are known currently, although theoretical data[41b] indicate that the B–Si π-bond strength in $H_2Si{=}B{-}H$ is 27.0 kcal mol^{-1}.[41b] No heavier group 13 element species featuring full-fledged metal carbon double bonds have been isolated as stable compounds, but see section IV.D. Calculations on $H_2C{=}AlH$ and $H_2Si{=}AlH$ indicate that the Al–C and Al–Si π bonds are quite weak having values of 9.4 and 14.1 kcal mol^{-1}.[41b]



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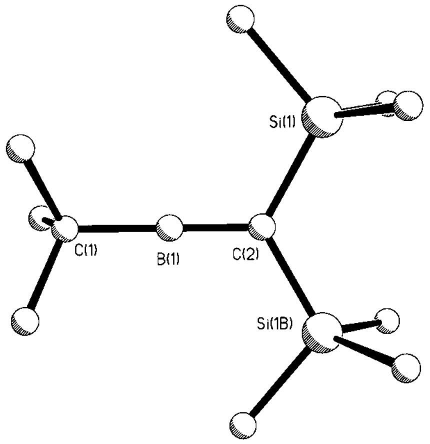


Figure 6. Schematic drawing of boraalkene t-Bu–B=C(SiMe$_3$)$_2$.[44]

C. Dianions of Formula $[R_2E{=}ER_2]^{2-}$ (E = Group 13 Element)

Compounds of formula $[R_2EER_2]^{2-}$ are the third class of group 13 double bonded species to be considered. They are isoelectronic with alkenes but possess a double negative charge on the central group 13 element moiety. This introduces significant Coulombic repulsion across the double bond. In effect, the formal addition of one electron to each group 13 element may be considered as having increased its effective radius (since the nuclear charge is unchanged) which should lead to a lengthening of the

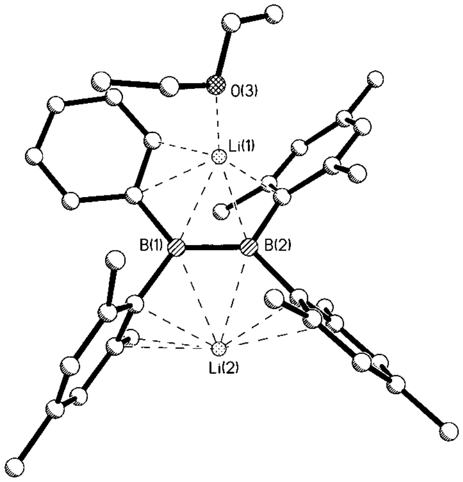


Figure 7. Schematic drawing of the boron−boron double bonded species $\{(Et_2O)Li\}_2\{Mes_2BB(Ph)Mes)\}$.[63a]

E−E bond. As a result the difference between the lengths of the single bond in the unreduced neutral R_2EER_2 species and the double bond in the reduced species may not be as great as expected. Only two acyclic examples,[62] the boron derivatives $\{(Et_2O)Li\}_2\{Mes_2BB(Ph)Mes\}$[63a] (Figure 7) and $\{(Et_2O)Li\}_2\{Me_2N(Ph)BB(Ph)NMe_2\}$,[63b] have been structurally characterized. Since boron is a first-row element, full participation of the s-electrons and planar coordination at boron is expected, and this is what is suggested by their structures. The B−B bond lengths are 1.636(11) and 1.631(9) Å, which may be compared with the normal B−B single bond lengths of 1.706(12) and 1.714(4) Å in the respective neutral precursors.[63c,d] The shortening in each case is on the order of 0.07−0.08 Å (between 4% and 5%) which is much less than the >10% value that might be expected for the difference in length between a carbon−carbon single and double bond (cf. 1.54 Å in ethane vs 1.34 Å in ethylene).[64] However, if the boron−boron double bond lengths are compared with the 1.859(6) Å B−B distance in the compound $[\{BC(SiMe_3)_2Mes\}_2]$,[2−65] which has a B−B single bond between two negatively charged three-coordinate boron atoms, the bond shortening is a much more impressive 0.22 Å or almost 12%. Singly reduced diborane (4) compounds, which have a formal B−B bond order of 1.5, are also known.[66,67] The structures of two compounds, the contact ion pair $\{(Et_2O)_2Li\}\{MeO(Ph)BB(Ph)OMe\}$[67a] and the solvent-separated ion pair [K(THF)(18-crown-6)] $[Mes_2BB(Ph)Mes]$,[67b] which have B−B bond lengths of 1.636(7) and 1.649(11) Å, have been reported. These distances are just slightly longer than the corresponding ones in the doubly reduced dianions.[63a,b] Apparently, the increased Coulombic repulsion produced by the addition of a second electron approximately counterbalances the expected shortening produced by the increase in bond order from 1.5 to 2. Calculations on the hypothetical species $Li_2B_2H_4$,[68a] $[Ph_2BBPh_2]^-$,[68b] and $[Ph_2BBPh_2]^{2-}$ [68b] afford results which are in good agreement with the experimental findings and indicate the presence of strong B−B π bonding.

No doubly reduced heavier element $[R_2E{=}ER_2]^{2-}$ (E = Al, Ga, In or Tl) compounds are known at present, but several species of considerable relevance have been characterized. Attempted reduction of tetraalkyls and -aryls of aluminum and gallium has led to the isolation of the singly reduced radical species $[R_2EER_2]^{-\bullet}$ (E = Al or Ga; R = $-CH(SiMe_3)_2$[10] or Trip[11]), which were crystallized as solvent-separated ion pairs with a variety of countercations. The four structures[10,11] determined to date show that E−E bond shortenings of up to 0.18 Å (ca. 7%)[11] relative to the neutral precursors can be achieved. Attempts at further reduction of the aluminum alkyl species in ether solvents led not to the dianions but to the isolation of products with Al−O bonds which derived from interaction of the reduced species with the solvent.[69] If ether is replaced by the less reactive solvent NEt_3, further reduction of the gallium aryl $Trip_2GaGaTrip_2$ can be achieved.[70] However, the product does not contain the doubly reduced $[Trip_2GaGaTrip_2]^{2-}$ ion but the rearranged species $[Ga(GaTrip_2)_3]^{2-}$ which features a central gallium coordinated to three $-GaTrip_2$ groups. The Ga_4 metal array is planar, and the sodium countercations are coordinated between four of the six Trip aryl ring substituents. The formal Ga−Ga bond order is 1.33, and the average Ga−Ga bond length is 2.39(2) Å. Two-electron oxidation produces the neutral $Ga(GaTrip_2)_3$ molecule with longer Ga−Ga distances that average 2.476(7) Å in length. Apparently, two-electron reduction of $Trip_2GaGaTrip_2$ leads to cleavage of at least two Ga−C bonds in the rearrangement sequence. It is notable that the interaction of $NaSi(t\text{-}Bu)_3$ with $GaCl_3$ gave the radical $(t\text{-}Bu)_3Si_2GaGaSi(t\text{-}Bu)_3$[12] (Figure 8) which can be further reduced with sodium to the anion $[\{(t\text{-}Bu_3)Si\}_2GaGaSi(t\text{-}Bu)_3]^-$.[71] These compounds also feature relatively short Ga−Ga distances of 2.420(1) and 2.38 Å. These results show that species of the type R_2EER_2 (E = Al or Ga) have a strong tendency to undergo cleavage of a metal−ligand bond.

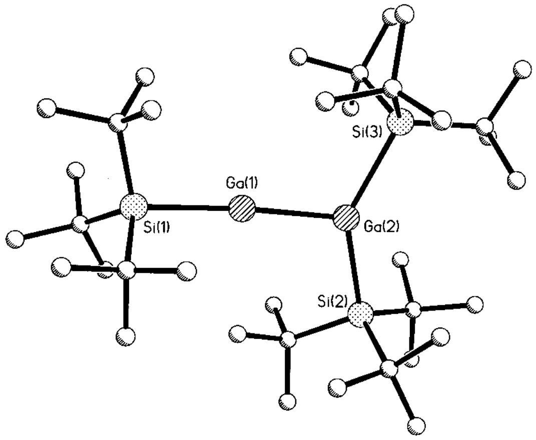


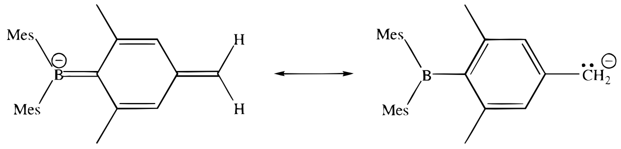
Figure 8. Schematic drawing of the multiply bonded gallium centered radical $\{(t\text{-}Bu)_3Si\}_2GaGaSi(t\text{-}Bu)_3$.[12]

An interesting aspect of the dianions $[R_2E{=}ER_2]^{2-}$ (E = Al or Ga) is that they are isoelectronic to the corresponding neutral silicon and germanium compounds. The tendency of the latter to assume pyramidal geometry at silicon or germanium is well-known, and it is probable that $[R_2E{=}ER_2]^{2-}$ (E = Al or Ga) may have the same tendency. Indeed, it could be argued that since aluminum or gallium is more electropositive than either silicon or germanium, the pyramidalization tendency in the group 13 dianions should be greater in accordance with MO theory.[33] However, this hypothesis has not been substantiated by experimental or theoretical data.[68b] It may be that owing to the relative weakness of the bonds between group 13 elements, the potential energy curve for the pyramidalization process may be relatively flat.

Unsymmetric $[R_2E{=}E'R_2]^{2-}$ dianions involving multiple bonding between different group 13 elements have not been reported. However, it is probable that some of these ions, especially those involving boron, will be synthesized in the future.

D. Monoanions of Formula $[R_2E{=}E'R_2]^-$ (E = Group 13; E′ = Group 14 Element)

Ions corresponding to the formula $[R_2E{=}E'R_2]^-$ (E = group 13; E′ = group 14 element) are isoelectronic to those in the previous section. A number of stable examples featuring the $[R_2B{=}CR_2]^-$ moiety have been structurally characterized (vide infra). In these lighter derivatives no trans-bent pyramidalization of the geometry is predicted. However, steric protection of the boron center is necessary to ensure stability since there is a strong tendency to form a four-coordinate borate salt rather than a deprotonated multiply bonded species upon addition of a nucleophile. The $[R_2B{=}CR_2]^-$ compounds may be considered as boron-stabilized carbanions[72] which have found application in organic synthesis as boron ylide reagents.[73] The first crystal structure of a boron-stabilized carbanion (in which boron is not part of a ring) involved the species $[Li(12\text{-crown-}4)_2][CH_2C_6H_2(3,5\text{-}Me_2)(4\text{-}BMes_2)]$,[74] which was synthesized by the treatment of $BMes_3$ with n-BuLi[75] followed by the addition of 12-crown-4.[74] It features a planar-coordinated boron bound to two Mes groups and to a further Mes group whose *para*-methyl substituent has been deprotonated. The B–C bond to the deprotonated Mes group is 1.522(10) Å, which is almost 0.1 Å shorter than the B–C distances to the intact Mes groups. The deprotonated *p*-CH_2 group also features a short C–C distance (1.349(10) Å) to the aryl ring. This suggests that the structure of the anion may be viewed as a composite of the two canonical forms



The addition of 12-crown-4 to a solution of $LiCH_2BMes_2$ (generated from $MeBMes_2$ and LiMes)[73a,b] gives $[Li(12\text{-crown-}4)_2][Mes_2B{=}CH_2]$ which has boron–carbon double bond distance of 1.438(9) Å.[76] Somewhat longer B=C distances of 1.475(8) and 1.509(8) Å were observed in the 2,3-diboratabutadiene $Li_2[\{BMesC(SiMe_3)_2\}_2]$,[65] and in the 1,3-diborataallene compound $\{(Et_2O)Li\}_2(Mes(t\text{-}Bu)BCB(t\text{-}Bu)Mes)$ where the B=C distance is 1.450(5) Å.[77a] No heavier group 13 metal analogues of these boron compounds have been reported. However, $(Cy_2N)_2(Me)PC(SiMe_3)GaMe_2$, which is related to the $[R_2C{=}ER_2]^-$ class, has a short Ga–C distance of 1.935(6) Å.[77b]

E. Compounds of Formula $R_2E{-}\ddot{E}'R_2$ (E = Group 13; E′ = Group 15 Element)

Compounds of formula $R_2E{-}\ddot{E}'R_2$ (E = group 13; E′ = group 15 element) may have formal double bonding through delocalization (dative π bonding) of the group 15 element lone pair into a p orbital on the group 13 element.[16,78] However, efficient delocalization requires planar geometries at both atoms and the alignment of their coordination planes. These conditions become increasingly difficult to achieve owing to the large inversion barriers in the heavier pnictogens as exemplified by the structure of the phosphinoborane Mes_2BPPh_2 (Figure 9). As already discussed, the much higher barriers and preference for pyramidal geometries in the heavier elements are a result of a second-order Jahn–Teller interaction of σ^* and π levels.[33] The lone pair character at the heavier pnictogen and the presence of an adjacent empty orbital at the group 13 element ensures that associated species with head to tail dimeric or trimeric structures and four-coordinate E and E′ centers are normally observed for heavier element derivatives. Steric crowding is thus necessary to produce monomeric structures in all molecules except the $R_2B{-}\ddot{N}R_2$ species where ready delocalization of the nitrogen lone pair can occur owing to the very low nitrogen inversion barrier.[15,79] A very large number of aminoboranes are known, but for reasons of space and the fact that neither of these elements is a heavy one, they cannot be treated in detail here. Up to the mid-1980s only a handful of monomeric heavier element congeners had been characterized. Currently, the structures of almost 100 compounds[80–94] of various classes (Tables 4–6), in which either E or E′ (or both) is a heavy group 13 and 15 element, have been determined and some of these species have been discussed in a number of reviews.[16,78] No unassociated derivatives of either antimony or bismuth have been structurally characterized as yet. The structures and spectroscopic measurements and computational data[95] enable the following generalizations to be made: (i) In the absence of geometrical constraints, all nitrogen derivatives have planar coordination at

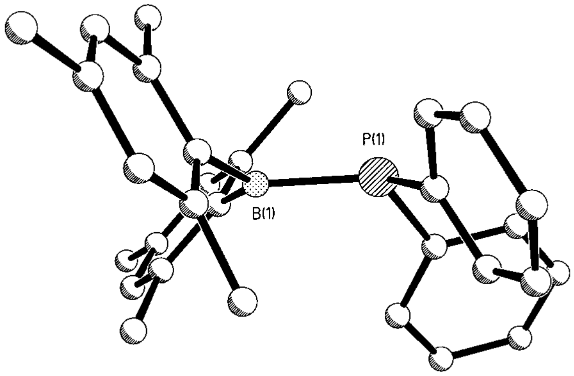


Figure 9. Illustration of the structure of Mes_2BPPh_2 showing the lone pair character of the phosphorus atom. The phosphorus coordination geometry ($\Sigma°P = 339.4$) and the B–P distance 1.859(3) Å (cf. B–P single bond = 1.96 Å[97]) indicate that there is some delocalization of the phosphorus lone pair.[89d]

Table 4. Metal−Nitrogen Bond Lengths and Torsion Angles between the Metal and Nitrogen Coordination Planes for Three-Coordinate Aluminum, Gallium, Indium, and Thallium Amides

compound	M−N (Å)	torsion Angle[a] (deg)	ref
Aluminum			
	Monoamides		
Trip$_2$AlN(H)Dipp	1.784(3)	5.5	80a
t-Bu$_2$AlNMes$_2$	1.823(4)	49.5	80b
t-Bu$_2$AlN(Dipp)SiPh$_3$	1.834(3)	16.1	80b
t-Bu$_2$AlN(1-Ad)SiPh$_3$	1.849(4) (av)	86.3 (av)	80b
Me(Cl)Al{SiPh(t-Bu)$_2$}{SiMe(t-Bu)$_2$}	1.852(1)	57.5	80c
Me$_2$AlN{SiPh(t-Bu)$_2$}$_2${SiMe(t-Bu)$_2$}	1.869(2)	57.5	80c,d
t-Bu$_2$AlN(SiPh$_3$)$_2$	1.879(4) (av)	64.3 (av)	80b
	Diamides		
Mes*Al{N(H)Ph}$_2$	1.794(4)	16.9 (av)	81b
MesAl{N(SiMe$_3$)$_2$}$_2$	1.804(2)	49.7	81a
	1.809(2)	44.5	
ClAl(Tmp)$_2$	1.785(4)	75.3	81c,d
	1.810(4)	41.5	
BrAl(Tmp)$_2$	1.782(6)	77.4	81c,d
	1.814(6)	39.0	
IAl(Tmp)$_2$	1.788(3)	77.3	81c,d
	1.803(3)	42.2	
DippOAl(Tmp)$_2$	1.808(2) (av)	59.8 (av)	81d
PhSAl(Tmp)$_2$	1.805(5) (av)	38.4, 71.4	81d
t-BuSAl(Tmp)$_2$	1.819(2) (av)	72.0, 67.3	81d
Ph$_2$PAl(Tmp)$_2$	1.819(2) (av)	66.0, 69.9	81d
Ph$_2$AsAl(Tmp)$_2$	1.819(3) (av)	67.6, 65.5	81d
PhAl(Tmp)$_2$	1.826(2) (av)	70.5	81d
Fc{Al(Tmp)$_2$}$_2$	1.825(2) (av)	71.9, 61.8	81d
(Me$_3$Si)$_3$SiAl(Tmp)$_2$	1.846(2) (av)	79.7, 63.4	81d
(η^5-C$_5$H$_5$)(CO)$_2$FeAl(Tmp)$_2$	1.847(4)	73.0, 69.6	81d
	1.802(4)		
ClAl{N(Ph)SiMePh$_2$}$_2$	1.829(2) (av)		81e
	Triamides		
Al{N(SiMe$_3$)$_2$}$_3$	1.78(2)	50	82b
Al{N(i-Pr)$_2$}$_3$	1.791(4) (av)	36.6 (av)	81a
	1.794(4) (av)	38.3 (av)	
	1.801(4) (av)	75.5 (av)	
(Tmp)$_2$AlN(H)Ph	1.813(2)	68.3	81d
	1.822(2)	69.2	
	1.790(2)		
Gallium			
	Monoamides		
Mes*Ga(Cl)N(H)Ph	1.832(10) (av)	2.4 (av)	81a
Trip$_2$GaN(H)Dipp	1.847(12) (av)	9.0	80a
Mes*$_2$GaN(H)Ph	1.874(4)	6.7	81a
Trip$_2$GaNPh$_2$	1.878(7)	0	80a
t-Bu$_2$GaN(t-Bu)SiPh$_3$	1.906(5)	88.7	80a
t-Bu$_2$GaN(1-Ad)SiPh$_3$	1.924(2)	71.8	80a
Et$_2$GaN(t-Bu)BMes$_2$	1.937(3)	69.7	83
	Diamides		
PhOGa(Tmp)$_2$	1.818(3)		84a
	1.849(3)		84a
Mes*Ga{N(H)Ph}$_2$	1.837(8)	7.3	81a
ClGa{N(SiMe$_3$)$_2$}$_2$	1.834(4)	40.5	81a
	1.844(4)	49.5	
Dipp{(Me$_3$Si)N}(Cl)GaN(Dipp) SiMe$_2$N(Dipp)SiMe$_3$	1.845(3)		84b
	1.898(3)		84b
PhGa(Tmp)$_2$	1.883(2)		84a
(Me$_3$Si)$_3$SiGa(Tmp)$_2$	1.908(3)	79.2	84b
	1.913(2)	64.3	
(Tmp)$_2$GaP(t-Bu)$_2$	1.908(6)		84d
[{Tmp)$_2$Ga}(t-Bu)P]$_2$	1.895(2)		84d
(Tmp)$_2$GaGa(Tmp)$_2$	1.901(4)	53	84e
	Triamides		
Ga{N(SiMe$_3$)$_2$}$_3$	1.868(1)	48.6	82a,81a,85a,f
	1.870(6)	50	
Indium			
	Monoamides		
t-Bu$_2$InN(Dipp)SiPh$_3$	2.104(3)	15.5	86a
Et$_2$In(NC$_4$H$_4$)	2.166(4)	16.1	86b
Me$_2$In(NC$_4$Me$_4$)	2.197(3)		86c
	Triamides		
In{N(SiMe$_3$)$_2$}$_3$	2.049(1)	48.6	82a,85a,86a
In{N(H)Mes*}$_3$	2.061(9)		87a
	2.067(7)		
	2.075(7)		
In(Tmp)$_3$	2.068(5)		87b
	2.068(5)		
	2.087(5)		
Thallium			
Tl{N(SiMe$_3$)$_2$}$_3$	2.089(18)	49.1	82a,88a
[TlN(SiMe$_3$)Dipp]$_4$	2.306(6)		88b

[a] Angle between the perpendiculars to the MC$_2$ and NC$_2$ coordination planes.

Table 5. Selected Structural Data for Some Boron−Pnictogen (E) Compounds with Varying Degrees of Multiple Bonding

compound	B−E (Å)	Σ°E[a]	ref
	Monophosphinoboranes		
Mes$_2$BPMes$_2$	1.839(8)	360	89a
Mes$_2$P(t-Bu)$_2$	1.839(8)	352.0	89a
	1.843(8)	359.2	
Mes$_2$BP(Ph)SiPh$_3$	1.842(6)	358.2	89a
Mes$_2$B(1-Ad)SiMe	1.846(8)	348.7(3)	89b
{Mes$_2$BP(1-Ad)}$_2$	1.852(9)	359.4	89c
Mes$_2$BPPh$_2$	1.859(3)	339.4	89d
Mes$_2$BP(H)(1-Ad)	1.897(3)	315	89a
Tmp(Cl)BP(H)Mes	1.948(3)	307.1[b]	89e
	Diphosphinoboranes		
BrB(PMes$_2$)$_2$	1.82(1)	347.1	90a
	1.84(1)	346.1	
PhB{P(Mes)BMes$_2$}$_2$	1.847(13)−1.869(14)	~360	90b
MesB(PPh$_2$)$_2$	1.879(2)	324.5	90c
	1.901(2)	318.8	
Ph$_2$NB{P(SiMe$_3$)$_2$}$_2$	1.896(7)	341	90d
(Me$_3$Si)$_2$NB[P(H)B{N(i-Pr)$_2$} N(SiMe$_3$)$_2$]	1.918		90e
	Diborylphosphines		
MesP{B(Cl)Mes}$_2$	1.853(4)	354.3	91
	1.859(4)		
PhP(BMes$_2$)$_2$	1.871(2)	360	90c
	Borylphosphides		
MesP{B(Trip)P(H)Mes} {B(Trip)P(Mes)Li(OEt$_2$)$_2$}	1.810(4)	359.4	92b
	1.927(3)	306.7	
Mes$_2$BP(Mes)Li(OEt$_2$)$_2$	1.823(7)	359.9	92a,b
Mes$_2$B(1-Ad)Li(OEt$_2$)$_2$	1.823(8)	357.4	89a
Mes$_2$BP(Cy)Li(OEt$_2$)$_2$	1.832(6)	357.7	92a,b
Mes$_2$BP(SiMe$_3$)Li(THF)$_3$	1.833(6)	357.7	92b
Trip$_2$BP(t-Bu)Li(OEt$_2$)$_2$	1.836(2)	356.1	92b
[Li(12-crown-4)$_2$][Mes$_2$BP(Mes)]	1.835(13)	- -	92a
	Monoarsinoboranes		
Mes$_2$BAs(Ph)SiMe$_3$	1.999(8)	323	93a
	2.031(8)	322	
Mes$_2$BAs(i-Pr)$_2$	2.019(7)	325.5	93b
(η^1-Cp*)(Cl)BAs(t-Bu)$_2$	2.085(4)	312	93a
C$_{20}$H$_{30}$BAs(t-Bu)$_2$	2.084(5)	322	93a
	Diarsinoboranes		
PhB{As(t-Bu)$_2$}$_2$	2.034(5)	320	93a
	2.065(5)	316	
	Borylarsenides		
Mes$_2$BAs(Ph)Li(THF)$_3$	1.926(6)	340.9	93a,c
[Li(TMEDA)$_2$][Mes$_2$BAsPh]	1.936(11)		93a,c

[a] Σ° = sum of the interligand angles at E. [b] A considerable number of compounds, in which three-coordinate boron is bound to both phosphorus and nitrogen, are known. These are not generally listed since the competitive π bonding interaction of the nitrogen lone pair usually dominates the interaction with phosphorus lone pair.

nitrogen whereas for the heavier pnictogen derivatives, such as those of phosphorus and arsenic, varying degrees of pyramidal coordination at the pnictogen are always observed unless there are very electropositive or crowding substituents at the pnictogen.

(ii) In the boron derivatives relatively strong π bonding (>20 kcal mol^{-1}) to nitrogen,[96] phosphorus,[89a,92a,b] and arsenic[93a,c] can exist. In such cases the boron-pnictogen bond distances have proven to be much shorter than the sum of the covalent radii[97] even when they are corrected for σ-rehybridization and ionic effects.

(iii) In aluminum−, gallium−, indium−, or thallium−nitrogen derivatives, metal−nitrogen bond lengths up to 0.2 Å shorter than the sum of the covalent radii may be observed. Although the nitrogen coordination is invariably planar, this is not indicative of strong π bonding since rotational barriers around these bonds are small. Empirical corrections[98] of the bond distances for ionic effects lead to values that are close to those observed experimentally. Furthermore, metal−nitrogen bond lengths are in the order monoamide > diamide > triamide, which is opposite to what is expected if strong π bonding existed and is consistent with a decreasing effective ionic radius with an increasing number of electronegative substituents.

(iv) In aluminum, gallium, indium, or thallium derivatives of the heavier pnictogens, pyramidal coordination is, with rare exceptions,[94b] observed at the pnictogen even where electropositive substituents are used to promote π bonding. Moreover, the experimentally observed bond lengths are consistent with single bonding.

These data lead to the generalization that although strong π bonding can be observed in B−N, B−P, and B−As derivatives, it is relatively weak (ca. ≤10 kcal

Table 6. Selected Structural Data for Heavier Unassociated Group 13 Element−Pnictogen Derivatives

compound	M−E (Å)	torsion angle (deg.)	Σ°P (deg)	ref
Aluminum				
$Trip_2AlP(Mes)SiPh_3$	2.342(2) (av)	47.5 (av)	330.0	94a
$Trip_2AlPPh_2$	2.377(1)		316.2	81d
$Tmp_2AlAsPh_2$	2.485(2)		308.1	81d
Gallium				
	Monophosphides			
$MesP\{Ga(Trip)_2\}_2$	2.256(3)	14.7	358.8	94b
	2.258(3)	15.6		
$t\text{-}Bu_2GaP(Mes^*)SiPh_3$	2.295(3)	3.2	346.4	94c
$t\text{-}Bu_2GaP(Trip)SiPh_3$	2.296(1)	1.9	340.5	94d
$t\text{-}Bu_2GaP(Ph)BMes_2$	2.319(1)	56.4	344.2	94e
$t\text{-}Bu_2GaP(SiMe_3)SiPh_3$	2.358(4)	76.5	326.2	94d
$Tmp_2GaP(t\text{-}Bu)_2$	2.375(3)		331.8	84d
$\{Tmp_2GaP(t\text{-}Bu)\}_2$	2.4225(8)		317.69	84d
	Diphosphides			
$t\text{-}BuGa\{P(Ph)BMes_2\}_2$	2.194(2)		351.8	94e
	2.390(2)	347.7		
$t\text{-}BuGa(PHMes^*)_2$	2.326(4)			94f
	2.323(5)			
	Triphosphides			
$Ga(PHMes^*)_3$	2.34(1) (av)			
	Monoarsenides			
$PhAs\{Ga(Trip)_2\}_2$	2.401(1)	41.7	329.8	94b
	2.418(1)	81.3		
$(\eta^1\text{-}Cp^*)_2GaAs(SiMe_3)_2$	2.433(4)	∼90	∼320	94i
$t\text{-}Bu_2GaAs\{CH(SiMe_3)_2\}SiPh_3$	2.459 (av)	70.6 (av)	316 (av)	94c
$t\text{-}Bu_2GaAs\text{-}t\text{-}Bu_2$	2.466(3)	90	317.0	94j
	Triarsenides			
$Ga\{As(SiMe_3)_2\}_3$	2.421(4)	-	101.85	94k
$Ga(AsMes_2)_3$	2.470(1)	52	320.2	
	2.498(1)	58	310.5	
	2.508(1)	86	313.6	94l

mol^{-1}) for the other currently known aluminum, gallium, indium, and thallium compounds of this class. The weakness of the bonding in the latter compounds has been accounted for in terms of the relatively large sizes and electropositive character of the group 13 metals which result in large electronegativity and size differences across the bonds.[78,81d] These lead to increased ionic character and reduced orbital overlap which reduce the π-bond strengths. This circumstance, allied with the large inversion barriers at three-coordinate heavier pnictogens, ensures a preference for increased lone pair character over π bonding in the heavy atom compounds. A recent, systematic study of a series of aluminum amides has also supported the presence of highly polar Al−N bonds and the absence of significant Al−N π-bonding.[81d]

F. Compounds of Formula $R_2E–E′R$ and $[R_2E–E′]^-$ (E = Group 13, E′ = Group 16 Element)

A very large number of the light atom R_2BOR compounds are known, but there are surprisingly few structures available on species of the specific formula R_2BOR'. They will not be discussed further here except to note that B−O π bonding as estimated from rotation barriers appears to be in the range 9−12 kcal mol^{-1}.[99a,b] However, theoretical data[99b] lead to the conclusion that this relatively low value is a result of the stabilization of the transition state by oxygen π donation. In effect the oxygen can behave as a two-sided π donor owing to the ability of its valence s and p orbitals to hybridize relatively easily. This affords wider bond angles at oxygen and relatively good π overlap in the transition state. For heavier chalcogen derivatives, hybridization is energetically disfavored and there is little stabilization of the transition state. In essence, the −E′R groups (E′ = S, Se, or Te) are one-sided donors since one of the lone pairs, mainly s in character, cannot easily participate in π bonding.[99b] For such compounds the measured rotation barrier gives a relatively accurate estimate of the strength of the B−E′ π bond which is ca. 18 kcal mol^{-1} in the compounds Mes_2BSPh[100a] and Mes_2BSMe[99b] (Figure 10). It seems probable that the strengths of the B−O and B−S π bonds are very similar in $R_2B−E′R$ (E′ = O, S) compounds. Apparently, the greater ionic character of the B−O bond plays a role in keeping the π-bond strength of the lighter pair at about the same level as that of its heavier sulfur congener. The B−S rotational barrier in the dithiolate compound $TripB(SPh)_2$ is ca. 12 kcal

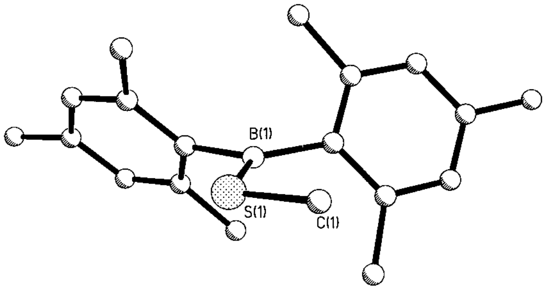


Figure 10. Structure of Mes_2BSMe[99b] illustrating the alignment of the boron and sulfur coordination planes. The 109.8(3)° interligand angle at sulfur is narrower than the 123.6(3)° angle observed in its oxygen congener Mes_2BOMe which is consistent with the greater s-character in the sulfur lone pair.

Table 7. Selected Structural Data for Some Thioborane Derivatives[a]

compound	B–S Å	B–S–R (deg)	ref
$\{Mes(t\text{-}BuS)B\}_2$	1.771(4)	114.1(2)	101c
Me_2BSMe	1.779(5)	107.2(10)	101a
Mes_2BSMe	1.787(6)	109.8(3)	99b
Mes_2BSPh	1.790(6)	107.0(2)	100b
$TripB(SPh)_2$	1.799(6)	100.4(3)	100b
	1.802(6)	106.6(3)	
$B(SMe)_3$	1.805(2)	104.5(3)	101b
$TbtB(SH)_2$	1.81(2)		101d

[a] There are a very large number of compounds with boron–sulfur bonds. Those which form part of a ring or have a π-donor substituent (e.g., $-NR_2$) at boron are not considered here.

mol^{-1},[100b] which is less than those in the monothiolates and is consistent with the delocalization of the π bond over the three-atom BS_2 moiety. Nonetheless, the B–S distances [99–101] in the six structurally characterized compounds (Table 7) fall within the very narrow range of 1.77–1.805 Å, which is significantly shorter than the sum of the covalent radii of boron and sulfur, ca. 1.87 Å.[97] There have been no structures or VT NMR studies of the heavier selenium[102] or tellurium analogues of formula $R_2BE'R$ (E′ = Se or Te). Presumably these would have slightly lower π-bond strengths than the corresponding oxygen or sulfur compounds.

The π bonding of the heavier main group 13 elements to chalcogenides[103–106] has also been the subject of recent attention (Tables 8 and 9). Calculations,[95f] however, suggest that π bonding in such compounds is quite weak—for example, rotation barriers of only 1.72 and 3.48 kcal mol^{-1} were calculated for the hypothetical alkoxide compounds Me_2AlOMe and H_2AlOH. The weakness of the π bonding is probably a result of the large size differences and polar character of these bonds.[78] Significantly higher barriers were calculated for the sulfur derivatives H_2AlSH (7.34 kcal mol^{-1}) and H_2GaSH (8.44 kcal mol^{-1}). It may be noted that the values for these compounds are less than one-half those (ca. 18 kcal mol^{-1}) for Mes_2BSPh or Mes_2BSMe. A VT ^1H NMR study of $Mes^*{}_2GaSMe$[104b] indicates that the Ga–S rotation barrier is ca. 10 kcal mol^{-1}. Although this result is in reasonable agreement with the calculated value, the observed dynamic process may be a result of steric effects similar to those seen in the VT NMR study of $\{(Me_3Si)_2HC\}_2GaTeSi(SiMe_3)_3$.[105b] A further interesting point regarding the calculations[95f] is that the rotational barrier predicted for the Ga–S bond is slightly higher than that for Al–S. Although it has not been confirmed experimentally, this prediction is consistent with the smaller size and less electropositive character of gallium, which affords a less ionic bond to the chalcogen.

Solvent-separated ion pairs of formula $[R_2E{-}E']^-$ (E = group 13 and E′ = group 16 element) have not been structurally characterized. However, the structures of several alkali metal salts of formula $\{(L)MOBR_2\}_n$ (M = Li or Na; n = 1, 2, or 4) have been reported.[107] The species $(TMEDA)LiOB\{CH(SiMe_3)_2\}_2$[107b] is the only monomer, and it features a short B–O bond of length 1.308(8) Å (cf. 1.352(5) Å in Mes_2BOMe)[99b] signifying enhanced B–O bond strength. The gem-dithiolate salt $(LiS)_2BTbt$ has been generated in solution, but it has not been characterized structurally, although a number of its deriva-

Table 8. Selected Structural Data for Monomeric–OR Derivatives of Three Coordinate Heavier Group 13 Elements

compound	M–O (Å)	M–O–C angle (deg)	torson angle[a] (deg)	ref
Aluminum				
	Monoalkoxides			
$t\text{-}Bu_2AlOMes^*$	1.709 (av)	135.2 (av)	12.8	103a
$t\text{-}Bu_2Al(O\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)$	1.710(2)	129.4(1)	3.0	103a
$(Tmp)_2AlODipp$	1.696(2)	158.4(2)		81d
	Bisalkoxides			
$MeAl(O\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)_2$	1.685(2)	148.8(2)		103b
	1.687(2)	140.5(2)		
$i\text{-}BuAl(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_2$	1.682(1)	157.3(1)		103c
	1.702(1)	134.7(1)		
$(\eta^5\text{-}C_5H_5)Al(O\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)_2$	1.736(2)	134.8(2)		103d
	Trisalkoxides			
$Al(O\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)_3$	1.648(7) (av)	177.2 (av)		103e
	Aluminoxane			
$O[Al\{CH(SiMe_3)_2\}_2]_2$	1.6877(4)	180[b]	0	103f
$O[Al\{CH(SiMe_3)_2\}_2]_2{\cdot}ONMe_3$	1.753(3)	162.3(2)		103g
Gallium				
	Monoalkoxides			
$O\{Ga(Mes^*)Mn(CO)_5\}_2$	1.784(11)	150.2(5)[c]		84e
	1.789(11)			
$t\text{-}Bu_2Ga(O\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)$	1.821(3)	125.0(2)	1.5	103a
$(Tmp)_2GaOPh$	1.822(3)	128.6(2)	23.5	84a
$t\text{-}Bu_2GaOCPh_3$	1.831(4)	127.5(3)	~90	103h
	Bisalkoxides			
$Mes^*Ga(OSiPh_3)_2$	1.783(8)	140.3(5)[d]		103i
	1.814(8)	141.9(5)		

[a] The torsion angle given is the angle between the O–C vector and the plane at the metal. [b] Al–O–Al angle. [c] Ga–O–Ga angle. [d] Ga–O–Si angle.

Table 9. Selected Structural Data for Low Coordinate Heavier Group 13 Derivatives of Chalcogenolate and Chalcogenido Ligands

compound	M−E	M−E−C	torson angle (deg)	ref
Aluminum				
Al(SMes*)$_3$	2.185(2)	100.4(1)	20.7	104a
n-BuAl(SMes*)$_2$	2.188(9)	98.5(2.0)	14.8	104b
t-BuAl(SMes*)$_2$	2.196(3)	102.7(3)	19.8	104b
(Tmp)$_2$Al(SPh)	2.229(4)	106.2(5)		81d
(Tmp)$_2$AlS(t-Bu)	2.200(1)	106.5(1)		81d
S[Al{CH(SiMe$_3$)$_2$}$_2$]$_2$	2.187(4)	117.5(3)^a	39.9	104c
Se[Al{CH(SiMe$_3$)$_2$}$_2$]$_2$	2.319(1)	114.71^a		104d
Te[Al{CH(SiMe$_3$)$_2$}$_2$]$_2$	2.549(1)	110.40(6)^a		104e
Gallium				
Ga(SMes*)$_3$	2.205(1)	100.4(1)	20.5	104a
n-BuGa(SMes*)$_2$	2.210(11)	99.9(4.5)	4.1, 14.2	104b
Mes*$_2$GaSMe	2.271(2)	102.9(3)	14.4	104b
Ga(SeMes*)$_3$	2.324(1)	93.9(2)	10.3	105a
{(Me$_3$Si)$_2$CH}$_2$GaTeSi(SiMe$_3$)$_3$	2.535(1)	117.4(1)	0	105b
Ga{TeSi(SiMe$_3$)$_3$}$_3$	2.496(6)	111.5(10)		105c
S[Ga{CH(SiMe$_3$)$_2$}$_2$]$_2$	2.2197(7)	117.04(5)^a		104d
Se[Ga{CH(SiMe$_3$)$_2$}$_2$]$_2$	2.3439(5)	113.45(3)^a		104d
Te[Ga{CH(SiMe$_3$)$_2$}$_2$]$_2$	2.552(4)	109.82(2)^a		105d
Indium				
In(SMes*)$_3$	2.398(3)	98(1)	22.0	106a
In(SeMes*)$_3$	2.506(1)	93.7(1)	11.5	106a
In[SeC(SiMe$_3$)$_3$]$_3$	2.527(12)	117.3		105c
Mes*In(SePh)$_2$	2.538(12)	100.1(20)		106b
S[In{CH(SiMe$_3$)$_2$}$_2$]$_2$	2.40(3)	114.6(20)^a		106c
Se[In{CH(SiMe$_3$)$_2$}$_2$]$_2$	2.5187(5)	109.96(3)^a		106c
Te[In{CH(SiMe$_3$)$_2$}$_2$]$_2$	2.7140(7)	105.4(2)^a		106c

^{a} M−E−M angle (M = Al, Ga, In; E = S, Se, or Te).

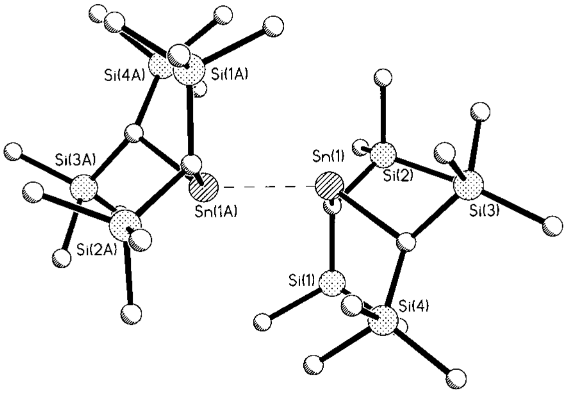


Figure 11. Structure of {Me$_3$Si)$_2$CH}$_2$SnSn{CH(SiMe$_3$)$_2$}$_2$[110b] illustrating the large out of plane angle at the tins. Further details are in Table 11.

tives with the moieties (η^5-C$_5$H$_5$)$_2$Ti, GeMes$_2$, and SnPh$_2$ are known.[108]

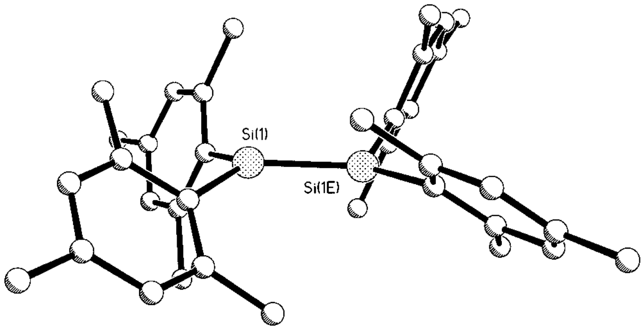


Figure 12. Structure of Mes$_2$SiSiMes$_2$ illustrating the very slight pyramidalization of the silicon geometries.[112a] Further details are in Table 10.

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

The compounds $R_2E{=}ER_2$ (E = Si, Ge, Sn, or Pb), which are analogous to the archetypical doubly bonded alkenes, have played a central role in the study of multiple bonding in the heavier main group elements. The first well-characterized example was the compound {(Me$_3$Si)$_2$CH}$_2$SnSn{CH(SiMe$_3$)$_2$}$_2$, which was reported in 1973.[109] Its structure[110] (Figure 11) showed that it had the, now familiar, trans-bent geometry (out of plane angle[110b] = 41°) and a Sn−Sn distance[110b] of 2.768(1) Å, which is slightly shorter than that of a single bond. However, it was found to dissociate to stannanediyl (SnR$_2$) monomers in hydrocarbon solution.[109,110] As a result of this and its trans-bent geometry, the SnSn bonding was deemed to consist of two weak semipolar, donor−acceptor bonds[110c] as described earlier.

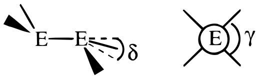
Another major breakthrough came with the synthesis of the stable disilene Mes$_2$SiSiMes$_2$ in 1981.[111] Three, separate X-ray crystal structures[112] of this compound have shown that the Si−Si distance is ca. 0.2 Å shorter than a single bond and that the out of plane angle (0−18°) (Figure 12) is much less than that in the tin species. It showed no tendency to dissociate in solution, and subsequent studies have shown that most stable disilenes have very similar structural characteristics. In effect disilenes bear a close structural (and some chemical) resemblance to alkenes, whereas the {(Me$_3$Si)$_2$HC}$_2$SnSn{CH(SiMe$_3$)$_2$}$_2$ compound is at a point of incipient dissociation and, for the most part, its chemistry is that of a monomeric stannanediyl.[113]

The physical and chemical properties of the disilenes[114] and the tin dialkyl provide pointers for bonding trends within the heavier group 14 alkene analogues. This area is under very active current inves-

Table 10. Selected Structural Data for Disilenes and Some Related Si=Si Double-Bonded Species

compound	Si−Si (Å)	δ (deg)[a]	γ (deg)[a]	ref
(*E*)-[Si(1-Ad)Mes]$_2$	2.138(2)	2.8	0	115a
[Si(Dep)$_2$]$_2$	2.140(3)	10	0	115b
[Si(Mes)$_2$]$_2$	2.1433(2)	12	3	112b
[Si(Mes)$_2$]$_2$	2.146	0	13	112c
[Si(Mes)$_2$]$_2$	2.160(1)	18	6.5	112a
[Si(Trip)$_2$]$_2$	2.144	3	0	115c
(*E*)-[Si(t-Bu)Mes]$_2$	2.143(1)	0	0	112a
(*E*)-[Si(SiMe$_3$)Trip]$_2$	2.152(3)	0	0	115d
(*E*)-[Si(t-Bu)Trip]$_2$	2.157(2)	0	0	115d
(*Z*)-[Si(Mes)(Tbt)]$_2$	2.195(4)	ca. 8.7	14	115e
[Si{Si(t-Bu)Me$_2$}$_2$]$_2$	2.202(1)	0	8.9	115f
[Si{Si(i-Pr)$_2$Me}$_2$]$_2$	2.228(2)	5.4	0	115f
(*E*)-[Si(Mes)(Tbt)]$_2$	2.228(3)	ca. 12	8.7	115e,g
[Si{Si(i-Pr)$_3$}$_2$]$_2$	2.251(1)	10.2	0	115f
R$_2$SiSiRSiR (R = SiMe(t-Bu)$_2$)	2.138(2)		30.9(2)	116a
RSiSi(R)SiR$_2$SiR$_2$ (R = {SiMe$_2$(t-Bu)})	2.174(4)	13.3	12.3	116b
(Trip)$_2$SiSi(Trip)Si(Trip)Si(Trip)$_2$	2.175(2)			116c
RSiSi(R)Si(I)RSiR (R = Si(t-Bu)$_3$)	2.257(2)		30.8	116d
R$_2$Si(SiR)(SiR)SiR$_2$E (R = Trip)				
E = S	2.170(1)			116e
E = Se	2.181(1)			116e
E = Te	2.198(2)			116e

[a] The angle δ and γ are represented by



tigation, and to date approximately 30 stable disilenes[114i] have been isolated and characterized. The structures of 12 of these have been determined,[112,115] as well as the structures of two tetrasilacyclobutenes, a tetrasilabuta-1,3-diene, a trisilacyclopropene and three 5-membered Si$_4$E (E = S, Se, or Te) ring compounds which contain Si−Si double bonds[116] (Table 10). The silicon analogues of alkenes have double bond distances in the range 2.138(2)−2.251(1) Å as well as planar, or almost planar, core geometries. The Si−Si π-bond strength ranges from 25.4 to 30.3 kcal mol^{-1},[117] which is consistent with theoretical data.[41a,b,118] Long silicon−silicon double-bonded distances in excess of 2.20 Å are observed when extremely hindering ligands are used, and one of these undergoes dissociation (ΔH_{diss} = ca. 26 kcal mol^{-1}) to monomers at elevated temperatures.[115g] However, solid state ^{29}Si NMR studies of a range of strongly bonded disilenes lend experimental support to the classical double-bond model for the Si−Si bond.[119]

The structures of 10 R$_2$GeGeR$_2$ compounds have been published[117b,120,121] (Table 11). The Ge−Ge distances and out of plane angles range from 2.213(2) to 2.460(1) Å and from 0° to 42°. The four compounds with the longest Ge−Ge bonds are dissociated to monomers in solution.[120d−g] The Ge−Ge π bonds may be similar in strength to those in their silicon analogues, although[122a] a variable temperature electronic spectrum of the very crowded species [Ge(Mes)-Tbt]$_2$ shows that it exists in a monomer−dimer equilibrium in hexane with a ΔH of 14.7 kcal mol^{-1} for dissociation (cf. ΔH_{diss} = ca. 26 kcal mol^{-1} for the corresponding silicon derivative).[122b] In addition, there are other Ge−Ge multiply bonded species, e.g., the cylic trigermanium compound {(t-Bu)$_3$Si}$_2$Ge-{GeSi(t-Bu)$_3$}$_2$,[120h] the cyclic cation, [GeSi(t-Bu)$_3$]$^+$,[120i] the cyclic radical {GeC$_6$H$_3$-2,6-Mes$_2$}$_3^{\bullet}$,[120j] and allyl anion analogue [GeC$_6$H$_3$-2,6-Mes$_2$]$_3^-$ [120j] all of which contain multiple Ge−Ge bonds including a short Ge−Ge double bond of 2.239(4) Å for the former species.[120h]

Five tin[109,110,123] (featuring three-coordinate metals) and six lead[124] analogues have been structurally characterized (Table 11). As far as is known, all these examples are dissociated to monomers in hydrocarbon solution. Furthermore, they all possess trans-bent structures with substantial out of plane angles and E−E distances that are approximately equal to or greater than that of a single bond. However, the remarkable tetrasilatristannaallene Sn$_3${Si(t-Bu)$_3$}$_4$ and the tristannacyclopropene analogue {t-Bu$_3$Si}$_2$Sn-{SnSi(t-Bu)$_3$}$_2$ contain Sn−Sn multiply bonded and double-bonded Sn−Sn distances as short as ca. 2.68 and 2.59 Å, respectively.[123g] The latter value in particular shows that with suitable steric and electronic ligand properties, strong π bonding is possible for tin.

The structures and solution properties of these homonuclear heavier group 14 ethylene analogues thus present a pattern of decreasing strength of the element−element bond as the group is descended, which is manifested in less shortening and an increasing tendency toward trans-bent structures in the solid state, as well as monomeric structures in solution. An increasing amount of effort is now being devoted to investigating the factors that control the EE bond strength. In a manner that is analogous to the factors which affect inversion barriers in mononuclear compounds,[33,34] molecular orbital theory predicts[29b,32] that the ability of the two :ER$_2$ fragments to π bond to each other should be enhanced by more electropositive and π-acceptor substituents whereas more electronegative and π-donating substituents will decrease this tendency. Such effects can be investigated experimentally, and the currently available data support these predictions. For ex-

Table 11. Selected Structural Data on Symmetric Heavier Main Group 14 Element Alkene Congeners

compound	E−E (Å)	δ (deg)[a]	γ (deg)[a]	ref
Germanium				
$[Ge(Dep)_2]_2$	2.213(2)	12	10	120a
$[Ge(Trip)_2]_2$	2.213(1)	12.3	13.7	120k
$[Ge(C_6HMe_3\text{-}2,3,4\text{-}t\text{-}Bu\text{-}6)_2]_2$	2.2521(8)	0	20.4	120b
$[Ge\{SiMe(i\text{-}Pr)_2\}_2]_2$	2.267(1)	0	6.5	120c
$[Ge\{Si(i\text{-}Pr)_3\}_2]_2$	2.298(1)	0	16.4	120c
$[Ge(Mes)(Dipp)]_2$	2.301(1)	36	7	117b
$[Ge\{CH(SiMe_3)_2\}_2]_2$	2.347(2)	32	0	110b,120d
$[Ge(Cl)C_6H_3Mes_2\text{-}2,6]_2$	2.443(2)	39	0	120e
$\{GeN(t\text{-}Bu)(CH_2)_2N(t\text{-}Bu)SiN(t\text{-}Bu)(CH_2)_2N(t\text{-}Bu)\}_2$	2.454(2)	41.3	42.3	120f
$\{GeN(i\text{-}Pr)(CH_2)_2N(i\text{-}Pr)SiN(t\text{-}Bu)(CH_2)_2N(t\text{-}Bu)\}_2$	2.460(1)	47.3	0	120g
Tin				
$[Sn\{CH(SiMe_3)_2\}_2]_2$	2.768(1)	41	0	110b
$[Sn\{Si(SiMe_3)_3\}_2]_2$	2.8247(6)	28.6	63.2	123a
$[Sn\{C_6H_2(CF_3)_3\text{-}2,4,6\}\{Si(SiMe_3)_3\}]_2$	2.833(1)	41.5	0	123b
$[Sn(C_6HMe_3\text{-}2,3,4\text{-}t\text{-}Bu\text{-}6)_2]_2$	2.910(1)	21.1,64.4		123c
$Cl_2SnSn\{C(H)SiMe_3C_9H_5N\}_2$	2.961(1)			123d
$[Sn_2(\lambda^3,\lambda^5)(C_{10}H_6\text{-}1,8\text{-}\{NCH_2(t\text{-}Bu)\}_2)_4]_2$	3.087(2)			123e
$[Sn(C_6H_2(CF_3)_3\text{-}2,4,6\}_2]_2$	3.639(1)	46	0	123f
Lead				
$[Pb\{Si(SiMe_3)_3\}Trip]_2$	2.9899(5)	42.7	0	124a,c
$[PbTrip_2]_2$	3.0515(3)	43.9,51.2		124b
$[PbMes_2]_2\cdot 2MgBr(THF)_4$	3.3549(6)	71	0	124c
$[Pb\{Si(SiMe_3)_3\}(C_6H\text{-}2,3,4\text{-}Me_3\text{-}6\text{-}t\text{-}Bu)]_2$	3.3695(11)	46.5	0	124b
$[Pb\{C_6H_2(CF_3)_3\text{-}2,4,6\}\{Si(SiMe_3)_3]_2$	3.537(1)	40.8	0	123b
$[Pb\{CH(SiMe_3)_2\}_2]_2$	4.129	34.2		124d

[a] The angle δ and γ are represented by

ample, the number of dimeric $R_2E{=}ER_2$ compounds that carry electronegative and π-donor substituents (e.g., amides or halides) is limited to three germanium derivatives[120e,f,g] which are characterized by long (2.44−2.46 Å) Ge−Ge bonds and pyramidal coordination at germanium. These Ge−Ge distances are similar to that of a Ge−Ge single bond 2.45 Å,[97] and the compounds are dissociated in solution.

Predicting the effect of changes in the steric and electronic properties of the ligands on the strength of the E−E bond is not a straightforward matter, however. Ideally, decreasing the size of the ligand to the minimum amount necessary to prevent oligomerization and increasing its electron-releasing character should result in the strengthened E−E bond as well as a flatter coordination geometry at E. However, there may not be the expected correlation between these variables. For example, the compound $\{(i\text{-}Pr)_3Si\}_2GeGe\{Si(i\text{-}Pr)_3\}_2$ has a Ge−Ge distance of 2.298(1) Å[120c] and a 0° out of plane angle, whereas (Dipp)(Mes)GeGe(Mes)(Dipp) has an almost identical GeGe distance of 2.301(1) Å but an out of plane angle of 36°.[117b] The currently known tin and lead derivatives also show the same lack of correlation between the out of plane angle and bond length.

The synthetic methods for disilenes are quite different from those of their heavier congeners which all have stable divalent precursors readily available. Thus, the latter species are usually obtained by the reaction of the lithium salt of the ligand with a germanium, tin, or lead dihalide. For the silicon species, a variety of methods, including the photolysis of linear and cyclic trisilanes and dehalogenation of dihalosilanes and 1,2-dihalodisilanes, have been used.[114] As is true elsewhere in organometallic chemistry, the type of ligand transfer agent or starting materials used may have a very large effect on the success of the synthetic approach. For example, the recently reported $Trip_2PbPbTrip_2$ (Figure 13), which has a Pb−Pb distance similar to that of a single bond, was isolated from the reaction of $PbCl_2$ with TripMgBr at −110 °C, whereas the attempted synthesis with TripLi at −78 °C in the same solvent did not result in the isolation of $Trip_2PbPbTrip_2$, but of $Trip_3PbCl$ and TripH, upon warming to room temperature.[124b] Similarly, $\{(Me_3Si)_2CH\}_2PbPb\{CH(SiMe_3)_2\}_2$ was originally isolated by using $Pb\{N(SiMe_3)_2\}_2$ rather than $PbCl_2$ as the starting material.[125] The latter species has a very long Pb−Pb interaction of

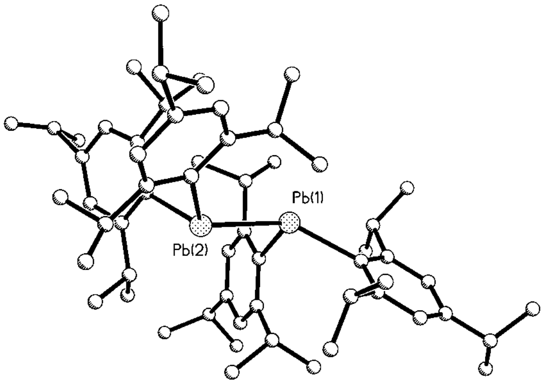
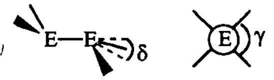


Figure 13. Structure of $Trip_2PbPbTrip_2$.[124b] The Pb−Pb distance, 3.0515(3) Å, is longer than a normal single bond in R_3PbPbR_3 compounds. The large out of plane angles of 43.9° and 51.2° are readily apparent.

Table 12. Selected Structural Data on Unsymmetric Heavier Main Group 14 Alkene Congeners and Related Species

compound	E=C (Å)	δ (deg)[a]	γ (deg)[a]	ref
$(Me_3Si)_2Si{=}C(OSiMe_3)(1\text{-}Ad)$	1.764	0	14.6	129b
$Me_2Si{=}C(SiMe_3)SiMe(t\text{-}Bu)_2$	1.702(5)	0	1.6	130a
$\{(t\text{-}Bu)Me_2Si\}(Me_3Si)Si{=}(2\text{-}Ad)$	1.741(1)	0	4.6	130b
$1,2\text{-}C_6H_4\{(R)N\}_2SiC\{N(R)\}C_6H_4\text{-}1,2$ $(R = CH_2(t\text{-}Bu))$	2.162(5)	77(Si) 28(C)		130c
$Trip_2Si{=}C{=}C(Ph)(SiMe_3)$	1.693(3)			131b
$Mes^*(1\text{-}Ad)Si{=}Fluorenyl$	1.704			131a
$Mes_2Ge{=}Fluorenyl$	1.803(4)	0	6	133a
$\{(Me_3Si)_2N\}_2Ge{=}CB(t\text{-}Bu)C(SiMe_3)_2B(t\text{-}Bu)$	1.827(4)	1.7	36	133b
$Trip_2Ge{=}C{=}C(Ph)(t\text{-}Bu)$	1.783(2)			134a
$\{(Me_3Si)_2HC\}_2SnCB(t\text{-}Bu)\{C(SiMe_3)_2\}B(t\text{-}Bu)$	2.025(4)		31	135a
$(6\text{-}t\text{-}Bu\text{-}2,3,4\text{-}Me_3HC)_2SnCB(t\text{-}Bu)\{C(SiMe_3)_2\}B(t\text{-}Bu)$	2.032(5)		36	135b
$Trip_2SnCN(i\text{-}Pr)(CH_2)_2N(i\text{-}Pr)$	2.379(5)	68.6		135c
$Trip_2PbCN(i\text{-}Pr)(CH_2)_2N(i\text{-}Pr)$	2.540(5)	70		135d

[a] The angle δ and γ are represented by



4.129 Å[124d] and, like the other low-coordinate Pb(II) compounds,[124,126] it is monomeric in solution.

Unsymmetrical species involving a multiple bond between two different group 14 elements have been the subject of considerable theoretical[28,41a,b,127] and experimental attention.[128] They are less extensively investigated than their symmetric counterparts at present. An exception is the important silene class of compounds featuring double bonds between carbon and silicon. The first stable example was synthesized in 1981 by the rearrangement of silyl-substituted acylsilanes.[129] Subsequent synthetic approaches have involved a variety of methods including LiF elimination upon treatment of a fluorosilylalkane bearing an α-hydrogen[129a,130a] with an organolithium reagent or a sila-Peterson-type reaction.[130b] In addition, the first crystal structure of a weak adduct between a stable carbene and silylene (i.e., $1,2\text{-}C_6H_4\{NR\}_2CSi\{NR\}\text{-}C_6H_4\text{-}1,2$; $R = -CH_2(t\text{-}Bu)$) has been reported.[130c] This compound features a long C−Si interaction (2.162(5) Å) with significant $C^+{-}Si^-$ bond polarity and little C=Si double bond character. Although several stable, quasi-stable, or Lewis base complexed silenes have been described,[128] only three stable, uncomplexed silenes have been characterized structurally[114j,128b,129,130] (Table 12). In addition, the structures of two silaallenes, which contain Si−C double bonds, have been published.[131] Like disilenes, the doubly bonded silenes possess planar or almost planar geometries at silicon. The Si−C double bond distances are in the range 1.702−1.764 Å, which is considerably shorter than that of a single Si−C bond (ca. 1.87−1.93 Å).[132] The above experimental Si=C distances may be compared to the calculated values of 1.687−1.694 Å[28,41a,b] in $H_2C{=}SiH_2$ which has a planar structure. The strength of the C=Si π bond has been calculated to be ca. 35 kcal mol^{-1},[41a,b] which is slightly more than one-half the strength of a C=C π bond.

The remaining stable heavier group 14 element compounds with potential double bonds to carbon involve a handful of germanium and tin species and a single lead derivative. At least seven stable germenes are currently known.[121] The structures of two, $Mes_2Ge{=}Fluorenyl$[133a] and $\{(Me_3Si)N\}_2Ge{=}C{-}B(t\text{-}Bu)C(SiMe_3)_2B(t\text{-}Bu)$,[133b] which have Ge=C distances of 1.803(4) and 1.827(4) Å, have been determined (Table 12). The fluorenyl derivative has planar germanium and carbon geometries with a small torsion angle of 6°. The other has pyramidal germanium coordination and a significantly longer Ge=C bond. In addition, the structure of germaallene $Trip_2Ge{=}C{=}C(Ph)(t\text{-}Bu)$ has a short Ge−C double bond of 1.783(2) Å and essentially planar geometry at germanium.[134a] As in the case of the silicon analogues, it is believed that the sp hybridization at the central carbon has contributed to the shortening. The germaallene $Tbt_2Ge{=}C{=}Fluorenyl$ has also been synthesized and spectroscopically characterized, although no structure has been published.[134b] The synthesis and spectroscopic characterization of 1-germa-3-phosphaallene has also been reported.[134c] A comparison of the experimental Ge=C distances with the calculated values of 1.770−1.814 Å for H_2GeCH_2 reveals relatively good agreement with the $Mes_2Ge{=}$Fluorenyl structure. Recent calculations[134d] on the hypothetical 1,4-digermabutadiene $H_2GeCHCHGeH_2$ show that there is stronger conjugation through the central C−C bond than in butadiene.

For the tin derivatives $(t\text{-}Bu)B(Me_3Si)_2C(t\text{-}Bu)\text{-}BCSn\{CH(SiMe_3)_2\}_2$[135a] and $(t\text{-}Bu)B(Me_3Si)_2C(t\text{-}Bu)\text{-}BCSn\{C_6H\text{-}Me_3\text{-}2,3,4\text{-}6\text{-}t\text{-}Bu\}_2$[135b] (Table 12), the Sn−C double bond distances are 2.025(4) and 2.032(5) Å, which represent about 6% shortening with respect to the single bond. Yet they are significantly longer than the distances 1.945 and 1.982 Å calculated for planar H_2SnCH_2.[28,127a] Although the tin coordination is almost planar in both structures, there are quite large torsion angles of 31° and 36° which signify a weakness of the π overlap and probably polar character in the Sn−C bond. The structure of the formally double-bonded carbene−stannylene adduct $(i\text{-}Pr)\text{-}N(CH_2)_2(i\text{-}Pr)NCSnTrip_2$ has pyramidally coordinated tin and a very long Sn−C bond, 2.379(5) Å.[135c] For this reason it is thought to have a zwitterionic structure with considerable polarity in the C−Sn bond. Its recently reported lead analogue, which has a very long Pb−C bond length of 2.540(5) Å, is thought to possess similar bonding.[135d] Both compounds possess very large out of plane angles of ca. 70° at both tin and lead.

Unsymmetrical $R_2E{=}E'R_2$ species with two different heavier group 14 elements are quite rare. The species $Mes_2Si{=}GeMes_2$[136] has been obtained by thermolysis or photolysis of the digermasilirane and characterized by ^{29}Si NMR spectroscopy and trapping reactions. Mixed silylene−stannylene adducts have also been proposed as intermediates in metathesis reactions.[137] The Ge−Sn combination is represented by the species $Mes_2GeSnTrip_2$[138] and $1,8\text{-}(t\text{-}BuH_2CN)\text{-}H_6C_{10}GeSnC_{10}H_8\text{-}1,8\text{-}\{NCH_2(t\text{-}Bu)\}_2$,[123e] which was also characterized spectroscopically and by trapping reactions. It undergoes rearrangement to give a distannagermirane among the products.

The dianionic compounds $[R{-}\ddot{E}{=}\ddot{E}{-}R]^{2-}$ (E = Ge, Sn, Pb) were unknown until recently. Since they are isoelectronic to the corresponding neutral group 15 dipnictenes (vide infra), they are expected to be formally double-bonded and to have a trans-bent structure. Only two examples have been reported to date. These are the germanium and tin derivatives $Na_2(2,6\text{-}Trip_2H_3C_6GeGeC_6H_3\text{-}2,6\text{-}Trip_2)$ (Figure 14) and the tin compound $K_2(2,6\text{-}Trip_2H_3C_6SnSnC_6H_3\text{-}2,6\text{-}Trip_2)$, which have planar C(ipso)EEC(ipso) arrays and EE distances of 2.3943(13) and 2.7763(9) Å, respectively.[36] The angles at germanium and tin are 102.37(8)° and 107.50(14)°. These EE distances are marginally (0.03−0.06 Å) shorter than single bonds. However, the presence of a dianionic charge at the EE moiety probably imposes some lengthening of the E−E bond. This is consistent with the observation of a long Sn−Sn single-bonded distance of ca. 2.90 Å in the dianion $[Ph_2SnSnPh_2]^{2-}$.[139] The germanium and tin compounds are also notable since they represent examples of heavier multiply bonded main group species for which no lighter element (i.e., carbon) analogue has been structurally characterized.

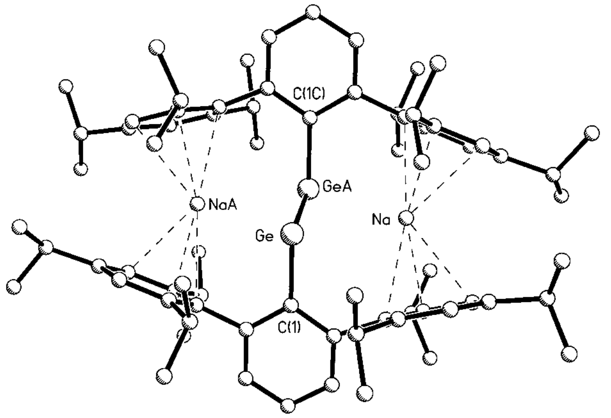


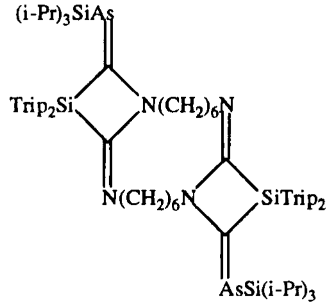
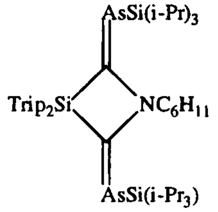
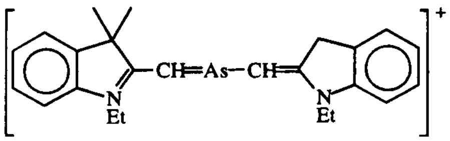
Figure 14. Structure of $Na_2(2,6\text{-}Trip_2H_3C_6GeGeC_6H_3\text{-}2,6\text{-}Trip_2)$[36] which has a Ge−Ge distance of 2.394(1) Å and a Ge−Ge−C angle of 102.37(8)°.

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

These compounds are heavier element analogues of the imines. The first stable derivative to be isolated and characterized was the phosphaalkene $t\text{-}Bu(Me_3SiO)C{=}P{-}R$ which was reported in 1976.[140] In the ensuing period there has been a very large volume of work in the phosphaalkene area. At present approximately 80 structures of phosphaalkenes and related species have been published. The very large number of publications (>300), especially if phosphopolyenes or phosphacumulenes are included, do not permit a detailed account of them in this review. Two books[141a,b] offer very useful overviews of phosphaalkenes and related multiply bonded phosphorus compounds. In addition, a broad overview of phosphorus chemistry (including many multiply bonded species) has been published recently.[141c]

Insofar as the theoretical, spectroscopic, and structural data for phosphaalkenes relate to the theme of this review, it can be noted that the P−C double bond lengths lie in the range 1.62−1.71 Å with 1.67 Å being a typical value. The increased s-character of the phosphorus lone pair (in comparison to the nitrogen lone pair in imines) can be seen in the calculated geometries of $H_2C{=}\ddot{P}{-}H$ and $H_2C{=}\ddot{N}{-}H$ where HPC and HNC angles of 97.4° and 111.4° were obtained.[142] The fundamental differences between nitrogen and phosphorus are also reflected in the valence orbital energies.[143] In the imine $H_2C{=}\ddot{N}{-}H$ the HOMO (−10.62 eV) represents the lone pair orbital on nitrogen and the HOMO-1 is associated with the C−N π orbital at −12.49 eV. In the corresponding phosphaalkene, the HOMO (−10.30 eV) is the P−C π bond and the HOMO-1 is the phosphorus lone pair orbital which lies very close in energy at −10.70 eV. This, combined with the much lower polarity of the P−C pair, ensures that the chemistry of the phosphaalkene bears a considerably closer resemblance to alkenes than it does to imines.[141a,b]

Table 13. Selected Structural Data for Some Arsaalkenes

compound	As=C (Å)	R–As–C (deg)	ref
t-Bu_2Fluorenyl=AsMes*	1.794(11)	105.0(4)	148a
$(Mes_3SiS)_2C{=}As\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}\{Cr(CO)_5\}$	1.800(5)	113.0(2)	148b
	1.816(6)	113.4(2)	148c
$(t\text{-}Bu)(Me_3SiO)C{=}As\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}$	1.821(2)	111.4(1)	148d
	1.827(3)	115.5(1)	148e
	1.831(1)	101.5	148b
$(Et_2N)(F)C{=}AsCF_3$	1.867(9)	94.3(4)	148g
$(Me_2N)_2C{=}As\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}$	1.876(8)	116.2(3)	148h

This is especially true if the lone pair is protected by coordination to a transition metal fragment. Calculations on $H_2C{=}\ddot{P}{-}H$ lead to the value of 43.1 kcal mol^{-1} (cf. 65 kcal mol^{-1} for a C=C double bond[41a]) for the strength of the P–C π bond. This demonstrates that there is quite strong overlap between the phosphorus and carbon p orbitals. This bond strength is near the mean value for C=C (65 kcal mol^{-1}) and P=P (35 kcal mol^{-1}) bonds. The strength of the P=C π bond enables *E* and *Z* isomers to be isolated, and structures of a pair of these have been reported.[144]

Arsaalkenes are much rarer than their phosphorus counterparts. The first neutral, stable example was reported in 1977.[145] They have been synthesized by a variety of methods that include 1,2-elimination of HCl,[146a] condensation reactions,[146b] and 1,3-trimethylsilyl migration.[145] The chemistry of species with arsenic–carbon multiple bonds has been reviewed recently.[147] Approximately two dozen species (including *E* and *Z*) isomers have been isolated,[147] and eight compounds that do not involve doubly bonded arsenic as part of a ring have been structurally characterized[148] (Table 13). In addition, there are a number of cyclic species that incorporate As=C double bonds[149] and zwitterionic species with longer As=C double bonds.[150] The structure of an arsaphosphaallene has also been determined, but owing to disorder problems, no details were given.[151] The compounds in Table 13 display As–C double-bonded distances in the range from 1.794(11) (as illustrated in Figure 15) to 1.876(3) Å (cf. theoretical value of 1.79 Å[152] in H_2CAsH). Thus, these bonds are elongated to varying degrees in comparison with the calculated value of 1.79 Å[152a] (cf. single bond calculated value = 1.96 Å[41a]). In many instances the bond lengthening can be traced to interactions between the As=C double bond and a heteroatom substituent lone pair.

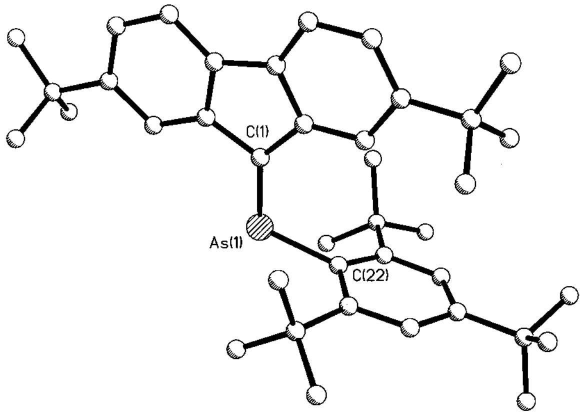


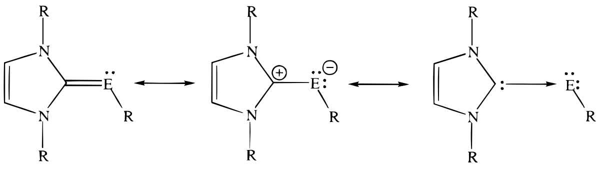
Figure 15. Structure[148a] of t-Bu_2Fluorenyl=AsMes*. The As–C double bond distance is 1.794(11) Å, and the interligand angle at arsenic is 105.0(4)°.

Table 14. Some Important Structural Data for Imino Derivatives (R$_2$E=E′R) of the Heavier Group 14 Elements

compound	E=N (Å)	E−N−R (deg)	ref
Silicon			
t-Bu$_2$Si=N−Si(t-Bu)$_3$	1.568(3)	177.8(2)	158c,d
t-Bu$_2$Si=N−Si(t-Bu)$_2$Ph	1.573(3)	170.1(18)	159
Germanium			
[{(Me$_3$Si)$_2$CH}$_2$Ge=N]$_2$SiMes$_2$	1.681(8)	137.3(5)	162a
η^3-{(μ-t-BuN)$_2$(MeSiN(t-Bu))$_2$Ge=N−SiMe$_3$	1.688(9)	151.2(7)	162b
{Mes(Me$_3$Si)N}$_2$Ge=N-Mes	1.691(3)	139.0(2)	162c
{(Me$_3$Si)$_2$N}N(CH$_2$)$_2$(t-Bu)N(Me)Si(t-Bu)NGe=N−SiMe$_3$	1.701(5)		162d
{Dipp(Me$_3$Si)N}$_2$Ge=N-Dipp	1.703(2)	134.2(2)	162c
{(Me$_3$Si)$_2$CH}$_2$Ge=N−Si(t-Bu)$_2$(N$_3$)	1.704(5)	136.0(4)	162a,e
Tin			
{(Me$_3$Si)$_2$HC}$_2$Sn=N−Si(t-Bu)$_2$(N$_3$)	1.905(5)	130.6(3)	162d
{(Me$_3$Si)$_2$N}$_2$Sn=N-Dipp	1.921(2)	120.6(2)	164

The calculations[152] on arsaalkenes give a very similar picture of the orbital energy levels to that of the phosphaalkenes. The HOMO represents the π molecular orbital at an energy of −9.26 eV (cf. −9.91 eV for P). The lone pair orbital appears 1.21 eV lower in energy at −10.47 eV (cf. −10.71 eV for P). The energy of the π bond, as measured by the rotational barrier, has been calculated to be 38.2 kcal mol^{-1} (cf. 44.2 kcal mol^{-1} for the phosphorus analogue and 29.5 and 26.4 kcal mol^{-1} for the stiba,[152] and bismaalkenes[153]).

An interesting recent development[154] has been the investigation of a number of substituted 1,3-imidazol-2-ylidene complexes of :ER (E = P or As). Although their formulas correspond to phosphaalkenes or arsaalkenes, their bonding differs considerably. For example other canonical forms of the pnictaalkene (a) may be written as structures b and c. Spectroscopic and structural data show essentially free rotation around the E−C bond, and E−C distances (near 1.76 Å for P and 1.90 Å for As)[154b] between single and double bonds indicate that the polarized form (b) may be the most representative structure while the carbene−phosphinidene/arsinidene donor−acceptor bonding may (c) be appropriate for the fluorenylidine derivatives.



(a) (b) (c)

Three compounds displaying Sb−C double bonds have been structurally characterized.[155] The 2,3-distibabutadiene compound [Sb=C(OSiMe$_3$)Mes*]$_2$,[155a] which was synthesized by treatment of Mes*C(O)Cl with LiSb(SiMe$_3$)$_2$, has a Sb−C distance of 2.056(10) Å (somewhat longer than the calculated 2.01 Å[152] in H$_2$C=SbH) and a narrow angle of 94.7(3)° at the antimony. The Sb−Sb distance 2.774(1) Å (cf. Sb−Sb = 2.837(1) Å in Ph$_2$SbSbPh$_2$[156]) is short, and this, coupled to the trans-planar CSbSbC array, may suggest some conjugation across the Sb−Sb bond. The less crowded 2,3-distibabutadiene species [Sb=C(OSiMe$_3$)Mes]$_2$,[155b] which has a Sb=C double-bonded distance of 2.066(5) Å with a Sb−Sb−C angle of 92.99(13)°, was isolated in a similar manner. In addition the stibaalkene, Mes*(O)C−Sb=C(OH)-Mes*[155b] has a Sb=C double bond length of 2.078(3) Å and an angle of 91.31(12)° at antimony and was obtained by treatment of the lithium enolate (Dme)$_n$-LiOC(Mes*)SbMes*O with HCl. The enolate[155c] was produced during the reaction of LiSb(SiMe$_3$)$_2$ with Mes*COCl. The stibaalkene 2-Py(Me$_3$Si)$_2$−Sb=C-(SiMe$_3$)$_2$Py has also been synthesized by Me$_3$SiCl elimination from [2-Py(Me$_3$Si)C]SbCl. It exists as a red oil which has not been structurally characterized.[155d] At present there are no stable examples of bismaalkenes.

Table 15. Selected Structural Data for Compounds with Double Bond between a Heavier Group 14 Element (E) and a Phosphorus or Arsenic (E′)

compound	E=E′ (Å)	E−E′−X (deg)	ref
Trip(t-Bu)Si=PSi(Trip)(t-Bu)F	2.053(2)	104.60(9)	169c
Trip(t-Bu)Si=PSi(i-Pr)$_3$	2.062(1)	112.79(2)	169b
{(Ph$_2$P)Mes*P}(t-Bu)Si=PMes*	2.094(3)	104.2(2)	169a
Trip(t-Bu)Si=AsSi(i-Pr)$_3$	2.164(1)	110.92(4)	169b
Mes$_2$Ge=PMes*	2.138(3)	112.9(4)	170a
Mes(t-Bu)Ge=PMes*	2.144(3)	110.9(5)	170b

Several stable compounds featuring multiple bonds between heavier group 14 elements and the pnictogens are now well characterized (Tables 14 and 15). For nitrogen derivatives,[114j,128b,157] the first reported stable example was the silaimine t-Bu$_2$Si=N−Si(t-Bu)$_3$[158] which featured a Si−N double bond length of 1.568(3) Å.[158c,d] The coordination geometry at nitrogen is almost linear 177.8(2)° (Figure 16). Slightly longer Si=N distances and narrower N=Si−N angles are seen in the adducts (THF)Me$_2$Si=NSi(t-Bu)$_3$ (1.5889(9) Å, 161.5(5)°) and (Ph$_2$CO)(t-Bu)$_2$Si=N−Si-(t-Bu)$_3$ (1.601(2) Å, 169.3(2)°)[158d] which have THF or Ph$_2$CO complexed to the doubly bonded silicon. Longer Si−N distances in the range ca. 1.606−1.619 Å are seen in lithium halide adducts such as (THF)$_3$LiF·(i-Pr)$_2$Si=N-Mes*,[158e,f] (THF)$_3$LiF·(t-Bu)-MeSi=NMes*,[158g] and (THF)$_3$LiF·(t-Bu)$_2$Si=NSi(t-Bu)$_2$Ph.[158e,f] Considerably longer Si−N bonds (ca. 1.71 Å) are seen in aluminum halide complexes t-Bu$_2$-SiNC(H)(t-Bu)$_2$·AlCl$_3$[80c] and t-Bu$_2$SiN(t-Bu)·AlCl$_3$[158h] which have zwitterionic structures with short Si−Cl contacts. The recently reported t-Bu$_2$Si=N−Si(t-Bu)$_2$Ph displays very similar structural parameters, Si=N = 1.573(3) Å, Si−N−Si = 170.1(18)°,[159] to those of the original reports,[158c,d] and all these are close to

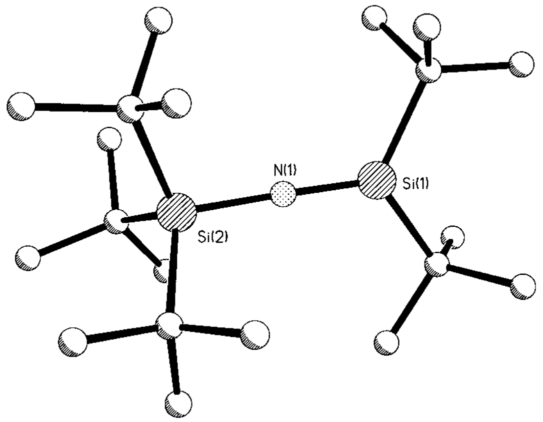


Figure 16. Structure[158c,d] of t-$Bu_2Si{=}N{-}Si(t\text{-}Bu)_3$ showing the almost linear nitrogen coordination as a result of the electronic effects of the silyl substituent at nitrogen.

the calculated values[41,160] in the hydrogen derivatives. The very wide angle at nitrogen is due to electronic rather than steric effects, since the relatively electropositive silyl substituents ensure a very low barrier to cis/trans or syn/anti isomerization[160,41a,b] (i.e., linear inversion). In silaimines such as $H_2Si{=}NH$ (Si−N−H = 125.2°), this barrier is 5.6 kcal mol^{-1} but the π bond strength, as measured by the rotation barrier, is 37.9 kcal mol^{-1}.[41a,160b] Calculations[160b] on silaimine with a carbon substituent at nitrogen have a smaller valence angle at nitrogen and a longer Si−N double bond. However, these parameters have not been confirmed experimentally since no structures of such compounds have been determined.

Stable germaimines and stannaimines (Table 14) are obtained by the reaction of azides with a Ge(II) or Sn(II) precursor.[121] Bulky groups are generally required for stability, although there are exceptions, for example, H_2GeNCF_3,[161] which was syntheized by the reaction of GeH_4 with H_2NCF_3. Five crystal structures of germaimines,[162] including a Lewis base complexed species,[162b] have been reported. They feature planar geometries at germanium and bent geometries at the nitrogen and Ge−N distances in the range 1.681(8)−1.704(5) Å in good agreement with the calculated value.[163] Stannaimines have also been synthesized by the reaction of silyl azides with a Sn(II) precursor. The structure of $\{(Me_3Si)_2N\}_2Sn{=}NDipp$,[164] for example, shows a Sn−N double-bonded distance of 1.921(2) Å, a planar geometry at tin, and an interligand angle at nitrogen of 120.6(2)°. The Sn−N distance in $\{(Me_3Si)_2CH\}_2Sn{=}N\{(Si(t\text{-}Bu)_2(N_3)\}$ has a shorter value of 1.905(3) Å.[162d]

The isolation and characterization of several stable examples of $R_2E{=}E'R$ compounds in which both the E and E′ elements are heavier group members have been reported[166] (Table 15). The first quasi-stable phosphasilene (or silylidenephosphane) was reported in 1984 and characterized spectroscopically.[166] Theoretical data[167] for H_2SiPH predicted a Si=P bond length of 2.044 Å and a Si−P−H angle of 93°. More recent calculations[168] on Si=P and Si=As doubly bonded species with silyl substituents at the pnictogen predicted distances of 2.053 and 2.161 Å and wider Si−E−Si (E = Si or As) angles near 100°. This relatively narrow angle (cf. almost linear geometry in the silaamines) reflects the much larger barrier to linear inversion as a result of the increased s character of the phosphorus or arsenic lone pair. The Si−P rotation barrier in H_2SiPH is 34 kcal mol^{-1}, in agreement with previous results,[35,41b,167] and the value for H_2SiAsH has been calculated to be 30 kcal mol^{-1}.[168] The first structurally characterized example was the compound $\{Ph_2P(Mes^*)P\}(t\text{-}Bu)SiPMes^*$ which featured a Si=P distance of 2.094(3) Å and a slightly pyramidalized silicon geometry which was thought to be a result of second order Jahn−Teller mixing of Si−P σ^* and π orbitals.[168,169a] The structure of $Trip(t\text{-}Bu)SiPSi(i\text{-}Pr)_3$ (Figure 17), however, displays a slightly shorter Si=P double bond distance of 2.062(1) Å, and the silicon has trigonal planar geometry.[169b] Isomerization of such species has not been observed experimentally. A recent report has disclosed the syntheses and structure of Trip(t-Bu)-Si=P−Si(Trip)(t-Bu)F which undergoes a 1,3-sigmatropic migration of the fluorine.[169c] The Si−P double bond distance is 2.053(2) Å. A stable arsasilene $Trip(t\text{-}Bu)SiAsSi(i\text{-}Pr)_3$ has also been structurally characterized.[169b] It has a very similar structure to the phosphorus derivative already discussed. It features a Si−As double bond 2.164(1) Å in length and a planar coordination geometry at silicon. Phosphagermenes, which predate the phosphasilenes, were the first doubly bonded species involving a heavier element from both group 14 and group 15. They display planar geometry at germanium and bent geometry at phosphorus.[121] The Ge−P double bond distances in the compounds $Mes_2GePMes^*$[170a] and $Mes(t\text{-}Bu)GePMes^*$[170b] are 2.138(3) and 2.144(3) Å, which represent a shortening of ca. 8% with respect to a single bond. The bond angles at phosphorus are 112.9(4), and 110.9(5)°, respectively. No other heavier main group compounds of this class have been structurally characterized.

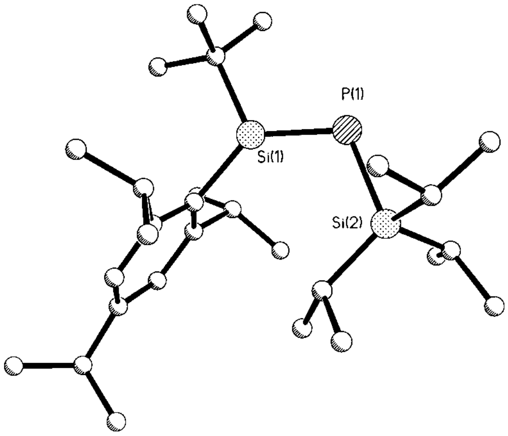


Figure 17. Structure[169b] of the silaphosphene (t-Bu)(Trip)-$Si{=}PSi(i\text{-}Pr)_3$ (Si = P = 2.062(1) Å) illustrating that the Si−P−Si angle (112.79(2)°) is much narrower than the almost linear angle in the related silicon−nitrogen species.

I. Compounds of Formula $[R_2E{=}E'R_2]^+$ (E = Group 14; E′ = Group 15 Element)

The simplest compounds of this class are the well-known iminium ions of the general formula $[R_2CNR_2]^+$ which normally possess planar geometries and strong C−N π bonding. These species will not be discussed further. However, the heavier pnictogen analogues, which have attracted increasing attention, are closely related to the $R_2B-\ddot{E}'R_2$ (E = pnictogen) species discussed earlier in section IV.E owing to the isoelectronic relationship between $-BR_2$ and $[CR_2]^+$. These compounds have been comprehensively reviewed recently,[171] and only a brief outline can be given here. The simplest heavier element derivative is the methylenephosphonium ion $[H_2C{=}PH_2]^+$, and calculations on this ion as well as various methyl- or silyl-substituted congeners indicate a planar geometry at both phosphorus and carbon with P=C distances and rotation barriers in the ranges 1.62−1.64 Å and 31−48 kcal mol^{-1}, indicating strong P−C π bonding.[172a−h] However, a frequency analysis[172f] of $[Me_2C{=}PMe_2]^+$ indicated a low-energy vibrational mode involving pyramidalization at phosphorus, indicating that the P=C bond is a “soft double bond”.[171] In other words, the tendency toward pyramidalization and lone pair character at phosphorus is very similar to the behavior of the neutral boron−phosphorus analogue[95] and is a consequence of the reduced tendency of the phosphorus s and p orbitals to hybridize. The structures of a number of methylenephosphonium ions have been determined.[171,172g−k] These were usually synthesized by the treatment of ylid $R_2C{=}P(t\text{-}Bu)_2Cl$ with $AlCl_3$ in CH_2Cl_2. They include $[Ph_2C{=}P(t\text{-}Bu)_2]^+$ [172i] (P=C = 1.683(11) Å), $[Ph(2\text{-}MeH_4C_6)C{=}P(t\text{-}Bu)_2]^+$ (P=C = 1.680(8) Å),[172g] and $[(Me_3Si)(H)C{=}P(t\text{-}Bu)_2]^+$ (P=C = 1.69(4) Å)[172j] which feature relatively low (20°, 22°, and 11°) torsion angles between the phosphorus and carbon coordination planes. Rotational barriers of >20 kcal mol^{-1} were estimated for the P=C double bond.[172g] A much shorter P=C distance of 1.620(3) Å was measured for $[(Me_3Si)_2C{=}P\{N(i\text{-}Pr)_2\}_2]^+$.[171,172k] However, the shortening is due to Coulombic interactions rather than a strengthening of the double bond since there is a torsion angle of 60° between the carbon and phosphorus coordination planes.

Recent calculations[172h] have shown that the heavier pnictogens arsenic and antimony are also capable of stabilizing the carbenium ion, although in these cases it is the increased inversion barrier at these elements which reduces their capability of doing so rather than any inherent weakness in the carbon−pnictogen π bond.

J. Compounds of Formula $R_2E{=}E'$ (E = Group 14; E′ = Group 16 Element)

The prototypical compounds of this class are the aldehydes and ketones. Sulfur-, selenium-, and tellurium-substituted analogues of the aldehydes[173a] and ketones[173b] become progressively less stable and rarer as the group is descended owing to a tendency to associate. The first stable thio-[173c] and selenoaldehydes,[173d] without an electronically stabilizing substituent, were obtained using the Mes* group. A telluroketone 1,2-$(Me_2C)_2H_4C_6Te$, which is stable enough to be observed spectroscopically in solution, has been reported recently.[173e] The use of the very bulkyl Tbt substituent has also resulted in the synthesis of the thio-[174a,b] and selenoaldehydes[174c] TbtC(E)H (E = S or Se). The selenoaldehyde is stable in dilute hydrocarbon solution but dimerizes upon concentration.[174c] However, it is stable when η^1-complexed to $W(CO)_5$ via selenium.[175] The C−Se distance in this species, $Tbt(H)C(Se)W(CO)_5$, is 1.782(14) Å. The difficulty in preparing the heavy aldehydes and ketones probably does not arise from the weakness of the CE π bond. In fact π bonds between carbon (and to a certain extent silicon and germanium) and the heavier chalcogens are among the strongest π bonds between heavier elements.[176a] It seems probable that the lack of a steric hindrance at the chalcogen combined with the three-coordination at carbon renders these compounds particularly susceptible to further reaction.

Table 16. Important Structural Data for Heavier Main Group 14 (E) Chalcogen (E′) Multiple-Bonded Compounds

compound	E=E′ (Å)	ref
Silicon		
Tbt(Trip)SiS	1.948(4)	177
Np(η^2-$C_{10}H_6NMe_2$)SiS	2.013(3)	178
Germanium		
Tbt(Trip)GeS	2.049(3)	185a,d
η^3-$\{(\mu\text{-}t\text{-}BuN)_2(MeSiN(t\text{-}Bu))_2\}GeS$	2.063(3)	181
$\{(Me_3Si)_2N\}N(CH_2)_2(t\text{-}Bu)N(Me)Si(t\text{-}Bu)NGeS$	2.090(2)	162d
[η^4-Me_8taa]GeS	2.110(2)	182
Tbt$\{(Me_3Si)_2HC\}$GeSe	2.173(3)	185d
Tbt(Trip)GeSe	2.180(2)	185b,d
[η^2-CyNC(t-Bu)NCy]$_2$[η^1-CyNC(t-Bu)NCy]GeSe	2.196(4)	183a
[η^2-CyNC(t-Bu)NCy]$\{(Me_3Si)_2N\}$GeSe	2.2212(3)	183a
[η^4-Me_8taa]GeSe	2.247(1)	182
(η^2-$\{2\text{-}(Me_3Si)_2CH\}C_5H_4N)_2GeSe$	2.2472(7)	184
Tbt(Dipp)GeTe	2.384(2)	185c
Tbt(Trip)GeTe	2.398(1)	185c,d
$\{\eta^4$-Me_8taa$\}$GeTe	2.466(1)	182
(η^2-$\{2\text{-}(Me_3Si)_2CH\}C_5H_4N)_2GeTe$	2.4795(5)	184
Tin		
[η^4-Me_8taa]SnS	2.274(3)	186
[η^2-CyNC(t-Bu)NCy]$_2$SnS	2.280(5)	183b
Tbp{Ditp}SnSe	2.375(3)	188a
[η^4-Me_8taa]$_2$SnSe	2.394(1)	186
η^2-[$(C_9H_6N)(Me_3Si)CH$]SnSe	2.398(1)	187
η^2-[$(C_9H_6N)(Me_3Si)CH$]SnTe	2.618(1)	187

The chemistry of silicon and group 14 element−chalcogen multiply bonded species has been reviewed recently.[176b] For the heavier group 14 elements (Table 16), silicon chalcogenide derivatives, the silanones (monomeric silicones), have not been isolated as stable species. The difficulty in isolating stable examples of such compounds probably arises from the polarity of the group 14 oxygen bond (as in $R_2E{=}O \leftrightarrow R_2E^+{-}O^-$) which renders high reactivity to the group 14 element center. However, the corresponding sulfur analogue, a silanethione with three-coordinate silicon, can be stabilized by the use of bulky substituents.[177] The compound (Tbt)TripSi=S (Figure 18) has a short Si−S bond length of 1.950(4) Å (cf. ca. 2.18 Å for the Si−S single bond in $(Tbt(Mes)SiS)_2$[177c]) with planar geometry at silicon. The 1.950(4) Å Si−S double bond length is very close to the ca. 1.93 Å distance reported for the gas-phase molecule SiS.[18,177d] Lewis base stabilized silanethiones were isolated in 1989[178] with use of a chelating aryl ligand as in the species (Naphthyl)(10-Me_2N-naphthyl)Si=S, which has a somewhat longer Si−S distance of 2.013(3) Å. The related silaneselenone species Ph(10-Me_2N-

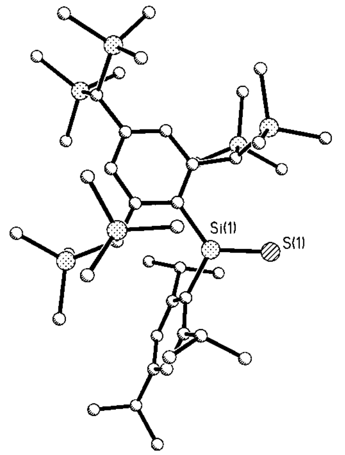


Figure 18. Structure of the silanethione Tbp(Trip)Si=S[177c] which has a short Si−S distance of 1.950(4) Å.

naphthyl)Si=Se was also synthesized.[178] No stable silanetellones have been isolated.

More germanium compounds with multiple bonds to chalcogens are known than for any other heavier group 14 element. The germanone Tbt(Trip)GeO,[179] which is stable in solution for short periods, has been formed by treatment of the diarylgermylene with $(PhCH_2)_3NO$. The germanone Mes*$_2$GeO[180a] and its sulfur congener[180b] are unstable in solution and rearrange to give a species in which germanium has formed a bond to a carbon from an *ortho*-t-Bu group and hydrogen is added to oxygen or sulfur. They were characterized spectroscopically and chemically.[180] The first structurally characterized germanethione was the base-stabilized compound η^3-{μ-t-BuN)$_2$-(MeSiN(t-Bu))$_2$}GeS which had a Ge−S distance of 2.063(3) Å.[181] It was synthesized by the direct reaction of the germanium amide with elemental sulfur. Other base-stabilized terminal chalcogenides have been isolated and characterized. These include derivatives of the tetradentate ligand Me_8taa^{2-}, which has allowed the synthesis of the first completely characterized series of heavier element chalcogenide species (η^4-Me_8taa)GeE (E = S, Se or Te).[182] The high (>3) coordination number of germanium in these complexes may compromise the strength of the π-bond to some extent. However, they have short Ge−E distances of 2.110(2) Å (E = S), 2.247(1) Å (E = Se), and 2.466(1) Å (E = Te). The use of bidentate amidinate ligands CyNC(t-Bu)NCy$^-$ [183] or chelating ligands such as η^2-{2-$(Me_3Si)_2$CH}-$C_5H_4N_2^-$ [184] also stabilize germaselenones and tellones featuring four- or five-coordinate germaniums. Employment of the Tbt group in combination with Trip or the related Dipp ligand also stabilize a complete series of heavier element chalcogenides featuring three-coordinate germanium.[185] The germanium double-bonded distances to sulfur, selenium, and tellurium are 2.049(3), 2.180(2), and 2.398(1) Å (cf. single bond distances of GeS, GeSe, and GeTe of 2.255, 2.384, and 2.595 Å). These distances are ca. 0.06−0.07 Å shorter than those in the η^4-Me_8taa complexes, and are in good agreement with calculations[177c] on H_2GeS (2.042 Å) and H_2GeSe (2.174 Å). At present there is no homologous series of tin compounds with multiple bonds to heavier chalcogenides. In addition, no stable stannone has been synthesized. The compounds (η^4-Me_8taa)SnS[184] and (η^2-CyNC(t-Bu)NCy)$_2$SnS[183] have Sn−S double bond lengths of 2.274(3) and 2.280(5) Å (cf. Sn−S single bond = 2.522 Å). Structurally characterized stable stannaselenones are represented by the compounds (η^4-Me_8taa)SnSe (Sn−Se = 2.394(1) Å)[186] and η^2-[$(C_9H_6N)(Me_3Si)$CH]SnSe (Sn−Se = 2.398(1) Å)[187] and the recently reported Tbp(Ditp)SnSe which featured a three-coordinate tin and a Sn−Se distance of 2.375(3) Å.[188] The sole example of a stable Sn−Te double-bonded species is η^2-[$(C_9H_6N)(Me_3Si)$CH]SnTe (Sn−Te = 2.618(1) Å).[189] At present there are no compounds with stable multiple bonds between lead and a chalcogen. Calculations[189] have shown that the oxo compounds have a tendency to rearrange to single-bonded species. However, compounds such as Tbt(R)Pb=S (R = Tbt, Trip) can be obtained in solution and trapped by reaction with unsaturated molecules.[190]

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

Like the heavier group 14 alkene analogues, the main group dipnictenes have played a central role in the development of the chemistry of multiply bonded heavier main group element compounds. The lightest derivatives are the ubiquitous diimines which are not considered further here. The first stable iminophosphane (t-Bu)N=P−N($SiMe_3$)(t-Bu) was synthesized in 1973[191] by a 1,2-elimination from a β-functionalized iminophosphane FP{N(t-Bu)-$SiMe_3$}$_2$. This route remains the most important synthetic approach to these compounds.[192] Their structure and bonding have also been the subject of considerable research.[192] The crystal structures of almost 60 acylic iminophosphines have been reported. These usually have a trans structure with small or zero torsion angles between the nitrogen and phosphorus coordination planes and a P−N double bond distance in the range 1.46−1.63 Å with an average value near 1.56 Å. The angle at phosphorus is typically (but not always) narrower than the angle at nitrogen.[192]

Ab initio calculations[193a] on the hypothetical H−P=N−H species show that the trans isomer is slightly (ca. 1.5 kcal mol^{-1})[193b] more stable than the cis isomer. The π-bond energy, as defined by the P−N rotational barrier, is in the range 40−50 kcal mol^{-1}. However, cis−trans isomerization can take place via a ‘linear inversion’ of the nitrogen geometry which has a much lower barrier near 15 kcal mol^{-1}.[193a] The corresponding inversion barrier at phosphorus is considerably higher, and it was calculated that there is an overall barrier of 115 kcal mol^{-1} to complete linearization of the molecule.[193a] The σ and π donor−acceptor properties of the phosphorus and nitrogen substituents have large effects on the P−N bond strength.[194] Thus, σ-acceptor (more EN) substituents at phosphorus and σ-donor (more electropositive) substituents at N strengthen the P−N double bond and vice versa. The effects of π ligands are more complex, and the presence of a π donor (e.g., $-NR_2$) at phosphorus strengthens σ bonding but weakens

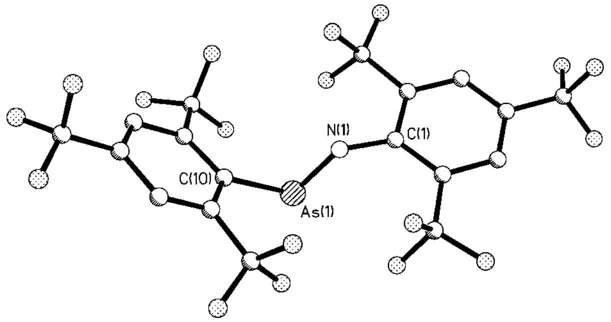


Figure 19. Structure of the *trans*-arsaimine 2,4,6-$(CF)_3H_2C_6NAsC_6H_2$-2,4,6-$(CF_3)_3$.[199] The As=N distance is 1.707(2) Å, and the angles at nitrogen and arsenic are 125.6(2)° and 96.3(1)°.

the R_2NP=NR π bond by conjugation (the R_2N−P=N−R system is analogous to an allyl anion). The presence of a π donor at nitrogen weakens both the σ and π components of the P−N double bond. Nitrogen σ-donor substituents (e.g., SiR_3) also decrease the linear inversion barrier at nitrogen, whereas σ-acceptor groups increase it in a manner very similar to the substituent effects on amines.[195] An interesting illustration of the variation of the substituents in iminophosphanes has concerned the pentamethylcyclopentadienyl (Cp*) substituted phosphorus derivatives.[196] When an aryl group substituent is employed at nitrogen, η^1 attachment of the Cp* ligand is observed. With an electron-releasing $-Si(i\text{-}Pr)_3$ group at nitrogen, nonclassical η^2 complexation of the Cp* to phosphorus is seen as well as a shortened P−N bond and a wide P−N−Si angle. The structure may be considered as an intramolecular π complex between the Cp* anion and the triply bonded $[N{\equiv}P{-}Si(i\text{-}Pr)_3]^+$ cation.

The first stable compound with an As(III)−N double bond was Mes*(H)NAsNMes*, which undergoes slow prototropy in benzene.[197] Partly in consequence, the As−N double bond distance measured was 1.714(7) Å, which is just slightly shorter than the other As−N bond of 1.745(7) Å. The N−As−N angle was 98.9(3)°. Anions of formula [DippNAsNDipp]$^-$, which are obtained by diprotonation of the corresponding Dipp-substituted amine species, have been shown to behave as ligands to Zn^{2+} or Cd^{2+} cations such as their phosphorus congeners.[198] These display AsN distances in the range 1.695(3)−1.744(2) Å. An iminoarsine without delocalization or prototropic characteristics has been synthesized with use of the tris(trifluoromethyl)phenyl substituent. Treatment of 2,4,6-$(CF_3)_3H_2C_6AsCl_2$ with 2 equiv of KN(H)C_6H_2-2,4,6-$(CF)_3$ gives the bisaminoarsane which can eliminate $H_2NC_6H_2$-2,4,6-$(CF_3)_3$ to afford 2,4,6-$(CF_3)_3H_2C_6AsNC_6H_2$-2,4,6-$(CF_3)_3$[199] (Figure 19). This has a trans structure and features an As−N distance of 1.707(2) Å and angles of 96.3(1)° and 125.6(2)° at arsenic and nitrogen, respectively. Currently, no stable stibaimines or bismaimines have been well-characterized.

The remaining dipnictenes all involve bonding between two heavier group 15 atoms (Tables 17 and 18). The most famous of these is the landmark diphosphene Mes*PPMes* (Figure 20) which was reported in 1981.[200] Numerous other diphosphenes with a variety of substituents (including transition metal fragments) have been synthesized and structurally characterized.[201] In addition, there are several transition metal complexes where the diphosphene behaves as an end-on donor through one or both phosphorus atoms and the P−P double bond is maintained essentially intact.[201] Most uncomplexed diphosphenes[203−215] have trans structures with angles at phosphorus that are strongly influenced by the electronic effects of the substituents. The P−P

Table 17. Selected Structural Data for Uncomplexed Diphosphenes

compound	P=P (Å)	X−P−P (deg)	P−P−Y (deg)	ref
***trans*-diphosphenes**				
2,6-$Xyl_2H_3C_6PPC_6H_3$-2,6-Xyl_2	1.954			203a
2,6-$Mes_2H_3C_6PPC_6H_3$-2,6-Mes_2	1.985(2)	109.8(1)	97.5(1)	203b
$(Me_3Si)_3CPPC(SiMe_3)_3$	2.002(3) (av)	108.5(4) (av)		204a
	2.009(6) (av)	108.6(4) (av)		204b,c
$(Me_3Si)_3CPPSiPh_3$	2.005(2)	110.5(1)	98.65(8)	204d
i-$Pr_2NPPN\{SiMe_2(t\text{-}Bu)\}_2$	2.011(2)	110.5(1)	89.8(1)	205a
$(\eta^5\text{-}C_5H_5)(CO)_2FePPC(SiMe_3)_3$	2.017(3)	111.2(1)	107.4(2)	205b
(i-$Pr_2N)_2$PPNMes*	2.018(1)	101.2(1)	92.3(1)	205a
2,6-$(CF_3)_2H_3C_6PPC_6H_3$-2,6-$(CF_3)_2$	2.019(2)	98.0(1)		205c
$(Cl_3Si)(Me_3Si)_2CPPC(SiMe_3)_2SiCl_3$	2.019(2)	106.9(4)		205d
$(Cl_3Ge)(Me_3Si)_2CPPC(SiMe_3)_2GeCl_3$	2.019(2)	106.6(2)		205d
2,4,6-$(CF_3)_3H_2C_6PPC_6H_2$-2,4,6-$(CF_3)_3$	2.022(2)	97.8(1)		206a
$(\eta^5\text{-}C_5H_5)(CO)_2$FePPMes*	2.027(3)	109.8(1)	102.4(1)	206b
i-Pr_2NPPTmp	2.029(2)	114.8(1)	89.4	205a
$(\eta^1\text{-}C_5Me_5)PP(\eta^1\text{-}C_5Me_5)$	2.031(3)	103.4	103.9	207
Mes*PPTmp	2.033(2)	89.4(3)	115(1)	208
Mes*PPSn(t-Bu)$_3$	2.033(3)	102.2(2)	100.6(1)	209
Mes*PPMes*	2.034(2)	102.8(1)	200,210	
$\{(t\text{-}Bu)Me_2Si\}_2NPPN\{SiMe_2(t\text{-}Bu)\}_2$	2.034(2)	102.2	211	
Mes*PPN$(SiMe_3)N(SiMe_3)_2$	2.037(2)	97.6(1)	106.1(1)	212
2,4,6-$(CF_3)_3H_2C_6$PPN(Mes)Fluorenyl	2.040(2)	90.4(2)	104.5(2)	213
Mes*PPC$(OSiMe_3)$PMes*	2.04	97		214
***cis*-diphosphenes**				
Mes*PPN$(SiMe_3)N(SiMe_3)_2$	2.027(3)	121.4(3)	126.3(3)	211
Mes*PPN(H)(t-Bu)	2.038(2)	102.0(2)	109.9(2)	215
Mes*PPN(H)(1-Ad)	2.044(2)	102.2(2)	109.2(2)	215

Table 18. Selected Structural Data for Heavier Element Symmetric and Unsymmetric Dipnictenes

compound	E=E (Å)	X–E–E (deg)	E–E–Y (deg)	ref
Arsenic				
$(Me_3Si)_3CAsAsC(SiMe_3)_3$	2.224(1)	106.4(2)		220c
Mes*AsAsCH$(SiMe_3)_2$	2.224(3)	93.6(3),99.9(3)		220a
2,6-$Mes_2H_3C_6AsAsC_6H_3$-2,6-Mes_2	2.276(3)	97.5(4)		9c
2,6-$Trip_2H_3C_6AsAsC_6H_3$-2,6-$Trip_2$	2.285(3)	96.4(2), 107.8(2)		9c
Antimony				
TbtSbSbTbt	2.642(1)	101.4(1)		9a
2,6-$Mes_2H_3C_6SbSbC_6H_3$-2,6-Mes_2	2.6558(5)	94.1(1)		9c
2,6-$Trip_2H_3C_6SbSbC_6H_3$-2,6-$Trip_2$	2.668(2)	98.9(2)		9c
Bismuth				
TbtBiBiTbt	2.8206(8)	100.5(2)		9b
2,6-$Mes_2H_3C_6BiBiC_6H_3$-2,6-Mes_2	2.8327(14)	92.5(4)		9c
Unsymmetric Species				
Mes*PAs{CH$(SiMe_3)_2$}	2.124(2)	101.2(2)	96.4(2)	222
$MesPAsC_6H_3$–2,6-$Trip_2$	2.134(2)	96.7(2)	101.5(2)	223
$MesPSbC_6H_3$–2,6-$Trip_2$	2.335(2)	95.7(3)	100.9(2)	223

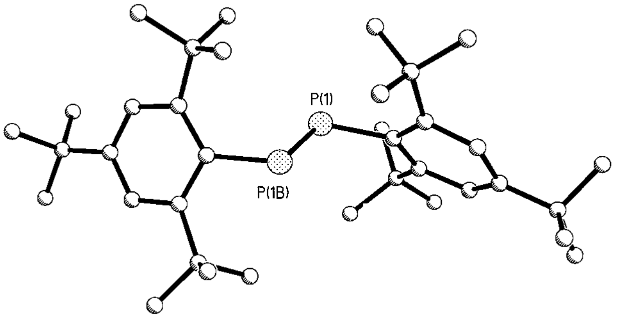


Figure 20. Structure of Mes*$\ddot{\mathrm{P}}$=$\ddot{\mathrm{P}}$Mes*[200] which features a planar C(ipso)PPC(ipso) core, a P=P distance of 2.034(2) Å, and a P–P–C angle of 102.8(1)°.

distances are in the range 1.954–2.044(2) Å (cf. single PP bond length of 2.22 Å). Numerous theoretical[25a,28,41a,216,217] studies on diphosphenes have been made. For the hypothetical HPPH species, the cis configuration (P=P = 2.010 Å) is only slightly (ca. 3.5 kcal mol^{-1}) less stable than the trans form[216i] (P=P = 2.004 Å). In reality, the cis form can be difficult to isolate owing to unfavorable steric interactions that ensue from the use of large substituents which are required to protect the double bond. However, stabilization can be achieved by forming a transition metal complex[217] or by using amino substituents at phosphorus.[211,215] Unlike the iminophosphanes, cis–trans isomerization takes place via rotation (34 kcal mol^{-1}) rather than by linear inversion (66 kcal mol^{-1}).[216i] Laser irradiation studies[218] of Mes*PPMes* show that the free energy of activation of the cis–trans isomerization is 20.3 kcal mol^{-1}. The frontier orbitals of HPPH show that the LUMO is the P=P π^* orbital ($2b_g$) and that the two HOMO's are the π orbital ($2a_u$) and the n_+ lone pair combination. These are very close in energy with the lone pair being slightly (ca. 0.1 eV) more stable.[219] Consistent with the increasing s-character of the lone pairs, calculations on the series HEEH (E = P, As, Sb, Bi) show that the n_+ lone pair molecular orbital becomes progressively more stable relative to the π level such that in HBiBiH there is a difference of ca. 1 eV between them. Electron deformation density studies combined with density functional theory clearly indicates that there exist both σ and π components of the double bond and that HOMO-1 is the P–P π orbital.[210]

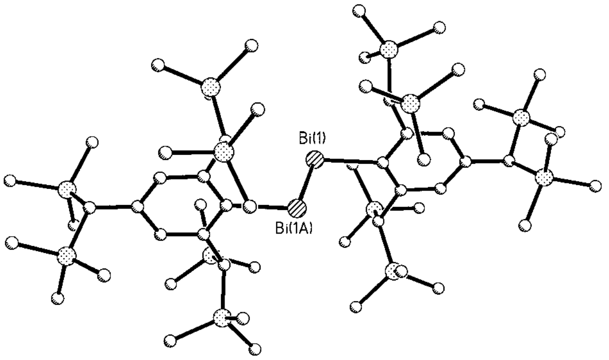


Figure 21. Structure of the dibismuthene[9b] Tbt$\ddot{\mathrm{B}}$i=$\ddot{\mathrm{B}}$iTbt. The Bi=Bi double bond distance is 2.8206(8) Å, and the CBiBi angle is 100.5(2)°.

Diarsenes were reported shortly after the first diphosphenes. Until recently, only two, Mes*AsAsCH$(SiMe_3)_2$[220a] and $(Me_3Si)_3CAsAsC(SiMe_3)_3$,[220c] had been structurally characterized. These featured As–As distances of 2.276(3) and 2.244(1) Å (cf. As–As single bond 2.44 Å). The diarsenes were synthesized by base-assisted dehydrohalogenation or by reduction of an arsenic halide with alkali metal. These two compounds have now been supplemented by the structures of the diarsenes 2,6-$Mes_2H_3C_6AsAsC_6H_3$-2,6-Mes_2 (As–As = 2.276(3) Å) and 2,6-$Trip_2H_3C_6$-$AsAsC_6H_3$-2,6-$Trip_2$ (As–As = 2.285(3) Å) which were synthesized by the reduction of the appropriate halide precursor with potassium or magnesium.[9c] The currently known As–As distances thus span the relatively narrow range 2.244(1)–2.285(3) Å, which represents a shortening of 8.03–6.35% with respect to the single bond.

The first stable distibene and dibismuthene (Figure 21) compounds were synthesized recently by the deselenation of the six-membered E_3Se_3 (E = Sb or Bi) cyclic trimers [E(Se)Tbt]$_3$.[9a,b] The very bulky aryl group Tbt ensures the protection of the double bond. In addition, the use of the *m*-terphenyl ligands $-C_6H_3$-2,6-Mes_2 and $-C_6H_3$-2,6-$Trip_2$ has afforded stable dipnictenes and dibismuthenes by direct reduction of the corresponding dihalides.[9c] The Sb–Sb double bond distances are in the range 2.642(1)–

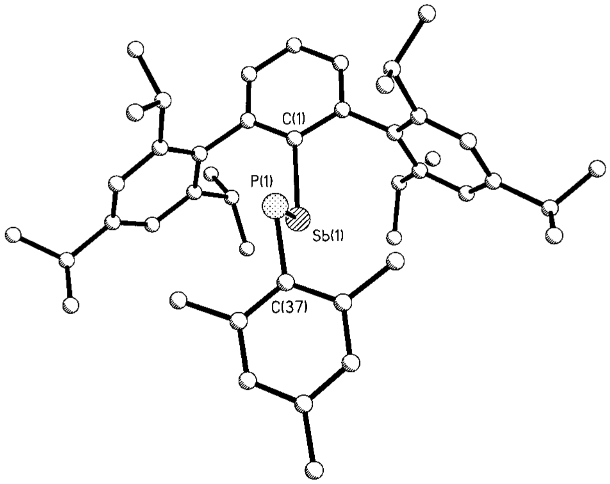


Figure 22. Structure of $\mathrm{Mes\ddot{P}{=}\ddot{S}bC_6H_3}$-2,6-$\mathrm{Trip_2}$[223] featuring a stable P=Sb double bond 2.335(2) Å long.

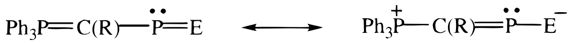
2.668(2) Å[9a,c] and the two known dibismuthenes[9b,c] have Bi−Bi double-bonded distances of 2.8206(8) and 2.8327(14) Å (cf. Sb−Sb or Bi−Bi single bond distances of 2.837 and 2.990(2) Å in Sb_2Ph_4[221a] and Bi_2Ph_4[221b]). To summarize, the amount of shortening from a single to double bond in the heavier dipnictenes is in the range 11.18−7.75% for diphosphenes, 8.03−6.35% for diarsenes, 6.87−5.96% for distibenes, and 6.15−5.26% for dibismuthenes. The percentage shortening decreases with increasing atomic number and, roughly speaking, falls by about 25% going from phosphorus to bismuth. Nonetheless the actual amount of the shortening falls less sharply: ca. 0.2 Å for diphosphenes, ca. 0.18 Å for diarsenes, ca. 0.18 Å for distibenes, and ca. 0.16 Å for dibismuthenes. The structurally characterized unsymmetric dipnictenes tell a very similar story. The phosphorus−arsenic double bonds,[222,223] which are ca. 2.13 Å long are mid-way between the values measured for P−P and As−As double bonds, while the only structurally characterized P−Sb double bond (in the compound $\mathrm{MesPSbC_6H_3}$-2,6-$\mathrm{Trip_2}$ (Figure 22)[223] has a distance of 2.335(2) Å which lies halfway between typical distances for P−P and Sb−Sb double bonds. The use of the terphenyl ligand $-\mathrm{C_6H_3}$-2,6-$\mathrm{Mes_2}$ has also allowed a complete homologous series of dipnictenes 2,6-$\mathrm{Mes_2H_3C_6EEC_6H_3}$-2,6-$\mathrm{Mes_2}$ (E = P, As, Sb, or Bi) to be prepared.[9c] The structures of these show that the E−E−C angles decrease in the sequence 103.7°(P) > 98.5(4)°(As) > 94.1(1)°(Sb) > 92.5(4)°(Bi). This reflects the increasing s character of the lone pair and the increasing p character of the σ and π bonding.[219]

L. Compounds of Formula RE=E′ (E = Group 15, E′ = Group 16 Element)

These compounds have a formal double bond between the pnictogen and chalcogen. Therefore, there is a stereochemically active lone pair at the pnictogen and a bent geometry is predicted at this atom. The simplest molecules in this class are the organonitrosyls which are generally metastable compounds. Stability is enhanced by the use of more electronegative substituents (e.g., fluorine, aminyl, alkoxyl) at nitrogen.[224] The parent molecule nitroxyl HNO has been detected spectroscopically in the gas phase[225a] and in an argon matrix.[225b] It can be stabilized by complexation (η^1 through the nitrogen) to transition metals, and a number of complexes involving osmium,[226a] rhodium,[226b,c] and rhenium[226d] have been synthesized. The structure of $\mathrm{Os(Cl)_2(CO)(HNO)(PPh_3)_2}$[226c] features an NO distance of 1.173(7) Å and a HNO angle of 99(7)° (cf. 1.211 Å and 108.5° in the unstable free molecule).[225a] It may be also noted that RNO complexes of heme proteins have been known for many years and several structures have been determined.[227] The X-ray crystal structure of ClNO shows that, at −160 °C, the NO distance is 1.102(1) Å and there is a Cl−N−O angle of 112.10(6)°.[228] For the heavier chalcogen analogues of the nitrosyl halides, the isomeric forms having the chalcogen as the middle atom are more stable.[229] Thionitrosyls (NS) have been stabilized on transition metals where nitrogen is in the middle of the MNS moiety.[230a] Very recently a stable osmium selenonitrosyl featuring the moiety OsNSe has been isolated and structurally characterized.[230b] However, the character of the MN bond in both these classes of complexes is multiple, and as transition metal derivatives they do not fall within the scope of the review.

The remaining compounds in this class involve bonding to the heavier pnictogens. Although the phosphorus compounds[231] have received most attention, data are scant and stable examples incorporating either phosphorus or the remaining elements in the group have not been structurally characterized as free species. Nonetheless, several examples have been isolated as transition metal complexes or spectroscopically characterized in solution. For oxo species (oxophosphanes), the complexes $\mathrm{(CO)_5CrP(O)N(i\text{-}Pr)_2}$[232a] and $\mathrm{ReCl(Ph_2PCH_2CH_2PPh_2)_2\{P(O)CH_2(t\text{-}Bu)\}}$[232b] have been structurally characterized. These compounds have P−O double-bonded distances of 1.475 and 1.499(3) Å with PN and OPC angles of 120.6° and 104.9(2)°, respectively. Calculations[233] on HP=O show that the HOMO is a phosphorus lone pair orbital with the HOMO-1 π orbital 1.6 eV more stable. The PO bond length is calculated to be 1.51 Å or slightly longer than the PO distances in the transition metal complexes above.[232] Several unstable oxophosphines have been characterized spectroscopically (e.g., IR, MS, or PES) either in the gas phase or trapped in an argon matrix.[234,235] These include the halides X−P=O (X = F, Cl, Br), the phosphenous acid HOP=O,[236] and the phosphenite 2,6-t-$\mathrm{Bu_2}$-4-$\mathrm{MeH_2C_6O{-}P{=}O}$.[237] The latter compound was obtained by thermolysis of its corresponding trimer followed by condensation of the vapor at 12 K. The condensate showed a strong P−O stretching frequency at 1235 $\mathrm{cm^{-1}}$. The ^{31}P NMR spectrum (signal at δ = 238 ppm) could also be observed during the thawing of a solution obtained by rapid condensation of the vapor in dichloromethane with cooling in liquid nitrogen.[237] Photoelectron spectroscopy and theoretical data indicate that in ClP=O the PO bond length is 1.44 Å and the ClPO angle is 109°.[235]

The corresponding phosphorus−sulfur compounds, the thioxophosphanes, have also been the subject of several investigations. The halides X−P═S (X = F, Cl, or Br) have been studied by various spectroscopies in the gas phase, and for ClPS a P═S distance of 1.86 Å and a ClPS angle of 110° was calculated.[235,238] In addition, thioxophosphanes and selenoxophosphane of formula Ar−P═S or Ar−P═Se (Ar = $-C_6H_2$-6-NMe_2-2,4-t-Bu_2) have been characterized spectroscopically in solution.[239] More recently, several ylidylphosphorus sulfides and selenides of formula $Ph_3P(R)C-PE$ (R = Me, Et, Ph, 3-MeC_6H_4, 2,6-$Cl_2C_6H_3$, $SiMe_3$) have been characterized.[240] However, these differ in the sense that stabilization is achieved by a major contribution from a zwitterionic resonance form (b) as depicted by



$$\underset{\text{(a)}}{Ph_3P{=}C(R){-}\ddot{P}{=}E} \longleftrightarrow \underset{\text{(b)}}{Ph_3\overset{+}{P}{-}C(R){=}\ddot{P}{-}E^-}$$

(a) (b)

A structural determination of $Ph_3PC(Et)PSe$ showed that it displayed a short C−P(Se) bond of 1.702(6) Å and a long P−Se distance of 2.129(2) Å (cf. P−Se single bond 2.06−2.12 Å) signifying that structure b is the dominant form. About a dozen compounds of this type, where E = S or Se, have been isolated and characterized by combustion analyses, various NMR spectroscopies, and their reaction chemistry.

The very simplest thioxophosphane H−P═S and its tautomer H−S−P have been shown to be stable in the gas phase.[241] The tautomeric form HSP was the first example of a compound of formula "XPS" (X = F, Cl, or Br) in which phosphorus did not occupy the central position. Several thioxophosphanes and selenoxophosphanes have been stabilized in the coordination sphere of various transition metal complexes. They may be η^2-bonded to a single metal as in Os(η^2-R−P═E)$(CO)_2(PPh_3)_2$ (E = S, R = H, Me; E = Se, R = H)[242a] or η^2-bonded as a bridging ligand between two metals as in $(\eta^5-C_5H_5)_2Mo_2(CO)_4$(4-$MeOC_6H_4PS$)[242b] or $(\eta^5-C_5H_5)_2Mo_2(CO)_4(PhPS)$.[242c] Work on the heavier pnictogen derivatives X−E═O (E = As, Sb, or Bu) has been confined for the most part to the halogens. These are formed under low pressure and high temperature by the reduction of a mixture of the trihalide and oxygen with silver. The oxohalides of antimony and bismuth have been known for many years and exist as ionic polymers. The structures of the antimony compounds are quite different from those of bismuth. For example, SbOCl consists of puckered sheets in which two-thirds of the antimony atoms are bound to two oxygens and one chlorine and the remaining third to four oxygens.[243a] In contrast, BiOCl has a complex layer structure in which a central planar sheet of O atoms has a sheet of halogens at either side with the bismuth atoms between the Cl−O−Cl sheets.[243b]

V. Compounds with Formal Bond Order >2 and Triply Bonded Compounds

A. Range of Compounds

The number of potentially triply bonded species listed in Table 2 is considerably less than the large variety of doubly bonded species given in Table 1. The major reason for this is that the use of three orbitals from each of the atoms forming the triple bond leaves only one orbital available for bonding to a substituent or for occupation by a lone pair. The number of available combinations of bonding and ligand orbitals is thereby greatly restricted. The restriction to a maximum of one substituent at each atom also means that the steric protection of the triple bond usually requires exceptionally large ligands. It may be noted that in molecules where there is a substituent at each heavier main group atom, the triple bonding will involve the use of s electrons. As in the double-bonded compounds, the reluctance of such electrons to participate in bonding is manifested in the appearance of lone pair character at the heavier main group element. This results in a trans-bent structure with a reduced bond strength between the main group elements.

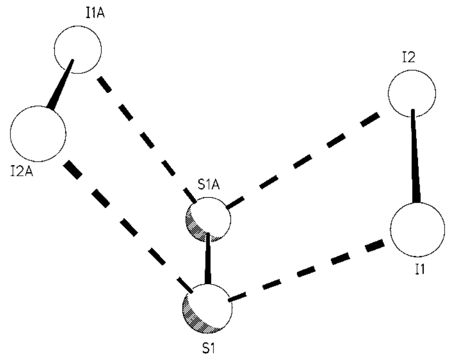
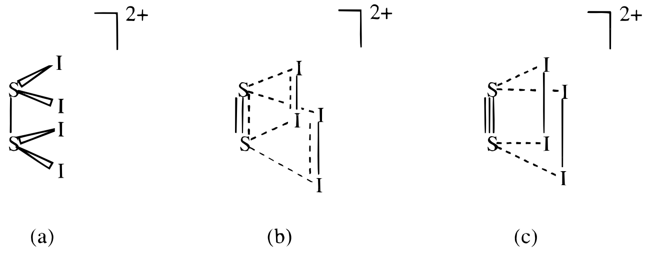


Figure 23. Structure of the $[S_2I_4]^{2+}$ in $[S_2I_4][SbF_6]_2$[244b] which features a very short sulfur−sulfur bond of 1.818(1) Å.

Among heavier element compounds where π bonding is strongest (i.e., between the smaller elements such as sulfur or phosphorus), the requirement for very large substituents may be relaxed to some extent. The foremost example of this is provided by the unusual compounds $S_2I_4(MF_6)_2$ (M = As or Sb) which consist of $S_2I_4^{2+}$ cations and MF_6^- anions with weak cation−anion interactions.[244] The structure of the $[S_2I_4]^{2+}$ ions (Figure 23) is composed of two planar quadrilateral S_2I_2 units with a common S−S bond and interplanar angles near 90°. The overall geometry may be described as a distorted right triangular prism. There are distortions from the ideal geometry which result from different lengths of the S−S, S−I, and I−I bonds. For the SbF_6^- salt, the S−S, S−I, and I−I distances are 1.818(1), 2.993(4), and 2.571(2) Å, respectively, whereas in the AsF_6^- salt the corresponding distances are 1.843(6), 3.02(16) (avg), and 2.5987(17) Å.[244b] These lengths may be compared with the singly bonded values for S−S, S−I, and I−I of 2.048 (in S_8),[245] 2.38 (sum of radii of I and S), and 2.666 Å (I_2).[18] Clearly, the S−S distances are 0.205−0.23 Å shorter than a single bond and the S−I distances are 0.33−0.35 Å longer than the single bond while the I−I bonds are 0.067−0.095 Å shorter than the single bond in I_2. It is important to note that the 'I_2' units in each molecule are separated from each other by a distance slightly greater than 4.2 Å.

The bonding in $S_2I_4^{2+}$ has been approached from the point of view that it involves an interaction between the two unpaired electrons in the orthogonal

π^* orbitals of S_2 with an unpaired electron from a π^* orbital in each I_2^+ ion. This is consistent with the ca. 90° dihedral angle between the two S_2I_2 planes. Since the electronegativities of sulfur and iodine are very similar, an approximately equal distribution of the 2+ change over the six atoms could occur, which leaves the S_2 units with a formal charge of +0.66 and a formal S−S bond order of 2.33. Nonetheless, the S−S distance in $S_2I_4(SbF_6)_2$ suggests a bond order as high as 2.7 by the Pauling formula.[6b] Another, less sophisticated, view of the bonding is through the resonance forms a, b, and c.



The two extremes are represented by a and c. The bonding in a is single throughout with a structure that is analogous to the eclipsed form of neutral P_2I_4, which is isoelectronic to $[S_2I_4]^{2+}$. Structure c represents another extreme in which a triply bonded S_2^{2+} moiety (isoelectronic to P_2) interacts weakly with two I_2 molecules, while b more closely represents the experimental findings, which show some multiple I−I bond character as well as a SS bond order between double and triple.

The unique structure of the $[S_2I_4]^{2+}$ cation is dependent on the approximate equality of the ionization energy and electronegativity of iodine and sulfur as well as the strength of S−S π bonding. The lower ionization energy and weaker π bonding characteristics of the next heaviest element selenium result in a different structure for the corresponding $[Se_2I_4]^{2+}$ dication which may be regarded as consisting of two $[SeI_2]^+$ radical cations linked by weak $\pi^*-\pi^*$ interactions to give a cage structure with relatively weak Se−Se bonds and strengthened Se−I bonds. The SS bond in $[S_2I_4]^{2+}$ is, by a large margin, the shortest currently known stable, homonuclear multiple bond between two heavier main group elements. Furthermore, the bond order[6b] of 2.7 is the highest for a stable homonuclear heavier element multiply bonded species.

Further examples of stable, relatively high bond order molecules without great steric congestion involve bonding to phosphorus—an element whose low-coordinate chemistry compares closely with that of carbon.[141b] The triply bonded phosphaalkynes[246] (see below) are the most relevant molecules to the subject matter of this review, but there are several other examples of triply bonded phosphorus that are outside the present scope, e.g., the transition metal phosphides[247a] and certain transition metal phosphinidene complexes.[247b] An important feature of phosphaalkynes is that they can be stabilized without the use of extremely large substituents. The first stable example was the landmark compound t-Bu−C≡P:[248a] (Figure 24). The steric protection afforded the phosphorus center by the t-Bu group would be, by itself, inadequate to protect the triple bond from attack. The P−C π bonds are inherently of almost sufficient strength to ensure stability at room temperature. In fact, the parent molecule HC≡P: can be kept for extended periods at room temperature under sufficiently reduced pressure.[248b] All of the other currently known species in Table 20 require the presence of large ligands to ensure stability.

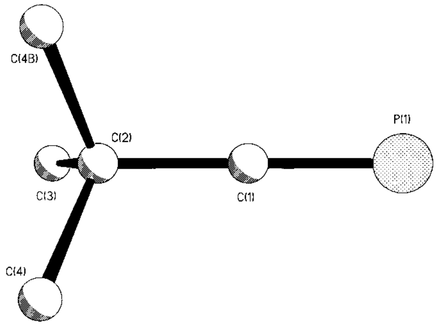


Figure 24. Structure of t-Bu−C≡P[271] featuring an essentially linear carbon geometry and P≡C triple bond distance of 1.548(1) Å.

B. Compounds with Potential Triple Bonding to a Group 13 Element

The first four columns in Table 2 fall into this category. At present, no ionic compounds with anions of formula $[-B\equiv B-]^{2-}$ have been isolated. Several attempts at synthesizing these via reduction of a organoborondihalide RBX_2 with bulky alkyl aryl or amido ligands have led to various products in which a boranediyl (borylidene), RB:, moiety has inserted into C−H or C−C bonds of various organic substituents.[54,55]

In contrast to these results, reduction of the gallium dihalide $GaCl_2C_6H_3$-2,6-$Trip_2$ (generated in situ from $GaCl_3$ and LiC_6H_3-2,6-$Trip_2$) with sodium metal affords the unique compound $Na_2\{GaC_6H_3\text{-2,6-}Trip_2\}_2$[24a] (Figure 25). It crystallizes as an ion triple in which the Na^+ ions are complexed via Na^+−Trip

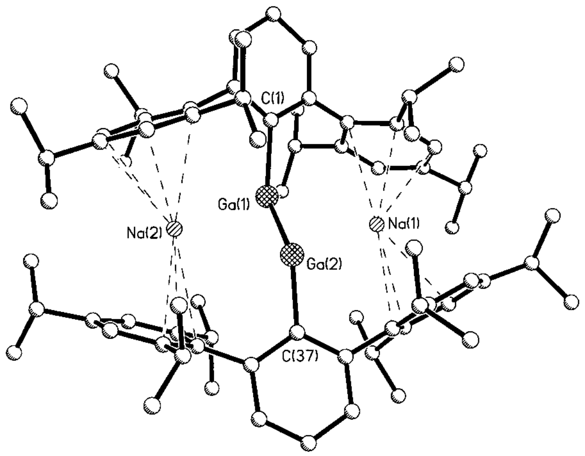
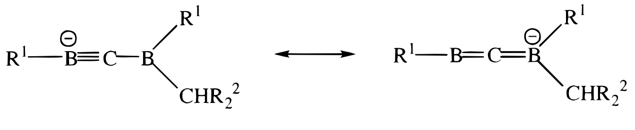


Figure 25. Structure of $Na_2\{GaC_6H_3\text{-2,6-}Trip\}_2$[24a] featuring a Ga−Ga distance of 2.319(3) Å and a Ga−Ga−C angle near 130°.

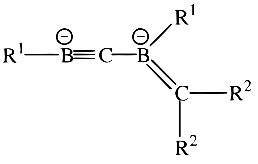
interactions to the $\{GaC_6H_3\text{-}2,6\text{-}Trip_2\}_2^{2-}$ dianion. The latter has a planar, trans-bent C(ipso)GaGaC(ipso) array rather than a linear one. The Ga−Ga distance is 2.319(3) Å, and the angles at the galliums are near 130°. The bending is consistent with the development of lone pair electron density at the metals, and molecular orbital[25b,d] and density functional[25a] calculations have shown that one of the three orbitals associated with the Ga−Ga bond is essentially nonbonding in character. The Ga−Ga distance, which is the shortest reported to date, is marginally shorter than some Ga−Ga single bonds[249] and may be compared to the 2.343(2) Å length in the ion $\{GaTrip_2\}_2^-$ which has a formal Ga−Ga bond order of 1.5.[11a] The density functional calculations[25a] have indicated that the Na^+ countercations may play a role in shortening the Ga−Ga bond through their interaction with the *ortho*-aryl substituents. Thus, in the hypothetical compound $Na_2\{GaC_6H_3\text{-}2,6\text{-}Ph_2\}_2$, which has Na^+−aryl interactions, the Ga−Ga distance is 2.36 Å, whereas in $Na_2\{GaPh_2\}_2$ which has no Na^+-aryl interactions, the Ga−Ga distance is 2.46 Å. The latter distance is comparable to those calculated, i.e., 2.508 and 2.522 Å, for $Na_2\{GaMe\}_2$ and $\{GaMe\}_2^{2-}$ which also possess a trans-bent structure.[24b] The Ga−Ga bonds in these were described as consisting of two weak dative (polar dative) and one σ bond and as being of between double and triple in character, although it was concluded that there was little Ga−Ga bond order—a bond distance relationship which is suggestive of weak Ga−Ga bonding. Other calculations on $\{GaMe\}_2^{2-}$ or $\{GaH\}_2^{2-}$ also yield similar Ga−Ga bond lengths and show that the bent geometry has a lower energy than the linear form.[25d] As previously mentioned, this geometry results from mixing of a Ga−Ga σ^* and a π level to give an essentially nonbonded orbital which has also been described as a “slipped” π bond.[24c] Although there has been a lively literature debate over bond orders involving gallium, all the calculations suggest that the Ga−Ga multiple bonds are not especially strong. No compounds related to the $Na_2\{GaC_6H_3\text{-}2,6\text{-}Trip_2\}_2$ species have been reported for aluminum, indium, or thallium.

The second class of group 13 triply bonded compounds concerns monoanionic species in which the group 13 element is triply bonded to elements of the carbon group. At present, the isolated compounds concern only the lightest atom boron−carbon moiety $[-B{\equiv}C-]^-$ which is not expected to manifest lone pair character at the first-row boron atom. These were first shown to exist in the stable system described by the schematic drawing



(R^1 = Mes, R^2 = $SiMe_3$)

which has partial triple bond character as indicated by a B−C distance of 1.339(6) Å.[250a] A reduction of the corresponding borinarylideneborane leads to the dianion



(R^1 = Dur, R^2 = $SiMe_3$)

which has a B−C distance of 1.323(9) Å (Figure 26).[250b] These B−C distances are longer than that calculated for the parent anion $[H-B{\equiv}C-H]^-$ which has a B−C triple bond distance of 1.319 Å.[251a] However, they are shorter than the 1.43 Å calculated distances[251b] for the isoelectronic BC^{3-} species.

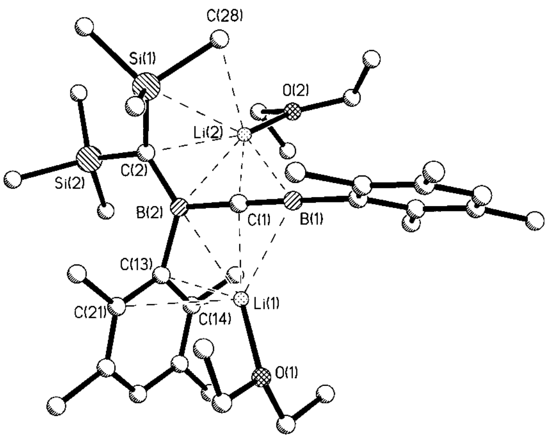


Figure 26. Structure of the compound $Li_2DurBCB(Dur)C(SiMe_3)_2$[251b] which features a B−C triple bond 1.323(9) Å long.

Stable compounds with triple bonds between boron and pnictogens are known only for the lightest element boron−nitrogen pair.[252] Several examples have been structurally characterized, and recently a molecule incorporating two B−N triple bonds, which are stable at temperatures as high as 300 °C, has been reported.[253] The structural[15,252] data show that both the boron and the nitrogen atom have linear or near linear coordination with B−N bond distances in the range 1.23−1.26 Å. The B−N triple bond in $H-B{\equiv}N-H$ was calculated to have an energy of 88 kcal mol^{-1}.[254] These parameters may be compared to a CC triple bond distance of ca. 1.18 Å in the alkynes[64] and a calculated $C{\equiv}C$ triple bond energy of 94 kcal mol^{-1}. The B−N triple bond is thus somewhat weaker than the isoelectronic C−C moiety.

Attempts to synthesize stable phosphorus analogues of iminoboranes have not been successful to date. Calculations on the idealized hydrogen derivative HBPH have shown that, unlike iminoboranes, the minimum energy species has a bent geometry (H−P−B = 94.5°) at phosphorus with a B−P distance of 1.756 Å,[89e] signifying the presence of a double rather than a triple BP bond. The narrow angle at phosphorus is consistent with considerable lone pair character at this atom, which is much more energetically preferred than a linear form with a second π bond. The linear form is in fact ca. 23 kcal mol^{-1} higher in energy, and there is a dimerization energy

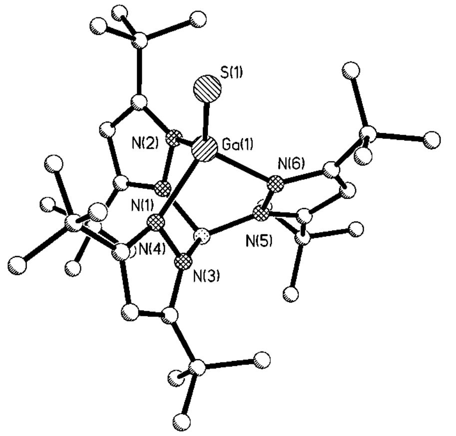


Figure 27. Structure of $Tp(t\text{-}Bu)_2GaS$[264c] which has a Ga=S double bond distance of 2.093(2) Å.

Table 19. Selected Structural Data for Heavier Group 13 Metal Chalcogenides

compound	bond length (Å)	ref
$\{Tp(t\text{-}Bu)_2\}GaS$	2.093(2)	264c
$\{Tp(t\text{-}Bu)_2\}GaSe$	2.214(1)	264b
$\{Tp(t\text{-}Bu)_2\}GaTe$	2.422(1)	264b
$\{Tp(t\text{-}Bu)_2\}InSe$	2.376(1)	264a

of −54 kcal to the four-membered diphosphadiboretane ring compound. For H_2NBPCH_3 the calculated dimerization energy is 90 kcal mol^{-1}, for which reaction the activation energy is only 5 kcal mol^{-1}.[255] Attempts to prevent dimerization by using sterically crowding substituents, as well as the use of an amine substituent at boron to relieve its electron deficiency, have not effected stabilization of the boranylidene phosphane monomer. Efforts[89e] toward this objective have involved heating the sterically crowded $(TmpBPMes^*)_2$ (prepared by dehydrohalogenation of Tmp-B(Cl)P(H)Mes*) under reduced pressure. The mass spectrum afforded peaks attributable to the monomer TmpBPMes*, which was not trapped. Reaction of TmpB(Cl)P(H)Mes* with alkyllithium reagents at room temperature did not result in dehydrohalogenation but in the boranyl phosphide Li{P(Mes*)B-(R)Tmp} (R = Me or t-Bu). Nonetheless, photolysis of the diphosphadiboretane $(TmpBPCEt_3)_2$ in the presence of $Cr(CO)_6$ allows trapping of boranylidene phosphane $TmpBPCEt_3$ as its $Cr(CO)_5$ complex.[256] A very short B−P bond length of 1.743(5) Å was observed, which is quite close to that calculated for the bent form HBPH.[89e] No analogous boron derivatives of the heavier pnictogens have been reported. Neither have any heavier group 13−15 compounds from this class been isolated as stable species, although dimeric and trimeric species related to the diphosphadiboretanes[16] have been isolated for heavier pairs such as Al−N,[257a−d] Ga−N,[257e] or Ga−P.[258] Theoretical data[257f−h] for various $(HAlNH)_n$ ($n = 1-4$) species indicate the presence of double rather than triple bonding in HAlNH.

The class of compounds defined by the formula RBE (E = chalcogen) may exhibit triple-bonded character if one of the E lone pairs is delocalized onto boron. However, no stable compounds have been isolated at room temperature, although several have been studied in the gas phase.[259] The multiple bond distances in these gas-phase species are quite short. For example, the B=S and B=Se distances in HBS[259b−d] and ClBSe[259i] are 1.599 and 1.751 Å, respectively. At room temperature the lowest stable aggregates are usually their dimers or trimers, although monomeric thioxoborane TbtBS has been generated in solution and trapped by further reaction with dienes.[260] The lowest degree of aggregation which has been attained in alumoxanes derivatives is four as in $(RAlO)_4$,[261a,b] and a dimeric aluminum sulfide species $(Mes^*AlS)_2$ has been reported recently.[261c] As in the case of the boron chalcogen species above, molecules such as X−Al=O (X = F, Cl) are stable only in the gas phase.[262] However, it has been possible to structurally characterize several molecular gallium (Figure 27) and indium species of formula $Tp(t\text{-}Bu)_2EE'$ (E = Ga, E′ = S, Se, or Te; E = In, E′ = Se) with terminal bonds to chalogens.[263] They are stabilized by use of the tridentate t-Bu-substituted pyrazolylborate ligand $Tp(t\text{-}Bu)_2^-$. Accordingly, the metals are four-coordinate, which reduces conjugation of the chalcogen lone pair. Nonetheless, it can be seen from Table 19 that the formally double-bonded metal chalcogen distances are much shorter than those seen earlier in the chalcogenato derivatives in Table 9.

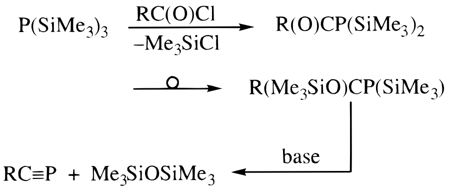
C. Compounds with Potential Triple Bonding to a Group 14 Element

The heavier group 14 analogues of alkynes, in which one or both carbon atoms are replaced by the atoms Si−Pb, are not currently represented by a stable compound, although molecules such as MeSiSiMe have been proposed as intermediates in thermolysis reactions.[264] Several calculations[29b] have been carried out on the hypothetical hydrogen and methyl derivatives of formula E_2H_2 and E_2Me_2 (E = Si[265] or Ge[29b,267]). The unique hydrogen species possess energetically low-lying doubly bridged, monobridged, or vinylidene structures in preference to the yne form.[265] Spectroscopic studies[266] on Si_2H_2 have identified both mono-[266a] and dihydrogen bridged structures $H\overline{Si(\mu\text{-}H)Si}$ and $\overline{Si(\mu\text{-}H)_2Si}$ which have short Si−Si distances of 2.119 and 2.2079 Å. Studies of silicon or germanium species with substituents other than hydrogen have shown that consistent with the appearance of lone pair density, the yne form exists in trans-bent instead of linear configuration.[29b,265−267] Recent calculations[268] show that electronic properties and the size of the substituent play a large role in the geometry of the yne analogues. For example, the use of bulky silyl substituents such as R = $-Si(t\text{-}Bu)_3$ or $-Si(Dep)_3$ in RSiSiR render the trans-bent disilyne form ca. 10 kcal mol^{-1} more stable than the vinylidene isomer. Furthermore, the trans-bent disilyne is only ca. 5 kcal mol^{-1} more stable than the linear species. This suggests that it is probable that species with Si−Si triple bonds will be stabilized in the future and these will have Si−Si distances of ca. 2.07 Å (cf. 2.34 Å for Si−Si single bond). Calculations[269a−l] on CH_2Si indicate that the 1-silavinylidene form is ca. 35 kcal mol^{-1} more stable than silaacetylene, which is predicted to have a trans-bent structure with a HSiC angle near 130° and an angle of ca. 150° at carbon. The predicted C−Si bond length is 1.632 Å.[269l] Similarly, calculations[269m] on $GeCH_2$ show that the germavinylidene isomer is ca. 43 kcal mol^{-1} more stable than the trans-bent germyne, which was predicted to have a Ge−C distance of 1.727 Å and angles near 145° and 128° at germanium and carbon, respectively. More recent computational data[269l,n] on HCSiX (X = F or Cl) also indicated that halide substituents at silicon greatly enhance the stability of the silyne isomer. Moreover, the barrier to interconversion of various isomers is increased, and this has prompted spectroscopic work[269n] which has resulted in the first experimental evidence for C≡Si triple bonds.

The singly reduced radical anions $[K(THF)_6][\{SnC_6H_3\text{-}2,6\text{-}Trip_2\}_2]$,[13] $[K(dibenzo\text{-}18\text{-}crown\text{-}6)(THF)_3][\{SnC_6H_3\text{-}2,6\text{-}Trip\}_2]$,[13] and $(THF)_3Na\{SnC_6H_3\text{-}2,6\text{-}Trip_2\}_2$,[270] whose anions contain one electron more than the corresponding neutral compounds, are closely analagous to the dimetallyne heavier group 14 species. These salts were obtained by the reduction of the aryl tin halide $2,6\text{-}Trip_2H_3C_6SnX$ (X = Cl or Br) with sodium or potassium. The anions possess an essentially planar trans-bent C−Sn−Sn−C array in which the Sn−Sn distance is ca. 2.81 Å and the interligand angles at the tins are in the range 95.20(13)−98.0(4)°. The EPR spectra display small couplings (ca. 8−9 G) to the ^{117}Sn or ^{119}Sn nuclei which are consistent with the location of the unpaired electron in a π orbital. This, together with the narrow angles at the tins, suggests that the bonding at tin primarily involves p orbitals with the lone pair occupying an orbital that is primarily s in character. Two of the p orbitals at each tin are employed in σ bonding so that the Sn−Sn π orbital is derived from overlap of the remaining p orbitals. A second electron can be added to this π orbital to afford the already discussed (section IV.G) doubly reduced species $K_2\{SnC_6H_3\text{-}2,6\text{-}Trip_2\}_2$[36] (Sn−Sn = 2.7763(9) Å) whose dianion is isoelectronic to the neutral distibene $\{SbC_6H_3\text{-}2,6\text{-}Trip_2\}_2$.[9c] The dianion and monoanion have formal Sn−Sn bond orders of 1.5 and 2.0. In view of these findings, the as yet uncharacterized, neutral dimer $\{SnC_6H_3\text{-}2,6\text{-}Trip_2\}_2$ is expected to have substantial lone pair character at each tin and an electronic structure lying somewhere between structure a and b in Figure 4. Preliminary calculations have indicated a trans-bent structure and a Sn−Sn distance of 2.65 Å which suggests some multiple character in the Sn−Sn bond.[271] The trans-bent structure[36] of the dianionic germanium species $Na_2\{GeC_6H_3\text{-}2,6\text{-}Trip_2\}_2$ also suggests that a trans-bent CGeGeC skeleton in a neutral RGeGeR species may have multiple character in the Ge−Ge bond, which is in agreement with calculations.[29b,267]

D. Compounds with Triple Bonding between Group 14 and 15 Elements

These compounds[247] are analogues of the nitriles. The pnictogen lone pair which will have increasing s character is accommodated in an orbital opposite the triple bond in all cases so that no geometrical changes (other than bond lengths) are expected for the heavier element derivatives. The first stable compound involving a heavier element was the previously mentioned landmark compound t-Bu−C≡P:.[249] It was synthesized for the general reaction described by



In the solid state the geometry at carbon is linear and the P−C distance is 1.548(1) Å[271] cf. P−C single bond of 1.85 Å[97] and a spectroscopically measured P−C triple bond distance of 1.5421 Å in H−C≡P: with similar values in other phosphaalkynes.[272] The first and second ionization potentials of t-Bu-C≡P are lower than those of nitriles and involve the π-MO at 9.61 eV and the phosphorus lone pair at 11.44 eV,[273] a difference of 1.83 eV. Like the imines and phosphaalkenes, nitriles and phosphaalkynes also differ in that the polarity of the −C≡E bond is changed since the electronegativity of phosphorus is lower than that of carbon. The presence of a negative charge at the alkyne carbon and a positive charge at phosphorus has been supported by electron density measurements[271] and by protonation studies.[274] The chemistry of the phosphaalkynes, in fact, more closely resembles alkynes than nitriles, which underlines the "carbon-copy" principle for low-coordinate phosphorus derivatives.[141b] There now exists an extensive body of data concerning the chemistry of the phosphaalkynes.[141b,246] This involves some reactions that might be expected for unsaturated species, e.g., 1,2-addition reactions and various cycloadditions (i.e., [2+1], [2+2], [3+2], [4+2]). In addition, the oligomerization of phosphaalkynes (in particular t-Bu-C≡P:) to tetramers, pentamers, and hexamers and the interaction of phosphaalkynes with various transition metal complexes have received considerable attention.

Table 20. Selected Structural Data for Phosphalkynes

phosphaalkyne	P≡C (Å)	X−C−P (deg)	ref
Mes*-C≡P	1.516(13)	-	272a
Mes*-C≡P	1.550	177.8	272b
t-Bu-C≡P	1.536	180	272c
t-Bu-C≡P	1.548(1)	179.5(1)	271
Ph_3C−C≡P	1.537	178.8	272b
1-Ad-C≡P	1.54	180	272b
F−C≡P	1.541	180	272d
CF_3−C≡P	1.542	180	272e
H−C≡P	1.542	180	272f
Me-C≡P	1.544	180	272g
Ph-C≡P	1.544	180	272h
$i\text{-}Pr_2N$−C≡P	1.552(2)	179.2(2)	272i
$[Li(Dme)_3]$ [S−C≡P]	1.555(11)	178.9	272j
$2(Dme)_2Li$−O−C≡P	1.555	178.5	272k

The structures of about 12 uncomplexed phosphaalkynes have been determined in the crystal and gas phases (Table 20). They are all characterized by linear or almost linear coordination at carbon and

P−C triple bond distances in the range from 1.516(13) Å in Mes*−C≡P:[272a] to 1.555(11) Å in [Li(Dme)$_3$][S−C≡P]. The structure of the former compound has been redetermined,[272b] however, and the P−C distance was reported to be 1.550 Å, so that the experimental range of phosphorus−carbon triple bonds is actually much narrower (1.536−1.555 Å)—a variation of only 0.02 Å. The longest P≡C distances are observed when the carbon substituents bear lone pairs which interact with the triple bond as in [E−C≡P]$^-$ (E = O[272k] or S[272j]) or i-Pr$_2$NCP.[272i]

Only one example of a stable arsaalkyne has been structurally characterized. The species Mes*−C≡As: was obtained from the reaction of Mes*C(O)Cl with LiAs(SiMe$_3$)$_2$.[275] The As−C triple bond has a length of 1.657(7) Å, and there is an angle of 175.9(5)° at the central carbon. These values are very similar to those calculated (1.661 Å and 180°) for Ph-C≡As:[277] or the As−C triple bond distance measured spectroscopically in Me-C≡As,[278] which was prepared from the reaction of HC≡C−AsH$_2$ with Na$_2$CO$_3$ at 80 °C.[279] It can be stored in solution at −60 °C, and it has a half-life of 1 h at 0 °C in CDCl$_3$ solution. Theoretical data for the hypothetical species H−C≡As: at the 3-21G* level show that the two degenerate As−C π-MOs are the HOMOs of the molecule at a level of −9.82 eV whereas the energy of the nonbonded orbital at arsenic is −12.93 eV.[152a] This represents a difference of over 3 eV or ca. 70 kcal mol^{-1} which may be attributed to the increased s character of the arsenic lone pair. These calculated data may be compared to experimental data from the photoelectron spectrum of Me−C≡As: which includes bands at 9.6 and 12.1 eV.[279]

At present there are no stable compounds that involve triple bonding between antimony and carbon, although transition metal stibido complexes containing triple bonds to antimony have been reported.[280] In addition, no stable compounds involving triple bonds between pnictogen and the heavier group 14 elements are known at present, although species such as silaisocyanides R−N≡Si (R = H[281a] or Ph[281b]) which contain very short Si−N distances near 1.57 Å have been detected spectroscopically. More recently, matrix isolation spectroscopy has provided proof for the existence of silane nitrile H−Si≡N via IR spectroscopy.[281c]

E. Compounds with Triple Bonding between Group 15 Elements

Dinitrogen is currently the only stable homonuclear neutral molecule involving triple bonding between group 15 elements. The corresponding heavier element analogues have been obtained in the vapor phase, however. The internuclear distances of many of these diatomic molecules (including unsymmetric species) have been determined by spectroscopy.[18] All show distances that are substantially shorter than the corresponding pair of doubly bonded atoms in dipnictenes (section IV.K). For example, a P−P distance of 1.8934 Å was estimated for the triple bond length in P$_2$ which can be compared to an average value of ca. 2.02 Å for a P−P double bond (Table 17). Similarly, the very heaviest element diatomics such as SbP, Sb$_2$, or Bi$_2$ feature short distances of 2.205,[282b] 2.3415,[282c] or 2.6594 Å[282d] consistent with triple bonding (cf. corresponding double-bond lengths in Table 18).

At present, stable examples which include a heavy element are limited to iminophosphenium salts of the type [P≡N−R]$^+$[X]$^-$ which are phosphorus−nitrogen analogues of diazonium salts. The cations are also isoelectronic to the corresponding phosphaalkynes. The first example to be characterized was the salt [P≡N-Mes*][AlCl$_4$],[283a] which has essentially linear (P−N−C = 177.0(7)°) geometry at nitrogen and a P≡N distance of 1.475(8) Å, which is very close to that calculated for [P≡N−H]$^+$, 1.476 Å.[283b] The structure also features interactions between the phosphorus and three chlorines from [AlCl$_4$]$^-$ groups. The salt [P≡N-Mes*][SO$_3$CF$_3$][283c] displays very similar structural features with a P≡N distance of 1.467(4) Å and a P−N−C angle of 176.4(3)°. In addition, it has been shown that the [P≡N-Mes*]$^+$ cation can behave as a Lewis acid toward arene rings and species such as [η^6-C$_6$H$_6$·P≡N-Mes*][GaCl$_4$],[283d,e] [η^6-PhMe·P≡N-Mes*][Ga$_2$Cl$_7$],[282d,e] and [η^6-Mesitylene·P≡N-Mes*][Ga$_2$Cl$_7$],[282e] which feature very slightly lengthened P≡N bonds, have been isolated, and structurally and spectroscopically[282f] characterized. Finally, although it is possible to regard the ion [Mes*PP(PPh$_3$)]$^+$ as a base-stabilized phosphanetriylphosphonium cation, i.e., [RP≡P]$^+$, the structure of the compound (Mes*P−P = 2.025(1) Å and Mes*−P−P angle of 96.78(5)°) indicates a phosphinidenediylphosphenium cation [Mes*−$\ddot{\text{P}}$=P:]$^+$ formulation.[284]

VI. Conclusions

The appearance of lone pair character in unsaturated compounds of the heavier main group elements is a persistent phenomenon which arises from the less efficient mixing of their s and p valence orbitals. However, it is often masked in compounds where stereochemically active lone pairs form part of the structure of the original lighter element congeners, for example, in imines and heavier dipnictenes where, apart from the increasing bond length, the only structural change is a narrowing of the angle at the pnictogen. The double bonds in all the dipnictenes do indeed consist of two covalent bonds, but the increasingly nonbonding character of the s electrons is clearly manifested in the ordering of the energies of the frontier orbitals and, consequently, in the chemistry of these molecules. In contrast, when all the available valence s and p electrons are required for bonding, as they are in the prototypical ethylenes and acetylenes, the appearance of lone pair character in their heavier congeners often results in drastic and much more obvious changes in the molecular architecture and bond strengths. In these cases, the gradual transition from π bonded electron pairs to lone pairs in the heavier elements can result in complete bond dissociation as it does in solutions of the heavier (Pb, Sn, and some Ge) ethylene analogues. The bonding in such compounds no longer consists of two covalent bonds but of weak polar dative ones often similar in strength to hydrogen bonds. Similarly, it is probable that the bonding in the acetylene analogues of these elements will increasingly resemble a single bond instead of a triple one, as depicted in Figure 4a as atomic number increases. The geometries of these molecules can, of course, be influenced by the electronic manipulation of substituent groups. The use of σ-donor and π-acceptor ligands make π bonding more likely, whereas σ-withdrawing and π-donor groups are expected to work in the opposite sense. The substituent effects have been exploited only to a limited extent up to now, but more extensive investigations of these are very likely to open new vistas for multiply bonded heavier main group element compounds.

An important finding that has emerged from theoretical and experimental work is that inherent π-bonding ability remains strong in the heaviest main group elements (e.g., refs 9, 172h, and 282). The common misconception that π-overlap involving orbitals such as 4p, 5p, or 6p is very weak or ineffective is gradually giving way to the recognition that, under suitable electronic and steric conditions, relatively strong π-bonding is possible even among the heaviest group members.

With regard to bonding models, the molecular orbital bonding approach provides a readily accessible, consistent, and useful theoretical underpinning of the bonding in the compounds discussed in this review. It readily explains the weakening of the heavier element multiple bonds and the reduction in bond order through mixing of σ^* and π orbitals. It also accounts for the effects of various substituents (σ-donor, π-acceptor, etc.) on the strength of the multiple bond. Moreover, it preserves to a large extent the long standing relationship between bond strength, bond order, and bond length.[285]

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VIII. References

(1) In this review the word ‘stable’ means that the compounds can be isolated under ambient conditions and can be stored without decomposition, either indefinitely or for long periods at room temperature, in the absence of air or moisture.

(2) A widely cited references in connection with such ‘rules’ is the classic book: *Non Existent Compounds−Compounds of Low Stability*; Dasent, W. E.; Marcel Dekker: New York, 1965. This work, now over a third of a century old, is “*about compounds* (among which are the heavier main group multiply bonded species) *whose structures do not offend the simpler rules of valence, but which nevertheless are characterized by a low stability*”. The author made it clear that even though many of the compounds discussed had never been prepared, it did not imply that they could not be synthesized in the future. The main themes of the book involved discussions of the factors that might account for the relative instability of such compounds.

(3) The origin of the double bond rule is obscure. Although it is an expression that is often used in the literature, a recent review (ref 4) has drawn attention to the fact that there does not appear to exist an original, authoritative, literature citation for such a rule. For earlier discussions, see also the following references: (a) Goubeau, J. *J. Angew. Chem.* **1957**, *69*, 77. (b) Jutzi, P. *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 232. (c) Guseln’ikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

(4) Kuchta, M. C.; Parkin, G. *Coord. Chem. Rev.* **1998**, *176*, 323.

(5) Norman, N. C. *Polyhedron* **1993**, *12*, 2431.

(6) (a) The chemical bond has been defined by Pauling as follows: “there is a chemical bond between two atoms or groups of atoms in case that the forces acting between them are such as to lead to the formation of an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species”. See: Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: 1960; p 6. (b) The term bond order is used to indicate the multiple character of a bond in molecular compounds. For “classical” homonuclear multiple bonds, an empirical curve relating single, double, and triple bond order to bond length may be drawn. In the case of carbon−carbon bonding, this curve is described by the empirical equation $D(n') = D_1 - (0.71\ \text{Å}) \log n'$ (where n' = bond order, D_1 = single bond length; ref 6a, p 239). In such relationships there is an underlying assumption that a homonuclear multiple bond will invariably be shorter than a single one since it is usually assumed that homonuclear multiple bonds arise from the sharing of more than one bonding electron pair between atoms and are thus stronger than single ones. For heavier element molecules, such relationships may become problematical since what are often described as “multiple” bonds do not involve the equal sharing of electron pairs and they are frequently not shortened in comparison to single bonds. In fact, in several cases the so-called “multiple” bonds are found to be longer than single bonds. Nonetheless, it is possible to calculate what the idealized double or triple bond distances in heavier analogues of ethylene or acetylene should be by restricting these hypothetical species to planar or linear geometries. These calculated molecular forms, which do not represent energy minima, may have very short bonds as exemplified by the SiSi and GeGe triple bond lengths of 2.07 and 2.13 Å for the linear disilyne HSiSiH and digermyne HGeGeH. These distances, along with those experimentally found for double and single bonds, can be used to generate an empirical relationship similar to that used for carbon bonds. See later in sections IV. F and V.C of this review for further data and ref 265h for the bond distances in linearized HSiSiH and HGeGeH.

(7) Power, P. P. *J. Chem. Soc., Dalton Trans.* **1998**, 2939.

(8) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373.

(9) (a) Tokitoh, N.; Arai, Y.; Sasamori, T.; Okazaki, R.; Nagase, S.; Uekusa, H.; Ohashi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 433. (b) Tokitoh, N.; Arai, Y.; Okazaki, R.; Nagase, S. *Science* **1998**, *120*, 433. (c) Twamley, B.; Sofield, C. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1999**, *121*, 5357.

(10) (a) Pluta, K.-R.; Pörschke, C.; Kruger, K.; Hildenbrand, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 388. (b) Uhl, W.; Vester, A.; Kaim, W.; Poppe, J. *J. Organomet. Chem.* **1993**, *454*, 9. (c) Uhl, W.; Schutz, U.; Kaim, E.; Waldhör, E. *J. Organomet. Chem.* **1995**, *501*, 79.

(11) (a) He, X.; Bartlett, R. A.; Olmstead, M. M.; Ruhlandt-Senge, K.; Sturgeon, B. E.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 717. (b) Wehmschulte, R. J.; Ruhlandt-Senge, K.; Olmstead, M. M.; Hope, H.; Sturgeon, B. E.; Power. P. P. *Inorg. Chem.* **1993**, *32*, 2983.

(12) Wiberg, N.; Amelunxen, H.; Nöth, H.; Schwenk, H.; Kaim, W.; Scheiring, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1213.

(13) Olmstead, M. M.; Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *166*, 1920.

(14) Haiduc, I.; Sowerby, D. B. *The Chemistry of Inorganic Homo- and Heterocycles*; Academic Press: London, 1987.

(15) (a) Niedenzu, K.; Dawson, J. W. *Boron−Nitrogen Compounds*; Springer: Berlin, 1965. (b) Boron and Nitrogen. *Gmelin Handbook of Inorganic and Organometallic Chemistry*, 4th Supplement; Springer-Verlag: Berlin, 1991 (Vol. 3a) and 1992 (Vol. 3b).

(16) (a) Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 449. (b) Paine, R. T.; Nöth, H. *Chem. Rev.* **1995**, *95*, 343.

(17) (a) Petrie, M. A.; Olmstead, M. M.; Hope, H.; Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* **1993**, *115*, 3221. (b) Mardones, M. A.; Cowley, A. H.; Contreras, L.; Jones, R. A.; Carrano, C. J. *J. Organomet. Chem.* **1993**, *455*, C1−C7.

(18) Numerous examples of formally multiply bonded diatomic molecules have been identified in the gas phase. Most of these are unstable under ambient conditions (ref 1) and thus will not, in general, be discussed here. Important structural and spectroscopic data for many of these diatomic species are given in the following references: (a) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*, 1st ed.; Van Nostrand: Toronto, 1979. (b) *Spectroscopic Data*; Suchard, S. N., Ed.; IFI/Plenum: Newark, 1975.

(19) (a) Hascall, T. K.; Ruhlandt-Senge, K.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 356. (b) Westerhausen, M.; Krofta, M.; Pfitzner, A. *Inorg. Chem.* **1999**, *38*, 598.

(20) Clark, A. H.; Haaland, A. *J. Chem. Soc., Chem. Commun.* **1969**, 912.

(21) Niemeyer, M.; Power, P. P. *Inorg. Chem.* **1997**, *36*, 4682.

(22) (a) Pohl, S.; Niecke, E.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 261. (b) Bjorgvinsson, M.; Roesky, H. W. *Polyhedron* **1991**, *10*, 2353. (c) Chivers, T.; Gao, X. L.; Parvez, M. *Inorg. Chem.* **1996**, *35*, 4336. (d) Fleischer, R.; Stalke, D. *Coord. Chem. Rev.* **1998**, *176*, 431. (e) Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 361.

(23) However, it is doubtful that d-orbitals play a major valence role in the bonding of most hypervalent main group species. For discussions of this question in the context of various main group element compounds, see: (a) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434. (b) Gilheany, D. *Chem. Rev.* **1994**, *94*, 1339. (c) Magnusson, E. *J. Am. Chem. Soc.* **1993**, *115*, 1051.

(24) (a) Su, J.; Li, X.-W.; Crittendon, R. C.; Robinson, G. H. *J. Am. Chem. Soc.* **1997**, *119*, 5471. (b) Xie, Y.; Grev, R. S.; Gu, J.; Schaefer, H. F.; Schleyer, P. v. R.; Su, J.; Li, X.-W.; Robinson, G. R. *J. Am. Chem. Soc.* **1998**, *120*, 5471. (c) Klinkhammer, K. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2320. For more recent discussions, see also: (d) Downs, A. J. *Coord. Chem. Rev.* **1999**, *189*, 59. (e) Robinson, G. H. *Acc. Chem. Res.* **1999**, *22*, 773.

(25) (a) Cotton, F. A.; Cowley, A. H.; Feng, X. *J. Am. Chem. Soc.* **1998**, *120*, 1795. (b) Bytheway, I.; Lin, Z. *J. Am. Chem. Soc.* **1998**, *120*, 12133. (c) Cotton, F. A.; Feng, X. *Organometallics* **1998**, *17*, 128. (d) Allen, T. L.; Power, P. P.; Funk, W. H. *J. Chem. Soc., Dalton Trans.* in press.

(26) Other approaches to bonding have also been proposed, see: Epiotis, N. D. *Deciphering the Chemical Code*; VCH: Weinheim, 1996.

(27) (a) Fjeldberg, T.; Haaland, A.; Lappert, M. F.; Schilling, B. E. R.; Seip, R.; Thorne, A. J. *J. Chem. Soc., Chem Commun.* **1982**, 1407. (b) Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Fjelberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2387.

(28) Jacobsen, H.; Zeigler, T. *J. Am. Chem. Soc.* **1994**, *116*, 3667.

(29) (a) Apeloig, Y. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley, New York, 1989; p 57. (b) Grev, R. S. *Adv. Organomet. Chem.* **1991**, *33*, 125.

(30) Carter, E. A.; Goddard, W. A. *J. Phys. Chem.* **1986**, *90*, 998.

(31) (a) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 5303. (b) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1989**, *111*, 5916. (c) Trinquier, G.; Malrieu, J.-P. In *The chemistry of functional groups, Suppl. A: The chemistry of double bonded functional groups*; Patai, S., Ed.; Wiley: Chichester, 1989; Vol. 2, Part 1, p 1. (d) Trinquier, G.; Malrieu, J.-P.; Rivière, P. *J. Am. Chem. Soc.* **1982**, *104*, 4529.

(32) For a concise account of this approach to the bonding in heavier main group analogues of carbenes, olefins, and small rings, see: Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 828.

(33) (a) Levin, C. C. *J. Am. Chem. Soc.* **1975**, *97*, 5649. (b) Schwerdtfeger, P.; Laakkonen, L. J.; Pyykkö, P. *J. Chem. Phys.* **1992**, *96*, 6807. (c) Cherry, W.; Epiotis, N.; Borden, W. T. *Acc. Chem. Res.* **1977**, *10*, 167.

(34) (a) Bader, R. F. W. *Can. J. Chem.* **1962**, *40*, 1164. (b) Pearson, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 4947.

(35) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

(36) Pu, L.; Senge, M. O.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1998**, *120*, 12682.

(37) Bader, R. F. W. *Atoms in Molecules*—*A Quantum Theory*; Clarendon: Oxford, 1990.

(38) (a) Magnusson, E. *J. Am. Chem. Soc.* **1984**, *106*, 1177. (b) Magnusson, E. *J. Am. Chem. Soc.* **1984**, *106*, 1185.

(39) The reasons for the rapid decline in the hybridization levels of the s and p orbitals in the heavier main group elements has been the subject of much discussion. Perhaps the most plausible explanation, which has been advanced by Kutzelnigg (ref 35), is that in the lighter main group elements of principal quantum number $n = 2$ hybridization is facilitated by the fact that the s and p orbitals occupy the same region of space. In the higher rows the p-orbitals are much more extended into space than the s-orbitals, which makes hybridization more difficult. This difference was rationalized on the basis that in elements of principal quantum number $n = 2$, the p-electrons experience no Pauli repulsion from the $n = 1$ (He) core which is composed exclusively of s-electrons. In contrast, for the higher rows (principal quantum number ($n \geq 3$) the p-electrons are subject to Pauli repulsion (which increases their distance from the nucleus) since these cores contain p-orbitals. It is doubtful that the reduced hybridization in the heavier element is due to increasing energy differences between the s and p-orbitals (thereby requiring larger promotion energies) as a particular group is descended. In fact, such energy differences do not display a large increase (refs 32 and 35) except in the heaviest elements where relativistic effects are important (ref 40). Furthermore, calculations (ref 38) have shown that interligand angles at the main group element are an unreliable guide to the hybridization of the orbitals corresponding to those bonds. Thus, while it appears to be true that for interligand angles near 90°, s orbital participation in bonding is very low, it does not necessarily follow that the percentage s orbital hybridization at higher interligand angles such as 120° or 180° corresponds to sp^2 or sp hybridization.

(40) The energy difference between s and p-orbitals in the heaviest elements is increased by relativistic effects which stabilize s electrons to a greater extent than p-electrons, see: Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271. Pyykkö, P.; Desclaux, J.-P. *Acc. Chem. Res.* **1979**, *12*, 276. Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563. Kaltsoyannis, N. *J. Chem. Soc., Dalton Trans.* **1997**, 1.

(41) Normally, both σ and π-bonds between main group elements are expected to decrease in strength going down a group, which is attributable to steric effects and Pauli repulsion rather than less efficient orbital overlap (ref 28). The largest decrease (usually more than 50%) occurs between the first and second rows (refs 28 and 41a,b; for reviews see refs 2, 4, 5, 7, and 35). However, the presence of adjacent lone pairs on lighter atoms comprising those bonds greatly weakens the σ-bond strength (e.g., in H_2O_2 and N_2H_4) owing (it is thought) to interelectronic repulsion between lone pairs. This factor is sufficient to render N—N and O—O σ-bond strengths much weaker than those of corresponding P—P or S—S bonds. In contrast, N—N and O—O π bonds are quite strong owing to the small size of these atoms and the fact that π bond formation either diminishes or eliminates lone pair—lone pair repulsion. It has also been proposed that the strengths of π-bonds decrease at a much greater rate than those of σ bonds, descending a group as a result of the differences between the s and p-orbital overlaps (refs 28 and 42a). However, other data (ref 42b) including recent experimental findings (e.g., ref 9) do not support this view: (a) Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5217. (b) Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105.

(42) (a) Pitzer, K. S. *J. Am. Chem. Soc.* **1948**, *70*, 2140. (b) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 4496.

(43) The inert pair effect, in which p-block elements increasingly show a tendency to form compounds in an oxidation state which is two less than the total number of available valence electrons (thereby giving the appearance of increasing inertness to the s electrons), is the result of several influencing factors. Perhaps the most significant of these is the decreasing bond strengths in the heavier element compounds, see: (a) Sidgwick, N. V. *The Chemical Elements and Their Compounds*; Clarendon: Oxford, 1950; Vol. 1, p 287. (b) Drago, R. S. *J. Phys. Chem.* **1958**, *62*, 353. In addition, relativistic effects (ref 40) undoubtedly render particular stability to the s electrons in the heaviest members of the groups (i.e., Tl, Pb, Bi). The decreasing hybridization tendency of the s and p-orbitals (ref 35 and 39) further differentiates the s and p-electrons in heavier element compounds. The term "lone pair effect" rather than "inert pair effect" has been used in this review in recognition of the fact that the electron pairs are not truly inert since in some instances they participate (albeit weakly) in bonding.

(44) (a) Schumann, H.; Janiak, C.; Görlitz, F.; Loebel, J.; Dietrich, A. *J. Organomet. Chem.* **1989**, *363*, 243. (b) Schumann, H.; Pickhardt, J.; Börner, U. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 790. (c) Jutzi, P.; Schnittger, J.; Hursthouse, M. B. *Chem. Ber.* **1991**, *124*, 1693. (d) Jutzi, P.; Wegener, D.; Hursthouse, M. B. *Chem. Ber.* **1991**, *124*, 295.

(45) For In—In and Tl—Tl single bond distances in molecular species, see in ref 7 and (a) Uhl, W.; Layh, M.; Hiller, W. *J. Organomet. Chem.* **1989**, *368*, 1213. (b) Brothers, P. J.; Olmstead, M. M.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2355. (c) Wiberg, N.; Amelunxen, K.; Nöth, H.; Schmidt, H.; Schwenk, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 65.

(46) For reviews of monovalent Al(I) and Ga(I) species and bulky organometallic and pyrazolylborate derivatives of heavier group 13 elements, see: (a) Dohmeier, C.; Loos, D.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 129. (b) Reger, D. L. *Coord. Chem. Rev.* **1996**, *147*, 571.

(47) (a) Haaland, A.; Martinsen, K.-G.; Volden, H. V.; Kaim, W.; Waldhör, E.; Uhl, W.; Schutz, U. *Organometallics* **1996**, *15*, 1146. (b) Haubrich, S. T.; Power, P. P. *J. Am. Chem. Soc.* **1998**, *120*, 2202. (c) Niemeyer, M.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1277.

(48) (a) Palagyi, Z.; Grev, R. S.; Schaefer, H. F. *J. Am. Chem. Soc.* **1993**, *115*, 1936. (b) Treboux, G.; Barthelat, J.-C. *J. Am. Chem. Soc.* **1993**, *115*, 4870. (c) Palagyi, Z.; Schaefer, H. F.; Kapuy, E. *Chem. Phys. Lett.* **1993**, *203*, 195.

(49) Uhl, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1386.

(50) (a) Janiak, C.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1688. (b) Hoffmann, R.; Janiak, C. *J. Am. Chem. Soc.* **1990**, *112*, 5924.

(51) Budzelaar, P. H. M.; Boersma, J. *Recl. Trav. Chem. Pays-Bas.* **1990**, *109*, 187.

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

(53) (a) Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3402. (b) Armstrong, D. R. *Theor. Chim. Acta* **1981**,

60, 159. (c) Jouany, C.; Barthelat, J.-C.; Daudey, J. P. *Chem. Phys. Lett.* **1987**, *136*, 52.

(54) (a) Mennekes, T.; Paetzold, P.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 398. (b) Grigsby, W. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 7981.

(55) See: (a) Meller, A.; Maringgele, W.; Elter, G.; Bromm, D.; Noltemeyer, M.; Sheldrick, G. M. *Chem. Ber.* **1987**, *120*, 1437. (b) Meller, A.; Bromm, D.; Maringgele, W.; Bohler, D.; Elter, G. *J. Organomet. Chem.* **1988**, *347*, 11. (c) Meller, A.; Seebold, U.; Maringgele, W.; Noltemeyer, M.; Sheldrick, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 8299. (d) Meller, A.; Bromm, D.; Maringgele, W.; Heine, A.; Stalke, D.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1990**, 741. (e) Meller, A. *Pure Appl. Chem.* **1991**, *63*, 395.

(56) (a) Meller, A.; Maringgele, W. *Advances in Boron Chemistry*; Siebert, W., Ed.; Royal Society of Chemistry Special Publication 201; 1997, p 224. (b) Maier, C.-J.; Pritzkow, H.; Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1666.

(57) (a) Glaser, B.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 416. (b) Henkelmann, J.; Maier, G.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1065. (c) Glaser, B.; Hanecker, E.; Nöth, H.; Wagner, H. *Chem. Ber.* **1987**, *120*, 659. (d) Boese, R.; Paetzold, P.; Tapper, A. *Chem. Ber.* **1987**, *120*, 1069. (e) Boese, R.; Paetzold, R.; Tapper, A.; Ziembinski, R. *Chem. Ber.* **1989**, *122*, 1057.

(58) (a) Berndt, A.; Klusik, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 877. (b) Hunold, R.; Pilz, M.; Allwohn, J.; Stadler, M.; Massa, W.; Schleyer, P. v. R.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 781. (c) Pilz, M.; Stadler, M.; Hunold, R.; Allwohn, J.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 784. (d) Wieczorek, C.; Allwohn, J.; Schmidt-Lukasch, G.; Hunold, R.; Massa, R.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 398. (e) Menzel, M.; Winkler, H. J.; Abelom, T.; Fau, S.; Frenking, G.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1340. (f) Allwohn, J.; Hunold, R.; Pilz, M.; Müller, R.-G.; Massa, W.; Berndt, A. *Z. Naturforsch.* **1990**, *45b*, 290. (g) Willershausen, P.; Höfner, A.; Allwohn, J.; Pilz, M.; Massa, W.; Berndt, A. *Z. Naturforsch.* **1992**, *47b*, 983.

(59) Höfner, A.; Ziegler, B.; Hunold, R.; Willershausen, P.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 594.

(60) Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 985.

(61) (a) Channareddy, S.; Linti, G.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 199. (b) Gunale, A.; Pritzkow, H.; Siebert, W.; Steiner, D.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1111. (c) Gunale, A.; Steiner, D.; Schweikart, D.; Pritzkow, H.; Berndt, A.; Siebert, W. *Chem. Eur. J.* **1998**, *4*, 44.

(62) Power, P. P. *Inorg. Chim. Acta* **1992**, *200*, 443.

(63) (a) Moezzi, A.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1992**, *114*, 2715. (b) Moezzi, A.; Bartlett, R. A.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1082. (c) Moezzi, A.; Olmstead, M. M.; Bartlett, R. A.; Power, P. P. *Organometallics* **1992**, *11*, 2383. (d) Moezzi, A.; Olmstead, M. M.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **1992**, 2429.

(64) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; Chapter 1.

(65) Pilz, M.; Allwohn, J.; Willershausen, P.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1030.

(66) (a) Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 870. (b) Klusik, H.; Berndt, A. *J. Organomet. Chem.* **1981**, *222*, C25.

(67) (a) Grigsby, W. J.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1996**, 2235. (b) Grigsby, W. J.; Power, P. P. *Chem. Eur. J.* **1997**, *3*, 368.

(68) (a) Kaufman, E.; Schleyer, P. v. R. *Inorg. Chem.* **1980**, *27*, 3987. (b) Hamilton, E. L.; Pruis, J. G.; DeKock, R. L.; Jalkanen, K. J. *Main Group Metal Chem.* **1998**, *21*, 219.

(69) (a) Uhl, W.; Vester, A.; Fenske, D.; Baum, G. *J. Organomet. Chem.* **1994**, *464*, 23. (b) Uhl, W.; Gerding, R.; Vester, A. *J. Organomet. Chem.* **1996**, *513*, 613. (c) Uhl, W. *Coord. Chem. Rev.* **1997**, *163*, 132.

(70) Wehmschulte, R. J.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3152.

(71) The result is cited in Wiberg, N. *Coord. Chem. Rev.* **1997**, *163*, 217.

(72) (a) Zweifel, G.; Brown, H. C. *J. Am. Chem. Soc.* **1961**, *83*, 3834. (b) Zweifel, G.; Arzoumanian, H. *Tetrahedron Lett.* **1966**, 2535. (c) Matteson, D. S. *Synthesis* **1975**, 147. (d) Rathke, M. W.; Kow, R. *J. Am. Chem. Soc.* **1972**, *94*, 6854; **1973**, *95*, 2715.

(73) (a) Brown, N. M. D.; Davidson, F.; Wilson, J. W. *J. Organomet. Chem.* **1980**, *185*, 277. (b) Wilson, J. W. *J. Organomet. Chem.* **1980**, *136*, 297. (c) Pelter, A.; Singaram, B.; Williams, L.; Wilson, J. W. *Tetrahedron lett.* **1983**, *24*, 621. (d) Pelter, A.; Briaden, G.; Roesser, R. *Tetrahedron Lett.* **1985**, *26*, 5097.

(74) Bartlett, R. A.; Power, P. P. *Organometallics* **1986**, *5*, 1916.

(75) Ramsey, B. G.; Isabelle, L. M. *J. Org. Chem.* **1981**, *46*, 179.

(76) Olmstead, M. M.; Power, P. P.; Weese, K. J.; Doedens, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 2541.

(77) (a) Pilz, M.; Allwohn, J.; Hunold, R.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1370. (b) Cowley, A. H.; Gabbai, F. P.; Carrano, C. J.; Mokry, L. M.; Bond, M. R.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 578.

(78) Brothers, P. J.; Power. P. P. *Adv. Organomet. Chem.* **1996**, *39*, 1.

(79) Several classes of boron−nitrogen compounds closely related to aminoboranes have been investigated. Among these are the amino−iminoboranes (ref 79a), bis(dialkyalamino)boron cations (ref 79b), and bis(diorganoboron)amido amines (ref 79c): (a) Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1603. (b) Kölle, P.; Nöth, H. *Chem. Rev.* **1985**, *85*, 399. (c) Bartlett, R. A.; Chen, H.; Dias, H. V. R.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1988**, *110*, 446.

(80) (a) Petrie, M. A.; Ruhlandt-Senge, K.; Wehmschulte, R. J.; He, X.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 2557. (b) Petrie, M. A.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 1135. (c) Niesmann, J.; Klingebiel, U.; Röpken, C.; Noltemeyer, M.; Herbst-Irmer, R. *Main Group Chem.* **1998**, *2*, 297. (d) Niesmann, J.; Klingebiel, U.; Noltemeyer, M.; Boese, R. *J. Chem. Soc., Chem. Commun.* **1997**, 365.

(81) (a) Brothers, P. J.; Wehmschulte, R. J.; Olmstead, M. M.; Parkin, S. R.; Power, P. P. *Organometallics* **1994**, *13*, 2792. (b) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 791. (c) Krossing, I.; Nöth, H.; Tacke, C.; Schmidt, M. *Chem. Ber., Recl.* **1997**, *130*, 1047. (d) Knabel, K.; Krossing, I.; Nöth, H.; Schwenk-Kirchner, H.; Schmidt-Amelunxen, M.; Seifert, T. *Eur. J. Inorg. Chem.* **1998**, 1095. (e) Waezsada, S. D.; Rennekamp, C.; Roesky, H. W.; Röpken, C.; Parsini. *Z. Anorg. Allg. Chem.* **1998**, *624*, 987.

(82) (a) Bürger, H.; Cichon, J.; Goetze, U.; Wannagat, W.; Wismar, H. J. *J. Organomet. Chem.* **1971**, *33*, 1. (b) Sheldrick, G. M.; Sheldrick, W. S. *J. Chem. Soc. A* **1969**, 2279.

(83) Linti, G. *J. Organomet. Chem.* **1994**, *465*, 79.

(84) (a) Linti, G.; Frey, R.; Polborn, K. *Chem. Ber.* **1994**, *127*, 1387. (b) Linti, G.; Frey, R. *Z. Anorg. Allg. Chem.* **1997**, *623*, 531. (c) Frey, R.; Linti, G.; Polborn, K. *Chem. Ber.* **1994**, *127*, 101. (d) Linti, G.; Frey, R.; Köstler, W.; Schwenk, H. *Chem. Ber., Recl.* **1997**, *130*, 663. (e) Cowley, A. H.; Decken, A.; Olazabal, C.; Norman, N. C. *Inorg. Chem.* **1994**, *33*, 3435.

(85) Although full structural details were not given, the compounds $M\{N(SiMe_3)_2\}_3$ (M = Ga or In) were reported to be isomorphous to $Fe\{N(SiMe_3)_2\}_2$ with Ga−N and In−N bond lengths of 1.857(8) and 2.057(12) Å. (a) Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. *Coord. Chem. Rev.* **1977**, *24*, 1. (b) Atwood, D. A.; Atwood, V. O.; Cowley, A. H.; Jones, R. A.; Atwood, J. L.; Bott, S. *Inorg. Chem.* **1994**, *33*, 3251.

(86) (a) Petrie, M. A.; Ruhlandt-Senge, K.; Hope, H.; Power, P. P. *Bull. Soc. Chem. Fr.* **1993**, *130*, 851. (b) Porchia, M.; Benetello, F.; Brianese, N.; Rosetto, G.; Zanella, P.; Bombieri, P. *J. Organomet. Chem.* **1992**, *424*, 1. (c) Tödtmann, J.; Schwartz, W.; Weidlein, J.; Haaland, A. *Z. Naturforsch., B.* **1993**, *48*, 1437.

(87) (a) Silverman, J. S.; Carmalt, C. J.; Cowley, A. H.; Culp, R. D.; Jones, R. A.; McBurnett, B. G. *Inorg. Chem.* **1999**, *38*, 296. (b) Frey, R.; Gupta, V. D.; Linti, G. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1060.

(88) (a) Allman, R.; Henke, W.; Krommes, P.; Lorberth, J. *J. Organomet. Chem.* **1978**, *162*, 183. (b) Walzsada, S. D.; Belgardt, T.; Noltemeyer, M.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1351.

(89) (a) Pestana, D. C.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8426. (b) Nöth, H.; Staude, S.; Thomann, M.; Paine, R. T. *Chem. Ber.* **1993**, *126*, 611. (c) Pestana, D. C.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 6887. (d) Feng, X.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1986**, *25*, 4615. (e) Arif, A. M.; Cowley, A. H.; Pakulski, M.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1986**, 889.

(90) (a) Karsch, H. H.; Hanika, G.; Huber, B.; Mundle, K.; Krönig, S.; Krüger, C.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1989** 373. (b) Pestana, D. C.; Power, P. P. *Organometallics* **1992**, *11*, 98. (c) Bartlett, R. A.; Dias, R. H. V.; Power, P. P. *Inorg. Chem.* **1988**, *27*, 3919. (d) Dou, D.; Westerhausen, M.; Wood, G. L.; Linti, G.; Duesler, E. N.; Nöth, H.; Paine, R. T. *Chem. Ber.* **1993**, *126*, 379. (e) Dou, D.; Fan, M.; Duesler, E. N.; Nöth, H.; Paine, R. T. *Inorg. Chem.* **1994**, *33*, 2151.

(91) Data cited in ref 16b.

(92) (a) Bartlett, R. A.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 6817. (b) Bartlett, R. A.; Dias, H. V. R.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 1306.

(93) (a) Petrie, M. A.; Olmstead, M. M.; Hope, H.; Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* **1993**, *115*, 3221. (b) Mardones, M. A.; Cowley, A. H.; Contreras, L.; Jones, R. A.; Carrano, C. J. *J. Organomet. Chem.* **1993**, *455*, C1−C2. (c) Petrie, M. A.; Shoner, S. C.; Dias, H. V. R.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1033.

(94) (a) Wehmschulte, R. J.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 3205. (b) Petrie, M. A.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 1309. (c) Petrie, M. A.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1992**, *31*, 4038. (d) Petrie, M. A.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **1993**, 1737. (e) Ellison, J. J.; Ruhlandt-Senge, K.; Power, P. P. Unpublished results. (f)

Atwood, D. A.; Cowley, A. H.; Jones, R. A.; Mardones, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 7050. (g) Arif, A. M.; Benac, B. L.; Cowley, A. H.; Geerts, R.; Jones, R. A.; Kidd, K. B.; Power, J. M.; Schwab, S. T. *J. Chem. Soc., Chem. Commun.* **1986**, 1543. (h) Alcock, N. W.; Degnan, I. A.; Wallbridge, M. G. H.; Powell, H. R.; McPartlin, M. *J. Organomet. Chem.* **1989**, *361*, C33. (i) Byrne, E. K.; Parkany, L.; Theopold, K. H. *Science* **1988**, *241*, 332. (j) Higa, K. T.; George, C. *Organometallics* **1990**, *9*, 275. (k) Wells, R. L.; Self, M. F.; Baldwin, R. A.; White, P. S. *J. Coord. Chem.* **1994**, *33*, 279. (l) Pitt, C. G.; Higa, K. T.; McPhail, A. T.; Wells, R. L. *Inorg. Chem.* **1986**, *25*, 2483.

(95) (a) Allen, T. L.; Scheiner, A. C.; Schaefer, H. F. *Inorg. Chem.* **1990**, *29*, 1930. (b) Allen, T. L.; Fink, W. H. *Inorg. Chem.* **1992**, *31*, 1703. (c) Allen, T. L.; Fink, W. H. *Inorg. Chem.* **1993**, *32*, 4230. (d) Davy, R. D.; Jaffrey, K. L. *J. Phys. Chem.* **1994**, *98*, 8930. (e) Müller, J. *J. Am. Chem. Soc.* **1996**, *118*, 6370. (f) Fink, W. H.; Power, P. P.; Allen, T. L. *Inorg. Chem.* **1997**, *36*, 1431.

(96) (a) Barfield, P.; Lappert, M. F.; Lee, J. *Proc. Chem. Soc. London* **1961**, 421. (b) Barfield, P.; Lappert, M. F.; Lee, J. *Trans. Faraday Soc.* **1968** *64*, 2571. (c) Watanabe, H.; Totini, T.; Tori, K.; Nakagawa, T. *Proc. Colloq. AMPERE* **1965**, *13*, 374. (d) Imbrey, P.; Jaeschke, A.; Friebolin, H. *Org. Magn. Reson.* **1970**, *2*, 271. (e) Neilson, R.; Wells, R. L. *Inorg. Chem.* **1977**, *16*, 7.

(97) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford 1984.

(98) The most well-known empirical correction formulae are those of Shomaker and Stevenson ($r_{A-B} = r_A + r_B - 0.09|EN_A - EN_B|$) (ref 98a) and Blom and Haaland ($r_{AB} = r_A + r_B - 0.085|EN_A - EN_B|^{1.4}$) (ref 98b). The former scheme has been criticized for its inaccuracy and empirical character (ref 98c). Nonetheless, there can be little doubt that the correction schemes (especially that given in ref 98b) give approximately correct answers in many instances. (a) Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37. (b) Blom, R.; Haaland, A. *J. Mol. Struct.* **1985**, *128*, 21. (c) Wells, A. F. *J. Chem. Soc.* **1949**, 55.

(99) (a) Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 7029. (b) Ashby, M. T.; Sheshtawy, N. A. *Organometallics* **1994**, *13*, 236.

(100) (a) Davidson, F.; Wilson, J. W. *J. Organomet. Chem.* **1981**, *204*, 147. (b) Wehmschulte, R. J.; Ruhlandt-Senge, K.; Olmstead, M. M.; Petrie, M. A.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **1994**, 2113.

(101) (a) Brandhaugen, K.; Wisloff-Nielssen, E.; Seip, H. M. *Acta Chem. Scand.* **1973**, *27*, 2965. (b) Johansen, R.; Wisloff-Nielssen, E.; Seip, H. M.; Siebert, W. *Acta Chem. Scand.* **1973**, *27*, 3015. (c) Hommer, H.; Nöth, H.; Knizek, J.; Ponikwar, W.; Schwenk-Kirchner, H. *Eur. J. Inorg. Chem.* **1998**, 1519. (d) Tokitoh, N.; Ito, M.; Okazaki, R. *Organometallics* **1995**, *14*, 4460.

(102) The structures of a number of compounds with bonding between three-coordinate boron and two-coordinate selenium are known. However, the boron center forms part of a ring or is substituted by $-NR_2$ groups which may compromise B−Se π bonding, see: Hanecker, E.; Nöth, H.; Wietelman, U. *Chem. Ber.* **1996**, *119*, 1904. Herberhold, M.; Dorfler, U.; Milius, W.; Wrackmeyer, B. *J. Organomet. Chem.* **1995**, *492*, 59.

(103) (a) Petrie, M. A.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8704. (b) Shreve, A. P.; Mulhaupt, R.; Fultz, W.; Calabrese, J.; Robbins, W.; Ittel, S. D. *Organometallics* **1988**, *7*, 409. (c) Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufinska, A.; Angermund, K.; Betz, P.; Goddard, R.; Krüger, C. *J. Organomet. Chem.* **1991**, *411*, 37. (d) Fisher, J. D.; Shapiro, P. J.; Budzelaar, P. H.; Staples, R. J. *Inorg. Chem.* **1998**, *37*, 1295. (e) Healy, M. D.; Barron, A. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 921. (f) Uhl, W.; Koch, M.; Pohl, S.; Saak, W.; Hiller, W.; Heckel, M. *Z. Naturforsch., B* **1995**, *50*, 635. (g) Uhl, W.; Hiller, W.; Heckel, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 989. (h) Cleaver, W. M.; Barron, A. R. *Organometallics* **1993**, *12*, 1001. (i) Brothers, P. J.; Ruhlandt-Senge, K.; Power, P. P. Unpublished results. For a review of bulky aryloxide derivatives of aluminum, see: (j) Healy, M. D.; Power, M. B.; Barron, A. R. *Coord. Chem. Rev.* **1994**, *130*, 63.

(104) (a) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 2633. (b) Wehmschulte, R. J.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1995**, *34*, 2593. (c) Uhl, W.; Vester, A.; Hiller, J. *J. Organomet. Chem.* **1993**, *443*, 9. (d) Uhl, W.; Gerding, R.; Hahn, I.; Pohl, S.; Saak, W.; Reuter, H. *Polyhedron* **1996**, *15*, 3987. (e) Uhl, W.; Schütz, U. *Z. Naturforsch., B* **1994**, *49*, 931.

(105) (a) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 3683. (b) Uhl, W.; Layh, M.; Becker, G.; Klinkhammer, K. W.; Hildenbrand, T. *Chem. Ber.* **1992**, *125*, 1547. (c) Wuller, S. P.; Seligson, A. L.; Mitchell, G. P.; Arnold, J. *Inorg. Chem.* **1995**, *34*, 4854. (d) Uhl, W.; Schütz, U.; Hiller, W.; Heckel, M. *Organometallics* **1995**, *14*, 1073.

(106) (a) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 3478. (b) Rahbarnoohi, H.; Wells, R. L.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **1996**, *15*, 3898. (c) Uhl, W.; Graupner, R.; Reuter, H. *J. Organomet. Chem.* **1996**, *523*, 227.

(107) (a) Weese, K. J.; Bartlett, R. A.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1987**, *26*, 2409. (b) Beck, G.; Hitchcock, P. B.; Lappert, M. F.; McKinnon, I. A. *J. Chem. Soc., Chem. Commun.* **1989**, 1312. (c) Köster, R.; Seidel, G.; Bläser, D.; Boese, R. *Z. Naturforsch., B* **1994**, *49*, 370. (d) Gibson, V. C.; Redshaw, C.; Clegg, W.; Elsegood, M. R. J. *Polyhedron* **1997**, *16*, 2637.

(108) Ito, M.; Tokitoh, N.; Okazaki, R. *Organometallics* **1997**, *16*, 4314.

(109) Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 317.

(110) (a) Goldberg, D. E.; Harris, D. H.; Lappert, M. F.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1976**, 261. (b) Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Fjelberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2387. (c) Lappert, M. F. *Adv. Chem. Ser.* **1976**, *150*, 256.

(111) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343.

(112) (a) Fink, M. J.; Michalczyk, M. J.; Haller, K.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793. (b) Shepherd, B. D.; Campana, C. F.; West, R. *Heteroatom. Chem.* **1990**, *1*, 1. (c) Wind, M.; Powell, D. R.; West, R. *Organometallics* **1996**, *15*, 5772.

(113) There are, however, a number of reactions of $[Sn\{CH(SiMe_3)_2\}_2]_2$ which give products with Sn−Sn bonds, see: (a) Weidenbruch, M.; Schäfer, A. M.; Kilian, H.; Pohl, S.; Saak, W.; Marsmann, H. *Chem. Ber.* **1992**, *125*, 563. (b) Grützmacher, H.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1017. (c) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 834.

(114) Since the publication of the first stable disilene, the area has been regularly reviewed, see: (a) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 413. (b) Cowley, A. H. *Acc. Chem. Res.* **1984**, *17*, 386. (c) Cowley, A. H. *Polyhedron* **1984**, *3*, 389. (d) Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1. (e) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (f) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York 1989; p 1015. (g) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (h) Weidenbruch, M. *Coord. Chem. Rev.* **1994**, *130*, 275. (i) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. For a recent review of the structural chemistry of organosilicon compounds including disilenes and other silicon−element multiply bonded species, see: (j) Kaftory, M.; Kapon, M.; Botoshansky, M. *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds., Wiley: Chichester, 1998; Vol. 2, Part 1, Chapter 5, pp 181−265.

(115) (a) Shepherd, B. D.; Powell, D. R.; West, R. *Organometallics* **1989**, *8*, 2664. (b) Masamune, S.; Murakami, S.; Snow, J.; Tobita, H.; Williams, D. J. *Organometallics* **1984**, *3*, 333. (c) Watanabe, H.; Takeuchi, K.; Fukawa, N.; Kato, M.; Goto, M.; Nagai, Y. *Chem. Lett.* **1987**, 1341. (d) Archibald, R. S.; van den Winkel, Y.; Millevolte, A. J.; Desper, J. M.; West, R. *Organometallics* **1992**, *11*, 3276. (e) Suzuki, H.; Tokitoh, N.; Okazaki, R.; Harada, J.; Ogawa, K.; Tomoda, S.; Goto, M. *Organometallics* **1995**, *14*, 1016. (f) Kira, M.; Maruyama, T.; Kabuto, C.; Ebata, K.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1489. (g) Tokitoh, N.; Suzuki, H.; Okazaki, R.; Ogawa, K. *J. Am. Chem. Soc.* **1993**, *115*, 10428.

(116) (a) Ichinoke, M.; Matsuno, T.; Sekiguchi, A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2194. (b) Kira, M.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1996**, *118*, 10303. (c) Weidenbruch, M.; Wilms, S.; Saak, W.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2503. (d) Wiberg, N.; Auer, H.; Nöth, H.; Knizek, J.; Polborn, K. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2869. (e) Grybat, A.; Boomgaarden, S.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2010.

(117) The earliest measurements of cis−trans isomerization afforded free energies of activation in the range 24.4−27.0 kcal mol^{-1} for the disilenes $[Si(Mes)R]_2$ [R = t-Bu or $-N(SiMe_3)_2$], see: (a) Michalczyk, M. J.; West, R. J.; Michl, J. *Organometallics* **1985**, *4*, 826. Further measurements are in refs 114 g and 117a and (b) Batcheller, S. A.; Tsumuraya, T.; Tempkin, O.; Davis, W. M.; Masamune, S. *J. Am. Chem. Soc.* **1990**, *112*, 9394.

(118) Olbrich, G.; Potzinger, P.; Riemann, B. *Organometallics* **1984**, *3*, 1267.

(119) West, R.; Cavalieri, J. D.; Buffy, J. J.; Fry, C.; Zilm, K. W.; Duchamp, J. C.; Kira, M.; Iwamoto, T.; Müller, T.; Apeloig, Y. *J. Am. Chem. Soc.* **1997**, *117*, 4972.

(120) (a) Snow, J. T.; Murukami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, *25*, 4191. (b) Weidenbruch, M.; Stürmann, M.; Kilian, H.; Pohl, S.; Saak, W. *Chem. Ber., Recl.* **1997**, *130*, 735. (c) Kira, M.; Iwamoto, T.; Miruyama, T.; Kabuto, C.; Sakurai, H. *Organometallics* **1996**, *15*, 3767. (d) Hitchcock, P. B.; Lappert, M. F.; Miles, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 480. (e) Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, *16*, 1920. (f) Schäfer, A.; Saak, W.; Weidenbruch, M.; Marsmann, H.; Henkel, G. *Chem. Ber., Recl.* **1997**, *130*, 1733. (g) Schäfer, A.; Saak, W.; Weidenbruch, M. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1405. (h) Sekiguchi, A.; Yamazaki, H.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1995**, *117*, 8025. (i) Sekiguchi, A.; Tsukamoto, M.; Ichinoke, M. *Science* **1997**, *275*, 5296. (j) Olmstead, M. M.; Pu, L.; Simons, R. S.; Power, P. P. *J. Chem. Soc., Chem. Commun.*

1997, 1595. (k) Schäfer, H.; Saak, W.; Weidenbruch, M. *Organometallics* **1999**, *18*, 3159.

(121) For recent reviews on various aspects of multiply bonded compounds of germanium and tin, see ref 9 and (a) Escudie, J.; Couret, C.; Ranaivonjatovo, H.; Satgé, J. *Coord. Chem. Rev.* **1994**, *130*, 427. (b) Rivière, P.; Rivière-Baudet, M.; Satgé, J. *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Ed. Davies, A. G., Elsevier: Oxford, 1995; Vol. 2, Chapter 5, p 137. (c) Davies, A. G. *Comprehensive Organometallic Chemistry II*; Elsevier: Oxford, 1995;Chapter 6, p 305. (d) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275. (e) Escudie, J.; Couret, C.; Ranaivonjatovo, H. *Coord. Chem. Rev.* **1998**, *178−180*, 565. (f) Barrau, J.; Rima, G. *Coord. Chem. Rev.* **1998**, *178−180*, 593. (g) Rivière-Baudet, M. *Main Group Metal Chem.* **1995**, *118*, 353. (h) Escudie, J.; Ranaivonjatovo, H. *Adv. Organomet. Chem.* **1999**, *44*, 113.

(122) (a) Grev, R. S.; Schaefer, H. F.; Baines, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 9458. (b) Kishikawa, K.; Tokitoh, N.; Okazaki, R. *Chem. Lett.* **1998**, 239.

(123) (a) Klinkhammer, K. W.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1334. (b) Klinkhammer, K. W.; Fässler, T. F.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 124. (c) Weidenbruch, M.; Kilian, H.; Peters, H.; Schnering, H. G. V.; Marsmann, H. *Chem. Ber.* **1995**, *128*, 983. (d) Leung, W. P.; Kwok, W.-H.; Xue, F.; Mak, T. C. W. *J. Am. Chem. Soc.* **1997**, *119*, 1145. (e) Drost, C.; Hitchcock, P. B.; Lappert, M. F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1113. (f) Layh, U.; Pritzkow, H.; Grützmacher, H. *J. Chem. Soc., Chem. Commun.* **1992**, 260. (g) Wiberg, N.; Lerner, H.-W.; Visisht, S.-K.; Wagner, S.; Karaghiosoff, K.; Nöth, H.; Ponikwar, W. *Eur. J. Inorg. Chem.* **1999**, 1211.

(124) (a) Stürmann, M.; Weidenbruch, M.; Klinkhammer, K. W.; Kissner, F.; Marsmann, H. *Organometallics* **1998**, *17*, 4425. (b) Stürmann, M.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 187. (c) Stürmann, M.; Saak, W.; Weidenbruch, M.; Klinkhammer, K. W. *Eur. J. Inorg. Chem.* **1999**, 579. (d) Data for this compound were cited in ref 124a.

(125) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268.

(126) For a review of low-coordinate organolead compounds, see: Kano, N.; Tokitoh, N.; Okazaki, R. *Synth. Org. Chem. Jpn.* **1998**, *56*, 919.

(127) (a) Dobbs, K. D.; Hehre, W. *Organometallics* **1996**, *5*, 2057. (b) Trinquier, J. *J. Am. Chem. Soc.* **1990**, *112*, 2130. (c) Windhus, T. L.; Gordon, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 9559.

(128) For recent reviews, see ref 121e and (a) Brook A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71. (b) Müller, T.; Ziche, W.; Auner, N. *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Z. Y., Eds.; Wiley: Chichester, 1998; Vol. 2, Part 2, Chapter 16.

(129) (a) Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R. *J. Chem. Soc., Chem. Commun.* **1981**, 191. (b) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ny, W. *J. Am. Chem. Soc.* **1982**, *104*, 567.

(130) (a) Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229. (b) Apeloig, Y.; Bendikov, M.; Yuzefovich, M.; Nakash, M.; Bravo-Zhivotovskii, D.; Bläser, D.; Boese, R. *J. Am. Chem. Soc.* **1996**, *118*, 12228. (c) Boesfeld, W. M.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1999**, 755.

(131) (a) Miracle, G. E.; Ball, J. L.; Powell, D. R.; West, R. *J. Am. Chem. Soc.* **1993**, *115*, 11958. (b) Trommer, M.; Miracle, G. E.; Eichler, B. E.; Powell, D. R.; West, R. *Organometallics* **1997**, *16*, 5737.

(132) Lukevics, E.; Pudova, O.; Sturkovich, R. *Molecular Structure of Organosilicon Compounds*; Ellis Horwood: Chichester, 1989.

(133) (a) Lazraq, M.; Escudie, J.; Couret, C.; Satgé, J.; Drager, M.; Dammel, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 828. (b) Meyer, H.; Baum, G.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 798.

(134) (a) Eichler, B. E.; Powell, D. R.; West, R. *Organometallics* **1998**, *17*, 2147. (b) Tokitoh, N.; Kishikawa, K.; Okazaki, R. *Chem. Lett.* **1998**, 811. (c) Ramdane, H.; Ranaivonjatovo, H.; Escudie, J.; Mathieu, S.; Knouzi, N. *Organometallics* **1996**, *15*, 3070. (d) Jouany, C.; Trinquier, G. *Organometallics* **1997**, *16*, 3148.

(135) (a) Meyer, H.; Baum, G.; Massa, W.; Berger, S.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *26*, 5546. (b) Weidenbruch, M.; Kilian, H.; Stürmann, M.; Pohl, S.; Saak, W.; Marsmann, H.; Steiner, D.; Berndt, A. *J. Organomet. Chem.* **1997**, *530*, 255. (c) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1157. (d) Weidenbruch, M.; Stabenow, F.; Saak, W. *J. Chem. Soc., Chem. Commun.* **1999**, 1131.

(136) (a) Baines, K. M.; Cooke, J. A. *Organometallics* **1991**, *10*, 3419. (b) Baines, K. M.; Cooke, J. A. *Organometallics* **1992**, *11*, 3487. (c) Baines, K. M.; Cook, J. A.; Dixon, C. E.; Liu, H. W.; Netherton, M. R. *Organometallics* **1994**, *13*, 631.

(137) (a) Drost, P. B.; Hitchcock, P. B.; Lappert, M. F.; Pierssens, L. J.-M. *Chem. Commun.* **1997**, 1141. (b) Drost, C.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1997**, 1845.

(138) Chaubon, M.-A.; Escudie, J.; Ranaivonjatovo, H.; Satgé, J. *J. Chem. Soc., Chem. Commun.* **1996**, 2621.

(139) Scotti, N.; Zachwieja, U.; Jacobs, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1503.

(140) Becker, G. *Z. Anorg. Allg. Chem.* **1976**, *423*, 242.

(141) (a) Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart 1990; Section D, Chapter 4. (b) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998. (c) Corbridge, D. E. C. *Phosphorus: An Outline of its Chemistry, Biochemistry and Technology*, 5th ed.; Elsevier: Amsterdam, 1995.

(142) Bruna, P. J.; Krumbach, V.; Peyerimhoff, S. D. *Can. J. Chem.* **1985**, *63*, 1594.

(143) Lacombe, S.; Gorbeau, D.; Cabioch, J.-L.; Pellerin, B.; Denis, J.-M.; Pfister-Guillozo, G. *J. Am. Chem. Soc.* **1988**, *110*, 6964.

(144) (a) Appel, R.; Menzel, J.; Knoch, F.; Volz, P. *Z. Anorg. Allg. Chem.* **1986**, *534*, 100. (b) Yoshifuji, M.; Toyota, K.; Shibayama, K.; Inamoto, N. *Chem. Lett.* **1983**, 1183. (c) Yoshifuji, M.; Toyota, K.; Inamoto, N. *Tetrahedron Lett.* **1985**, *26*, 1727.

(145) Becker, G.; Gutekunst, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 463.

(146) (a) Klebach, T. C.; van Dongen, H.; Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 395. (b) Märkl, G.; Lieb, F. *Tetrahedron Lett.* **1967**, *8*, 3484.

(147) Weber, L. *Chem. Ber.* **1996**, *129*, 367.

(148) (a) Decken, A.; Carmalt, C.; Clyburne, J. A. C.; Cowley, A. H. *Inorg. Chem.* **1997**, *36*, 3741. (b) Weber, L.; Uthmann, S.; Torwieke, B.; Kirchoff, R. *Organometallics* **1997**, *16*, 3188. (c) Driess, M.; Pritzkow, H. *J. Chem. Soc., Chem. Commun.* **1993**, 1585. (d) Weber, L.; Meine, G.; Boese, R.; Bungardt, D. *Z. Anorg. Allg. Chem.* **1987**, *549*, 73. (e) Driess, M.; Pritzkow, H.; Sander, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 283. (f) Gamon, N.; Reichardt, C.; Allmann, R.; Waskowska, A. *Chem. Ber.* **1981**, *114*, 3289. (g) Albers, T.; Grobe, J.; Le Van, D.; Krebs, B.; Läge, M. *Z. Naturforsch., B* **1995**, *50*, 94. (h) Weber, L.; Kaminski, O.; Stammler, H. G.; Neumann, B. *Chem. Ber.* **1996**, *129*, 223.

(149) (a) Becker, G.; Becker, W.; Schmidt, M.; Schwartz, W.; Westerhausen, M. *Z. Anorg. Allg. Chem.* **1991**, *605*, 7. (b) Driess, M.; Pritzkow, H.; Sander, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 283.

(150) Weber, L.; Scheffer, M.; Stammler, H.-G.; Neumann, B. *Eur. J. Inorg. Chem.* **1998**, 55.

(151) Ranaivonjatovo, H.; Ramdane, H.; Gornitzka, H.; Escudie, J.; Satgé, J. *Organometallics* **1998**, *17*, 1631.

(152) (a) Dobbs, K. D.; Boggs, J. E.; Cowley, A. H. *Chem. Phys. Lett.* **1987**, *141*, 372. (b) Lohr, L. L.; Scheiner, A. C. *J. Mol. Struct.* **1984**, *109*, 195.

(153) Data for Sb and Bi compounds were cited in ref 147.

(154) (a) Arduengo, A. J.; Carmalt, C. J.; Clyburne, J. A. C.; Cowley, A. H.; Pyati, R. *J. Chem. Soc., Chem. Commun.* **1997**, 981. (b) Arduengo, A. J.; Calabrese, J. C.; Cowley, A. H.; Dias, H. V. R.; Goerlich, J. R.; Marshall, W. J.; Reigel, B. *Inorg. Chem.* **1997**, *36*, 2151.

(155) (a) Hitchcock, P. B.; Jones, C.; Nixon, J. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 492. (b) Jones, C.; Steed, J. W.; Thomas, R. C. *J. Chem. Soc., Dalton Trans.* **1999**, 1541. (c) Durkin, J.; Hibbs, D. F.; Hitchcock, P. B.; Hursthouse, M. B.; Jones, C.; Jones, J.; Malik, K. M. A.; Nixon, J. F.; Parry, G. *J. Chem. Soc., Dalton Trans.* **1996**, 3277. (d) Andrews, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1997**, 1183.

(156) Bürger, H.; Eujen, R. *J. Mol. Struct.* **1983**, *98*, 265.

(157) (a) Walter, S.; Klingebiel, U. *Coord. Chem. Rev.* **1994**, *130* 481. (b) Hemme, I.; Klingebiel, U. *Adv. Organomet. Chem.* **1996**, *39*, 159.

(158) (a) Wiberg, N.; Schurz, K.; Fischer, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1053. (b) Wiberg, N.; Schurz, K. *Chem. Ber.* **1988**, *121*, 581. (c) Wiberg, N.; Schurz, K.; Reber, G.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1986**, 591. (d) Reber, G.; Riede, J.; Wiberg, N.; Schurz, K.; Müller, G. *Z. Naturforsch, B* **1988**, *44B*, 786. (e) Grosskopf, D.; Marcus, L.; Klingebiel, U.; Noltemeyer, M. *Phosphorus Sulfur Silicon Relat. Elem.* **1994**, *97*, 113. (f) Boese, R.; Klingebiel, U. *J. Organomet. Chem.* **1986**, *315*, C17. (g) Stalke, D.; Piper, U.; Vollbrecht, S.; Klingebiel, U. *Z. Naturforsch.* **1990**, *45b*, 1513. (h) Klingebiel, U.; Noltemeyer, M.; Schmidt, H.-G.; Schmidt-Bäse, D. *Chem. Ber, Recl.* **1997**, *130*, 753.

(159) Niesmann, J.; Klingebiel, U.; Schäfer, M.; Boese, R. *Organometallics* **1998**, *17*, 947.

(160) (a) Schleyer, P. v. R.; Stout, P. D. *J. Chem. Soc., Chem. Commun.* **1986**, 1373. (b) Truong, T. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 1775.

(161) Ang, H. G.; Lee, F. K. *J. Chem. Soc., Chem. Commun.* **1989**, 310.

(162) (a) Ando, W.; Ohtaki, T.; Kabe, Y. *Organometallics* **1994**, *13*, 434. (b) Veith, M.; Becker, S.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 216. (c) Meller, A.; Ossig, G.; Maringgele, W.; Stalke, D.; Herbst-Irmer, R.; Freitag, S.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1991**, 1123. (d) Veith, M.; Rammo, A. *Z. Anorg. Allg. Chem.* **1997**, *623*, 861. (e) Ohtaki, T.; Kabe, Y.; Ando, Y. *Heteroatom Chem.* **1994**, *5*, 313.

(163) Trinquier, G.; Barthelat, J.-C.; Satgé, J. *J. Am. Chem. Soc.* **1982**, *104*, 5931.

(164) Ossig, G.; Meller, A.; Freitag, S.; Herbst-Irmer, R. *J. Chem. Soc., Chem. Commun.* **1993**, 497.

(165) (a) Driess, M. *Coord. Chem. Rev.* **1995**, *145*, 1. (b) Driess, M. *Adv. Organomet. Chem.* **1996**, *39*, 193.

(166) Smit, C. N.; Look, F. M.; Bickelhaupt, F. *Tetrahedron Lett.* **1984**, *25*, 3011.

(167) (a) Dykema, K. J.; Truong, T. N.; Gordon, M. *J. Am. Chem. Soc.* **1985**, *107*, 4535. (b) Lee, L. G.; Boggs, J. E.; Cowley, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 773.

(168) Driess, M.; Janoschek, R. *J. Mol. Struct.* **1994**, *313*, 129.

(169) (a) Bender, H. R.; Niecke, E.; Nieger, M. *J. Am. Chem. Soc.* **1993**, *115*, 3314. (b) Driess, M.; Rell, S.; Pritzkow, H. *J. Chem. Soc., Chem. Commun.* **1995**, 253. (c) Driess, M.; Pritzkow, H.; Rell, S.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1326.

(170) (a) Drager, M.; Escudie, J.; Couret, C.; Ranaivonjatovo, H.; Satgé, J. *Organometallics* **1988**, *7*, 1010. (b) Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Satgé, J.; Drager, M. *New J. Chem.* **1989**, *13*, 389.

(171) (a) Grützmacher, H.; Marchand, C. M. *Coord. Chem. Rev.* **1997**, *163*, 287. (b) Guerret, O.; Bertrand, G. *Acc. Chem. Res.* **1997**, *20*, 4436.

(172) (a) Bernardi, F.; Csizmadia, I. G.; Epiotis, N. D. *Tetrahedron* **1975**, *31*, 3085. (b) Lohr, L. L.; Schegel, H. B.; Morokuma, K. *J. Chem. Phys.* **1984**, *88*, 1981. (c) Schade, C.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1399. (d) Schleyer, P. v. R. *Pure Appl. Chem.* **1987**, *59*, 1647. (e) White, J. C.; Cave, R. J.; Davidson, E. R. *J. Am. Chem. Soc.* **1988**, *110*, 6308. (f) Ehrig, M.; Horn, H.; Kölmel, C.; Ahlrichs, R. *J. Am. Chem. Soc.* **1991**, *113*, 3701. (g) Heim, U.; Pritzkow, H.; Schönberg, H.; Grützmacher, H. *J. Chem. Soc., Chem. Commun.* **1993**, 673. (h) Kapp, J.; Schade, C.; El-Nahas, A. M.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2236. (i) Grützmacher, H.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 99. (j) Grützmacher, H.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 709. (k) Igau, A.; Baceiredo, A.; Grützmacher, H.; Pritzkow, H.; Bertrand, G. *J. Am. Chem. Soc.* **1989**, *111*, 6853.

(173) For a review of stable thio- and selenoaldehydes and ketones, see: (a) Tokitoh, N.; Okazaki, R. *Polish J. Chem.* **1998**, *72*, 971. (b) Okazaki, R. In *Organosulfur Chemistry*; Page, P. D., Ed.; Academic Press: London, 1995; Chapter 5, p 225. (c) Okazaki, R.; Ishii, A.; Fukuda, N.; Oyama, H.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1982**, 1187. (d) Okazaki, R.; Kumon, N.; Inamoto, N. *J. Am. Chem. Soc.* **1989**, *111*, 5949. (e) Minoura, M.; Kawashima, T.; Okazaki, R. *Tetrahedron Lett.* **1997**, *38*, 2501.

(174) (a) Tokitoh, N.; Takeda, N.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 7907. (b) Takeda, N.; Tokitoh, N.; Okazaki, R. *Chem. Eur. J.* **1997**, *3*, 62. (c) Takeda, N.; Tokitoh, N.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 660.

(175) (a) Takeda, N.; Tokitoh, N.; Okazaki, R. *Tetrahedron* **1997**, *53* 12167. (b) For a review of transition metal complexes of heavier element aldehydes and ketones, see: Fischer, H.; Stumpf, R.; Roth, G. *Adv. Organomet. Chem.* **1998**, *43*, 125.

(176) (a) Tokitoh, N. *J. Synth. Org. Jpn.* **1994**, *52*, 58 (see also ref 177b). (b) Tokitoh, N.; Okazaki, R. *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; Vol. 2, Part 2, Chapter 17.

(177) (a) Suzuki, H.; Tokitoh, N.; Nagase, S.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 11578. (b) Tokitoh, N.; Suzuki, H.; Matsumoto, T.; Matsuhashi, Y.; Okazaki, R.; Goto, M. *J. Am. Chem. Soc.* **1991**, *113*, 7047. (c) Suzuki, H.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Goto, M. *J. Am. Chem. Soc.* **1998**, *120*, 11096. (d) Hoeft, J.; Lovas, F. J.; Tiemann, E.; Törring. *Z. Naturforsch/* **1969**, *24A*, 1422.

(178) Arya, P.; Boyer, J.; Carré, F.; Corriu, R.; Lanneau, G.; Lapasset, M.; Perrot, M.; Priou, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 6.

(179) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *Chem. Lett.* **1995**, 1087.

(180) (a) Jutzi, P.; Schmidt, H.; Neumann, B.; Stammler, H.-G. *Organometallics* **1996**, *15*, 741. (b) Lange, L.; Meyer, B.; du Mont, W.-W. *J. Organomet. Chem.* **1987**, *328*, C17.

(181) Veith, M.; Becker, S.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1988**, *28*, 1237.

(182) Kuchta, M. C.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1994**, 1351.

(183) (a) Foley, S. A.; Bensimon, C.; Richeson, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 10359. (b) Zhou, Y.; Richeson, D. S. *J. Am. Chem. Soc.* **1996**, *118*, 10850.

(184) Ossig, G.; Meller, A.; Brönneke, C.; Müller, O.; Schäfer, M.; Herbst-Irmer, R. *Organometallics* **1997**, *16*, 2116.

(185) (a) Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855. (b) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2316. (c) Tokitoh, N.; Matsuhashi, Y.; Shibata, K.; Matsumoto, T.; Suzuki, H.; Saito, M.; Manmaru, K.; Okazaki, R. *Main Group Metal Chem.* **1994**, *17*, 55. (d) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1999**, *121*, 8811.

(186) Kuchta, M. C.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 8372.

(187) Leung, W.-P.; Kwok, W.-H.; Low, T. C.; Zhou, Z. Y.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1996**, 505.

(188) (a) Saito, M.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1997**, *119*, 11124. For the synthesis of Tbt(Ditp)Sn=Se, see: (b) Saito, M.; Tokitoh, N.; Okazaki, R. *J. Organomet. Chem.* **1995**, *499*, 43.

(189) Kapp, J.; Remko, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1996**, *118*, 5745.

(190) Kano, N.; Tokitoh, N.; Okazaki, R. *Chem. Lett.* **1997**, 277.

(191) Niecke, E.; Flick. W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 585.

(192) Niecke, E. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, 1990; Section D, Chapter 8. Niecke, E.; Gudat, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 217.

(193) (a) Trinquier, G. *J. Am. Chem. Soc.* **1982**, *104*, 6969. (b) Nguyen, M.-T.; McGinn, M. A.; Hegarty, A. F. *J. Am. Chem. Soc.* **1985**, *107*, 3029. (c) Gonbeau, J.-L.; Garcia, J.-L.; Pfister-Guillouzo, G. *Can. J. Chem.* **1986**, *64*, 1530.

(194) Schoeller, W. W.; Busch, T.; Niecke, E. *Chem. Ber.* **1990**, *123*, 1653.

(195) For a concise discussion of theoretical data on iminophosphines and related multiply bonded phosphorus species, see: Schoeller, W. W. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, 1990, Section B.

(196) Gudat, D.; Schiffner, H. M.; Nieger, M.; Stalke, D.; Blake, A. J.; Grondey, H.; Niecke, E. *J. Am. Chem. Soc.* **1992**, *114*, 8857.

(197) Hitchcock, P. B.; Lappert, M. F.; Rai, A. K.; Williams, H. D. *J. Chem. Soc., Chem. Commun.* **1986**, 1633.

(198) Wirringa, U.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1628.

(199) Ahlemann, J.-T.; Künzel, A.; Roesky, H. W.; Noltemeyer, M.; Markovskii, L.; Schmidt, H.-G. *Inorg. Chem.* **1996**, *35*, 6644.

(200) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587.

(201) For reviews see, refs 5, 114b−d, and (a) Yoshifuji, M. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, 1990; Section D, Chapter 9. (b) Yoshifuji, M. *J. Chem. Soc., Dalton Trans.* **1998**, 3343.

(202) The most recent comprehensive treatment is in Weber, L. *Chem. Rev.* **1992**, *92*, 1839.

(203) (a) This datum was cited as unpublished in Shah, S.; Burdette, S. C.; Swavey, S.; Urbach, F. L.; Protasiewicz, J. D. *Organometallics* **1997**, *16*, 3395. (b) Urnezius, E.; Protasiewicz, J. D. *Main Group Chem.* **1996**, *1*, 369.

(204) (a) Escudie, J.; Couret, C.; Ranaivonjatovo, H.; Satgé, J.; Jaud, J. *Phosphorus Sulfur* **1983**, *17*, 221. (b) Cowley, A. H.; Kilduff, J. E.; Norman, N. C.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 4845. (c) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Mehrotra, S. K.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R.; Atwood, J. L.; Hunter, W. E. *Inorg. Chem.* **1984**, *23*, 2582. (d) Cowley, A. H.; Knuppel, P. C.; Nunn, C. M. *Organometallics* **1989**, *8*, 2490.

(205) (a) Busch, T.; Schoeller, W. W.; Niecke, E.; Nieger, M.; Westermann, H. *Inorg. Chem.* **1989**, *28*, 4334. (b) Weber, L.; Kirchoff, R.; Boese, R.; Stammler, H.-G.; Neumann, B. *Organometallics* **1993**, *12*, 731. (c) Duboury, A.; Declereq, J.-P.; Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Lazraq, M. *Acta Crystallogr. C* **1988**, *C44*, 2004. (d) Zanin, A.; Karnop, M.; Jeske, J.; Jones, P. G.; du Mont, W.-W. *J. Organomet. Chem.* **1994**, *475*, 95.

(206) (a) Lübben, T.; Roesky, H. W.; Gornitzka, H.; Steiner, A.; Stalke, D. *Eur. J. Solid State Inorg. Chem.* **1995**, *32*, 121. (b) Weber, L.; Reizig, K.; Bungardt, D.; Boese, R. *Organometallics* **1987**, *6*, 110.

(207) Jutzi, P.; Meyer, U.; Krebs, B.; Dartmann, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 919.

(208) (a) Markovski, L. N.; Romanenko, V. D.; Ruben, A. V. *Chemistry of Acyclic Compounds of Two-coordinated Phosphorus*; Naukova Dumka: Kiev, 1988; p 199. (b) Chernega, A. N.; Antipin, M. Yu.; Struchkov, Yu. T.; Romanenko, V. D. *Zh. Strukt. Khim.* **1990**, *31*, 108.

(209) Hänssgen, D.; Aldenhoven, H.; Nieger, M. *J. Organomet. Chem.* **1989**, *375*, C9.

(210) Cowley, A. H.; Decken, A.; Norman, N. C.; Krüger, C.; Lutz, F.; Jacobsen, H.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 3389.

(211) Niecke, E.; Rüger, R.; Lysek, M.; Pohl, S.; Schoeller, W. W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 486.

(212) Niecke, E.; Altemeyer, O.; Nieger, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1136.

(213) Yoshifuji, M.; Abe, M.; Toyota, K.; Mijahara, I.; Hirotsu, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3831.

(214) Appel, R.; Niemann, B.; Schuhn, W.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 932.

(215) Niecke, E.; Kramer, B.; Nieger, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 215.

(216) (a) Yoshifuji, M.; Hashida, T.; Inamoto, N.; Hirotsu, K.; Nishimoto, K. *J. Am. Chem. Soc.* **1983**, *105*, 2495. (b) Cetinkaya, B.; Lappert, M. F.; Staufer, J. G.; Suffolk, R. J. *J. Electron Spectrosc. Phenom.* **1983**, *32*, 133. (c) Lee, J.-G.; Cowley, A. H.; Boggs, J. E. *Inorg. Chim. Acta* **1983**, *77* L61. Galasso, V. *Chem. Phys.* **1984**, *83*, 407. (d) Schoeller, W. W.; Stammler, H.-G. *Inorg. Chem.* **1984**, *23*, 3369. (e) Elbel, S.; Ellis, A.; Niecke, E.; Egsgaard, H.; Carlsen, L. *J. Chem. Soc., Dalton Trans.* **1985**, 879. (f) Yoshifuji, M.; Inamoto, N.; Ito, K.; Nagase, S. *Chem. Lett.* **1985**, 437. (g) Trinquier, G.; Bertrand, G. *Inorg. Chem.* **1985**, *24*, 3842. (h) Schmidt, M. W.; Gordon, M. S. *Inorg. Chem.* **1986**, *25*, 248. (i) Allen, T. L.; Scheiner, A. C.; Yamaguchi, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1986**, *108*, 7579. (j) Ito, K.; Nagase, S. *Chem. Phys. Lett.* **1986**, *126*, 531. (k) Allen, T. L.; Scheiner, A. C.; Schaefer, H. F. *J. Phys. Chem.* **1990**, *94*, 7780.

(217) Yoshifuji, M.; Hashida, T.; Inamoto, N.; Hirotsu, K.; Horiuchi, T.; Higuchi, T.; Ito, K.; Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 211.

(218) Caminade, A.-M.; Verrier, M.; Ades, C.; Paillous, N.; Koenig, M. *J. Chem. Soc., Chem. Commun.* **1984**, 875.

(219) Nagase, S.; Suzuki, S.; Kurakake, T. *J. Chem. Soc., Chem. Commun.* **1990**, 1724.

(220) (a) Cowley, A. H.; Lasch, J. G.; Norman, N. C.; Pakulski, M. *J. Am. Chem. Soc.* **1983**, *105*, 5506. (b) Couret, C.; Escudie, J.; Madaule, Y.; Ranaivonjatovo, H.; Wolf, J.-G. *Tetrahedron Lett.* **1983**, *24*, 2769. (c) Cowley, A. H.; Norman, N. C.; Pakulski, M. *J. Chem. Soc., Dalton Trans.* **1985**, 383. (d) Weber, L.; Sonneberg, U. *Chem. Ber.* **1989**, *122*, 1809.

(221) (a) Bürger, H.; Eujen, R. *J. Mol. Struct.* **1983**, *98*, 265. (b) Calderazzo, F.; Poli, R.; Pelizzi, G. *J. Chem. Soc., Dalton Trans.* **1984**, 2365.

(222) Cowley, A. H.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R. *J. Chem. Soc., Chem. Commun.* **1983**, 5659.

(223) Twamley, B.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1998**, 1979.

(224) Nguyen, M. T.; van Keer, A.; Vanquackenborne, L. G. *J. Organomet. Chem.* **1997**, *529*, 3 and references therein.

(225) (a) Dalby, F. W. *Can. J. Phys.* **1958**, *36*, 1336. (b) Brown, H. W.; Pimentel, G. C. *J. Chem. Phys.* **1958**, *29*, 883.

(226) (a) Collman, J. P.; Hoffman, N. W.; Morris, D. E. *J. Am. Chem. Soc.* **1969**, *91*, 5659. (b) Grundy, K. R.; Reed, C. A.; Roper, W. R. *J. Chem. Soc. Chem. Commun.* **1970**, 1501. (c) Wilson, R. D.; Ibers, J. A. *Inorg. Chem.* **1979**, *18*, 336. (d) Southern, J. S.; Hillhouse, G. L.; Rheingold, A. H. *J. Am. Chem. Soc.* **1997**, *119*, 12406.

(227) See: Godbout, N.; Sanders, L. K.; Salzmann, R.; Havlin, R. H.; Wojdelski, M.; Oldfield, E. *J. Am. Chem. Soc.* **1999**, *121*, 3829.

(228) Obermeyer, A.; Borrmann, H.; Simon, A. *J. Am. Chem. Soc.* **1995**, *117*, 7887.

(229) Binnewies, M.; Schnöckel, H. *Chem. Rev.* **1990**, *90*, 321.

(230) (a) Pandey, K. K. *Prog. Inorg. Chem.* **1992**, *40*, 2145. (b) Crevier, T. J.; Lovell, S.; Mayer, J. M.; Rheingold, A. L.; Guzei, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 6607.

(231) Quin, L. O.; Szewezyk, J. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, 1990; Section D, Chapter 11, p 352.

(232) (a) Niecke, E.; Engelmann, M.; Zorn, H.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 710. (b) Hitchcock, P. B.; Johnson, J. A.; Lemos, M. A. N. D. A.; Meidine, M. F.; Nixon, J. F.; Pombiero, A. J. L. *J. Chem. Soc., Chem. Commun.* **1992**, 645.

(233) Schoeller, W. W.; Niecke, E. *J. Chem. Soc., Chem. Commun.* **1982**, 569.

(234) (a) Binnewies, M.; Lakenbrink, M.; Schnöckel, H. *Z. Anorg. Allg. Chem.* **1983**, *497*, 7. (b) Binnewies, M. *Thermochim. Acta* **1983**, *67*, 387. (c) Binnewies, M.; Lakenbrink, M.; Schnöckel, H. *High Temp. Sci.* **1986**, *22*, 83. (d) Alrichs, R.; Becherer, R.; Binnewies, M.; Borrmann, H.; Lakenbrink, M.; Schunck, S.; Schnöckel, H. *J. Am. Chem. Soc.* **1986**, *108*, 7905.

(235) Binnewies, M.; Solouki, B.; Bock, H.; Becherer, R.; Alrichs, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 731.

(236) Schnöckel, H.; Schunck, S. *Z. Anorg. Allg. Chem.* **1987**, *548*, 161.

(237) Quin, L. D.; Jankowski, S.; Sommese, A. G.; Lahti, P.; Chesnut, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 11009.

(238) (a) Binnewies, M.; Borrmann, H. *Z. Anorg. Allg. Chem.* **1987**, *552*, 147. (b) Schnöckel, H.; Schunck, S. *Z. Anorg. Allg. Chem.* **1987**, *552*, 163. (c) Binnewies, M. *Z. Anorg. Allg. Chem.* **1983**, *507*, 66. (d) Schnöckel, H.; Lakenbrink, M. *Z. Anorg. Allg. Chem.* **1987**, *552*, 155.

(239) (a) Yoshifuji, M.; Hirano, M.; Toyota, K. *Tetrahedron Lett.* **1993**, *34*, 1043. (b) Yoshifuji, M.; Sangu, S.; Hirano, M.; Toyota, K. *Chem. Lett.* **1993**, 1715.

(240) Jochem, G.; Karaghiosoff, K.; Plank, S.; Dick, S.; Schmidpeter, A. *Chem. Ber.* **1995**, *128*, 1207.

(241) Wong, T.; Terlouw, J. K.; Keck, H.; Kuchen, W.; Tommes, P. *J. Am. Chem. Soc.* **1992**, *114*, 8208.

(242) (a) Bohle, D. S.; Rickard, C. E. F.; Roper, W. R.; Schwerdfeger, P. *Organometallics* **1990**, *9*, 2068. (b) Alper, H.; Einstein, F. W. B.; Petrignani, J.-F.; Willis, A. C. *Organometallics* **1983**, *2*, 1422. (c) Hussong, R.; Heydt, H.; Maas, G.; Regitz, M. *Chem. Ber.* **1987**, *120*, 1263.

(243) (a) Reference 97, p 896. (b) Reference 97, pp 486, 897.

(244) (a) Passmore, J.; Sutherland, G. W.; Whidden, T. K.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1980**, 288. (b) Murchie, M. P.; Johnson, J. P.; Passmore, J.; Sutherland, G. W.; Tajik, M.; Whidden, T. K.; White, P. S.; Grein, F. *Inorg. Chem.* **1992**, *31*, 273.

(245) Coppens, P.; Yang, Y. W.; Blessing, R. H.; Cooper, W. F.; Larsen, F. K. *J. Am. Chem. Soc.* **1997**, *99*, 7760.

(246) (a) Regitz, M. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, 1990; Section C, Chapter 2. (b) Regitz, M. *Chem. Rev.* **1990**, *90*, 191.

(247) (a) Scheer, M. *Coord. Chem. Rev.* **1997**, *163*, 271. (b) Cowley, A. H. *Acc. Chem. Res.* **1997**, *30*, 445.

(248) (a) Becker, G.; Gresser, G.; Uhl, W. *Z. Naturforsch.* **1981**, *36B*, 16. (b) Gier, T. E. *J. Am. Chem. Soc.* **1961**, *83*, 1769.

(249) (a) Saxena, A. K.; Zhang, M.; Maguire, J. A.; Hosmane, N. S.; Cowley, A. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 332. (b) Brown, D. S.; Decken, A.; Cowley, A. H. *J. Am. Chem. Soc.* **1995**, *117*, 5421.

(250) (a) Hunold, R.; Allwohn, J.; Baum, G.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 961. (b) Allwohn, J.; Pilz, M.; Hunold, R.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1032.

(251) (a) Alberts, I. L.; Schaefer, H. F. *Chem. Phys. Lett.* **1990**, *165*, 250. (b) Pyykkö, P. *Mol. Phys.* **1989**, *67*, 871.

(252) Paetzold, P. *Prog. Inorg. Chem.* **1987**, *31*, 123.

(253) Albrecht, T.; Elder, G.; Meller, A. *J. Chem. Soc., Chem. Commun.* **1998**, 2583.

(254) (a) Armstrong, D. R.; Clark, D. T. *Theor. Chim. Acta* **1972**, *24*, 307. (b) Baird, C.; Datta, R. K. *Inorg. Chem.* **1972**, *11*, 17.

(255) Kölle, P.; Linti, G.; Nöth, H.; Wood, G. L.; Narula, C. K.; Paine, R. T. *Chem. Ber.* **1987**, *121*, 871.

(256) Linti, G.; Nöth, H.; Polborn, K.; Paine, R. T. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 682.

(257) (a) Schutz, S.; Häming, L.; Herbst-Irmer, R.; Roesky, H. W.; Sheldrick, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 969. (b) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 791. (c) Fisher, J. D.; Shapiro, P. J.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 271. (d) Schulz, S.; Voigt, A.; Roesky, H. W.; Häming, L.; Herbst-Irmer, R. *Organometallics* **1996**, *15*, 5252. (e) Jutzi, P.; Neumann, B.; Reumann, G.; Stammler, H.-G. *Organometallics* **1999**, *18*, 2037. (f) Davy, R. D.; Jaffrey, K. L. *J. Phys. Chem.* **1994**, *98*, 8930. (g) Hamilton, T. P.; Shaikh, A. W. *Inorg. Chem.* **1997**, *36*, 754. (h) Davy, R. D.; Schaefer, H. F. *Inorg. Chem.* **1998**, *37*, 2291.

(258) (a) Atwood, D. A.; Cowley, A. H.; Jones, R. A.; Mardones, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 7050. (b) Hope, H.; Pestana, D. C.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 691.

(259) (a) Lory, E. R.; Porter, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 6301. (b) Kirk, R. W.; Timins, P. L. *J. Chem. Soc., Chem. Commun.* **1967**, 18. (c) Pearson, E. F.; McCormick, R. V. *J. Phys. Chem.* **1973**, *58*, 1619. (d) Pearson, E. F.; Norris, C. L.; Flygane, W. H. *J. Chem. Phys.* **1974**, *60*, 1761. (e) Fehlner, T. P.; Turner, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 7173. (f) Kroto, H. W.; Suffolk, R. J.; Westwood, N. C. P. *Chem. Phys. Lett.* **1973**, *22*, 495. (g) Kirby, C.; Kroto, H. W.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* **1978**, 19. (h) Kroto, H. W. *Chem. Soc. Rev.* **1982**, *11*, 435. (i) Cooper, T. A.; King, M. A.; Kroto, H. W.; Suffolk, R. J. *J. Chem. Soc., Chem. Commun.* **1981**, 354.

(260) Tokitoh, N.; Ito, M.; Okazaki, R. *Tetrahedron Lett.* **1996**, *37*, 5145.

(261) (a) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971. (b) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 8387. (c) Wehmschulte, R. J.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1998**, 335.

(262) (a) Schnöckel, H. *J. Mol. Struct.* **1978**, *50*, 267. (b) Alrichs, L.; Zhengyan, L.; Schnöckel, H. *Z. Anorg. Allg. Chem.* **1984**, *519*, 155.

(263) (a) Kuchta, M. C.; Parkin, G. *J. Am. Chem. Soc.* **1995**, *117*, 12651. (b) Kuchta, M. C.; Parkin, G. *Inorg. Chem.* **1997**, *36*, 2492. (c) Kuchta, M. C.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **1998**, 2279.

(264) Sekiguchi, A.; Zigler, S. S.; West, R. *J. Am. Chem. Soc.* **1986**, *108*, 4241.

(265) (a) Lischka, H.; Kohler, H.-J. *J. Am. Chem. Soc.* **1983**, *105*, 6646. (b) Binkley, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 603. (c) Kalcher, J.; Sax, A.; Olbrich, G. *Int. J. Quantum Chem.* **1984**, *25*, 543. (d) Kohler, H.-J.; Lischka, H. *Chem. Phys. Lett.* **1984**, *112*, 33. (e) Clabo, D. A.; Schaefer, H. F. *J. Chem. Phys.* **1986**, *84*, 1664.

(f) Thies, B. S.; Grev, R. S.; Schaefer, H. F. *Chem. Phys. Lett.* **1987**, *140*, 355. (g) Koseki, S.; Gordon, M. S. *J. Phys. Chem.* **1988**, *92*, 364. (h) Koseki, S.; Gordon, M. S. *J. Phys. Chem.* **1989**, *93*, 118. (i) Colegrove, B. T.; Schaefer, H. F. *J. Phys. Chem.* **1990**, *94*, 5593. (j) Colegrove, B. T.; Schaefer, H. F. *J. Am. Chem. Soc.* **1991**, *113*, 1557. (k) Grev, R. S.; Schaefer, K. F. *J. Chem. Phys.* **1992**, *97*, 7990.

(266) (a) Cordonnier, M.; Bogey, M.; Demuynck, C.; Destombes, J.-L. *J. Chem. Phys.* **1992**, *97*, 7984. (b) Bogey, M.; Bolvin, H.; Demuynck, C.; Destombes, J. L. *Phys. Rev. Lett.* **1991**, *66*, 413.

(267) (a) Grev, R. S.; De Leeuw, B. J.; Schaefer, H. F. *Chem. Phys. Lett.* **1990**, *165*, 257. (b) Palagyi, Z.; Schaefer, H. F.; Kapuy, E. *J. Am. Chem. Soc.* **1993**, *115*, 6901.

(268) Kobayashi, K.; Nagase, S. *Organometallics* **1997**, *16*, 2489.

(269) (a) Murrell, J. N.; Kroto, H. W.; Guest, M. F. *J. Chem. Soc., Chem. Commun.* **1977**, 619. (b) Hopkinson, A. C.; Lien, M. H. *J. Chem. Soc., Chem. Commun.* **1980**, 107. (c) Gordon, M. S.; Koob, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 2939. (d) Gordon, J. A.; Pople, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 2945. (e) Gordon, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 4352. (f) Hoffmann, M. R.; Yoshioka, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1983**, *105*, 1084. (g) Hopkinson, A. C.; Lien, M. H.; Csizmadia, I. G. *Chem. Phys. Lett.* **1983**, *95*, 232. (h) Sherill, C. D.; Schaefer, H. F. *J. Phys. Chem.* **1995**, *99*, 1949. (i) Nguyen, M. T.; Sengupta, D.; Vanquackenborne, L. G. *Chem. Phys. Lett.* **1995**, *244*, 83. (j) Stegman, R.; Frenking, G. *J. Comput. Chem.* **1996**, *17*, 781. (k) Hilliard, R. K.; Grev, R. S. *J. Chem. Phys.* **1997**, *107*, 8823. (l) Apeloig, Y.; Karni, M. *Organometallics* **1997**, *16*, 310. (m) Stogner, S. M.; Grev, R. S. *J. Chem. Phys.* **1998**, *108*, 5458. (n) Karni, M.; Apeloig, Y.; Schröder, D.; Zummack, W.; Rabezzana, R.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 332.

(270) Pu, L.; Haubrich, S. T.; Power, P. P. *J. Organomet. Chem.* **1999**, *582*, 100.

(271) Antipin, M. Y.; Chernega, A. N.; Lysenko, K. A.; Struchkov, Y. T.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1995**, 505.

(272) (a) Arif, A. M.; Barron, A.; Cowley, A. H.; Hall, S. W. *J. Chem. Soc., Chem. Commun.* **1988**, 171. (b) Data cited in ref 272k. (c) Oberhammer, G.; Becker, G.; Gresser, G. *J. Mol. Struct.* **1982**, *79*, 215. (d) Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C. *J. Mol. Spectrosc.* **1980**, *82*, 185. (e) Burckett-St. Laurent, J. C. T. R.; Cooper, T. A.; Kroto, H. W.; Nixon, J. F.; Ohashi, O.; Ohno, K. *J. Mol. Struct.* **1982**, *79*, 215. (f) Tyler, J. K. *J. Chem. Phys.* **1964**, *40*, 1170. (g) Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C. *J. Mol. Spectrosc.* **1979**, *77*, 270. (h) Burckett-St. Laurent, J. C. T. R.; Kroto, H. W.; Nixon, J. F.; Ohno, K. *J. Mol. Spectrosc.* **1982**, *92*, 158. (i) Becker, G.; Bohringer, M.; Gleiter, R.; Pfeifer, K.-H.; Grobe, J.; LeVan, D.; Hegemann, M. *Chem. Ber.* **1994**, *127*, 1041. (j) Becker, G.; Hubler, K. *Z. Anorg. Allg. Chem.* **1994**, *620*, 405. (k) Becker, G.; Schwarz, W.; Seidler, N.; Westerhausen, M. *Z. Anorg. Allg. Chem.* **1992**, *612*, 72.

(273) Burckett-St. Laurent, J. C. T. R.; King, M. A.; Kroto, H. W.; Nixon, J. F.; Suffolk, R. J. *J. Chem. Soc., Dalton Trans.* **1983**, 755.

(274) Laali, K. K.; Geissler, B.; Regitz, M.; Houser, J. J. *J. Org. Chem.* **1995**, *60*, 6362.

(275) Märkl, G. Seijka, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 286.

(276) Hitchcock, P. B.; Jones, C.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1994**, 2061.

(277) Schmidt, H. M.; Stoll, H.; Preuss, H.; Becker, G.; Mundt, O. *J. Mol. Struct.* (*THEOCHEM*) **1992**, *262*, 171.

(278) Guillemin, J.-C.; Lasalle, L.; Dreán, P.; Wlodarczak, G.; Demaison, J. *J. Am. Chem. Soc.* **1994**, *116*, 8930.

(279) Metail, V.; Serio, A.; Lasalle, L.; Guillemin, J.-C.; Pfitzner-Guillozo, G. *Organometallics* **1995**, *14*, 4732.

(280) Arnold, F. P.; Ridge, D. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1995**, *117*, 4427.

(281) (a) Ogilvie, J. F.; Cradock, S. *J. Chem. Soc. Chem Commun.* **1966**, 264. (b) Bock, H.; Dammel, R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 111. (c) Maier, G.; Glatthaar, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 473.

(282) (a) Creutzberg, F. *Can. J. Phys.* **1966**, *44*, 158. (b) Jones, W. E.; Flinn, C. G.; Yee, K. K. *J. Mol. Struct.* **1974**, *52*, 344. (c) Almy, G. M.; Schutz, H. A. *Phys. Rev.* **1937**, *51*, 62. (d) Data cited in ref 18b.

(283) (a) Niecke, E.; Nieger, M.; Reichert, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1715. (b) Buenker, R. J.; Bruna, P. J.; Peyerimhoff, S. *Isr. J. Chem.* **1980**, *19*, 309. (c) Niecke, E.; Detsch, R.; Nieger, M.; Reichert, F.; Schoeller, W. W. *Bull. Soc. Chim. Fr.* **1993**, *130*, 25. (d) Burford, N.; Clyburne, J. A. C.; Bakshi, P. K.; Cameron, T. S. *J. Am. Chem. Soc.* **1993**, *115*, 8829. (e) Burford, N.; Clyburne, J. A. C.; Bakshi, P. K.; Cameron, T. S. *Organometallics* **1995**, *14*, 1578. (f) Burford, N.; Clyburne, J. A. C.; Silvert, D.; Warner, S.; Whitla, A.; Darvesh, K. V. *Inorg. Chem.* **1997**, *36*, 482.

(284) Romanenko, V. D.; Rudzevich, V. L.; Rusanov, E. B.; Chernega, A. N.; Senio, A.; Sotiropoulos, J.-M.; Pfister-Guillouzo, G.; Sanchez, M. *J. Chem. Soc., Chem. Commun.* **1995**, 1383.

(285) While this relationship is usually observed, there are a few exceptions: Kaupp, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 1061.

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