

Reviews

Bonding and Reactivity of Heavier Group 14 Element Alkyne Analogues

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In this short review recent developments in the synthesis and spectroscopic characterization, as well as the bonding and reactivity, of heavier group 14 element alkyne analogues (REER, R = large aryl or silyl group; E = Si–Pb) are summarized. Stable¹ examples of such compounds have been known only since 2000, although their bonding has been studied by theoretical methods since the early 1980s. The use of very large substituents has enabled their isolation and the study of their reactions at room temperature. All the currently known compounds possess trans-bent planar core structures and nonbonded electron density at the tetrel (group 14 element). The bending increases with increasing atomic number, and when E = Pb the triple bonding seen in the lighter carbon homologue has been transformed into a single bond and two nonbonded electron pairs. To a crude approximation the bond order decreases by ca. 0.5 of a unit between elements upon descending the group. Currently available reactivity data show that the silicon and germanium derivatives are significantly more reactive than their tin or lead analogues. A “digermynes” has been shown to react directly with hydrogen under ambient conditions, suggesting the presence of some singlet diradical character. The “distannynes” have been shown to adopt either a multiply bonded structure similar to its germanium analogue or a singly bonded structure like the lead species. Much further work will be required to obtain a clearer picture of this exciting new class of molecules.

1. Introduction

Heavier group 14 element alkyne analogues are compounds of formula REER (R = H, alkyl, aryl, or silyl group; E = Si, Ge, Sn, or Pb). They have been a focus of theoretical and experimental interest since the early 1980s.^{2–39} Beginning in 1982² computational data on model species with hydrogen or

simple organic substituents indicated that their most stable structures differed greatly from that of their carbon congeners.

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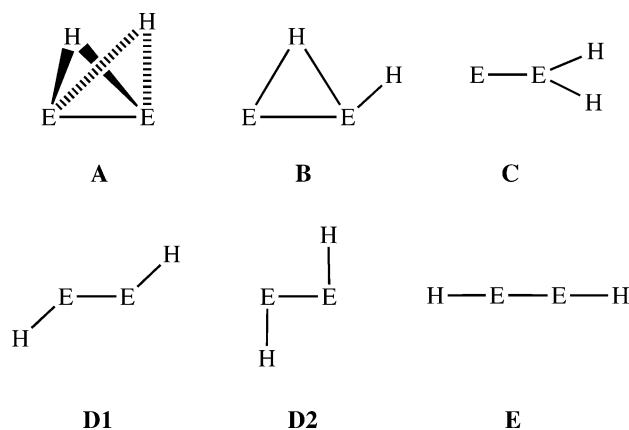
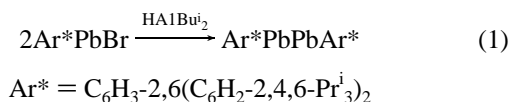


Figure 1. Some structures of the alkyne analogues E_2H_2 ($E = Si-Pb$). The structures **A**, **B**, **C**, and **D1** have been identified as minima on the potential energy surface (PES) and in terms of their relative energy lie in the order **D1** > **C** > **B** > **A**. Neither **D2** nor **E** is a minimum on the PES.²⁹

For example the hydrogen derivatives HEEH can adopt several isomeric forms that correspond to minima on the potential energy surface (PES), with bridged structures **A** and **B** being favored due in part to the excellent bridging properties of hydrogen (Figure 1).^{2-4,6-11,17,29} For methyl-substituted model species the vinylidene (**C**) and planar trans-bent forms (**D**) become more stable than the bridged forms, and as the size of the substituent is increased further, the vinylidene form becomes disfavored for steric reasons, leaving the trans-bent structure **D1** as the energy minimum. It is notable that the linear structure **E** analogous to that seen in acetylenes is never a minimum on the PES for any of the heavier elements. It is also noteworthy that a more strongly trans-bent species, **D2**, is given as a possible structure in Figure 1. This structure is not a minimum on the PES when the substituent is H. However, as shown by Frenking and co-workers, this arrangement can become an energy minimum when large substituents such as terphenyls are employed.¹⁸

The synthesis, isolation, and characterization of the first stable heavier ditetrel alkyne analogues have occurred only since 2000.⁴⁰⁻⁴⁷ The first example was obtained fortuitously⁴⁰ during the attempted synthesis of a divalent lead(II) hydride as shown by



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Table 1. Selected Structural Data for the First Structurally Characterized "Ditetrelynes" with Comparison Data for the Carbon Analogue and Single Bonds^a

$R-E \equiv E-R$	$E \equiv E$ (Å)	E-E-C (deg)	E-E (Å, Single Bond)	Ref
$R-C \equiv C-R$	1.2	180	1.54	-
	2.0622(9)	137.44(4)	2.34	43
	2.2850(6)	128.67(8)	2.44	42
	2.6675(4)	125.1(2)(avg)	2.81	41
	3.1881(1)	94.26(4)	2.9	40

^a $R' = SiPr^i\{CH(SiMe_3)_2\}_2$, $Ar' = C_6H_3-2,6(C_6H_3-2,6-Pr^i_2)_2$; $Ar^* = C_6H_3-2,6(C_6H_2-2,4,6-Pr^i_3)_2$.

Prior to this work, and beginning in 1997,^{45,48-50} attempts to synthesize germanium and tin alkyne analogues by reduction of Ar^* or Ar' ($C_6H_3-2,6(C_6H_3-2,6-Pr^i_2)_2$) substituted^{50,51} divalent halides Ar^*ECl ($Ar = Ar'$ or Ar^* ; $E = Ge$ or Sn) with alkali metals or KC_8 led to singly or doubly reduced products in accordance with eq 2.



($M = Li, Na, K, \text{ or } KC_8$; $E = Ge$ or Sn ; $Ar = Ar'$ or Ar^*)

More careful control of the reaction conditions and stoichiometry led to the isolation of the neutral $ArEEAr$ ($Ar = Ar'$ or Ar^* ; $E = Ge$ or Sn) species in 2002.^{41,42} Work by Sekiguchi,⁴³ Wiberg,⁴⁴ and their co-workers afforded the first stable disilynes in 2004 by reduction of 1,2-dihalogendisilyl precursors in which large silyl substituents provide the stabilization necessary for the isolation of the disilynes. Some geometrical parameters of the first four structurally characterized examples are given in Table 1. More recently, Tokitoh and co-workers have synthesized the digermynes $BbtGeGeBbt$ ($Bbt = C_6H_2-2,6\{CH(SiMe_3)_2\}_2-4-C(SiMe_3)_3$; $Ge-Ge = 2.22 \text{ \AA}$ av; $Ge-Ge-C = 131^\circ$ av). The more strongly trans-bent distannyne $Me_3Si-4-Ar'SnSnAr'-4-SiMe_3$ ($Ar'-4-SiMe_3 = C_6H_2-2,6(C_6H_3-2,6-Pr^i_2)_2-4-SiMe_3$; $Sn-Sn = 3.066(1) \text{ \AA}$; $Sn-Sn-C = 99.25(14)^\circ$) has also been synthesized and characterized.⁴⁷ In all cases the data show that the compounds have a trans-bent, planar core arrangement in which the trans-bending increases as the group is descended. The silicon, germanium, and tin derivatives have element-element bond lengths that are significantly shorter than those of single bonds. For the silicon compound the distance $2.0622(9) \text{ \AA}$ ⁴³ is shorter than the range (ca. 2.14 to 2.25 Å) observed in double-bonded disilenes.^{53,54} For the germanium and tin compounds, however, the distances are similar to those

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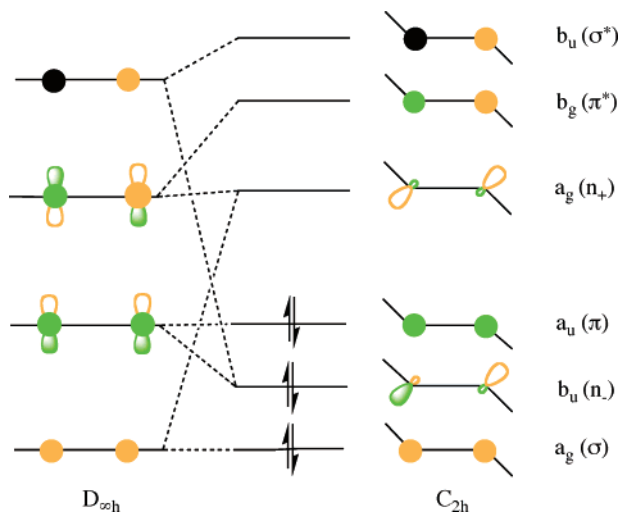
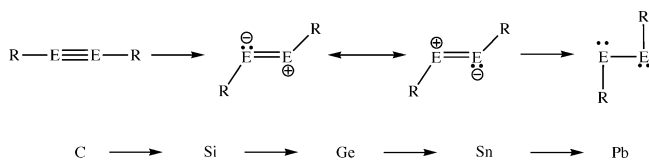


Figure 2. Selected orbital interactions in the C_{2h} -symmetric trans-bent REER molecule. The opposite phases for s and p orbitals are indicated by black and green shading, respectively.

measured for double bonds.^{53,55} In the case of $\text{Ar}^*\text{PbPbAr}^*$ it can be seen that the trans-bending approaches 90° and that the lead–lead distance is longer than the ca. 2.9 Å generally associated with R_3PbPbR_3 derivatives.^{56,57} The greater degree of trans-bending and length of the Pb–Pb bond in $\text{Ar}^*\text{PbPbAr}^*$ were rationalized on the basis that the $6s^2$ valence electrons are also stabilized by relativistic effects,^{58,59} as a result of which they participate less in bonding.⁶⁰ The PbPb single bond can be formed by head-to-head overlap of 6p orbitals, which have a larger radius than that of 6s and hence form bonds longer than those with more 6s character. In sum, the structural trends in Table 1 correspond to a rough pattern in which the amount of bending increases and the amount of bond shortening decreases with increasing atomic number.

The trans-bending may be explained on the basis of the mixing of a σ^* and the in-plane π levels, which have the same symmetry properties in the C_{2h} point group (Figure 2). The mixing can occur to a significant extent in the heavier element compounds, where the separation of the bonding and antibonding levels is approximately half or less than half of that in the carbon analogues. This is a result of the weaker bonding between the heavier elements, itself a consequence of their greatly increased core–core repulsion.⁶⁰ The mixing of the σ^* and π levels affords an accumulation of nonbonding electron density at the tetrel, thereby causing bending of the geometry at these centers by interelectronic repulsion. These distortions result in the conversion of first one and then the second of the two π components of the triple bond to two nonbonding lone pairs, leaving a single bond between the tetrels as in the lead species $\text{Ar}^*\text{PbPbAr}^*$. This progression may be illustrated schematically by the sequence



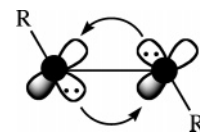
Thus the bond order decreases from 3 at carbon to 1 at lead with the bond orders for E = Si, Ge, or Sn lying between these

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extremes: greater than 2 for silicon, about 2 or slightly greater than 2 for germanium, and near 2 or less than 2 for tin. To a first approximation the bond order seems to decline by about 0.5 of a unit upon descending each row, although this is a great oversimplification. For silicon the mixing of the σ^* and π level is incomplete such that the in-plane π level is not fully converted to an n– level but retains considerable ($\geq 50\%$) bonding character and resembles a skewed or slipped π orbital.^{43,61} For germanium the conversion seems almost complete and the bond order is approximately 2. Tin appears to be a borderline case, in which the bonding is finely balanced between single and double.³²

An alternative view of the bonding for REER, E = Si, Ge, or Sn, is illustrated by



For this model there are two donor–acceptor bonds plus a π bond that is perpendicular to the core array. When the bending is increased to 90° , the donor–acceptor bonds become nonbonded electron pairs and the remaining π bond is converted to a σ bond to afford single bonding as in the case of E = Pb. Thus, in this approach, formal triple bonding is maintained as far as E = Sn. This alternative model draws attention to the fact that the description of bonding in both of these complexes and the neighboring group 13 dianions^{62–64} has been, and remains, a very contentious issue, as demonstrated by the recent series of publications^{28,30,31} on the Si–Si bond order in the compound RSiSiR (R = $\text{SiPr}^i\{\text{CH}(\text{SiMe}_3)_2\}_2$).⁴³ On the basis of calculations^{28,31} the Si–Si multiple bond in this compound was described as a double one, whereas its discoverer and others assert that it is a triple one.³⁰ It should be noted that in this compound the Si–Si bond length (2.0622(9) Å)⁴³ is shorter than the shortest known Si–Si double bonds (ca. 2.15 Å)^{65,66} in disilenes having “classical” planar or nearly planar geometries. Although some of the shortening in the “disilyne” may be due to σ -hybridization effects, the Si–Si distance suggests that the bond order is significantly greater than 2. This is borne out by recent solid-state ^{29}Si NMR⁶⁷ and reactivity studies.⁶⁸ Also of relevance to the debate is the fact that triple bonds^{69–75} between

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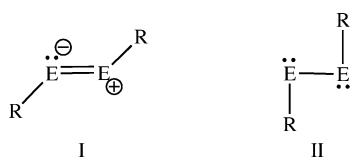
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germanium,^{69–71,75} tin,⁷² or lead^{73,74} and transition metals have been known since the first example was reported a decade ago.⁶⁹ In these compounds the tetrel centers have linear or almost linear geometry as well as very short tetrel–transition metal distances that are consistent with full-fledged triple bonds.⁷⁶

2. Bonding, Reactivity, and Calculations

The changes in the structure of the REER species as the group is descended indicate that the E–E bond order decreases rapidly. Electron density is removed from the bonding region between the E atoms to a nonbonding location at each E atom. This leads to the prediction that reactivity toward Lewis bases should increase and that the Lewis base character of the E centers should increase with increasing atomic number. Furthermore, the weakening of the E–E bond, the larger size of the heavier elements, and the greater E–C bond polarity suggest an increased reactivity upon descending the group. Nonetheless, the chemical behavior and reactivity patterns^{77–81} of the germanium and tin derivatives that have been discovered so far (see below) do not conform to the trend suggested by the structural data for the neutral species. The chemical investigations revealed a noticeable discontinuity in chemical behavior between the germanium and tin compounds, which led us to suggest that the much higher reactivity of the germanium compounds toward molecules such as hydrogen or benzonitrile (see below) might be a result of their greater singlet diradical character.⁸² In response to the large disparity in the chemical properties of some of the germanium and tin alkyne analogues, high-level calculations were undertaken on the simple model species MeEEMe (E = Si–Pb) to explain the much higher reactivity of the germanium compounds.³² These showed that the frontier orbitals of these species change upon descending the series and that the Si–Pb derivatives fall into two categories, in which the pattern for silicon and germanium differ considerably from that of tin and lead, as shown in Figure 3. The calculated geometries for these simple model species are given in Table 2. The general trends in bond lengths and angles are broadly similar to numerous previous results with various substituents over the past two and a half decades. However, for the MeEEMe model species there is obviously a discontinuity between Si and Ge versus Sn and Pb. The E–E bond length jumps by almost 1.0 Å and the bending angle decreases by almost 30° between the two pairs of compounds. These changes can be associated with a change in hybridization such that the Si and Ge derivatives are closer to structure I and those of Sn and Pb are close to II.



The isosurfaces shown in Figure 3 are in agreement with these structural trends. For both the Si and Ge species the HOMO

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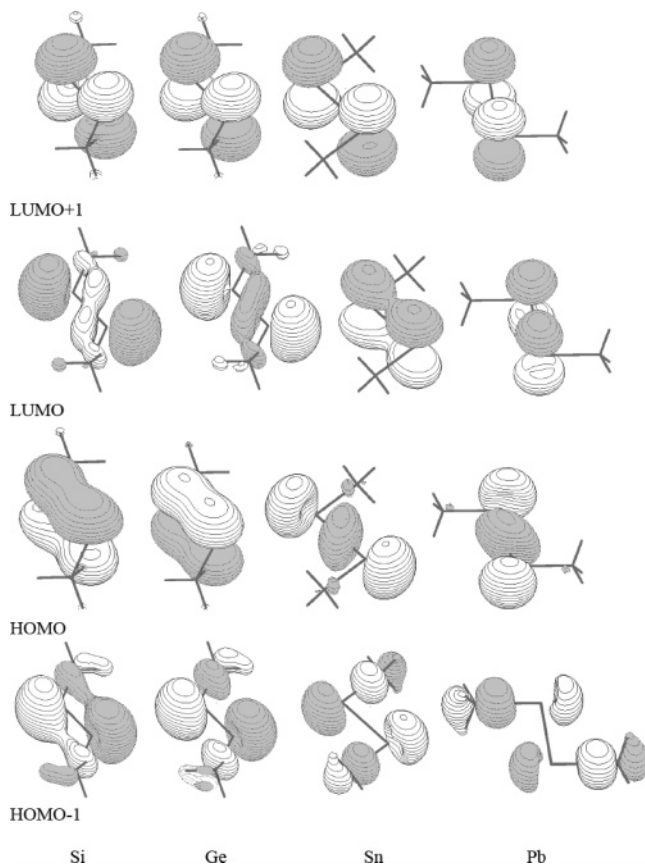


Figure 3. Frontier orbitals for MeEEMe (E = Si–Pb) model species determined from the triplet ground state reference calculations in spin-flip (SF)-TDDFT to avoid spin contamination. In SF-TDDFT calculations, the ground state is taken as the triplet, and singlets are described as linear combinations of spin-flipping excitations, which yields a description of singlet diradicaloid species that is nearly free of spin contamination.³²

Table 2. Calculated (spin-unrestricted DFT at the B3LYP/CRENBL* level) Structural Parameters for Planar MeMMMMe (M = Si–Pb)³²

	MeMMMMe			
	Si	Ge	Sn	Pb
M–M (Å)	2.1	2.3	3.1	3.3
M–M–C (deg)	128.4	125.7	100.0	95.7

(a_u symmetry) is the out-of-plane π orbital. For Si the HOMO–1 (n_-, b_u symmetry) is a skewed or slipped in-plane π orbital, and for Ge the HOMO–1 (also n_-, b_u) resembles an in-plane nonbonding lone pair orbital for Ge. In both cases the LUMO is an essentially nonbonding lone pair orbital (n_+, a_g symmetry). Thus, taking into account the σ -bonding orbital (HOMO–2) the bond order for Si is greater than 2, whereas for Ge the bond order is about 2. In contrast, for the tin and lead species, it can be seen from Figure 3 that the positions of the HOMO and LUMO seen for Si and Ge are switched so that the HOMO is now the n_+, a_g nonbonding orbital and the LUMO is the π, a_u bonding combination. Thus the Sn and Pb methyl-substituted species are singly bonded, in contrast to their Si and Ge congeners. However the calculations also show that the energy

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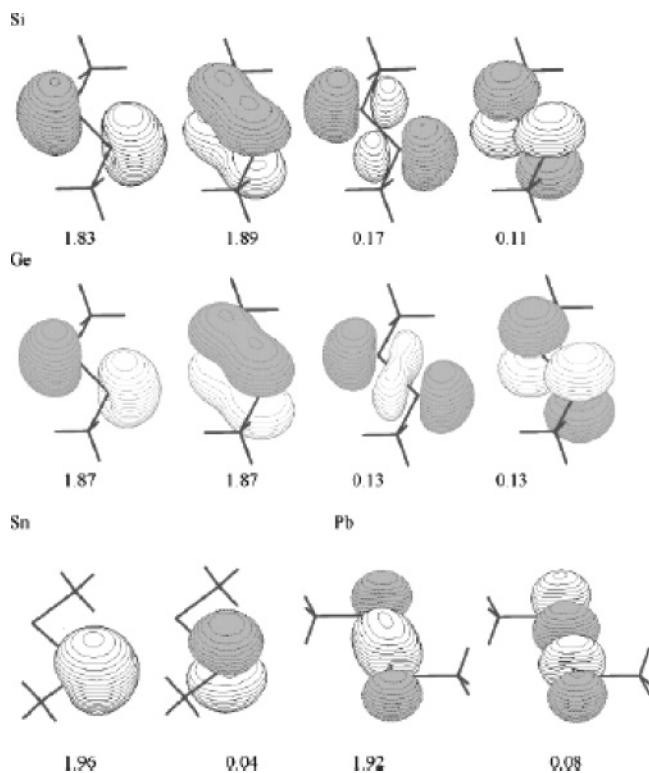
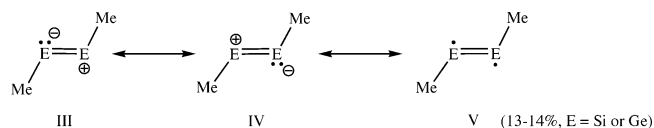


Figure 4. The most strongly correlated (diradicaloid) imperfect-pairing (IP) orbitals for MeEEMe (E = Si, Ge, Sn, Pb). For Sn, the correlated orbital pair essentially corresponds to an atomic excitation, and so for brevity, the same correlation but centered on the other Sn atom is not shown.³²

required to convert the tin species from one category to the other is small and is less than 5 kcal·mol⁻¹.

These differences do not explain the large variation in reactivity between the germanium and tin derivatives. Instead a partial explanation was sought in the differences in the singlet diradical character of the molecules. The diradical character of the MeEEMe models was evaluated by calculation of the occupation numbers of antibonding orbitals. This was done using inexpensive, perfect pairing or imperfect pairing approximations to complete active space, self-consistent-field calculations that allow all valence orbitals to be treated as active.³² The Si and Ge species have strong π to π^* and n_- to n_+ correlations that yield 0.11 and 0.17 unpaired electron density for Si and 0.13 and 0.13 unpaired electron density for Ge in the higher energy orbitals, as shown in Figure 4 and representation V.



In contrast, the Sn and Pb species have smaller “antibonding” occupations that are close to those expected for normal, closed-shell compounds. The occupation numbers for the higher levels in the Si and Ge compounds suggest significant diradical character in those derivatives. The difference in the diradical character for the Si and Ge versus the Sn and Pb species is consistent with some of the differences in the chemical behavior of these compounds that will be described in the next section. In essence it will be shown that tin alkyne analogues are easier to reduce but display much lower reactivity, and since this behavior is contradicted by (i) the more electropositive character of Sn, (ii) the lower bond energies and greater bond

polarities, and (iii) the spatially more open environment at Sn, the diradical character of the Ge alkyne supplies a partial explanation for the observed differences in reactivity toward molecules such as H₂, although the lower bond energies in tin compounds are obviously a factor.

The calculations also reveal several other important features. The first of these is that the planar geometry of the core may be easily distorted to a gauche configuration with associated bond length changes. This is especially true for the germanium, tin, and lead derivatives, where the gauche, unsymmetrically bridged structures are more stable than the trans-bent structures by 2–4 kcal·mol⁻¹ and have E–E bond distances that are ca. 0.4 Å longer. This can be explained by favorable donor–acceptor interaction between the E–C σ bond and the empty π orbital. As mentioned earlier, the calculations for the tin species indicate only a small (<5 kcal·mol⁻¹) energy difference between the multiple (I) and singly bonded form (II). That such large bond length changes occur with such small energy changes is remarkable. This finding is in agreement with the earlier calculations of Takagi and Nagase²⁰ on species with larger substituents, which also afforded only small energy differences between the structures. For example with Ar*SnSnAr* the computed structure with Sn–Sn = 2.66 Å is more stable than the singly bonded isomer with Sn–Sn = 3.09 Å by 4.8 kcal·mol⁻¹. Finally it is notable that the planar cis conformation is higher in energy than the planar trans conformation. This may be due to repulsions between the E–C bonds and also the lone pairs, which are now on the same side rather than the opposite side of the molecule.

3. Chemical Behavior

As stated above, stable examples of reduced ditetrelynes of formula M(ArEEAr) or M₂(ArEEAr) (M = Li, Na, or K; Ar = Ar' or Ar*) have been known since 1997.^{45,48–50} Comparison of their structural data with those of the neutral species provides insight into the EE bonding. Successive one-electron reduction of Ar'GeGeAr' yields progressive closure of the bending angle and a modest lengthening of the GeGe bond (Table 3).⁴⁵ Very recent work by Sekiguchi and co-workers has shown that reduction of his disilyne also leads to the monoanion [(Me₃Si)₂HC]₂Pr(Si)SiSi(SiPr{CH(SiMe₃)₂})₂]⁻, which has a Si–Si multiple bonded distance of 2.1728(14) Å and a bending angle of ca. 113.4°.⁸³ Data for the reduction of Ar'SnSnAr' indicate a sharp decrease of the bending angle and a considerable lengthening of the Sn–Sn distance when one electron is added. The addition of the second electron decreases the Sn–Sn bond length but also decreases the bending angle. These changes differ from those found for the germanium species. However it is notable that the role the counteraction plays in these changes is not well-explored. The data for the Ar*-substituted anions and dianions tell a similar story to that found for the Ar' series, although the detailed structures of the neutral Ar*EEAr* (E = Ge or Sn) molecules remain unknown.⁴⁵

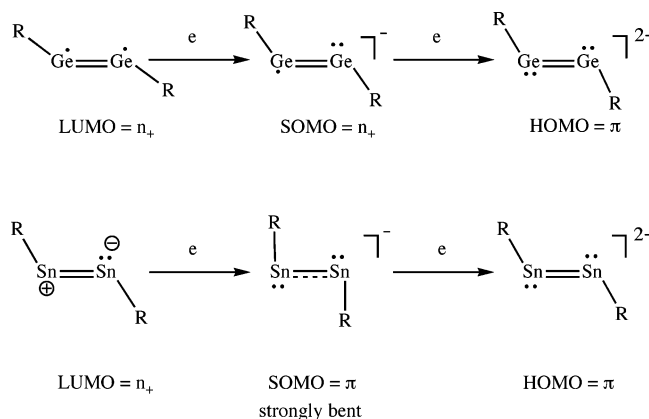
The structural changes undergone by the germanium and tin derivatives are consistent with either the “relaxation” of Ar'SnSnAr' to a more strongly bent, single-bonded structure in solution or a change to a strongly bent geometry that is induced by the act of reduction itself (Scheme 1). The strongly bent structure of the singly reduced species contains a single electron in the LUMO, π orbital. The addition of the electron to the LUMO results in a large shortening of the Sn–Sn distance from

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Table 3. Structural Data for Ge and Sn Alkyne Analogues and Their Reduced Salts⁴⁵

parameter	Ar'GeGeAr'	KAr'GeGeAr'	Li ₂ Ar'GeGeAr'	
Ge–Ge (Å)	2.2850(8)	2.3331(4)	2.455(9)	
Ge–Ge–C (deg)	128.67(8)	114.0(1.5)	102.98(7)	
parameter	Ar*GeGeAr*	NaAr*GeGeAr*	Na ₂ Ar*GeGeAr*	K ₂ Ar*GeGeAr*
Ge–Ge (Å)		2.3089(8)	2.394(1)	2.3912(6)
Ge–Ge–C (deg)		114.8(5)	102.37(8)	102.14(7)
parameter	Ar'SnSnAr'	K(THF) ₆ Ar'SnSnAr'	K ₂ Ar'SnSnAr'	
Sn–Sn (Å)	2.6675(4)	2.8081(9)	2.7754(3)	
Sn–Sn–C (deg)	125.24(7)	97.9(2)	106.02(5)	
parameter	Ar*SnSnAr*	[ML _n][Ar*SnSnAr*]	Na ₂ Ar*SnSnAr*	K ₂ Ar*SnSnAr*
Sn–Sn (deg)		2.782(1)–2.8123(9)	2.789(1)	2.7763(9)
Sn–Sn–C (Å)		95.0(4)–98.0(4)	104.8(2)	107.5(1)

Scheme 1. Illustration of the Structural Changes Undergone by the Ge and Sn Alkyne Analogues upon Reduction

Table 4. ¹¹⁹Sn Solid-State NMR and Mössbauer Parameters for Ar'SnSnAr' and Ar*SnSnAr*⁸⁵

		Ar'SnSnAr'	Ar*SnSnAr*
NMR	δ_{11} (ppm)	+1125.2	+726.1
	δ_{22} (ppm)	+740.4	+193.3
	δ_{33} (ppm)	-860.3	-1028.0
	δ_{iso} (ppm) ^a	+335.1	-36.2
	η^b	0.32	0.54
Mössbauer ^c	IS (mm·s ⁻¹)	2.658(2)	2.69(3)
	QS (mm·s ⁻¹)	2.995(2)	3.730(3)
	d IS/dT (μm·s ⁻¹ ·K ⁻¹)	-0.24(0.027)	-0.496(0.106)
	d QS/dT (μm·s ⁻¹ ·K ⁻¹)	-1.98(62)	-2.52(7)

^a The isotropic chemical shift is defined as $\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$.

^b The asymmetry parameter is defined as $\eta = (\delta_{11} - \delta_{22})/(\delta_{33} - \delta_{\text{iso}})$. ^c The IS scale reference point is the centroid of a room temperature absorption spectrum of BaSnO₃.

the 3.06 Å predicted for a neutral singly bonded species²⁰ to ca. 2.80 Å (cf. Table 2) and a relatively small (ca. 3°) change in the bending angle. Addition of the second electron affords a further shortening of the Sn–Sn bond, which now becomes a double one analogous to the isoelectronic neutral aryl-substituted distibene.⁸⁴

Mössbauer and solid-state ¹¹⁹Sn NMR spectroscopy supply evidence for the existence of different degrees of bending in the tin alkyne analogue structures in the solid state. These data are presented for Ar'SnSnAr' and Ar*SnSnAr* in Table 4 and Figure 5.⁸⁵ It can be seen that significantly different spectroscopic parameters are obtained for each compound. The extent

of these differences is unlikely to be a result of the σ inductive effects of the Ar* and Ar' ligands, which differ only by the presence of a *p*-Prⁱ substituent on the flanking rings of the Ar* ligand. Instead, molecular models suggest that the structure of Ar*SnSnAr* may differ from that of Ar'SnSnAr' for steric reasons. Inspection of the molecular structure of Ar'SnSnAr' shows that the central aryl rings of the Ar' substituents lie in the same plane as the CSnSnC core. This is possible because the Ar' groups lack *p*-Prⁱ substituents on the flanking rings. The presence of such groups would cause steric interference to the extent that the central aryl rings would be twisted out of the CSnSnC plane and may give a structure that is closer to that observed in the strongly bent lead derivative Ar*PbPbAr*. Repeated attempts to obtain X-ray crystal structures of Ar*EEAr* (E = Ge or Sn) were unsuccessful because of the poor diffraction characteristics of the crystals.

We sought other approaches to obtain detailed structural information on a strongly trans-bent tin alkyne analogue by suitable electronic modification of the terphenyl ligand with minimal changes in its steric properties. This may be achieved by maintaining the flanking rings unchanged while at the same time introducing different substituents at the para (or less often) meta positions of the central aryl ring. In this way the doublet–quartet energy difference for the monomeric fragment EAr can be altered. Changing the ΔE_{D-Q} energy can affect the strength of the interaction between the EAr moieties in the manner outlined diagrammatically in Scheme 2. This approach was originally developed by Trinquier and Malrieu⁸⁶ in a general treatment of the formation of multiple bonds between heavier main group atoms and has been applied by Tokitoh, Nagase, and co-workers to rationalize the wider bending angle and shorter GeGe distance in BbtGeGeBbt (Bbt = C₆H₂-2,6-{CH-(SiMe₃)₂}₂-4-{C(SiMe₃)₃}) in terms of the greater electron-releasing character of the ligand and hence a lower ΔE_{D-Q} .⁴⁶

The synthesis of the modified terphenyl ligands with a variety of substituents at the para position of the central aryl ring can be expected to modify the ΔE_{D-Q} values. Preliminary data for the model species GeC₆H_{*n*-4}X_{*n*} (*n* = 1, 2) show that ΔE_{D-Q} can be varied by about 4.5 kcal·mol⁻¹ in the series listed in Table 5.⁸⁷ Since the actual molecules are composed of two EAr fragments, the energy range available is thus almost 9 kcal·mol⁻¹, which should be (according to the calculations) sufficient to effect structural changes.^{20,32} The application of this approach to “distannynes” has resulted in the recent synthesis and characterization of the modified terphenyl derivative Me₃Si-4-Ar'SnSnAr'-4-SiMe₃, in which the para-H on the central aryl ring has been replaced by an SiMe₃ group.⁴⁷ The

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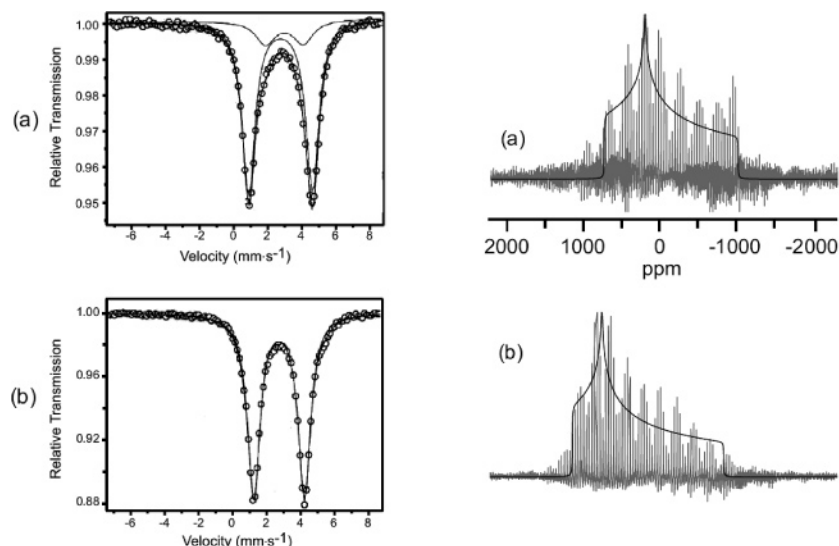


Figure 5. Mössbauer and ^{119}Sn NMR solid-state NMR data for (a) $\text{Ar}^*\text{SnSnAr}^*$ and (b) $\text{Ar}'\text{SnSnAr}'$.⁸⁵

Scheme 2. Schematic Representations of the Energetics of Triple-Bond Formation in Group 14 Elements

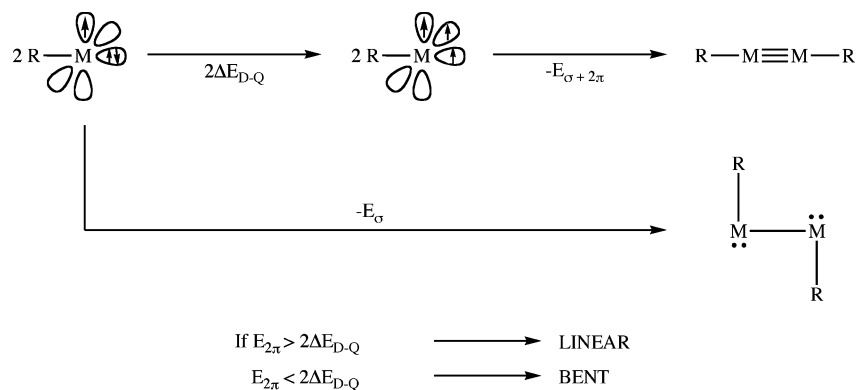
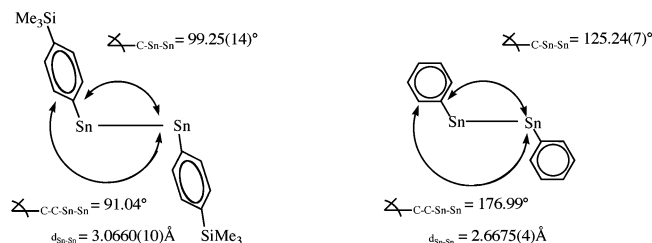


Table 5. Calculated ΔE_{D-Q} Values of Some Germanium Model Species at the B3LYP/LANL2DZ Level^a

moiety	ΔE_{D-Q} (kcal·mol ⁻¹)
H ₃ C ₆ Ge	47.8
4-Cl H ₄ C ₆ Ge	47.2
3,5-Cl ₂ H ₃ C ₆ Ge	50.5
4-H ₃ SiH ₄ C ₆ Ge	48.0
4-Me ₂ NH ₄ C ₆ Ge	46.9

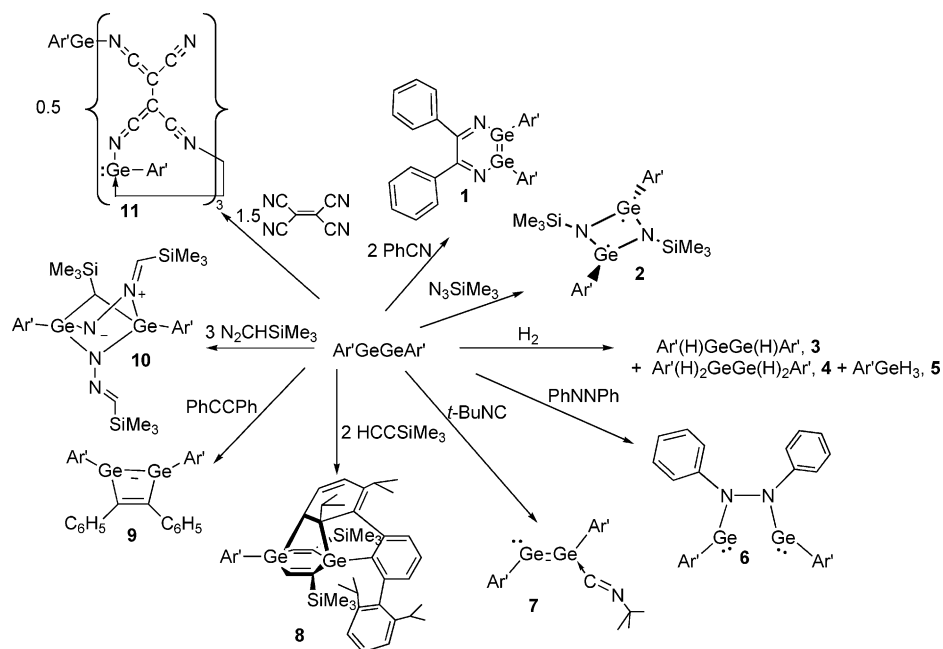
^a Brynda, M.; Power, P. P. Unpublished work.

Scheme 3. Comparison of Core Geometries for Me₃Si-4-Ar'SnSnAr'-4-SiMe₃ and Ar'SnSnAr'



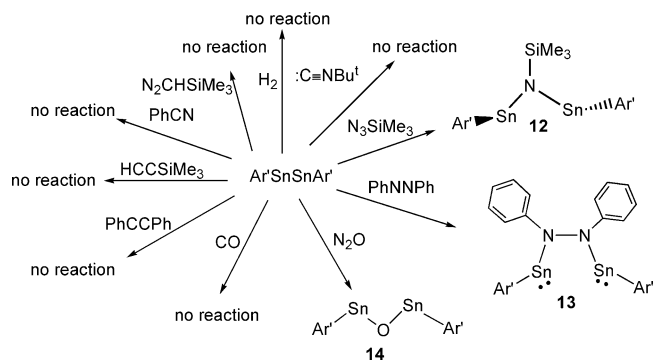
structure of this compound differs greatly from that of the original multiple-bonded structure of $\text{Ar}'\text{SnSnAr}'$, whose core structural parameters are given in Table 1. Key data for the two structures are given in Scheme 3. It can be seen that the Sn–Sn bond length in $\text{Me}_3\text{Si-4-Ar}'\text{SnSnAr}'\text{-4-SiMe}_3$ is 3.066(1) Å, which is almost 0.4 Å longer than the 2.6675(4) Å in $\text{Ar}'\text{SnSnAr}'$. In addition, the Sn–C bond angle is 99.25-(4)°, a decrease of about 26° in comparison to the 125.24(7)°

in $\text{Ar}'\text{SnSnAr}'$. In effect, the structural parameters resemble those of $\text{Ar}^*\text{PbPbAr}^*$ (Pb–Pb = 3.1881(1)°, Pb–Pb–C = 94.26-(4)°) more than those of $\text{Ar}'\text{SnSnAr}'$ and are consistent with Sn–Sn single bonding. Similar to $\text{Ar}^*\text{PbPbAr}^*$ the central aryl ring of the ligand in $\text{Me}_3\text{Si-4-Ar}'\text{SnSnAr}'\text{-4-SiMe}_3$ lies perpendicularly to the CSnSnC core, in contrast to the coplanar arrangement observed in $\text{Ar}'\text{SnSnAr}'$. These results are in agreement with the theoretical prediction that relatively small amounts of energy separate the two different bonding modes (i.e., **D1** and **D2**) and that bulky ligands can favor **D2** over **D1** as illustrated in Figure 1.^{18,20} The apparently shallow potential well for the bending energies of the tin compounds and the fact that the more strongly bent structure was calculated for MeSnSnMe ,³² led us to suggest^{32,37} that they “relaxed” to a strongly bent structure in hydrocarbon solution. This suggestion is not supported by recent calculations⁸⁸ of Takagi and Nagase, who showed that the solution electronic spectra of $\text{Ar}'\text{EEAr}'$ (E = Ge or Sn) are consistent with a multiple-bonded structure with wide E–E–C angles. Moreover the multiple-bonded $\text{Ar}'\text{SnSnAr}'$ tin structure was calculated to be at least 5.3 kcal mol⁻¹ more stable than the strongly bent single-bonded form. Calculations were also carried out on $\text{Me}_3\text{Si-4-Ar}'\text{SnSnAr}'\text{-4-SiMe}_3$, which indicated that the multiple-bonded form is favored by a very similar energy difference. However, this is in disagreement to what is found in the X-ray crystal structure.⁸⁹ The calculations indicate that the spectra of the two compounds are expected to be similar and indicative of a multiple-bonded

Scheme 4. Reactions of $\text{Ar}'\text{GeGeAr}'$ with a Range of Saturated and Unsaturated Molecules⁸¹

structure in solution. Thus, the currently available theoretical and spectroscopic (UV–vis) evidence indicates the strongly bent crystal structure of $\text{Me}_3\text{Si}-4-\text{Ar}'\text{SnSnAr}'-4-\text{SiMe}_3$ relaxes to the more stable multiple-bonded form in solution.⁸⁸ It is also notable that the data for the model ligands given in Table 5 suggest that the difference between the $\Delta E_{\text{D-Q}}$ values for *p*-H- and *p*- SiMe_3 -substituted species is less than $1 \text{ kcal}\cdot\text{mol}^{-1}$. This finding also shows that the large change in structure in different phases cannot be due to the electronic effects induced by SiMe_3 . It seems probable therefore that the large structural changes between the solid and solution are due to packing forces.⁸⁹ A similar conclusion was reached from recent calculations on the lead species $\text{Ar}^*\text{PbPbAr}^*$, which indicated that it also relaxes to a multiple-bonded species in solution, although the energy difference between the two forms is only $1 \text{ kcal}\cdot\text{mol}^{-1}$.⁹⁰ Unfortunately the strength of the packing forces is not theoretically well-explored in sterically crowded molecular species. It is possible that a series of terphenyl ligands in which the substituents at the central phenyl ring are varied systematically will provide further information. This will entail a considerable synthetic effort that will involve the synthesis of a range of derivatized Ar' and Ar^* ligands as well as the synthesis and physical and chemical characterization of their group 14 element derivatives. Such data may provide key information especially with regard to the apparently fine energy balance that determines the geometrical parameters of these compounds.

The detailed calculations by Nagase and Takagi^{88,90} have demonstrated that the use of simple model ligands such as Me do not provide as accurate a picture as the more bulky ligands that are actually employed in the laboratory. All calculations so far published by various groups deal only with molecules that are isolated from their neighbors. Reliable predictions of

Scheme 5. Reactions of $\text{Ar}'\text{SnSnAr}'$ with a Range of Saturated and Unsaturated Molecules⁸¹

solid-state structures where there are interactions between neighboring molecules present a problem of considerably greater difficulty.

The reactivity of the germanium and tin species $\text{Ar}'\text{GeGeAr}'$ and $\text{Ar}'\text{SnSnAr}'$ has been examined in some detail.^{78–81} Summaries of most of their currently known reactions are given in Schemes 4 and 5. It will be immediately apparent that the reactivity of the “digermynes” is much greater than that of the corresponding tin molecule, which is not predictable on the basis of bond strengths, bond polarities, and steric effects. Several reactions of the germanium species are noteworthy and reveal much about the nature of the Ge–Ge bonding. For example, the addition of the isonitrile Bu^tNC affords the 1:1 complex $\text{Ar}'\text{GeGeAr}'\cdot\text{CNBu}^t$ (**7**).⁸¹ Significantly, the coordination occurs in the plane of the $\text{C}(\text{ipso})\text{GeGeC}(\text{ipso})$ core of the molecule as shown in Figure 6. Moreover, there is a relatively modest increase in the Ge–Ge bond length from 2.2850(6) to 2.3432(9) Å. These changes are consistent with the orbital illustrations in Figures 2 and 3, in which the LUMO is a nonbonding n_+ orbital whose occupancy by the added electron density from a donor molecule such as Bu^tNC would be expected to exert only a small effect on the Ge–Ge bond length. An additional feature of the structure is that the bending angle at the uncomplexed germanium (Ge_2) decreases to $102.8(2)^\circ$, which is ca. 26° narrower than that in $\text{Ar}'\text{GeGeAr}'$ (cf. Table 3). This narrowing is consistent with the simple bonding picture in which the

(89) The singly bonded structure of $\text{Me}_3\text{Si}-4-\text{Ar}'\text{SnSnAr}'-4-\text{SiMe}_3$ led us to consider the possibility that the compound was in fact the hydride $\text{Me}_3\text{Si}-4-\text{Ar}'\text{Sn}(\mu\text{-H})_2\text{SnAr}'-4-\text{SiMe}_3$, which would also afford a long Sn–Sn distance and an apparently strongly bent CSnSn angle. We have synthesized the hydride by a different route, and although the cell constraints for the crystals are similar, the compounds have different physical properties (color, melting point, and spectroscopic characteristics): Fischer, R. C.; Peng, Y.; Rivard, E.; Fettinger, J. C.; Power, P. P. Unpublished results.

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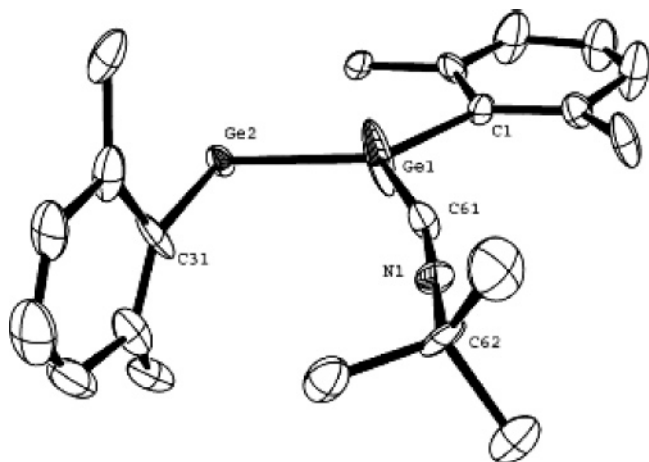


Figure 6. Thermal ellipsoid plot of **7**. Hydrogen atoms and C₆H₃-2,6-Pr₂ groups (except ipso carbon atoms) are not shown. Selected bond distances (Å) and angles (deg): Ge1–Ge2 2.3432(9), Ge1–C1 1.966(5), Ge1–C61 1.957(5), C61–N1 1.155(2), N1–C62 1.480(6), Ge2–C31 2.004(5); Ge2–Ge1–C1 129.62(14), Ge1–Ge2–C31 102.77(15), Ge2–Ge1–C61 127.61(2), C1–Ge1–C61 112.7(2), Ge1–C61–N1 164.2(6), C61–N1–C62 168.3(11).⁸¹

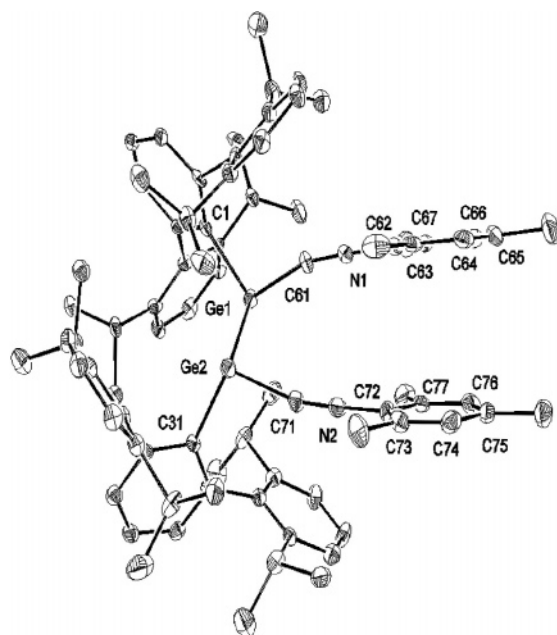
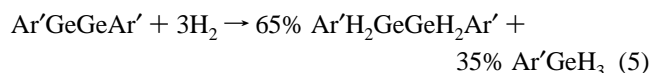
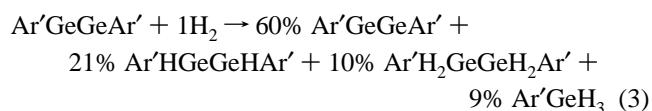


Figure 7. Thermal ellipsoid (30%) drawing of Ar'GeGeAr'-(CNMe)₂. H atoms are not shown. Selected bond lengths (Å) and angles (deg): Ge1–Ge2 2.6626(8), Ge1–C1 2.033(4), Ge1–C61 2.026(5), Ge2–C31 2.023(4), Ge2–C71 1.996(5), C61–N1 1.145(6), N1–C62 1.402(6), Ge2–C71 1.996(5), C71–N2 1.157(6), N2–C72 1.395(6); C1–Ge1–C61 100.09(18), Ge2–Ge1–C61 88.64(14), C1–Ge1–Ge2 104.45(12), C31–Ge2–C71 99.34(19), Ge1–Ge2–C71 88.00(14), C31–Ge2–Ge1 105.14(13), Ge1–C61–N1 159.5(4), C61–N1–C62 173.9(5), Ge2–C71–N2 159.4(4), C71–N2–C72 174.5(5).⁹¹

nonbonding pair of electrons that resonates between positions at the two germaniums as shown in structures III and IV becomes localized on one germanium only. This causes an increase in interelectronic repulsion between lone pair and bond pairs and a consequent closure of the bond angle. The narrower bond angle may indicate greater 4p character in the Ge(2) bonding orbital, which could contribute to the slight lengthening in the Ge–Ge bond. More recent work⁹¹ has shown that it is

possible to add a second isocyanide to the Ge–Ge bond. If MesNC: is used instead of Bu'NC:, the complex Ar'GeGeAr'-(CNMe)₂ (Figure 7) can be isolated. The structural details are consistent with the addition of the second molecule to a π* level, which produces a much greater lengthening of the Ge–Ge bond to 2.6626(8) Å. It has been proposed that the addition of two MesNC: molecules to Ar'GeGeAr' can occur because the Mes rings can be oriented parallel to each other (Figure 7), whereas two Bu'NC: molecules would cause greater steric pressure, which may prevent a second Bu'NC: from coordinating.

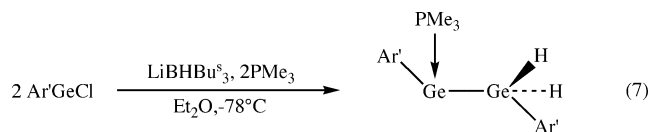
Several of the other reactions in Scheme 4 are noteworthy including the formally symmetry-forbidden addition of PhCCPh to afford the cyclic four-membered ring product **9**. Addition of a second alkyne can occur with Me₃SiCCH, which may proceed through an intermediate 1,4-digermbenzene, which then activates a flanking aryl ring of the Ar' ligand to yield the product **8**. However it is the room-temperature reaction of Ar'GeGeAr' with H₂ that is perhaps the most unusual among the series of reactions in Scheme 4.⁸¹ The addition occurs within a few minutes at room temperature and pressure. Three products, the digermene Ar'HGeGeHAr', the digermene Ar'H₂GeGeH₂Ar', and the germane Ar'GeH₃, are obtained for 1:1 and 1:2 stoichiometries of the Ar'GeGeAr'/H₂ reactants. At Ar'GeGeAr':H₂ ratios of 1:3 or greater, an approximately 2:1 ratio of Ar'H₂GeGeH₂Ar' and Ar'GeH₃ is obtained in accordance with eqs 3–5.



The occurrence of the monogermane Ar'GeH₃ could be a result of an equilibrium shown in eq 6,



in which the “digermene” Ar'HGeGeHAr' dissociates to two germylene monomers Ar'GeH. The latter may then add H₂ to form Ar'GeH₃, although the details of such a reaction have not been studied. The digermene Ar'HGeGeHAr' can be synthesized independently by the reduction of Ar'GeCl with LiBHBu^s₃.⁹² If this reduction is carried out in the presence of 2 equiv of trimethylphosphine, the unusual adduct (Me₃P)Ar'GeGeH₂Ar', in which both hydrogens are bound to one germanium, can be isolated and structurally characterized in accordance with

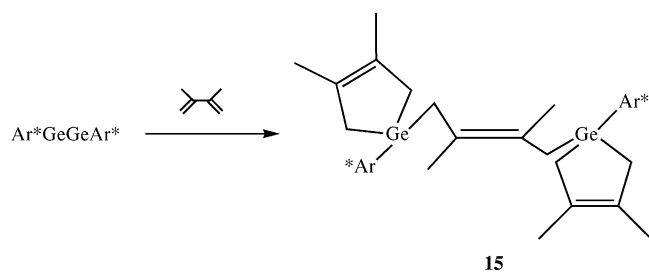


It was the facile reaction between Ar'GeGeAr' and H₂ that originally led to consideration of the extent of diradical character in Ar'GeGeAr' as a possible explanation for its high reactivity. Other reactions of Ar'GeGeAr' and the products obtained are

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suggestive of one-electron radical processes. For example reaction of $\text{Ar}'\text{GeGeAr}'$ with benzonitrile produces the cyclic product **1**, which contains a C–C bond due to coupling of two benzonitriles. This reaction is reminiscent of the coupling of nitriles by transition metal complexes, where it is believed the reaction occurs by initial one-electron reduction followed by dimerization of the radical thus generated to give a C–C bonded species.^{93–95} It is also noteworthy that the cyclic product $\text{Ar}'\text{Ge}(\mu\text{-NSiMe}_3)_2\text{GeAr}'$ (**2**) has singlet diradical character.⁷⁹ In contrast to other cyclic germanium–nitrogen compounds, it is deeply colored. It is a non-Kekulé molecule in which the formally trivalent germaniums are pyramidally coordinated. It is diamagnetic, and the “nonbonded” electrons at each germanium are apparently weakly coupled. Compound **2** is one of a growing number of singlet diradicaloid molecules whose importance in main group chemistry is only beginning to be realized.⁹⁶ The earlier discussed product **8** may also be a result of the singlet diradical character of the putative intermediate 1,4-digermbenzene, $\text{Ar}'\text{Ge}(\text{CHCSiMe}_3)_2\text{GeAr}'$, which is so reactive that it activates a flanking aryl ring of the Ar' ligand. The unusual product **10**, in which three $\text{N}_2\text{CHSiMe}_3$ molecules have interacted in a different manner with $\text{Ar}'\text{GeGeAr}'$, and the isolation of the unusual product **15**⁷⁷ in low yield in the reaction



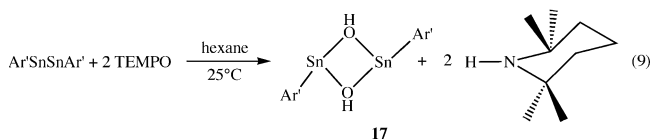
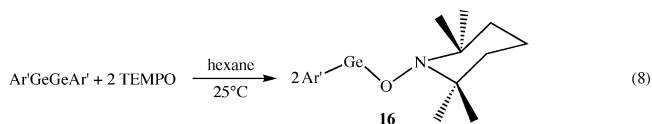
of $\text{Ar}'\text{GeGeAr}'$ with 2,3-dimethyl-1,3-butadiene also suggest the presence of some radical character in these “digermynes”.

Parallel investigations by Tokitoh and co-workers⁴⁶ on the BbtGeGeBbt compound reveal a different reactivity pattern from that of $\text{Ar}'\text{GeGeAr}'$. The most significant difference perhaps is the fact that BbtGeGeBbt does not react with Et_3SiH , suggesting that it has little diradical or germylene character. In addition the pattern of reactivity with 2,3-dimethyl-1,3-butadiene also differs in that no product analogous to **15** was obtained. Instead

the cyclic species $\text{CH}_2\text{C}(\text{Me})\text{C}(\text{Me})\text{CH}_2(\text{Bbt})\text{GeGeBbt}$ or $\text{CH}_2\text{C}(\text{Me})\text{C}(\text{Me})\text{CH}_2(\text{Bbt})\text{GeGe}(\text{Bbt})\text{CH}_2\text{C}(\text{Me})\text{C}(\text{Me})\text{CH}_2$ was isolated. The shorter GeGe bond in BbtGeGeBbt ($\text{Ge}-\text{Ge} = 2.21 \text{ \AA}$) suggests greater electronic coupling in the “slipped” π bond consistent with lower singlet diradical character. In principle, it should be possible to test the variation of the proposed diradical character with changes in the bond length and the amount of bending with use of a range of stabilizing ligands.

In contrast to the high reactivity seen for $\text{Ar}'\text{GeGeAr}'$, its tin analogue displays a much lower reactivity pattern. Reactions with most of the reagents in Scheme 5 do not proceed at a rate that is faster than the slow oxidation or hydrolysis of $\text{Ar}'\text{SnSnAr}'$ when stirring this compound in solution for prolonged periods. The exceptions involve the reaction with azobenzene, which produces the tin analogue **13** of the germanium species **6**

although the reaction occurs at a slower rate. A reaction between $\text{Ar}'\text{SnSnAr}'$ and N_3SiMe_3 is also observed, but in this case the unique product $\text{Me}_3\text{SiN}(\text{SnAr}')_2$, **12**, is obtained.⁸¹ Attempts to make a cyclic product analogous to the germanium derivative $\text{Ar}'\text{Ge}(\mu\text{-NSiMe}_3)_2\text{GeAr}'$ by the addition of excess N_3SiMe_3 were unsuccessful. The species **12** features two SnAr' and an SiMe_3 group bound to nitrogen, which has approximately planar coordination. The two Sn–N distances, 2.111(6) and 2.055(6) Å, differ slightly. The shorter distance is correlated with a wider Sn–N–Si angle ($134.6(3)^\circ$ vs $115.8(3)^\circ$) and lower degree of twisting of the tin coordination planes, 22° vs 45° , which suggests that some N–Sn π delocalization exists. However, this is unlikely to be extensive due to the disparity in size and polarity of the atoms in the Sn–N unit. A further recently reported example of reactivity differences between $\text{Ar}'\text{GeGeAr}'$ and $\text{Ar}'\text{SnSnAr}'$ involves their reaction with tetramethylpiperidineoxide (TEMPO) as shown in eqs 8 and 9.⁹⁷



The reaction of $\text{Ar}'\text{GeGeAr}'$ with TEMPO can be considered a two-step oxidation of the digermine unit by the sequential interaction of the SOMO of the two TEMPO molecules with the LUMO of $\text{Ar}'\text{GeGeAr}'$ (i.e., the n_+ combination). Steric crowding and electronic effects caused by the addition of TEMPO induce dissociation to the monomeric germylene product $\text{Ar}'\text{GeTEMPO}$, **16**. The corresponding reaction of TEMPO with $\text{Ar}'\text{SnSnAr}'$ proceeds more slowly than that of its germanium counterpart. A tin analogue of **16** was not obtained from this reaction. Instead the hydroxide-bridged dimer **17** was isolated. This product may be a result of N–O bond cleavage in the putative $\text{Ar}'\text{SnTEMPO}$ intermediate, where the NO bond may be weakened by coordination to the more electropositive tin. The $\text{Ar}'\text{SnO}$ and NR_2 fragments may then abstract hydrogen from the solvent to afford **17** and 2,2,6,6-tetramethylpiperidine. More recent results indicate that small quantities of the $\text{O}(\text{SnAr}')_2$ species are obtained during this reaction, and this observation is consistent with the generation of $\text{Ar}'\text{SnO}$, which may then react with $\text{Ar}'\text{SnSnAr}'$ to form $\text{O}(\text{SnAr}')_2$ and SnAr' .

At present the reactivity of the lead compound $\text{Ar}'\text{PbPbAr}'$ (or $\text{Ar}'\text{PbPbAr}'$, which has not yet been characterized) is unexplored.⁹⁸ The chemistry of this compound can be expected to be consistent with its structure. The lead centers should have good Lewis basicity in comparison to the (as yet scarcely investigated) Lewis basicity of the germanium and tin species. The $\text{Ar}'\text{PbPbAr}'$ species should also display Lewis acidity due to the presence of two empty 6p orbitals at each lead. It should also be possible to reduce the lead compound to mono- or

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dianions to give multiply bonded compounds in the manner of the germanium and tin species listed in Table 3.

4. Outlook and Conclusions

The results described in this review represent only the initial stages of the study of heavier group 14 alkyne analogues. Some fundamental trends can be discerned from the initial structural, spectroscopic, reactivity, and theoretical data. Much remains to be accomplished however. The synthesis and characterization of a much wider range of the complexes will be required to obtain a more complete picture. These data, combined with electrochemical studies, solid-state NMR (for the Si, Sn, and Pb derivatives, and Mössbauer (Sn derivatives) and electronic spectroscopy, will provide vital details of the nature of the EE bonds. Suitable ligand manipulation should lead to considerable variation in the structures and degree of multiple bonding in these compounds. In addition the synthesis and characterization of heteronuclear compounds, including those incorporating multiple bonding to carbon, can be anticipated. It is notable that the bonding trends within the group 14 ditetrelynes could be interpreted in terms of very weak or nonexistent π bonding especially for the heaviest derivatives of tin and lead. But several studies have shown that π bonding remains important in the fifth and sixth periods,⁹⁹ especially when considered in relation

to the weaker σ bonding also displayed by elements in these periods. The trans-bending is more a manifestation of the trend toward stabilization of the s-valence electrons (and their consequent lower involvement in bonding as the group is descended) than any inherent weakness of the π bonding. It appears from recent results that the increasing stabilization of the s electrons and the strength of the π bond are in approximate balance by the fifth period (i.e., tin in group 14), and even minor changes in the ligand are sufficient to effect large changes in the structure by relatively minor electronic and packing effects. However further theoretical and experimental work will be required to establish this more firmly.

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