

Reactions of Heavier Main-Group Compounds with Hydrogen, Ammonia, Ethylene and Related Small Molecules

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ABSTRACT: The first reaction between hydrogen and a main-group compound under ambient conditions was reported in 2005. This unexpected result has been followed by numerous others which show that such reactivity is widespread in unsaturated and multiple bonded main-group species. These may react spontaneously not only with hydrogen, but also with ethylene, ammonia and related molecules. This account focuses on results from the author's laboratory but also on parallel work by other groups. The link between HOMO-LUMO separations, symmetry considerations and reactivity of the main-group species is emphasized as is their similarity in reactivity to transition-metal organometallic compounds. **DOI 10.1002/tcr.201100016**

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1. Introduction and Background

It is well known that the chemistry of compounds of the heavier main-group elements in many instances bears only a limited resemblance to that of their lighter element congeners.^{1,2} However, the differences between the lighter and heavier elements are especially accentuated in several classes of heavier element derivatives whose chemistry is the subject of increasingly intensive investigations.^{3–10} These compounds are characterized by “strained” geometries or by open, or relatively open, valence shells that confer high reactivity. Examples include multiple bonded heavier element congeners of alkenes or alkynes,¹¹ lower oxidation state unsaturated derivatives of the Group 13⁹ and Group 14 elements as well as a variety of non-Kekulé compounds.¹² The latter are species which appear to be missing a bond according to the normal rules of valence. However, they are generally not paramagnetic but instead

feature weakened electronic coupling or bonding between two atoms of the structure and may be described as singlet diradicaloids or, less often, as open shell singlets. Examples from the above compound classes are given in Figure 1 and indicate the weaker electronic coupling in one of the bonds of the diradicaloids (c) indicated by dashed lines. An important feature of all the species featured in Figure 1 is that they are almost always colored, which indicates that the frontier orbitals are not widely separated (cf. the visible region of the electronic spectrum is in the range ca. 1.5–3.0 eV). This characteristic, as well as other aspects of their behavior, have led to analogies being drawn between the chemistry of these compounds and that of transition elements.¹³ However it is the propensity of some of the heavier element derivatives in Figure 1 (a) and (b) above to interact with unactivated small molecules such as hydrogen or

simple olefins that has underlined their unique reactivity. The main objective of this account is to provide a summary of the recent work of the author's group with compounds (a) and (b) of Figure 1.

Since the initial discovery of the first isolable compounds featuring multiple bonds between heavier main-group atoms, their chemistry has been of high interest. A major justification for these studies was to establish how their bonding and reactivity differed from those of their lighter element congeners. For example, as early as 1976 Lappert had uncovered the *trans*-pyramidalized, "strained" geometry of the "distannene" $\{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{SnSn}\{\text{CH}(\text{SiMe}_3)_2\}_2$ ¹⁴ and showed that its reactivity was consistent with its extensive dissociation into two monomeric singlet stannylenes $\text{Sn}\{\text{CH}(\text{SiMe}_3)_2\}_2$ in solution.¹⁵ In contrast West's disilene $\text{Mes}_2\text{Si}=\text{SiMes}_2$ ($\text{Mes} = \text{C}_6\text{H}_2-2,4,6-\text{Me}_3$),¹⁶ which was the first compound to feature a non-dissociating, stable, homonuclear double bond between the heavier elements, displayed reactivity that was more characteristic of a reactive olefin. In general, disilenes were found to react readily at room temperature with molecules such as hydrogen halides, alcohols, aldehydes, ketones, azides, isonitriles, nitrous oxide, oxygen, sulfur or selenium.^{17,18} This heightened reactivity is consistent with their weaker π bonding, which features a $\pi-\pi^*$ energy separation near 3 eV (cf. 5–6 eV in olefins). Even so, their $[2+2]$ cycloaddition reactions with 1-alkynes were relatively sluggish and no reactions were observed with more hindered alkynes.¹⁹ The tetraaryldisilenes also did not react with nonpolar alkenes or conjugated dienes. However, tet-

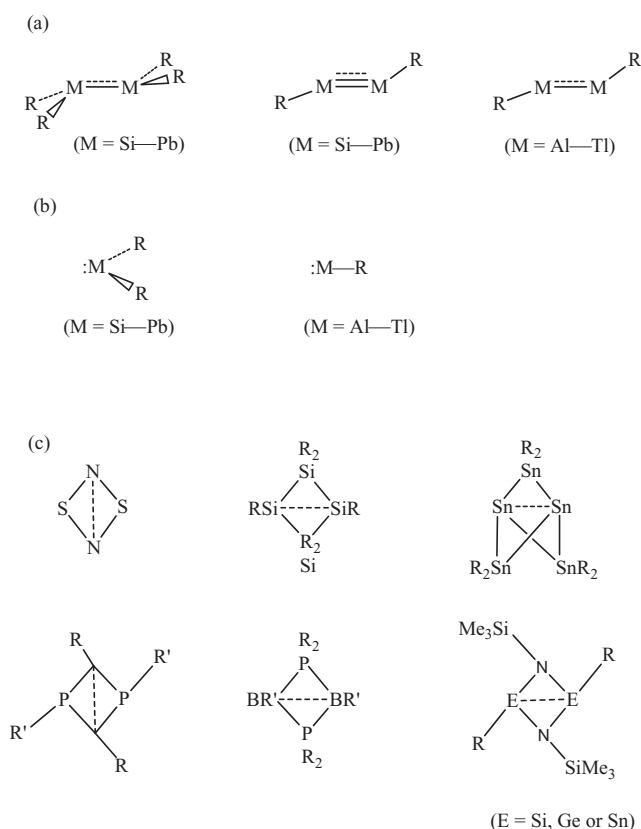


Fig. 1. Schematic drawing of a selection of reactive heavier main-group molecules: (a) multiple bonded Group 13 and 14 species with strained (i.e., pyramidalized or bent) geometry; (b) lower-valent Group 13 and 14 species featuring occupied and empty valence orbitals; (c) non-Kekulé, singlet diradicaloids.

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



raalkyl disilenes were shown to react under photolysis in a $[2+4]$ manner with 2,3-dimethylbutadiene,^{20,21} cyclopentadiene or furan.²² In contrast, by using silyl substituents the resultant tetrakis(trialkylsilyl)disilene²³ reacted with 1-butene and styrene to give $[2+2]$ cyclic addition products.²⁴ Tetramesityldigermene and tetramesitylgermasilene were found to react with dimethylbutadiene^{25,26} and the latter also reacts in a $[2+2]$ fashion with styrene.²⁶

The chemistry of these heavier Group 14 element alkene analogues thus presented a picture of considerably increased reactivity in comparison to the parent carbon-based olefins. Nonetheless, this reactivity could be restricted because of the steric crowding introduced by the bulky substituents²⁷ required to stabilize the compounds. Electronic effects, for example those induced by silyl substituents, were also shown to affect reactivity.²⁴

The geometries and reactivity of the disilene and digermene molecules has been compared to those of crystalline silicon or germanium (100) faces where the exposed tetrel

atoms at the surface form dimeric units featuring multiple Si-Si or Ge-Ge bonds.²⁸ In contrast to the molecular species these dimeric units are unencumbered by large organic groups being bonded only to the adjacent layer of silicon or germanium atoms below the surface. As a result they exhibit a *cis*-bent geometry and very high reactivity toward a variety of molecules including hydrogen or ethylene.^{28,29}

2. Heavier Group 14 Element Alkyne Analogues, Group 13 Dimetallenes and Unsaturated Low-Valent Group 13 and 14 Element Species—Developments in the New Millennium

Since the year 2000 there have been several major advances in the chemistry of multiple bonded heavier main-group complexes. For the Group 14 elements Si-Pb the synthesis and stabilization of their alkyne analogues REER (E = Si-Pb, R = large organic or silyl substituent) was a major advance. Beginning with the diplumbyne $\text{Ar}^{\text{Pr}^i}_6\text{PbPbAr}^{\text{Pr}^i}_6$ ($\text{Ar}^{\text{Pr}^i}_6 = \text{C}_6\text{H}_3-2,6(\text{C}_6\text{H}_2-2,4,6-\text{Pr}^i_3)_2$) in 2000,³⁰ examples for tin,³¹ germanium³² and silicon^{33,34} had been prepared³⁴ by 2004. The latter species was published by Sekiguchi and his group.³³ It is interesting to note that the first reports of each dimetallene were published in reverse order to their atomic number. The preparative methods for the compounds involved reduction of a precursor (either monomeric or dimeric organo or silyl sub-

stituted element halides) by alkali metals or organoaluminum hydrides. The synthesis of neutral germanium and tin alkyne derivatives had been foreshadowed by the isolation of their singly and doubly reduced salts M_nREER (M = Li, Na or K; $n = 1$ or 2) beginning in 1997^{35–38} and the compound $(\eta^2\text{-C}_5\text{H}_5)(\text{CO})_2\text{MoGeC}_6\text{H}_3-2,6\text{-mesityl}_2$ in 1996, which featured a $\text{Mo}\equiv\text{Ge}$ triple bond.³⁹ The key structural parameters of the first example of ditetrelynes from each element are listed in Table 1.

All have essentially planar, *trans*-bent core structures with substantial deviation from linearity. The bending increases and the bond order diminishes with increasing atomic number so that at the heaviest element lead the Pb-Pb bonding is essentially single in character. The bending of the linear geometry in these compounds has been viewed^{40–43} as arising from a second-order Jahn-Teller effect mainly involving a σ^* orbital and the in-plane π orbital, which are vibrationally coupled by one of the doubly degenerate symmetric bending modes which permits mixing of these two orbitals ($\sigma^*(b_u)$ and $\pi(b_u)$) in the C_{2h} (local symmetry) structure (Figure 2). The deviation from triple bonding can also be interpreted in terms of singlet diradical character especially in the case of the germanium and tin compounds where the bond order has been diminished to about two. These compounds are thus “missing” a bond and can be classified as non-Kekulé singlet diradical species.^{42–44} Several further ditetrelynes have also been synthesized and currently almost twenty stable examples have been isolated or

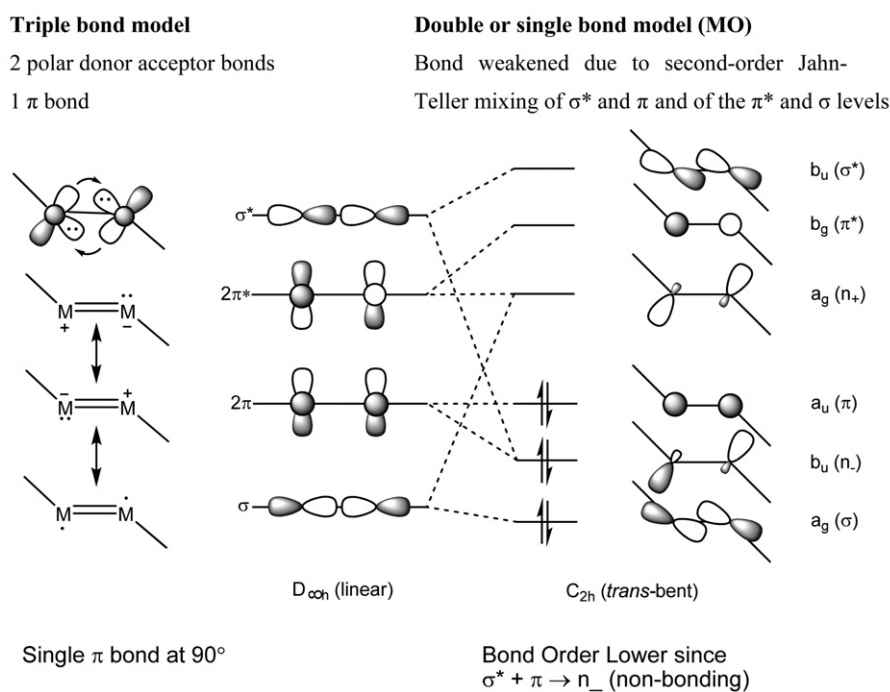


Fig. 2. Schematic drawing of the second-order Jahn-Teller mixing in heavier Group 14 element alkyne analogues.

Table 1. First examples of stable heavier Group 14 element alkyne analogues.^[a]

	E°E (Å)	E-E-C (°)	E-E (Å, single bond)	Reference
H—C≡C—H	1.2	180	1.54	—
$\begin{array}{c} \text{R} \\ \\ \text{Si} \equiv \text{Si} \\ \\ \text{R} \end{array}$	2.0622(9)	137.44(4)	2.34	[33]
$\begin{array}{c} \text{Ar}^{\text{Pr}^i_4} \\ \\ \text{Ge} = \text{Ge} \\ \\ \text{Ar}^{\text{Pr}^i_4} \end{array}$	2.285(6)	128.67(8)	2.44	[31]
$\begin{array}{c} \text{Ar}^{\text{Pr}^i_4} \\ \\ \text{Sn} \equiv \text{Sn} \\ \\ \text{Ar}^{\text{Pr}^i_4} \end{array}$	2.6675(4)	125.1(2)	2.81	[30]
$\begin{array}{c} \text{Ar}^{\text{Pr}^i_6} \\ \\ \text{Pb} - \text{Pb} \\ \\ \text{Ar}^{\text{Pr}^i_6} \end{array}$	3.1811(1)	94.26(4)	2.9	[29]

[a] R = SiPrⁱ₃{CH(SiMe₃)₂} Ar^{Prⁱ₄} = C₆H₃-2,6(C₆H₃-2,6-Prⁱ₂)₂; Ar^{Prⁱ₆} = C₆H₃-2,6(C₆H₂-2,4,6-Prⁱ₃)₂.

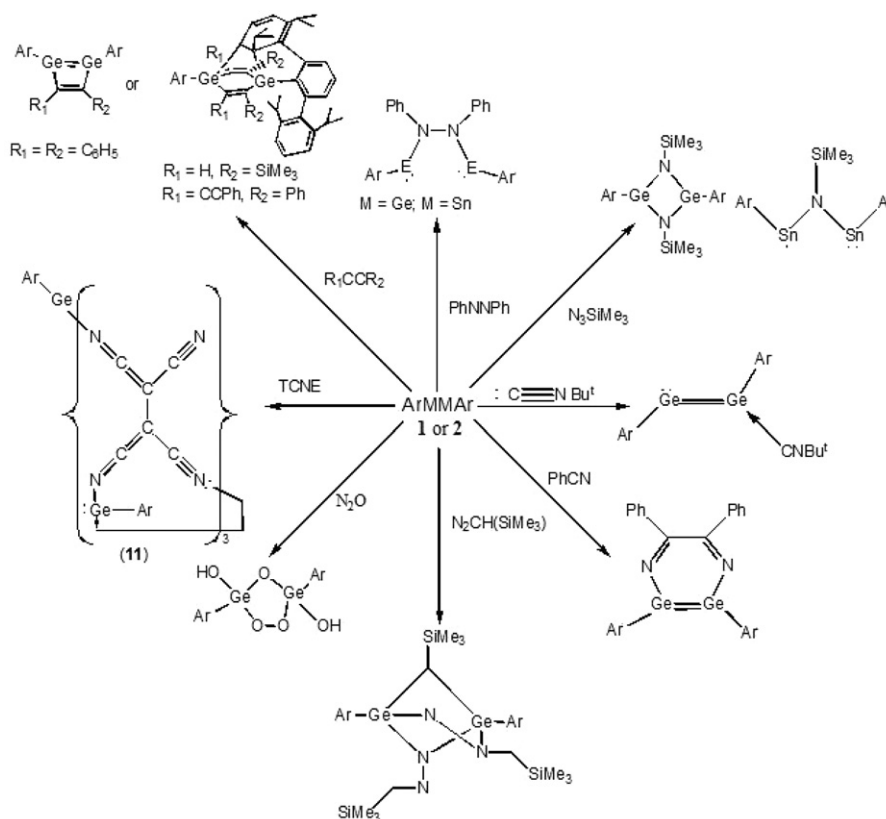
structurally characterized.^{45–48} The tin alkyne analogues are noteworthy because they can exist in two isomeric forms in the solid state. Five of the seven structurally characterized distannynes have a structure very similar to that of Ar^{Prⁱ₄}SnSnAr^{Prⁱ₄} (Table 1) with short tin-tin bonds near 2.65 Å and a bending angle near 124°, whereas two of the distannynes (differentiated only by –SiMe₃ or –GeMe₃ *para* substituents on the central aryl ring of the terphenyl ligand) have tin-tin distances near 3.06 Å and a bending angle near 98°.^{45,47} The structures of the latter resemble that of the lead species Ar^{Prⁱ₆}PbPbAr^{Prⁱ₆} and have single bonds. The existence of the two isomeric forms is possible because there is a very small energy difference (ca. 5 kcal mol^{–1}) between them that allows the structures in the solid state to be affected by packing forces.^{43,47} All seven distannyne structures have the multiple bonded structure in solution as determined by electronic spectroscopy. Only multiple bonded forms have been observed for the digermynes both in solution and the solid state, which is consistent with the fact that this form has been calculated to be more stable than the single bonded arrangement by ca. 15 kcal mol^{–1}.⁴⁹ This is apparently too large to allow significant structural changes as a result of packing forces in the digermynes.

The chemistry of compounds with multiple bonds between the heavier Group 13 metals is less developed than that of their Group 14 neighbors.^{8,9,11,50,51} Although low-valent

M(I) metal-metal bonded clusters had been known for over twenty years,^{8,52} the metals in them generally had a coordination number of four or greater, which tends to saturate the metal valence orbitals. Even in the dimers [M{η⁵-C₅(CH₂Ph)₃}]₂ (M = In or Tl)⁵³ the ligands are η⁵-bound, which leaves no valence orbitals available for further interactions. The M–M bonds are weak as evidenced by the M–M distances which are longer than ca. 3.6 Å. Our interest in this area stemmed from attempts to synthesize species with multiple bonds between Group 13 metals with use of terphenyl ligands. It was shown that the use of the large Ar^{Prⁱ₆} terphenyl substituent (cf. Table 1) could stabilize the highly colored, monomeric, univalent species :InAr^{Prⁱ₆}^{54a} and (in collaboration with M. Niemeyer) :TlAr^{Prⁱ₆}.^{54b} In these derivatives the metals featured a non-bonded pair and two unoccupied valence p orbitals. In 2002 it was shown that the slightly less crowding Ar^{Prⁱ₄} ligand permitted dimerization to afford the In–In bonded dimer Ar^{Prⁱ₄}InInAr^{Prⁱ₄}, which had a *trans*-bent structure and a nominal double bond with an In–In bond length of 2.9786(5) Å.⁵⁵ It was also shown that its gallium⁵⁶ and thallium⁵⁷ analogues Ar^{Prⁱ₄}GaGaAr^{Prⁱ₄} and Ar^{Prⁱ₄}TlTlAr^{Prⁱ₄} had *trans*-bent, planar, core structures with Ga–Ga and Tl–Tl distances of 2.6268(7) and 3.0936(8) Å. All three dimers were extensively dissociated to monomers in hydrocarbon solution and subsequently the use of extremely large terphenyls such as C₆H-2,6(C₆H₂-2,4,6-Prⁱ₃)₂-3,5-Prⁱ₂ (abbreviated Ar^{Prⁱ₈}) at gallium was shown to stabilize monomeric structures featuring one-coordinate gallium in the solid state.⁵⁸ Attempts to synthesize the aluminum dimer Ar^{Prⁱ₄}AlAlAr^{Prⁱ₄} led to a reaction with solvent toluene to give a [2 + 4] cycloaddition product.^{59a} Apparently the putative Ar^{Prⁱ₄}AlAlAr^{Prⁱ₄} species, which can be reduced to form Na₂Ar^{Prⁱ₄}AlAlAr^{Prⁱ₄},^{59b} has extremely high reactivity partly as a result of its singlet diradical character.⁶⁰ Investigations of the reactivity of the gallium, indium and thallium dimetallenes have shown that they behave as good σ-donor ligands^{54a,57,61} as well as reacting with a large variety of reagents to give transition-metal complexes,^{8,54a} imides,⁶² phosphinidenes⁶³ or chalcogenide derivatives.⁶⁴

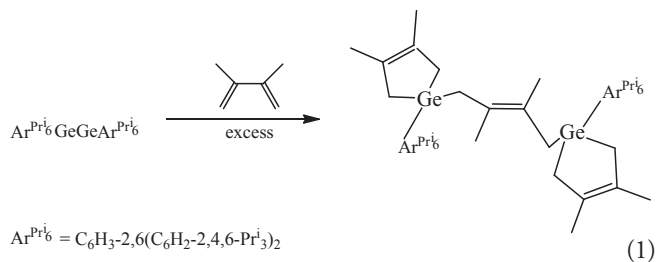
3. Reactions with Unsaturated Small Molecules

The synthesis of the nominally triple bonded Group 14 and double bonded Group 13 dimers afforded a range of new main-group compounds that were distinguished by low coordination numbers (1 or 2) at these elements. Furthermore, all the compounds were deeply colored due to one or more electronic absorptions involving their frontier orbitals which are separated by modest energies (<4 eV). Another feature of the compounds is that calculations indicate that they have a singlet diradical character.^{43,60} Taken together, these properties sug-



Scheme 1. Summary of reactions undergone by the germanium and tin alkyne analogues ArEEAr ($\text{M} = \text{Ge}$, **1**; Sn , **2**; $\text{Ar} = \text{Ar}^{\text{Pr}^4} = \text{C}_6\text{H}_3-2,6(\text{C}_6\text{H}_3-2,4,6-\text{Pr}^i_2)_2$) with unsaturated molecules.

gested a particularly high reactivity for these species. This was borne out by our early investigation in 2002 which showed that the stable digermene $\text{Ar}^{\text{Pr}^4}\text{GeGeAr}^{\text{Pr}^4}$ readily underwent a cyclization with dimethylbutadiene to give the unique product depicted in Eq. (1),⁶⁵ which suggested the involvement of radicals.

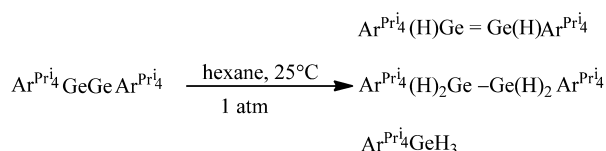


In 2004 Wiberg and coworkers showed that the quasi-stable disilyne $\text{RSi}\equiv\text{SiR}$ ($\text{R} = \text{SiMe}(\text{SiBu}^t_3)_2$) reacted with ethylene and butadiene to give [2 + 2] and [2 + 4] addition products.^{34b} In addition Sekiguchi reported that his stable disilyne $\text{RSi}\equiv\text{SiR}$ ($\text{R} = \text{SiPr}^i\{\text{CH}(\text{SiMe}_3)_2\}_2$) reacted stereospecifically with *cis*- and *trans*-but-2-ene.⁶⁶

Earlier, we had already initiated a wide-ranging investigation of the chemical properties of the digermene and distannene. These showed that they reacted readily with a wide range of unsaturated substrates as shown in Scheme 1,⁶⁷ which underscored their highly reactive character. This high reactivity led us to investigate their reactions with saturated molecules, of which the simplest example is hydrogen.⁶⁸

Although no reactions had been reported between any main-group compound and hydrogen under ambient conditions, calculations by Himmel and Schnöckel⁶⁹ had shown that the model species $\text{HGe}\equiv\text{GeH}$ exhibited a highly exothermic heat of hydrogenation ($\Delta H^\circ_{\text{R}} = \text{ca. } -250 \text{ kJ mol}^{-1}$) to give H_2GeGeH_2 which in turn displays a $\Delta H^\circ_{\text{R}} = -150 \text{ kJ mol}^{-1}$ for a reaction with further equivalent of hydrogen to give H_3GeGeH_3 . We discovered that the digermene $\text{Ar}^{\text{Pr}^4}\text{GeGeAr}^{\text{Pr}^4}$ reacted readily at room temperature and atmospheric pressure to give a mixture of hydrogenated products as shown in Scheme 2.⁶⁷

This reaction was the first experimental evidence that a main-group compound reacted with H_2 under mild conditions. The addition of 1, 2 or 3 equiv of H_2 produced different ratios of the three products shown in Scheme 2. However, with



Scheme 2. Reaction of the digermine $\text{Ar}^{\text{Pr}^i_4}\text{GeGeAr}^{\text{Pr}^i_4}$ ($\text{Ar}^{\text{Pr}^i_4} = \text{C}_6\text{H}_3-2,6(\text{C}_6\text{H}_3-2,6-\text{Pr}^i_2)_2$) with H_2 under ambient conditions.

Table 2. Kohn-Sham valence orbitals for the model species MeGeGeMe.

Orbital	E (kcal mol ⁻¹)	Kohn-Shamorbital
LUMO+1	86.1	
LUMO	48.4	
HOMO	0.0	
HOMO-1	-34.2	
HOMO-2	-80.8	

excess H_2 two products, $\text{Ar}^{\text{Pr}^i_4}(\text{H})_2\text{GeGe}(\text{H})_2\text{Ar}^{\text{Pr}^i_4}$ and $\text{Ar}^{\text{Pr}^i_4}\text{GeH}_3$, are obtained in an approximately 2:1 ratio. The mononuclear germane $\text{Ar}^{\text{Pr}^i_4}\text{GeH}_3$ is noteworthy since its appearance in the reaction products necessarily involves cleavage of the Ge-Ge bond in the digermine. The monogermane could arise via partial dissociation of the digermine $\text{Ar}^{\text{Pr}^i_4}(\text{H})\text{Ge} = \text{Ge}(\text{H})\text{Ar}^{\text{Pr}^i_4}$ to germylene, $:\text{Ge}(\text{H})\text{Ar}^{\text{Pr}^i_4}$, monomers in solution, in which case H_2 may add to the $:\text{Ge}(\text{H})\text{Ar}^{\text{Pr}^i_4}$ unit to yield the monogermane $\text{Ar}^{\text{Pr}^i_4}\text{GeH}_3$. The initial step of the reaction most probably involves the interaction of H_2 with the frontier orbitals at one of the germanium atoms. Some of the calculated valence orbitals for the model species MeGeGeMe are illustrated in Table 2,⁷⁰ where it can be seen that the HOMO-LUMO energy separation is less than 50 kcal mol⁻¹.

Thus a possible reaction sequence as illustrated in Scheme 3 where H_2 is activated synergistically via interaction of its σ and σ^* orbitals with the HOMO and LUMO of the digermine. It is noteworthy that the proposed reaction

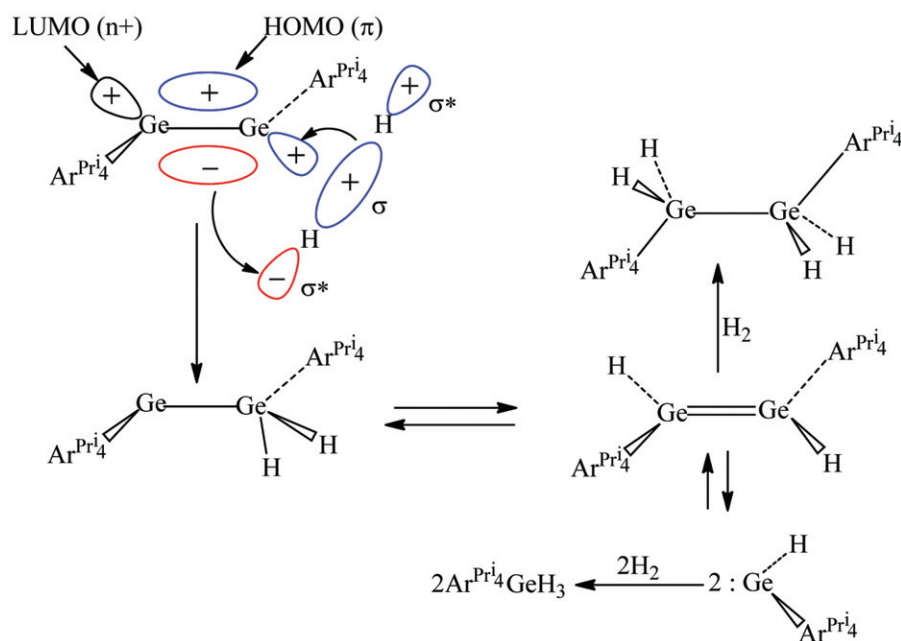
sequence involves the production of $\text{Ar}^{\text{Pr}^i_4}\text{GeGe}(\text{H})_2\text{Ar}^{\text{Pr}^i_4}$ initially, which can quickly rearrange to its digermine isomer, probably via a bridged intermediate. The unsymmetric $\text{Ar}^{\text{Pr}^i_4}\text{GeGe}(\text{H})_2\text{Ar}^{\text{Pr}^i_4}$ can be stabilized as the adduct $\text{Ar}^{\text{Pr}^i_4}(\text{PMe}_3)\text{GeGe}(\text{H})_2\text{Ar}^{\text{Pr}^i_4}$.⁷¹

Calculations⁷² on the corresponding distannylene system indicate a similar initial activation pathway in which the unsymmetric $\text{Ar}'\text{SnSn}(\text{H})_2\text{Ar}'$ is generated in the first instance. However, neither a distannene nor a distannane or monostannane has been isolated so far from this system. Instead, for most terphenyl substituents a symmetrically bridged Sn(II) hydride structure of the type $\text{ArSn}(\mu\text{-H})_2\text{SnAr}$ is isolated. With very bulky terphenyl groups such as $\text{C}_6\text{H}-2,6(\text{C}_6\text{H}_3-2,6-\text{Pr}^i_2)_2-3,5-\text{Pr}^i_2$ ($\text{Ar}^{\text{Pr}^i_8}$) the unsymmetric stannylstannane $\text{Ar}^{\text{Pr}^i_8}\text{SnSn}(\text{H})_2\text{Ar}^{\text{Pr}^i_8}$ is isolated in accordance with Scheme 4.⁷³

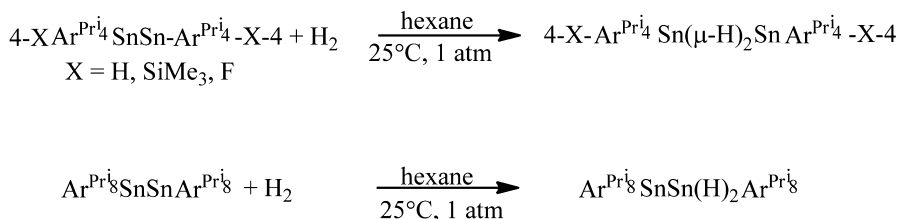
In a more detailed investigation⁷⁴ we showed that the tin hydride products could also be synthesized by reduction of aryl tin halide precursors with a variety of reducing agents. Calculations on the various hydride products showed that they had similar stability but that as the bulk of the substituents increases ($\text{Ar}^{\text{Pr}^i_4}$, $\text{Ar}^{\text{Pr}^i_6}$, $\text{Ar}^{\text{Pr}^i_8}$ cf. Table 1) the bridged form (III) and the distannene form (II) became more disfavored (Figure 3). Oddly, only the symmetric forms $\text{Ar}^{\text{Pr}^i_4}\text{Sn}(\mu\text{-H})_2\text{SnAr}^{\text{Pr}^i_4}$ and $\text{Ar}^{\text{Pr}^i_6}\text{Sn}(\mu\text{-H})_2\text{SnAr}^{\text{Pr}^i_6}$ are seen in the crystal phase even though they are calculated to be the least stable (albeit by only ca. 7 kcal mol⁻¹) of the three structural isomers. We proposed that the apparent inconsistency was due to packing forces which can favor the symmetrically bridged isomers. The existence of isomeric forms of the hydrides is thus a peculiarity of the tin species and mirrors our earlier findings on related tin compounds with small organic substituents, such as Me or Ph instead of hydrogen, which can also have unsymmetric structures.⁷⁵

Related work by Stephan⁷⁶ and Bertrand⁷⁷ show that hydrogen could be activated under mild conditions by phosphine boranes (reversibly) and also by carbenes which could also activate ammonia. The common feature of these results and ours was that the activation occurred by the use of donor and acceptor orbitals in a synergistic fashion at one or more main-group elements (B, C, P, Ge or Sn). In this sense the activation resembles that of H_2 with transition-metal complexes where interactions with d orbitals (rather than s and p orbitals) affect the activation.⁷⁸

In order to explore this theme further we had also been investigating the reactivity of other main-group molecules with hydrogen. The most obvious candidates were the divalent germylene, stannylene and plumbynes.¹⁰ Highly colored bis(terphenyl) derivatives of these elements were already available in our laboratory.⁷⁹ Investigation⁸⁰ of the reactions of germanium and tin divalent diaryls with H_2 or NH_3 afforded considerable variation in behavior



Scheme 3. Schematic illustration of the activation of H_2 by a digermene.



Scheme 4. Reaction of H_2 with various distannynes ($\text{Ar}^{\text{Pr}^i_4}\text{-4-X} = \text{C}_6\text{H}_2\text{-2,6}(\text{C}_6\text{H}_3\text{-2,4,6-Pr}^i_2)_2\text{-4-X}$ where $\text{X} = \text{H}$, SiMe_3 or F ; $\text{Ar}^{\text{Pr}^i_8} = \text{C}_6\text{H}_2\text{-2,6}(\text{C}_6\text{H}_2\text{-2,4,6-Pr}^i_3)_2\text{-3,5-Pr}^i_2$).⁷³

as shown in Scheme 5. Treatment of the germylene $\text{Ge}(\text{Ar}^{\text{Me}_6})_2$ ($\text{Ar}^{\text{Me}_6} = \text{C}_6\text{H}_3\text{-2,6}(\text{C}_6\text{H}_2\text{-2,4,6-Me}_3)_2$) with H_2 or NH_3 afforded the tetravalent products $(\text{Ar}^{\text{Me}_6})_2\text{GeH}_2$ and $(\text{Ar}^{\text{Me}_6})_2\text{Ge}(\text{H})\text{NH}_2$ exclusively.

For the bulkier $\text{Ar}^{\text{Pr}^i_4}$ substituted $\text{Ge}(\text{Ar}^{\text{Pr}^i_4})_2$, however, treatment with H_2 affords the tetravalent $\text{Ar}^{\text{Pr}^i_4}\text{GeH}_3$ with $\text{Ar}^{\text{Pr}^i_4}\text{H}$ elimination whereas the reaction with NH_3 yields $\text{Ar}^{\text{Pr}^i_4}\text{Ge}(\text{H})\text{NH}_2$ in quantitative yield. In contrast to these results, the reactions of $\text{Sn}(\text{Ar}^{\text{Me}_6})_2$ and $\text{Sn}(\text{Ar}^{\text{Pr}^i_4})_2$ with H_2 or NH_3 yield only divalent products with $\text{Ar}^{\text{Me}_6}\text{H}$ or $\text{Ar}^{\text{Pr}^i_4}\text{H}$ elimination. Oddly, no reaction between hydrogen and $\text{Sn}(\text{Ar}^{\text{Me}_6})_2$ was observed up to 70°C in toluene. The more crowded $\text{Sn}(\text{Ar}^{\text{Pr}^i_4})_2$ readily formed the symmetrically bridged $\text{Ar}^{\text{Pr}^i_4}\text{Sn}(\mu\text{-H})_2\text{SnAr}^{\text{Pr}^i_4}$, which was identical to that obtained by the reaction of H_2 with $\text{Ar}^{\text{Pr}^i_4}\text{SnSnAr}^{\text{Pr}^i_4}$ described above. The corresponding reaction with deuterium afforded $\text{Ar}^{\text{Pr}^i_4}\text{Sn}(\mu\text{-D})_2\text{SnAr}^{\text{Pr}^i_4}$ with elimination of $\text{Ar}^{\text{Pr}^i_4}\text{D}$. The reactions between NH_3 and either $\text{SnAr}^{\text{Me}_6}$ or $\text{SnAr}^{\text{Pr}^i_4}$ afforded

the symmetrically bridged parent amido products $\text{Ar}^{\text{Me}_6}\text{Sn}(\mu\text{-NH}_2)_2\text{SnAr}^{\text{Me}_6}$ or $\text{Ar}^{\text{Pr}^i_4}\text{Sn}(\mu\text{-NH}_2)_2\text{SnAr}^{\text{Pr}^i_4}$ with $\text{Ar}^{\text{Me}_6}\text{H}$ or $\text{Ar}^{\text{Pr}^i_4}\text{H}$ elimination. The structure of the germanium and tin amido products closely resemble those of $\text{Ar}^{\text{Pr}^i_6}\text{E}(\mu\text{-NH})_2\text{EAr}^{\text{Pr}^i_6}$ ($\text{E} = \text{Ge}$ or Sn), which were obtained from the reaction of NH_3 with the corresponding divalent halides $\text{Ar}^{\text{Pr}^i_6}\text{ECl}$ ($\text{E} = \text{Ge}$ or Sn).⁸¹ It is noteworthy that the elimination of ArH upon reaction of MAR_2 with NH_3 is also observed for iron and manganese diaryls.⁸²

DFT calculations of the reactions of H_2 with EAR_2 ($\text{E} = \text{Ge}$ or Sn) showed that they initially proceed via interaction of the σ orbital of H_2 with the $4p(\text{Ge})$ or $5p(\text{Sn})$ orbital with back donation of electron density from the Ge or Sn lone pair orbital to the H_2 σ^* orbital.⁸³ The subsequent reaction proceeds by an oxidative addition or a concerted pathway. The data show that the bond strength differences between Ge and Sn , as well as greater non-bonded electron pair stabilization for tin, are in general more important than steric factors in determining the

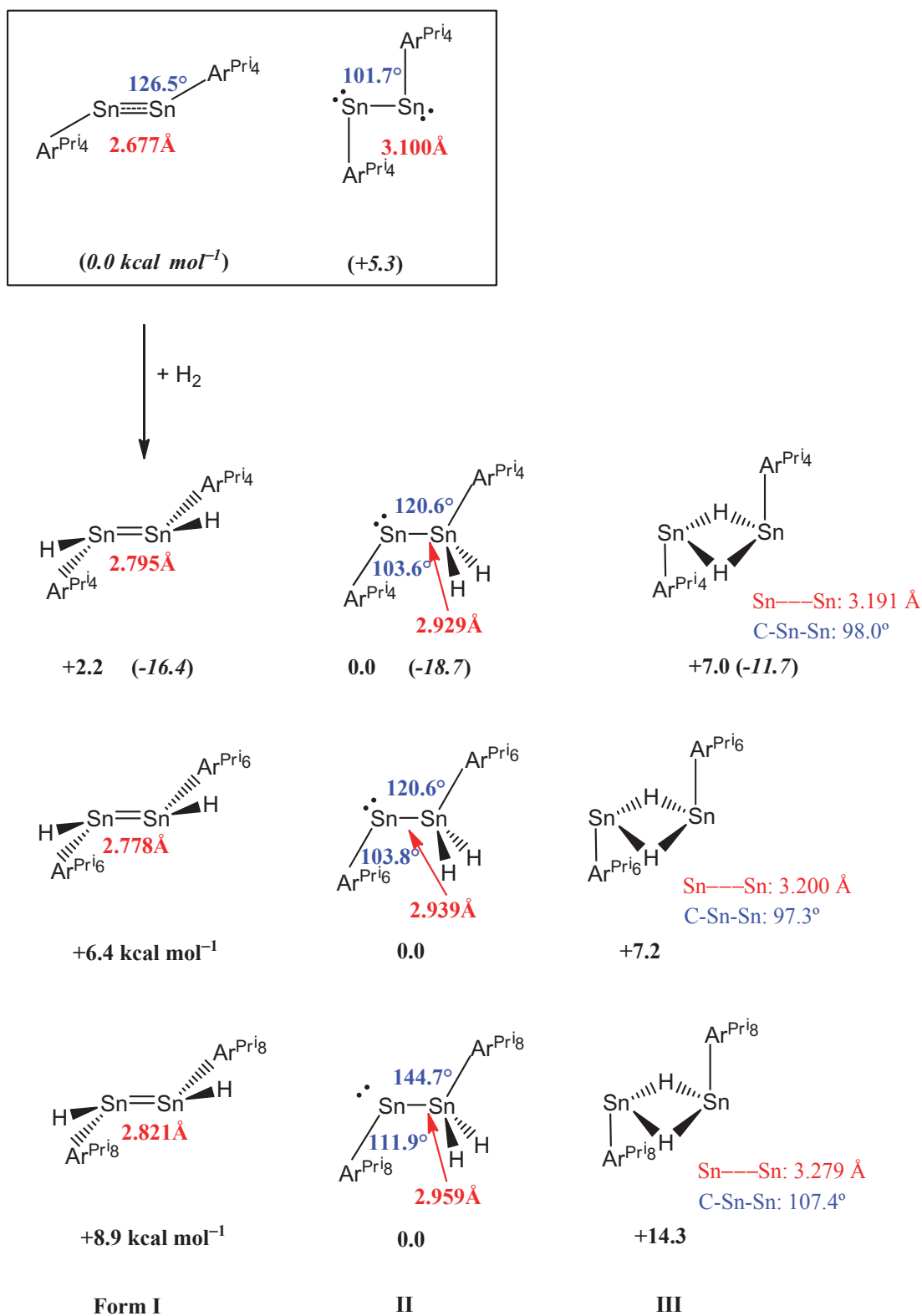
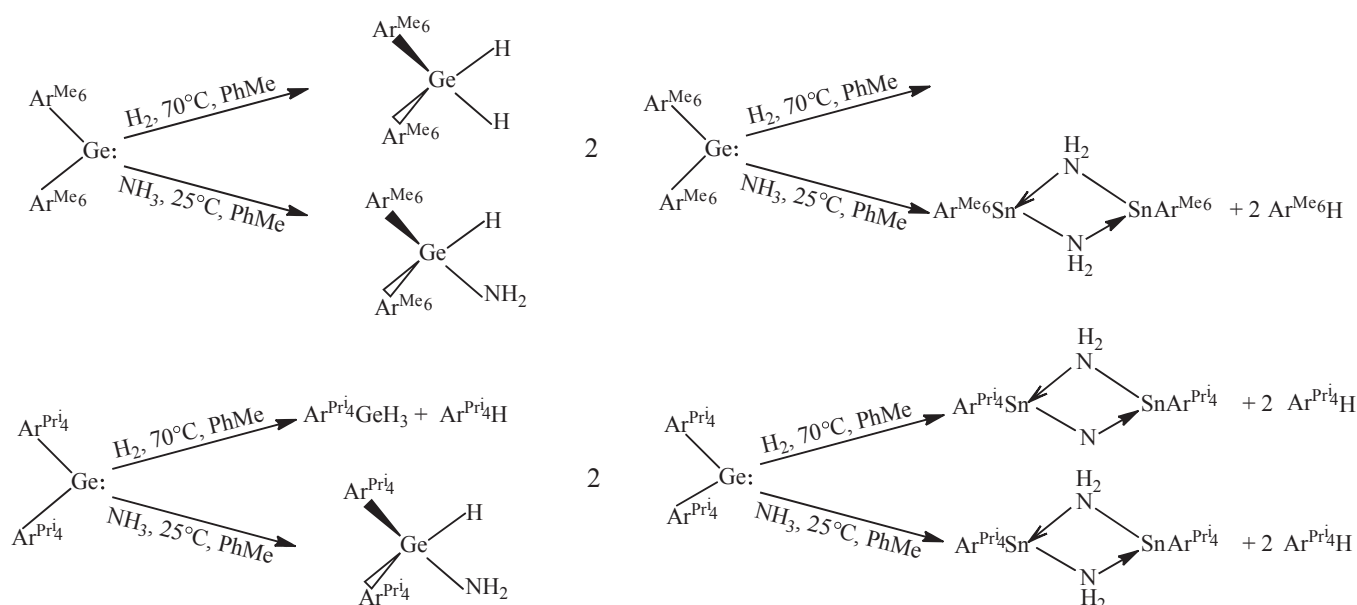


Fig. 3. Calculated relative energies and selected geometric parameters for various isomer forms of $(\text{Ar}^{\text{Pri}}_4\text{SnH})_2$, $(\text{Ar}^{\text{Pri}}_6\text{SnH})_2$ and $(\text{Ar}^{\text{Pri}}_8\text{SnH})_2$ at the B3W91 level. Numbers in parenthesis refer to the energy of the $(\text{Ar}^{\text{Pri}}_4\text{SnH})_2$ hydrides relative to $\text{Ar}^{\text{Pri}}_4\text{SnSnAr}^{\text{Pri}}_4$.



Scheme 5. Summary of the reactions of EAr_2 ($\text{E} = \text{Ge}, \text{Sn}$; $\text{Ar} = \text{Ar}^{\text{Me}_6}$ ($\text{C}_6\text{H}_3\text{-}2,6\text{-(C}_6\text{H}_2\text{-}2,4,6\text{-Me}_3)_2$) or Ar^{Pri_4} ($\text{C}_6\text{H}_3\text{-}2,6\text{-(C}_6\text{H}_3\text{-}2,6\text{-i-Pr}_2)_2$) with H_2 and NH_3 .

product obtained. The calculations indicated that $\text{Ar}^{\text{Me}_6}\text{GeH}_2$ or $\text{Ar}'\text{GeH}$ were thermodynamically preferred with a further reaction between the latter and H_2 yielding $\text{Ar}'\text{GeH}_3$. For the reactions of NH_3 with EAr_2 ($\text{E} = \text{Ge}$ or Sn ; Ar^{Me_6} and Ar^{Pri_4}) the divalent ArENH_2 products were also calculated to be the most stable for both Ge or Sn . However, the tetravalent amido species $\text{Ar}_2\text{Ge(H)NH}_2$ was obtained for kinetic reasons. The reactions with ammonia differ from those with H_2 in that they involve not one but two ammonia molecules in which the lone pair of one NH_3 becomes associated with the empty $4p$ or $5p$ orbital while a second NH_3 solvates the complexed NH_3 via an intermolecular $\text{N-H}\cdots\text{N}$ interaction (Figure 4).

Computations for the reaction of the low-valent Group 13 dimetallene HMMH ($\text{M} = \text{Al}$ or Ga) either in the triplet state or the more stable low-valent bridged species $\text{M}(\mu\text{-H})_2\text{M}$ with H_2 to give H_2MMH_2 showed that the heats of reaction are negative which tend to support the view that the addition of H_2 to isolable dimetallenes should also be favored.⁶⁹ We found that the H_2 reacted readily (Scheme 6) at ca 25°C and 1 atmosphere pressure with dark green toluene solutions of $\text{Ar}^{\text{Pri}_4}\text{GaGaAr}^{\text{Pri}_4}$ (which dissociates at least in part to $:\text{GaAr}^{\text{Pri}_4}$ monomers in solution) to produce bleaching of the color. Work-up provided crystals of the product $\text{Ar}^{\text{Pri}_4}(\text{H})\text{Ga}(\mu\text{-H})_2\text{Ga}(\text{H})\text{Ar}^{\text{Pri}_4}$ in 62% yield. Characterization by X-ray crystallography, NMR and IR spectroscopy showed that the structure was centrosymmetric with two bridging hydrogen atoms and a terminally bound hydrogen atom at each gallium center. Attempts to synthesize the dihydride

product by reduction of $\text{Ar}^{\text{Pri}_4}\text{GaCl}_2$ with hydride sources such as $(\text{Bu}'\text{AlH})_2\text{NaH}$, LiBH_4 and LiBHET_3 afforded a mixture of products which did not contain the target dihydride species.

Similarly the reaction of $\text{Ar}^{\text{Pri}_4}\text{GaGaAr}^{\text{Pri}_4}$ with liq. NH_3 at ca -78°C afforded a 73% yield of the product $\text{Ar}^{\text{Pri}_4}(\text{H})\text{Ga}(\mu\text{-NH}_2)_2\text{Ga}(\text{H})\text{Ar}^{\text{Pri}_4}$ in which gallium has inserted into an N-H bond of ammonia. The gallium centers are bridged symmetrically by two NH_2 moieties and the hydrogen atoms are terminally bound at each gallium. The structure is a relatively rare example⁸⁴ of a parent amido gallium complex and is unique in that the coordination sphere also contains a hydride. Reaction between $\text{Ar}^{\text{Pri}_4}\text{InInAr}^{\text{Pri}_4}$ and H_2 did not occur under ambient conditions although a reaction with NH_3 was observed.⁸⁵

4. Reactions with Olefins and Related Unsaturated Molecules

The early reactivity studies on the ditetrelynes showed that they displayed considerable reactivity toward a variety of unsaturated molecules^{6,7,34b,41,42} including alkynes, nitriles, azides and N_2O as well as some diolefins.^{34b,65} It was also demonstrated that the quasi-stable disilyne $\text{R}^*\text{Si}\equiv\text{SiR}^*$ ($\text{R}^* = \text{SiMe}(\text{SiBu}^t)_2$) reacted with the parent olefin ethylene at or below room temperature.^{34b} The stable disilyne $\text{RSi}\equiv\text{SiR}$ ($\text{R} = \text{SiPr}^i\{\text{CH}(\text{SiMe}_3)_2\}_2$) was also shown to react with some mono-olefins, *cis* and *trans* butenes.⁶⁶

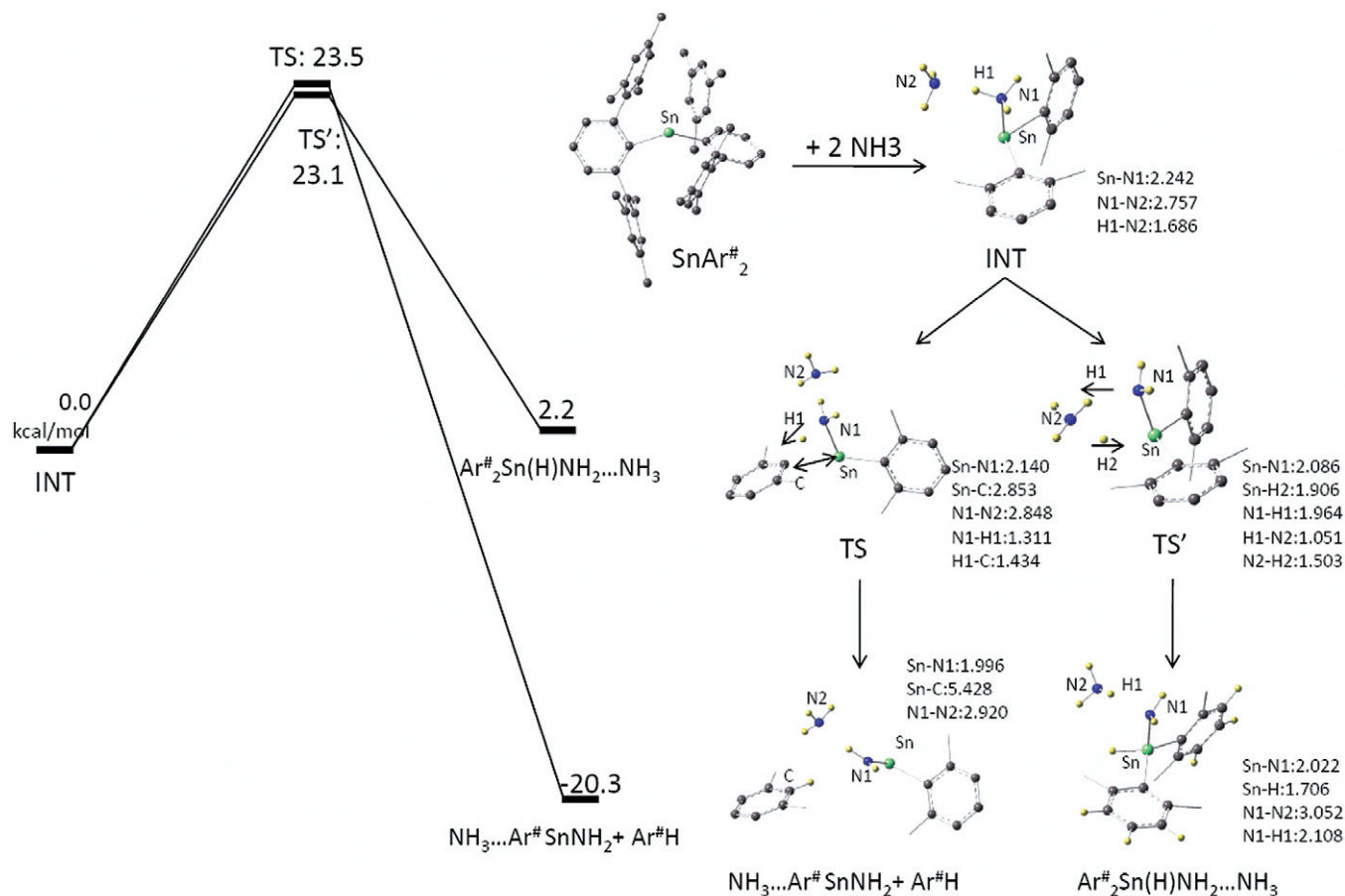
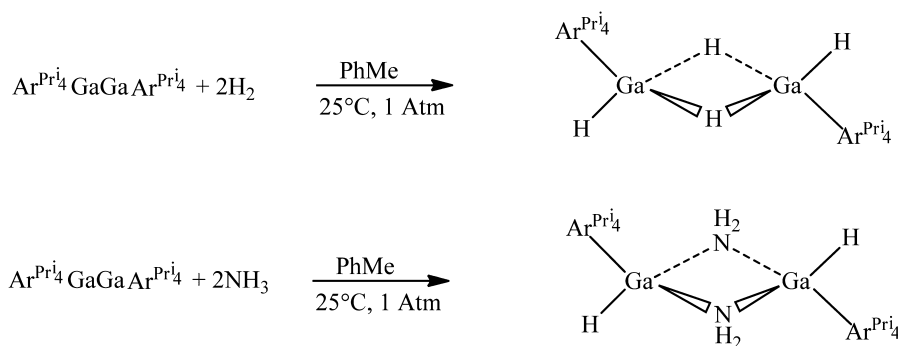
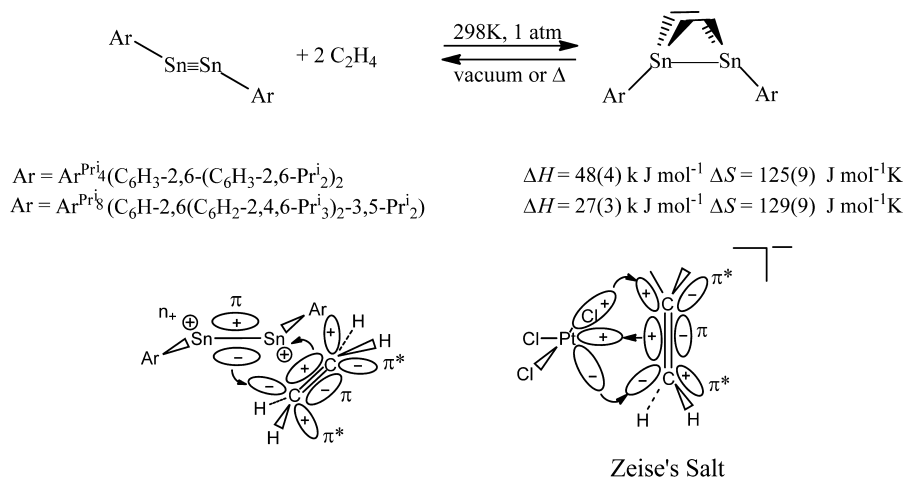


Fig. 4. Calculated energy and drawings of intermediates and transition states with selected distances (Å) and angles (°) for the reaction of $\text{SnAr}^{\text{Me}_6}$ ($\text{Ar}^{\text{Me}_6} = \text{C}_6\text{H}_3\text{-}2,6(\text{C}_6\text{H}_2\text{-}2,4,6\text{-Me}_3)_2$) with NH_3 at the B3PW91 level. In the figure, $\text{Ar}^\# = \text{Ar}^{\text{Me}_6}$.



Scheme 6. Reaction of $\text{Ar}^{\text{Pri}_4}\text{GaGaAr}^{\text{Pri}_4}$ ($\text{Ar}^{\text{Pri}_4} = \text{C}_6\text{H}_3\text{-}2,6\text{-(C}_6\text{H}_3\text{-}2,6\text{-Pri}_2)_2$) with H_2 and NH_3 .

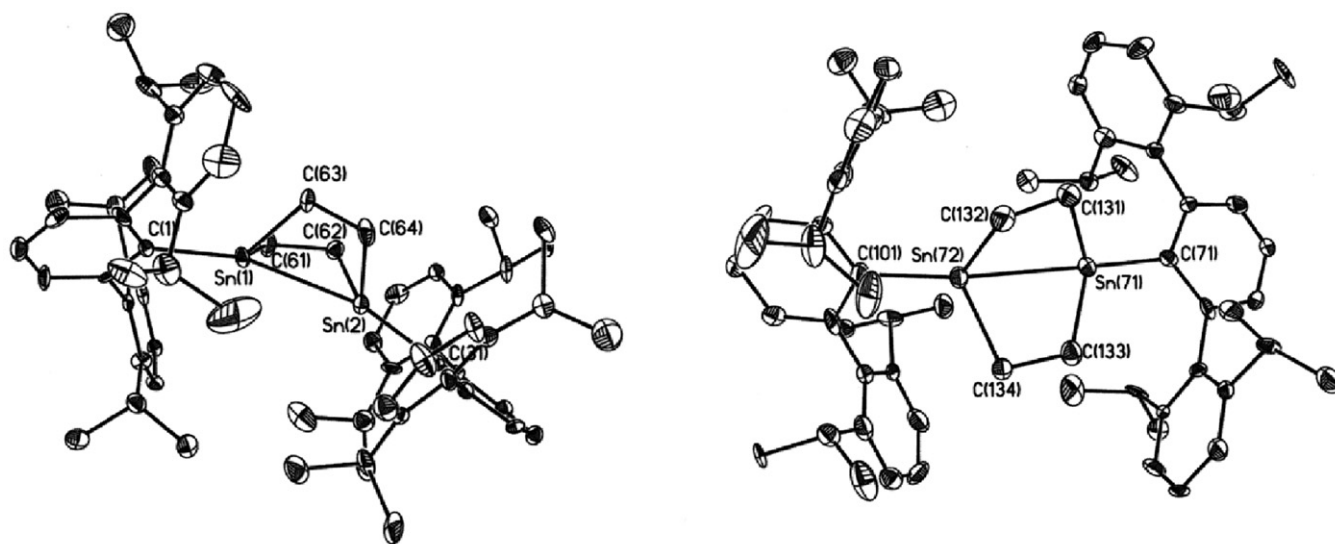


Scheme 7. Reversible reactions of two distannynes with ethylene.

The facile reaction⁶⁴ of Ar^{Pr₆}GeGeAr^{Pr₆} with 2,3-dimethyl-1,3-butadiene suggested that similar reactions with olefins should also be feasible for the slightly less bulky ditrelynies Ar^{Pr₄}GeGeAr^{Pr₄} and Ar^{Pr₄}SnSnAr^{Pr₄}. We tested the reaction of a green toluene solution of Ar^{Pr₄}SnSnAr^{Pr₄} under an atmosphere of ethylene at 25 °C and 1 atmosphere pressure (Scheme 7).⁸⁶ This produced an almost immediate color change from green to amber. To our surprise, workup in the usual fashion, involving the reduction of the solvent volume under reduced pressure (to induce product crystal growth), restored the original green color to the solution. Moreover, treatment of the solution with ethylene regenerated the amber color which persisted if the solution was stored under ethylene. Storage of the solution under ethylene atmosphere at ca. −18 °C afforded crystals of the ethylene adduct as yellow plates.

X-ray crystallographic analysis of these showed that the distannynone had complexed two ethylene units as shown in Figure 5. The two CH₂CH₂ units are η¹,η¹:μ₂ bound to the ditin moiety in a *Z* fashion in the two structurally similar, but crystallographically independent, molecules to afford a 1,4-distannabicyclo[2.2.0]butane core structure. It can be seen that the terphenyl ligands are in the *Z* configuration with respect to each other with Sn-Sn-C(*ipso*) angles of 163.2(1.2)° and tin-tin distances of 2.886(6) Å. The average Sn-CH₂ bond length is 2.19(2) Å, which is indistinguishable from the SnC(Ar^{Pr₄}) distance. The key C-C bond distance within the CH₂CH₂ units averages 1.54(5) Å, which is typical for a C-C single bond. The structure thus has C-C, Sn-C and Sn-Sn bond lengths in the {C(*ipso*)}Sn₂(CH₂CH₂)₂ cores that are all consistent with single bonds. Furthermore, the ¹H, ¹³C and ¹¹⁹Sn NMR data supported this conclusion. Structural and spectroscopic data for the related but slightly more crowded distannynone Ar^{Pr₈}SnSnAr^{Pr₈}(C₂H₄)₂ present a similar picture to the data for Ar^{Pr₄}SnSnAr^{Pr₄}(C₂H₄)₂.

Despite the apparently normal structural and spectroscopic data that support core single bonding, both complexes readily dissociate ethylene. A van't Hoff analysis of variable-temperature ¹H NMR spectra afforded relatively small molar enthalpies of association of −48 and −27 kJ mol^{−1} for the Ar^{Pr₄}SnSnAr^{Pr₄}(C₂H₄)₂ and Ar^{Pr₈}SnSnAr^{Pr₈}(C₂H₄)₂ complexes (Scheme 7, Figure 5). DFT calculations on the model species PhSnSnPh(C₂H₄)₂ reproduced the core structural parameters and afforded a more negative Δ*H*_{assn} value of −133 kJ mol^{−1}, which can be rationalized on the basis of the reduced steric crowding in the model complex. The DFT calculations also indicated that the initial step, involving the synergistic interaction of the frontier orbitals of the distannynone and ethylene (cf. Zeise's salt, Scheme 7), involved a very low energy barrier. The apparent paradox of weak Sn-C bond strength in the face of normal Sn-C bonds lengths can be accounted for, at least in part, on the basis of the distorted geometries at the ethylene complexes, which suggest considerable internal strain energy. For example, the interatomic angles at the four-coordinate tin atoms vary from ca. 70 to 160° and there is a mutually *Z* orientation of large terphenyl groups. In addition, the Sn-Sn bond is lengthened and compared to the distance of 2.8 Å in elemental tin. These parameters may be contrasted to the *trans*-planar structure and short Sn-Sn distances in uncomplexed Ar^{Pr₄}SnSnAr^{Pr₄}. It thus seems that the energy gained in the formation of four Sn-C σ bonds is in approximate balance with the loss of two ethylene C-C π bonds plus the increase in strain energy. As a result the equilibrium in Scheme 7 is strongly affected by the entropic *T*Δ*S* factor and relatively small physical changes can induce rapid and complete dissociation of the ethylene units. Because of this internal strain the distannynone-ethylene complexes need just a small outside stimulus (e.g., gentle heating or vacuum) and are analogous to the compressed spring of a jack-in-the-box toy in their dissociative behavior. The jack-in-the-box



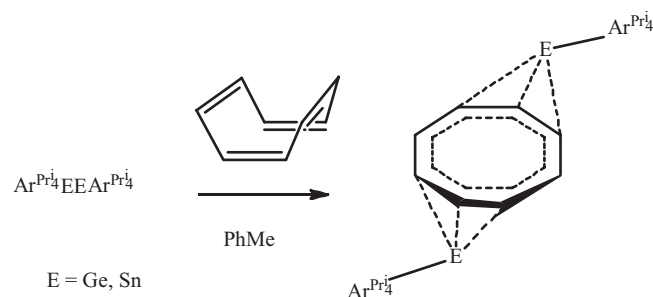
^1H NMR: 1.94 (d, -CHCH-), 0.99 (d, -CHCH-)
 δ ^{119}Sn : 344 (^1J ^{119}Sn - ^{117}Sn : 3130 Hz)

Fig. 5. Structure of $\text{Ar}^{\text{Pr}^i_4}\text{SnSnAr}^{\text{Pr}^i_4}(\text{C}_2\text{H}_4)_2$ ($\text{Ar}' = \text{C}_6\text{H}_3\text{-}2,6(\text{C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2)_2$ (two molecules per unit cell) Selected bond lengths (Å) and angles ($^\circ$): Sn1-Sn2 2.8997(3), Sn1-C1 2.191(1), Sn1-C61 2.08(2), Sn1-C63 2.22(1), Sn2-C31 2.22(1), Sn2-C62 2.22(1), Sn2-C64 2.17(1), C61-C62 1.59(2), C63-C64 1.47(2); C1-Sn1-Sn2 163.0(3), C31-Sn2-Sn1 163(3).

analogy was originally made for sterically encumbered dipnictanes⁸⁷ which dissociate to persistent diorganopnictinyl radicals with concomitant ligand conformational changes when dissolved in hydrocarbons.

Further experiments with other olefins showed that $\text{Ar}^{\text{Pr}^i_4}\text{SnSnAr}^{\text{Pr}^i_4}$ formed a dissociating complex $\text{Ar}^{\text{Pr}^i_4}\text{SnSnAr}^{\text{Pr}^i_4}(\text{nbd})_2$ (nbd = norbornadiene) with two norbornadiene molecules, which exhibited slightly stronger binding than the ethylene complex. However, propene did not display any olefin complex formation. DFT calculations⁸⁸ on the $\text{Ar}^{\text{Pr}^i_4}\text{SnSnAr}^{\text{Pr}^i_4}$ ethylene system showed that the initial interaction involved one of the tin atoms as illustrated in Scheme 7, which shows a synergic interaction between the n_+ (LUMO) and π (HOMO) orbitals of ethylene. The calculations also showed that the subsequent steps (which bear a similarity to those reported by Sekiguchi for the stereospecific interaction of his disilylne with one equivalent of a *cis* or *trans* but-2-ene)⁶⁶ in the formation of the adducts involved essentially zero activation barriers. Investigation of the corresponding reactions of ethylene and norbornadiene with $\text{Ar}^{\text{Pr}^i_4}\text{GeGeAr}^{\text{Pr}^i_4}$ resulted in the isolation of products analogous to those observed for $\text{Ar}^{\text{Pr}^i_4}\text{SnSnAr}^{\text{Pr}^i_4}$, but no dissociation of the olefin could be detected at temperatures below their decomposition points.⁸⁹

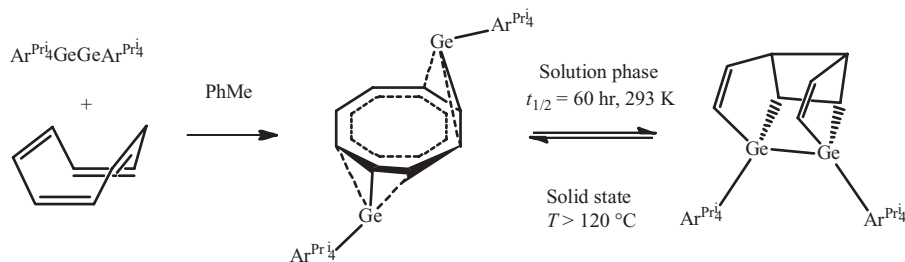
More recent investigations have uncovered further reactions with olefins. Thus treatment of $\text{Ar}^{\text{Pr}^i_4}\text{MMAr}^{\text{Pr}^i_4}$



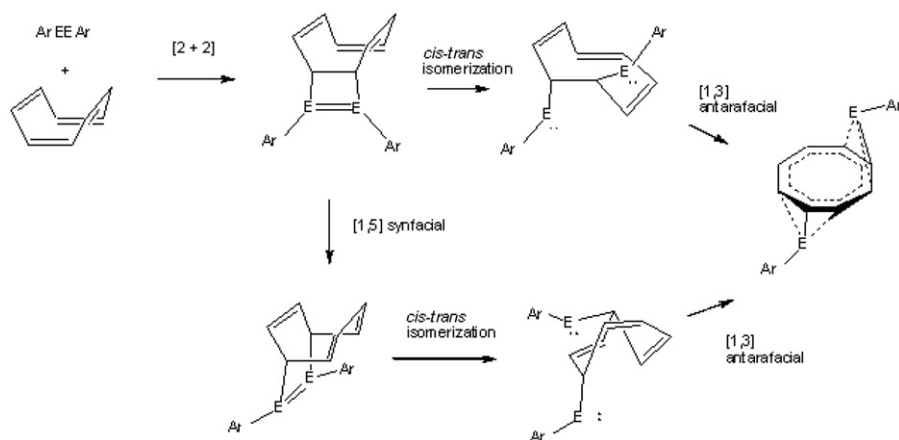
Scheme 8. Multiple bond cleavage of a distannyne or digermayne by cyclooctatetraene. Fluxional behavior, single COT resonance: ^1H NMR (δ , ppm): 5.36 (Sn) and 5.32 (Ge) [cf. 5.79 for free COT, 5.73 for Li_2COT]; ^{13}C NMR (δ , ppm): 96.4 (Sn) and 100.0 (Ge) [cf. 132.4 for free COT, 87.5 for Li_2COT].

($\text{M} = \text{Ge}$ or Sn) with COT (1,3,5,7-cyclooctatetraene) results in complete cleavage of the M-M multiple bonds with the formation of inverted sandwich complexes as shown in Scheme 8.⁹⁰

In this reaction the COT rings have been reduced to afford $\text{C}_8\text{H}_8^{2-}$ in an almost planar 10- π aromatic ring for which the spectroscopic and structural properties are consistent with π -electron delocalization. However the germanium inverse sandwich compound isomerizes in solution^{90b} to afford a digermanium substituted analogue of the hydrocarbon



Scheme 9. Reversible isomerization of $(\text{Ar}^{\text{Pr}^i_4}\text{Ge})_2(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-COT})$ occurs with C-C and Ge-Ge multiple bond cleavage. Isomerization occurs in solution to give thermodynamic product with first order kinetics: activation parameters $\Delta H^\ddagger = 14.9 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -6.2 \text{ cal mol}^{-1} \text{ K}^{-1}$.



Scheme 10. A possible route to Group 14 element inverse sandwich compounds. $\text{Ar} = \text{Ar}^{\text{Pr}^i_4}$ ($\text{C}_6\text{H}_3\text{-}2,6(\text{C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2)_2$).

molecule hypostrophene as illustrated in Scheme 9. Variable-temperature ^1H NMR studies afforded an activation enthalpy near 15 kcal mol^{-1} . However, in the solid-state upon heating above 120°C the inverted sandwich structure is regenerated. For the tin system the inverse sandwich structure alone is observed under analogous conditions.

The mechanism of this reversible rearrangement remains under computational study (in collaboration with G. Merino) but it is a possibility that the reaction initially involves interaction in a $[2+2]$ fashion of the dimetallene with a double bond from the COT ring as shown in Scheme 10. The heavier ditetrelene double bond of the $[2+2]$ product may then dissociate to give a digermylene species and allow generate the inverse sandwich product in which each $\text{EAr}^{\text{Pr}^i_4}$ fragment is complexed on opposite sides of the COT ring as observed in both the tin and germanium (kinetic) products.

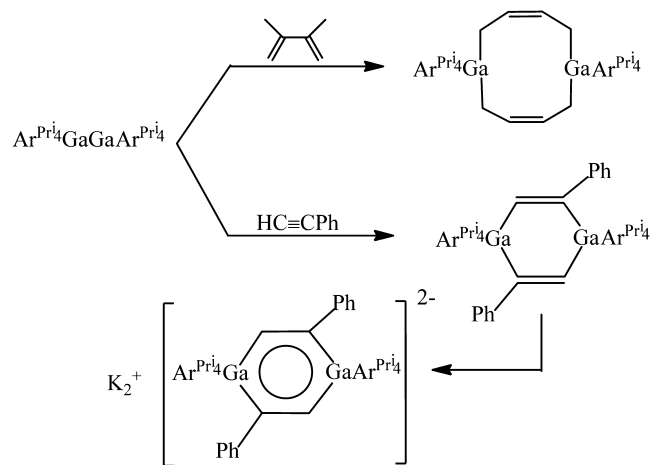
Current work involves a general exploration of the reactions of a wider variety of olefins with unsaturated heavier main-group molecules. The latter include the Group 13 element dimetallenes such as the earlier mentioned digallene

$\text{Ar}^{\text{Pr}^i_4}\text{GaGaAr}^{\text{Pr}^i_4}$ and this species has already been shown to display a higher reactivity with a wider variety of olefins than its Group 14 counterpart $\text{Ar}^{\text{Pr}^i_4}\text{EEAr}^{\text{Pr}^i_4}$ ($\text{E} = \text{Ge}$ or Sn). Currently, the only reactions with unsaturated hydrocarbons that have been reported involve 2,3-dimethyl-1,3-butadiene which affords an unusual 1,6-digalla-2,3,8,9-tetramethylcyclodeca-3,8-diene ring.⁸ In addition, it was shown that $\text{Ar}^{\text{Pr}^i_4}\text{GaGaAr}^{\text{Pr}^i_4}$ reacts with phenylacetylene to afford the unsaturated digallacyclohexadiene (Scheme 11), which can be readily reduced by potassium to give a delocalized quasi-aromatic digallatabenzene ring.⁹¹

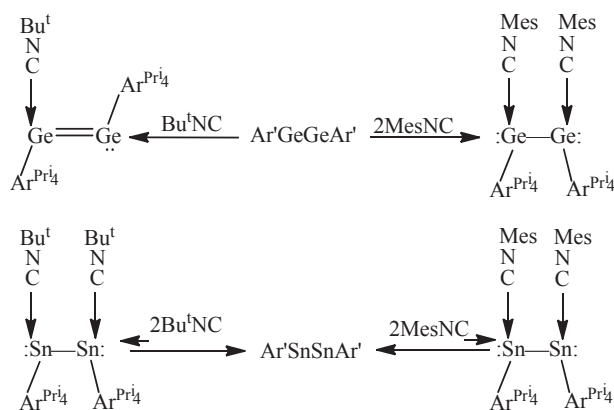
We have also recently shown that $\text{Ar}^{\text{Pr}^i_4}\text{GaGaAr}^{\text{Pr}^i_4}$ reacts with ethylene, propene as well as a variety of other olefins both cyclic and non-cyclic. Details of these reactions will be reported in the near future.⁹²

5. Reactions with Other Unsaturated Molecules

Both the digermylene $\text{Ar}^{\text{Pr}^i_4}\text{GeGeAr}^{\text{Pr}^i_4}$ and distannyne $\text{Ar}^{\text{Pr}^i_4}\text{SnSnAr}^{\text{Pr}^i_4}$ react readily with the isocyanides Bu^tNC and



Scheme 11. Reaction of $\text{Ar}^{\text{Pr}_4}\text{GaGaAr}^{\text{Pr}_4}$ with 2,3-dimethyl-1,3-butadiene or phenylacetylene and the reduction of the latter product to give a delocalized digallatabenzene.



Scheme 12. Reactions of $\text{Ar}^{\text{Pr}_4}\text{MMAr}^{\text{Pr}_4}$ ($\text{M} = \text{Ge}$ or Sn) with isocyanides.

MesNC to afford products that display interesting variation as shown in Scheme 12.^{7,93,94}

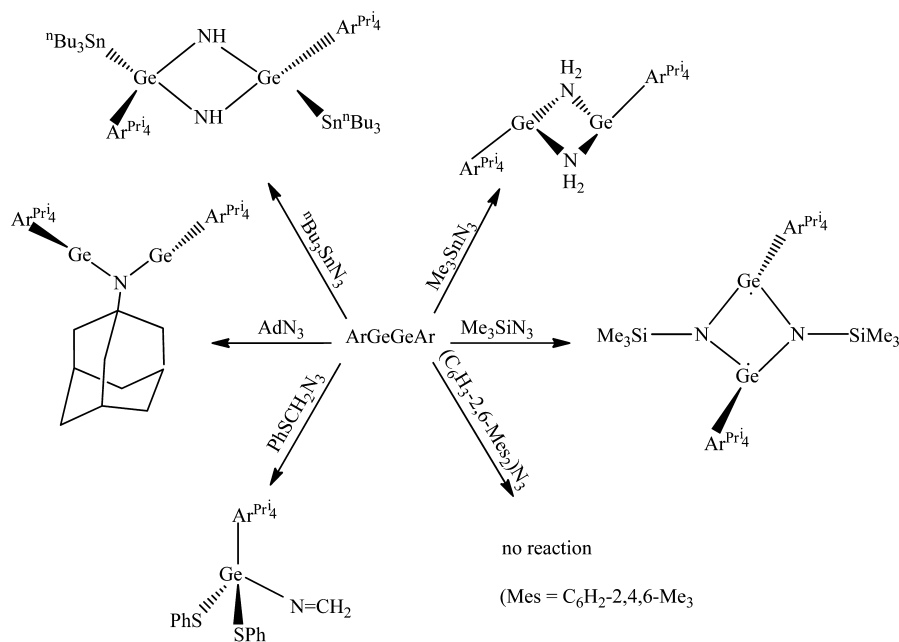
The reaction of Bu^tNC with $\text{Ar}^{\text{Pr}_4}\text{GeGeAr}^{\text{Pr}_4}$ is noteworthy because of the light it sheds on the electronic structure. The structure of the 1:1 adduct $\text{Ar}^{\text{Pr}_4}\text{GeGeAr}^{\text{Pr}_4}(\text{CNBu}^t)$ (a 2:1 adduct was not observed presumably because coordination of a second Bu^tNC unit is prevented for steric reasons) shows that the isocyanide binds to one of the germaniums in the $\text{Ge}_2\{\text{C}(\text{ipso})\}_2$ core plane and not perpendicular to it as would be expected if it bonded to a π^* orbital. Moreover the Ge-Ge bond distance increases only slightly from 2.2850(6) Å to 2.3432(9) Å. This finding is entirely consistent with the MO picture shown in Table 2, where the LUMO to which the isocyanide binds is only slightly bonding in character and lies in the $\text{Ge}_2\{\text{C}(\text{ipso})\}_2$ plane. In contrast, use of the essentially two-dimensional MesNC : ($\text{Mes} = \text{mesityl}$) permits binding of

two isocyanide units, the second of which interacts with the lowest energy orbital available, the LUMO+1. This produces a large increase ($>0.4\text{Å}$) in the Ge-Ge bond length at 2.6626(8) Å and this finding is consistent with the antibonding character of this orbital.

The less sterically crowded distannyne bonds two equiv of both Bu^tNC : and MesNC :.⁹⁴ Attempts to synthesize 1:1 complexes were unsuccessful. The 2:1 complexes are unstable with respect to dissociation in toluene solution at room temperature although they can be isolated and structurally characterized at low temperature. The complexes feature relatively long Sn-Sn bonds of 2.928(2) Å for $\text{Ar}^{\text{Pr}_4}\text{SnSnAr}^{\text{Pr}_4}(\text{CNBu}^t)_2$ and 3.0412(3) Å for $\text{Ar}^{\text{Pr}_4}\text{SnSnAr}^{\text{Pr}_4}(\text{CNMes})_2$ that are consistent with Sn-Sn single bonds. Each complex was isolated as red crystals, but when these crystals are dissolved in hexane at room temperature, a green solution is obtained that displays two absorption maximum at 410 and 597 nm that are characteristic of the $\pi \rightarrow n_+$ and $n_- \rightarrow n_+$ transitions of $\text{Ar}^{\text{Pr}_4}\text{SnSnAr}^{\text{Pr}_4}$. Cooling the solution to ca. -40° restores the red color, which is associated with an absorption at 510–520 nm. Van't Hoff analysis of the variable-temperature ^1H NMR spectra afforded $\Delta H_{\text{assn}} = -25(3)$ and $-127(4)$ kJmol $^{-1}$ for the Bu^tNC and MesNC adducts, respectively, the difference being attributable to the higher steric requirement of the Bu^tNC unit, which promotes dissociation. Coordination occurs in the empty 5p orbital perpendicular to the coordination plane. Sekiguchi⁹⁵ and co-workers have also shown that addition of the nitrile Me_3SiCN to his disilyne RSiSiR ($\text{R} = \text{Si}\{\text{CH}(\text{SiMe}_3)_2\text{Pr}^i\}$) affords the bis(isocyanide) adduct $\text{RSiSiR}(\text{CNSiMe}_3)_2$ as a coproduct which probably arises from the existence of the Me_3SiNC in equilibrium with Me_3SiCN .

The reactivity of the ditertiarylynes with CO was also tested. No reaction between $\text{Ar}^{\text{Pr}_4}\text{EEAr}^{\text{Pr}_4}$ ($\text{E} = \text{Ge}$ or Sn) and CO was observed under ambient conditions. However, diarylgermylenes were found to react with CO to give double CO insertion into a Ge-C bond with activation of alkyl groups from the flanking rings of the terphenyl substituents.⁹⁶

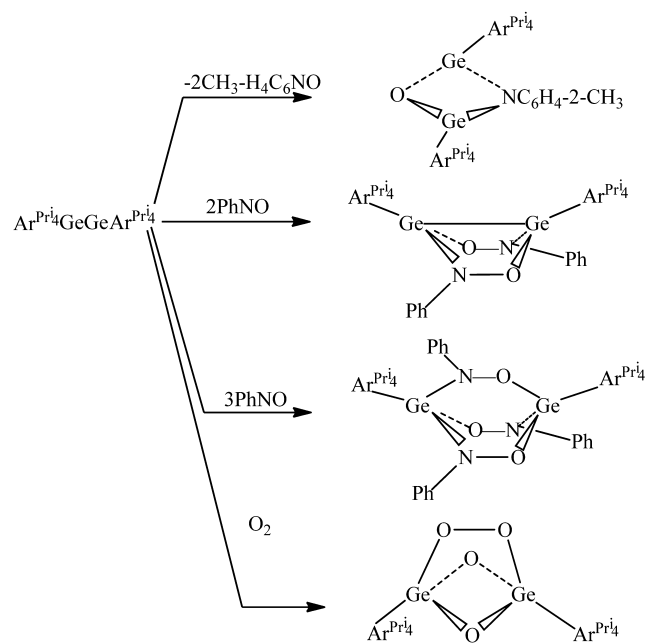
The reaction of $\text{Ar}^{\text{Pr}_4}\text{MMAr}^{\text{Pr}_4}$ ($\text{M} = \text{Ge}$ or Sn) with azides led to a number of different products.⁹⁷ Treatment of $\text{Ar}^{\text{Pr}_4}\text{GeGeAr}^{\text{Pr}_4}$ with N_3SiMe_3 gave the singlet diradicaloid $\text{Ar}^{\text{Pr}_4}\text{Ge}(\mu\text{-NSiMe}_3)_2\text{GeAr}^{\text{Pr}_4}$,^{12f} whose core structure features a four-membered Ge_2N_2 ring which is non-Kekulé in character with a Ge-Ge separation of 2.7550(4) Å and a low, calculated energy difference between singlet and triplet state of 17.51 kcal mol $^{-1}$. Recent work has shown that the reaction of the disilyne RSiSiR ($\text{R} = \text{SiPr}^i\{\text{CH}(\text{SiMe}_3)_2\}_2$) with the diaryl diimine ArNNAr ($\text{Ar} = \text{C}_6\text{H}_3\text{-3,5-Me}_2$) yielded the related silicon species $\text{RSi}(\mu\text{-NAr})_2\text{SiR}$ which has an Si-Si separation of 2.6380(9) Å.^{12g} In contrast, the reaction of $\text{Ar}^{\text{Pr}_4}\text{SnSnAr}^{\text{Pr}_4}$ leads to the product $\text{Me}_3\text{SiN}(\text{SnAr}')_2$ in which two SnAr' moieties and a SiMe_3 group are coordinated to the nitrogen atom.



Scheme 13. Reaction of $\text{Ar}^{\text{Pr}_4}_4\text{GeGeAr}^{\text{Pr}_4}_4$ with various azides.⁹⁷

The reaction of $\text{Ar}^{\text{Pr}_4}_4\text{GeGeAr}^{\text{Pr}_4}_4$ with a variety of other azides RN_3 ($\text{R} = \text{SiMe}_3$, SnBu^n_3 , CH_2SPh or 1-admantanyl (1-Ad)) led to a variety of products (Scheme 13), none of which was analogous to the diradicaloid above.⁹⁷ However, the adamantanyl substituted azide afforded $(1\text{-Ad})\text{N}(\text{GeAr}^{\text{Pr}_4}_4)_2$ whose structure is analogous to the corresponding $\text{Me}_3\text{SiN}(\text{SnAr}^{\text{Pr}_4}_4)_2$ species.

The reaction of $\text{Ar}'\text{GeGeAr}'$ with the nitrosoarene 2- $\text{CH}_3\text{H}_4\text{C}_6\text{NO}$ led cleanly to the unsymmetric oxo/imido bridged germanium centered singlet diradicaloid $\text{Ar}^{\text{Pr}_4}_4\text{Ge}(\mu\text{-O})(\mu\text{-NC}_6\text{H}_4\text{-2-CH}_3)\text{GeAr}^{\text{Pr}_4}_4$ (Scheme 14).^{98a} The Ge_2NO four-membered ring is planar with a Ge-Ge separation of 2.7280(16) Å and it is similar in its physical and spectroscopic properties to the symmetric NSiMe_3 bridged diradicaloid discussed above. Further experiments with the parent nitrosoarene PhNO and $\text{Ar}^{\text{Pr}_4}_4\text{GeGeAr}^{\text{Pr}_4}_4$ showed that it was also possible to add two or three equivalents of the nitrosoarene to afford the products shown in Scheme 14.^{98b} The X-ray data for the two equivalent products showed that it had a bicyclic structure with a lengthened Ge-Ge bond of (2.4731(7) Å), and the fold angle between the two almost planar GeNOGe rings is 110°. The Ge coordination is extremely distorted and there is an almost linear arrangement of the $\text{C}(\text{ipso})\text{GeGeC}(\text{ipso})$ atoms. Use of the larger $\text{Ar}^{\text{Pr}_4}_4$ substituent at germanium results in a similar structure but with a longer Ge-Ge bond of 2.5403(3) Å. Reaction of $\text{Ar}^{\text{Pr}_4}_4\text{GeGeAr}^{\text{Pr}_4}_4$ with three equivalents of PhNO afforded a



Scheme 14. Reaction of $\text{Ar}^{\text{Pr}_4}_4\text{GeGeAr}^{\text{Pr}_4}_4$ with nitrosoarenes or oxygen.^{98a,98b}

tris(nitrosobenzene)-1,4-digermabicyclo[2.2.2] octane structure which features a Ge-Ge separation of ca. 3.0 Å consistent with the absence of a Ge-Ge bond.⁹⁸

6. Summary and Outlook

The multiple bonded and open shell heavier main-group compounds possess unique reactivity in many instances. In the author's laboratory the key factor in their isolation has been the use of terphenyl ligands which provide the steric hindrance necessary for stability but yet allow access of many small molecules. The reactions usually occur under ambient conditions and proceed in near quantitative yield. Many of the reactions, for example those with hydrogen or ammonia, provide the simplest and highest yielding routes to the respective hydride or amido products. The discovery of reversible olefin and isocyanide complexation as well as various isomerization equilibria involving heavier Group 14 element derivatives show that the heavier main-group species can engage in dynamic processes. This opens the possibility that these and related main-group compounds may have catalytic properties.

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