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Mechanisms of Reactions of Open-Shell, Heavier Group 14 Derivatives with Small Molecules: n−π* Back-Bonding in Isocyanide Complexes, C−H Activation under Ambient Conditions, CO Coupling, and Ancillary Molecular Interactions†

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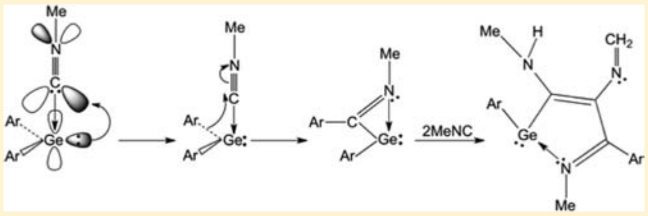

ABSTRACT: The main themes of this review are the mechanisms of the reactions of germanium and tin analogues of carbenes with isocyanides, CO, ammonia, and related molecules. The treatment of Ge(Ar^{Me_6})$_2$ (Ar^{Me_6} = C_6H_3-2,6(C_6H_2-2,4,6-Me_3)$_2$) with MeNC or Bu^{t}NC afforded 1:1 complexes, but the increase in the electron density at germanium leads to C−H activation at the isocyanide methyl or *tert*-butyl substituents. For MeNC, the initial adduct formation is followed by a migratory insertion of the MeNC carbon into a Ge−C(ipso) bond of an aryl substituent. The addition of excess MeNC led to sequential insertions of two further MeNC molecules. The third insertion led to methylisocyanide methyl group C−H activation, to afford an azagermacyclopentadienyl species. The Bu^{t}NC complex (Ar^{Me_6})$_2$GeCNBu^t spontanously transforms into (Ar^{Me_6})$_2$Ge(H)CN and isobutene with C−H activation of the Bu^t substituent. The germylene Ge(Ar^{Me_6})(Ar$^{Pr^i_4}$) [Ar$^{Pr^i_4}$ = C_6H_3-2,6(C_6H_3-2,6-Pr^i_2)$_2$] reacted with CO to afford α-germyloxyketones. The initial step is the formation of a 1:1 complex, followed by migratory insertion into the Ge−C bond of the Ar$^{Pr^i_4}$ ligand to give Ar^{Me_6}GeC(O)Ar$^{Pr^i_4}$. Insertion of a second CO gave Ar^{Me_6}GeC(O)C(O)Ar$^{Pr^i_4}$, which rearranges to afford α-germyloxyketone. No reaction was observed for Sn(Ar^{Me_6})$_2$ with RNC (R = Me, Bu^t) or CO. Spectroscopic (IR) results and density functional theory (DFT) calculations showed that the reactivity can be rationalized on the basis of Ge−C (isocyanide or CO) Ge(n) → π* (ligand) back-bonding. The reaction of Ge(Ar^{Me_6})$_2$ and Sn(Ar^{Me_6})$_2$ with ammonia or hydrazines initially gave 1:1 adducts. However, DFT calculations show that there are ancillary N−H---N interactions with a second ammonia or hydrazine, which stabilizes the transition state to form germanium(IV) hydride (amido or hydrazido) products. For tin, arene elimination is favored by a buildup of electron density at the tin, as well as the greater polarity of the Sn−C(ipso) bond. Germanium(IV) products were observed upon reaction of Ge(Ar^{Me_6})$_2$ with acids, whereas reactions of Sn(Ar^{Me_6})$_2$ with acids did not give tin(II) products. In contrast to reactions with NH_3, there is no buildup of negative charge at tin upon protonation, and its subsequent reaction with conjugate bases readily affords the tin(IV) products.

■ INTRODUCTION

The low-valent derivatives of the heavier group 14 elements silicon, germanium, tin, and lead have played a central role in the development of modern main-group chemistry.[1−5] A major objective of the early studies was the isolation of two-coordinate, monomeric, divalent analogues (i.e., metallanediyls or tetrylenes) of carbenes (at that time also unknown as stable species) via the use of sterically crowding ligands, which could stabilize the compounds by preventing association and/or element−element bond formation. The earliest studies by Lappert and coworkers on germanium, tin, and lead dialkyls,[6] and by Lappert[7a] and Zuckerman[7b] on bis(amido) derivatives, afforded the first stable compounds that were two-coordinate monomers [e.g., M{CH($SiMe_3$)$_2$}$_2$ or M{N($SiMe_3$)$_2$}$_2$ (M = Ge, Sn, or Pb) in solution]. However, the alkyl dervatives dimerized weakly in the solid state to give heavier-element olefin analogues that had distorted trans-pyramidalized geometries, unlike the planar structures in olefins. In contrast, West and co-workers showed that the silicon species $Mes_2SiSiMes_2$ (Mes = C_6H_2-2,4,6-Me_3) maintained its dimeric structure in solution and had almost planar silicon coordination, thus providing the first stable example of a homonuclear multiple bond between two heavier main-group elements in a neutral molecule.[8]

Studies of the unusual bonding and high reactivity of the heavier group 14 element analogues of carbenes and olefins continue to be a very active area, as exemplified by the recent synthesis of the first examples of stable acyclic silylenes; the compounds $\mathrm{Si\{\overline{BN(Dipp)CHCHN}(Dipp)\}\{N(Dipp)SiMe_3\}}$ (Dipp = C_6H_3-2,6-Pr^i_2)[9] and Si(SAr^{Me_6})$_2$ (Ar^{Me_6} = C_6H_3-2,6-(C_6H_2-2,4,6-Me_3)$_2$).[10] Hitherto, stable monomeric silylenes could only be isolated at room temperature, where the silicon

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† This Award Article summarizes, including more recent results, one of the themes of a lecture presented on March 26th, 2012, at the 243rd Chemical Society National Meeting American in San Diego, CA, in receipt of the 2012 Award in Organometallic Chemistry sponsored by the Dow Corporation.

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atom was part of a ring structure.[1−5] The heavier group 14 element analogues of alkynes,[11,12] first reported in 2000,[11] have also proven to have a very rich chemistry. In 2005, it was discovered that the germanium derivative, a digermyne, reacted directly with dihydrogen (H_2) at 25 °C and atmospheric pressure (Figure 1). This was the first demonstration that main-group compounds could react with H_2 under ambient conditions.[13] We postulated that the reaction with H_2 was synergistic and involved interaction of the σ-bond molecular orbital of H_2 with the n_+-type lowest unoccupied molecular orbital (LUMO) of the digermyne, coupled with nucleophilic interaction of the highest occupied molecular orbital π-HOMO with the H_2 σ^* orbital, leading to facile cleavage of the H−H bond in a manner analogous to that seen for transition-metal complexes.[13,14] This discovery resulted in a broad investigation of the reactions of low-valent (e.g., germylenes or stannylenes) or multiple-bonded heavier group 14 element compounds (e.g., dimetallynes) possessing either open-shell or quasi-open-shell electron configurations with a range of small molecules, which have been summarized in several review articles.[15]

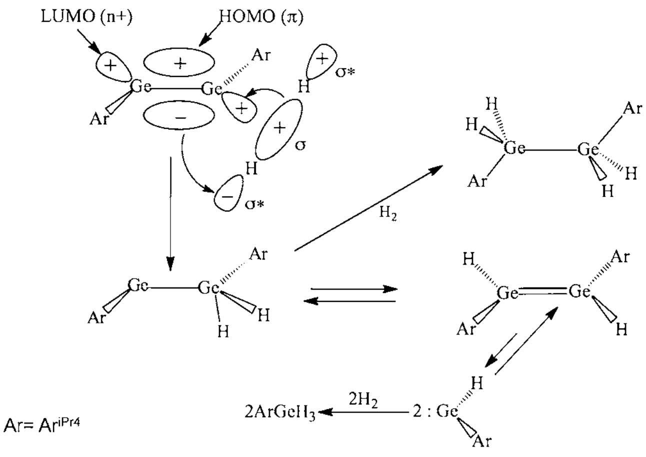


Figure 1. Schematic drawing of the synergic activation of H_2 by a digermyne and subsequent reactions with further equivalents of H_2.[13]

In a remarkable development in 2006, Stephan and co-workers introduced the frustrated Lewis pair (FLP) concept using a sterically crowded phosphine donor, in combination with a Lewis acidic boron center to effect reversible, metal-free hydrogen activation.[16] In this case, the activation pathway involves synergism in which the HOMO and LUMO of H_2 interact with a borane acceptor and phosphine donor. Bertrand and co-workers showed in 2007 that carbenes reacted directly with hydrogen or ammonia under ambient conditions and described a related synergistic activation pathway that was supported by density functional theory (DFT) calculations (Figure 2).[17]

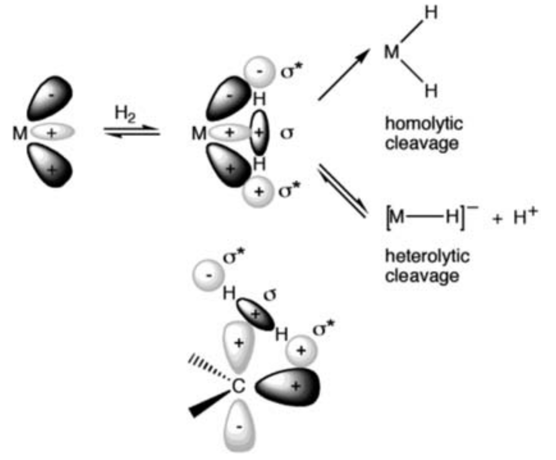


Figure 2. Comparison of the synergistic interactions of H_2 with a transition-metal center[14] and a singlet carbene.[17]

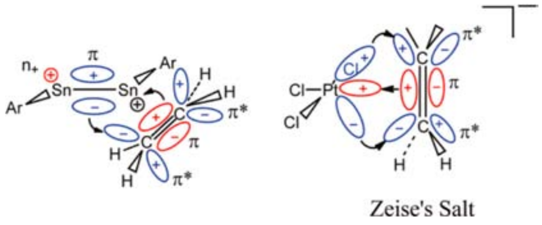


Figure 3. Schematic drawing of the synergic interactions of ethylene with a distannyne and their similarity to those in Zeise's salt.[20]

The synergistic interaction between H_2 and main-group complexes with energetically accessible donor and acceptor frontier orbitals is now becoming well accepted and mirrors[18] the synergic reaction pathways seen for transition-metal complexes.[19] A similar comparison between main-group and transition-metal complexation to small molecules was drawn in work describing the reversible, π-type binding between ethylene and a distannyne (Figure 3).[20] In a companion article[21] to this review, we discussed the reactions of open-shell main-group 13 and 14 species with hydrogen and olefins. We now focus on our recent investigations of the reactivity of monomeric germylenes and stannylenes with isocyanides, CO, ammonia, hydrazines, and various protic molecules. In particular, we will emphasize the effects of synergism on the subsequent reactivity, as well as the role their ambiphilicity plays in determining subsequent reaction products.

■ SYNERGISTIC INTERACTIONS BETWEEN HEAVIER GROUP 14 METALLENES AND ISOCYANIDES: C−H ACTIVATION

As mentioned earlier, the ambiphilic nature of the heavier group 14 carbenes and their heavier analogues (tetrylenes) plays a central role in their reactivity. Because the ability to donate and accept electron density concurrently is central to the reactivity of these species, the synthesis of heavier group 14 "push−pull" complexes, complexes where the tetrel atom is simultaneously acting as a Lewis acid and Lewis base, has garnered considerable interest. Rivard and co-workers have published notable examples of this type, and they have illustrated that the group 14 dihydrides, heavy analogues of methylene, could be stabilized by complexation with a suitable Lewis acid and Lewis base (related to the FLP complexes of Stephan).[22,23] Similarly, various Lewis base adducts of heavier group 14 element metallanediyls have been isolated using various coordinating ligands, most notably isocyanides.[24−29] Tetrylene isocyanide complexes may be divided into two categories that are defined by two bonding extremes. The first involves multiple bonding between the isocyanide carbon and the main-group element in which the isocyanide is subsumed into a heterocumulene structure (Figure 4, **A**).[24]

The other extreme involves a simple donor−acceptor interaction between the carbon and main-group atom, in other words, a single σ bond illustrated by **C** in Figure 4. To date, the limited number of spectroscopically characterized stannylene

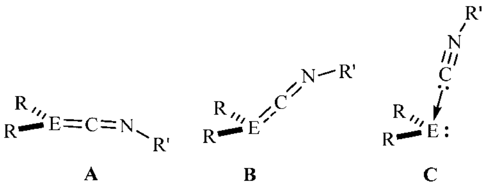


Figure 4. Schematic drawings of the bonding in R_2E isocyanide complexes. R′ = alkyl or aryl groups; E = Si−Pb.

and plumbylene isocyanide complexes are Lewis base adducts, as in **C**, while the silicon isocyanide complexes tend to form heterocumulenes, as in **A**. However, when very bulky isocyanides are used, Lewis base adducts with silylenes can also be isolated.[25] We could isolate the first structurally characterized germylene isocyanide complexes by the addition of an excess of various, simple isocyanides to stirred solutions of a germylene, $Ge(Ar^{Me_6})_2$.[26,27] Three germylene isocyanide adducts, $(Ar^{Me_6})_2GeCNR$ (R = Me, Bu^t, C_6H_{11}), were independently prepared, and their crystal structures initially suggested simple *σ*-type bonding between the isocyanide ligand and the germanium atom (Figure 5).

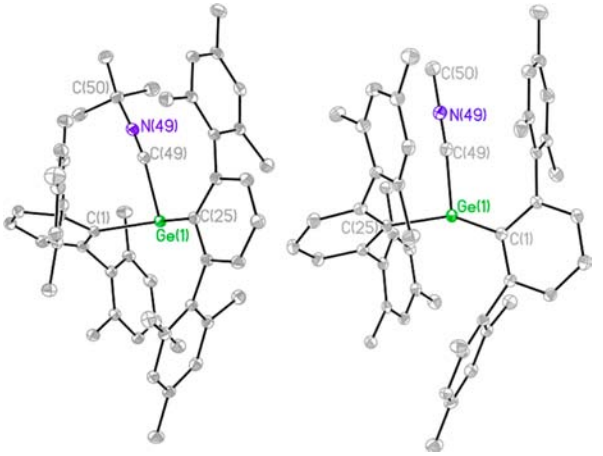


Figure 5. Thermal ellipsoid drawings (30%) of the structures of $(Ar^{Me_6})_2GeCNBu^t$ and $(Ar^{Me_6})_2GeCNMe$. Hydrogen atoms are not shown.[26,27]

However, a detailed investigation of the IR spectroscopy of these complexes revealed a more complex picture.[30] Examination of the C−N stretching frequencies reported for the tetrylenes yields an interesting trend where the heavier congeners (Sn and Pb) display C−N stretching bands shifted to much higher frequencies and the silicon complexes display shifts to much lower frequencies (Table 1). The C−N stretching frequency of the germylene isocyanide adducts falls between these two extremes, with very small shifts in the C−N bands being observed.

The shift to a higher C−N stretching frequency for *σ*-bonded isocyanide complexes is thought to be due to an increase in the effective positive charge on the carbon atom upon donation of its lone pair, which leads to an increase in the polarity of the C−N bond and, hence, to an increase in its strength and stretching frequency.[31] In effect, the larger the shift of the C−N stretching band to higher frequency, the stronger the M−C bond. For the silicon congeners, the greatly reduced C−N stretching frequency can easily be rationalized by a heteroallenic structure, which formally lowers the C−N triple bond order to that of a double bond and which weakens the bond and decreases the frequency of the C−N stretching band. For the germylene isocyanide adducts, the isocyanide fragment is *σ*-bound and the crystal structure suggests there is little to no Ge−C multiple-bond character. However, the reduced C−N stretching frequency suggests an interaction between the lone pair of electrons on the germanium atom and the *π** orbital of the isocyanide. From these data, we concluded that a back-bonding interaction exists between the lone pair of electrons on the germylene and the *π** orbital of the isocyanide, a bonding interaction typically seen for transition metals.

Table 1. Various C−N Stretching Frequency Shifts of Tetrylene Isocyanide Complexes

adduct[a]	ν(CN) [cm^{-1}]	change [cm^{-1}]	ref
$Ar^F{}_2SnCNMes$	2166	+48	28
$(Ar^{Me_6})_2SnCNMe$	2197	+36	27
$[(SiMe_3)_3Si]_2PbCN^tBu$	ca. 2164	+30	29
$[(SiMe_3)_3Si]_2SnCNCy$	ca. 2171	+30	29
$(Ar^{Me_6})_2GeCNMe$	2165	+4	27
$(Ar^{Me_6})_2GeCNCy$	2134	−2	27
$(Ar^{Me_6})_2GeCNBu^t$	2135	−5	26
Mes[Tbt]SiCNMes*	1919	−89	24
Mes[Tbt]SiCNTrip	2002	−111	24

[a] Ar^F = C_6H_2-2,4,6-$(CF_3)_3$, Cy = cyclohexyl, Tbt = C_6H_2-2,4,6-$\{CH(SiMe_3)_2\}_3$, and Mes* = C_6H_2-2,4,6-$Bu^t{}_3$.

The formation and bonding of the germylene isocyanide adducts was further investigated by DFT calculations. The optimized structure of $(Ar^{Me_6})_2GeCNBu^t$ was in good agreement with the X-ray data,[26] and the calculated dissociation energy was 47 kJ mol^{-1} (cf. 54 kJ mol^{-1} for experimentally determined ΔH_{diss}). Similarly, the ν(CN) stretching band of $(Ar^{Me_6})_2GeCNBu^t$[26] (2234 cm^{-1}) was shifted to lower frequency in comparison to the stretching frequency of the free isocyanide (2247 cm^{-1}). The HOMO of $(Ar^{Me_6})_2GeCNBu^t$ is a Ge−C bonding combination between the lone pair of electrons on the germanium atom and the C−N *π** orbital of the isocyanide ligand (Figure 6), indicative of the presence of a significant back-bonding interaction.

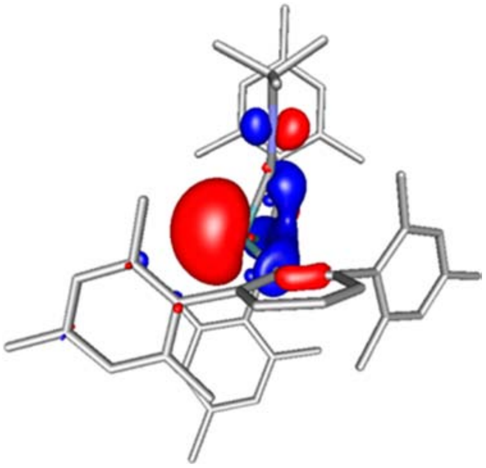


Figure 6. Highest occupied Kohn−Sham orbital of $(Ar^{Me_6})_2GeCNBu^t$ (contour value ± 0.04). Hydrogen atoms are not shown for clarity.[26]

The bonding was examined in more detail with energy decomposition analysis (EDA) and by investigation of the corresponding natural orbitals of chemical valence (NOCVs). The results showed that the instantaneous interaction energy between the *tert*-butylisocyanide and diarylgermylene fragments was −78 kJ mol^{-1}. This consists of Pauli repulsion (716 kJ mol^{-1}), quasi-classical electrostatic interaction (−437 kJ mol^{-1}), and orbital interactions (−357 kJ mol^{-1}). Because of the lack of symmetry in the adduct $(Ar^{Me_6})_2GeCNBu^t$, the orbital interaction term cannot easily be expressed as a sum of σ and π contributions.[26] However, an estimate of the relative importance of bonding and back-bonding components to the total orbital interaction was obtained by using the constrained-space orbital variation procedure. If the unoccupied orbitals of the diarylgermylene fragment are removed from the EDA calculation, only back-bonding interactions are possible and the total orbital interaction term decreases to 148 kJ mol^{-1}. Similarly, by removal of the unoccupied orbitals from *trt*-butylisocyanide, the back-bonding interaction was eliminated and the calculated orbital interaction energy became 244 kJ mol^{-1}. This indicated that the back-bonding interaction constitutes about 37% of the total orbital energy of the interaction. Qualitatively similar results were obtained by analyzing the NOCVs calculated for $(Ar^{Me_6})_2GeCNBu^t$, wherein the two most important orbitals correspond to the relevant σ and π interactions with energy contributions of 225 and 84 kJ mol^{-1} (24%), respectively. Consequently, these data indicate that the back-bonding interaction represents roughly one-third of the total orbital bonding interaction.

The computational data for the back-bonding interaction in $(Ar^{Me_6})_2GeCNBu^t$ prompted us to study a series of R'_2MCNR complexes to elucidate any trend in back-donation when M = Si, Ge, or Sn.[27] The metal isocyanide bond distances change in the C−N stretching frequency from the free ligand, as well as in the respective σ and π contributions for the total M−C interaction, which were calculated for the model complexes listed in Table 2.

Table 2. Calculated Data for R'_2MCNR Complexes with Relative σ and π Contributions[27]

M	R′	R	*r*(M−C)	Δ*ν*(C−N) [cm^{-1}]	σ/π contribution [kJ mol^{-1}]
Si	^{t}Bu	^{t}Bu	1.806	−235	−150/−591
	^{t}Bu	Ph	1.786	−285	−149/−704
	Ph	^{t}Bu	1.869	−87	−135/−382
	Ph	Ph	1.88	−7	−141/−345
Ge	^{t}Bu	^{t}Bu	2.019	−13	−241/−75
	^{t}Bu	Ph	1.984	−27	−238/−124
	Ph	^{t}Bu	2.052	30	−250/−55
	Ph	Ph	2.023	8	−249/−83
Sn	^{t}Bu	^{t}Bu	2.357	29	−144/−32
	^{t}Bu	Ph	2.318	−2	−122/−75
	Ph	^{t}Bu	2.39	56	−146/−26
	Ph	Ph	2.37	35	−145/−34

Each tetrel atom exhibited nearly constant values for the σ contribution to bonding. Because of their preference to form cumulene-type structures, the silicon isocyanide complexes, predictably, have very large π contributions for the overall interaction, which are indicative of significant Si−C(isocyanide) multiple bonding.[24] In comparison, the stannylene model complexes can be described as Lewis acid−base adducts and possess Sn−C bonding that is based largely on σ interactions. The germylene isocyanide model complexes afforded data that fell between these two extremes and provided evidence for the existence of a back-bonding interaction.[26,27] The back-bonding present in the complexes, however, masked the increase of the C−N stretching band caused by the strong σ contribution to M−C bonding. Furthermore, the change in the C−N stretching frequency was determined to be a good predictor of the total π contribution for the metal isocyanide bond in the tetrylene isocyanide complexes, R'_2MCNR (Figure 7).

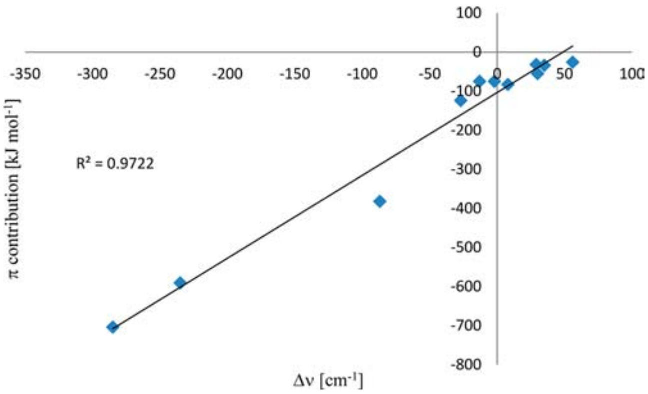


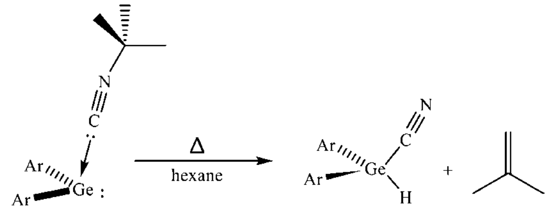
Figure 7. Correlation between Δ*ν*(C−N) and total π contribution to M−C bonding of model complexes (cf. Table 2).

As mentioned above, the shift to a higher C−N stretching frequency for datively bound isocyanide complexes is due to an increase in the effective positive charge on the carbon atom upon donation of its lone pair, and the larger the shift of the C−N stretching band to higher frequency, the stronger the M−C bond. The tin congener of $(Ar^{Me_6})_2SnCNMe$[27] was isolated at low temperatures upon reaction with 10-fold excess of methylisocyanide. It readily dissociated to free $Sn(Ar^{Me_6})_2$ and CNMe above ca. −50 °C, consistent with weak Sn−C bonding. Although the bonding between CNMe and $Sn(Ar^{Me_6})_2$ is very weak, the C−N stretching band in the IR spectrum of $(Ar^{Me_6})_2SnCNMe$ is shifted by 36 cm^{-1} to higher frequency relative to free MeNC. The direct comparison between isoleptic tetrylene isocyanide adducts illustrates the fact that the traditional view that the hypsochromic shift of the C−N stretching band is directly proportional to the M−C bond strength is not borne out by our data.

The bonding in $(Ar^{Me_6})_2GeCNR$ may also be compared to that in other known heavier group 14 element congeners $[(CH_2)C(SiMe_3)_2]_2SiCNR$ (R = C_6H_3-2,6-Pr^i_2, 1-adamantyl),[31] $Ar^F_2SnCNMes$ [Ar^F = C_6H_2-2,4,6-$(CF_3)_3$],[32] and $[Si(SiMe_3)_3]_2ECNBu^t$ (E = Sn, Pb),[29] which have been structurally characterized. The tin isocyanide adduct, $Ar^F_2SnCNMes$, exhibited weak binding, ΔH_{diss} = 29.6(4) kJ mol^{-1} [cf. 53(5) kJ mol^{-1} in **1**], and the C−N frequency is 48 cm^{-1} higher than that in the free isocyanide, indicating that the Sn−C bonding is primarily of a σ-donor type.[32] Although the C−N stretching frequencies in $(Ar^{Me_6})_2GeCNR$ are shifted slightly in comparison to the free ligand, it stands in sharp contrast to other σ-bonded main-group isocyanide adducts where the C−N stretching frequencies increase proportionally to the strength of the E−C bond, typically by several tens of wavenumbers (Table 1). Thus, a comparison of the experimental data for $(Ar^{Me_6})_2GeCNR$ and their group 14 element analogues indicates that the back-donation of electrons (and degree of multiple-bond formation) from the group 14 element to the isocyanide ligand decreases in the heavier atoms, and the back-donation of electron density for the germylene isocyanide adducts arises from having a relatively electron-rich germanium atom.

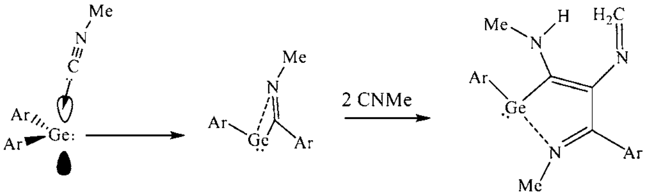
The adduct species $(\mathrm{Ar^{Me_6}})_2\mathrm{GeCNR}$ possess a highly reactive germanium atom because of the large accumulation of electron density localized on the germanium atom, but the adducts $(\mathrm{Ar^{Me_6}})_2\mathrm{GeCNBu^t}$ and $(\mathrm{Ar^{Me_6}})_2\mathrm{GeCNMe}$ can be shown to be intermediates for two highly divergent reactions. The germylene *tert*-butylisocyanide adduct $(\mathrm{Ar^{Me_6}})_2\mathrm{GeCNBu^t}$ undergoes C–H activation with mild heating of hexane solutions to produce the germanium(IV) hydride/cyanide complex $(\mathrm{Ar^{Me_6}})_2\mathrm{Ge(H)CN}$ and isobutene (Scheme 1) in quantitative yield.

Scheme 1. Reaction of $\mathrm{Bu^tNC}$ with $\mathrm{Ge(Ar^{Me_6})_2}$[26]



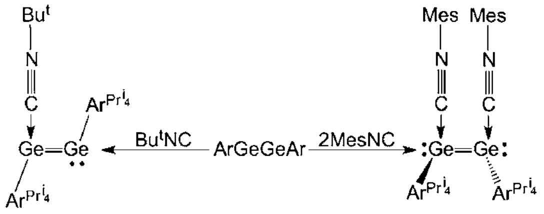
We also found that the coordinated methylisocyanide molecule in $(\mathrm{Ar^{Me_6}})_2\mathrm{GeCNMe}$ undergoes spontaneous migratory insertion into a Ge–C(Ar) bond to form $(\mathrm{Ar^{Me_6}})\mathrm{Ge(CNMe)(Ar^{Me_6})}$. If the germylene is treated with an excess of the isocyanide, two additional molecules of methylisocyanide are incorporated into $(\mathrm{Ar^{Me_6}})\mathrm{Ge(CNMe)(Ar^{Me_6})}$ to form $(\mathrm{Ar^{Me_6}})\text{-}\mathrm{GeC(NHMe)C(NCH_2)C(Ar^{Me_6})NMe}$ (Scheme 2). Both reaction mechanisms were studied via DFT and were found to be predicated on decreasing the electron density on the germanium atom and removing the formal charge separation in the complexes.

Scheme 2. Reaction of MeNC with $\mathrm{Ge(Ar^{Me_6})_2}$[21]



The reaction of isocyanides with digermyne and distannyne $\mathrm{Ar^{Pr^i_4}MMAr^{Pr^i_4}}$ (M = Ge or Sn) also afforded complexed species. The reaction of $\mathrm{Bu^tNC}$[33] or MesNC (Mes = $\mathrm{C_6H_2\text{-}2,4,6\text{-}Me_3}$)[34] with $\mathrm{Ar^{Pr^i_4}GeGeAr^{Pr^i_4}}$ afforded either the mono or bis Lewis acid–base complexes, as shown by Scheme 3. For the $\mathrm{Bu^tNC}$ monoadduct, the Ge–Ge bond length [2.343(2) Å] increases slightly in comparison to the uncomplexed digermyne [2.2850(6) Å]. This is consistent with the interaction of the isocyanide carbon lone pair with the essentially nonbonding n_+ LUMO of the digermyne.

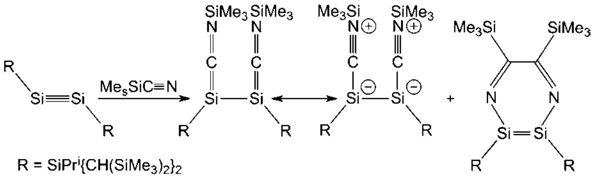
Scheme 3. Reaction of $\mathrm{Bu^tNC}$ or MesNC with $\mathrm{Ar^{Pr^i_4}GeGeAr^{Pr^i_4}}$[34,35]



On the other hand, when two less-crowded mesityl isonitriles complexes to $\mathrm{Ar^{Pr^i_4}GeGeAr^{Pr^i_4}}$, the lone pair of the second isonitrile occupies LUMO+1 (a π*-antibonding orbital) so that the Ge–Ge bond becomes a single one and lengthens to 2.6626(8) Å, which is ca. 0.38 Å (ca. 16%) longer than that in the digermyne. The C–N stretching bonds in the $\mathrm{Bu^tNC}$ and MesNC complexes appear at 2092 and 2113 $\mathrm{cm^{-1}}$, respectively, and are lower than those of the free isocyanides (2134 and 2118 $\mathrm{cm^{-1}}$), indicative of significant back-bonding. It is worth noting that the value for $\mathrm{Ar^{Pr^i_4}GeGeAr^{Pr^i_4}(CNBu^t)}$ is lowered to a greater extent, suggesting that there is a significant interaction between the out-of-plane π orbital of the digermyne and the π* orbital of $\mathrm{CNBu^t}$. Both $\mathrm{Bu^tNC}$ and MesNC form 2:1 complexes with $\mathrm{Ar^{Pr^i_4}SnSnAr^{Pr^i_4}}$,[34] but these are weak and dissociation readily occurs at room temperature. The C–N stretching frequencies for $\mathrm{Ar^{Pr^i_4}SnSnAr^{Pr^i_4}(CNBu^t)_2}$ (2162 and 2175 $\mathrm{cm^{-1}}$) and $\mathrm{Ar^{Pr^i_4}SnSnAr^{Pr^i_4}}$ $\mathrm{(CNMes)_2}$ (2278 $\mathrm{cm^{-1}}$) are much higher than those in the free ligand, presumably for reasons similar to those proposed for higher frequencies in the stannanediyl complexes above. Neither the digermyne nor the distannyne isocyanide complexes had been shown to effect C–H activation at the time this review was written.

The formation of isocyanide complexes of disilynes was discovered in an unusual manner by Sekiguchi and co-workers, as shown in Scheme 4.[34] The treatment of the disilyne RSi≡SiR ($\mathrm{R = SiPr^i\{CH(SiMe_3)_2\}_2}$ with 2 equiv of (trimethylsilyl)cyanide affords a species resulting from the coordination of two isocyanides (16% yield) and a 1,4-diaza-2,3-disilabenzene (84% yield) as the minor and major products, respectively.

Scheme 4. Reaction of the Disilyne RSi≡SiR ($\mathrm{R = SiPr^i\{CH(SiMe_3)_2\}_2}$) with $\mathrm{Me_3SiCN}$[36]

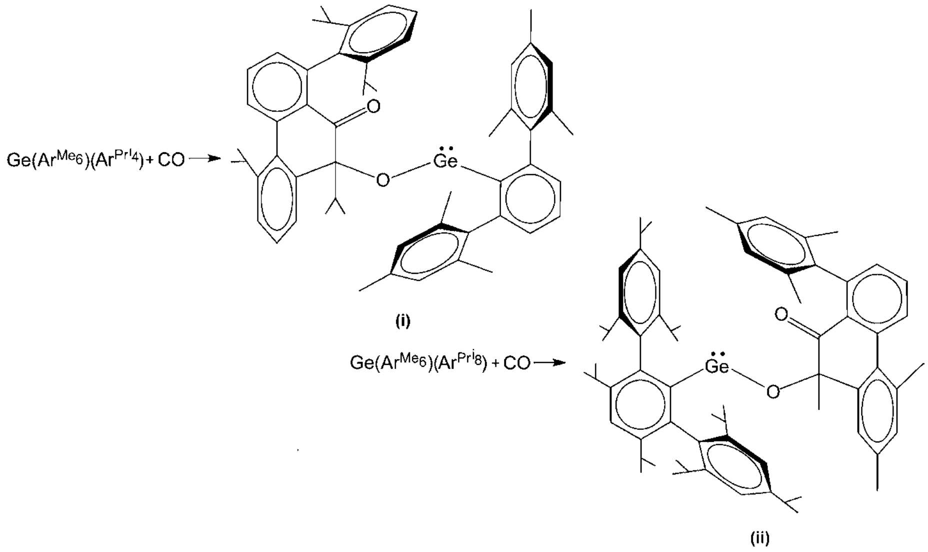


The yield of the bis(isocyanide)-coordinated species could be increased to 58% by performing the reaction with no solvent. X-ray crystallography showed that the C–Si bond lengths to the isocyanide were short [1.826(3) and 1.830(2) Å], which supported a silaketimine structure with zwitterionic contributions. The bis(isocyanide)-complexed product arises from the fact that the silylcyanide itself is in equilibrium with the silylisocyanide. The 1,4-diaza-2,3-disilabenzene product was structurally authenticated by reaction with 1,3-bis-(cyanodimethylsilyl)propane, which gave the cyclized product exclusively.[37] The reaction of the disilyne with isocyanides was confirmed by the formation of bis(isocyanide) complexes with $\mathrm{Bu^tNC}$:, which supported the contribution from a silaketimine structure as before.[38]

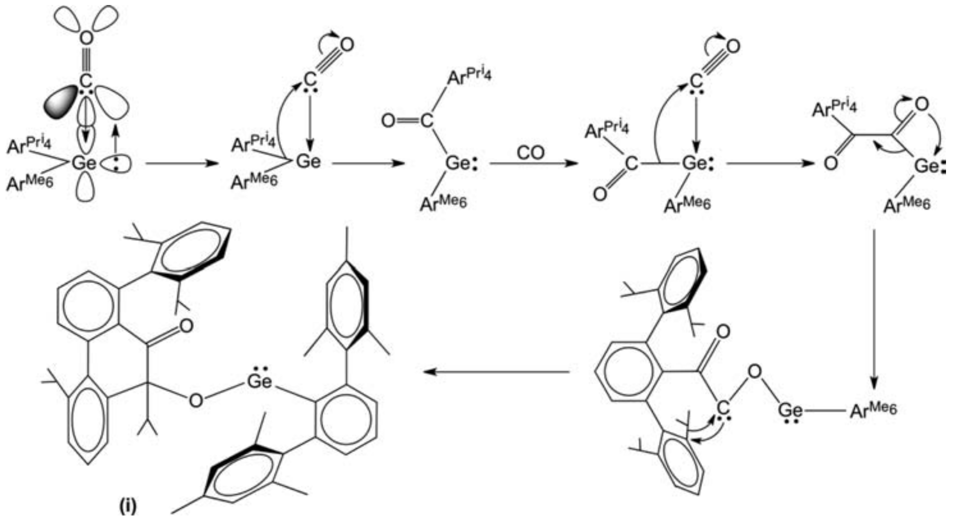
■ REACTIONS OF OPEN-SHELL GROUP 14 SPECIES WITH CARBON MONOXIDE (CO)

Reactions of transition-metal species with CO are one of the mainstays of organometallic chemistry. Although the insertion of

Scheme 5. Reactions of Ge(Ar$^{\mathrm{Me_6}}$)(Ar$^{\mathrm{Pr^i_4}}$) and Ge(Ar$^{\mathrm{Me_6}}$)(Ar$^{\mathrm{Pr^i_8}}$) with CO at 1 atm and 25 °C[43]



Scheme 6. Sequential Interaction of 2 equiv of CO with Ge(Ar$^{\mathrm{Me_6}}$)(Ar$^{\mathrm{Pr^i_4}}$)[43]



CO into transition metal−carbon bonds is well-known, its insertion into main-group element−carbon bonds is mainly associated with the more electropositive metals of groups 1, 2, and 13.[39] Insertion reactions with group 14 element compounds were and remain less well-known.[40] Carbenes react with CO to give ketenes,[41] but reactions with silylenes give complexes that are stable only at low temperatures, and readily dissociate CO when warmed to room temperature.[42] However, we could show that the treatment of diarylgermylenes with CO afforded pm multiple insertion of CO into the Ge−C bonds.[43]

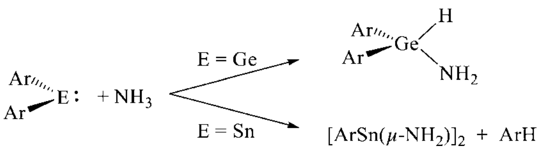
The germylenes Ge(Ar$^{\mathrm{Pr^i_4}}$)$_2$, Ge(Ar$^{\mathrm{Me_6}}$)$_2$, Ge(Ar$^{\mathrm{Me_6}}$)(Ar$^{\mathrm{Pr^i_4}}$), and Ge(Ar$^{\mathrm{Me_6}}$)(Ar$^{\mathrm{Pr^i_8}}$)$_2$ with CO at 1 atm of pressure all afforded reactions at room temperature in a toluene solution. However, only those with Ge(Ar$^{\mathrm{Me_6}}$)(Ar$^{\mathrm{Pr^i_4}}$) or Ge(Ar$^{\mathrm{Me_6}}$)(Ar$^{\mathrm{Pr^i_8}}$) afforded crystalline products, shown in Scheme 5 as (i) and (ii). X-ray crystallography showed that both compounds are racemates.

A coupled (CO)$_2$ unit is incorporated into the bond between germanium and the bulkier aryl ligand (Ar$^{\mathrm{Pr^i_4}}$) in the case of the reaction with Ge(Ar$^{\mathrm{Me_6}}$)(Ar$^{\mathrm{Pr^i_4}}$), whereas for Ge(Ar$^{\mathrm{Me_6}}$)(Ar$^{\mathrm{Pr^i_8}}$), the insertion occurs in the bond to the less bulky Ar$^{\mathrm{Me_6}}$ ligand. It seems likely that the initial step in the reaction sequence is complexation of CO to the germylene, as shown in Scheme 6. The initial interaction to give the germaketone is analogous to the interaction with MeNC discussed above. This apparently unstable species may then rearrange to an acylgermylene, which can then add a second 1 equiv of CO via a similar reaction pathway to give a doubly inserted product. This product then undergoes a rearrangement involving Ge−C bond cleavage and Ge−O bond formation to give an unstable germyloxy(aryl) carbene, which can insert into a C−C bond between a flanking aryl ring and one of its Pr$^{\mathrm{i}}$ substituents, as shown by structure (i) in Schemes 5 and 6. Structure (ii) may be generated in a similar fashion, except that in this case the final insertion step takes place into a C−C bond involving a methyl substituent on a flanking mesityl ring of the Ar$^{\mathrm{Me_6}}$ substituent. The instability of the doubly inserted product parallels that of the triple insertion of MeNC with Ge(Ar$^{\mathrm{Me_6}}$)$_2$ described earlier, except that in the CO reaction sequence a C−C bond, rather than a C−H bond, is activated.

■ REACTIONS OF GERMYLENES AND STANNYLENES WITH AMMONIA AND HYDRAZINES: AUXILIARY EFFECTS

Although they are formally characterized as having an empty p-type orbital, carbenes are not generally regarded as good Lewis acids, and their reactivity is dominated by their nucleophilic behavior. The heavier congeners, however, possess Lewis acidic properties that are much more pronounced, and numerous examples of Lewis acid−base adducts have been characterized wherein the tetrylene atom acts as a Lewis acid. Recently, we showed that when they are treated with NH_3, diarylgermylenes and -stannylenes, $E(Ar^{Me_6})_2$, or $E(Ar^{Pr^i_4})_2$ (E = Ge or Sn) insert into the N−H bond to form germanium(IV) amido hydrides or afford arene elimination to yield aryltin(II) amide dimers (Scheme 7).[44]

Scheme 7. Reaction of NH_3 with $GeAr_2$ or $SnAr_2$ ($Ar = Ar^{Me_6}$ or $Ar^{Pr^i_4}$) To Afford the Amido Hydride Germanium(IV) or Arene-Eliminated Tin(II) Products[44]



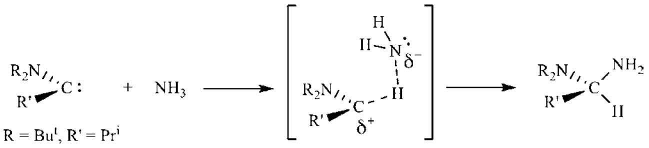
These reactions proceed initially by forming a Lewis acid−base adduct intermediate wherein the electron lone pair of ammonia attacks the empty p orbital of the tetrylenes. DFT calculations predicted that the decreased strength of the Sn−C bond and increased stability of the nonbonded pair of electrons on the tin(II) atom gave preference to the tin(II) species over a tin(IV) hydride/amido complex.

However, a particular aspect of the ammonia addition reactions was that the DFT calculations established that the additions involve not just one but two ammonia molecules. First, one of the ammonia molecules becomes associated with the empty 4p(Ge) or 5p(Sn) orbitals, and the second NH_3 solvates the complexed NH_3 via an intermolecular N−H---N interaction, which lowers the energy of the transition state (Figure 8) in the transformation of the initial adduct into the products.

The calculations also demonstrated that the reaction pathway, involving a single ammonia molecule, had a high energy barrier in which no transition state could be located. It is important to note that, in the reactions of both $Ge(Ar^{Me_6})_2$ and $Sn(Ar^{Me_6})_2$, the arene-eliminated product [i.e., the germanium(II) or tin(II) amides] are favored (by ca. 19 and 22 kcal mol^{-1}, respectively), but the transition state to the $Ge^{IV}(H)(NH_2)$ product, involving a concerted proton transfer to germanium by the ancillary NH_3, is more favorable than a proton transfer involving the complexed NH_3 by 5.7 kcal mol^{-1}, whereas in the case of the tin system, both proton-transfer pathways are almost equally favored. This may be due to the fact that the proton transfer from the complexed ammonia to the ipso carbon of the aryl ligand is more favored because of the greater polarity of the Sn−C(ipso) bond.[44]

Bertrand and co-workers showed that monoaminocarbenes could insert into the N−H bonds of ammonia, but the reactivity was heavily dependent on the singlet−triplet energy gap of the unsaturated carbene, and the reactions did not proceed if this energy gap exceeded ca. 50 kcal mol^{-1}.[17] It is important to note that DFT calculations showed that the mono(amino)carbenes react with ammonia first by a nucleophilic attack to a N−H antibonding orbital, with the lone pair of electrons on the nitrogen atom oriented away from the empty p orbital on the carbene (Scheme 8). Therefore, Lewis base σ-adduct formation

Scheme 8. Reaction of Ammonia with a Carbene[17]



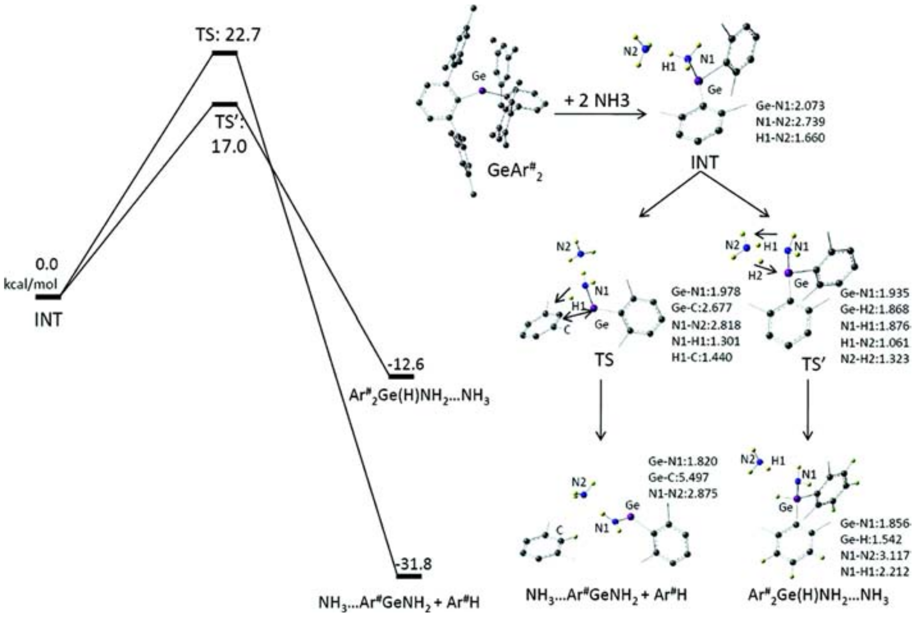


Figure 8. Calculated energies and drawings of the intermediates and transition states with selected distances (Å) and angles (deg) for the reaction of $Ge(Ar^{Me_6})_2$ (i.e., $GeAr^{\#}_2$) with NH_3 at the B3PW91 level.[44]

does not play a role in the N−H bond activation for carbenes, and the reactivity is predicated solely on the nucleophilic character of the carbene.[17]

We further explored the unusual reactivity of Ge(Ar^{Me_6})$_2$ and Sn(Ar^{Me_6})$_2$ with Lewis bases by treating the germylene Ge(Ar^{Me_6})$_2$ with hydrazine, methylhydrazine, and *N*,*N*-dimethylhydrazine.[45] Additionally, the diarylgermylene and -stannylene were treated with various Brønsted acids to probe the divergent reactivity seen in the case of ammonia. For the reactions with hydrazines, the germanium atom undergoes facile oxidative insertion into N−H bonds of hydrazine and methylhydrazine to yield the germanium(IV) hydride/hydrazide products (Ar^{Me_6})$_2$Ge(H)N_2H_3 and (Ar^{Me_6})$_2$Ge(H)N(H)NHMe (Figure 9), which are similar to that observed for NH_3. However, in contrast to the facile formation of these N−H bond insertion products at room temperature, the treatment of germylene with an excess of *N*,*N*-dimethylhydrazine afforded only the Lewis acid−base complex (Ar^{Me_6})$_2$Ge·NH_2NMe_2 (Figure 9).

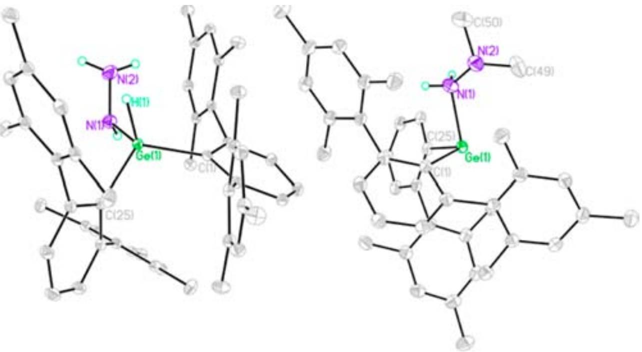


Figure 9. Thermal ellipsoid drawings (30%) of the germanium(IV) hydrazido hydride (Ar^{Me_6})$_2$Ge(H)$NHNH_2$ insertion product (left) and the germanium(II) *N*,*N*-dimethylhydrazine adduct (Me_2NNH_2)Ge(Ar^{Me_6})$_2$ (right). Hydrogen atoms except Ge−H and N=H are not shown.[45]

No formation of germanium(IV) hydrazide was observed even upon heating the reaction mixture and increasing the reaction time up to 3 weeks. In order to gain a greater understanding of this reaction, the mechanism for the formation of (Ar^{Me_6})$_2$Ge(H)N_2H_3 was studied computationally by DFT calculations (Figure 10).[45]

These calculations established that reaction intermediates and transition states that were similar to those calculated for the reaction with ammonia were also present in the hydrazine case. Transition state 1 (TS-1) involves the initial approach of a hydrazine molecule to Ge(Ar^{Me_6})$_2$, which is immediately followed by the formation of the adduct intermediate (INT-1). The approach of the second molecule of hydrazine (INT-2) unexpectedly does not lead to an increase in energy. The energy required to overcome the conformational change in the molecule to accommodate the second molecule of N_2H_4 is offset by an intermolecular hydrogen-bonding interaction, ca. 12 kcal mol^{-1}. Transition state 2 (TS-2) represents the concerted proton migration (H2) from the second hydrazine molecule to the electron-rich germanium atom with simultaneous transfer of H1 from the bound hydrazine to the adjacent molecule of hydrazine. This transition state is similar to that for the activation for ammonia by an analogous germanium species, and the total activation energy for the formation of (Ar^{Me_6})$_2$Ge(H)N_2H_3 is somewhat higher at 23.0 kcal mol^{-1} [cf. 17.0 kcal mol^{-1} for (Ar^{Me_6})$_2$Ge(H)(NH_2)].[44]

The calculated mechanism for the reaction of Ge(Ar^{Me_6})$_2$ with *N*,*N*-dimethylhydrazine (Figure 11) displayed transition states and intermediates, albeit with larger energy differences, similar to those of the reaction pathway for the formation of (Ar^{Me_6})$_2$Ge(H)N_2H_3.

Transition state 1 (TS-1) is higher in energy, ca. 5 kcal mol^{-1}, with respect to the starting materials in comparison to the reaction pathway for (Ar^{Me_6})$_2$Ge(H)N_2H_3 (Figure 9), where the two are nearly degenerate. As in (Ar^{Me_6})$_2$Ge(H)N_2H_3, a hydrogen-bonding interaction was predicted to stabilize INT-2, but in this case, steric repulsion between the terminal methyl groups of the hydrazine ligand and the adjacent molecule of

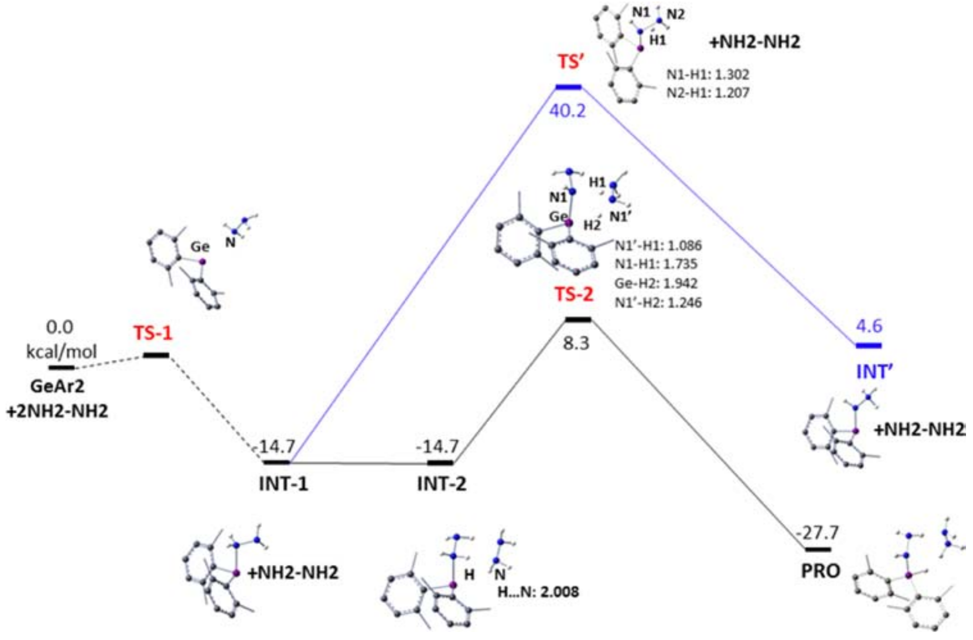


Figure 10. Reaction of a diarylgermanium with hydrazine showing calculated energies (kcal mol^{-1}) of the intermediates and transition states.[45].

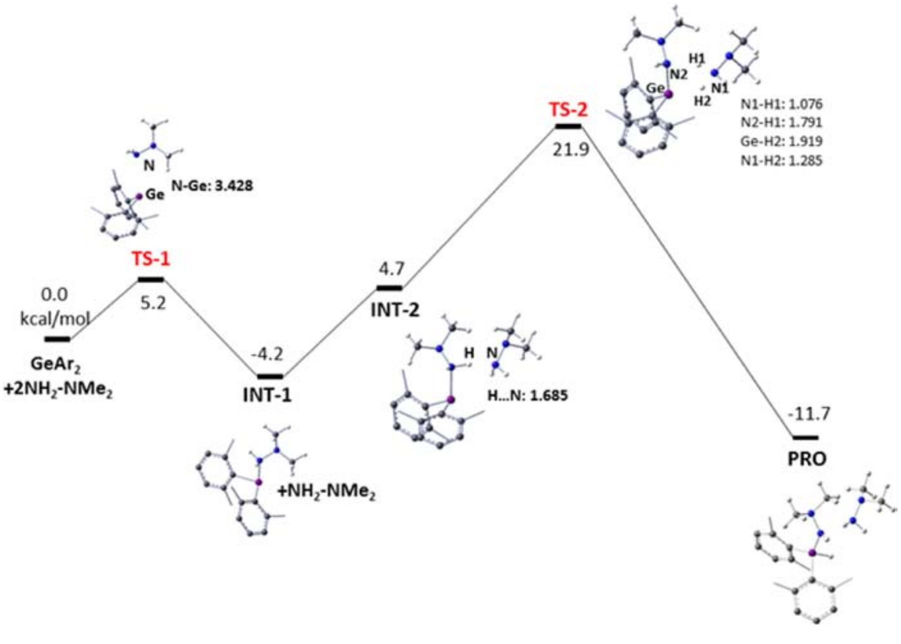


Figure 11. Calculated energies and drawings of the intermediates and reaction pathway of Me_2NNH_2 with $Ge(Ar^{Me_6})_2$.[45]

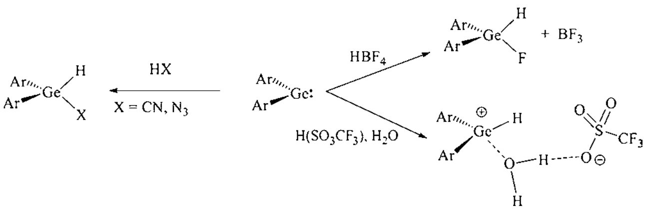
N,N-dimethylhydrazine significantly increased the energy required for a second molecule of NH_2NMe_2 to approach INT-1 ($(Ar^{Me_6})_2Ge \cdot NH_2NMe_2$); thus, INT-2 is less stable relative to INT-1 by ca. 9 kcal mol^{-1}. The activation energy for the formation of the theoretical product $(Ar^{Me_6})_2Ge(H)N(H)NMe_2$ is only 3.1 kcal mol^{-1} higher than that for $(Ar^{Me_6})_2Ge(H)N_2H_3$ (26.1 kcal mol^{-1}), but the transition state is 21.9 kcal mol^{-1} higher in energy than the fully dissociated starting materials, whereas in $(Ar^{Me_6})_2Ge(H)N_2H_3$, the energy difference is 8.3 kcal mol^{-1}. These differences may be rationalized in terms of the increased steric strain of the $-NMe_2$ end of the bound hydrazine decreasing the dissociation energy of the Ge−N dative bond and preventing subsequent hydrogen bonding with the second molecule of hydrazine. Thus, there is a steep rise in energy of the key transition state (TS-2) with respect to $Ge(Ar^{Me_6})_2$ and free NH_2NMe_2. This inhibits the N−H bond activation of *N,N*-dimethylhydrazine, and the adduct $(Ar^{Me_6})_2Ge \cdot NH_2NMe_2$ is the only product isolated.[45]

■ GERMYLENE AND STANNYLENE REACTIVITY WITH PROTIC REAGENTS

As mentioned above, the facile nature of the N−H bond insertion by the diarylgermylene to afford the germanium(IV) hydrido amide product is in stark contrast to its tin congener, which undergoes arene elimination to yield $\{ArSn(\mu\text{-}NH_2)\}_2$ and ArH.[44] The divergent reactivity prompted us to further examine the reactions of the diarylgermylene with other protic reagents with significantly enhanced acidity to probe whether arene elimination could be induced, as well as to explore routes of synthesizing functionalized germanium complexes analogous to lighter organic congeners. The treatment of $Ge(Ar^{Me_6})_2$ with the inorganic acids HN_3, HCN, HBF_4, and $H(SO_3CF_3)$ showed that they afford oxidized products in which germanium inserts into an E−H bond (Scheme 9).[46]

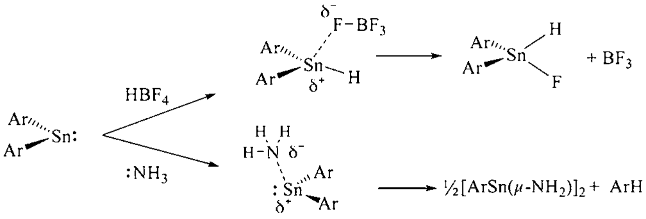
The reaction of $Ge(Ar^{Me_6})_2$ with HCN and HN_3 led to the formation of the corresponding insertion products $(Ar^{Me_6})_2Ge(H)X$ (X = CN, N_3). The diarylgermylene was very resistant to arene elimination, as demonstrated by the reaction with an ethereal solution of HBF_4, which yielded the germanium(IV) product $(Ar^{Me_6})_2Ge(H)F$ with BF_3 elimination. We believe that the initial step of this reaction is protonation of the germanium to form a three-coordinate, cationic germanium complex. The increased reactivity of the cationic species is sufficient to abstract a fluoride from the BF_4^- anion. This phenomenon has also been reported during attempts to form analogous cationic silicon complexes.[47,48] Although germanium and silicon(IV) aryl bonds have been shown to be cleaved by hydrohalic acids,[47,49,50] their low-valent counterparts prefer oxidative reaction pathways.[51] However, these reactions tend to be dependent upon the nature of the connectivity between the tetrel and the aryl ligand. Tokitoh and co-workers have similarly shown that a base-stabilized silylene can oxidatively add hydrochloric acid;[52] conversely, Jutzi and co-workers have shown that π-bound cyclopentadienyl ligands can be readily protonated by ethereal solutions of HBF_4.[53]

Scheme 9. Reaction of $GeAr_2$ ($Ar = Ar^{Me_6}$) with Various Protic Acids[46]



Although the oxidative addition of stannylenes into aryl[54] and alkyl halides,[55] water,[56] and methanol[57] has been well explored by Lappert and co-workers, we expected to see arene elimination upon treatment of the diarylstannylene $Sn(Ar^{Me_6})_2$ with strong acids analogous to the loss of an arene ligand for reactions with hydrogen or ammonia.[41] However, the tin(IV) hydride fluoride complex $(Ar^{Me_6})_2Sn(H)F$ was isolated in the reaction of a diarylstannylene with HBF_4. The divergence of reactivity for the stannylene in comparison to the products obtained for the reaction with hydrogen or ammonia can be rationalized by differing reaction pathways (Scheme 10).

Scheme 10. Reaction of $SnAr_2$ (Ar = Ar^{Me_6}) with HBF_4 or NH_3[46]



We reported that the initial intermediate for the reaction of $Sn(Ar^{Me_6})_2$ with ammonia was the formation of a Lewis acid−base adduct species with a high degree of electron density located on the metal atom.[45] The resulting effective negative charge, coupled with the enhanced stability of the tin lone pair in comparison to its germanium congener and the more ionic character of the Sn−C bond, is sufficient to facilitate cleavage of the Sn−C bond to form the dimeric amido species. Conversely, the initial intermediate for the reactions of the germylenes and stannylenes with the acids is oxidation of the metal by protonation. This is followed by subsequent attack by the conjugate base. The pseudocationic intermediate in the preparation of $(Ar^{Me_6})_2Sn(H)F$ avoids an electron-rich intermediate and prevents the loss of the arene.

■ CONCLUSIONS

In this short review, we have discussed our most recent investigations of the reactions of open-shell main-group compounds with small molecules. These have concerned germanium and tin analogues of carbenes. We described the first germylene isocyanide complexes, $(Ar^{Me_6})_2GeCNR$ (R = Me, Bu^t, C_6H_{11}), and have shown that they can exhibit further reactivity involving C−H bond activation. The Ge−C(isocyanide) bond is characterized by strong $n \rightarrow \pi^*$ back-bonding interactions normally seen only in transition-metal species. The isocyanide complexation increases the electron density localized on the germanium atom, which induces subsequent reactivity involving the $CNBu^t$ and CNMe ligands that is predicated on effecting a decrease of the electron density on the germanium atom and the removal of the formal charge separation created in the Lewis adduct complexes. In contrast, the corresponding stannylene isocyanide adducts have very weak Sn−C(isocyanide) bonds, are unstable, and do not display any evidence of onward reaction. It was also shown that the electronically related Lewis base CO displays a reactivity pattern similar to that of the initial formation of a complex with $Ge(Ar^{Me}{}_6)_2$ and further reactivity that resulted in C−C, rather than C−H, bond activation.

The formation of Lewis acid−base complexes is also the initial step in their reactions with ammonia and hydrazines. This is in contrast to carbenes, where nucleophilic attack on the N−H bond in ammonia is the initial step (cf. Scheme 8). A germanium(IV) hydride/amido product is formed, whereas arene elimination was observed for the stannylene to afford a dimeric aryltin(II) amide. The arene elimination by the tin complex and the increased polarity of the Sn−C(ipso) bond is due to the buildup of the electron density of the Lewis adduct intermediate rather than the protic nature of the reagent. This was confirmed by the treatment of a diarylstannylene with ethereal solutions of HBF_4, which yielded tin(IV) oxidative addition products, and no arene elimination was observed.

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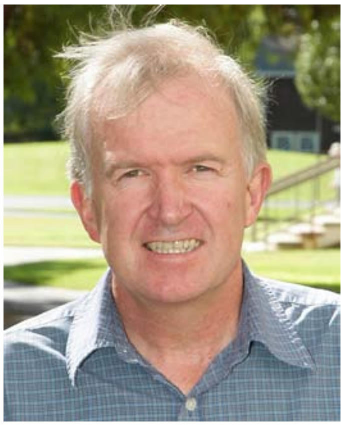
Notes

The authors declare no competing financial interest.

Biographies

Zachary Brown received a B.S. from Butler University in 2007 in Indianapolis, IN. He joined the Power group as a graduate student at the University of California at Davis in early 2008, where he studied the synthesis and reaction chemistry of the heavier group 14 carbene and alkyne analogues. He received his Ph.D. in 2012 and soon thereafter joined the group of Professor Paul Chirik at Princeton University as a postdoctoral research associate, where he focused on hydrogenation reactions of ketones and carbon dioxide using base-metal catalysts. He is currently an R&D chemist for The Shepherd Chemical Company in Norwood, OH.



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 types 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), and the ACS Award in Organometallic Chemistry (2012) and was elected Fellow of the Royal Society of London (2005).

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