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A Germanium Isocyanide Complex Featuring (n → π*) Back-Bonding and Its Conversion to a Hydride/Cyanide Product via C−H Bond Activation under Mild Conditions

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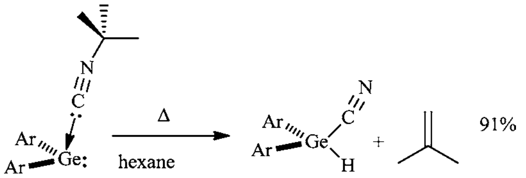
Supporting Information

ABSTRACT: Reaction of the diarylgermylene Ge(Ar^{Me_6})$_2$ [Ar^{Me_6} = C_6H_3-2,6-(C_6H_2-2,4,6-$(CH_3)_3$)$_2$] with *tert*-butyl isocyanide gave the Lewis adduct species (Ar^{Me_6})$_2$GeCNBu^t, in which the isocyanide ligand displays a decreased C−N stretching frequency consistent with an n → π* back-bonding interaction. Density functional theory confirmed that the HOMO 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. The complex undergoes facile C−H bond activation to produce a new diarylgermanium hydride/cyanide species and isobutene via heterolytic cleavage of the N−Bu^t bond.

Synergism is a central concept for the understanding of bonding in organometallic compounds, most notably in transition-metal complexes of σ-donor/π-acceptor ligands.[1] Carbonyl (CO) and isocyanide (CNR) molecules are among the most widely studied ligands of this type, and the latter generally display stronger σ-donor and weaker π-acceptor character than carbonyls.[1,2] In addition, whereas the C−O stretching frequency is always lowered upon complexation to a transition metal, the C−N frequency of an isocyanide can shift to either higher or lower frequency. The shifts to higher frequency generally occur in transition-metal complexes wherein the π-donating tendency toward the isocyanide is weak and the M−C bond is dominated by σ effects.[2,3]

Tetrylene−isocyanide complexes (isocyanide complexes of divalent diorgano derivatives of the group 14 (tetrel) elements) 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.[4] The other extreme involves a simple donor−acceptor interaction between the carbon and the main-group atom (i.e., a single σ bond). To date, the limited number of spectroscopically characterized stannylene− and plumbylene−isocyanide complexes are Lewis adducts and display higher ν(CN) stretching frequencies than the free ligand, indicating primarily a σ-donor bond with little or no π back-bonding to the isocyanide. Silicon−isocyanide complexes tend to form heterocumulenes, however, when very bulky isocyanides are used, Lewis adducts that exhibit ν(CN) stretching frequencies lower than that of the free ligand have been isolated.[5] Although the possibility of π back-bonding in these adducts has not been explored, there have been numerous recent reports of the activation of small molecules such as H_2, NH_3, or C_2H_4 via synergistic pathways in which a main-group atom(s) behaves as both an electron donor and acceptor.[6−8] We now report that the addition of *tert*-butyl isocyanide to the diarylgermylene Ge(Ar^{Me_6})$_2$ [Ar^{Me_6} = C_6H_3-2,6-(C_6H_2-2,4,6-$(CH_3)_3$)$_2$] leads to the formation of the Lewis adduct (Ar^{Me_6})$_2$GeCNBu^t (**1**). Further analysis of the metal−isocyanide bonding mode in **1** by density functional theory (DFT) indicated that **1** displays back-bonding from the lone pair on germanium to the π* orbital of the isocyanide ligand.[9] Adduct **1** also undergoes C−H activation upon mild heating of its hexane solutions to produce the Ge(IV) hydride/cyanide complex (Ar^{Me_6})$_2$Ge(H)CN (**2**) and isobutene in essentially quantitative yield (Scheme 1).

Scheme 1. C−H Bond Activation of *tert*-Butyl Isocyanide by Diarylgermylene



Complex **1** was initially obtained by the addition of 1.1 equiv of *tert*-butyl isocyanide to a stirred solution of Ge(Ar^{Me_6})$_2$[10] in toluene. Concentration of the solution and overnight storage at ca. −20 °C afforded a crystalline mixture of **1** and unreacted Ge(Ar^{Me_6})$_2$. UV−vis spectroscopy showed that **1** was in equilibrium with freely dissociated Ge(Ar^{Me_6})$_2$ and CNBu^t in solution. However, **1** was isolated pure by reaction of a 5-fold excess of *tert*-butyl isocyanide and Ge(Ar^{Me_6})$_2$ in pentane at room temperature. The reaction was rapid, and its completion was indicated by the fading of the characteristic deep-purple color of the germylene to yellow. The removal of all volatile fractions afforded **1** as a yellow powder in quantitative yield. Crystals of **1** suitable for single-crystal X-ray diffraction (XRD) were grown from a concentrated hexane solution of **1** in the presence of excess *tert*-butyl isocyanide by slow cooling to ca.

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−20 °C. X-ray crystallographic analysis of **1** showed that the germanium is three-coordinate and is bound to two aryls and an isocyanide ligand (Figure 1). The complexation of the isocyanide ligand is almost perpendicular to the Ge−C(ipso)$_2$ plane, with an angle of ca. 103° between the Ge(1)−C(49) bond and the Ge(1)−[C(ipso)]$_2$ plane. In the isocyanide moiety, the Ge(1)−C(49) and C(49)−N(49) bond distances are 2.075(3) and 1.159(4) Å, and the C(49)−N(49)−C(50) moiety is almost linear, with a bond angle of 175.0(2)°.

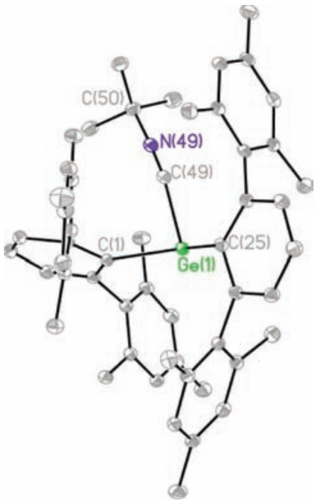


Figure 1. Thermal ellipsoid plot (30%) of **1**. H atoms and solvent molecules are not shown. Selected bond distances (Å) and angles (deg) [calculated values]: Ge(1)−C(Ar) (ave) = 2.052(3) [2.051], Ge(1)−C(49) = 2.075(3) [2.041], C(49)−N(49) = 1.159(4) [1.164], N(49)−C(50) = 1.455(9) [1.438], C(Ar)−Ge(1)−C(49) (ave) = 93.8(1) [95.1], Ge(1)−C(49)−N(49) = 156.9(2) [155.7], C(49)−N(49)−C(50) = 175.1(6) [174.4], C(1)−Ge(1)−C(25) = 118.7(2) [123.0].

^{1}H NMR spectroscopy of **1** at room temperature in the presence of an excess of *tert*-butyl isocyanide showed only one Bu^t signal, indicating rapid exchange of complexed and uncomplexed isocyanide ligands, but two signals were observed at temperatures below −25 °C. Dissolving pure **1** in hexane at room temperature afforded a green solution that changed to yellow upon cooling and deep-purple upon warming. Van't Hoff analysis of the UV−vis spectra of **1** recorded at different temperatures indicated that $\Delta H_{\mathrm{diss}} = 53(5)$ kJ mol^{-1} for **1**. The IR spectrum of **1** displayed an absorption at 2132 cm^{-1}, which is slightly lower than the stretching frequency of the free isocyanide (2134 cm^{-1}). The dissociation enthalpy determined for **1**, coupled with the shift to lower frequency of the C−N stretching band, suggested the existence of back-bonding between the lone pair on germanium and the π^* orbital of the isocyanide.

The formation and bonding of **1** was investigated computationally using DFT [see the Supporting Information (SI)]. The optimized structure of the adduct was in good agreement with the X-ray data (Figure 1), and the calculated dissociation energy was 47 kJ mol^{-1}. Similarly, the calculated ν(CN) stretching band of **1** (2234 cm^{-1}) was shifted to lower frequency relative to the stretching frequency of the free isocyanide (2247 cm^{-1}). The HOMO of **1** 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 2), and is indicative of the presence of a back-bonding interaction. Consequently, the bonding was examined in more detail with energy decomposition analysis (EDA) and by investigation of the corresponding natural orbitals of chemical valence (NOCVs) (see the SI). The results showed that the instantaneous interaction energy between the *tert*-butyl isocyanide and diarylgermylene fragments is −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 adduct **1**, the orbital interaction term cannot easily be expressed as a sum of σ and π contributions. However, an estimate of the relative importance of the bonding and back-bonding components to the total orbital interaction was obtained using the constrained space orbital variation procedure. When the unoccupied orbitals of the diarylgermylene fragment were removed from the EDA calculation, only back-bonding interactions were possible, and the total orbital interaction term decreased to 148 kJ mol^{-1}. Similarly, removing the unoccupied orbitals from *tert*-butyl isocyanide rendered the back-bonding interaction impossible, and the calculated orbital interaction energy decreased to 244 kJ mol^{-1}. These results indicate that the back-bonding interaction constitutes ca. 40% of the total orbital interaction. Qualitatively similar results were obtained by analyzing the NOCVs calculated for **1**: the two most important orbitals corresponded 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 interaction.

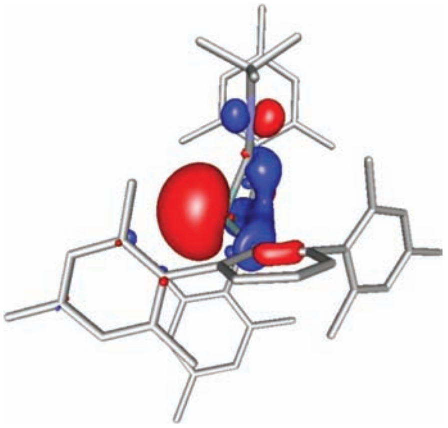
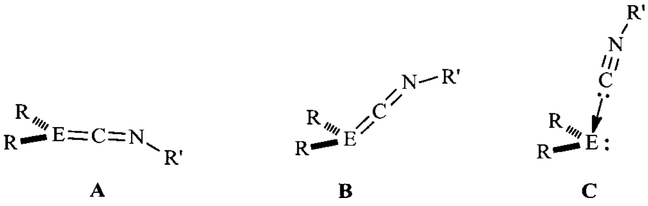


Figure 2. Highest occupied Kohn−Sham orbital of **1** (contour value ±0.04). H atoms have been omitted for clarity.

The bonding in **1** may be compared to that in the few known congeners containing heavier group-14 elements, including $[(\mathrm{CH_2})\mathrm{C}(\mathrm{SiMe_3})]_2\mathrm{SiCNR}$ (R = $\mathrm{C_6H_3}$-2,6-$\mathrm{Pr}^i{}_2$, 1-adamantyl),[11] $\mathrm{Ar^F}_2\mathrm{SnCNMes}$ ($\mathrm{Ar^F}$ = $\mathrm{C_6H_2}$-2,4,6-$(\mathrm{CF_3})_3$; Mes = mesityl),[12] and $[\mathrm{Si(SiMe_3)_3}]_2\mathrm{ECNBu}^t$ (E = Sn, Pb).[13] The silicon species have bonding similar to that in the carbon-based cumulenes, as illustrated by **A** in Scheme 2.[14] Unlike the silicon species, the tin and lead complexes form Lewis adducts with the isocyanide ligands (**C**). The tin−isocyanide adduct $\mathrm{Ar^F}_2\mathrm{SnCNMes}$ exhibits weak binding [$\Delta H_{\mathrm{diss}} = 29.6(4)$ kJ mol^{-1} vs 53(5) kJ mol^{-1} in **1**],[12] and the C−N frequency is 48 cm^{-1} higher than in the free isocyanide, indicating that the Sn−C bonding is primarily of the σ-donor type.[15] Although the C−N stretching frequency in **1** is only slightly less than that in the free ligand, it stands in sharp contrast to other σ-bonded main-group isocyanide adducts, where the C−N stretching frequencies increase proportionally

Scheme 2. Tetrylene–Isocyanide Bonding Modes



to the strength of the E–C bond, typically by several tens of wavenumbers.[15] Thus, the comparison of the experimental data for **1** and its group-14-element analogues indicates that the back-donation of electrons (and the degree of multiple-bond formation) from the group-14 element to the isocyanide ligand decreases very rapidly in the heavier atoms.

The hydride/cyanide complex **2** was first isolated and structurally characterized as an unexpected minor product (>0.5%) from a synthesis of **1**. A more rational synthesis of **2** was performed by heating a stirred solution of **1** in hexane to ca. 75 °C under static vacuum with a 5-fold excess of *tert*-butyl isocyanide in order to support the formation of **1** instead of the dissociated starting materials. The color of the solution changed from yellow to colorless overnight. The volatile materials were removed, and the white residue was washed with a small amount of pentane and dried under reduced pressure to afford **2** in 91% yield. Colorless single crystals of **2** suitable for XRD studies were grown by slow cooling of a toluene/pentane solution (1:2 v/v) to ca. −20 °C overnight, and the structure of **2** (Figure 3) was found to be similar to those of other published germanium(IV) cyanide complexes.[16] A broad absorption at 2117 cm^{-1} in the FT-IR spectrum was predicted to be due to the terminal Ge–H stretching mode (calculated value 2218 cm^{-1}), and the weak absorption at 2177 cm^{-1} was attributed to the terminal C–N stretching mode (calculated value 2326 cm^{-1}). Monitoring the ^1H NMR spectrum of a sample of **1** during heating with excess isocyanide showed the clean formation of isobutene with no other side products as well as bleaching of the yellow color of the solution.

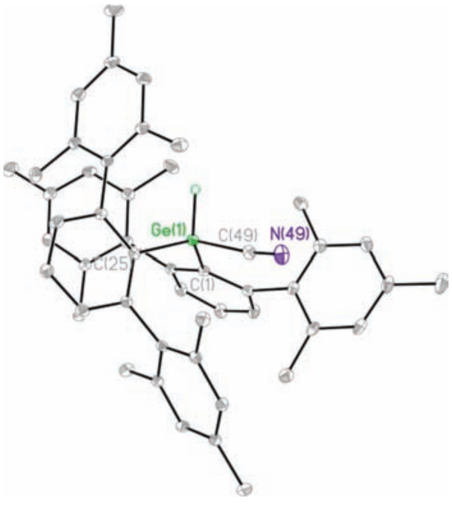
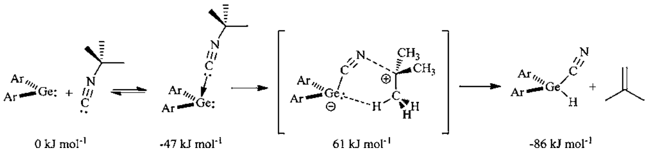


Figure 3. Thermal ellipsoid plot (30%) of **2**. C-bound H atoms are not shown. Selected bond distances (Å) and angles (deg) [calculated values]: Ge(1)–C(Ar) (ave) = 1.972(2) [1.998], Ge(1)–C(49) = 1.952(2) [1.953], Ge(1)–H(1) = 1.48(3) [1.527], C(49)–N(49) = 1.145(3) [1.153], C(Ar)–Ge(1)–C(49) (ave) = 106.01(8) [104.3], Ge(1)–C(49)–N(49) = 170.1(2) [172.9], C(1)–Ge(1)–C(25) = 124.9(1) [136.0].

Until now, mechanistic insight into the dealkylation and insertion products of metal–isocyanide complexes has been limited. It was reported that the activation of *tert*-butyl isocyanide by the iron(0) phosphine complex $Fe(PMe_3)_2(CNBu^t)_3$ gave $Fe(PMe_3)_2(CNBu^t)_2(H)(CN)$ via homolytic cleavage of the N–Bu^t bond, with the subsequent Bu^t radical acting as a hydrogen donor to yield isobutene.[17] Silylenes have been reported to insert into the N–R bond of cyclohexyl isocyanide, and the rearrangement was attributed to an alkyl shift from the isocyanide ligand to silicon upon formation of the adduct.[18] Tokitoh and co-workers also reported ^1H NMR characterization of C–H bond activation resulting from the reaction of a transient silylene with *tert*-butyl isocyanide. They proposed a mechanism involving a concerted proton migration from the *tert*-butyl group to the silaketimine accompanied by isobutene elimination.[5]

The formation of **2** and isobutene from **1** was examined with DFT calculations to elucidate a possible transition state for the reaction. Attempts to remove a proton from the *tert*-butyl group led to a steep rise in the total energy, inconsistent with the facile nature of the reaction. Consequently, we turned our attention to a concerted mechanism related to the reaction pathway proposed by Tokitoh. The calculations led to the characterization of a transition state corresponding to the formation of a formally anionic germanium and a Bu^t cation (i.e., heterolytic bond cleavage), as shown in Scheme 3. Following the internal reaction coordinate along the reaction path led to complete dissociation of the Bu^t cation coupled with a simultaneous C–H proton transfer to germanium. The conversion of **1** to **2** was found to be exothermic by 39 kJ mol^{-1}, and the calculated activation energy was 108 kJ mol^{-1}. Despite an extended search, no other transition states could be located on the potential energy surface, nor did the calculations give any support for a pathway involving homolytic N–Bu^t bond cleavage, as there was no indication of an internal instability in the Kohn–Sham determinant.[19]

Scheme 3. Calculated Energies for the Formation of 1 and 2



The decomposition was studied experimentally by heating hexane solutions of **1**, prepared in the presence of excess *tert*-butyl isocyanide, to temperatures of 40–70 °C. The disappearance of the UV–vis absorptions at 400 and 579 nm were monitored in order to measure the rate of formation of **2.** An Eyring plot afforded E_{act} = 74 kJ mol^{-1} for the formation of **2**, which is ca. 30 kJ mol^{-1} lower than other reported examples of C–H bond activation of *tert*-butyl isocyanide by transition-metal complexes.[17] These data confirm the presence of a highly activated germanium center coupled with the high stability of the reaction products. A radical mechanism involving homolytic cleavage of the N–Bu^t bond of **1** was deemed unlikely because heating adduct **1** (with a 5-fold excess of isocyanide) in the presence of excess 1,4-cyclohexadiene yielded no trace of isobutane by ^1H NMR spectroscopy.

In conclusion, structural and spectroscopic characterization of the first germylene−isocyanide complex indicates the formation of an adduct with $n \rightarrow \pi^*$ back-bonding from Ge to the isocyanide ligand. This species readily undergoes C−H bond activation to form the Ge(IV) hydride/cyanide product **2**. Although main-group isocyanide species that display lowered C−N stretching frequencies have been reported,[20] the possibility of back-bonding had not yet been explored. Further theoretical explorations of these interactions are underway and will be reported in a future publication.[21]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and characterization of **1** and **2**, tables of crystallographic data, details of kinetic measurements, details of computational analyses, and CIFs for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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■ REFERENCES

(1) Elschenbroich, C. *Organometallics; 3rd ed.*; Wiley: Weinheim, Germany, 2006, p. 382.

(2) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209.

(3) The shift to a higher C−N stretching frequency for σ-bonded isonitrile complexes is thought to be due to an increase in the effective positive charge on the carbon atom upon donation of its lone pair. This leads to an increase in the polarity of the C−N bond and hence to an increase in its strength and stretching frequency, see: Nakamoto, K. *Infrared and Raman Spectra Of Inorganic and Coordination Compounds. 4th ed.*; Wiley: New York, 1986.

(4) For a review of group-14 heterocumulenes, see: Escudie, J.; Ranaivonjatovo, H. *Organometallics* **2007**, *26*, 1542.

(5) Takeda, N.; Kajiwara, T.; Suzuki, H.; Okazaki, R.; Tokitoh, N. *Chem.—Eur. J.* **2003**, *9*, 3530.

(6) Stephan, D. W.; Erker, G. *Angew. Chem. Int. Ed.* **2010**, *49*, 46.

(7) Power, P. P. *Acc. Chem. Res.* **2011**, *44*, 627.

(8) Martin, D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2011**, *2*, 389.

(9) Initial attempts to isolate a tin or lead analogue of **1** by the addition of *tert*-butyl isonitrile to $E(Ar^{Me_6})_2$ (E = Sn, Pb) were unsuccessful. There was no apparent reaction between the stannylene or plumbylene and *tert*-butyl isonitrile.

(10) Simons, R. S.; Pu, L. H.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, *16*, 1920.

(11) Abe, T.; Iwamoto, T.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2006**, *128*, 4228.

(12) Grützmacher, H.; Freitag, S.; Herbst-Irmer, R.; Sheldrick, G. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 437.

(13) Klinkhammer, K. *Polyhedron* **2002**, *21*, 587.

(14) Furthermore, the nitrogen atoms in these complexes are distinctly sp^2-hybridized and have C−N−R bond angles of 146.3 and 130.7°, respectively. This is in contrast to the sp-hybridized nitrogen in **1**, which has a C−N−R bond angle of 175.1(6)°.

(15) Trialkylaluminum−isocyanide adducts, which possess an essentially pure σ-donor interaction, are reported to have ν(CN) shifts ca. 85 cm^{-1} higher in frequency. See: Fisher, J. D.; Wei, M. Y.; Willett, R.; Shapiro, P. J. *Organometallics* **1994**, *13*, 3324.

(16) Hihara, G.; Hynes, R. C.; Lebuis, A. M.; Riviere-Baudet, M.; Wharf, I.; Onyszchuk, M. *J. Organomet. Chem.* **2000**, *598*, 276.

(17) Tennent, C. L.; Jones, W. D. *Can. J. Chem.* **2005**, *83*, 626.

(18) Xiong, Y.; Yao, S.; Driess, M. *Chem.—Eur. J.* **2009**, *15*, 8542.

(19) As no other mechanism was apparent from the calculations, the difference between the experimental and calculated values of E_{act} can be attributed at least in part to the neglect of multiple polarization and diffuse functions in the basis set, leading to an inferior description of the transition state in comparison with the reactant and products. We note that the choice of the basis set was determined by the size of the systems in question, and its enlargement would have made the calculations prohibitively time-consuming.

(20) The digermyne−isocyanide adducts $[Ar^{^iPr_4}GeGeAr^{^iPr_4}](CNR)_n$ [R = Bu^t, $n = 1$; R = Mes, $n = 2$; $Ar^{iPr_4} = C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}Pr^i{}_2)_2$] [see: (a) Cui, C. M.; Olmstead, M. M.; Fettinger, J. C.; Spikes, G. H.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 17530. (b) Spikes, G. H.; Power, P. P. *Chem. Commun.* **2007**, 85.] have been reported to have lower ν(CN) stretching frequencies than their tin analogues [see: (c) Peng, Y.; Wang, X.; Fettinger, J. C.; Power, P. P. *Chem. Commun.* **2010**, *46*, 943]. Explorations of the back-bonding in these complexes are underway and will be reported in a full accout of this work.

(21) An experimental and computational investigation of a full series of tetrylene−isocyanide complexes is currently underway in order to examine the variations in bonding with increased atomic number (cf. ref 9). We have also prepared other germylene−isonitrile adducts, $(Ar^{Me_6})_2GeCNR$ (R = Me, C_6H_{11}, Mes), which exhibit ν(CN) shifts similar to that in **1**.