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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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ABSTRACT: Reaction of the dialkygermylene, Ge(ÂMe6); (ÂArMe6 = C6H3-2,6-(C6H2-2,4,6-(CH3)3)2) with tert-butylisocyanide gave the Lewis adduct species, (ÂArMe6)GeCtBu, in which the isocyanide ligand displays a decreased C-N stretching frequency consistent with an n–π* back-bonding interaction. Density functional theory confirms that the HOMO is a Ge-C bonding combination between the lone pair of electrons at 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 dialkygermylene hydride/cyanide species and isobutene via heterolytic cleavage of the N-Bu1 bond.

Synergism is a central concept for the understanding of bonding in organometallic compounds—notably in transition metal complexes of σ-donor/π-acid ligands. Carbonyl (CO) and isocyanide (CNR) molecules are amongst the most widely studied ligands of this type, and the latter generally displays stronger σ-donor and weaker π-acceptor character than carbonyls. 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 higher as well as lower frequency. The shifts to higher frequency generally occur in transition metal complexes with a weak π-donating tendency toward the isocyanide and the M-C bond is dominated by σ effects.

Tetraylene – isocyanide complexes may be divided into two categories which 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. The other example involves a simple donor–acceptor interaction between the carbon and main group atom—in other words 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 low or zero π-backbonding to the isocyanide. Silicon – isocyanide complexes tend to form heterocumulenes, however, when very bulky isocyanides are used, Lewis adducts have been isolated which exhibit ν(CN) stretching frequencies lower than that of the free ligand.

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 H2, NH3, or C2H4 via synergistic pathways in which a main group atom(s) behaves as both electron donor and acceptor. We now report that the addition of tert-butylisocyanide to a dialkygermylene leads to the formation of a Lewis adduct, (ÂArMe6)GeCtBu (1) [ÂArMe6 = C6H3-2,6-(C6H2-2,4,6-(CH3)3)2]. Further analysis of the metal – isocyanide bonding mode in 1 by density functional theory (DFT) indicates that I displays back-bonding from the lone pair on germanium to the π* orbital of the isocyanide ligand. The adduct, I, also undergoes C-H activation with mild heating of hexane solutions to produce the Ge(IV) hydride/cyanide complex (ÂArMe6)GeH(CN) (2) and isobutene (Scheme 1) in quantitative yield.

Complex 1 was initially obtained by the addition of 1.1 eq. tert-butylisocyanide to a stirred solution of Ge(ÂMe6)2 in toluene. Concentration of the solution and overnight storage at ca. -20 °C afforded a crystalline mixture of 1 and unreacted Ge(ÂMe6)2. UV-visible spectroscopy showed that 1 was in equilibrium with freely dissociated Ge(ÂMe6)2 and CNBu in solution. However, 1 was isolated pure by reaction of a fivefold excess of tert-butylisocyanide and Ge(ÂMe6)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 the adduct, 1, as a yellow powder in quantitative yield. Crystals of 1 suitable for single crystal X-ray diffraction were grown by slow cooling to ca. -20 °C a concentrated hexane solution of 1 in the presence of excess tert-butylisocyanide. X-ray crystallographic analysis of 1 showed that the germylene 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) plane with an angle of ca. 103° between the Ge(1) – C(49) bond and the Ge(1) – [C(ipso)]; 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) bond angle of 175.0(2)° is almost linear.

1H NMR spectroscopy of 1 at room temperature in the presence of an excess of tert-butylisocyanide shows only one Bu signal indicating rapid exchange of complexed and uncomplexed isocyanide ligands, but two signals were observed at temperatures below -25 °C. When pure 1 was dissolved in hexane at room temperature, a green solution was obtained, which changes to yellow upon cooling and to deep purple on warming. Van’t Hoff analysis of UV-visible spectra of 1 recorded at different temperatures revealed a bond order of ca. 3.35. Further analysis of the metal – isocyanide bonding in 1 via DFT indicates that the C=N (CN) stretching frequencies than the free ligand, indicating primarily a σ donor bond with low or zero π-backbonding to the isocyanide. Silicon – isocyanide complexes tend to form heterocumulenes, however, when very bulky isocyanides are used, Lewis adducts have been isolated which exhibit ν(CN) stretching frequencies lower than that of the free ligand. 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 H2, NH3, or C2H4 via synergistic pathways in which a main group atom(s) behaves as both electron donor and acceptor. We now report that the addition of tert-butylisocyanide to a dialkygermylene leads to the formation of a Lewis adduct, (ÂArMe6)GeCtBu (1) [ÂArMe6 = C6H3-2,6-(C6H2-2,4,6-(CH3)3)2]. Further analysis of the metal – isocyanide bonding mode in 1 by density functional theory (DFT) indicates that I displays back-bonding from the lone pair on germanium to the π* orbital of the isocyanide ligand. The adduct, I, also undergoes C-H activation with mild heating of hexane solutions to produce the Ge(IV) hydride/cyanide complex (ÂArMe6)GeH(CN) (2) and isobutene (Scheme 1) in quantitative yield.

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temperatures indicates a $\Delta H_{\text{diss}} = 53(5)$ kJ mol$^{-1}$ for 1. The IR spectrum of 1 displayed an absorption at 2132 cm$^{-1}$ which is slightly lower than the 2134 cm$^{-1}$ stretching frequency of the free isocyanide. 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 ligand.

The formation and bonding of 1 was investigated computationally using DFT (Supporting Information). 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 v(CN) stretching band of 1 (2234 cm$^{-1}$) was shifted to lower frequency when compared 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 at the germanium atom and the C-N π* orbital of the isocyanide ligand (Figure 2), indicative of the presence of a back-bonding interaction. Consequently, the bonding was examined in more detail with energy decomposition analysis and by investigation of the corresponding natural orbitals of chemical valence (EDA and NOCV, respectively; Supporting Information). The results show the instantaneous interaction energy between the tert-butylisocyanide 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$^{-1}$). Due to the lack of symmetry in the 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 bonding and back-bonding components to the total orbital interaction can be obtained 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 decreases to 148 kJ mol$^{-1}$. Similarly, by removing the unoccupied orbitals from tert-butylisocyanide, the back-bonding interaction is made impossible and the calculated orbital interaction energy is now 244 kJ mol$^{-1}$. This indicates that the back-bonding interaction constitutes about 40% of the total orbital interaction. Qualitatively similar results are obtained by analyzing the NOCV’s calculated for 1: 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 interaction.

The bonding in 1 may be compared to that in the few known heavier group 14 element congeners [(CH$_3$)$_2$SiMe$_3$]$_2$SiCNR (R = CsH$_2$-2,6-Pr$_2$, 1-Adamantyl)$_{11}$, Ar$_2$Sn(C$_6$H$_4$)(CNMe)$_2$Mes (Ar$^2$ = C$_6$H$_2$-2,4,6-CF$_3$; Mes = mesityl)$_{12}$ and [(SiMe$_3$)$_2$]$_2$E=CNBu$_2$ (E = Sn, Pb)$_{13}$]. The silicon species have similar bonding to the carbon based cumulenes as illustrated by A (Scheme 2). Unlike the silicon species, the tin and lead complexes form Lewis adducts with the isocyanide ligands (C). The tin isocyanide adduct, Ar$_2$Sn(C$_6$H$_4$)(CNMe)$_2$Mes, exhibits weak binding, $\Delta H_{\text{diss}} = 29.6(4)$ kJ mol$^{-1}$, (cf. 53(5) kJ mol$^{-1}$ in 1)$_{12}$ 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 π-donor type$_{13}$. Although the C-N stretching frequency in 1 is only slightly less than that on the free ligand, it stands in sharp contrast to other π-bonded main group isocyanide adducts where the C-N stretching frequencies increase proportionally to the strength of the E-C bond, typically several tens of wavenumbers.$^{13}$ Thus, the comparison of experimental data for 1 and its group 14 element analogues indicate that the back donation of electrons (and 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 five-fold excess of tert-butylisocyanide 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 X-ray diffraction studies were grown by slow cooling of a toluene/pentane solution (1:2 V/V) to ca. -20 °C overnight, and is structurally similar to other published germanium(IV) cyanide complexes.$^{14}$ 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 $^1$H NMR spectrum of a sample of 1 during heating with excess isocyanide showed the clean formation of isobutenone with no other side products as well as bleaching of the yellow color of the solution.

Until now, mechanistic insight on the dealkylation and insertion products of metal isocyanide complexes has been limited. It was reported that the activation of tert-butylisocyanide by the iron(0) phosphine complex Fe(PMe$_3$)(CNBu$_2$), gave Fe(PMe$_3$)(CNBu$_2$)(H-CN). via homolytic cleavage of the N-Bu bond, and the subsequent Bu$^+$ radical acts as a hydrogen donor to yield isobutenone.$^{15}$ Silylenes have been reported to insert into the N-R bond of cyclohexylisocyanide, and the rearrangement was attributed to an alkyl shift from the isocyanide ligand to silicon upon formation of the adduct.$^{16}$ Tokitoh and coworkers also characterized C-H bond activation by $^1$H NMR spectroscopy formed from a transient silylene with tert-butylisocyanide. They proposed a mechanism involving a concerted proton migration from the tert-butyl group to the silylamine accompanied by isobutenone elimination.$^{17}$

The formation of 2 and isobutenone 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 steep rise in 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 which corresponds to the formation of a formally anionic germanium and a Bu$^+$ cation i.e. heterolytic bond cleavage (Scheme 3). Following the internal reaction coordinate along the reaction path led to complete dissociation of the Bu$^+$ 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-But bond cleavage as there was no indication of an internal instability in the Kohn-Sham determinant.$^{18}$

The decomposition was studied experimentally by heating hexane solutions of 1, prepared in the presence of excess tert-butylisocyanide, to temperatures in the range of 40 to 70 °C. The disappearance of the UV-visible absorptions at 400 and 579 nm were monitored in order to measure the rate of formation of 2. An Eyring plot afforded an $E_{\text{act}} = 74$ 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-butylisocyanide by transition metal complexes.$^{19}$ 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-But bond of 1 is unlikely because heating the adduct, 1 (with a fivefold 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 π−π* back-bonding 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, which display lowered C-N stretching frequencies have been reported,[23] 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]

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Supporting Information Available: 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.

Scheme 1. C-H Bond Activation of tert-Butylisocyanide by Diarylgermylene

Scheme 2. Tetrylene–Isocyanide Bonding Modes

Scheme 3. Calculated Energies for the Formation of 1 and 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) [0.041], 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].

Figure 2. Highest occupied Kohn-Sham orbital of 1 (contour value ±0.04). Hydrogen atoms are not shown for clarity.
REFERENCES

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 stretching frequency.
4 For a review of group 14 heterocumules, see Escudie, J.; Ranaivonjatovo, H. Organometallics 2007, 26, 1542.
9 Initial attempts to isolate a tin or lead analogue of 1 by the addition of tert-butylisonitrile to E(ArMe$_3$)$_2$ (E = Sn, Pb) were unsuccessful. There was no apparent reaction between the stannylene or plumbylene and tert-butylisonitrile.
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 Trialkylaluminium isocyanide adducts, which possess an essentially pure σ-donor interaction, are reported to have ν(CN) shifts of ca. 85 cm$^{-1}$ to higher frequency. Fisher, J. D.; Wei, M. Y.; Willett, R.; Shapiro, P. J. Organometallics. 1994, 13, 3324.
19 As no other possible mechanism was apparent from the calculations, the difference in experimentally determined E$_c$ relative to the calculations can, at least in part, be attributed to the neglect of multiple polarization and diffuse functions in the basis set, leading to an inferior description of the transition state in comparison to 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 calculations prohibitively time-consuming.
20 The germylene isocyanide adducts, [ArGeGeAr=CN(R)]$_2$ (R = Bu', n = 1; R = Mes, n = 2) (Ar$^{28}$Ge=CN$_2$ has a C-N-R bond angle of 175.1(6)° have been reported to have lower ν(CN) stretching frequencies when compared to their tin analogs. Explorations into the back-bonding in these complexes are underway and will be reported in a full account 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. Reference 9). We have also prepared other germylene-isonitrile adducts, (ArGe)$^2$GeCN (R = Me, C$_6$H$_5$, Mes), which exhibit similar ν(CN) shifts to that in 1.