Nitrogen Insertion

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End-On Nitrogen Insertion of a Diazo Compound into a Germanium(II) Hydrogen Bond and a Comparable Reaction with Diethyl Azodicarboxylate**

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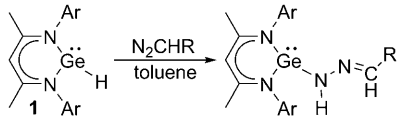
Dedicated to Professor Martin Jansen on the occasion of his 65th birthday

The reaction of diazoalkanes with transition metals has a long history in the cyclopropanation of olefins.[1] Moreover, metal carbene complexes play an important role in olefin metathesis,[2] C–H bond activation,[3] and the synthesis of reactive ylides.[4] In all these examples, diazoalkane either interacts with the metal center to form a metal diazoalkane complex or subsequently releases dinitrogen from diazoalkane to form the metal carbene complex. In contrast, the reaction of diazoalkane with main group metals is scarcely known in literature.[5]

Recently we reported on the synthesis of a germanium(II) hydride [LGeH] (**1**; L = [HC{(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)}$_2$]) and its reactivity towards multiply-bonded carbon–carbon and carbon–oxygen multiple bonds,[6] and were subsequently interested in studying the reactivity of **1** with a diazoalkane. Some reactions between metal hydrides and diazoalkanes have been reported.[7] From the reaction of diazoalkane with **1**, we expected one of the following products: [LGe(H)NNCHR], [LGeNNCH$_2$R], [LGe(H)CHR], or [LGeCH$_2$R]. To our surprise, none of these species was formed. Treatment of **1** with ethyl diazoacetate and trimethylsilyldiazomethane leads to the first stable germanium(II)-substituted hydrazone derivative, [LGeN(H)NCHR], where R = CO$_2$Et (**2**) or SiMe$_3$ (**3**), in high yields (Scheme 1). The reaction proceeds by the unprecedented end-on insertion of diazoalkane into the Ge–H bond.

Dinitrogen elimination with subsequent insertion or an oxidative addition reaction is generally accepted. Accordingly, the end-on N$_2$CHR insertion into the Ge–H bond unambiguously reveals the initial interaction between the germanium center and the terminal nitrogen atom of the diazo group followed by hydrogen transfer from the germanium center to nitrogen. This type of reaction is, to the best of our knowledge, unknown, although in 2005 we reported the first end-on azide insertion into an Al–C bond of an aluminacyclopropene and the formation of aluminaazacyclobutene.[8]



Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

R = CO$_2$Et (**2**) and SiMe$_3$ (**3**)

Scheme 1. Synthesis of **2** and **3**.

Compounds **2** and **3** were characterized by spectroscopic, analytical, and X-ray crystallographic measurements. The ^{1}H NMR spectra of **2** and **3** have singlets that are shifted upfield ($\delta = 7.25$ and 6.37 ppm) that can be assigned to the N*H* proton. Furthermore, **2** and **3** have singlet resonances ($\delta = 6.62, 4.91$ ppm and $\delta = 6.44, 4.96$ ppm) that correspond to the imine and γ C*H* protons. The IR spectrum of **2** has bands at 3188, 2700, and 1641 cm^{-1}, which are tentatively assigned to the N-H, C-H, and C=O stretching frequencies.

Compounds **2** and **3** are both soluble in benzene, THF, *n*-hexane, and *n*-pentane, and show no decomposition on exposure to air. In the solid state, **2** and **3** are yellow solids. Compound **2** crystallizes after one day from a saturated toluene solution at room temperature in the tetragonal space group $P4_2/ncm$ with one molecule in the asymmetric unit (Figure 1).[9] Compound **3** has one SiMe$_3$ group, and a singlet is observed in the ^{29}Si NMR spectrum ($\delta = 6.28$ ppm). Compound **3** crystallizes after two days from saturated *n*-hexane solution at room temperature in the monoclinic space group $C2/m$ with one molecule in the asymmetric unit (Figure 2).[9]

To investigate the electronic structure and bonding properties of **2** and **3**, we performed ab initio DFT calculations as implemented in the Gaussian 03 package.[10] We adopted the hybrid B3LYP[11] exchange and correlation functional with the LANL2DZ[12] basis set in all the calculations. The molecular structures of **1**–**3** as obtained from X-ray crystallography were used for the calculations; since the hydrogen atom positions could not be precisely located by X-ray crystallography, we relaxed all the hydrogen atoms in

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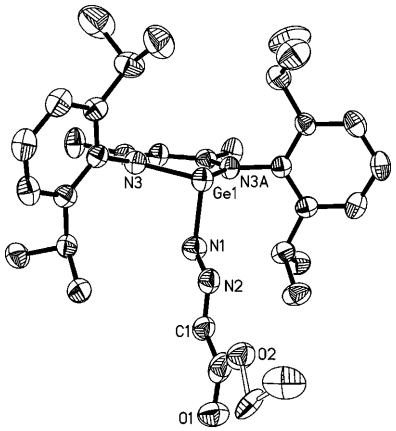


Figure 1. Molecular structure of **2**. Thermal ellipsoids are shown at 50% probability; H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–N1 1.915(7), N1–N2 1.344(10), N2–C1 1.273(10), Ge1–N3 2.015(5), Ge1–N3A 2.015(5); Ge1-N1-N2 117.0(6); N1-N2-C1 118.7(7), N3-Ge1-N3A 94.2(2).

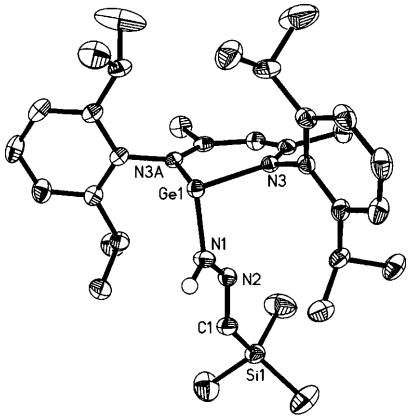


Figure 2. Molecular structure of **3**. Thermal ellipsoids are shown at 50% probability; H atoms (except N1-H) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–N1 1.878(3), N1–N2 1.351(4), N2–C1 1.303(4), Ge1–N3 1.9913(17), Ge1–N3A 1.9913(17); Ge1-N1-N2 130.6(2), N1-N2-C1 117.4(3), N3-Ge1-N3A 90.41(10).

the experimentally obtained structures. We also optimized the precursor geometries (N_2CHR, $R = CO_2Et/SiMe_3$) and performed vibrational energy calculations to confirm the global minimum structures.

We found large stabilization energies for both **2** (−0.894 eV) and **3** (−1.30 eV). The stabilization energy E_{stab} was calculated as $E_{stab}(\mathbf{2/3}) = E(\mathbf{2/3}) - E(\mathbf{1}) - E(N_2CHR)$, with $R = CO_2Et$ and $SiMe_3$. To obtain insight into the charge density profile and bonding aspects, we performed natural atomic orbital (NAO) and Wiberg bond order calculations. Mulliken charge analysis shows a drastic electron density shift from the germanium center to the nitrogen atom of the diazo ligand in **2** and **3** (see the Supporting Information). A closer look at the natural atomic orbitals reveals that the electrons migrate mainly from the p orbital of germanium and s orbital of hydrogen to the p orbital of ligating nitrogen atom of the diazo group (see the Supporting Information). Similar observations are reflected in the HOMO plots of compounds **1**–**3** and the reagents (Figure 3): the hybrid orbitals of germanium are mostly dominated by s character in **1**–**3**. The calculations also reveal that the stabilities of compounds **2** and **3** arise from the electron density shift from the N–N bond of the diazoalkane reagent (N–N bond order: 2.4 ($R = CO_2Et$), 2.3 ($R = SiMe_3$)) to the Ge–N bond between germanium and ligating nitrogen (see bond order data in the Supporting Information). As a consequence, the N–N bond deviates from a triple bond and the initial linear geometry of the ligating end in N_2CHR transforms into a planar zigzag structure in **2** and **3**. The relative stability analysis shows that the structure and geometry of compound **1** in the crystalline state is about 0.4 eV more stable than those for compounds **2** and **3**, as observed in the case of other stable heteronuclear rings.[13] These observations unambiguously show that although the ring structure in compound **1** is destabilized upon ligation, the formation of a Ge–N bond by end-on insertion of diazoalkane in compounds **2** and **3** leads to the stable germanium-substituted hydrazone derivatives. The similarity in electronic structures and bonding characteristics of compounds **2** and **3** suggests that the diazoalkane R groups play a negligible role in the stability, as they lack conjugation with the rest of the molecule.

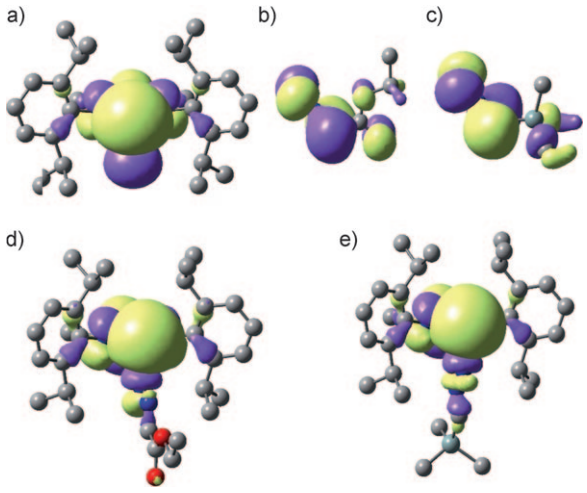
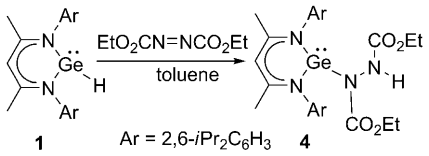


Figure 3. The HOMOs of a) **1**, b) N_2CHCO_2Et, c) $N_2CHSiMe_3$, d) **2**, and e) **3**.

We carried out the reaction of **1** with diethyl azodicarboxylate (DEAD). This reaction (Scheme 2) proceeds rapidly at room temperature under oxidative addition to give compound **4** in high yield. Compound **4** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. Single crystals were obtained after three days from a saturated *n*-hexane solution at −32 °C



Scheme 2. Synthesis of **4**.

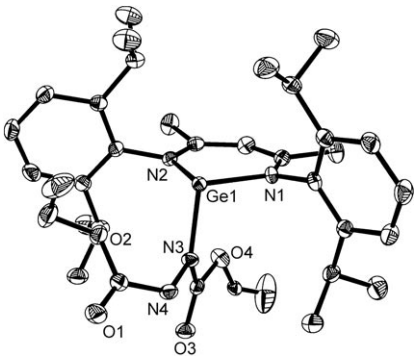


Figure 4. Molecular structure of **4**. Thermal ellipsoids are shown at 50% probability; H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–N1 2.009(2), Ge1–N3 1.990(2), N3–N4 1.418(14); N1-Ge1-N2 90.94(9), N1-Ge1-N3 98.93(9).

(Figure 4).[9] The coordination polyhedron around the germanium atom features a distorted tetrahedral geometry with a stereochemically active lone pair. The IR spectrum has bands at 3245 and 1752 cm^{-1}, which are tentatively assigned to the N-H and C=O stretching frequencies.

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