ChemPubSoc Europe
DOI: 10.1002/chem.201603544
CHEMISTRY
A European Journal
Communication

Main Group Chemistry

A Germylene/Borane Lewis Pair and the Remarkable C=O Bond Cleavage Reaction toward Isocyanate and Ketone Molecules

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Abstract: A germylene/borane Lewis pair (**2**) was prepared from a 1,1-carboboration of amidinato phenylethynylgermylene (**1**) by $B(C_6F_5)_3$. Compound **2** reacted with *i*PrNCO and $(4\text{-MeOC}_6H_4)C(O)Me$, respectively, with cleavage of the C=O double bond. In the first instance, O and *i*PrNC insert separately into the Ge–B bond to yield a $GeBC_2O$-heterocycle (**3**) and a $GeBC_3$-heterocycle (**4**). In the second case $(4\text{-MeOC}_6H_4)(Me)C$ inserts into the Ge–N bond of **2** while O is incorporated in the Ge–B bond to form a Ge-centered spiroheterocycle (**5**). The reaction of **2** with *t*BuNC to give **6**, which has almost the same structure as **4**, proved the formation of the isonitrile during transformation from **2** and *i*PrNCO to **3** and **4**. The kinetic study of the reaction of **2** and *i*PrNCO gave evidence of proceeding through a $GeBC_3O$-heterocycle intermediate. In addition, a DFT study was performed to elucidate the reaction mechanism.

The deoxygenation reaction of carbonyl compounds is an important process, which has been extensively utilized to produce a variety of organic molecules such as imines, hydrocarbons, carbene-like species, and others.[1] It is essential that this reaction proceeds with a multiple bond cleavage of the C=O functionality, during which the deoxygenated remaining moiety couples with the functional group to form the target product. The condensation reaction of aldehydes or ketones with amines has been well-known to yield the imines. This process exhibits a deoxygenation under elimination of water, which is accompanied with the C=N bond formation. However, the reaction mechanism is quite complex.[2] The Fischer–Tropsch synthesis converts CO and H_2 to hydrocarbons, carrying a hydrogenation deoxygenation reaction through elimination of water as well, but operates under catalytic conditions when using transition metals.[3] Recently, Erker and Stephan independently illustrated this reaction process using P/B frustrated Lewis pairs (FLPs) with or without an excess of the Lewis acid as stoichiometric reactant.[4] Also well-known is the cross-coupling reaction of the Wittig[5a,b] and Tebbe[5c,d] reagents. These reagents efficiently deoxygenate aldehydes, ketones, and/or carboxylic acid derivatives, respectively, and couple with the remaining fragment to yield α-olefins. The organophosphorus and -titanium oxides are formed as the respective byproducts.

The deoxygenation of the carbonyl compounds directing to the free carbene-like species appears to be difficult and to date only rare examples have been reported.[6] Efficient and selective reducing agents are indeed rare. In recent years, the groups of Kira, Cui, and Roesky have reported on silylenes involved in the deoxygenation of aldehydes and ketones.[7] Nonetheless, such compounds are still limited. Moreover, the related reaction mechanisms are not clear due to the complicated process that is induced by these too reactive moieties. Recently we worked on the synthesis of the germylenes[8] and the Ge^{IV}/P FLP.[9] The reactions of some of these compounds with aldehydes, ketones, or their derivatives have also been carried out. However, only the C=O bond activation or addition reactions were found.[8d,e,9] We were then intrigued with the deoxygenation of the carbonyls by germylenes in a reaction similar to that of the silylenes. A new germylene that has an intramolecular borane connectivity was synthesized (**2**, Figure 1), which has been tested to function as a deoxygenation compound for isocyanate by forming the respective GeC_2BO- and GeC_3B-heterocycles. Remarkably, during the reaction, the formation of the free isonitrile was detected. However, the deoxygenation reaction of **2** with a ketone resulted in a Ge-centered spiroheterocycle as the single product.

Amidinato phenylethynyl germylene **1** was prepared (see Experimental Section in the Supporting Information) and then treated with $B(C_6F_5)_3$ in toluene at 65 °C for 12 h to give compound **2** with 92 % isolated yield (Figure 1). The ^{19}F NMR spectrum displayed two sets of C_6F_5 resonances ($\delta = -129.1$ (*o-F*),

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201603544.

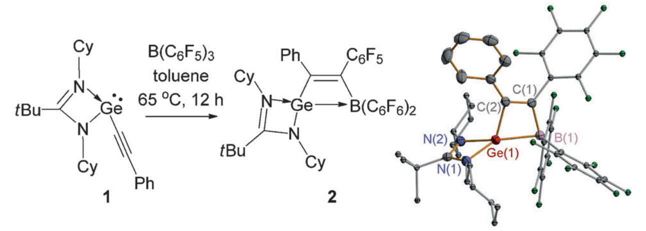
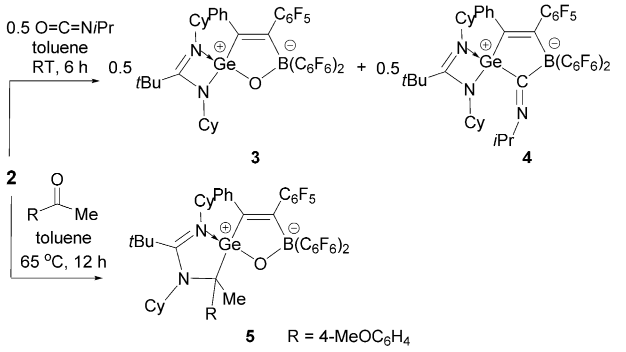


Figure 1. Synthesis and X-ray crystal structure of **2** (H-atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Ge(1)-C(2) 1.935(2), C(2)-C(1)1.359(3), C(1)-B(1) 1.659(3), B(1)-Ge(1) 2.160(2), Ge(1)-N(1) 1.933(2), Ge(1)-N(2) 1.939(2); Ge(1)-C(2)-C(1) 93.9(1),C(2)-C(1)-B(1) 111.9(2), C(1)-B(1)-Ge(1) 78.2(1), B(1)-Ge(1)-C(2) 75.2(1), N(1)-Ge(1)-N(2) 67.5(1).

−158.4 (*p-F*), −164.2 ppm (*m-F*) vs. $\delta = -139.0$ (*o-F*), −157.8 (*p-F*), −163.2 ppm (*m-F*)), in a 2:1 ratio. This is supportive of a 1,1-carboboration reaction that involves a probable abstraction of the $PhCC^-$ anion by $B(C_6F_5)_3$ from the Ge atom to form $[PhCCB(C_6F_5)_3]^-$ and the Ge^{II} cation. Then one C_6F_5 group from the B center migrated to the adjacent acetylenic carbon atom, following by a back-bonding of another acetylenic carbon atom to the Ge center.[10] As a consequence, the respective $=CB(C_6F_5)_2$ and $=C(C_6F_5)$ groups were formed. The ^{11}B NMR resonance was observed at $\delta = -16.6$ ppm, which is in the range of germylene-borane adducts ($\delta = 2.8$ to −42.0 ppm),[11] but significantly deviates from that found in three-coordinate boron compound $Ge[C(Ph)C(Ph)B(NDippCH)_2][N(SiMe_3)_2]$ ($\delta = 43.5$ ppm).[12] These data indicate the formation of a four-coordinate B atom reminiscent of a $Ge^{II} \rightarrow B$ donor–acceptor interaction present in **2**. The X-ray crystal structure analysis unambiguously evidenced **2** as a 1,1-carboboration product that had a *cis*-arrangement of the $[tBuC(NCy)_2]Ge$ and $B(C_6F_5)_2$ moieties along the vinyl C(1)–C(2) bond (1.359(3) Å). A Ge–B bond (2.160(2) Å) is indicated by comparison with the germylene-borane adducts (2.015(7) −2.186(3) Å)[11] and borylgermanium compounds (2.141(2) Å).[13] The four-membered $GeBC_2$-heterocycle forms a distorted plane ($\Delta = 0.0446$ Å). However, the Ge(1)-C(2)-C(1) (93.94(13)°) and C(2)-C(1)-B(1) (111.88(17)°) bond angles are deviated from the ideal 90° due to the ring strain. To the best of our knowledge heterocycles containing the $Ge^{II} \rightarrow B$ bond motif have not been reported so far. Compound **2** can be well ascribed as a Lewis pair.[14]

The reaction of **2** with isopropyl isocyanate was carried out by using toluene as solvent. Thus, at room temperature this reaction proceeded smoothly. However, the product formation depended on the molar ratio of the two precursors (see Sections IV and V in the Supporting Information). The reaction on an NMR-scale in $[D_8]$toluene solution showed that a strict molar ratio (1:0.5) of the precursors was necessary to obtain two clean products in an almost equal amount, as indicated by the presence of two sets of the proton resonances after about 6 h (see Figures S1 and S2 in the Supporting Information). A scaled-up reaction of **2** and half equivalent of isopropyl isocyanate was then accomplished, which expectedly gave compounds **3** (colorless crystals) and **4** (yellow crystals; Scheme 1).



Scheme 1. Reactions of **2** with the respective isocyanate and ketone molecules.

The X-ray single-crystal diffraction study revealed that **3** is a $GeBC_2O$-heterocycle, whereas **4** showed a $GeBC_3$-heterocyclic arrangement (Figure 2). This result indicates a clear C=O bond cleavage of the isopropyl isocyanate and the O and *i*PrNC insert, respectively, into the Ge–B bond of **2**. These two new heterocycles keep the planarity as well ($\Delta = 0.0518$ Å for **3** and 0.0268 Å for **4**). Note that, within the $GeBC_2O$-heterocycle, the Ge(1)–O(1) bond length (1.721(2) Å) is between those of the Ge=O double bond of germanones (1.646(2)–1.672(3) Å)[15] and the single bond of germoxanes (1.765(4)–1.820(2) Å).[16] These data suggest a probable $Ge{=}O \rightarrow B$ bonding and their resonance form ($Ge^+{-}O{-}B^-$) is attributable to the polarity of the Ge=O bond intensively discussed in the literature.[15] In contrast, within the $GeBC_3$-heterocycle the $Ge{-}C_{C=NiPr}$ bond length (2.019(5) Å) is longer by about 0.10 Å than that of the $Ge{-}C_{C=C}$ (1.918(6) Å) and much longer than those of the Ge=C double bonds of known compounds (1.761(2)–1.840(4) Å).[17]

The ^1H NMR data indicated that in the above-NMR-scale reaction compound **3** appeared to form as the major product when an excess of the isopropyl isocyanate was employed (Figures S3 and S4 in the Supporting Information). To elucidate this reaction process in detail, kinetic study of the reaction of **2** and 0.5 *i*PrNCO was conducted. As can be seen from the data recorded in Figure S2 in the Supporting Information, the consumption of **2** and *i*PrNCO is observed while products **3** and **4** are gradually generated. It was noted that this reaction process was clearly accompanied with the formation of an intermediate and its further reaction to the new products. We have tried to isolate the intermediate by controlling the reaction time and temperature, but failed. Furthermore, we treated **2** directly with *tert*-butyl isonitrile, which reacted very fast (within several minutes) in toluene at room temperature and yielded compound **6** (Figure 3). Compound **6** has almost the same structure as that of **4** in which only the *i*Pr group of the *i*PrNC part is replaced by the *t*Bu group. Compound **6** was characterized on the basis of NMR spectroscopy, X-ray crystallography, and CHN element analysis. Similar reaction patterns have been observed in the reaction of the P/B Lewis pair with isonitriles. The resulting PBC_3-heterocycles were formed by synergistic 1,1-addition of the P/B LP to the terminal C atom of the isonitriles.[18] In compound **2** the borane part serves as a ligand acceptor

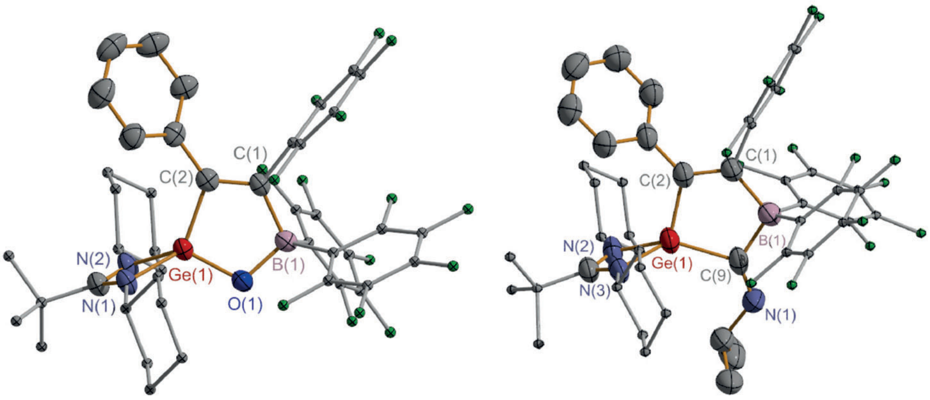


Figure 2. Crystal structures of **3** (left) and **4** (right). H-atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: for **3**, Ge(1)-C(2) 1.914(3), C(2)-C(1)1.347(4), C(1)-B(1) 1.653(4), Ge(1)-O(1) 1.721(2), B(1)-O(1) 1.512(4), Ge(1)-N(1) 1.894(2), Ge(1)-N(2) 1.905(2); Ge(1)-C(2)-C(1) 103.7(2), C(2)-C(1)-B(1) 119.1(2), C(1)-B(1)-O(1) 106.8(2), Ge(1)-O(1)-B(1) 109.4(2), O(1)-Ge(1)-C(2) 99.3(1), N(1)-Ge(1)-N(2) 69.1(1); for 4, Ge(1)-C(2) 1.918(6), C(2)-C(1)1.363(8), C(1)-B(1) 1.659(8), Ge(1)-C(9) 2.019(5), B(1)-C(9) 1.623(9), C(9)-N(1) 1.273(8), Ge(1)-N(2) 1.931(5), Ge(1)-N(3) 1.937(4); Ge(1)-C(2)-C(1) 108.6(4), C(2)-C(1)-B(1) 122.1(5), C(1)-B(1)-C(9) 108.6(5), Ge(1)-C(9)-B(1) 104.5(4), C(9)-Ge(1)-C(2) 96.0(2), N(2)-Ge(1)-N(3) 68.7(2).

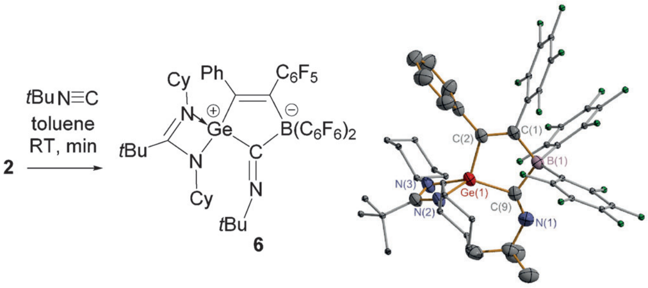


Figure 3. Reaction of **2** with *tert*-butyl isonitrile and X-ray crystal structure of product **6** (H-atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Ge(1)-C(2) 1.919(3), C(2)-C(1) 1.352(4), C(1)-B(1) 1.658(4), B(1)-C(9) 1.655(4), Ge(1)-C(9) 2.031(3), C(9)-N(1) 1.244(4), Ge(1)-N(2) 1.924(2), Ge(1)-N(3) 1.919(2); Ge(1)-C(2)-C(1) 109.6(2), C(2)-C(1)-B(1) 121.6(2), C(1)-B(1)-C(9) 108.9(2), Ge(1)-C(9)-B(1) 103.3(2), C(9)-Ge(1)-C(2) 95.8(1), N(2)-Ge(1)-N(3) 68.0(1).

while the Ge^{II} atom behaves as a donor coordinating at the terminal C atom of the isonitriles. To the best of our knowledge, the formation of such a Ge–C bond is unprecedented among known organogermanium compounds.[8,19]

Even with these experimental results in hand it was not possible to understand the reaction mechanism in detail with respect to the C=O double bond cleavage of the isopropyl isocyanate when interacting with **2**. Moreover, both compounds **3** and **4** were formed in different yields when the molar ratio of the precursors changed. The Ge-based Lewis pair reaction chemistry has been rarely reported.[9] Therefore we performed DFT calculations (see Section VI in the Supporting Information) to illustrate the bonding scenario of **2** and also to predict a probable reaction pathway of **2** and isopropyl isocyanate. The formation of **2** from the initial precursor **1** is exergonic ($\Delta G_L^S = -22.0\ \mathrm{kcal\,mol^{-1}}$) and also highly exothermic ($\Delta H_L^S = -38.9\ \mathrm{kcal\,mol^{-1}}$), suggesting a facile conversion. The Ge–B bond (2.199 Å) in **2** with occupancy of 1.872 e is almost equally shared between the bonding partners (B: 44%) because of nearly the same electronegativity. The natural population analysis (NPA) charges on Ge and B atoms are +1.702 and +0.066, respectively. The Wiberg bond index (WBI) calculated for the Ge–B bond is 0.824. The KS-HOMO and KS-LUMO of **2** comprise the Ge–B σ orbital and C–C π* orbital as pictorially represented in Figure S5.

The reaction of **2** with *i*PrNCO might involve a dipolar addition of **2** to the C=O bond of *i*PrNCO as a similar reaction pattern has been reported for the P/B FLP toward the isocyanates.[20a] Then an intermediate **D** was formed, which is calculated to be relatively more stable than **2** in energy by 9.6 kcal $\mathrm{mol^{-1}}$ (Figure 4). The calculated activation barrier for the step is moderate ($\Delta^{+}G_L^S = 20.1\ \mathrm{kcal\,mol^{-1}}$). Nonetheless, a transition state **[2-D]**$^{+}$ is possible, which is characterized by a single imaginary frequency with respect to the simultaneous formation of Ge–C and B–O bonds. In the next step, the oxygen atom approaches Ge, resulting in the formation of **3** and *i*PrNC. This step, corresponding to an activation barrier of 29.4 $\mathrm{kcal\,mol^{-1}}$, is referred to as the rate-determining step. The single imaginary frequency in **[D-3]**$^{+}$ depicts the Ge–O bond formation and concomitant cleavage of the Ge–C and C–O bonds. The B–O bond (1.518 Å) in **3** with occupancy of 1.957 e is polarized toward the more electronegative oxygen atom (O: 79%). The NPA analysis reveals +2.261 and +0.536 charges on Ge and B atoms, respectively. Furthermore, approach of the isopropyl isonitrile carbon towards the electron-deficient boron in **2** leads to **4A**, which shows the typical features of a strong Lewis acid adduct (B–C3 = 1.604 Å) with a shorter C3–N bond length (1.173 Å).[18,20b] This process occurs through the relatively lower energy ($\Delta^{+}G_L^S = 16.2\ \mathrm{kcal\,mol^{-1}}$) transition state **[2-4A]**$^{+}$. The imaginary mode of the transition-state vector portrays the formation of the B–C bond. The final step is a barrierless process, where the isopropyl isonitrile carbon atom in **4A** approaches the Ge to furnish product **4**, as has been substantiated by the experimental findings from the reaction of **2** with *tert*-butyl isonitrile to produce **6**.

It appears that the calculated activation barriers for the reactions between **2**+*i*PrNCO ($\Delta^{+}G_L^S = 20.1\ \mathrm{kcal\,mol^{-1}}$) and **2**+ *i*PrNC ($\Delta^{+}G_L^S = 16.2\ \mathrm{kcal\,mol^{-1}}$) are somewhat comparable.

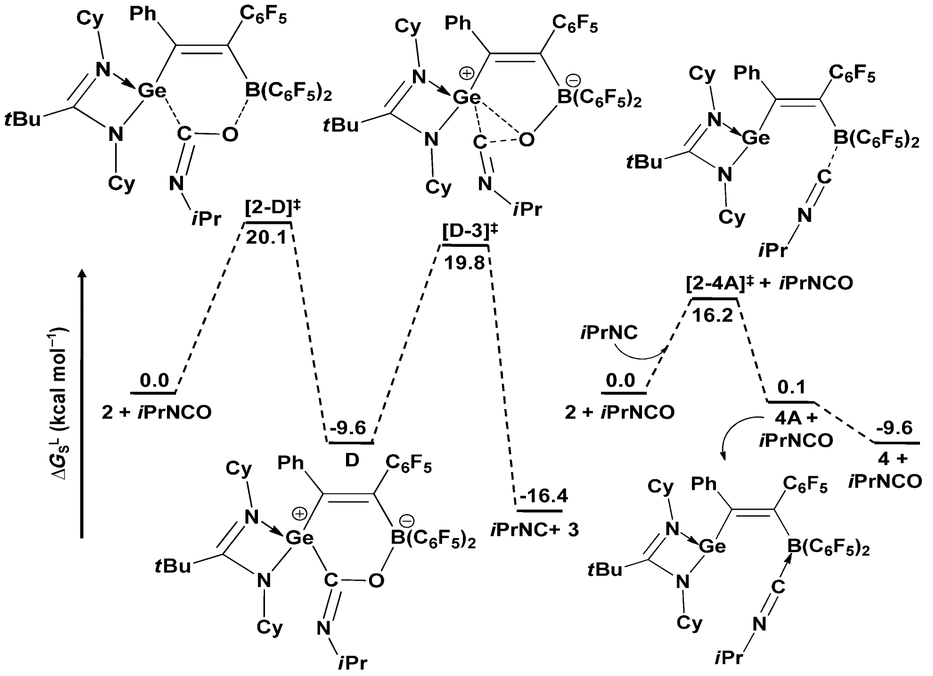
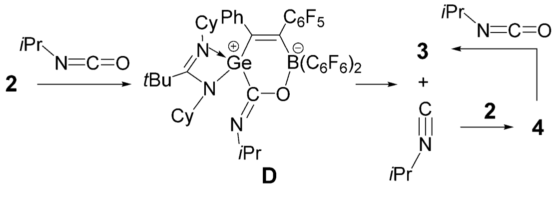


Figure 4. Energy profile for the reaction of **2** with isopropyl isocyanate at R-M06-2X(SMD)/def2-TZVP//ONIOM{R-BP86/def2-SVP:HF/STO-3G} level of theory.

Moreover, compound **3** is only a little more stable than **4** in energy by 6.8 kcal mol^{-1}. Accordingly, when isopropyl isocyanate was excessively added the reaction appeared to not stop at the formation of **3** and **4** as the final products in equal amounts. As further reaction of **4** with the excess isopropyl isocyanate continued, **3** accumulated to become a major part under release of the isopropyl isonitrile as a free compound while **4** decreased to become the minor product (Scheme 2). This result is in line with the experiment by the reaction of **2** with three equivalent *i*PrNCO to give *i*PrNC, **3** (major), and **4** (minor; see Figures S3 and S4 in the Supporting Information). It is worth mentioning that this reaction reveals indeed a cooperative interaction of the Ge^{II}/B Lewis pair with the isocyanate and isonitrile. We have investigated the reaction using either **1** or [*t*BuC(NCy)$_2$]GeCl[21] in the absence or presence of $B(C_6F_5)_3$. However, no reaction occurred, while the reactions of the related amidinato silylenes with ketones and 3,5-di-*tert*-butyl-*o*-benzoquinone yielded the SiCO- and SiC_2O_2-heterocycles.[22]

Finally, we used **2** for the reaction with the ketone molecule. The reaction of **2** and one equivalent 4-methoxyacetophenone was accomplished in toluene at 65 °C and resulted in **5** as a pure product of colorless crystals (Scheme 1). No other compound was formed even when an excess of 4-methoxyacetophenone was employed. Compound **5** is a Ge-centered spiroheterocycle with two five-membered rings (Figure 5). The $GeBC_2O$-heterocycle is comparable in structure to that of **3**. The GeC_2N_2-heterocycle deviates a little from the planarity ($\Delta_{GeC2N2} = 0.0835$ Å) when compared with the $GeCN_2$-heterocycles found in **2**–**4** ($\Delta_{GeCN2} = 0.0032$–0.0176 Å). The Ge–C bond length within the GeC_2N_2-heterocycle is 1.975(3) Å, typical of a single bond feature, which is a little longer than the Ge–$C_{C=C}$ distance (1.930(3) Å) in the adjacent $GeBC_2O$-heterocycle. The formation of **5** can be considered as a result of the C=O bond cleavage of 4-methoxyacetophenone, but the (4-$MeOC_6H_4$)(Me)C reacts differently and inserts into the Ge–N bond while the O is simultaneously located in the Ge–B bond. Computational results showed that the reaction proceeds through a $GeBC_3O$-heterocycle **E** as the intermediate, similar to **D** in the C=O bond insertion (Figure S9 in the Supporting Information).



Scheme 2. Proposed reaction mechanism of **2** with excess isopropyl isocyanate.

In conclusion, we have developed a germylene/borane Lewis pair **2** that features the $GeBC_2$-heterocycle having the Ge–B donor–acceptor bond. Compound **2** has been tested to be capable of cleaving the C=O double bond of the isocyanate (*i*PrNCO) and ketone ((4-$MeOC_6H_4$)C(O)Me) molecules. The reaction mechanism of **2** and isopropyl isocyanate was studied in detail both experimentally and theoretically. The reaction of **2** with an excess of isopropyl isocyanate to yield isopropyl isonitrile may find application in the deoxygenation of the isocyanates in the synthesis of the free isonitriles by using **2** as a precursor. We are working on the progress of this study.

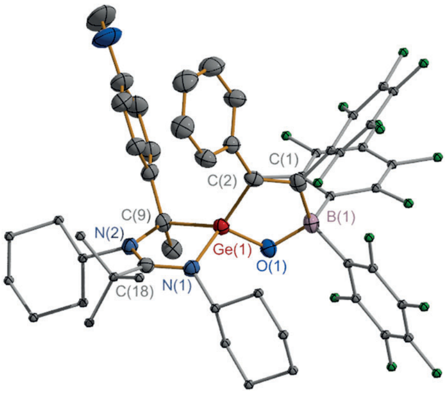


Figure 5. Crystal structure of **5** (H-atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Ge(1)-C(2) 1.930(3), C(2)-C(1)1.342(4), C(1)-B(1) 1.676(5), Ge(1)-O(1) 1.737(2), B(1)-O(1) 1.490(4), Ge(1)-N(1) 1.899(3), Ge(1)-C(9) 1.975(3), C(9)-N(2) 1.514(4); Ge(1)-C(2)-C(1) 106.8(2), C(2)-C(1)-B(1) 117.1(3), C(1)-B(1)-O(1) 107.0(2), Ge(1)-O(1)-B(1) 112.7(2), O(1)-Ge(1)-C(2) 96.3(2), N(1)-Ge(1)-C(9) 87.6(2).

Acknowledgements

H.Z. acknowledges the National Nature Science Foundation of China (21473142), the 973 Program (2012CB821704), and the Program for Innovative Research Team in Chinese Universities (2013B019 and IRT_14R31) for financial support. H.W.R. thanks the Deutsche Forschungsgemeinschaft (DFG RO 224/64-1) for financial support. S.D. is thankful to the CSIR for the JRF fellowship. D.K. acknowledges IISER-Kolkata for start-up grant and SERB for DST fast track fellowship (SR/FT/SC-72/2011).

Keywords: $C{=}O$ bond cleavage · coordination chemistry · density functional calculations · germylene/borane Lewis pairs · isonitrile

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Received: July 27, 2016

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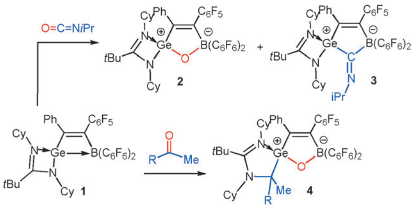
■■ – ■■

A Germylene/Borane Lewis Pair and the Remarkable C=O Bond Cleavage Reaction toward Isocyanate and Ketone Molecules



Give it a break: Germylene/borane Lewis pair **1** reacts with *i*PrNCO and (4-MeOC$_6$H$_4$)C(O)Me, respectively, with cleavage of the C=O double bond (see scheme). Fragments O and *i*PrNC insert separately into the Ge–B bond to yield **2** and **3**, and O and (4-MeOC$_6$H$_4$)(Me)C into the respective Ge–B and Ge–N bonds to form **4**. The reaction of **1** with an excess of *i*PrNCO leads to *i*PrNC, **2** (major) and **3** (minor).