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Facile B−H Bond Activation of Borane by Stable Carbenoid Species

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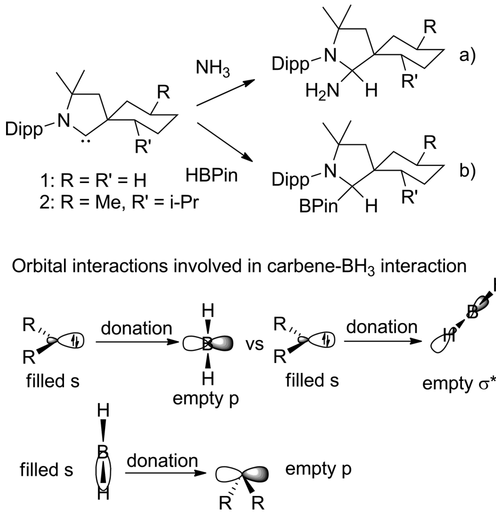
Ⓢ *Supporting Information*

ABSTRACT: Stable nucleophilic carbene compounds have recently been shown to be able to mimic in some instances the reactivity of metal fragments in the reaction of unactivated E−H bonds (E = H, R_3Si, NH_2, R_2P). However, the insertion into a B−H bond of the strongly Lewis acidic BH_3 molecule has never been observed at a single C atom or even at a metal fragment. Our results show that designed stable, highly electrophilic carbenoid fragments in compounds **4** and **6** can achieve this reactivity in a controlled manner. Density functional theory calculations corroborated the experimental results on the presently designed systems as well as the lack of reactivity on nucleophilic carbenes.

Scheme 1. (a, b) Activation of NH_3 and HBPin by CAACs; (c) Orbitals Involved in Carbene−BH_3 Activation



Activation of small molecules and unactivated bonds is one of the greatest challenges of 21st century chemistry. For many years, it has been thought that only transition metal (TM) fragments are capable of activating such bonds because of an appropriate double electron transfer involving donation from the electron pair of the bond to the metal center and back-donation from the metal into the corresponding antibonding orbital. However, in 2005, Power and co-workers proved that activation of H_2 under mild conditions with heavier group-14 metals (Ge, Sn) is feasible.[1] Then, in 2006, the Stephan group demonstrated that a system featuring a P/B frustrated Lewis pair (FLP) could cleave dihydrogen heterolytically,[2] opening ways for further transformations.[3] Shortly thereafter, the Bertrand group showed that stable singlet carbenes can also act as mimics of TMs[4] to activate a number of small reactive molecules such as CO[5] and white phosphorus.[6] The more remarkable splittings of the H−H bond of H_2, a N−H bond of NH_3 (Scheme 1a),[7] and other unactivated E−H bonds (E = Si, P) have also been reported.[8] Furthermore, B−H bond activation of the hydridic substrate pinacolborane (HBPin) by stable singlet carbenes (Scheme 1b)[8] and an FLP[9] has been observed. This 1,1-addition at a single carbon center is reminiscent of the oxidative addition of R_2BH on TM fragments, which has been extensively studied because it is a key step in TM-catalyzed 1,2-addition over a π system. In contrast, the 1,1-addition of a B−H bond of the much stronger Lewis acid BH_3 at a single metallic[10] or organic center is not known, although the 1,2-addition to a π system is one of the most famous reactions in organic chemistry. The 1,1-activation of BH_3 at a C center is most difficult for several reasons. The formation of two novel bonds, C−BH_2 and C−H, from BH_3 and a designed "C" fragment requires the efficient double electron transfer mentioned above. However, in the case of BH_3, the preferred orbital interaction involves donation of the lone pair at C to the empty orbital at B (Scheme 1c, left). Comparatively, the donation to the BH σ^* orbital is less efficient (Scheme 1c, right). Moreover, the BH σ orbital is a weak donor, and the orbital overlap with the empty p orbital at C is poor. Overall, the formal oxidative addition at a single "C" center is thus typically an endergonic process ($\Delta G° > 0$), and even the most reactive systems presented above failed to split the BH bond of BH_3. Instead, the Lewis acid−base adduct was obtained with cyclic alkyl amino carbenes (CAACs), and ring opening was observed with N-heterocyclic carbenes (NHCs).[8,11]

Strategies for B−H bond activations have thus relied on suppressing the strong Lewis acidity of BH_3 in a preliminary step via the formation of strong Lewis acid−base adducts such as phosphine−borane, amine−borane, or NHC−borane adducts.[12] In particular, it has been shown that only the transiently generated dichlorocarbene reacted with L→BH_3 adducts (L = tertiary amine or phosphine).[13]

To favor the double electron transfer, we reasoned that the nucleophilic character of a carbene-like species should be decreased whereas the electrophilic character should be

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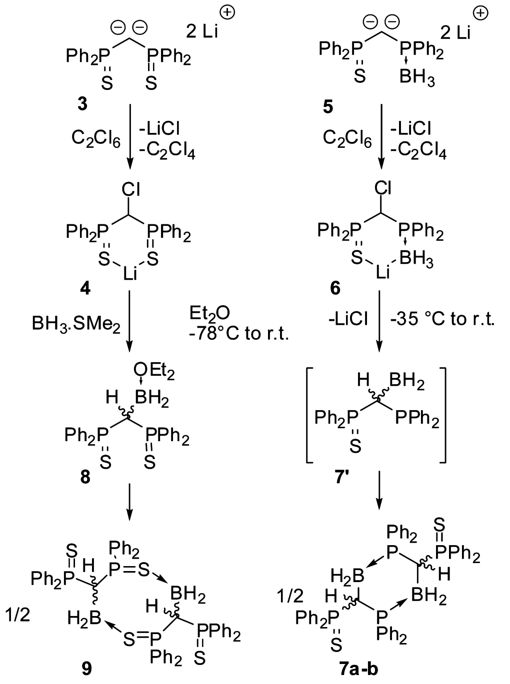
increased compared with the stable carbenes such as NHCs and CAACs. Our group has been working for some years on the use of geminal dianions such as **3** (Scheme 2) as carbene precursors for TMs as well as lanthanides and actinides.[14] We have shown experimentally and corroborated by density functional theory (DFT) calculations that the very highly nucleophilic character brought by the two lone pairs at C is decreased by very efficient electron transfer to the strongly accepting phosphorus substituents. It was thus hypothesized that oxidation of such a dianion would result in the formation of a carbene fragment with reduced nucleophilic character but also with significant electrophilic character because of a lack of significant stabilization of the empty p orbital. In 2007, the oxidation of dianion **3** with hexachloroethane was studied, and the first example of a carbenoid species that is stable at room temperature (compound **4** in Scheme 2) was obtained.[15] In line with our hypothesis, **4** was shown to be a competent precursor of a Pd carbene complex upon reaction with an electron-rich Pd(0) precursor. This first carbenoid was used in the present work to probe the intermolecular reactivity with BH_3. A second carbenoid/carbene species, **6**, derived from the dianionic derivative **5** (Scheme 2)[16] was envisaged to probe thermodynamically more favorable intramolecular reactivity. In this contribution, we present a novel example of very rare isolable, stable carbenoid species as well as intramolecular and intermolecular 1,1-additions of a B−H bond of BH_3 at a C center. DFT calculations providing mechanisms of these unprecedented activations by the aforementioned carbenoid species as well as comparisons with the stable CAAC and NHC systems are also presented.

Scheme 2. Activation of BH_3 by Carbenoid Species



In a first approach, the more favorable intramolecular reactivity was probed. The oxidation of dianion **5** was studied in diethyl ether (Scheme 2), as this highly reactive species decomposes in most organic solvents, including tetrahydrofuran (THF) (quantitative deprotonation). The total conversion of **5** was observed after only 15 min at room temperature. The formation of a single new species, **6**, was confirmed by ^{31}P NMR spectroscopy (a doublet at $\delta_P = 45.5$ ppm and a broad signal centered at $\delta_P = 30$ ppm). Although **6** was stable at −35 °C for over a month, it reacted further at room temperature (vide supra). Yellow single crystals were thus grown from Et_2O at −35 °C and analyzed by X-ray diffraction (XRD). This analysis confirmed the formation of carbenoid **6** (Figure 1). Low-temperature ^{31}P NMR spectra confirmed the assignment. The most important feature of **6** is the separation of Li^+ and Cl^-, which explains the stability of **6** at such a high temperature compared with other carbenoid species.[17] It resembles compound **4** in this sense. The Cl atom is bound to the C center, whereas the Li cation is bound to the S atom and also to the BH_3 moiety via interactions with two B−H bonds. The lower thermal stability of **6** (stable up to −20 °C) compared with **4** (stable at room temperature) is obviously due to the weaker coordination of Li^+ by the BH_3 moiety in **6** compared with the S atom in **4**. Following the evolution of **6** in solution revealed the expected reactivity. Two new products (**7a** and **7b**) were identified by NMR spectroscopy. Both compounds were characterized by two sets of well-resolved multiplets at $\delta_P = 46.1$ and 45.9 ppm (3:2 ratio) as well as a broad signal at $\delta_P = 19$ ppm. Also, both compounds featured one H atom on the P−C−P bridge, as evidenced by the ^1H NMR spectrum, which contained two highly coupled signals at $\delta_H = 3.37$ and 2.96 ppm that simplified upon ^{31}P decoupling and appeared as the expected multiplets because of coupling with one B center. Moreover, the ^{13}C NMR spectrum showed a C−B coupling pattern for the corresponding carbon in the two compounds.

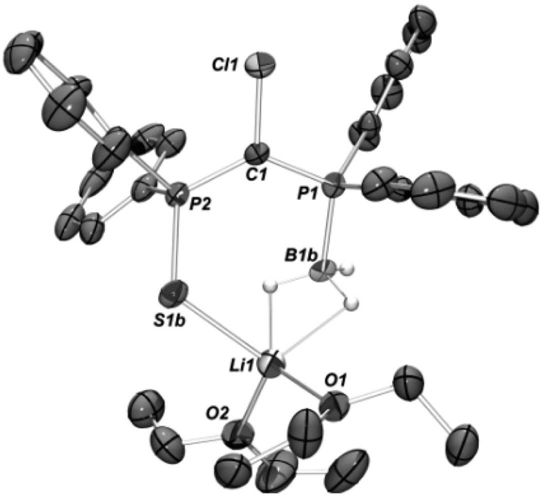


Figure 1. Crystal structure of **6** with 50% thermal ellipsoids. H atoms on the phenyl rings and on the solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C1−P1, 1.722(3); C1−P2, 1.728(3); C1−Cl1, 1.775(3); P1−B1b, 1.89(3); P2−S1b, 2.0526(8); S1b−Li1, 2.42(1); Li1−O1, 1.999(5); Li1−O2, 1.972(6); P1−C1−P1, 126.7(2); P2−C1−Cl1, 118.5(2); P1−C1−Cl1, 114.5(2).

The rest of the NMR data suggested that these two products were structurally very similar. These compounds were crystallized from the crude mixture, and XRD analysis on each compound proved the formation of diastereomeric pairs. The structures of compounds **7a** and **7b** are presented in the Supporting Information (SI). Both **7a** and **7b** are six-membered $P_2C_2B_2$ rings; **7a** adopts a boat conformation, whereas **7b** adopts a chair conformation. More interesting is the mechanism of their formation (Scheme 2). They most likely result from a common reaction intermediate, **7′**, which is formed by intramolecular insertion of the carbenoid center into a B−H bond of the BH_3 moiety. The dimerization of **7′** is thermodynamically favored by the formation of two strong P→B bonds.

Motivated by this result, we then focused our attention on the more challenging intermolecular reaction involving the room-temperature-stable carbenoid **4**. Most satisfyingly, addition of 2 equiv of BH_3·SMe_2 to a solution of **4** in Et_2O resulted in the formation of compound **8** after one night at room temperature (Scheme 2). Compound **8** was characterized by a singlet at δ_P = 52 ppm in the $^{31}P\{^1H\}$ NMR spectrum. A resonance corresponding to the H atom on the P−C−P bridge was seen at δ_H = 3.62 ppm. This resonance exhibited a characteristic H−B coupling pattern upon ^{31}P decoupling. Crystallization of **8** resulted in the formation of a dimer, **9**. As for compounds **7a** and **7b**, dimerization of **8** is favorable because of the formation of two S→B bonds. It is the only example to date of a $P_2S_2C_2B_2$ eight-membered ring.

Mechanistic investigations were carried out by means of deuterium labeling experiments. Most importantly, the reaction of **4** with BH_3·SMe_2 in C_6D_6 did not lead to any deuterated products, such as "C(D)(BH_2)" species. Moreover, the reaction with commercial BD_3·THF (containing ca. 2% BD_2H) in Et_2O led to the formation of the corresponding "C(D)(BD_2)" species **8-*d*$_3$** (singlet at δ_P = 49 ppm in the $^{31}P\{^1H\}$ NMR spectrum) as well as a very minor species (singlet at δ_P = 50 ppm in the ^{31}P NMR spectrum) corresponding to the "C(D)(BDH)"/"C(H)(BD_2)" species in the expected 98/2 ratio. These experiments support the B−H insertion at C rather than a radical process involving abstraction of H from the solvent.

DFT calculations were performed to provide further insights into the mechanisms of the transformations and the requirements for B−H activation of BH_3 by metal-free organic fragments. Optimizations were conducted on model compounds, in which the Et_2O solvent was modeled by Me_2O. Full details on the calculations are given in the SI. The two mechanisms bear some resemblance, especially from the point where BH_3 is coordinated to the central C atom. Thus, only the "intermolecular" mechanism involving compound **A** is presented here. The "intramolecular" process is presented in the SI.

A low-energy path was found, in accord with the experimental results. The computed energies for the mechanism are shown in Figure 2. The transformation of **A** into **E** is highly exergonic (ΔG = −59.5 kcal/mol). In the first step, the coordination of BH_3 to the carbon center of **A** is favorable by only 14.6 kcal/mol, as expected for a rather weak nucleophilic center. In the second step, from carbenoid **B**, the Li−Cl interaction develops because of a facile rotation about the C−P bond (**TS$_{BC}$** was calculated to be 14.8 kcal/mol higher than **B**), forming compound **C**. Most remarkably, the key insertion step then proceeds with a very low activation barrier of 1.7 kcal/mol (**TS$_{CD}$**) and a large exergonicity (ΔG = −45.7 kcal/mol).

The structure of **TS$_{CD}$** (Figure 3) deserves some comments. First, the C−Cl distance of 2.342 Å is very long compared with those in **A** (1.781 Å) and **D** (1.889 Å), as this bond is broken in this step. The C−B bond at 1.550 Å is classical for Lewis acid−base adducts such as NHC−BH_3. In **TS$_{CD}$**, the B−H bond featuring the H atom to be transferred is only slightly elongated (1.271 Å vs 1.200 Å av for the two other BH bonds), as expected for an early transition state. Finally, the C−B−H angle of 78.06° is very acute and points an interaction of the H atom with the electrophilic C center. Natural bond order (NBO) charge analysis revealed that the migrating H in **TS$_{CD}$** bears a positive charge (0.16 vs 0.02 and −0.01 for the two other H atoms of BH_3), while it is almost neutral (−0.01) in **C** and becomes more positive in **D** (0.30). Finally, as expected, the dimerization to form **E** is slightly favorable because the newly formed RBH_2 species **D** is a Lewis acid. Overall, **TS$_{CD}$** was found to be 11.2 kcal/mol higher than compound **B**. As a comparison, the insertion step in the "intramolecular" process (see the SI) proceeds with a barrier of 10.7 kcal/mol, which is also readily overcome at room temperature.

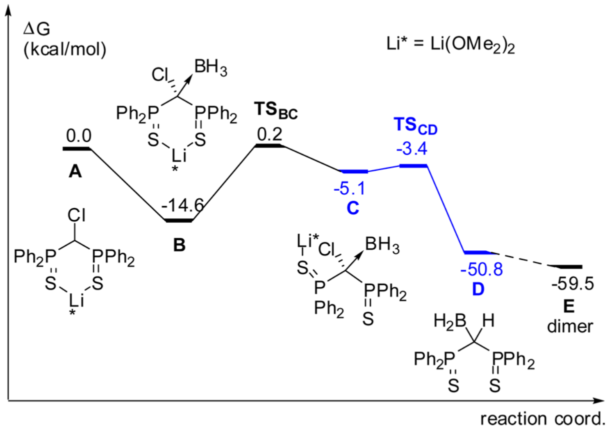


Figure 2. Free energy profile for the reaction between carbenoid **4** (modeled as **A**) and BH_3.

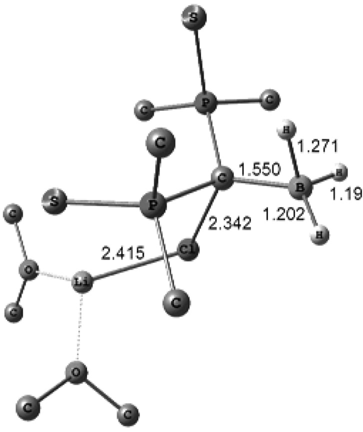


Figure 3. View of **TS$_{CD}$** with distances in Å. For clarity, only C_{ipso} of the phenyl groups and pertinent H atoms are shown.

To provide a better understanding of the difference between the reactivity of these two stable carbenoid species and that of stable nucleophilic carbenes, calculations on similar BH insertions with CAAC and NHC compounds were performed (Figure 4). In the case of the NHC, the Lewis acid−base adduct is very strong and the electrophilicity of the carbene is very weak, which makes not only the activation energy prohibitively high ($\Delta G^{\ddagger}$ = 44.5 kcal/mol) but also renders the reaction strongly endergonic (ΔG = 31.8 kcal/mol). The increased electrophilicity of the CAAC compared to the NHC decreases the activation barrier to a great extent ($\Delta G^{\ddagger}$ = 12.8 kcal/mol), but the reaction is nevertheless endergonic (ΔG = 11.1 kcal/mol), even when coordination with a solvent

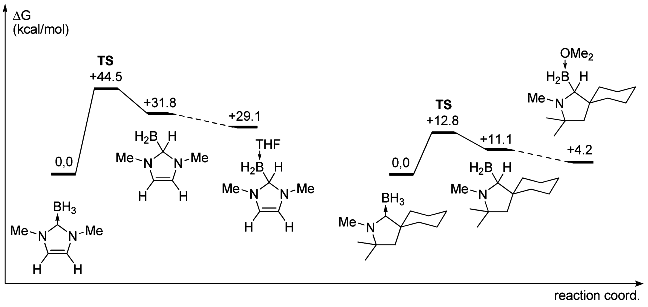


Figure 4. Free energy profiles for the activations of BH_3 by (left) NHC and (right) CAAC.

molecule is taken into account ($\Delta G = 4.2$ kcal/mol), because of their pronounced nucleophilic character.

In conclusion, we have shown that stable carbenoid species fill the void in the activation of strong unactivated E−H bonds [E = H, group 14 element (Si), group 15 element (N, P)], allowing the activation of the E−H bond for E = group 13 element (B) by non-TM fragments. In these compounds, the balance between the high electrophilicity and the reduced nucleophilicity provides both a low-energy path as well as the appropriate driving force for the 1,1-addition of a B−H bond at a single carbon center. Finally, the highly electrophilic character of the carbenoid species **4** and **6** presented here, which are stable at room temperature and −20 °C, respectively, allows the development of reactivity complementary to that of ubiquitous stable carbene compounds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, crystal data, and details of the theoretical calculations. 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.

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