Carbenes

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# Activation of Si–H, B–H, and P–H Bonds at a Single Nonmetal Center**

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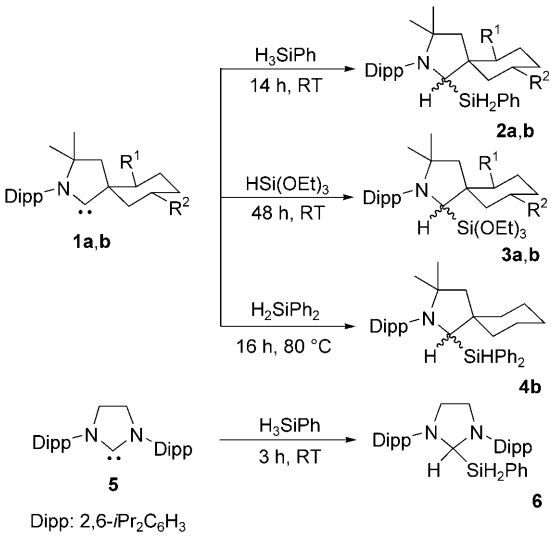
For many years, it was believed that only transition-metal centers could activate small molecules and enthalpically strong bonds. However, it has recently been shown that several nonmetallic systems are capable of some of these tasks.[1,2] For example, stable singlet carbenes can activate CO,[3a] $H_2$,[3b] and $P_4$.[3c–e] Such reactions have long been known for transition metals.[4,5] However, stable singlet carbenes can also activate $NH_3$;[3b] a much more difficult task for transition metals.[6,7] The oxidative addition of hydrosilanes, hydroboranes, and hydrophosphines at vacant coordination sites of transition metals are well-exemplified and are considered as key steps in the transition-metal-catalyzed hydrosilylation, hydroboration, and hydrophosphination of multiple bonds.[8] Herein, we report the first examples of the activation of E–H bonds (E = Si, B, P) at a single nonmetal center.

On the basis of our successful results with $H_2$,[3b] we began our study with the activation of Si–H bonds. Indeed, silanes are similar to $H_2$ in that they lack both nonbonding electron pairs and π electrons. They can bind to various metal centers to form stable Si–H σ complexes, which undergo subsequent oxidative addition.[4] To test the possible activation of Si–H bonds with carbenes, we treated the cyclic (alkyl)(amino)carbenes (CAACs) **1a** and **1b**[9] with primary, secondary, and tertiary silanes.

The addition of phenylsilane to **1a** and **1b** occurred readily at room temperature, and the corresponding adducts **2a**,**b** were isolated in 91 and 83% yield, respectively (Scheme 1). As expected, in the case of the enantiomerically pure CAAC **1a**, two diastereomers **2a**,**a′** were formed (in a 2:1 ratio), as shown by two singlets at $\delta = -36.4$ and $-29.3$ ppm in the $^{29}$Si NMR spectrum. The $^{13}$C NMR spectrum revealed the loss of the carbene signal and a new C–H peak at $\delta = 63.2$ (**2a**) and 65.5 ppm (**2b**). The $^1$H NMR spectrum of the major isomer **2a** revealed a pseudotriplet at $\delta = 4.78$ ppm (SiCH) and two doublets at $\delta = 4.29$ and 4.21 ppm corresponding to the diastereotopic hydrogen atoms of the $SiH_2$ fragment. The structure of **2a** was confirmed by X-ray crystallography[10] (Figure 1, top), whereas the presence of a triplet at $\delta = 4.53$ ppm and a doublet at $\delta = 4.08$ ppm in the $^1$H NMR spectrum confirmed the identity of adduct **2b**.




Dipp: 2,6-*i*Pr$_2$C$_6$H$_3$

**1a**, **2a**, **3a**: $R^1$ = *i*Pr, $R^2$ = $CH_3$; **1b**, **2b**, **3b**, **4b**: $R^1$, $R^2$ = H

***Scheme 1.*** Reaction of carbenes **1a**,**b** and **5** with silanes.

CAACs **1a**,**b** also reacted with $(EtO)_3SiH$ to afford **3a** (d.r. 3:1) and **3b** in 64 and 73% yield, respectively. However, when $Ph_2SiH_2$ was used, only the less bulky carbene **1b** underwent insertion into the Si–H bond (to give **4b** in 65% yield), and a reaction time of 16 hours at 80 °C was necessary for the reaction to reach completion. Surprisingly, although it has been shown that, in contrast to CAACs, N-heterocyclic carbenes (NHCs) do not react with $H_2$,[11] we found that imidazolidin-2-ylidene **5**[12] also reacted at room temperature with phenylsilane to afford the Si–H insertion product **6** in 88% yield (Figure 1, bottom).

The formation of **6** raises the question of the mechanism of the activation of Si–H bonds with carbenes. Why should NHCs react with silanes although they are inert towards hydrogen? The evident difference is the presence of low-lying vacant orbitals in silanes. In other words, the observed reactivity might be due to the Lewis acid character of silanes; indeed, several NHC–$SiX_4$ adducts are known.[13]

To test this hypothesis, we turned our attention to boranes, the prototypical Lewis acids. As early as 1993, Kuhn et al.[14] reported that imidazol-2-ylidenes (unsaturated NHCs) react

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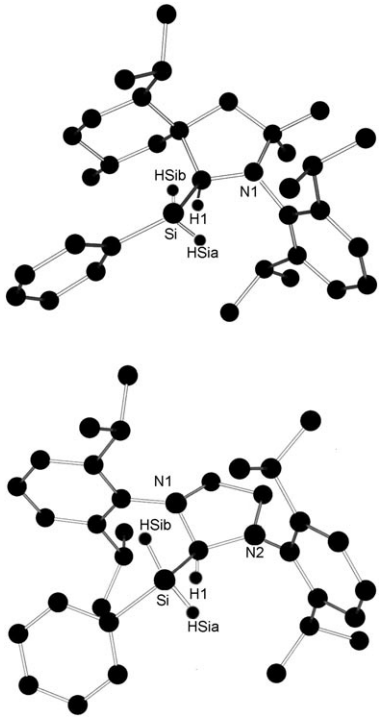
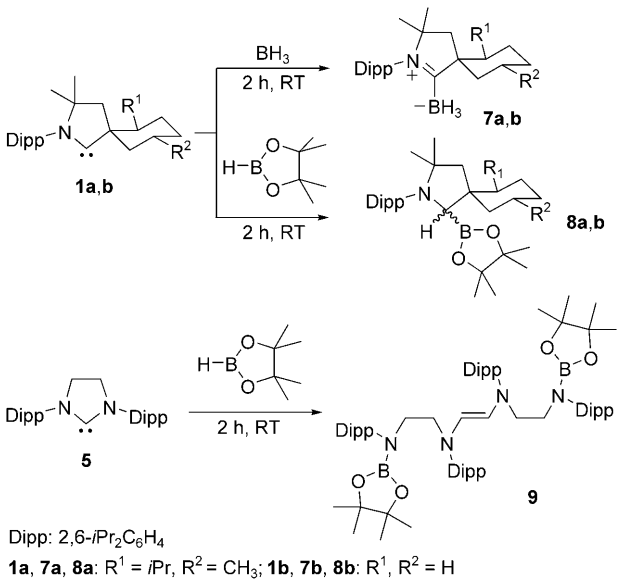



***Figure 1.*** Solid-state structures of **2a** (top) and **6** (bottom; hydrogen atoms have been omitted for clarity, except at the former carbene carbon atom and at the silicon atom).

with $BH_3$ to afford the corresponding NHC–$BH_3$ adducts.[15] Similarly, cyclic (alkyl)(amino)carbenes (CAACs) **1a**,**b** reacted at room temperature with $BH_3$ to give the corresponding Lewis acid–base adducts **7a**,**b** (in 96 and 84% yield, respectively); no trace of B–H bond activation was observed (Scheme 2, Figure 2). However, Dureen and Stephan[16] recently showed that the B–H bond of more hydridic catecholborane can be activated by a mixture of $tBu_3P$ and




***Scheme 2.*** Reaction of carbenes **1a**,**b** and **5** with boranes.

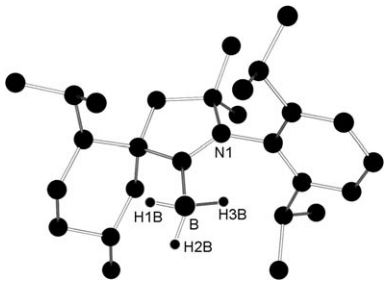



***Figure 2.*** Solid-state structure of **7a** (hydrogen atoms at the carbene fragment have been omitted for clarity).

$B(C_6F_5)_3$. They isolated $[(C_6H_4O_2)BPtBu_2R][HB(C_6F_5)_3]$. Similarly, CAACs **1a**,**b** reacted cleanly with pinacolborane to afford the desired oxidative-addition products **8a**,**b** after 2 hours at room temperature in 79 and 85% yield, respectively. As observed with the silanes, when enantiomerically pure **1a** was used, two diastereomers **8a**,**a′** were formed (in a 44:56 ratio). Interestingly, although the saturated NHC **5** also reacted with pinacolborane, a totally different and unexpected reaction took place, and the dimeric product **9** was isolated in 89% yield. The structure of **9** was ascertained by a single-crystal X-ray diffraction study (Figure 3). Although the mechanism of the reaction leading to **9** is not yet clear, these results demonstrate once again the very different chemical behavior of NHCs and CAACs.

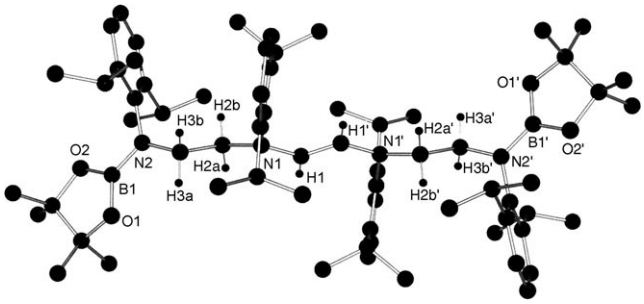
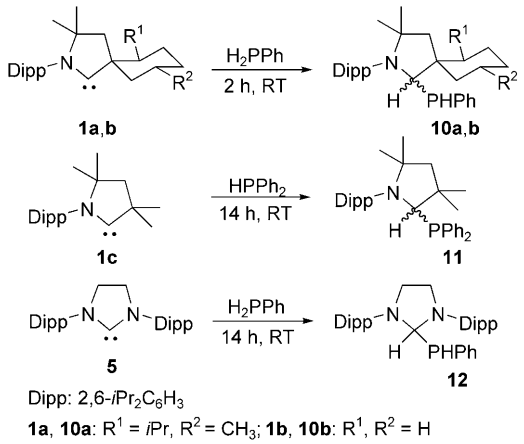



***Figure 3.*** Solid-state structure of **9** (hydrogen atoms at the aryl and pinacol fragments have been omitted for clarity).

The results obtained for the reactions between boranes and CAACs **1a**,**b** suggest that, as hypothesized for the silane substrates, the activation involves the Lewis acid character of the substrate and the initial formation of Lewis acid–base adducts, such as **7a**,**b**. Then, if the hydrogen atom is hydridic enough, a migration occurs from the main-group atom (Si or B) to the former carbene center.

Carbenes are known to form Lewis acid–base adducts[17] with other main-group elements. We therefore studied their reactivity with primary and secondary phosphanes (Scheme 3). Phenylphosphane reacted with CAACs **1a** and **1b** at room temperature to afford the oxidative-addition products **10a** and **10b** as mixtures of four (1.0:1.4:1.3:1.8) and two diastereomers (1.0:3.0) in 96 and 93% yield, respectively. When sterically more demanding diphenylphosphane was used, CAACs **1a**,**b** were inert, but the smaller CAAC **1c**




***Scheme 3.*** Reaction of singlet carbenes **1a–c** and **5** with phosphanes.

underwent a slow but clean reaction at room temperature to give **11** in 73% yield. Lastly, we found that although NHC **5** did not react with diphenylphosphane, it underwent insertion into the P–H bond of phenylphosphane to give adduct **12** in 84% yield after 14 hours at room temperature. The structure of **12** was confirmed by X-ray crystallography (Figure 4).

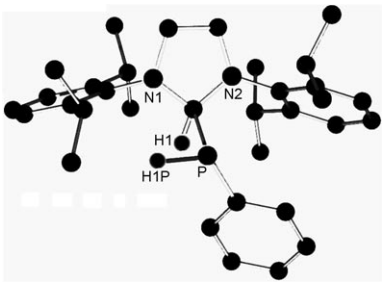



***Figure 4.*** Solid-state structure of **12** (hydrogen atoms have been omitted for clarity, except at the former carbene carbon atom and at the phosphorus atom).

These results demonstrate again that stable singlet carbenes can mimic to some extent the behavior of transition metals. They confirm that, in contrast with the electrophilic mode of activation observed with metals, carbenes act as nucleophiles towards the substrates. We envision the development of new catalytic processes that will capitalize upon this discovery and pave the way to metal-free systems capable of small-molecule transfer.

## *Experimental Section*

All manipulations were performed under an inert atmosphere of dry argon by using standard Schlenk techniques. Dry, oxygen-free solvents were used.

General procedure: A solution of the silane, borane, or phosphine (1.5 equiv) in hexanes (5 mL) was added to a stirred solution of the carbene (1 mmol) in THF, toluene, or hexanes (5 mL). The reaction mixture was stirred at the temperature and for the period of time indicated in Schemes 1–3, and then the solvents were removed, and the solid residue was washed with cold hexanes (1 mL). Adducts were isolated as white powders and recrystallized as indicated in the Supporting Information.

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