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Reactivity of Stabilized Li/Cl Carbenoids towards Lewis Base Adducts of BH_3: B−H Bond Activation versus Carbene Dimerization

Sebastian Molitor and Viktoria H. Gessner*[a]

For many years the activation of small molecules had been a research field limited to transition-metal complexes. However, the past few decades have revealed several examples of non-metallic systems also applicable in bond activation reactions.[1] Without doubt, one of the most prominent examples are singlet carbenes, which have been shown to activate a variety of small molecules amongst others dihydrogen, CO, P_4, and even ammonia.[2] Thereby, in some cases substituent effects at the carbene carbon atom have been shown to be crucial for the activity of a particular carbene. Another—not less impressive—non-metal system established in small molecule activation chemistry is that of the so-called frustrated Lewis pairs (FLPs).[3] Comparable to carbenes, this class of compounds has proven to be applicable in a variety of activation reactions. In recent years, the activation of B−H bonds has received special attention due to the versatile utility of boranes in many organic transformations. B−H activation or splitting had been reported with the aid of transition metals as early as the 1980s.[4] However, non-metallic systems have long been reluctant in this reaction. For example, N-heterocyclic carbenes (NHCs) generally react with the parent BH_3 and its Lewis base adducts under simple formation of the corresponding $NHC\cdot BH_3$ adduct (such as **A** Figure 1). No hydroboration of the carbene center is usually observed. The hitherto only example of B−H bond activation of a carbene species was reported by Bertrand and co-workers using a cyclic (alkyl)(amino)carbene (CAAC) in combination with the more hydridic pinacolborane to selectively form **1**.[5] Earlier the group of Stephan had shown that FLPs are also applicable in the B−H bond splitting reaction by formation of salt **2**.[6] An analogous salt formation was reported by Alcarazo and co-workers with carbodiphosphorane as Lewis base even allowing an activation of the less hydridic parent borane, BH_3.[7]

In the course of our investigations on the general reactivity patterns of electronically stabilized Li/Cl carbenoids we became interested in their reactivity towards boranes. Several reaction pathways are feasible: i) the formation of a simple carbene borane adduct such as **A** after elimination of lithium chloride, ii) formation of borate **B** analogous to organolithium compounds, or iii) B−H bond activation. In related work that appeared during the final stages of preparation of this Communication, So, Mézailles and co-workers reported on the B−H bond activation using a carbenoid stable at room temperature, which resulted in the formation of a dimeric borane adduct.[8] Herein however, we show that with more reactive carbenoids different reactivities are observed depending on the borane source. Whereas with borane–THF and thioether adducts B−H bond activation and subsequent formation of a borate species is observed, the carbenoids were shown to be unreactive towards trialkylamine adducts, leading to the dimerization of the corresponding carbene.

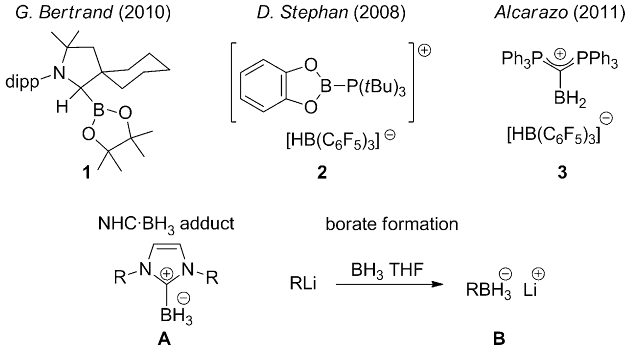

Figure 1. Compounds formed by B−H bond activation and selected reactivities towards boranes.

The α-chlorinated carbenoid precursor **2** was obtained by straightforward lithiation of the silyl-substituted phosphane sulfide **1** and subsequent chlorination with hexachloroethane (Scheme 1, see also the Supporting Information). As reported earlier, compound **2** is selectively deprotonated at low temperatures by using methyllithium as deprotonation reagent. The thus formed Li/Cl carbenoid **3** is stable at temperatures up to −30 °C and can be used for in situ transformations.[9] To examine the reactivity of carbenoid **3** towards B−H bonds we first studied the reactivity towards catecholborane and pinacolborane. However, the addition of both boranes resulted in the formation of a complex mixture of compounds, with **1** and **2** being the main products. This observation indicated that—amongst other pathways—hydride transfer (to form **1**) occurs during the reaction process.

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[a] S. Molitor, Dr. V. H. Gessner
Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
E-mail: vgessner@uni-wuerzburg.de

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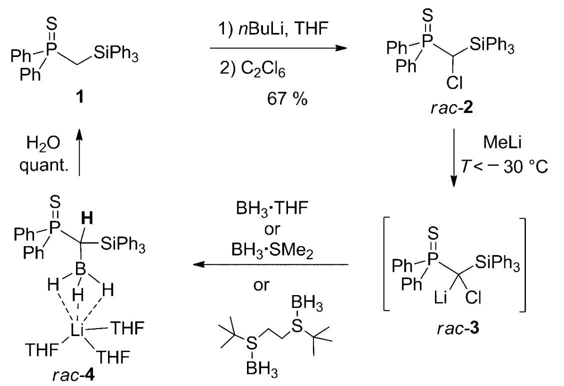


Scheme 1. Reactivity of carbenoid **3** towards different boranes; formation of borate **4**.

Thus, we turned our attention towards the less hydridic parent borane BH_3.

Warming of a solution of **3** in THF with an excess of $BH_3{\cdot}THF$ adduct from −78 °C to room temperature led to a complete decoloration of the yellowish carbenoid solution. NMR spectroscopic studies of the crude product showed the selective formation of a single new species featuring a signal at $\delta = 58.3$ ppm (C_6D_6) in the $^{31}P\{^1H\}$ NMR spectrum (**2**: $\delta = 46.3$ ppm). Work-up delivered a colorless, moisture-sensitive solid in 83 % yield, which was characterized by multinuclear NMR spectroscopy, as well as elemental and single-crystal X-ray diffraction analysis. All methods confirmed the unexpected formation of lithium borate **4** formed by additional protonation of the former carbenic carbon atom (Scheme 1). The proton is clearly evident as a broad doublet at $\delta = 2.66$ ppm in the ^1H NMR spectrum. The ^{11}B NMR resonance of **4** ($\delta = -28.6$ ppm; $^1J(^1H,^{11}B) = 81.4$ Hz) further confirms the four-coordinate boron atom involved in coupling to the adjacent hydrides. The ^7Li and ^{29}Si NMR signals appear at $\delta = 0.47$ and $\delta = -9.9$ ppm, respectively. Borate **4** is highly moisture sensitive and hydrolyzes quantitatively in the presence of water under formation of starting compound **1**. The formation of borate **4** is quite remarkable as lithium carbenoids usually react under elimination of lithium chloride.[10] Also the B−H bond activation product previously reported is formed by LiCl elimination.[8]

The selective formation of lithium borate **4** was also observed with $BH_3{\cdot}SMe_2$ and $(BH_3)_2{\cdot}t\mathrm{BuSCH_2CH_2S}t\mathrm{Bu}$ as borane sources, all leading to the THF-coordinated product. The same holds true for changing the silyl moiety in the carbenoid to $SiMePh_2$. In the resulting borate **4-SiMePh₂**, the phenyl substituents at both the silicon and phosphorus centers, become diastereotopic and appear as separate multiplets in the ^1H NMR spectrum. Due to the synthetic method, the lithium borates **4** and **4-SiMePh₂** are formed as racemic mixtures.

The molecular structure of lithium borate **4** and its derivative **4-SiMePh₂** are depicted in Figure 2. Compound **4** crystallizes as a monomer in the monoclinic space group $P2_1/n$, **4-SiMePh₂** as a *pseudo*-C_2 symmetric dimer in the triclinic space group $P\bar{1}$. The unit cell of **4-SiMePh₂** contains two molecules, one of which is depicted in Figure 2. Both dimers differ from each other in the configuration at the stereogenic carbon atom. In the crystal, only the homochiral dimers, (*R,R*)- and (*S,S*)-**4-SiMePh₂**, were found. Both structures clearly confirm the presence of the borate unit as well as the hydrogen atom at the central carbon atom. These hydrogen atoms were all found in the difference Fourier map and refined independently. The B−C distances (**4**: 1.660(2) Å; **4-SiMePh₂** (av) 1.664(6) Å) are in the range of known alkylborates.[11] The P-C-Si backbone shows only marginal differences compared with the PCH_2Si derivative **1** (see the Supporting Information). In both structures the lithium atoms show interactions with the hydridic hydrogen atoms at the boron atoms. Such stabilizing metal hydrogen interactions are typical for metal hydrides and have—in the case of lithium—first been introduced by Wade and co-workers.[12,13] In **4**, the coordination sphere of lithium is completed by coordi-

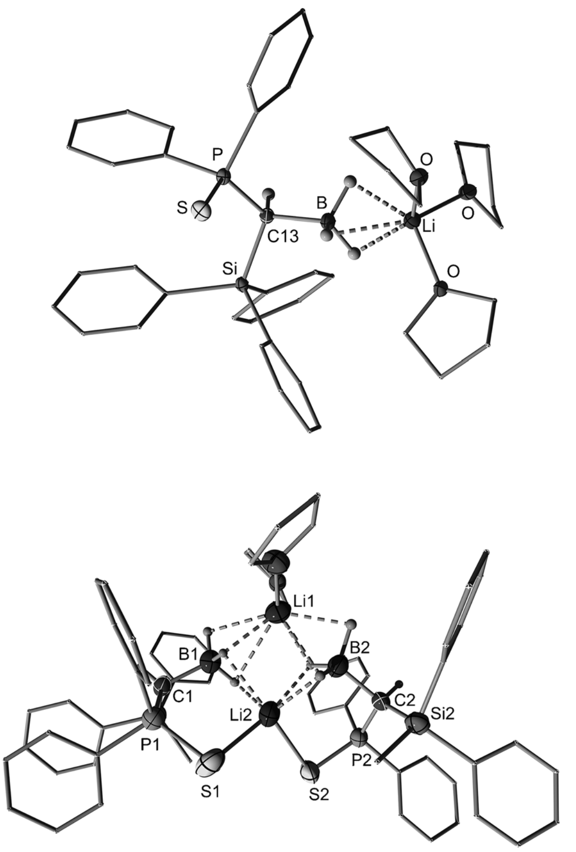
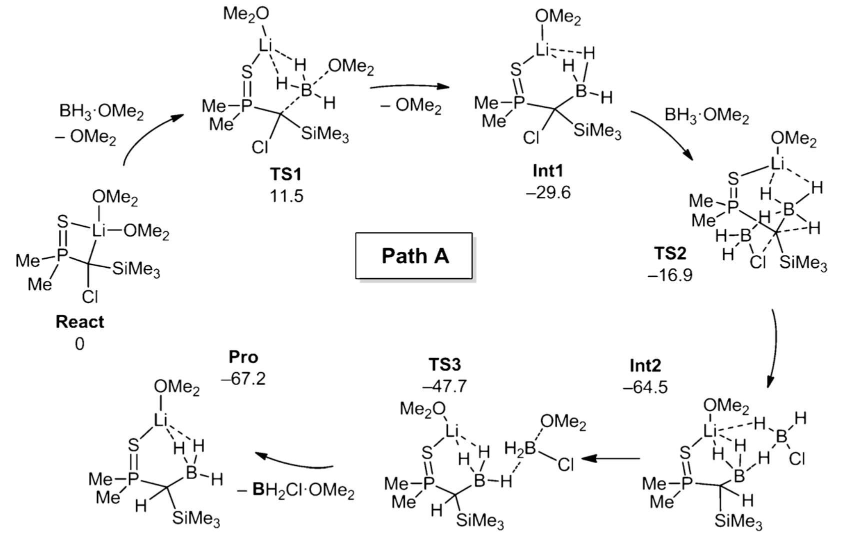


Figure 2. Molecular structures of lithium borate **4** (top) and (*S,S*)-**4-SiMePh₂** (bottom). Selected bond lengths [Å] and angles [°]: **4**: S−P 1.9622(6), P−C13 1.7926(15), Si−C13 1.8930(16), B−C13 1.660(2), B−Li 2.259(3); B-C13-P 111.2(1), B-C13-Si 109.3(1), P-C13-Si 117.25(8), C13-B-Li 173.76(14). **4-SiMePh₂**: S1−P1 1.990(2), S2−P2 1.984(2), S3−P3 1.9858(19), S4−P4 1.981(2), S1−Li1 2.548(8), S2−Li1 2.491(8), S3−Li4 2.431(8), S4−Li4 2.489(9), P1−C1 1.794(4), P2−C2 1.777(3), P3−C3 1.773(4), P4−C4 1.790(4), Si1−C1 1.913(5), Si2−C2 1.879(4), Si3−C3 1.882(4), Si4−C4 1.864(5), C1−B1 1.654(6), C2−B2 1.670(6), C3−B3 1.674(6), C4−B4 1.658(6); B1-C1-P1 107.5(3), B1-C1-Si1 110.7(3), P1-C1-Si1 117.7(2), B2-C2-P2 108.2(3), B2-C2-Si2 108.6(3), P2-C2-Si2 119.1(2), B3-C3-P3 107.4(3), B3-C3-Si3 108.4(3), P3-C3-Si 121.4(2), P4-C4-Si4 117.8(2) (toluene solvent omitted for clarity).

nation of three THF molecules, whereas in **4-SiMePh$_2$** additional coordination of the thiophosphinoyl moieties is observed.

The observed reactivity of the lithium carbenoids to form the corresponding borates **4** under simultaneous reduction is—to the best of our knowledge—unprecedented. The observed hydration reaction with the more hydridic catechol and pinacol borane suggests that the hydrogen chloride exchange proceeds via an intramolecular borane/borate species and thus via an overall B–H bond activation reaction. However, to exclude the involvement of the solvent in the course of the reaction, we performed additional deuteration experiments. In the past, protonation reactions in the presence of alkaline-earth metals have often been referenced to hydrogen abstraction from ethereal solvents.[14] Thus we repeated the reaction of **3**, prepared from solid methyllithium, with $(BH_3)_2{\cdot}tBuSCH_2CH_2StBu$ in deuterated [D$_8$]THF. No incorporation of deuterium could be identified in the ^{2}H NMR spectrum, but exclusive formation of the protonated compound **4**, as evidenced by ^{1}H and ^{11}B NMR spectroscopy. This strongly suggests that replacement of the chloride should occur via reduction by a borane/borate species.[10] We envisioned that in our case reduction would be facilitated by a second borane molecule, which would finally lead to **4** and the formation of a chloroborane species. Indeed, it was found that a slight excess of borane source is necessary for quantitative formation of **4**.[15] Repeating the reaction with BD$_3$.THF (freshly prepared from NaBD$_4$ and BF$_3$·OEt$_2$) finally confirmed the B–H splitting. No signal for the methylene proton was observed anymore in the ^{1}H NMR spectrum and only a singlet in the ^{11}B NMR spectrum at $\delta = -29.1$ ppm (see the Supporting Information).



Scheme 2. Calculated mechanism for the formation of **4**.

To gain further insight into the reaction mechanism, DFT calculations [B3LYP/6-311+g(d,p)] on a monomeric model system of **3** (Ph substituents and THF replaced by Me and Me$_2$O, respectively) were performed. Three reaction pathways were studied: i) formation of the corresponding lithium borate followed by chloride hydride exchange (Path A); ii) chloride hydride exchange followed by borate formation (Path B), and iii) formation of the corresponding free carbene after LiCl elimination and subsequent hydroboration via B–H bond activation (Path C). Due to the high nucleophilicity of carbenoid **3**, Path A was expected to be preferred over Path B. Furthermore, Path C can be ruled out, as no lithium chloride formation was observed in the experiment. Indeed, borate formation was found to possess the lowest reaction barrier of only 11.5 kcal mol^{-1}. The alternative carbene formation as well as hydride chloride exchange turned out to be much higher in energy with barriers of 34.3 and 50.4 kcal mol^{-1}, respectively (for details on alternative mechanisms and computational methods, see the Supporting Information). Scheme 2 depicts the whole reaction pathway for the formation of **4**, Figure 3 the energy profile of the reaction. The borate formation via **TS1** was found to be the crucial reaction step determining the course of the reaction. The formed intermediate borate **Int1** next reacts—mediated by a second borane molecule (**TS2**) under hydride chloride exchange—to form the alkylborane species **Int2**, thus completing the hydroboration at the carbenic carbon atom. Elimination of BH$_2$Cl finally furnishes the product.

Overall the mechanism can be described as a stepwise B–H bond splitting reaction through a nucleophilic attack of the carbenoid at the borane (borate formation) followed by hydride–chloride exchange. Surprisingly, despite the highly

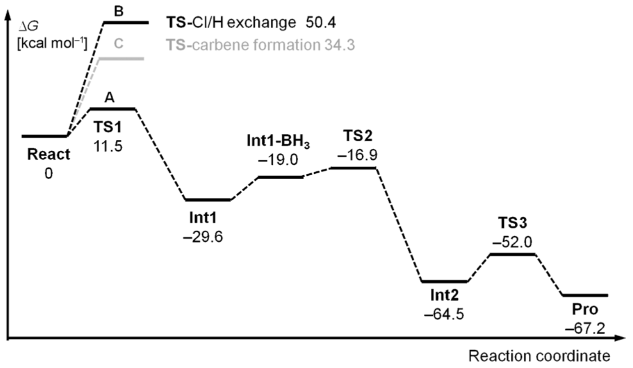
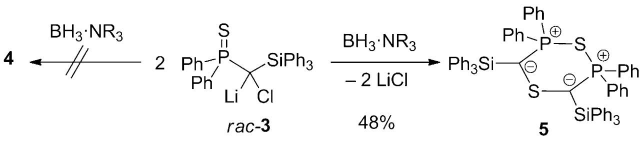


Figure 3. Energy profile of the calculated mechanism for the formation of **4** (=**Pro**); free energies are given in kcal mol^{-1}.

exergonic nature of this reaction ($\Delta G^{\neq} = -67.2$ kcal mol^{-1}) a different reactivity was observed when $BH_3{\cdot}NMe_3$ (or $BH_3{\cdot}NEt_3$) was used as borane source. In this case no borate formation was observed, but dimerization of the intermediate formed carbene. Interestingly, dimerization (CI/MS: m/z 976) did not lead to olefin formation as known for carbenes (such as in the Wanzlick equilibrium) and other carbenoids.[16,17] Instead the dimerization was found to occur via sulfur transfer to selectively form bis-ylide **5** (Scheme 3).



Scheme 3. Dimerization of carbenoid **3**.

Ylide **5** was isolated as an orange air-stable solid in 48 %. It is characterized by a single signal at $\delta = 37.8$ ppm in the ^{31}P NMR spectrum. In the ^{1}H NMR spectrum ([D$_8$]THF) only broadened resonances in the aromatic region were observed, which sharpened upon cooling of the sample to −80 °C (see Supporting Information for VT-NMR spectroscopy). X-ray diffraction analysis confirmed the constitution of **5**. The central structural motif consists of an S-P-C-S-C-P six-membered ring featuring saddle conformation, which explains the complex splitting in the ^{1}H NMR spectrum (axial and equatorial positions of the phenyl substituents at phosphorus). The carbon atom in **5** features a planar environment (sum of angles: 360.0(4)° and 159.1(4)°) with shortened P–C bond lengths due to electrostatic interactions (see Supporting Information).[18]

The formation of **5** is also observed without addition of any borane source. This is contrary to the methylsilyl-substituted derivatives of **3**, which solely furnished complex product mixtures upon warming, thus underlining the stabilization by the phenyl substituents.[9] Chivers and co-workers have recently reported on the formation of a dimeric species analogous to **5** as a by-product of a two-electron oxidation of a dilithio methandiide.[19,20] They suggested a carbene species as intermediate, which undergoes electrophilic attack at the sulfur of the P–S bond. An analogous mechanism might also be applicable for carbenoid **3**. Indeed computational studies confirm that borate formation possesses a much higher reaction barrier for the amine adduct, $BH_3{\cdot}NMe_3$, compared to the ether and thioether adducts. In fact, when using a phenyl-substituted model system the carbene formation ($\Delta G^{\neq} = 24.0$ kcal mol^{-1}) was revealed to be slightly favored over the nucleophilic attack of the carbenoid at the borane ($\Delta G^{\neq} = 30.2$ kcal mol^{-1}). These findings demonstrate that borate formation is the crucial step for the B–H bond activation of carbenoid species. This depends on the stability of the borane (as demonstrated above) but also on the nucleophilicity of the carbenoid itself. The formation of **5** accounts for the great electronic stabilization of the carbenoid by the thiophosphinoyl and silyl moiety. More nucleophilic carbenoids might also furnish the B–H bond activation with the less reactive $BH_3{\cdot}NMe_3$.

In conclusion, we have reported on the reactivity of electronically stabilized Li/Cl carbenoids towards different Lewis base adducts of parent BH_3. This reactivity strongly differs from the reactivity usually observed with simple organolithium compounds and NHCs. Depending on the stability of the borane adduct either B–H bond activation at the carbenic carbon center or dimerization of the carbene is observed. DFT calculations showed that the B–H bond activation proceeds in a stepwise fashion during which the nucleophilic attack of the Li/Cl carbenoid at $BH_3{\cdot}LB$ is the crucial reaction step. In the case of more stable borane adducts, borate formation competes with carbene formation and therefore further reaction pathways. These findings suggest that also other—less stable carbenoids—should be applicable in B–H bond activation reactions and that the choice of the borane source might be crucial for selective transformations.

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Keywords: bond activation · boranes · carbenoids · density functional calculations · lithium

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