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Generation of a Carbene-Stabilized Bora-borylene and its Insertion into a C−H Bond

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S *Supporting Information*

ABSTRACT: A novel NHC adduct of a dihalodiborane(4), **1**, is reduced by KC_8 with formation of the five-membered boracycle **2**. The reaction most likely proceeds via C−H insertion of an intermediate NHC-stabilized free bora-borylene species.

In 1967, at a time when few were focused on the element boron, P. L. Timms generated the free borylene ":BF" by passing BF_3 over solid boron at high temperature and low pressure.[1] Later, West provided more evidence for borylenes by photolyzing disilaboranes at low temperatures.[2] Timms' work was so far ahead of its time that it took another 31 years before a borylene could be stabilized as a terminal ligand on a transition metal[3,4] and a further 11 years before the elusive fluoroborylene in particular could be similarly tamed.[5] Although borylene chemistry took decades to gain a foothold, research interest in synthesizing or generating low-valent and reactive boron compounds, such as boron-centered anions, radicals, and multiply bound species, was undeterred.

In 2006, Yamashita and Nozaki turned on its head many years of unsuccessful attempts at generating a boryl anion (**I**, Figure 1),[6] spurring new interest in the stabilization of reactive boron compounds and inspiring us to synthesize two new families of formal boryl anions (**II** and **III**).[7,8] Recently, an interdisciplinary consortium comprising the groups of Curran, Malacria, Newcomb, Walton, Fensterbank, and Lacôte has revived the study of boryl radicals, using state-of-the-art techniques for their characterization (**IV**).[9] Their work has shown that by adding an N-heterocyclic carbene (NHC) to a boron center, radical abstraction of $H^\bullet$ can result in stable boron-centered radicals. Likewise, Power's group has a long history of reducing boron-containing compounds, including diboranes (**V**, leading to multiply bound B−B radical anions)[10] and dihaloboranes (**VII**, resulting in insertion of the boron fragment into a C−C bond, presumably via a two-coordinate borylene intermediate).[11]

Similarly, Robinson's group has also exploited NHC stabilization to synthesize a diborene (**VI**, Figure 1).[12] We recently reduced an NHC-stabilized dihaloborane and trapped the presumed borylene intermediate as its naphthalene adduct (**VIII**),[13] and related work by Robinson on the reduction of NHC-stabilized dihaloboranes and monohaloboronium cations showed hydrogen abstraction/boron coupling and C−H bond insertion reactivity (**IX**).[14] As we were preparing this manuscript, Bertrand and coworkers published the synthesis of a doubly carbene-stabilized terminal borylene (:BH), a compound isoelectronic to an amine and in possession of a boron-based lone pair of electrons. They also demonstrated the ability of this compound to undergo one-electron oxidation or add as a Lewis base to H^+ (**X**).[15]

In stark contrast to the aforementioned NHC−monoborane chemistry, the corresponding diborane(4)−mono-NHC species are restricted to only two partially characterized (^{11}B NMR) examples.[16a,b] However, sp^2−sp^3-hybridized mixed diboranes featuring other Lewis donors have been prepared,[16c,d] and some have been used for the copper-catalyzed β-boration of α,β-unsaturated conjugated compounds.[16e−g] Thus, on the basis of our borylene-trapping reaction and the work of Power, we set out to combine the concepts of NHC stabilization and diboranes with the reduction of BX_2 fragments to form borylenes. In this communication, we initially describe an unexpected rearrangement of the substituents on the diborane(4) framework upon addition of a carbene (see below). This fortuitous result provided compounds with a boron atom bearing two halides and a carbene donor. The unprecedented 1,1-dihalodiborane(4) connectivity pattern gave us a unique opportunity to probe the reduction chemistry of a BX_2 fragment directly connected to another boron atom. Electronic stabilization of the BX_2 fragment by the carbene donor and steric shielding by the surrounding mesityl substituents provided further encouragement. The results of the subsequent reduction attempts are also presented herein.

We became interested in the compound 1,2-dichloro-1,2-dimesityldiborane(4) (**1**; Scheme 1), as its mesityl groups impart considerable steric protection to the boron atoms while providing negligible electronic stabilization, thus making **1** much more reactive than traditional 1,2-dihalo-1,2-diaminodiboranes(4).[17] We reasoned that Lewis base adducts of **1** with one or two bulky NHCs would be promising precursors for reduction chemistry.

Treatment of **1** with 1,3-bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene (SIMes) in toluene resulted in new ^{11}B NMR signals at δ −0.17 and 87.4. The strong high-field shift of one boron nucleus relative to the starting material **1** (δ 85.2) clearly indicated the formation of a four-coordinate boron center in the product **2** (Scheme 1).

The identity of **2** was unambiguously determined by NMR spectroscopy, elemental analysis, and X-ray diffraction to be an NHC-stabilized 1,1-dichlorodiborane(4). This result was rather surprising because this rearrangement reaction necessarily requires the cleavage of at least one B−Cl and one B−C bond. However, we note that a similar rearrangement has been observed in the transhalogenation reactions of various

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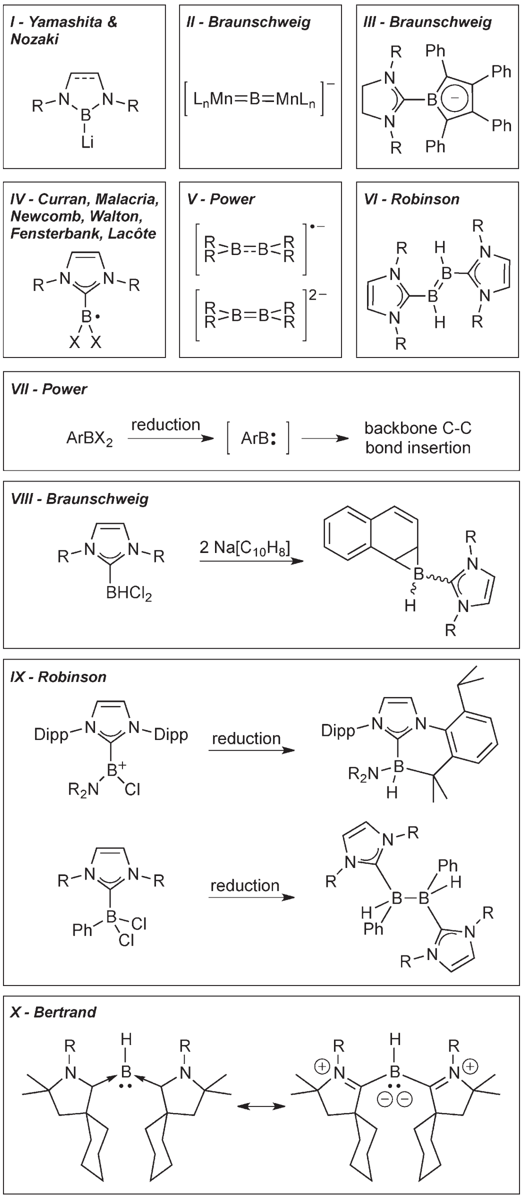
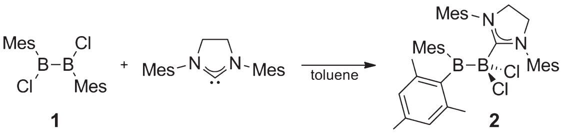


Figure 1. Relevant anionic and radical boron compounds or trapping products thereof.

Scheme 1. Carbene-Induced Rearrangement of 1,2-Dichlorodiborane(4) 1 To Form the Unsymmetrical Carbene-Stabilized 1,1-Dichlorodiborane(4) 2



1 2

1,2-dichloro-1,2-diaryldiboranes(4) with LiF.[18] The molecular structure of **2** in the solid state is shown in Figure 2. The B—B bond in **2** has a length of 1.774(3) Å, which is notably elongated relative to the B—B bond in **1** [1.680(6) Å].[19]

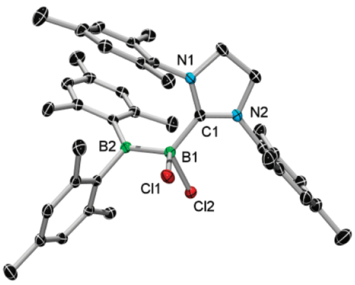


Figure 2. Structure of **2** in the solid state. Thermal ellipsoids are shown at 50% probability. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): B1—B2, 1.774(3); B1—C1, 1.653(2); B1—Cl1, 1.889(2); B1—Cl2, 1.906(2); $\Sigma\angle_{B2}$, 359.4; B2—B1—Cl1, 112.5(2); B2—B1—Cl2, 101.2(1); B2—B1—C1, 124.2(2).

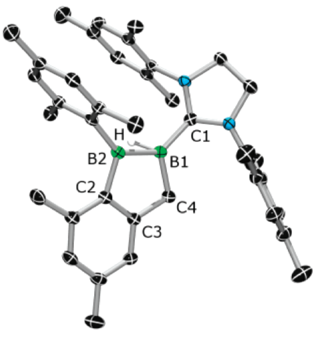


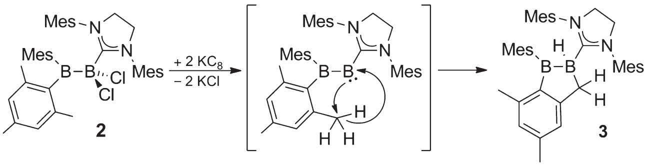
Figure 3. Structure of **3** in the solid state. Thermal ellipsoids are shown at 50% probability. Apart from that bound to B1, H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): B1—B2, 1.670(3); B1—C1, 1.553(3); B1—H1, 1.25(2); B2—H1, 1.51(2); $\Sigma\angle_{B2}$, 359.9; $\Sigma\angle_{B1}$, 357.5; H1—B1—B2, 60.1(9); H1—B2—B1, 45.8(8); B2—B1—C 128.1(2).

Subsequent reduction of NHC adduct **2** with 2 equiv of KC$_8$ resulted in the quantitative conversion to the new compound **3** as judged by ^{11}B NMR spectroscopy. The ^{11}B NMR spectrum shows a more upfield-shifted signal (δ 57.5) for the three-coordinate boron center than in **2** (δ 87.4), while the second signal at δ 0.15 lies in the expected range for four-coordinate boron nuclei. A broad signal at 0.81 ppm in the ^{1}H NMR spectrum, which sharpened considerably upon ^{11}B decoupling, was assigned to a boron-bound hydrogen atom. Although these data were insufficient to determine the connectivity of **3**, the molecular structure provided by X-ray crystallography allowed us to assign the highly unusual structure of **3** depicted in Figure 3.

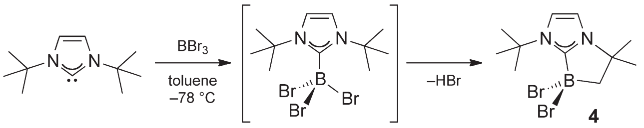
The protons of the CH$_2$ group bound to boron give rise to two doublet signals each (^2J = 19 Hz) at δ 1.82 and 2.57. The protons in the backbone of the NHC ligand show a complex multiplet, which may be an indication of hindered rotation of the NHC group. The most downfield ^{13}C NMR signal (δ 161.3) was assigned to the C3 nucleus connected to the CH$_2$ group at boron. The signals for the quaternary carbon atoms bound to boron (141.9, 145.5 ppm) were significantly broadened. The signal for the carbene center, however, could not be located.

The solid-state structure of **3** shows a B1—C1 distance of 1.553(3) Å, which is considerably shorter than that in **2** [1.653(2) Å]. The B—B distance [1.670(3) Å] in **3** is also shortened relative to that in the starting material [1.774(3) Å]. However, the most striking feature of the structure of **3** is the position of the boron-bound hydrogen atom, which was reliably located. This hydrogen appears to be strongly distorted toward

Scheme 2. Proposed Mechanism for the Formation of 3



Scheme 3. Synthesis of 4



the second boron atom (B1−H1, 1.25(2) Å; B2−H1, 1.51(2) Å). B2 lies in a trigonal-planar environment ($\Sigma\angle_{B2}$ = 359.9°), while the three non-hydrogen substituents of B1 are also bound in a planar fashion ($\Sigma\angle_{B1}$ = 357.5°). The hydrogen atom sits above the plane defined by the bicyclic rings, making a triangular H−B−B system with extremely acute H−B−B angles (H1−B1−B2, 60.1°; H1−B2−B1, 45.8°). Interestingly, the B2−B1−C1 angle [128.1(2)°] is significantly larger than that in **2** [124.2(2)°], although this distortion from true trigonal planarity is probably the result of steric interactions between the bulky adjacent *B*-Mes and *N*-Mes groups.

Thus, the solid-state structure of **3** includes a highly unusual planar R_2B−BR(NHC) system with a semibridging boron-bound hydrogen atom above this plane, making the compound difficult to classify. We are unaware of any diborane compound with comparable structural features. The high-field ^{11}B NMR signal of **3** (δ 0.15) is consistent with a tetracoordinate borane−base adduct or borate description, suggesting that a more conventional tetrahedral geometry of the NHC-bound boron atom prevails in solution. A ^{11}B,^{1}H HMQC NMR spectrum of **3** permitted the analysis of the cross-peak profile to determine the B−H coupling constant ($^{1}J_{B,H}$ = 160 Hz). The absence of a similar correlation for the second boron atom indicates that the proton is in this case terminally bound in solution.

Bicyclic diborane **3** might be considered the product of the formal insertion of an NHC-stabilized borylene into a methyl C−H bond of one mesityl group. Given the strongly reducing conditions of the reaction and previously observed "free" borylene reactivity patterns, we are inclined to propose a mechanism involving two-electron reduction of the dichloroboryl group to form a reactive bora-borylene intermediate, as shown in Scheme 2.

It should be noted that in our laboratories certain NHC-stabilized haloboranes have been shown to undergo thermally induced ring-closure reactions, which to the best of our knowledge have no precedent in NHC−borane chemistry. An example of this is the reaction of 1,3-di-*tert*-butylimidazol-2-ylidene (I^{t}Bu) with BBr_3, which affords the cyclic species **4** in high yield with spontaneous elimination of HBr (Scheme 3). However, the expected adduct I^{t}Bu·BBr_3 could also be observed as an intermediate at low temperatures by ^{11}B NMR spectroscopy, as it gave rise to a sharp singlet signal at δ −16.4. This chemical shift is comparable to those of other (NHC)·BBr_3 adducts but distinctly different from that of **4** (δ −6.85).[12] The ^{1}H, ^{11}B, and ^{13}C{^{1}H} NMR spectroscopic data for **4** are unobtrusive and in full agreement with its determined solid-state structure (Figure 4; see the Supporting Information for full experimental, spectroscopic, and structural details).

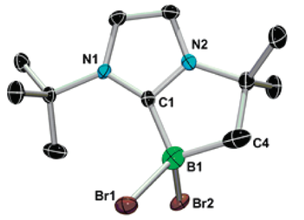


Figure 4. Molecular structure of **4** in the solid state.[20] Thermal ellipsoids are shown at 50% probability. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): B1−C1, 1.608(6); B−Br1, 2.041(5); B−Br2, 2.093(5); B1−C4, 1.671(6); $\Sigma\angle_{C1}$, 360.0; N1−C1−N2, 106.4(3); N2−C1−B1, 107.1(3); B1−C1−N1, 146.5(3).

To ensure that the formation of **3** was not the result of a comparable elimination process, we extensively heated solutions of the precursor **2** in various solvents. However, the NHC−diborane adduct **2** proved to be perfectly stable even under relatively harsh thermal conditions, thus providing further support for the proposed borylene mechanism (see above).

In conclusion, we have described the formation of a hitherto unknown NHC adduct of the 1,2-diaryl-1,2-dihalodiborane(4) **1**. Interestingly, an unprecedented rearrangement occurred upon adduct formation, furnishing the NHC-stabilized 1,1-dichlorodiborane(4) **2**. Its reaction with KC_8 afforded compound **3**, which is presumably formed by C−H insertion of an intermediate NHC-stabilized borylene. In contrast, the reaction of I^{t}Bu with BBr_3 led to the formation of a ring-closure product upon heating in solution. This behavior was not observed for **2** upon heating in solution, thus supporting the formation **3** via an NHC-stabilized bora-borylene intermediate.

■ ASSOCIATED CONTENT

S **Supporting Information.** Experimental details and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) The unit cell contains three independent molecules, which differ only marginally. For simplicity, only one of these molecules is depicted and discussed.