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Synthesis and Structure of a Carbene-Stabilized π-Boryl Anion**

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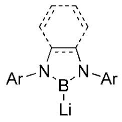
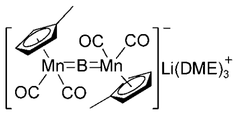
Dedicated to Professor Peter Paetzold on the occasion of his 75th birthday

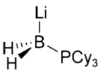
One of the vital research areas in modern main-group chemistry is focused on the synthesis of Group 13 carbene analogues. In contrast to the facile synthesis of anionic gallyl species,[1] the isolation of a boryl anion was only reported recently.[2] Chemical reduction of haloboranes with KC_8 or Na/K alloy generally yields products from radical reactions, that is, C−H bond insertion,[3] homocoupling, and rearrangement.[4,5] In 2006, the groups of Nozaki and Yamashita isolated the first structurally characterized boryllithium reagent of type **A** by reduction of the corresponding 2-halo-1,3,2-diazaborole.[2a] In addition to these NHC-analogous (NHC = N-heterocyclic carbene) boryl anions, reduction of the chloroborylene complex $[((\eta^5\text{-}C_5H_5)Mn(CO)_2)_2(BCl)]$[6] resulted in the formation of the corresponding linear anionic dimetalloborylene complex **B** (DME = 1,2-dimethoxyethane), which reacts as a boron-centered nucleophile.[7]



A



B

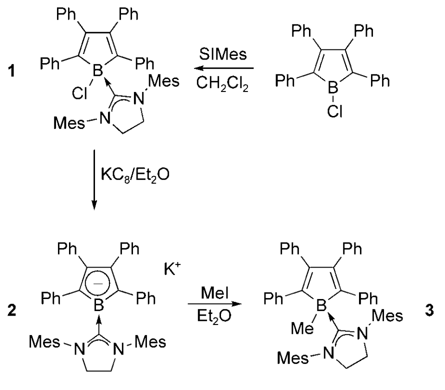


C

Prior to the isolation of **A**, a few studies suggested that base-stabilized sp^3 nucleophilic boryl anions (type **C**; Cy = cyclohexyl) could be generated by reduction of the corresponding triethylamine- or tricyclohexylphosphine-coordinated haloboranes.[8] However, definitive characterization of the base-stabilized boryl anion has never been reported.

In recent studies, NHCs have proven useful in stabilizing low-valent boron-containing molecules, such as neutral diborenes, borenium cations, and neutral 9-boraanthracenes.[9] Therefore, we decided to investigate whether an NHC is effective in stabilizing the borole-based boryl anion. Herein we describe the synthesis of a carbene-stabilized borole monoanion and its reactivity toward electrophiles. Structural and computational (DFT) data of the title compound are also discussed.

The SIMes (1,3-dimesitylimidazolidin-2-ylidene) adduct of 1-chloro-2,3,4,5-tetraphenylborole[10] was obtained by mixing equimolar amounts of the reagents in benzene and was isolated as a yellow solid after purification (Scheme 1).



Scheme 1. Synthesis and reactivity of SIMes-stabilized borole monoanion **2**. Mes = mesityl.

The resonance in the ^{11}B NMR spectrum of **1** detected at $\delta = -3.1$ ppm as a sharp singlet indicates the formation of a tetracoordinate boron center. The ^1H NMR spectrum of **1** exhibits only one set of signals for the methyl protons, suggesting free rotation of SIMes about the C−B bond in solution at ambient temperature.

Reduction of **1** with excess KC_8 in diethyl ether affords the monoanionic derivative **2** in 37% yield. Upon reduction, a deep reddish-purple color developed immediately and the completeness of reaction was monitored by ^{11}B NMR spectroscopy. The ^{11}B resonance of **2** observed at $\delta = 12$ ppm rules out the formulation of **2** as a borataalkene derivative, for which the ^{11}B NMR spectroscopy signals generally appear around $\delta = 40$ ppm.[11] The aforementioned ^{11}B chemical shift of **2** is also shifted considerable upfield compared to that for $[K_2(Ph_4C_4BPh)]$ ($\delta = 26$ ppm), thus emphasizing the difference in the electronic structure of **2** and borole dianions.[12] Therefore, compound **2** is better described as an NHC-stabilized boryl anion, in which the lone-pair electrons reside in the π-bonding orbital of the boron atom and are stabilized by delocalization over the C_4B ring (Figure 1).

Dark-purple crystals of **2** suitable for X-ray analysis were obtained from cooling a diethyl ether/pentane solution to −30 °C. Compound **2** crystallized as a potassium-bridged

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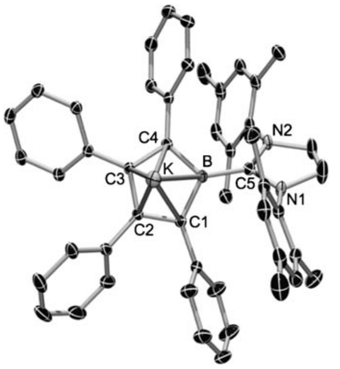


Figure 1. Crystal structure of **2**. Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: B–C5 1.541(2), B–C1 1.535(2), B–C4 1.541(2), C1–C2 1.431(1), C2–C3 1.446(1), C3–C4 1.41(1), C5–N1 1.371(1), C5–N2 1.374(1); C1-B-C5 128.55(10), C1-B-C4 104.95(9), C4-B-C5 125.79(10), B-C1-C2 107.21(9), C1-C2-C3 109.57(9), C2-C3-C4 111.36(9), C3-C4-B 106.86(9).

dimer in the space group $P\bar{1}$ (Figure 1; only one half is displayed; the dimer is depicted in Figure S1). Within the dimer unit, the potassium cation resides above one of the borole rings and coordinates to the phenyl substituent at the C2 atom of the other borole molecule through an intermolecular cation–π interaction (Figure S1 in the Supporting Information). The borole ring is essentially planar with an average displacement of the ring atoms above the C_4B plane of 0.0085 Å. The boron atom adopts the trigonal-planar geometry, as indicated by the sum of angles of 359.3°. In comparison with the neutral boroles, the intraannular C–C bond-length alternation within the C_4B ring is significantly decreased.[13] The B–C1 and B–C4 bonds are also shorter than those observed in neutral boroles.[12b] In fact, the structural features of **2** within the borole ring resemble those of borole dianions, thus emphasizing the aromatic character of the C_4B ring in **2**.[12b] The B–C5 bond of 1.5406(15) Å is also significantly shorter than that of the NHC-coordinated borabenzenes (1.596(2) Å)[14] or 9-boraanthracenes (1.607(4) Å).[9d] This finding together with a relatively small dihedral angle of 36.3° between the carbene ligand and borole moiety suggests non-negligible π bonding between the boron atom and the exocyclic carbene ligand.[15]

To better understand the electronic structure of **2**, computations of the model complex **2′** were performed with DFT methods at the B3LYP/6-31g* level of theory. Complex **2′**, in which the mesityl groups are replaced by 2,6-dimethylphenyl groups, was optimized as a monomer in the absence of the potassium ion coordination. The energy-optimized geometry of **2′** is in good agreement with that determined experimentally, thus indicating that the critical bonding features are captured in the model complex. Examination of the electron density distribution of the HOMO of **2′** indeed reveals a π-like bonding orbital between the boron atom and carbene carbon center with significant contribution from boron atom (14.6%), suggesting the presence of a π-nucleophilic boron atom (Figure 2). This finding also implies the existence of a considerable π-back-bonding contribution from boron to carbon to the overall borole–carbene bonding interaction. This electronic situation of **2** is somewhat inverse to that of boryl anions of type **A**, in which the lone-pair electrons occupy an exocyclic sp^2 orbital, while the p_z orbital of boron is stabilized by π bonding to the adjacent nitrogen atoms.[2d,16] In compound **2**, however, the electron density preferentially resides in the p_z orbital of the boron atom, while the NHC donates its lone pair into the equatorial sp^2 orbital. The NHC ligand serves not only as a strong σ donor but also as a π acceptor in delocalizing the electrons from the boron atom.

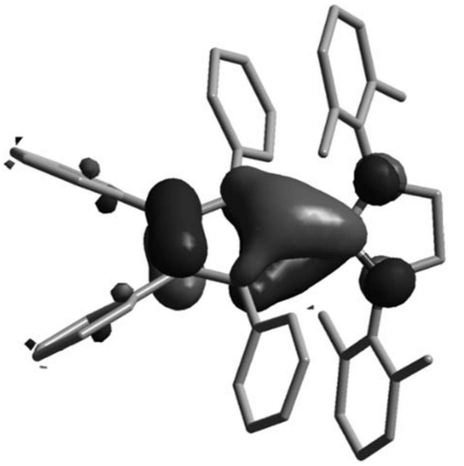


Figure 2. Depiction of the HOMO of **2′**.

For probing the nucleophilicity of the boron atom, compound **2** was treated with an excess of MeI in Et_2O at ambient temperature. After workup, the NHC-coordinated 1-methyl-2,3,4,5-tetraphenylborole (**3**) was isolated as a colorless solid in 71% yield. The resonance of **3** in the ^{11}B NMR spectrum detected at $\delta = -10.8$ ppm is significantly shifted upfield compared to that detected for **2**, in agreement with the formation of a tetracoordinate boron center. The ^{1}H resonance of the methyl (B–Me) group at $\delta = -0.4$ ppm is also shifted upfield with respect to those of the methyl protons of the mesityl groups. As a result of the quadrupolar coupling with the boron nuclei, the signal of the boron-bound methyl group in the ^{13}C NMR spectrum detected at $\delta = 8.2$ ppm is very weak and was only identified by HMQC methods.

Single crystals suitable for X-ray analysis were obtained from slow evaporation of a Et_2O/*n*-hexane solution of **3** at room temperature. Compound **3** crystallizes in the monoclinic $P2_1/c$ space group and displays two independent molecules in the asymmetric unit (Figure 3). These two independent molecules feature similar structural parameters and are arbitrarily denoted as molecule **I** and molecule **II**. The propeller-like arrangement of the phenyl groups with average dihedral angles of 53.2° (**I**) and 56.8° (**II**) represents the common structural feature of tetraphenyl-substituted boroles. The boron atom adopts a distorted tetrahedral environment, and all B–C bond lengths fall within the expected range for the corresponding single bonds. The significant elongation of the B–C1 [1.649(2) Å (**I**); 1.650(2) Å (**II**)] and B–C4 bonds [1.648(2) Å (**I**); 1.650(2) Å (**II**)] compared to those observed in **2** indicates the loss of π-electron delocalization over the C_4B ring mediated by the p_z orbital of the boron atom.

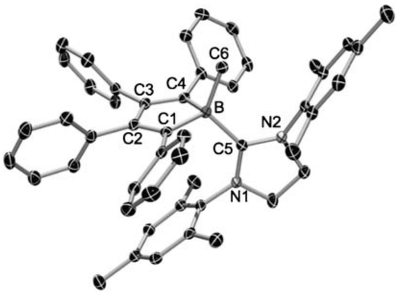
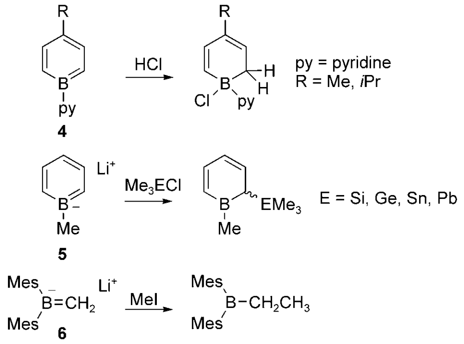


Figure 3. Crystal structure of one of the independent molecules of **3**. Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: molecule **I**: B–C6 1.633(2), B–C5 1.647(2), B–C1 1.649(2), B–C4 1.648(2), C1–C2 1.355(2), C2–C3 1.481(2), C3–C4 1.363(2), C5–N1 1.352(2), C5–N2 1.346(2); molecule **II**: B–C6 1.633(2), B–C5 1.649(2), B–C1 1.650(2), B–C4 1.650(2), C1–C2 1.364(2), C2–C3 1.479(2), C3–C4 1.359(2), C5–N1 1.342(2), C5–N2 1.357(2)

Lengthening of the B–C5 bond [1.647(2) Å (**I**); 1.649(2) Å (**II**)] in addition to the contraction of both C5–N bonds [C5–N1: 1.3524(17), C5–N2: 1.3460(18) Å (**I**); C5–N1: 1.3417(18), C5–N2: 1.3569(17) Å (**II**)] indicates canceling of π-electron back-donation from the boron atom to the carbene carbon center upon methylation.

The nucleophilic character of the boron atom in **2** as expressed in its reactivity towards MeI is highly unusual and unique in comparison with all other relevant six-π-electron boracycles (Scheme 2). Thus, in borabenzenes **4**, the boron atom acts as an electrophile and prompts nucleophilic addition.[17] Likewise, electrophilic quenching of boratabenzene **5** only results in the formation of a 2-substituted boracyclohexadiene.[18] Accordingly, the borataalkene **6** also represents a carbon-centered nucleophile and displays no nucleophilicity of the boron atom.[19]



Scheme 2. Reactivity of borabenzene **4**, boratabenzene **5**, and borataalkene **6** toward electrophiles.

In conclusion, an unprecedented NHC-stabilized borole anion was synthesized and structurally characterized. Computational and reactivity studies of **2** confirm the presence of a π-nucleophilic boron atom, which cleanly reacts with the electrophile MeI, thus establishing the first example of reactivity umpolung for such a boron heterocycle. Moreover, **2** opens up the possibility for the preparation of unusual 1-substituted borole derivatives, which are otherwise difficult to obtain. More detailed reactivity studies of **2** are currently underway.

Experimental Section

2: Compound **1** (20 mg, 0.028 mmol) and KC_8 (20 mg, 0.15 mmol) were mixed in a Young NMR tube and dissolved in diethyl ether (0.5 mL). The reaction was monitored with ^{11}B NMR spectroscopy until the total consumption of compound **1** was detected. After standing at ambient temperature for overnight, the dark reddish-purple solution was filtered through a filter pipette in a glovebox. Additional diethyl ether (2 × 0.5 mL) was used to wash the product from the solid residue. The combined filtrate was layered with one-tenth volume of pentane and kept at −30 °C for 10 days to give dark purple crystals. Yield 7.5 mg (37%). ^{1}H NMR (500 MHz, C_5D_5N, 297 K): $\delta = 2.06$ (s, 6H, *p*-MeMes), 2.30 (s, 12H, *o*-MeMes), 3.61 (s, 4H, NCH_2CH_2N), 6.49 (s, 4H, MesCH), 6.58–6.62 (m, 2H), 6.68–6.74 (m, 4H), 6.87–6.91 (m, 6H), 6.96–7.03 ppm (m, 8H). ^{13}C{^{1}H} NMR (126 MHz, C_5D_5N, 297 K): $\delta = 20.4$ (*o*-MeMes), 20.7 (*p*-MeMes), 51.3 (NCH_2CH_2N), 120.2 (Ph), 120.8 (Ph), 126.2 (Ph), 126.5 (Ph), 129.5 (Mes), 131.4 (Ph), 132.3 (Ph), 134.5, 140.0, 145.2, 152.7 ppm. ^{11}B{^{1}H} NMR (160 MHz, C_5D_5N, 297 K): $\delta = 12.7$ ppm. Elemental analysis (%) calcd. for $C_{51}H_{51}BKN_2O_{0.5}$: C 81.69, H 6.86, N 3.74; found: C 80.63, H 6.72, N 4.22.

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