

NHC-Stabilized 1-Hydro-1*H*-borole and Its Nondegenerate Sigmatropic Isomers

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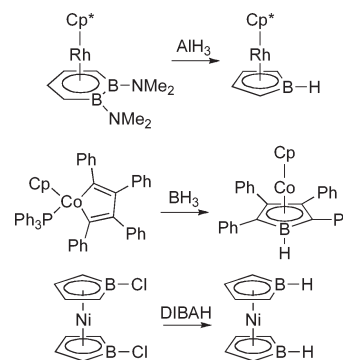
S Supporting Information

ABSTRACT: Electrophilic quenching of a carbene-stabilized π -boryl anion with the Brønsted acid Et_3NHCl provides a convenient synthetic route to the parent NHC-stabilized 1-hydroborole, which isomerizes to the corresponding 3-hydroborole via two successive nondegenerate [1,5]-sigmatropic hydrogen migrations. Molecular structures of both isomers have been determined by X-ray crystallography.

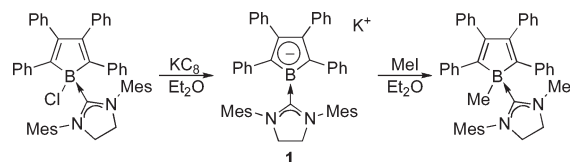
Being the smallest neutral antiaromatic boracycles, boroles have recently attracted considerable attention because of their potential application in optoelectronics.¹ The antiaromatic character of boroles entails strong electrophilicity of the boron center in combination with the presence of a highly activated conjugated carbon backbone, which readily participates in Diels–Alder reactions.² Accordingly, it is imperative to protect the C_4B core with bulky substituents in order to enable the isolation of monomeric, nonannulated borole derivatives.^{2,3} In the past few years, various substituents such as halide, aryl, and amino functionalities, as well as ferrocenyl and platinum complex fragments, have been successfully attached to the boron atom.⁴ By contrast, little is known for the parent unsubstituted 1-hydroborole. Apart from those generated within the coordination sphere of transition metals, the 1-hydro-1*H*-boroles were only studied by computational methods.⁵ However, preparation of the $\eta^5\text{-(C}_4\text{R}_4\text{BH)}$ -containing metal complexes is not straightforward either. These species were obtained via (i) AlH_3 -induced ring contraction of the 1,2-diboratabenzene in $[\text{Cp}^*\text{Rh}(\eta^5\text{-C}_4\text{H}_4\text{-(BNMe}_2)_2)]$,⁶ (ii) BH group insertion to the metal–C bonds of $\{\text{Cp}(\text{PPh}_3)_3\text{Co}(\kappa^2\text{-C}_4\text{Ph}_4)\}$,⁷ or (iii) reduction of η^5 -haloborole metal complexes with hydride reagents (Scheme 1).⁸

Prior to the isolation of boron nucleophiles,⁹ the generation of B–H bonds generally relied on the hydride reduction of haloboranes,¹⁰ chemical reduction of boron halides,¹¹ or reaction of $(\text{C}_6\text{F}_5)_3\text{B}$ and triethylsilane.¹² With the isolation of nucleophilic boryl anions, an alternative approach to the B–H bond was made accessible by means of protonation of the boron atom with weak acids.^{9a} In our previous study, chemical reduction of a SiMes–chloroborole adduct (SiMes: 1,3-dimesitylimidazolidin-2-ylidene) afforded the π -boryl anion **1**, which readily reacted with CH_3I to yield the carbene-stabilized 1-methylborole (Scheme 2).¹³ Because of the nucleophilicity of the boron center in **1**, this monoanionic borollide represents a unique precursor to various B-substituted borole derivatives, which are difficult to prepare by conventional methods. In this paper, we report on the

Scheme 1. Syntheses of $\eta^5\text{-(C}_4\text{R}_4\text{BH)}$ -Containing Metal Complexes



Scheme 2. Synthesis and Electrophilic Quench with MeI of **1**



synthesis of a NHC-stabilized 1-hydro-1*H*-borole via protonation of the corresponding π -boryl anion. In addition, the nondegenerate [1,5]-sigmatropic isomers of 1-hydro-1*H*-borole are also studied experimentally and computationally.

Protonation of **1** with excess triethylammonium chloride in Et_2O at room temperature resulted in a substantial color change from dark reddish purple to light orange within 10 min. After removal of the solvent under vacuum, **2-BH** (Figure 1) was isolated via hexane extraction of the reaction residue. The ^{11}B NMR resonance of **2-BH** is detected at -18 ppm with a $^1J_{\text{BH}}$ coupling of 85 Hz, which is comparable to that observed for trialkyl borohydrides¹⁴ and stable carbene–borane adducts.¹⁵ Consequently, the corresponding ^1H NMR signal of the B–H proton (δ 3.12) can only be identified in the ^{11}B -decoupled spectrum, thus confirming the direct bonding between boron and hydrogen. The symmetric ^1H NMR resonances of the mesityl groups suggest a free rotation of the SiMes ligand about the B–carbene bond in solution at room temperature.

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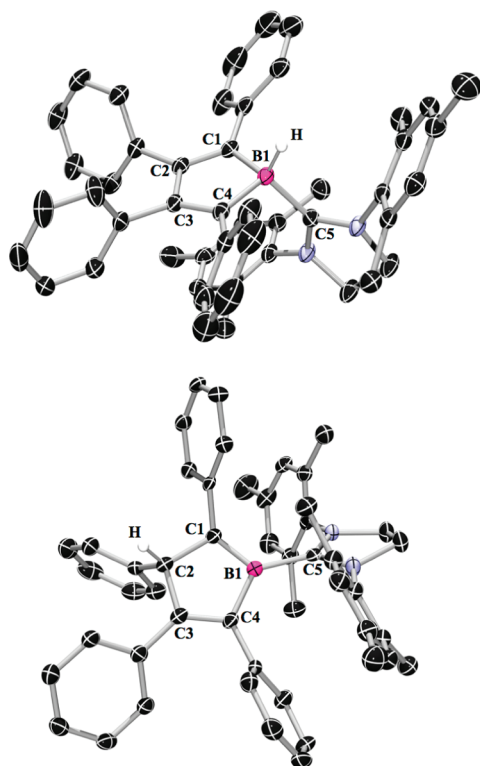
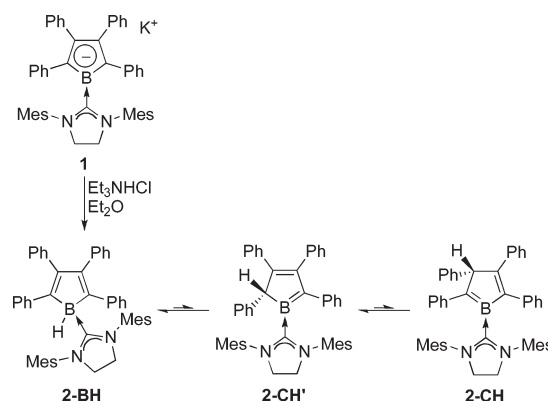


Figure 1. Molecular structures of **2-BH** (top) and **2-CH** with hydrogen atoms omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

Interestingly, slow evaporation of a **2-BH** solution in CH_2Cl_2 /hexane afforded two types of crystalline materials, i.e., (i) pale-yellow blocks and (ii) a very few orange needles, which were both suitable for X-ray diffraction.¹⁶ Analysis of the yellow blocks verified the formation of a 1-hydro-2,3,4,5-tetraphenyl-1H-borole SIMes adduct (**2-BH**). The presence of a tetracoordinate boron center is confirmed by the sum of the C–B–C angles around B1 of 326.8° . Rehybridization of the boron atom results in a significant elongation of the B–carbene bond distance [B1–C5 1.628(2) Å] with respect to that in **1** [1.541(2) Å], as well as a pronounced C–C bond length alternation within the butadiene backbone [C1–C2 1.359(2) Å; C2–C3 1.479(2) Å; C3–C4 1.363(2) Å], which strongly resembles those observed in NHC-stabilized 1-methyl-2,3,4,5-tetraphenylborole.¹³

X-ray diffraction of the orange needles, on the other hand, allowed for the structural characterization of the 3-hydroborole **2-CH**, one of the two possible nondegenerate [1,5]-sigmatropic isomers of **2-BH**. The shift of the hydrogen atom from B1 to C2 is authenticated by the presence of a tetrahedral C2 center ($\Sigma = 331.1^\circ$), whereas the remaining ring atoms still display their trigonal-planar geometry. The B1–C1 bond distance [1.463(4) Å] is noticeably shorter than the B–C bonds in **1** [B1–C1 1.535(2) Å; B1–C4 1.541(2) Å], which indicates a strong bonding interaction between B1 and C1 in **2-CH**. In fact, the B1–C1 bond distance is analogous to that reported for borataalkene compounds, in which the formal bond order for the B–C linkage is 2.¹⁷ Hence, **2-CH** can also be considered a carbene-stabilized boraalkene. Despite its structural elucidation in the solid state, **2-CH** consistently eluded spectroscopic characterization in solution, even if the crystalline mixture of **2-BH** and **2-CH** was used in the measurements. In any case, only the spectroscopic

Scheme 3. Synthesis of **2-BH** and Its [1,5]-Sigmatropic Isomers, **2-CH'** and **2-CH**



characteristics of **2-BH** have been detected in solution. In addition, all attempts to separate the crystals of **2-BH** and **2-CH** mechanically failed, and we were not able to obtain analytical data for **2-CH** by variable-temperature NMR spectroscopy or solid state UV–visible spectroscopy so far.

Even though sigmatropic rearrangements of this type are pretty common in cyclopentadienyl chemistry, only a few reports of a related reactivity have appeared in the literature for boracycles.¹⁸ In order to elucidate the relative stabilities of **2-BH** and **2-CH**, theoretical computations of the two isomers and its putative third isomer, namely, 2-hydroborole **2-CH'**, were performed with density functional theory (DFT) methods applying the B3LYP functional and 6-31G* basis sets. The optimized geometries of **2-BH** and **2-CH** are in fairly good agreement with those determined by X-ray diffraction. Examination of the enthalpies of the molecules in the gas phase revealed that **2-BH** is thermodynamically favored over **2-CH** and **2-CH'** by 9.0 and 4.6 kcal mol^{−1}, respectively. This result is consistent with the absence of any detectable quantities of **2-CH** and **2-CH'** in solution; i.e., the equilibrium between the three different isomers, as depicted in Scheme 3, most likely lies completely on the side of **2-BH**. Nevertheless, the fact that it has been possible to isolate single crystals of **2-CH** might be connected to its favorable crystallization properties, which are capable of shifting the equilibrium toward **2-CH** during the crystallization process. Although **2-CH'** is more stable than the **2-CH** isomer, all efforts toward the isolation and structural characterization of **2-CH'** remained unsuccessful.

In summary, the NHC-stabilized borole anion **1** represents a unique synthon for the generation of 1-hydro-1H-borole **2-BH**, which is related to **2-CH** by a sequence of two nondegenerate [1,5]-sigmatropic rearrangements of the boron-bound hydrogen atom. Two of three possible isomers were isolated and characterized in the solid state by single-crystal X-ray analysis (**2-BH** and **2-CH**). DFT studies indicate that the equilibrium between the three isomers lies completely on the side of **2-BH** in solution due to thermodynamics. Further reactivity studies of the π -boryl anion are currently ongoing.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental procedures, spectroscopic and crystallographic data, details on the theoretical calculations, and crystallographic material in CIF format. This

material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (16) Crystal data for **2-BH**: $C_{49}H_{47}BN_2$, $M_r = 674.70$, yellow block, $0.49 \times 0.38 \times 0.29 \text{ mm}^3$, monoclinic space group $P2_1/n$, $a = 12.5450(6) \text{ \AA}$, $b = 13.9877(7) \text{ \AA}$, $c = 22.8093(11) \text{ \AA}$, $\beta = 103.996(2)^\circ$, $V = 3883.7(3) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.154 \text{ g cm}^{-3}$, $\mu = 0.066 \text{ mm}^{-1}$, $F(000) = 1440$, $T = 100(2) \text{ K}$, $R_1 = 0.0738$, $wR_2 = 0.1402$, 9578 independent reflections [$2\theta \leq 56.64^\circ$] ($R_{\text{int}} = 0.0532$) and 475 parameters. Crystal data for **2-CH**: $C_{49}H_{47}BN_2$, $M_r = 674.70$, orange needles, $0.32 \times 0.09 \times 0.07 \text{ mm}^3$, monoclinic space group $P2_1/c$, $a = 9.8006(8) \text{ \AA}$, $b = 18.2005(13) \text{ \AA}$, $c = 21.5781(17) \text{ \AA}$, $\beta = 95.482(4)^\circ$, $V = 3831.4(5) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.170 \text{ g cm}^{-3}$, $\mu = 0.067 \text{ mm}^{-1}$, $F(000) = 1440$, $T = 100(2) \text{ K}$, $R_1 = 0.1029$, $wR_2 = 0.1454$, 8857 independent reflections [$2\theta \leq 56.7^\circ$] ($R_{\text{int}} = 0.0000$) and 552 parameters.
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