Inorganic Chemistry
COMMUNICATION
pubs.acs.org/IC

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

Holger Braunschweig,* Ching-Wen Chiu, Thomas Kupfer, and Krzysztof Radacki

Institut für Anorganische Chemie, Julius-Maximilians Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

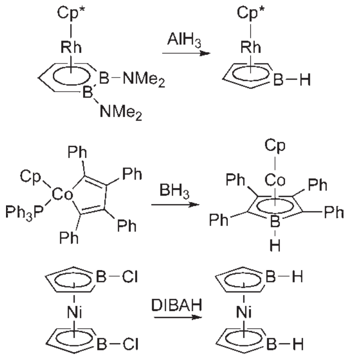
S *Supporting Information*

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.

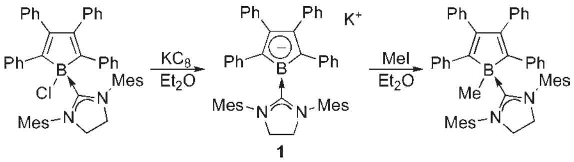
Being the smallest neutral antiaromatic boracycles, boroles have recently attracted considerable attention because of their potential application in optoelectronics.[1] The antiaromatic character of boroles entails strong electrophilicity of the boron center in combination with the presence of a highly 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 η^5-(C_4R_4BH)-containing metal complexes is not straightforward either. These species were obtained via (i) AlH_3-induced ring contraction of the 1,2-diboratabenzene in [Cp*Rh(η^6-C_4H_4-$(BNMe_2)_2$)],[6] (ii) BH group insertion to the metal–C bonds of {Cp(PPh_3)Co(κ^2-C_4Ph_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 $(C_6F_5)_3B$ 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 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.

Scheme 1. Syntheses of η^5-(C_4R_4BH)-Containing Metal Complexes



Scheme 2. Synthesis and Electrophilic Quench with MeI of 1



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 $^1J_{BH}$ coupling of 85 Hz, which is comparable to that observed for trialkyl borohydrides[14] 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.

Received: March 15, 2011
Published: April 11, 2011

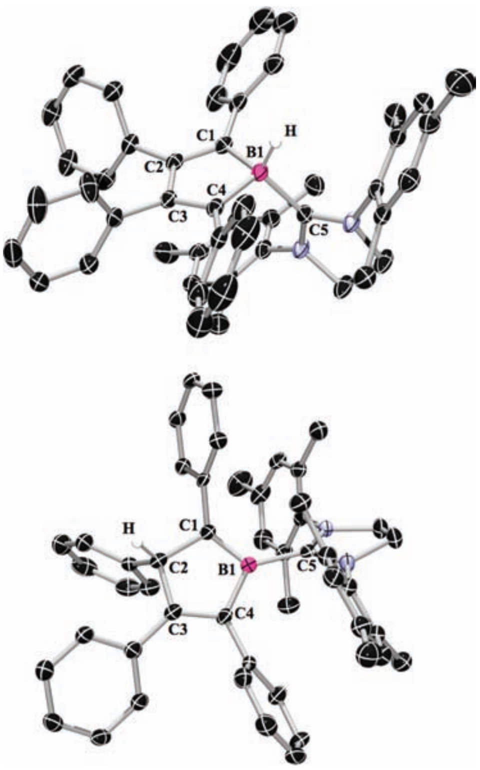
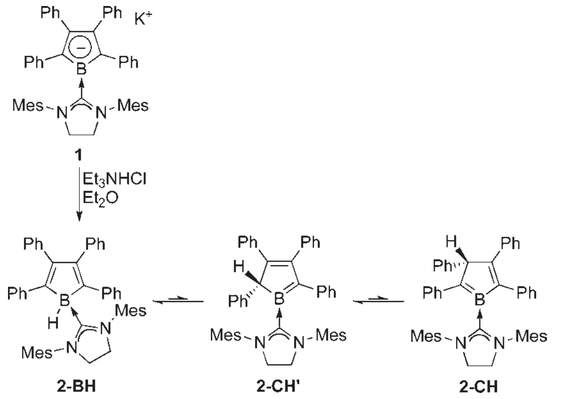


Figure 1. Molecular structures of **2-BH** (top) and **2-CH** with hydrogen atoms omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

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-1*H*-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 (Σ = 331.1°), 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 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.

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



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-1*H*-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

Ⓢ 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.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: h.braunschweig@mail.uni-wuerzburg.de.

■ ACKNOWLEDGMENT

C.-W.C. is grateful for a postdoctoral research fellowship from the Alexander von Humboldt Foundation.

■ REFERENCES

(1) (a) Yamaguchi, S.; Shirasaka, T.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2002**, *124*, 8816. (b) Kim, S.; Song, K.-H.; Kang, S. O.; Ko, J. *Chem. Commun.* **2004**, 68. (c) Thanthiriwatte, K. S.; Gwaltney, S. R. *J. Phys. Chem. A* **2006**, *110*, 2434. (d) Wakamiya, A.; Mishima, K.; Ekawa, K.; Yamaguchi, S. *Chem. Commun.* **2008**, 579.

(2) (a) Eisch, J. J.; Galle, J. E.; Kozima, S. *J. Am. Chem. Soc.* **1986**, *108*, 379. (b) Fagan, P. J.; Burns, E. G.; Calabrese, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 2979.

(3) (a) Eisch, J. J.; Hota, N. K.; Kozima, S. *J. Am. Chem. Soc.* **1969**, *91*, 4575. (b) Herberich, G. E.; Buller, B.; Hessner, B.; Oschmann, W. *J. Organomet. Chem.* **1980**, *195*, 253.

(4) (a) Braunschweig, H.; Fernández, I.; Frenking, G.; Kupfer, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 1951. (b) So, C.-W.; Watanabe, D.; Wakamiya, A.; Yamaguchi, S. *Organometallics* **2008**, *27*, 3496. (c) Braunschweig, H.; Kupfer, T. *Chem. Commun.* **2008**, 4487. (d) Fan, C.; Piers, W. E.; Parvez, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 2955. (e) Braunschweig, H.; Chiu, C.-W.; Radacki, K.; Brenner, P. *Chem. Commun.* **2010**, *46*, 916.

(5) (a) Schleyer, P. v. R.; Jiao, H.; Goldfuss, B.; Freeman, P. K. *Angew. Chem., Int. Ed.* **1995**, *34*, 337. (b) Cyrañski, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P. v. R. *J. Org. Chem.* **2002**, *67*, 1333.

(6) Herberich, G. E.; Hessner, B.; Hostalek, M. *J. Organomet. Chem.* **1988**, *355*, 473.

(7) (a) Palladino, D. B.; Fehlner, T. P. *Organometallics* **1983**, *2*, 1692. (b) Hong, F. E.; Eigenbrot, C. W.; Fehlner, T. P. *J. Am. Chem. Soc.* **1989**, *111*, 949.

(8) (a) Herberich, G. E.; Englert, U.; Hostalek, M.; Laven, R. *Chem. Ber.* **1991**, *124*, 17. (b) Aradi, A. A.; Hong, F. E.; Fehlner, T. P. *Organometallics* **1991**, *10*, 2726.

(9) (a) Segawa, Y.; Yamashita, M.; Nozaki, K. *Science* **2006**, *314*, 113. (b) Yamashita, M.; Suzuki, Y.; Segawa, Y.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 9570. (c) Segawa, Y.; Yamashita, M.; Nozaki, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 6710. (d) Yamashita, M.; Suzuki, Y.; Segawa, Y.; Nozaki, K. *Chem. Lett.* **2008**, *37*, 802. (e) Segawa, Y.; Suzuki, Y.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2008**, *130*, 16069. (f) Kajiwara, T.; Terabayashi, T.; Yamashita, M.; Nozaki, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 6606. (g) Braunschweig, H.; Burzler, M.; Dewhurst, R. D.; Radacki, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 5650. (h) Terabayashi, T.; Kajiwara, T.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14162. (i) Braunschweig, H.; Brenner, P.; Dewhurst, R. D.; Kaupp, M.; Müller, R.; Östreicher, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 9735.

(10) (a) Hooz, J.; Akiyama, S.; Cedar, F. J.; Bennett, M. J.; Tuggle, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 274. (b) Bestmann, H. J.; Arenz, T. *Angew. Chem.* **1986**, *98*, 571. (c) Ashe, A. J.; Klein, W.; Rousseau, R. *Organometallics* **1993**, *12*, 3225. (d) Parks, D. J.; Spence, R. E. v. H.; Piers, W. E. *Angew. Chem., Int. Ed.* **1995**, *34*, 809.

(11) (a) Mennekes, T.; Paetzold, P.; Boese, R. *Angew. Chem., Int. Ed.* **1990**, *29*, 899. (b) Grigsby, W. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 7981. (c) Wang, Y.; Quillian, B.; Wei, P.; Wannere, C. S.; Xie, Y.; King, R. B.; Schaefer, H. F.; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2007**, *129*, 12412.

(12) Parks, D. J.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5492.

(13) Braunschweig, H.; Chiu, C.-W.; Radacki, K.; Kupfer, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 2041.

(14) (a) Brown, H. C.; Hubbard, J. L.; Singaram, B. *J. Organomet. Chem.* **1979**, *44*, 5004. (b) Brown, H. C.; Kramer, G. W.; Hubbard, J. L.; Krishnamurthy, S. *J. Organomet. Chem.* **1980**, *188*, 1.

(15) Kuhn, N.; Henkel, G.; Kratz, T.; Kreutzberg, J.; Boese, R.; Maulitz, A. H. *Chem. Ber.* **1993**, *126*, 2041.

(16) Crystal data for **2-BH**: $C_{49}H_{47}BN_2$, M_r = 674.70, yellow block, 0.49 × 0.38 × 0.29 mm^3, monoclinic space group $P2_1/n$, a = 12.5450(6) Å, b = 13.9877(7) Å, c = 22.8093(11) Å, β = 103.996(2)°, V = 3883.7(3) Å^3, Z = 4, ρ_{calcd} = 1.154 g cm^{-3}, μ = 0.066 mm^{-1}, F(000) = 1440, T = 100(2) K, R1 = 0.0738, wR2 = 0.1402, 9578 independent reflections [$2\theta \leq 56.64°$] (R_{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 × 0.09 × 0.07 mm^3, monoclinic space group $P2_1/c$, a = 9.8006(8) Å, b = 18.2005(13) Å, c = 21.5781(17) Å, β = 95.482(4)°, V = 3831.4(5) Å^3, Z = 4, ρ_{calcd} = 1.170 g cm^{-3}, μ = 0.067 mm^{-1}, F(000) = 1440, T = 100(2) K, R1 = 0.1029, wR2 = 0.1454, 8857 independent reflections [$2\theta \leq 56.7°$] (R_{int} = 0.0000) and 552 parameters.

(17) (a) Bartlett, R. A.; Power, P. P. *Organometallics* **1986**, *5*, 1916. (b) Olmstead, M. M.; Power, P. P.; Weese, K. J.; Doedens, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 2541. (c) Hoefelmeyer, J. D.; Solé, S.; Gabbaï, F. P. *Dalton Trans.* **2004**, 1254. (d) Chiu, C.-W.; Gabbaï, F. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 6878.

(18) (a) Maier, G. N.; Henkelmann, J.; Reisenauer, H. P. *Angew. Chem., Int. Ed.* **1985**, *24*, 1065. (b) Herberich, G. E.; Rosenplänter, J.; Schmidt, B.; Englert, U. *Organometallics* **1997**, *16*, 926.