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Reactions of Boron-Substituted N-Heterocyclic Carbene Boranes with Triflic Acid. Isolation of a New Dihydroxyborenium Cation

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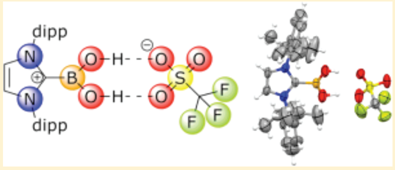
Supporting Information

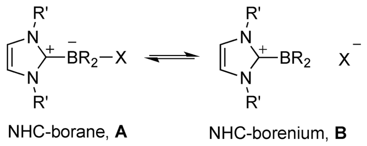
ABSTRACT: Reactions of NHC-BH_2X (where X = Cl, OTf and NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with 1 equiv of triflic acid provide the stable products of acid/base reactions NHC-$BH(OTf)_2$ and NHC-BH(OTf)Cl. Further reactions of these compounds with additional triflic acid (or direct reactions of NHC-BH_3 with excess triflic acid) produce the isolable dihydroxyborenium triflate $[NHC\text{-}B(OH)_2]^+TfO^-$. This first-in-class ligated borenium ion has been characterized by NMR spectroscopy and X-ray crystallography.



Tricoordinate boron cations $[L\text{-}BR_2]^+$ are commonly called borenium ions.[1] Formally, they are Lewis adducts of dicoordinate borinium cations (BR_2^+) and Lewis bases (L) such as amines, phosphines, and the so-called carbon(0) ligands.[2] Interest in borenium cations is growing because of their novel structures and their high reactivity as cationic Lewis acids[3] and electrophilic borylation agents.[4]

N-heterocyclic carbenes (NHC) have become popular ligands for the stabilization of unusual and otherwise unstable boron species, including borenium ions.[5,6] Most NHC-boranes bearing good leaving groups X on boron prefer structure **A**, with a tetracoordinate boron center and a covalent B–X bond (Figure 1).[7] Occasionally, when the groups R on boron are bulky or are capable of conjugation, the dissociation of **A** to planar, tricoordinate borenium form **B** becomes favorable because of steric destabilization of the tetracoordinate form **A**, electronic stabilization of the borenium center in **B**, or both.

a) NHC-boranes with leaving groups X usually exist in the tetracoordinate form **A** and rarely in the tricoordinate borenium form **B**



b) Known NHC-borenium ions **1–5** and a new dihydroxyborenium ion **6**

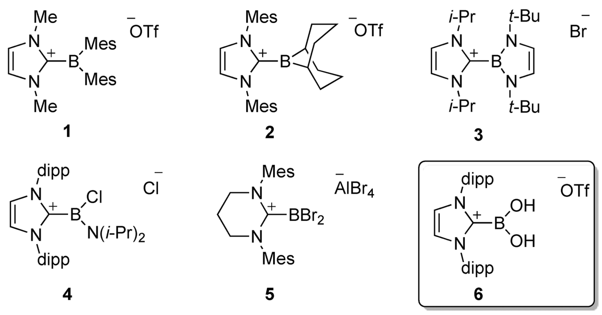


Figure 1. (a) General structures and (b) literature examples of NHC-borenium cations **1–5** along with the new borenium ion **6** (Mes = 2,4,6-trimethylphenyl; dipp = 2,6-diisopropylphenyl).

Five NHC-borenium cations with different boron substituents have been identified (Figure 1). Steric effects are likely responsible for the formation of Gabbaï's NHC-diarylborenium **1**[8] and Lindsay's NHC-dialkylborenium **2**.[9] Both steric and electronic effects account for the formation of Weber's NHC-diaminoborenium **3**,[10] Robinson's NHC-aminochloroborenium **4**,[6] and Aldridge's dibromoborenium ion **5**.[11]

The synthesis of NHC-boreniums **1–5** was achieved either by the direct substitution of X in R_2B-X by free NHC or by the treatment of NHC-BR_2–H with a strong acid H-X. These NHC-borenium ions all have amine–borenium analogues: $[DMAP\text{-}BMes_2]^+$,[12] $[Py\text{-}9\text{-}BBN]^+$,[13] $[Py\text{-}B(NR_2)_2]^+$,[14] the β-diketiminate-supported chloroborenium $[L\text{-}B(NR_2)Cl]^+$,[15] and $[2,6\text{-}diMes\text{-}Py\text{-}BBr_2]^+$.[11]

Here we describe the isolation and characterization of the new dihydroxyborenium cation **6**, $[NHC\text{-}B(OH)_2]^+TfO^-$. This cation lacks large groups R on boron, forms in an unusual way, and has no direct antecedent in other classes of ligated borenium ions.

The new borenium ion was discovered during a study of acid/base reactions of substituted NHC-boranes, as summarized in Scheme 1. Treatment of **7** with 1 equiv of triflic acid or HCl is known to provide monotriflate **8a** or monochloride **8b** in situ.[7] Reaction of **7** with 2.5 equiv of triflic acid provided the known but not previously isolated ditriflate **9a**.[7] This proved to be rather robust and was isolated in 54% yield after flash chromatography.

The reaction of NHC-BH_2Cl (**8b**) with TfOH (1.5 equiv) was quick and complete as well. NHC-BH(OTf)Cl (**9b**) was the only boron product observed in the reaction mixture by ^{11}B

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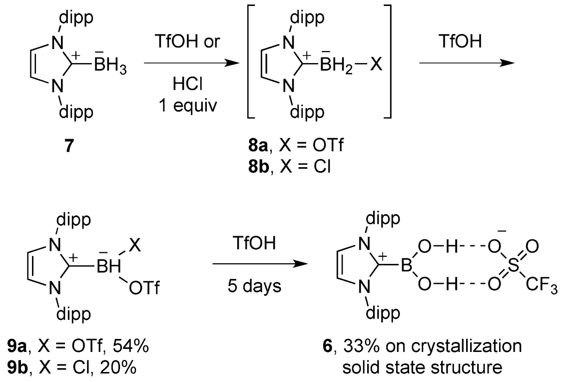
Scheme 1. Reactions of Boron Triflate 8a and Boron Chloride 8b with Additional Triflic Acid



NMR analysis (−3.1 ppm). This was less stable to moisture than **9a** and was isolated in 20% yield after flash chromatography. However, once isolated, **9b** can be handled under ambient laboratory conditions. The X-ray structure of compound **9b** is shown in the Supporting Information. Both **9a** and **9b** exist in the tetracoordinate form **A** in solution and in the solid state.

In an effort to replace the final "hydride" on the boron atom of these complexes by a third acid/base reaction, TfOH was added in excess (5 equiv) to either NHC-BH_3 (**7**) or NHC-BH_2Cl (**8b**) in $CDCl_3$. Quantitative formation of either NHC-$BH(OTf)_2$ (**9a**) or NHC-BH(OTf)Cl (**9b**) was again observed by ^{11}B NMR spectroscopy after 10 min. No signals attributable to NHC-$B(OTf)_3$ or NHC-$B(OTf)_2Cl$ were detected. However, keeping solutions of either **9a** or **9b** with an excess of TfOH at room temperature gave an even more interesting result. In both cases, there was slow formation over 5 days of the same new compound **6**.

The only signal in the ^{11}B NMR spectra of these crude products was a singlet at +22.5 ppm. This resonance is too far downfield for the expected tetracoordinate boron products and suggests instead a tricoordinate boron environment. The chemical shift of the triflate CF_3 signal in the ^{19}F NMR spectrum at −78.9 ppm is different from the resonances of triflates bound to the boron atom (−76.0 ppm in **8a** and **9a**,**b**) and is characteristic for the free TfO^- anion. Also, the product did not survive flash chromatography. Thus, the new product has the general structure $[NHC\text{-}BR_2]^+TfO^-$. But what is R, and how do the two different precursors give the same product? Crystallography answered these questions.

Colorless crystals of **6** (33% yield) were grown directly from the reaction mixture starting from **7** (see the Supporting Information). These crystals could be handled quickly in air, but the compound decomposed to the imidazolium triflate [NHC-H]OTf upon dissolution in Et_2O. X-ray crystallographic analysis established the structure of **6** as an NHC-dihydroxyborenium triflate. There are two similar molecules of **6** in the unit cell, and one of these is shown in Figure 2. The other is shown in Figure S1 of the Supporting Information.

The value of the N(1)−C(1)−N(2) angle (106.5°) lies between the values of this angle in NHC-BH_3 (**7**; 104.1°)[16] and in imidazolium chloride [NHC-H]Cl (107.7°).[17] The hydrogen atoms on the hydroxy groups of **6** were located, and they form hydrogen bonds with the triflate counterion to assemble an eight-membered ring with O−H···O bond distances of 2.681 and 2.780 Å. These H bonds serve to increase the stabilizing effect of the electron-donating hydroxy groups on the borenium ion.

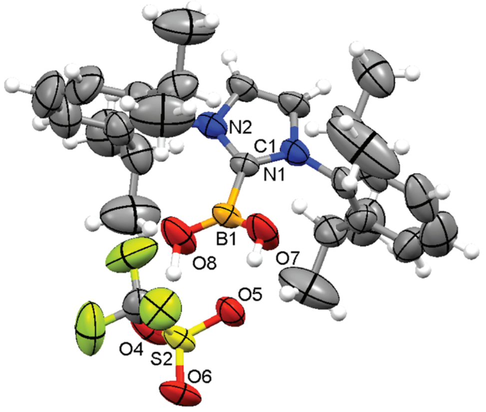
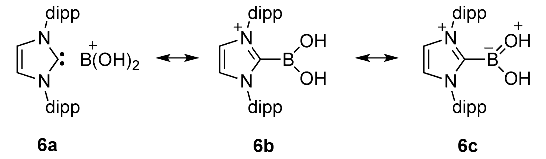


Figure 2. The X-ray crystal structure of $[NHC\text{-}B(OH)_2]OTf$ **6**. Selected distances (Å), angles (deg), and torsion angles: B(1)−C(1) 1.591(6), B(1)−O(7) 1.310(6), B(1)−O(8) 1.307(4), O(4)−S(2) 1.433(3), O(5)−S(2) 1.433(2), O(6)−S(2) 1.425(3), O(5)−O(7) 2.681(4), O(4)−O(8) 2.780(4), N(1)−C(1)−N(2) 106.5(2), C(1)−B(1)−O(7) 114.8(3), C(1)−B(1)−O(8) 117.0(3), O(7)−B(1)−O(8) 128.2(4); N(1)−C(1)−B(1)−O(7) 32.6(5).

We speculate that NHC-$BH(OH)_2$ might be an intermediate on the way from **9a**,**b** to **6**. This could be formed by hydrolysis with adventitious water. Further acid/base reaction of this intermediate with the excess triflic acid would then provide **6**.

The relative stability of amine−dihydroxyborenium ions $[H_3N\text{-}B(OH)_2]^+$ compared to that of other amine−borenium ions $[H_3N\text{-}BR_2]^+$ has been predicted by quantum calculations,[18] but stable ions in this dihydroxy class have yet to be described. The closest analogues to **6** are perhaps catecholborenium cations such as **10** and **11** ($[CatB\text{-}L]^+$, Figure 3), prepared and characterized by Stephan (L = $t\text{-}Bu_3P$),[19] Ingleson (L = NEt_3),[4b] and very recently Aldridge.[11]

a) resonance forms for **6**



b) comparables for **6**

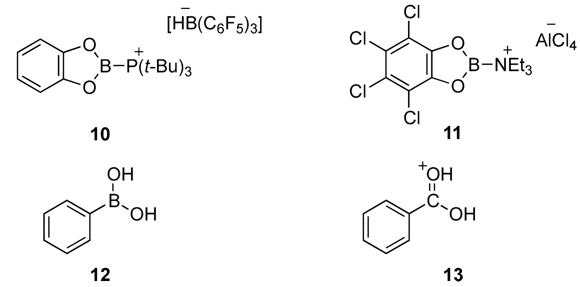


Figure 3. (a) Three of several resonance forms for **6** and (b) comparable species, including catecholborenium cations **10** and **11**, phenylboronic acid **12**, and protonated benzoic acid **13**.

The B−O distances (1.310 and 1.307 Å) in **6** are shorter than B−O bonds in catecholborenium cations **10** (1.350 Å)[19] and **11** (1.364 and 1.370 Å)[4b] or B−O bonds in $PhB(OH)_2$

(**12**; 1.37 Å)[20] and are significantly shorter than B−O bonds in NHC-BH_2OTs (1.522 Å)[7] and NHC-BH_2ONO (1.512 Å).[7] Apparently the B−O bonds in **6** have partial double-bond character, as reflected in resonance form **6c**. For comparison, the length of the B=O bond in a coordinated oxoborane (*β*-diketiminate)−B=O−$AlCl_3$ is 1.304(2) Å.[21]

We conclude that the borenium center in **6** is stabilized by the *π* donation of hydroxy groups in a manner analogous to the stabilization of borenium by two amine nitrogens, as in **3**. However, the diazaborole and NHC rings of **3** are orthogonal, while the torsion angle between the O−B−O plane and the plane of the NHC ring in **6** is about 30°. Thus, **6** benefits from additional conjugative stabilization across the two subunits (NHC and boron with its substituents) that is lacking in **3** and other NHC-borenium ions.

Moving farther afield, the NHC rings of NHC-borane reactive intermediates are sometimes compared to phenyl rings.[22] Therefore, **6** can be considered as a cationic analogue of the neutral phenylboronic acid ($PhB(OH)_2$). Because of the positive charge, $[NHC\text{-}B(OH)_2]^+$ must be a much stronger Lewis and Brønsted acid than $PhB(OH)_2$. The boron atom in **6** can further be replaced by a trivalent carbon atom; thus, **6** is a distant cousin of $[PhC(OH)_2]^+$, which is simply protonated benzoic acid.

In summary, acid/base reactions of NHC-BH_2X (X = Cl, OTf) provide the stable products NHC-BH(OTf)X. In the presence of triflic acid, these products slowly convert into $[NHC\text{-}B(OH)_2]^+TfO^-$. This borenium ion **6** was isolated and its ionic structure was established by spectroscopic and X-ray crystallographic methods. It is the first representative of a new class of borenium cation bearing two hydroxy groups on boron.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text and figures giving full experimental and compound characterization details and CIF files giving crystallographic data for all X-ray structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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