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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Weakly Stabilized Primary Borenium Cations and Their Dicationic Dimers

Aleksandrs Prokofjevs,[†] Jeff W. Kampf,[†] Andrey Solovyev,[‡] Dennis P. Curran,*[,‡] and Edwin Vedejs*[,†]

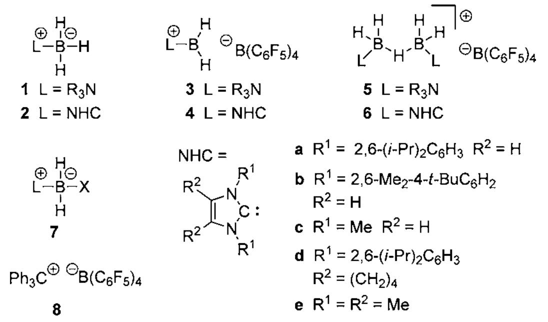
[†]Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, United States
[‡]Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States

Supporting Information

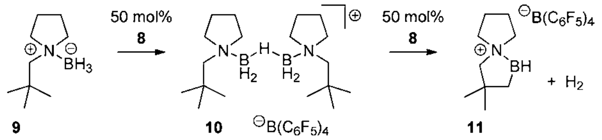
ABSTRACT: Hydride abstraction from monocationic hydride bridged salts $[H(H_2B{-}L)_2]^+$ $[B(C_6F_5)_4]^-$ (L = Lewis base) generates an observable primary borenium cation for L = iPr$_2$NEt, but with L = Me$_3$N, Me$_2$NPr, or several *N*-heterocyclic carbenes, highly reactive dicationic dimers are formed.

Borocations are accessible by activation of Lewis base−borane complexes with electrophiles.[1] Recent applications include aromatic or aliphatic C−H borylation and alkene hydroboration using activated reagents derived from amine boranes **1**[2,3] or *N*-heterocyclic carbene boranes (NHC boranes; **2**) (Scheme 1).[4,5] Both catalytic and stoichiometric activation methods were developed, but attempts to understand the stoichiometric activations encountered puzzling results. Thus, stoichiometric activation of typical **1** or **2** using strongly electrophilic "hydridophiles" was shown to generate transient species equivalent to the borenium cations **3** or **4**, but borenium intermediates were not detected. Instead, we observed intermediate cationic hydride-bridged "dimers" **5** or **6**,[6,7] apparently derived from a 3c2e interaction between the mostly empty borenium *p*-orbital and a nucleophilic B−H bond in the starting borane complex. In cases where nucleophilic anions were present, the tetracoordinate complexes **7** were observed instead of the borocations **5** or **6**. However, it soon became clear that additional activated intermediates would have to be considered.

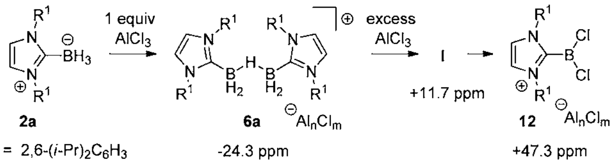
Scheme 1. Lewis Base Borane Complex Activation



In our recently reported example of activation using the trityl salt **8** as a hydridophile, amine borane **9** afforded a relatively stable H-bridged dimer **10** using 50 mol % of **8** (eq 1).[2a] No further reaction occurred over days at rt, but addition of a second 50 mol % portion of **8** to **10** resulted in facile (10 min, rt) conversion into the cationic borylation product **11**. Clearly, the final 1:1 stoichiometry of trityl salt **8** to **9** was responsible for greatly increased reactivity, but we could only speculate about the nature of the activating event(s) pending further evidence.

(1) 

Hints regarding the key activation process were obtained from several distinct directions, and the first important clue came from experiments with the NHC borane **2a**. Thus, treatment of **2a** with 1 equiv of AlCl$_3$ in CH$_2$Cl$_2$ (eq 2) gave the expected solution intermediate **6a** (^{11}B δ −24.3 ppm).[8] When the solution containing **6a** was treated with excess AlCl$_3$, a transient signal appeared at ^{11}B δ +11.7 ppm that was replaced by a dominant new signal at δ +47.3 ppm after 24 h at rt. Although neither the initial nor the final (relatively stable) solution species could be isolated, the dichloroborenium cation structure **12** for the final product was inferred from chemical shift comparisons with the analogous picoline-derived PicBCl$_2^+$ Al$_2$Cl$_7^-$ (δ +47.3 ppm).[9]

(2) 

The details of the presumed disproportionation leading to **12** were not investigated, but we were intrigued by the identity of the +11.7 ppm species (unknown **I**). This chemical shift is at least ca. 15 ppm downfield compared to any known, formally tetracoordinate NHC borane complex (NHC−BH$_2$X, **7** with L = NHC),[10] and suspicions inevitably turned to the borenium cation subunit of structure **4a**. However, this structure did not fit intuitive or computational chemical shift evaluations (see Supporting Information).

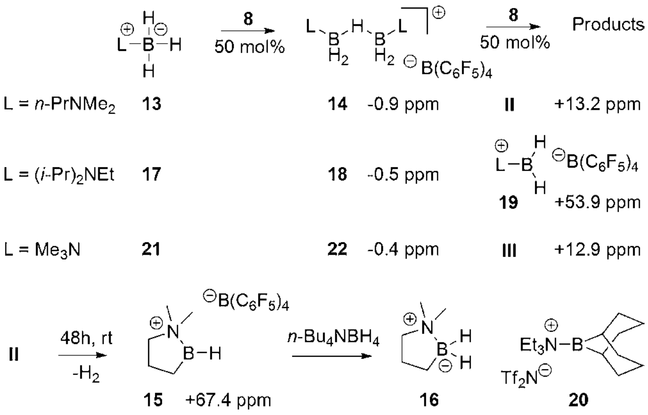
Additional clues were obtained by studying amine boranes under conditions (bromobenzene solution instead of CH$_2$Cl$_2$)

Received: July 19, 2013
Published: October 2, 2013

dx.doi.org/10.1021/ja407458k | *J. Am. Chem. Soc.* 2013, 135, 15686−15689

that afforded relatively long-lived activated intermediates. Thus, *N,N*-dimethylpropylamine borane **13** reacted with 50 mol % of trityl salt **8** in d_5-PhBr to give a stable solution of **14** (Scheme 2). Addition of a second 50 mol % of **8** not only drastically increased reactivity as usual but also afforded a transient ^{11}B signal at δ +13.2 ppm (unknown **II**), similar to the NHC-derived +11.7 ppm species (unknown **I**) mentioned above. Within 48 h at rt, the transient signals were almost entirely replaced by an H-coupled ^{11}B peak at δ +67.4 ppm. Along with observation of a very broad ^{1}H signal (1H) centered around 4.8 ppm, and by analogy with the cyclization of **9**, this species could be assigned as the secondary borenium cation **15**. The assignment is supported by reductive quenching with *n*-Bu$_4$NBH$_4$, which afforded ca. 80% of the borylation product **16**. These observations raise the possibility that the +13.2 ppm transient (unknown **II**) is an intermediate in the borylation. Although the time scale for survival of unknown **II** was quite long (hours at rt), the unknown could not be isolated.

Scheme 2. Amine Borane Activation

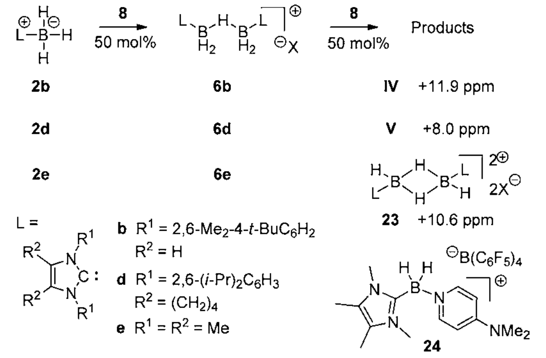


In an attempt to suppress internal borylation pathways and also to destabilize H-bridged intermediates, we explored activation of the hindered *N,N*-diisopropylethylamine borane **17**. Thus, treatment with 100 mol % of the trityl salt **8** in d_5-PhBr gave two new boron species (4:1 ratio after 5 min at rt) as evidenced by ^{11}B NMR assay. While the major new cationic product can be assigned as **18** (δ −0.5 ppm), the minor product (δ +53.9 ppm) is clearly a tricoordinate boron cation, tentatively assigned to the unprecedented nitrogen-bound primary borenium structure **19**.[11] This structure is also supported by the observation of a broad ^{1}H resonance near δ 4.8 ppm, typical for B−H resonances in tricoordinate boron cations.[12] Further characterization or isolation of **19** was precluded by rapid decomposition and formation of complex unidentified species within minutes at rt, not to mention partial degradation of the $[B(C_6F_5)_4]^-$ counterion over 2 h at rt according to ^{1}H and ^{19}F NMR data. Therefore, the structural assignment of **19** relies on comparisons with the known ^{11}B chemical shifts of nonstabilized, but more highly substituted borenium species including the tertiary cation **20** (δ +85.1 ppm in CD_2Cl_2)[2c] and the secondary cations **11** (δ +71.1 ppm in CD_2Cl_2, +69.5 ppm in d_5-PhBr) and **15** (δ +67.4 ppm in d_5-PhBr). Neglecting the structural differences between **20**, **11**, and **15**, replacement of a B-alkyl group by a hydrogen atom shifts the ^{11}B signal upfield by roughly 15 ppm. A comparable, additional upfield shift would be expected for the primary borenium cation **19**, qualitatively consistent with the observed chemical shift of +53.9 ppm. This value is also consistent with the ^{11}B chemical shift computed using the GIAO method (+55.8 ppm in PhBr).

Similar activation of trimethylamine borane **21** using 100 mol % of **8** in d_5-PhBr gave contrasting results (Scheme 2). Although the initially formed product at rt was the previously reported hydride-bridged dimer **22**,[6] formation of a second product (^{11}B δ +12.9 ppm; unknown **III**) occurred more slowly. After 24 h at rt, the ratio of unknown **III** to **22** reached 2.5:1, and decomposition occurred more slowly than in the experiments starting from **17**. Nevertheless, repeated efforts to isolate the highly sensitive unknown **III** by crystallization were not successful.

After a major effort in the amine borane series had encountered no example of an isolable species having the unexplained δ 11−13 ppm ^{11}B chemical shift, we opted to re-examine the NHC boranes. Activation of NHC−BH$_3$ complexes **2a−c** with 0.5 equiv of the trityl salt **8** predictably resulted in clean formation of solutions containing the H-bridged cations **6a−c**, respectively (X = $B[C_6F_5]_4$), with ^{11}B chemical shifts in the range of −22 to −25 ppm, ca. 10 ppm downfield compared to the starting **2a−c** (Scheme 3). Additionally, salt **6c** was prepared in a benzene suspension, isolated as a sensitive crystalline solid in 97% yield, and fully characterized by ^{1}H, ^{11}B, ^{13}C, and ^{19}F NMR spectroscopy.

Scheme 3. NHC Borane Activation



Subsequent addition of a second 50 mol % portion of **8** to the solution of **6b** resulted in another hydride abstraction event, producing additional Ph$_3$CH along with a new species having a ^{11}B NMR signal at δ +11.9 ppm (unknown **IV**), nearly identical to that (δ +11.7 ppm) observed initially for unknown **I** using AlCl$_3$ in the activation step (eq 2). Formation of the new product was rather slow, taking several hours at rt to reach completion. In contrast, a similar activation sequence starting from the more substituted NHC borane **2d** was quite fast, reaching full conversion of **6d** to a new product (^{11}B δ +8.0 ppm; unknown **V**) within 10 min at rt. Attempts to obtain X-ray quality crystals were not successful, but the improved reactivity of **2d** stimulated experiments with the analogous tetrasubstituted NHC borane **2e**.

The standard activation method from **2e** and trityl salt **8** afforded a finely divided solid having a solution ^{11}B chemical shift of δ +10.6 ppm, while activation with $Ph_3C^+ [HCB_{11}Cl_{11}]^-$ in PhF afforded single crystals suitable for X-ray crystallography. Two NHC subunits and two counterions were present, so the structure was clearly a dication. However, the boron atoms were disordered, and key features of the structure remained unresolved. On the other hand, the dicationic nature of the substance became obvious at this step and was also consistent with the limited solubility of the solid.

Finally, after a lengthy optimization study, activation of **2e** with Ph_3C^+ $Al_2Br_7^-$ in fluorobenzene afforded a relatively well behaved, but highly sensitive crystalline product that allowed acquisition of high quality X-ray diffraction data. Subject to the considerations discussed below, a definitive fit for the corresponding reactivity and X-ray data is the unprecedented dimeric hydride-bridged dication structure **23** ($X^- = Al_2Br_7^-$; Figure 1). By analogy, the standard activation procedure using **8** must afford a similar structure (**23** with $X^- = [B(C_6F_5)_4]^-$).

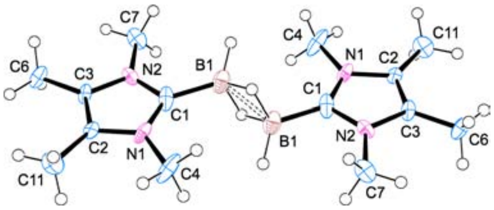
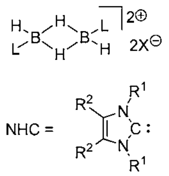


Figure 1. ORTEP plot of **23** ($X^- = Al_2Br_7^-$, the counterion has been omitted for clarity).

The X-ray structure of **23** conforms to the crystallographically imposed C_i symmetry, with the inversion center rendering both "NHC−BH_2^+" subunits equivalent. The same symmetry considerations define the mutually parallel orientation of the mean planes of both five-membered rings with interplane separation of 0.46 Å. Another bonding parameter of interest is the C−B bond distance of 1.58 Å, which is only marginally shorter than the corresponding C−B bond in the starting carbene borane **2e** (1.59 Å).[13] The crucial B···B distance in **23** is 1.78 Å and is essentially identical to B···B distances measured by X-ray crystallography in neutral RBH_2 dimers (1.78−1.79 Å)[14,15] as well as to the B···B distance in the parent B_2H_6 determined by electron diffraction (1.77 Å)[16] or X-ray methods (1.78 Å).[17] A substantially shorter B···B distance has been established for a structure containing a B−B bond (X-ray, 1.49 Å; neutron diffraction, 1.48 Å).[18] Hydrogens near the central boron atoms were located on difference Fourier maps and were allowed to refine isotropically as independent atoms. The exact location of the B−H hydrogens is uncertain due to their inherently low contribution to the electron density map. However, there can be little doubt that each boron retains two attached hydrogens, based on quenching studies described in the next paragraph, and no doubt that **23** has the indicated overall symmetry.

Addition of 4-dimethylaminopyridine to freshly generated **23** ($X = B[C_6F_5]_4$) as a suspension in bromobenzene afforded a homogeneous solution of the boronium salt **24** (^{11}B δ −14.7 ppm), identical to the fully characterized material prepared independently from **6e** (see Supporting Information). Furthermore, treatment of **23** with n-Bu_4NBH_4 resulted in clean conversion to the starting NHC borane **2e**. Finally, addition of **2e** to **23** afforded the monocationic **6e**. In each of these quenching experiments, a single product was formed exclusively according to NMR assay. This evidence provides strong support for the presence of an intact "NHC−BH_2^+" subunit in **23**, while the X-ray and ^{11}B chemical shift data support the dimeric, dicationic structure (GIAO computed chemical shift δ +10.8 ppm vs 10.6 ppm observed).

Based on the analogy of ^{11}B chemical shifts, all of the unknowns **I**−**V** can be assigned as the hydride bridged dicationic dimers with reasonable confidence (Figure 2), even though **23** is the only structure to be fully defined. Analogous hydride-bridged dications are known in transition metal chemistry,[19] but we could find no main group precedents for **23**. We did find diverse dicationic and tricationic boron-based structures,[20] but no hydride-bridged dimers potentially capable of dissociating into a primary borenium cation. In contrast, reversible dissociation is implicit for all of the species shown in Figure 2. Furthermore, the detection of a primary borenium monomer **19** under similar activation conditions indicates that the hydride bridged dimeric dications are thermodynamically more stable in most, but not all, of the cases studied.



I L = NHC, R^1 = 2,6-(i-Pr)$_2$C$_6$H$_3$ R^2 = H
II L = n-PrNMe$_2$
III L = Me$_3$N
IV L = NHC, R^1 = 2,6-Me$_2$-4-t-BuC$_6$H$_2$ R^2 = H
V L = NHC, R^1 = 2,6-(i-Pr)$_2$C$_6$H$_3$ R^2 = (CH$_2$)$_4$
23 L = NHC, R^1 = R^2 = Me

Figure 2. Proposed structures of unknowns **I**−**V**.

The balance between dimer and monomer depends on the interplay between steric and electronic factors. The monomeric borenium salt $[(Ph_3P)_2C{\rightarrow}BH_2]^+$ $[BH(C_6F_5)_3]^-$ isolated and characterized by Alcarazo et al. is stabilized by the sterically demanding Ph_3P subunits, as well as by σ and π donation from the carbon-bound ligand.[8a,21] In contrast, all of the NHC-derived (carbon-bound) borenium salts (Figure 2) prefer the unprecedented dicationic dimer structures (**I**, **IV**, **V**, **23**), presumably because of lower π donation from the NHC subunit. Analogous nitrogen-bound borocations are far more reactive due to minimal stabilizing factors and increased electron demand from the electronegative, cationic amine ligand. Thus, the dicationic dimer **II** was detected as a labile solution intermediate during the conversion of amine borane **13** into the cyclic borenium salt **15**, while the more hindered amine borane **17** was converted into an observable, but highly reactive primary borenium salt **19**. Apparently, **19** prefers the monomeric structure in part because steric repulsion between the isopropyl groups destabilizes the corresponding (undetected) dimeric dication.

Since the dimeric dication **23** is now proven to be an energy minimum, we assume that dicationic transition states are also possible. Thus, the direct interaction of **6e** with the trityl salt **8** becomes a plausible activation pathway leading to **23**.[22] The role of dication intermediates in the C−H borylation events also remains uncertain, but the options are more clear. The dissociation of dimeric dications into monomeric monocations followed by C−H insertion provides the simplest explanation, but the dimeric dications may already be sufficiently electrophilic for direct insertion into a C−H σ-bond.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental, X-ray crystallography data, NMR spectra, and computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

curran@pitt.edu
edved@umich.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Institute of General Medical Sciences, NIH (GM067146)

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