Cyclic boronium and borenium cations derived from borabenzene–pyridine complexes†

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A new class of boronium and borenium cations are prepared by reaction of pyridinium hydrochloride with pyridine stabilized borabenzene derivatives.

Cationic boron compounds are rare but important species in the chemistry of boron.[1] While stable, isolable examples are scarce, they are implicated as intermediates in several reactions including, possibly, ClSiMe₃ eliminating reactions that form pyridine adducts of borabenzene derivatives.[2] Given the growing importance of borabenzene and its derivatives as ligands in catalysis[3,4] and as components in materials for optoelectronic applications,[5] we decided to examine this aspect of borabenzene chemistry more closely.

While neutral borabenzene derivatives $C_5H_5B·L$ (L = py, PMe_3) typically react with nucleophiles to form isoelectronic anionic boratabenzene derivatives,[6] they are also susceptible to protic electrophilic attack at the α carbon atoms. This mode of reactivity has been exploited using neutral Brønsted acids like ROH or RNH_2 as an alternative route to boratabenzenes.[3d,7] We have found that use of cationic Brønsted acids, such as pyridinium salts $[C_5H_5NH]^+[A]^-$, provides a facile entry into a new family of cyclic four coordinate boronium and three coordinate borenium cations.

The chemistry described herein is depicted in Scheme 1. Pyridine adducts of borabenzene were used as synthons to prepare three and four coordinate boron cations. Reactions of pyridine borabenzenes **1a**[2] and **1b** with pyridinium hydrochloride at room temperature results in protonation of the B=C bond and addition of a second pyridine to the boron center to give colorless ionic compounds **2a,b** and **3a** in the case of the unsubstituted derivative. Isomers **2a** and **3a** were formed in a 1 : 1 ratio and no attempts were made to separate them. Boronium ions **2a,b** and **3a** are insoluble in hydrocarbons and give orange solutions when dissolved in dichloromethane. Their ¹¹B NMR spectra show singlets at ∼5 ppm for the 2,4 regioisomers and 0.4 ppm for the 2,5 regioisomer **3a**.

¹H NMR studies at variable temperatures suggest that the cationic species are in equilibrium with free pyridine and the neutral pyridine adducts of chloroboracyclohexadienes **4a,b** and **5a** *via* a chloride–pyridine exchange reaction. This equilibrium is probably responsible for the color change observed upon dissolution of colorless solids **2** and **3**. Dissociation of pyridine is suppressed by addition of excess pyridine or exchanging the
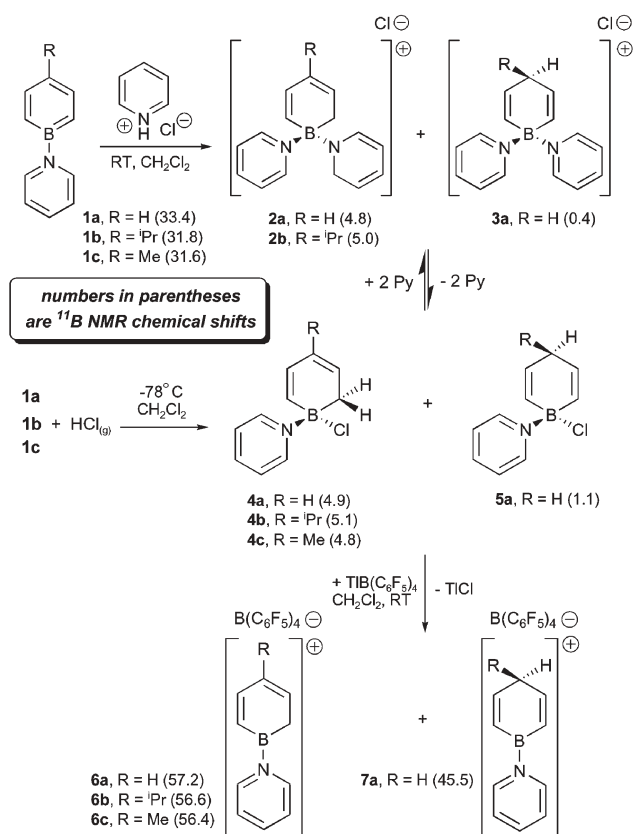
Scheme 1

chlorine anion for weakly coordinating $[B(C_6F_5)_4]^-$ *via* metathesis with $Tl[B(C_6F_5)_4]$.[8] Also, the equilibrium is shifted completely to the chloroboranes by trapping the free pyridine with the strong Lewis acid $B(C_6F_5)_3$.[9]

The neutral chloroboracyclohexadienes **4** and **5** can be generated in the absence of excess pyridine by treatment of precursors **1a–c** with HCl(g) in CH_2Cl_2 at −78 °C. The presence of tetracoordinate boron atoms in these adducts is demonstrated by their ¹¹B NMR spectra, which contain new signals at ∼5 ppm for the 2,4 regioisomers and 1.1 ppm for the 2,5 regioisomer **5a**. Notably, reaction of lutidine–borabenzene with HCl under the same conditions gave lutidine hydrochloride and chloroboracyclohexadiene, demonstrating the lability of the boron–pyridine linkage when substituents *ortho* to the pyridine nitrogen are incorporated. Solutions of **4a–c** and **5a**, in dichloromethane exhibit no ionization as evidenced by their ¹¹B and ¹H NMR spectra.

The absence of free pyridine allows for synthesis of cyclic three coordinate borenium cations **6a–c** and **7a** by treatment of **4a/5a** or

4b,c with $Tl[B(C_6F_5)_4]$.[8] This results in rapid chloride abstraction and partners the reactive borenium ions with the weakly coordinating $[B(C_6F_5)_4]^-$ anion. The ^{11}B NMR spectra of **6/7** contain singlets at ~ 57 ppm for the borenium cations and at ~ -17 ppm for the $B(C_6F_5)_4$ anions. Also, significant downfield shifts for the signals of both heterocyclic components of the molecules are observed in the ^{1}H NMR spectra after dehalogenation. ESI mass spectrometry (positive ion mode) confirmed molecular ions at $m/z = 156$, 198 and 170 for **6a**, **6b** and **6c**, respectively.

The molecular structures of **3a** and **4c** have been determined in order to establish their constitutions unambiguously and to study the influence of the positive charge on the boracyclohexadiene ring. Figs 1 and 2 show their molecular structures along with selected metrical data.

Despite the presence of sp^3 carbon and boron centers the boracyclohexadiene units are essentially planar. For example, only a small deviation from planarity is observed in the structure of **4c** with B(1) being situated 0.12 Å above the plane. The bonds within the boracyclic portion of the compounds indicate a localized π framework since the C–C bonds of the C_5B rings alternate between short (C(1)–C(2), C(4)–C(5) in **3a** and C(6)–C(7), C(8)–C(9) in **4c**) and long (C(2)–C(3), C(3)–C(4) in **3a** and C(7)–C(8), C(9)–C(10) in **4c**). The B–C bond lengths are typical for tetrahedral boron with the bonds of boron to sp^2 carbons (~ 1.58 Å) being shorter than that to the sp^3 carbon (B(1)–C(10) in **4c** = 1.614(4) Å).

The B–Cl bond length of 1.922(3) Å in **4c** is significantly longer than in boron trichloride–pyridine (1.835 Å)[10] or other tetra-coordinate boron chlorides and accounts for the increased tendency towards chloride ionization/abstraction observed at this bond.

All our attempts to grow single crystals of the three coordinate borenium cations **6/7** suitable for X-ray diffraction studies led to analyses that could not be refined satisfactorily possibly due to artifacts arising from crystal packing. Nonetheless, duplicate
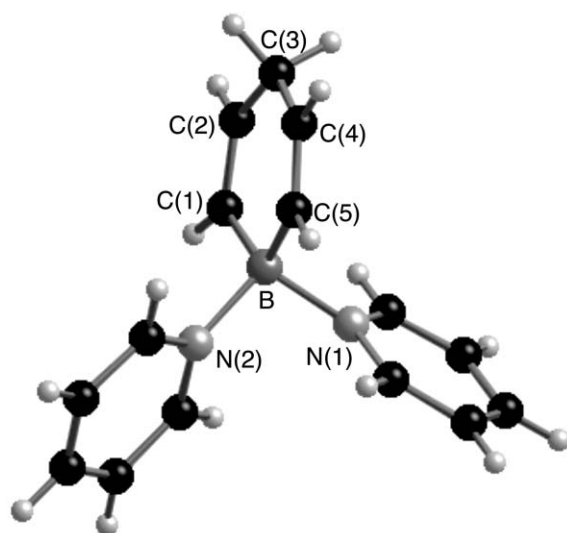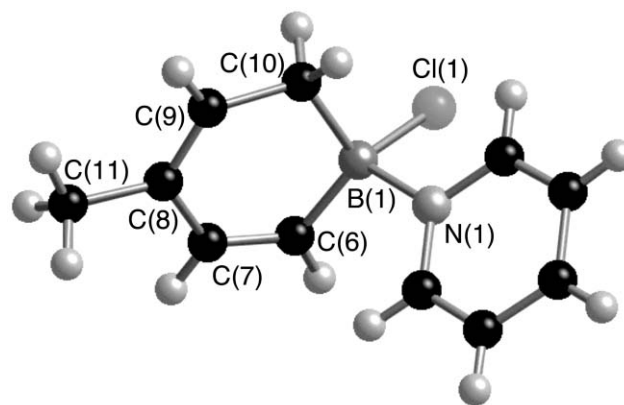

Fig. 2 Crystalmaker representation of **4c**. Selected bond lengths (Å): B(1)–N(1), 1.623(3); B(1)–Cl(1), 1.922(3); B(1)–C(6), 1.582(4); B(1)–C(10), 1.614(4); C(6)–C(7), 1.343(4); C(7)–C(8), 1.467(4); C(8)–C(9), 1.343(4); C(9)–C(10), 1.496(4). Selected bond angles (deg): N(1)–B(1)–Cl(1), 103.12(15); C(6)–B(1)–C(10), 112.9(2).

analyses of crystal samples of methyl substituted **6c** confirmed the assigned coordination number of three at boron and indicated that the boracycle and the pyridine rings were essentially co-planar.

While we have described these compounds as boronium (**2**, **3**) and borenium (**6**, **7**) ions, formal charge assignment to nitrogen would change the description to boracyclohexadiene substituted pyridinium salts and adducts thereof. Although the reality probably lies somewhere in between, assignment of a significant portion of the charge to the more electropositive boron is supported by computational studies on related borenium ions.[11] Furthermore, the behavior of compounds **6** and **7** as Lewis acids (these compounds react with pyridine to give the $[B(C_6F_5)_4]^-$ salts of **2** and **3**) demonstrates their boron cation character.

In conclusion, we have prepared a number of examples of a new class of boron cations, including rare examples of three coordinate borenium ions. There is a growing realization of the role these kinds of species play in catalysis[1b,12] and the borenium cations of the type reported herein may play a role in the synthesis of pyridine–borabenzene adducts **1**. Indeed, preliminary mechanistic studies indicate that intermediates with similar NMR signatures to compounds **6** appear *en route* to the pyridine adducts when larger *ortho* substituents are present in the pyridine reagent. For the synthesis of more complex derivatives of compounds **1**, it is important to determine the precise nature of these compounds and the factors that control their formation and equilibration with neutral analogs. Use of the weakly coordinating perfluoroarylborates provides an opportunity to study the chemistry of these elusive species in more detail; studies are continuing.‡

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Fig. 1 Crystalmaker representation of the cation of **3a**. Selected bond lengths (Å): B–N(1), 1.622(3); B–N(2), 1.609(3); B–C(1), 1.583(3); B–C(5), 1.588(3); C(1)–C(2), 1.339(3); C(2)–C(3), 1.439(4); C(3)–C(4), 1.450(4); C(4)–C(5), 1.318(3). Selected bond angles (deg): N(1)–B–N(2), 103.13(16); C(1)–B–C(5), 111.95(19); C(2)–C(3)–C(4), 118.1(2).

## Notes and references

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