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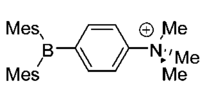
# Lewis Acidity Enhancement of Triarylboranes via Peripheral Decoration with Cationic Groups

Ching-Wen Chiu, Youngmin Kim, and François P. Gabbaï*

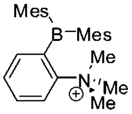
*Department of Chemistry, Texas A&M University, College Station, Texas 77843*

Received October 31, 2008; E-mail: francois@tamu.edu

The introduction of electron-withdrawing substituents in triarylboranes constitutes a well established method for enhancing their Lewis acidity. The success of this approach is nicely illustrated by the widespread use of fluorinated boranes as Lewis acids in both organic and organometallic chemistry.[1] As demonstrated by the properties of ferrocenium-boron compounds,[2] cationic substituents also exert a strong negative inductive effect which can be used to increase the Lewis acidity of the boron atom.

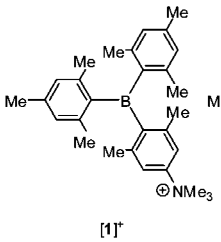


**[I]$^+$**

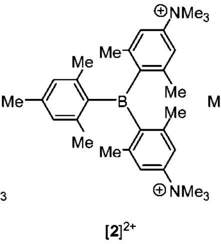


**[II]$^+$**

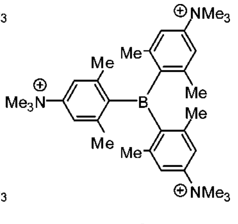
This strategy has also been applied to the case of triarylboranes[3] such as [$p$-$Mes_2B-C_6H_4-NMe_3$]$^+$ ([**I**]$^+$) and [$o$-$Mes_2B-C_6H_4-NMe_3$]$^+$ ([**II**]$^+$) which have been investigated for the complexation of fluoride and cyanide ions in aqueous media.[4] While neutral analogues of such boranes fail to capture fluoride or cyanide in aqueous solutions, we observed that [**I**]$^+$ and [**II**]$^+$ complex cyanide and fluoride, respectively, in aqueous solutions. These unusual properties demonstrate that the presence of a cationic group serves to enhance the Lewis acidity of the boron center. A question which remains unanswered is whether the introduction of multiple cationic groups would have additive effects on the electron deficiency and Lewis acidity of the boron center. To answer this question, we have decided to synthesize and study [**1**]$^+$, [**2**]$^{2+}$, and [**3**]$^{3+}$ which can be regarded as cationic analogues of trimesitylborane ($Mes_3B$).



**[1]$^+$**



**[2]$^{2+}$**



**[3]$^{3+}$**

***Scheme 1***[a]

$$Ar^NLi + Mes_2BF \xrightarrow{(a)} Ar^NBMes_2 \xrightarrow{(b)} [Ar^{N+}BMes_2]^+\ OTf^-$$

**[1]**OTf

$$MesLi + Ar^N{}_2BF \xrightarrow{(a)} Ar^N{}_2BMes \xrightarrow{(b)} [Ar^{N+}{}_2BMes]^{2+}\ 2OTf^-$$

**[2]**$OTf_2$

$$Ar^NLi + Ar^N{}_2BF \xrightarrow{(a)} Ar^N{}_3B \xrightarrow{(c)} [Ar^{N+}{}_3B]^{3+}\ 3OTf^-$$

**[3]**$OTf_3$

[a] (a) $Et_2O$, 25 °C. (b) MeOTf, $CH_2Cl_2$, 25 °C. (c) MeOTf, $CH_2Cl_2$/pyridine, 25 °C.

The salt [**1**]OTf was obtained by reaction of 1 equiv of $Ar^NLi$ ($Ar^N$ = 4-($Me_2N$)-2,6-$Me_2$-$C_6H_2$) with $Mes_2BF$ (Mes = mesityl) in $Et_2O$ followed by methylation with MeOTf (Scheme 1). Similarly, reaction of $Ar^N{}_2BF$[5] with MesLi and $Ar^NLi$ followed by methylation of the resulting boranes with MeOTf afforded [**2**]$OTf_2$ and [**3**]$OTf_3$, respectively (Scheme 1). The cationic boranes present in these salts are air- and moisture-stable, which possibly reflects the steric protection of the boron center by the six *ortho*-methyl groups. These salts have been characterized by $^1H$, $^{13}C$, and $^{11}B$ NMR spectroscopy as well as by elemental analysis. The $^{11}B$ NMR resonance of these new cationic boranes appear in the 83−89 ppm range, indicating the presence of a coordinatively unsaturated boron center. The $^1H$ NMR spectra confirm the presence of the trimethylammonium groups whose resonance can be detected in the 3.5−3.7 ppm range.

As recently shown by Norton and Jäkle who compared the reduction potential of $Mes_3B$, $Mes_2B(C_6F_5)$, and $MesB(C_6F_5)_2$ in THF,[6] the effects caused by the number of electron-withdrawing pentafluorophenyl groups are linearly additive and result in an increase of the reduction potential by ∼0.5 V per $C_6F_5$ groups.[6] Hoping to determine if the introduction of successive cationic [4-($Me_3N$)-2,6-$Me_2$-$C_6H_2$]$^+$ ($Ar^{N+}$) substituents would result in a similar additive effect, we have measured the reduction potential of $Mes_3B$,[6,7] [**1**]$^+$, [**2**]$^{2+}$, and [**3**]$^{3+}$ by cyclic voltammetry in $CH_3CN$ using a glassy carbon electrode and [$Bu_4N$][$PF_6$] (0.1 M) as a supporting electrolyte. The cyclic voltammograms of $Mes_3B$, [**1**]$^+$, and [**2**]$^{2+}$ show a reversible reduction wave at $E_{1/2}$ −2.57, −2.33, and −2.09 V vs Fc/Fc$^+$, respectively (Figure 1). By contrast, the CV of [**3**]$^{3+}$ features an irreversible reduction wave at $E_{peak}$ −1.86 V. Although it is unclear why this reduction is irreversible, a comparison of the peak potential of −2.63, −2.41, −2.16, and −1.86 V recorded for $Mes_3B$, [**1**]$^+$, [**2**]$^{2+}$, and [**3**]$^{3+}$, respectively, indicate that [**3**]$^{3+}$ is, as expected, the most electron-deficient derivative in the series. Remarkably, the reduction peak potential of the boranes shows a nearly linear dependence on the number of

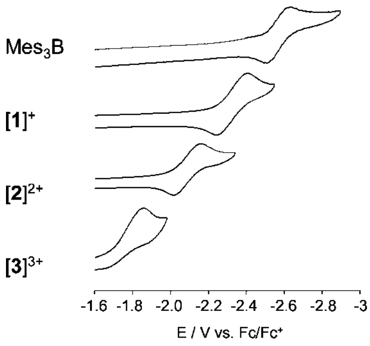


***Figure 1.*** Cyclic voltammograms of $Mes_3B$, [**1**]$^+$, [**2**]$^{2+}$, and [**3**]$^{3+}$ (1 mM) in MeCN with a glassy-carbon working electrode in 0.1 M of $nBu_4NPF_6$ solution with scan rate of $\nu$ = 300 mV s$^{-1}$.

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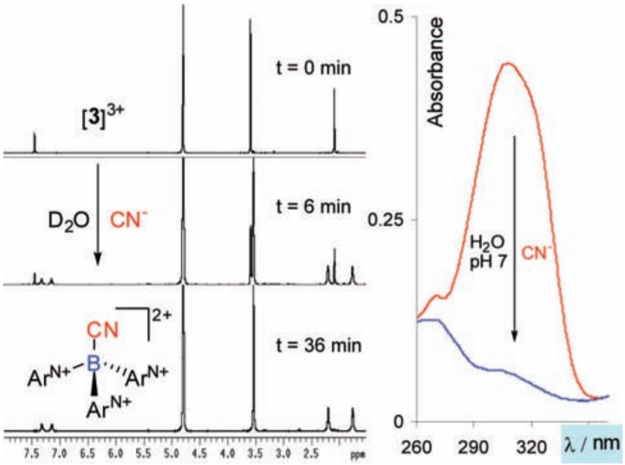

***Figure 2.*** Left: $^1$H NMR spectra of a sample of $[\mathbf{3}]^{3+}$ (14 mM) in $D_2O$ at 25 °C before ($t = 0$ min) and after addition of 2 equiv of KCN ($t = 6$ and 36 min). Right: Absorbance change of a solution of $[\mathbf{3}]^{3+}$ ($3.7 \times 10^{-5}$ M in $H_2O$; HEPES 9 mM, pH 7, $\epsilon([\mathbf{3}]^{3+}) = 12\,000$ $M^{-1}$ $cm^{-1}$) before (red line) and 1 h after addition of 10 equiv of KCN (blue line).

ammonium substituents. A least-squares analysis of these data shows that substitution of a Mes group by an $Ar^{N+}$ group leads to an increase of the reduction peak potential by 0.26 V. Similar measurements have been carried out in THF with $Mes_3B$, [**1**]OTf, and [**2**]$OTf_2$ but not [**3**]$OTf_3$ which is insoluble in this solvent. The resulting cyclic voltammograms show a reversible reduction wave at $E_{1/2} = -2.9$ V for $Mes_3B$, $-2.55$ V for $[\mathbf{1}]^+$, and $-2.19$ V for $[\mathbf{2}]^{2+}$, thus indicating that substitution of a Mes group by an $Ar^{N+}$ group leads to an increase of the reduction potential by 0.36 V in THF. This increment can be compared to the 0.5 V increase measured in THF for the $Mes_3B/Mes_2B(C_6F_5)/MesB(C_6F_5)_2$ series upon substitution of a mesityl group by a $C_6F_5$ group. From this comparison, it can be concluded that despite the presence of electron-releasing *ortho*-methyl groups, the electron-withdrawing properties of the $Ar^{N+}$ is ~70% that of a $C_6F_5$ group.

To better assess the effect caused by the introduction of multiple cationic moieties, we decided to investigate the use of these compounds for the complexation of small anions in water. Having established that only [**2**]$OTf_2$ (solubility <1 mM) and [**3**]$OTf_3$ (solubility = 17 mM) are soluble in pure water, we first studied their stability around neutral pH by monitoring the absorbance of the boron centered chromophore[8] measured at 308 nm for $[\mathbf{2}]^{2+}$ and at 307 nm for $[\mathbf{3}]^{3+}$. For each of these cations, the value of the absorbance remained unchanged between pH 6 and 8, indicating the absence of any decomposition. Next, we studied their $^1$H NMR spectra in the presence of KF and KCN. These experiments showed that neither $[\mathbf{2}]^{2+}$ or $[\mathbf{3}]^{3+}$ binds fluoride ions in pure water. The high hydration of the fluoride anion and the steric protection provided by the six *ortho*-methyl groups to the boron center are most likely responsible for this lack of reactivity. The dication $[\mathbf{2}]^{2+}$ also failed to react with cyanide under similar conditions. However, cyanide ion complexation was observed in the case of $[\mathbf{3}]^{3+}$ which was converted into $[\mathbf{3}\text{-CN}]^{2+}$ (Figure 2). Acidification of the solution does not lead to dissociation of $[\mathbf{3}\text{-CN}]^{2+}$ thus suggesting that its formation is irreversible. The contrasting behaviors of $[\mathbf{2}]^{2+}$ and $[\mathbf{3}]^{3+}$ underscore the dramatic effects caused by the increase in the number of cationic groups. The adduct $[\mathbf{3}\text{-CN}]^{2+}$ has been characterized by multinuclear NMR spectroscopy, and its structure studied computationally using DFT methods (see Supporting Information). The presence of a tetrahedral boron center was confirmed by the detection of a peak at −12.6 ppm in the $^{11}$B NMR spectrum.[4] In the $^1$H NMR spectrum, the *ortho*-methyl groups are detected as two singlets of equal intensity at 1.76 and 2.20 ppm. Similarly, the aromatic CH groups are detected as two singlets of equal intensity at 7.14 and 7.32 ppm. These observations show that $Ar^{N+}$ groups do not freely rotate about the B−C bonds. The IR spectrum features an intense band at 2172 $cm^{-1}$ confirming the presence of a boron-bound cyanide ion.[4] We have also studied this reaction at pH 7 (HEPES, 9 mM) by UV−vis spectroscopy. Addition of cyanide to this solution results in the progressive quenching of the absorbance at 307 nm indicating cyanide binding to the boron center (Figure 2). This reaction proceeds smoothly and is complete within 1 h when 10 equiv of cyanide are added to a $3.7 \times 10^{-5}$ M solution of $[\mathbf{3}]^{3+}$. Kinetic studies indicate that the second-order rate constant for this reaction is equal to 2.2 (±0.1) $M^{-1}$ $s^{-1}$. Finally, we note that $[\mathbf{3}]^{3+}$ is highly selective for cyanide and fails to react with $F^-$, $Cl^-$, $Br^-$, $I^-$, $OAc^-$, $NO_3^-$, $H_2PO_4^-$, and $HSO_4^-$.

In conclusion, we show that the electron deficiency and Lewis acidity of triarylboranes can be incrementally enhanced through peripheral decoration of the aryl ligands with cationic groups. This strategy provides control over the redox properties of these compounds. This approach can also be used to increase the anion affinity and water solubility of the boranes. These last effects are best illustrated by the behaviors of $[\mathbf{3}]^{3+}$ which complexes cyanide anions in pure water. Accordingly, polycationic boranes such as $[\mathbf{3}]^{3+}$ could become useful for the development of water compatible chemosensors for the highly toxic cyanide anion.[9]

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**Supporting Information Available:** Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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