Lewis acidity enhancement of organoboranes *via* oxidation of appended ferrocene moieties†

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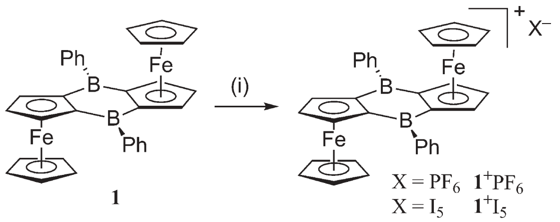
Received (in Berkeley, CA, USA) 8th February 2007, Accepted 10th April 2007
First published as an Advance Article on the web 1st May 2007
DOI: 10.1039/b701807j

The Lewis acidity of boron in diboradiferrocene 1 is strongly enhanced through oxidation of the iron atoms as evident from examination of X-ray structural parameters of the mixed-valent cation 1^+PF_6 and further confirmed from the strong complexation of MeCN to the dication in $2^{2+}(I_3)_2$.

Highly Lewis acidic organoboranes play key roles as sensor materials for nucleophiles, catalysts in organic and organometallic synthesis, and as activators in polymerization reactions.[1,2] One of the challenges has been to increase the Lewis acidity of the boranes, and thus to further improve their performance. In pursuit of this goal, the most widely applied method is the modification of aliphatic or aromatic side groups with electron-withdrawing fluorine substituents.[2,3] For instance, the Lewis acid strength of tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, has been shown to be in the same range as that of BF_3, and thus much higher than that of $B(C_6H_5)_3$.[2,3] In addition, various examples of bidentate[4] and polyfunctional[5] organoboranes have been reported, and the incorporation of boron into strained cyclics[6] or anti-aromatic ring-systems[7] has also been demonstrated, in some cases, to increase the binding strength. In a different approach, Gabbaï and Chiu,[8] and Kawashima *et al.*[9] demonstrated recently the strong binding affinity of boranes in the presence of covalently linked ammonium or phosphonium ions. We describe here an alternative method for the Lewis acidity enhancement of triarylboranes that takes advantage of the reversible oxidation of directly appended metallocene moieties.[10]

We have recently discovered the formation of the diboradiferrocene **1** (Scheme 1) through an unusual rearrangement reaction from 1,1′-distannylferrocene.[11] Cyclic voltammetry measurements provided evidence for two reversible oxidations that were attributed to changes in the oxidation states of the two iron centers from Fe(II) to Fe(III). We have also demonstrated from X-ray crystallography that the mixed-valent species $\mathbf{1}^+I_5$, which is obtained upon treatment of **1** with excess iodine, shows a valence-detrapped structure in the solid state.[11] Mössbauer studies further suggest that $\mathbf{1}^+I_5$ is delocalized on the Mössbauer timescale ($\sim 10^7$–$10^9\ s^{-1}$) in the solid state.[12] However, the low solubility of $\mathbf{1}^+I_5$ in non-coordinating solvents and the facile loss of I_2 prevented detailed studies on the solution properties of $\mathbf{1}^+I_5$.



Scheme 1 Synthesis of complexes $\mathbf{1}^+X$. (i) Excess I_2 or 1 equiv. $AgPF_6$ in CH_2Cl_2.

To gain further insight into the properties of the mixed-valent cation $\mathbf{1}^+$, we performed the oxidation of **1** with $AgPF_6$ in CH_2Cl_2 and isolated the PF_6 salt as a brown solid in 70% yield (Scheme 1).‡ A broad signal was observed in the ^{11}B NMR spectrum at 49.7 ppm, which is slightly upfield shifted compared to the neutral species (δ 57.7), an effect that is likely a result of the paramagnetic shift exerted by the oxidized ferrocene moiety. Only one set of ^1H NMR signals was observed for $\mathbf{1}^+PF_6$ in $CDCl_3$, with three averaged peaks at δ 21.1 (free-Cp), 19.4 (Cp-4) and 15.2 (Cp-3,5) that correspond to the ferrocene moieties (ferrocene: δ 4.0; ferrocenium: δ 31) and three signals at δ 3.78, 3.25, 2.92 for the phenyl groups, consistent with fast electron transfer on the NMR time scale in solution. Moreover, the near-IR spectrum of $\mathbf{1}^+PF_6$ in CH_2Cl_2 shows a broad intervalence charge transfer (IVCT) band at 1543 nm, indicative of rapid charge transfer between two localized states and thus consistent with Robin and Day Class II behavior.[13,14]

An X-ray structure analysis was performed on single crystals of $\mathbf{1}^+PF_6$ obtained from a $CHCl_3$–hexanes mixture, and the molecular structure of one of two independent molecules of $\mathbf{1}^+PF_6$ is shown in comparison to that of $\mathbf{1}^+I_5$ in Fig. 1.§ The structural features of the two molecules of $\mathbf{1}^+PF_6$ were found to be similar, but surprisingly different from those of $\mathbf{1}^+I_5$. Most notably, for each molecule one ferrocene moiety shows a longer Cp_{cent}–Cp_{cent} distance ($\mathbf{1}^+PF_6$-1: 3.411(1) Å; $\mathbf{1}^+PF_6$-2: 3.396(1) Å), which is

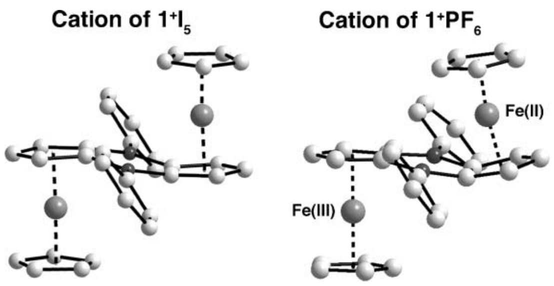


Fig. 1 Comparison of the structures of $\mathbf{1}^+I_5$-2 and $\mathbf{1}^+PF_6$-2. Only one of two independent molecules in the unit cell is shown, and the counterions, solvent molecules, and hydrogen atoms are omitted for clarity.

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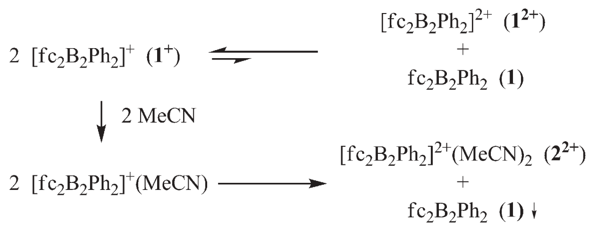
† Electronic supplementary information (ESI) available: Experimental methods, comparison of X-ray data, and ORTEP plots for all X-ray structures. See DOI: 10.1039/b701807j

indicative of iron in the +3 oxidation state, and one that is shorter ($\mathbf{1}^+PF_6$-1: 3.302(1) Å; $\mathbf{1}^+PF_6$-2: 3.306(1) Å) and thus consistent with Fe in the +2 oxidation state.[15] These observations are in stark contrast to the structural data of the two independent molecules of $\mathbf{1}^+I_5$, where the Cp_{cent}–Cp_{cent} distances for the two molecules of $\mathbf{1}^+I_5$ were found to be 3.355(1) and 3.357(2) Å, respectively, intermediate between those of **1** (3.308(1) Å) and typical oxidized ferrocenes (*ca.* 3.4 Å). Thus, while $\mathbf{1}^+I_5$ is valence-detrapped according to the X-ray analysis, the positive charge in $\mathbf{1}^+PF_6$ clearly is localized on one ferrocene moiety. The dissimilar behavior with different counterions can be traced back to differences in the symmetry, where both molecules of $\mathbf{1}^+I_5$ lie about a crystallographic inversion center, which in turn requires the ferrocene moieties to be identical. In contrast, the molecules $\mathbf{1}^+PF_6$-1 and $\mathbf{1}^+PF_6$-2 show no inversion symmetry and the distances to the anions, though long in all cases, are different for the two halves of the molecules. Similar anion and symmetry effects have been reported for a number of mixed-valent species derived from biferrocenes.[16]

The difference in oxidation state of the two iron centers has major consequences on the molecular conformation of $\mathbf{1}^+PF_6$. It is most instructive to compare the tilting between the substituted Cp rings and the central C_4B_2 ring that forms the double-bridge between the two ferrocene moieties. In highly Lewis acidic neutral ferrocenylboranes tilting of the borane group toward Fe is commonly observed and has been determined by Wagner and Holthausen *et al.* to be due to a delocalized interaction through the Cp ring, rather than due to direct orbital overlap between the electron-rich Fe atom and the electron-deficient boron atom.[17] For neutral **1**, the Cp//C_4B_2 interplanar angle was determined to be 15.9° and for the two independent valence delocalized molecules of $\mathbf{1}^+I_5$ similar values of 13.8° and 16.5° were determined; due to the inversion center, the angle is identical for both ferrocenes in each molecule. In contrast, the tilt angle for the ferrocenyl group in $\mathbf{1}^+PF_6$ differs from that of the ferricenyl moiety. For the oxidized ferricenyl group a relatively small angle was found ($\mathbf{1}^+PF_6$-1: 8.7(2)°; $\mathbf{1}^+PF_6$-2: 12.5(2)°), whereas the angle for the neutral ferrocenyl group ($\mathbf{1}^+PF_6$-1: 22.6(2)°; $\mathbf{1}^+PF_6$-2: 19.0(2)°) is even larger than that in **1**. As expected based on the bending angles for the boryl groups, the distances from boron to Fe(II) (2.869 to 2.885 Å) are considerably shorter than those to the Fe(III) centers (3.100 to 3.173 Å) in $\mathbf{1}^+PF_6$ and also shorter than those in **1** (2.957 Å). We attribute these effects to (i) strongly diminished interaction of Fe(III) of the ferricenyl moiety with the boron centers and (ii) enhanced interaction of Fe(II) of the ferrocenyl group with the boron centers. The latter is highly intriguing in that it provides strong evidence that the boron centers in $\mathbf{1}^+PF_6$ become more electron-deficient due to the presence of an oxidized ferricenyl moiety. These results are in excellent agreement with theoretical studies by Wagner and Holthausen *et al.* on the structural and electronic effects of oxidation of $FcBH_2$, which they predicted to lead to a decrease in the dip angle for the boryl group from 25.1 to 5.0° and a reduction of electron density not only at Fe but also B.[17]

To further investigate the apparent Lewis acidity enhancement of boron in the oxidized diboradiferrocene, we studied the complexation with nucleophiles. The neutral molecule **1** coordinates only weakly to pyridine and does not bind to MeCN.[18] However, when we treated $\mathbf{1}^+I_5$ with excess MeCN, the solution color turned from brown to green and a red precipitate formed.‡



Scheme 2 Disproportionation of $\mathbf{1}^+$ in acetonitrile.

The latter was filtered off and identified from ^1H NMR data as the neutral, non-coordinated species **1**. From the supernatant the MeCN complex $\mathbf{2}^{2+}(I_3)_2$ was isolated by recrystallization from MeCN as a dark green crystalline solid in 88% yield (Scheme 2).[19] It is noteworthy that $\mathbf{2}^{2+}$ can be obtained as the sole product upon addition of excess iodine or another oxidant.

Coordination of MeCN to $\mathbf{2}^{2+}(I_3)_2$ in solution is evident from the ^{11}B NMR signal at δ −0.2 ($\mathbf{1}^+PF_6$: δ 49.7), in a region typical of tetracoordinate boron species. Moreover, oxidation of both ferrocenes is reflected in a downfield shift of the Cp resonances to δ 32.5 ($\mathbf{1}^+PF_6$: δ 21.1). The crystal structure of $\mathbf{2}^{2+}(I_3)_2$ shows the cation lying about an inversion center (Fig. 2).§ The Cp_{cent}–Cp_{cent} distances of 3.414(2) Å are consistent with Fe(III) centers and, as expected for a tetracoordinate boron complex, the Cp//C_4B_2 angles of 2.4° are small. Most intriguingly, the relatively short B–N distance of 1.594(6) Å indicates strong binding of MeCN in the dication $\mathbf{2}^{2+}$. Similar B–N distances of 1.610(3) Å[20] and 1.616(3) Å[21] were reported by two different groups for the complex of MeCN with the fluorinated Lewis acid $B(C_6F_5)_3$. The C–N bond length of 1.122(7) Å for the bound MeCN in $\mathbf{2}^{2+}(I_3)_2$ is slightly shortened relative to that of a cocrystallized unbound molecule of MeCN with 1.163(10) Å (literature value for free MeCN: 1.141(2) Å[21]) and in a similar range as that of $(C_6F_5)_3B\cdot MeCN$ (1.124(3) Å).[21] While the relatively large standard deviations for the structure of $\mathbf{2}^{2+}(I_3)_2$ do not permit more detailed discussions, the IR data further support strong binding of MeCN. The C–N stretch at 2345 cm^{-1} in the IR spectrum of $\mathbf{2}^{2+}(I_3)_2$ is

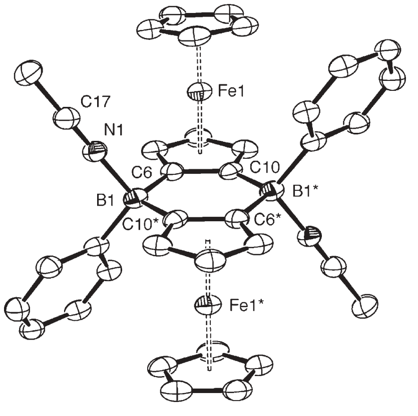


Fig. 2 ORTEP plot of $\mathbf{2}^{2+}(I_3)_2$. The I_3^- counterions and MeCN solvent molecules are omitted for clarity. The asterisks indicate atoms in equivalent positions (1 − *x*, 1 − *y*, 2 − *z*). Selected interatomic distances (Å) and angles (°) for $\mathbf{2}^{2+}(I_3)_2$: B1–C6 1.607(8), B1–C10* 1.626(8), B1–N1 1.594(6), B1–C11 1.617(7), C17–N1 1.122(7), C6–B1–N1 109.1(4), N1–B1–C10* 105.4(4), N1–B1–C11 106.7(4), C6–B1–C10* 110.7(4), C6–B1–C11 112.3(4), C10*–B1–C11 112.3(4), Cp_{cent}–C6–B1 175.6(1), Cp_{cent}–C10–B1* 177.6(1), Cp_{cent}–Cp_{cent} 3.414(2), Cp//Cp 5.8, Cp//C_4B_2 2.4.

only slightly lower than those of $(C_6F_5)_3B{\cdot}MeCN$ (2367 cm^{-1})[21] and $Br_3B{\cdot}MeCN$ (2362 cm^{-1}).[22] Importantly, the band is considerably shifted relative to the cocrystallized free MeCN (2246 cm^{-1}). A new band at 727 cm^{-1} is also observed, which from comparison to that of $Br_3B{\cdot}MeCN$ (715 cm^{-1})[22] is tentatively assigned to the B–N stretch.

In conclusion, oxidation of one of the iron centers in diboradiferrocene (**1**) leads to a mixed-valent species that, depending on the counterion, is valence delocalized or trapped in the solid state. The structural features of valence trapped $\mathbf{1}^+PF_6$ provide direct evidence that a ferricenyl group acts as a strongly electron-withdrawing substituent on boron. The enhanced Lewis acidity is further reflected in the facile binding of MeCN, with formation of the dioxidized species $\mathbf{2}^{2+}$, which shows spectroscopic and crystallographic features that are consistent with strong Lewis acid–base interactions. Further studies on the use of oxidized diboradiferrocenes as anion sensors and Lewis acid catalysts are in progress.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. FJ thanks the Alfred P. Sloan Foundation for a research fellowship and the National Science Foundation for a CAREER award. Funding for an X-ray diffractometer was provided by NSF (CRIF 0443538). We are grateful to Prof. Mendelsohn, Dr Carol Flach and Guojin Zhang for acquisition of IR data of compound $\mathbf{2}^{2+}(I_3)_2$ and to Prof. Lalancette and A. Doshi for helpful discussions.

Notes and references

‡ **Oxidation of 1 with $AgPF_6$**: to a solution of **1** (100 mg, 0.184 mmol) in CH_2Cl_2 (6 mL) was added $AgPF_6$ (46.4 mg, 0.184 mmol) in CH_2Cl_2 (3 mL) at −35 °C. The mixture was stirred at RT for 10 min, filtered, and the solvent removed under vacuum to give a crystalline brown solid. Yield: 111 mg (70%). X-Ray quality crystals were grown from a mixture of $CHCl_3$ and hexanes at −35 °C. ^1H NMR (500 MHz, $CDCl_3$, 25 °C) δ 21.1 (br, 10H, free-Cp), 19.4 (br, 2H, Cp-4), 15.2 (br, 4H, Cp-3,5), 5.31 (CH_2Cl_2), 3.78, 3.25, 2.92 (br, 10H, Ph). ^{11}B NMR (160 MHz, CD_2Cl_2, 25 °C) δ 49.7 ($w_{1/2}$ = 1600 Hz). UV-Vis (CH_2Cl_2, 2.60×10^{-3} M): λ_{max} = 1543 nm (ε = 330 M^{-1} cm^{-1}). Calcd for $C_{32}H_{26}B_2Fe_2PF_6{\cdot}2CH_2Cl_2$: C 47.56, H 3.52; found C 48.20, H 3.74%.

Binding of acetonitrile to $\mathbf{1}^+I_5$: synthesis of $\mathbf{2}^{2+}(I_3)_2$: MeCN (5 mL) was added to $\mathbf{1}^+I_5$ (34.3 mg, 29.1 μmol) at RT and the mixture stirred for 30 min. The color of the solution turned green with a red precipitate that was identified as **1** from ^1H NMR data (yield: 2.3 mg, 87%). The solution was filtered, the volume reduced to 2 mL, and the mixture kept for crystallization at −35 °C. Yield $\mathbf{2}^{2+}(I_3)_2(MeCN)_2$: 31.4 mg (88%). X-Ray quality crystals were grown by recrystallization from MeCN at −35 °C. ^1H NMR (500 MHz, CD_3CN, 25 °C) δ 32.5 (br, Cp), 5.42, 4.71, −3.32 (br, Ph), 1.94 (MeCN). ^{11}B NMR (160 MHz, CD_3CN, 25 °C) δ −0.2 ($w_{1/2}$ = 640 Hz). UV-Vis (MeCN, 3.29×10^{-4} M): λ_{max} (nm) = 553 (ε = 760 M^{-1} cm^{-1}), 644 (ε = 920 M^{-1} cm^{-1}). IR (KBr): ν (cm^{-1}) = 2345 (CN, bound MeCN), 2246 (CN, free MeCN), 727 (B–N). Calcd for $C_{36}H_{32}B_2Fe_2I_6N_2{\cdot}2MeCN$: C 32.69, H 2.61, N 3.81; found C 32.46, H 2.27, N 3.62%.

§ **Crystallographic data**: $\mathbf{1}^+PF_6{\cdot}2CHCl_3$, CCDC 635884: $C_{34}H_{28}B_2Cl_6F_6Fe_2P$, M = 927.55, T = 100(2) K, monoclinic, $P2_1/c$, a = 18.5711(3), b = 25.9704(4), c = 15.3244(3) Å, β = 100.0530(10)°, V = 7277.5(2) Å^3, Z = 8, μ = 11.374 mm^{-1}, R_{int} = 0.0493, $R1$ = 0.0513, w$R2$ = 0.1220 ($I > 2\sigma(I)$). $\mathbf{2}^{2+}(I_3)_2{\cdot}2MeCN$, CCDC 635885: $C_{40}H_{38}B_2Fe_2I_6N_4$, M = 1469.46, T = 100(2) K, monoclinic, $P2_1/c$, a = 11.7183(9), b = 8.9579(7), c = 21.3539(15) Å, β = 92.612(4)°, V = 2239.2(3) Å^3, Z = 2, μ = 37.924 mm^{-1}, R_{int} = 0.0353, $R1$ = 0.0455, w$R2$ = 0.1172 ($I > 2\sigma(I)$). For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b701807j

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