

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

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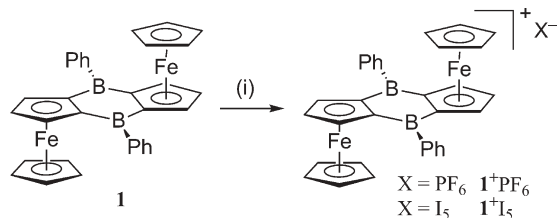
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The Lewis acidity of boron in diboradiferrocene **1** is strongly enhanced through oxidation of the iron atoms as evident from examination of X-ray structural parameters of the mixed-valent cation 1^+PF_6 and further confirmed from the strong complexation of MeCN to the dication in $2^{2+}(\text{I}_3)_2$.

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, $\text{B}(\text{C}_6\text{F}_5)_3$, has been shown to be in the same range as that of BF_3 , and thus much higher than that of $\text{B}(\text{C}_6\text{H}_5)_3$.^{2,3} In addition, various examples of bidentate⁴ and polyfunctional⁵ organoboranes have been reported, and the incorporation of boron into strained cyclics⁶ or anti-aromatic ring-systems⁷ has also been demonstrated, in some cases, to increase the binding strength. In a different approach, Gabbai 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



Scheme 1 Synthesis of complexes 1^+X . (i) Excess I_2 or 1 equiv. AgPF_6 in CH_2Cl_2 .

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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 1^+I_3 , which is obtained upon treatment of **1** with excess iodine, shows a valence-trapped structure in the solid state.¹¹ Mössbauer studies further suggest that 1^+I_3 is delocalized on the Mössbauer timescale ($\sim 10^7$ – 10^9 s⁻¹) in the solid state.¹² However, the low solubility of 1^+I_3 in non-coordinating solvents and the facile loss of I_2 prevented detailed studies on the solution properties of 1^+I_3 .

To gain further insight into the properties of the mixed-valent cation 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 ¹¹B 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 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 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 1^+PF_6 obtained from a CHCl_3 –hexanes mixture, and the molecular structure of one of two independent molecules of 1^+PF_6 is shown in comparison to that of 1^+I_3 in Fig. 1.§ The structural features of the two molecules of 1^+PF_6 were found to be similar, but surprisingly different from those of 1^+I_3 . Most notably, for each molecule one ferrocene moiety shows a longer Cp_{cent} – Cp_{cent} distance (1^+PF_6 -1: 3.411(1) Å; 1^+PF_6 -2: 3.396(1) Å), which is

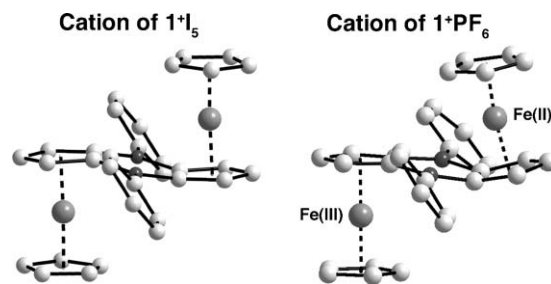
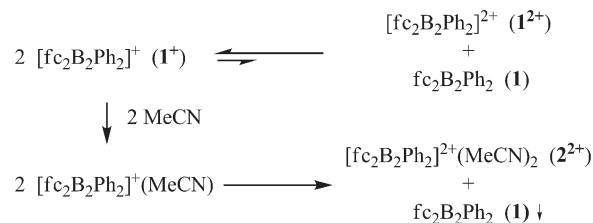


Fig. 1 Comparison of the structures of 1^+I_3 -2 and 1^+PF_6 -2. Only one of two independent molecules in the unit cell is shown, and the counterions, solvent molecules, and hydrogen atoms are omitted for clarity.

indicative of iron in the +3 oxidation state, and one that is shorter ($1^+\text{PF}_6\text{-1}$: 3.302(1) Å; $1^+\text{PF}_6\text{-2}$: 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 1^+I_5 , where the $\text{Cp}_{\text{cent}}\text{-Cp}_{\text{cent}}$ distances for the two molecules of 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 1^+I_5 is valence-detrapped according to the X-ray analysis, the positive charge in 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 1^+I_5 lie about a crystallographic inversion center, which in turn requires the ferrocene moieties to be identical. In contrast, the molecules $1^+\text{PF}_6\text{-1}$ and $1^+\text{PF}_6\text{-2}$ 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 biferoenes.¹⁶

The difference in oxidation state of the two iron centers has major consequences on the molecular conformation of 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 $\text{Cp}/\text{C}_4\text{B}_2$ interplanar angle was determined to be 15.9° and for the two independent valence delocalized molecules of 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 1^+PF_6 differs from that of the ferricenyl moiety. For the oxidized ferricenyl group a relatively small angle was found ($1^+\text{PF}_6\text{-1}$: 8.7(2)°; $1^+\text{PF}_6\text{-2}$: 12.5(2)°), whereas the angle for the neutral ferrocenyl group ($1^+\text{PF}_6\text{-1}$: 22.6(2)°; $1^+\text{PF}_6\text{-2}$: 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 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 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 1^+I_5 with excess MeCN, the solution color turned from brown to green and a red precipitate formed.‡



Scheme 2 Disproportionation of 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 $2^{2+}(\text{I}_3)_2$ was isolated by recrystallization from MeCN as a dark green crystalline solid in 88% yield (Scheme 2).¹⁹ It is noteworthy that 2^{2+} can be obtained as the sole product upon addition of excess iodine or another oxidant.

Coordination of MeCN to $2^{2+}(\text{I}_3)_2$ in solution is evident from the ^{11}B NMR signal at $\delta -0.2$ (1^+PF_6 : $\delta 49.7$), in a region typical of tetracoordinate boron species. Moreover, oxidation of both ferrocenes is reflected in a downfield shift of the Cp resonances to $\delta 32.5$ (1^+PF_6 : $\delta 21.1$). The crystal structure of $2^{2+}(\text{I}_3)_2$ shows the cation lying about an inversion center (Fig. 2).§ The $\text{Cp}_{\text{cent}}\text{-Cp}_{\text{cent}}$ distances of 3.414(2) Å are consistent with Fe(III) centers and, as expected for a tetracoordinate boron complex, the $\text{Cp}/\text{C}_4\text{B}_2$ 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 2^{2+} . Similar B–N distances of 1.610(3) Å²⁰ and 1.616(3) Å²¹ were reported by two different groups for the complex of MeCN with the fluorinated Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$. The C–N bond length of 1.122(7) Å for the bound MeCN in $2^{2+}(\text{I}_3)_2$ 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) Å²¹) and in a similar range as that of $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{MeCN}$ (1.124(3) Å).²¹ While the relatively large standard deviations for the structure of $2^{2+}(\text{I}_3)_2$ 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 $2^{2+}(\text{I}_3)_2$ is

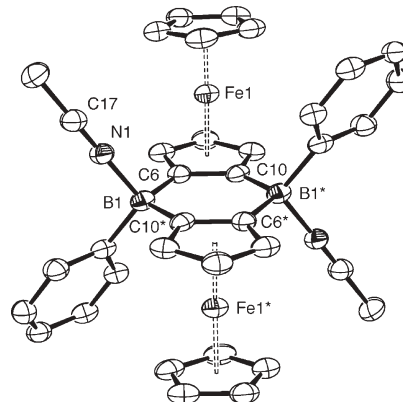


Fig. 2 ORTEP plot of $2^{2+}(\text{I}_3)_2$. The I_3^- counterions and MeCN solvent molecules are omitted for clarity. The asterisks indicate atoms in equivalent positions ($1-x, 1-y, 2-z$). Selected interatomic distances (Å) and angles (°) for $2^{2+}(\text{I}_3)_2$: B1–C6 1.607(8), B1–C10* 1.626(8), 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), $\text{Cp}_{\text{cent}}\text{-C6-B1}$ 175.6(1), $\text{Cp}_{\text{cent}}\text{-C10-B1}^*$ 177.6(1), $\text{Cp}_{\text{cent}}\text{-Cp}_{\text{cent}}$ 3.414(2), Cp/Cp 5.8, $\text{Cp}/\text{C}_4\text{B}_2$ 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 $1^+PF_6^-$ 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 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.

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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 $-35\text{ }^\circ\text{C}$. 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 $-35\text{ }^\circ\text{C}$. 1H NMR (500 MHz, $CDCl_3$, $25\text{ }^\circ\text{C}$) 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 , $25\text{ }^\circ\text{C}$) δ 49.7 ($w_{1/2} = 1600\text{ Hz}$). UV-Vis (CH_2Cl_2 , $2.60 \times 10^{-3}\text{ M}$): $\lambda_{max} = 1543\text{ nm}$ ($\epsilon = 330\text{ M}^{-1}\text{ cm}^{-1}$). 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 $1^+I_5^-$; synthesis of $2^{2+}(I_3)_2$: MeCN (5 mL) was added to $1^+I_5^-$ (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 $-35\text{ }^\circ\text{C}$. Yield $2^{2+}(I_3)_2(MeCN)_2$: 31.4 mg (88%). X-Ray quality crystals were grown by recrystallization from MeCN at $-35\text{ }^\circ\text{C}$. 1H NMR (500 MHz, CD_3CN , $25\text{ }^\circ\text{C}$) δ 32.5 (br, Cp), 5.42, 4.71, -3.32 (br, Ph), 1.94 (MeCN). ^{11}B NMR (160 MHz, CD_3CN , $25\text{ }^\circ\text{C}$) δ -0.2 ($w_{1/2} = 640\text{ Hz}$). UV-Vis (MeCN, $3.29 \times 10^{-4}\text{ M}$): λ_{max} (nm) = 553 ($\epsilon = 760\text{ M}^{-1}\text{ cm}^{-1}$), 644 ($\epsilon = 920\text{ M}^{-1}\text{ cm}^{-1}$). 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:** $1^+PF_6^- \cdot 2CHCl_3$, CCDC 635884: $C_{34}H_{28}B_2Cl_6F_6Fe_2P$, $M = 927.55$, $T = 100(2)\text{ K}$, monoclinic, $P2_1/c$, $a = 18.5711(3)$, $b = 25.9704(4)$, $c = 15.3244(3)\text{ \AA}$, $\beta = 100.0530(10)^\circ$, $V = 7277.5(2)\text{ \AA}^3$, $Z = 8$, $\mu = 11.374\text{ mm}^{-1}$, $R_{int} = 0.0493$, $R1 = 0.0513$, $wR2 = 0.1220$ ($I > 2\sigma(I)$). $2^{2+}(I_3)_2 \cdot 2MeCN$, CCDC 635885: $C_{40}H_{38}B_2Fe_2I_6N_4$, $M = 1469.46$, $T = 100(2)\text{ K}$, monoclinic, $P2_1/c$, $a = 11.7183(9)$, $b = 8.9579(7)$, $c = 21.3539(15)\text{ \AA}$, $\beta = 92.612(4)^\circ$, $V = 2239.2(3)\text{ \AA}^3$, $Z = 2$, $\mu = 37.924\text{ mm}^{-1}$, $R_{int} = 0.0353$, $R1 = 0.0455$, $wR2 = 0.1172$ ($I > 2\sigma(I)$). For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b701807j

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