Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Lewis Acidity Enhancement of Organoboranes via Oxidation of Appended Ferrocene Moieties

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Experimental Methods

Materials and General Methods. Acetonitrile was purchased from Pharmco and $AgPF_6$ from Aldrich. Compounds **1** and $\mathbf{1}^{+}I_5$ were prepared as previously reported.[1] All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box (Innovative Technologies). Hydrocarbon and chlorinated solvents were purified using a solvent purification system (Innovative Technologies), and the chlorinated solvents were subsequently degassed via several freeze-pump-thaw cycles. All 499.9 MHz ^{1}H NMR and 160.3 ^{11}B NMR spectra were recorded on a Varian INOVA NMR spectrometer (Varian Inc., Palo Alto, CA) equipped with a boron-free 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). ^{1}H NMR spectra were referenced internally to the solvent signals and ^{11}B NMR spectra were referenced externally to $BF_3{\bullet}Et_2O$ in C_6D_6 (δ = 0). UV-visible absorption data were acquired on a Varian Cary 500 UV-vis/NIR spectrophotometer. Solutions were prepared using a microbalance (±0.1 mg) and volumetric glassware and then charged into quartz cuvettes with sealing screw caps (Starna) inside the glovebox. Infrared spectra were obtained with a Nicolet IR-200 spectrometer. All samples were prepared as KBr pellets. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ. ^{57}Fe Mössbauer spectra were accumulated in transmission geometry as discussed previously in the literature [2] over the temperature range 86<T<342 K where appropriate. Samples were transferred from sealed ampoules to O-ring provided sample holders in an inert atmosphere glove box and immediately cooled to 78 K in liquid nitrogen prior to mounting in the pre-cooled cryostat. X-Ray data were collected on a Bruker SMART APEX CCD Diffractrometer using Cu-Kα (1.54178 Å) radiation. Crystallographic data for $\mathbf{1}^{+}PF_6$ and $\mathbf{2}^{2+}(I_3)_2$ and details of X-ray diffraction experiments and crystal structure refinements are given in Table S1. SADABS [3] absorption corrections were applied in both cases. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full matrix least squares procedures on reflection intensities ($F2$). All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms. All software and source scattering factors are contained in the SHELXTL program package.[4] Crystallographic data for the structures of $\mathbf{1}^{+}PF_6$ and $\mathbf{2}^{2+}(I_3)_2$ have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-635884 and CCDC-635885, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

[1] K. Venkatasubbaiah, L. N. Zakharov, W. S. Kassel, A. L. Rheingold and F. Jäkle, *Angew. Chem. Int. Ed.*, **2005**, *44*, 5428-5433.
[2] I. Nowik, R. H. Herber, *Inorg. Chim. Acta* **2000**, *310*, 191-195.
[3] Sheldrick, G.M. (2001). SADABS. Version 2. Multi-Scan Absorption Correction Program. University of Göttingen, Germany.
[4] Sheldrick, G. *SHELXTL* (5.10); Bruker XRD: Madison, WI.

Figure S1. ORTEP plots of the cations of the two independent molecules of $\mathbf{1}^{+}PF_6$ in the unit cell with thermal ellipsoids at the 50% probability level; the PF_6^- counterions, $CHCl_3$ solvent molecules, and hydrogen atoms are omitted for clarity.

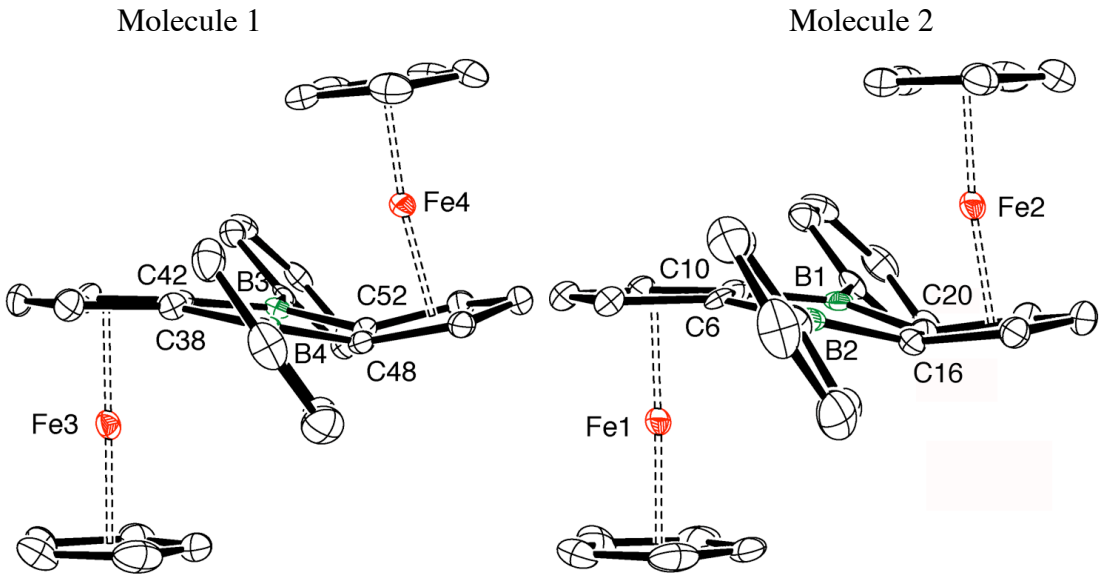

Table S1. Comparison of selected bond lengths (Å) and angles (°).

	1	**1**$^{+}$$I_5$		**1**$^{+}PF_6$				**2**$^{2+}$$(I_3)_2$
		1^{+}I_5-1	**1**$^{+}$$I_5$-2	**1**$^{+}PF_6$-1		**1**$^{+}PF_6$-2		
	Fe(II)			Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(III)
B-C_i(Cp)	1.546(2)	1.551(6)	1.543(6)	1.525(6)	1.570(6)	1.528(6)	1.562(6)	1.607(8)
	1.546(2)	1.542(6)	1.543(6)	1.531(6)	1.568(6)	1.543(6)	1.559(6)	1.626(8)
B-C_i(Ph)	1.564(2)	1.562(6)	1.566(6)	1.563(6) / 1.567(6)		1.561(6) / 1.556(6)		1.617(7)
$Cp_{cent}\cdots Cp_{cent}$	3.308(1)	3.355(1)	3.357(2)	3.302(1)	3.411(1)	3.306(1)	3.396(1)	3.414(2)
B···B*	3.103(3)	3.121(1)	3.097(5)	3.118(1)		3.105(1)		3.280(2)
Fe···Fe*	5.123(1)	5.076(8)	5.189(2)	5.090(1)		5.121(1)		5.937(2)
Fe···B	3.032(2)	2.924(3)	3.025(1)	2.885(1)	3.173(1)	2.870(1)	3.100(1)	3.364(3)
	2.957(2)	3.034(3)	3.018(1)	2.792(1)	3.113(1)	2.869(1)	3.144(1)	3.418(6)
C_{Cp}-B-C_{Cp}	115.8(1)	115.6(4)	115.5(3)	115.2(4)	115.1(4)	115.5(4)	115.2(4)	110.7(4)
Cp_{Cent}-C_i-B	167.9(1)	162.9(1)	167.9(1)	157.6(1)	174.1(1)	160.5(1)	171.2(1)	175.6(1) [a]
	164.4(1)	168.5(2)	167.8(1)	161.6(1)	171.6(1)	160.8(1)	172.3(1)	177.6(1) [a]
Cp // C_4B_2 angle	15.9	16.5	13.8	22.6	8.7	19.0	12.5	2.4
Cp tilt angle	1.2	3.2	2.6	5.3	1.8	5.2	2.5	5.8

[a] The boron substituents are upward tilted in the MeCN complex with respect to the ferrocene moieties (exo side).

Table S2. Details of X-ray crystal structure analyses of complexes $\mathbf{1}^{+}PF_6$ and $\mathbf{2}^{2+}(I_3)_2$.

	$\mathbf{1}^{+}PF_6 \bullet 2CHCl_3$	$\mathbf{2}^{2+}(I_3)_2 \bullet 2CH_3CN$
empirical formula	$C_{34}H_{28}B_2Cl_6F_6Fe_2P$	$C_{40}H_{38}B_2Fe_2I_6N_4$
MW	927.55	1469.46
T, K	100(2)	100(2)
wavelength, Å	1.54178	1.54178
crystal system	Monoclinic	Monoclinic
space group	P2(1)/c	P2(1)/c
a, Å	18.5711(3)	11.7183(9)
b, Å	25.9704(4)	8.9579(7)
c, Å	15.3244(3)	21.3539(15)
□, deg.	100.0530(10)	92.612(4)
V, Å^3	7277.5(2)	2239.2(3)
Z	8	2
□$_{calc}$, g cm^{-3}	1.693	2.179
□ (CuK□), mm^{-1}	11.374	37.924
F (000)	3720	1372
Crystal size, mm	0.25 x 0.13 x 0.06	0.28 x 0.18 x 0.16
□ range, deg	2.42-64.99	3.87-67.74
limiting indices	-21<=h<=21 -28<=k<=30 -15<=l<=17	-14<=h<=13 -10<=k<=8 -24<=l<=25
reflns collected	44369	14152
independent reflns	11958 [R(int) = 0.0493]	3956 [R(int) = 0.0353]
absorption correction	semi-empirical from equivalents	Numerical
refinement method	full-matrix least square on F^2	full-matrix least square on F^2
data / restraints / parameters	11958 / 0 / 919	3956 / 0 / 246
goodness-of-fit on F^2	1.012	1.065
final R indices	R1 = 0.0513	R1 = 0.0455
[I >2□(I)] [a]	wR2 = 0.1220	wR2 = 0.1172
R indices (all data) [a]	R1 = 0.0695	R1 = 0.0474
	wR2 = 0.1335	wR2 = 0.1193
peak$_{max}$/hole$_{min}$ (e Å^{-3})	1.644 and –0.897	1.940 and –0.700

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.