An Estimate of the Reduction Potential of $B(C_6F_5)_3$ from Electrochemical Measurements on Related Mesityl Boranes

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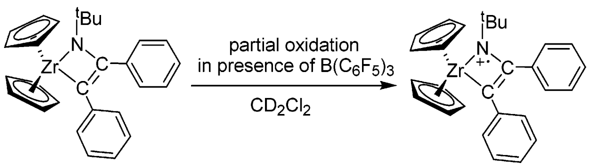
$MesB(C_6F_5)_2$ (**1**) has been prepared from MesMgBr and $FB(C_6F_5)_2{\cdot}OEt_2$, while $Mes_2B(C_6F_5)$ (**2**) is readily available from CuC_6F_5 and Mes_2BBr. The reduction potential $E°$ of **1** vs $Cp_2Fe^{0/+}$ in THF is −1.72 V, while that of **2** is −2.10 V, and that of Mes_3B (**3**) is −2.73 V. ^{11}B and ^{1}H NMR show that neither **1** nor **2** binds THF significantly. These results have been used to estimate the reduction potential of $B(C_6F_5)_3$ in THF as −1.17 V vs $Cp_2Fe^{0/+}$ or as −0.64 V vs SCE.

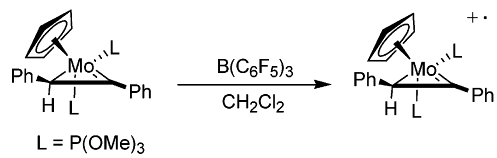
Introduction

$B(C_6F_5)_3$ has found wide application in the activation of catalysts for olefin polymerization.[1−3] It is known to be a powerful acceptor for lone-pair donors,[4] but there is relatively little information on its ability to serve as a one-electron acceptor. Some of us have reported the partial one-electron oxidation of an azazirconacycle in the presence of $B(C_6F_5)_3$ (eq 1).[5]



(1)

Green and co-workers have reported that $B(C_6F_5)_3$ does serve as a one-electron oxidant in eq 2 and that other products are obtained when traces of water form the highly acidic[6] adduct $H_2O{\rightarrow}B(C_6F_5)_3$.[7]



(2)

In neither case was the anion radical of $B(C_6F_5)_3$ observed, although some of us later prepared it by reducing $B(C_6F_5)_3$ with decamethylcobaltocene in THF (eq 3).[8]

$$B(C_6F_5)_3 \xrightarrow[\text{THF, }-50\text{ °C}]{Cp^*{}_2Co} B(C_6F_5)_3^{\bullet-} \qquad (3)$$

The reduction potential of $B(C_6F_5)_3$ is therefore of interest, but direct measurement has proven impossible. Little or no signal is observed when we attempt a CV of $B(C_6F_5)_3$,[5,9] apparently because the radical anion becomes absorbed on electrode surfaces.

Similar problems have been encountered in the electrochemistry of other triaryl boranes and have been solved by introducing mesityl substituents; even a single mesityl generally provides enough steric hindrance to preclude absorption of the radical anion.[10] We have therefore prepared the previously unreported $MesB(C_6F_5)_2$ (**1**) and $Mes_2B(C_6F_5)$ (**2**), examined the electrochemistry of **1**, **2**, and Mes_3B (**3**), and used the results to estimate the reduction potential of $B(C_6F_5)_3$.

Results and Discussion

The relatively unhindered $MesB(C_6F_5)_2$ (**1**) was prepared straightforwardly (eq 4) from MesMgBr and $FB(C_6F_5)_2{\cdot}OEt_2$.

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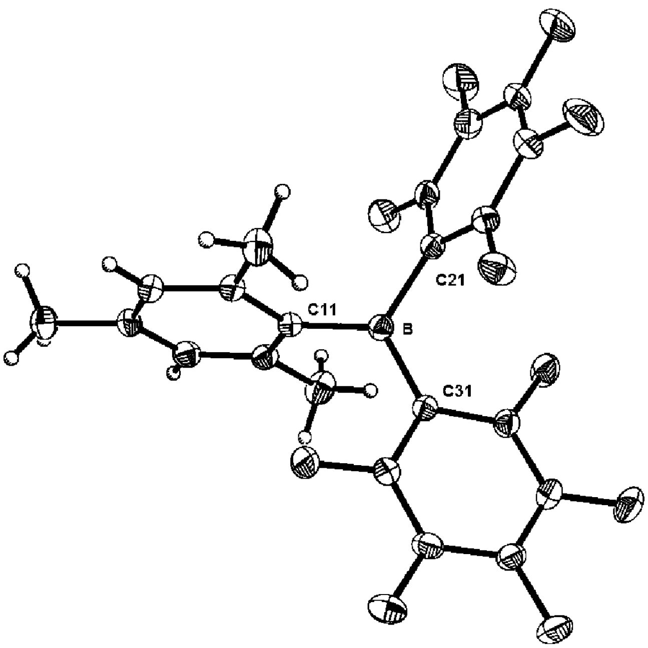

Figure 1. Thermal ellipsoid representation of $MesB(C_6F_5)_2$ (**1**). See Table 1 for selected bond lengths and angles and Table 2 for crystal data, data collection, and refinement parameters.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1

Bond Lengths	
B−C(11)	1.564(3)
B−C(21)	1.590(3)
B−C(31)	1.561(3)
Bond Angles	
C(11)−B−C(21)	121.97(18)
C(21)−B−C(31)	117.94(17)
C(31)−B−C(11)	122.67(17)

The latter was, as reported by Bochmann and co-workers,[11] readily accessible from $BF_3{\cdot}OEt_2$ and 2 equiv of C_6F_5MgBr.

$$FB(C_6F_5)_2{\cdot}OEt_2 + MesMgBr \xrightarrow[\substack{Et_2O \\ 40\%}]{-78\text{ to }20\ ^\circ C} MesB(C_6F_5)_2 + MgBrF \quad (4)$$

An X-ray structure of **1** shows the expected propeller shape (Figure 1) with a trigonal planar environment at boron. Its bulkier substituents cause the mesityl ring to make an angle of 72° with the BC_3 plane, while the C_6F_5 rings make angles of only 36° and 47°.

Due to the steric constraints of the mesityl substituent, the Lewis acidity of **1** is strongly reduced relative to that of $B(C_6F_5)_3$. The interaction between Et_2O or THF and **1** is very weak, although CH_3CN binds noticeably to **1**; the addition of two drops of CH_3CN to an NMR tube containing **1** in C_6D_6 shifts its ortho ^{19}F signal upfield by 3.4 ppm, its para ^{19}F signal upfield by 12.3 ppm, and its meta ^{19}F signal upfield by 4.3 ppm. The chemical shift difference $\Delta\delta_{m,p}$ between the meta and para fluorine substituents has been reported to be very sensitive to the electronic environment of fluorinated arylboranes.[1b] The observed 8.0 ppm decrease in $\Delta\delta_{m,p}$ confirms a considerable degree of CH_3CN binding to **1**.

The more hindered $Mes_2B(C_6F_5)$ (**2**) proved far more difficult to prepare. An attempt at the comproportionation of Mes_3B and $B(C_6F_5)_3$ gave negligible reaction even at elevated temperatures. The intermediate Mes_2BF is commercially available (Aldrich), but steric hindrance made its reaction with nucleophiles difficult, and the thermal instability of organometallic pentafluorophenyls $M{-}C_6F_5$ (e.g., LiC_6F_5, $BrMgC_6F_5$) made it impossible to run reaction 5 at elevated temperatures.

$$Mes_2BF + M{-}C_6F_5 \not\rightarrow Mes_2B(C_6F_5) + M{-}F \quad (5)$$

$$(M = Li, BrMg, Me_3Si, Me_3Sn)$$

As two of us had previously found CuC_6F_5 useful for replacing Br with C_6F_5 on sterically congested boranes,[12] we tried the same reagent with Mes_2BBr (eq 6). The reaction proved straightforward and gave good yields of **2**.

$$Mes_2BBr + CuC_6F_5 \rightarrow Mes_2B(C_6F_5) + CuBr \quad (6)$$

An alternative boron starting material was Mes_2BI, reported by Power and co-workers as a byproduct in the preparation of $[MesPI]_2$ by reactions 7 and 8.[13] Indeed, **2** was the major product when Mes_2BI was treated with AgC_6F_5 in DMF (eq 9).

$$Mes_2BF + MesPH_2 \xrightarrow{BuLi} Mes_2BPH(Mes) \xrightarrow{BuLi} Mes_2BP(Mes)Li \quad (7)$$

$$Mes_2BP(Mes)Li \xrightarrow{I_2} Mes_2BI + [Mes(I)P]_2 \quad (8)$$

$$Mes_2BI + AgC_6F_5 \xrightarrow[DMF]{} Mes_2B(C_6F_5) + AgI \quad (9)$$

Electrochemistry. While we know of no report of cyclic voltammetry on compounds **1** and **2** prior to the present work, there have been a number of reports (with different $E°$ values) of the reversible reduction of Mes_3B (**3**) under various conditions. In 1975 DuPont and Mills reported −3.0 V in THF at a Pt electrode vs Ag/Ag^+,[14] which (if we take Ag/Ag^+ as +0.49 vs SCE) suggests −2.5 V for **3** in THF vs SCE. The most recent and presumably more reliable values suggest considerably less negative reduction potentials for **3**. In 1986 Okhlobystin and co-workers reported −2.18 V in CH_3CN vs SCE, and −2.13 V in DMF vs SCE.[15] In 1989, Schultz and Kaim reported −1.94 V in DMF vs SCE,[10] and their value was used by Elschenbroich and co-workers when working in glyme.[16] In 1992, Okada and co-workers reported −2.18 V in DMF vs SCE.[17] The reduction potential $E°$ for **3** appears to vary little with solvent, as is expected in view of the fact that **3** is an extremely weak Lewis acid. Nevertheless, there is always an element of uncertainty when electrode potential data of a given compound, recorded with different solvents and supporting electrolytes and referenced against different reference electrodes or internal references, are to be compared. Therefore, we have investigated the cyclic voltammograms of **1**−**3** under identical conditions.

The cyclic voltammograms of the boranes **1**−**3** were recorded at 0 °C in THF containing 0.05 M $[Bu_4N][B(C_6F_5)_4]$ as the supporting electrolyte at Pt disk electrodes. The electrode potentials are reported vs $Cp_2Fe^{0/+}$. After first recording the

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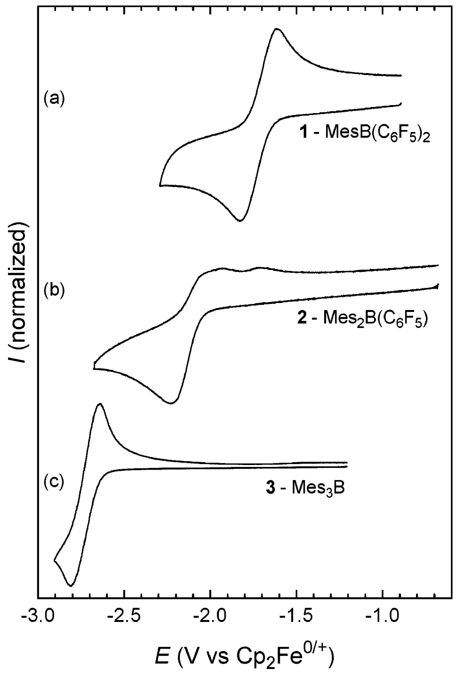

Figure 2. Cyclic voltammogram of a solution of (a) **1** at a voltage sweep rate of 5 V/s, (b) **2** at a voltage sweep rate of 10 V/s, (c) **3** at a voltage sweep rate of 1 V/s in THF/0.05 M $[Bu_4N][B(C_6F_5)_4]$ at $T = 0$ °C at a Pt disk electrode ($d = 0.2-1.0$ mm). The potential scales are referenced to the ferrocene/ferrocenium couple.

voltammograms of the boranes without ferrocene present, separate scans were recorded with ferrocene added for calibration purposes.

The cyclic voltammogram of **1** showed limited chemical reversibility at scan rates slower than 0.5 V/s. The scans became more reversible at faster scan rates. At 5 V/s (Figure 2a) the reoxidation of the radical anion $\mathbf{1}^{\bullet-}$ competed effectively with its decomposition, resulting in a convincingly reversible voltammogram. The reduction potential of **1** (eq 10, $n = 1$), taken as the midpoint between the reduction and oxidation peak potentials, is -1.72 V vs $Cp_2Fe^{0/+}$. The position of the peaks did vary somewhat from scan to scan (by up to 0.05 V) and depended on the conditioning of the electrode.

$$\mathrm{Mes}_n\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_{3-n} + \mathrm{e}^- \rightleftharpoons \mathrm{Mes}_n\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_{3-n}{}^{\bullet-} \qquad (10)$$

The cyclic voltammogram of **2** showed an ill-defined irreversible reduction at 0.2 V/s, but a partially reversible reduction (Figure 2b) above 10 V/s. The reduction potential for **2** (eq 10, $n = 2$) is estimated at -2.10 V vs $Cp_2Fe^{0/+}$. Again, the position of the peak potentials was highly dependent on the electrode history (varying by up to 0.1 V), and the data presented are taken from the most well-defined voltammograms. It is not clear to us why the cyclic voltammetry behavior of **2** was less chemically reversible, and also qualitatively less reproducible, than that of **1** and **3**.

The cyclic voltammogram of **3** exhibited a well-defined, reversible wave centered at -2.73 V vs $Cp_2Fe^{0/+}$ (Figure 2c), which was much more reproducible and independent of electrode history than the voltammograms of **1** and **2**.

To obtain $E°$ values vs SCE in THF from the measured values vs $Cp_2Fe^{0/+}$ in THF, an $E°$ for $Cp_2Fe^{0/+}$ vs SCE in that solvent is required. The value of $E°$ ($Cp_2Fe^{0/+}$ vs SCE in THF) has been given as $+0.52$ V with 0.2 M $[Bu_4N]PF_6$ at 20 °C[18] and as $+0.547$ with 0.1 M $[Bu_4N]PF_6$ at 20 °C.[19] Using the average, $+0.53$ V, our cyclic voltammetry data give $E°$ for $\mathbf{1}/\mathbf{1}^{\bullet-}$ as -1.19 V, for $\mathbf{2}/\mathbf{2}^{\bullet-}$ as -1.57 V, and for $\mathbf{3}/\mathbf{3}^{\bullet-}$ as -2.20 V, all reported vs SCE in THF.

Correction of $E°$ Values for the Coordination of THF? In principle these $E°$ values need correction for the coordination of THF in equilibria like eq 11. The THF adducts (e.g., THF•**1**) have no low-lying vacant orbitals and cannot easily undergo reduction. If we assume that these equilibria are rapidly maintained on the time scale of the CV experiments, and know their equilibrium constants K_{eq}, we can determine the reduction potentials $E°$ for the free boranes from eq 12.[20]

$$\underset{\mathbf{1}}{\mathrm{MesB}(\mathrm{C}_6\mathrm{F}_5)_2} + \mathrm{THF} \overset{K_{eq}}{\rightleftharpoons} \underset{\mathrm{THF}\cdot\mathbf{1}}{\mathrm{THF} \rightarrow \mathrm{BMes}(\mathrm{C}_6\mathrm{F}_5)_2} \qquad (11)$$

$$E = E^0 - \frac{RT}{nF}\ln(1 + K_{eq}[\mathrm{THF}]) \qquad (12)$$

However, K_{eq} is small for both **1** and **2**. The ^{11}B chemical shift of **1**, δ 69.7 in toluene-d_8, is little affected by THF: the addition of 30 equiv (1.12 M) of THF moves it only to 68.9, 0.8 ppm upfield, whereas the addition of 20 equiv of THF (1.12 M) to the strong Lewis acid $B(C_6F_5)_3$ moves its chemical shift from δ 58.1 to δ 3.0, over 50 ppm upfield. Comparison of these upfield ^{11}B shifts suggests that less than 2% of **1** is complexed in the presence of 30 equiv (1.12 M) of THF and that K_{eq} is <0.018, implying that the observed E is negligibly (<1 mV, far less than the experimental uncertainty) different from the $E°$ for (free $\mathbf{1}$)/$\mathbf{1}^{-\bullet}$.

The ^{1}H NMR chemical shifts of **2** in toluene-d_8 also show little change as THF is added, confirming that the equilibrium constant for association of **2** with THF is also negligible and that no correction is required to the $E°$ measured for **2**.

The equilibrium constant K_{eq} for association of **3** (Mes_3B) with THF is surely even smaller than that for **2**.

Estimate for $E°$ of $B(C_6F_5)_3$. By assuming a linear relationship between the reduction potential of the substituted boranes **1**, **2**, and **3** and the number of mesityl substituents, we can extrapolate an estimate for $E°$ of $B(C_6F_5)_3$. Our values of $E°$ for **1**, **2**, and **3** vs SCE lie on a reasonably straight line (Figure 3) and suggest that $E°$ for free $B(C_6F_5)_3$ in THF is about -0.64 V vs SCE. However, the accuracy of the extrapolation is limited by the likelihood of variations in structure within this series of compounds.

Experimental Section

General Comments. All reactions and manipulations were carried out using standard vacuum-line, Schlenk, and glovebox techniques, under an atmosphere of purified Ar/N_2 unless otherwise noted. All glassware was flamed out immediately prior to use or dried overnight at 160 °C. All solvents were purified and dried using standard procedures and were distilled immediately prior to use.

AgC_6F_5 was prepared by a recently reported method.[21] Mes_2BI was prepared from $Mes_2BP(Mes)Li$, in 10% yield, by iodine oxidation in ether as reported by Pestana and Power.[13] The complex

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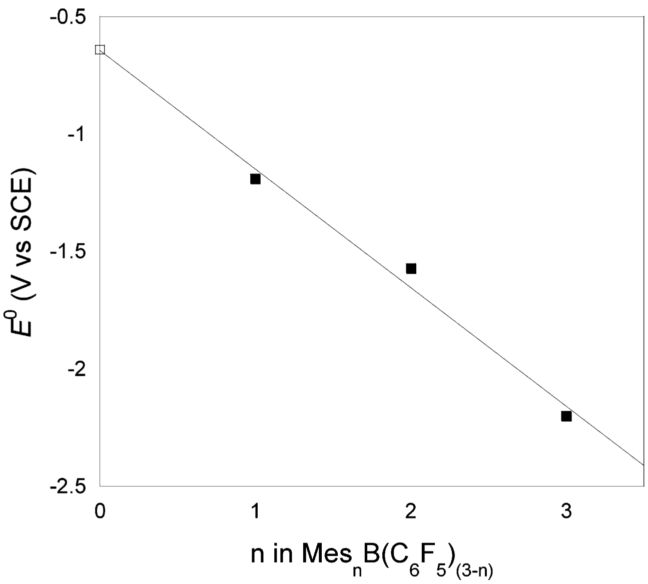

Figure 3. Reduction potential (vs SCE) vs number of mesityl substituents on boranes **1**, **2**, and **3**. The reduction potential for $B(C_6F_5)_3$ can be extrapolated to −0.64 V vs SCE.

$[Cu(C_6F_5)]_4(toluene)_2$ was prepared according to literature procedures[22] and dried at 60 °C under high vacuum for 24 h to remove the toluene. Mes_2BBr was prepared from $[CuMes]_5(toluene)$ and BBr_3.[23]

X-ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector, and crystal data, data collection, and refinement parameters are summarized in Table 2. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 5.03).[24]

$MesB(C_6F_5)_2$ (1). Two equivalents (40 mmol) of C_6F_5MgBr in Et_2O (40 mL of an 1.0 M solution) was added to BF_3 etherate (2.5 g, 18 mmol) in 40 mL of ether and stirred for 3 h at 0 °C, giving an orange-brown solution of crude $FB(C_6F_5)_2{\cdot}OEt_2$. One equivalent (20 mmol) of MesMgBr (20 mL of a commercial 1.0 M ether solution) was then added at 0 °C, and the combined solution allowed to warm to room temperature while stirring overnight. Removing all volatiles left an orange-brown oil. Extracting with 3:1 toluene−hexane (with sonication), allowing the suspension to settle, removing and filtering the top layer, and removing the solvent under vacuum gave an orange oil; upon standing a colorless solid separated from a brown oil. Recrystallization of the solid from ether and hexane at −30 °C gave colorless **1** in 40% yield. ^{1}H NMR (300 MHz, C_6D_6): δ 6.68 (2H), 2.11(3H), 1.99 (6H). ^{19}F NMR (282 MHz, C_6D_6): δ −128.3, −143.9, −159.8. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 146.2 (CF), 142.7 (CF), 137.5 (CF), 141.2, 140.9, 140.6, 129.0, 120.0, 22.9, 21.5. ^{11}B NMR (32.1 MHz, toluene-d_8): δ 69.7. Anal. Calcd for $C_{21}H_{11}BF_{10}$: C, 54.35; H, 2.39. Found: C, 54.17; H, 1.83.

$Mes_2B(C_6F_5)$ (**2**) was prepared by cooling a solution of CuC_6F_5 (0.60 g, 2.60 mmol) in toluene (20 mL) to −37 °C and adding it to a solution of Mes_2BBr (0.81 g, 2.45 mmol) in toluene (25 mL) at the same temperature. Upon heating the mixture to 85 °C, a white precipitate gradually formed; the mixture was kept at this temperature for 16 h. It was then cooled to room temperature, the insoluble precipitate was removed by filtration, and the volatile components were removed under vacuum. The spectroscopic yield of **2** is 90% according to ^{1}H NMR analysis; sublimation at 75 °C under high vacuum gave 0.67 g (66%) of pure product. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.81 (4H), 2.30 (6H), 2.08 (12H). ^{19}F NMR (470.4 MHz, $CDCl_3$): δ −131.9, −151.9, −162.8. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 146.2 (CF), 142.7 (CF), 137.5 (CF), 141.2, 140.9, 140.6, 129.0, 120.0, 22.9, 21.5. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ 72.6. Anal. Calcd for $C_{24}H_{22}BF_5$: C, 69.25; H, 5.33. Found: C, 69.30; H, 5.15.

Table 2. Summary of Data Collection, Solution, and Refinement Parameters for 1

empirical formula	$C_{21}H_{11}BF_{10}$
fw	464.11
T (K)	233(2)
wavelength (Å)	0.71073
cryst syst/space group	monoclinic, *Cc*
a (Å)	13.877(10)
b (Å)	20.404(10)
c (Å)	7.706(5)
α (deg)	90
β (deg)	116.153(14)
γ (deg)	90
volume (Å^3)	1959(2)
Z	4
D_{calc} (Mg/m^3)	1.574
absorp coeff (mm^{-1})	1.646
cryst size (mm^3)	0.70 × 0.40 × 0.40
θ range for data collection (deg)	1.92 to 28.04
index ranges	$-18 \le h \le 17$, $-9 \le k \le 23$, $-10 \le l \le 10$
no. reflns collected/unique	4733/3780 [R_{int} = 0.0680]
absorp corr	SADABS
no. of data/restraints/params	3780/2/294
goodness-of-fit on F^2	1.058
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0393$, $wR_2 = 0.1089$
R indices (all data)	$R_1 = 0.0423$, $wR_2 = 0.1117$

Formation of **2** was also observed (^{19}F NMR) when a J-Young NMR tube was charged with Mes_2BI (ca. 0.020 g, 0.054 mmol), excess AgC_6F_5 (0.055 g, 0.200 mmol), and DMF-d_7, degassed by freezing under vacuum, wrapped in aluminum foil, and kept at 30 °C for 2 h. The reaction appeared to be complete after 9 h.

Cyclic voltammetric measurements were performed with a three-electrode CV cell, using an EG&G-PAR Model 273 potentiostat/galvanostat driven by an external HP 33120 function generator. The signals were fed to a National Instruments DAQ interface card for on-line processing on a personal computer using in-house-designed National Instruments LabView software. The working electrodes were Pt-disk electrodes (d = 0.2−1.0 mm depending on voltage scan rates), the counter electrode was a Pt wire, and the Ag-wire reference electrode assembly was filled with acetonitrile/0.01 M $AgNO_3$/0.1 M $[Bu_4N]BF_4$. The reference electrode was calibrated against Cp_2Fe in the THF/$[Bu_4N][B(C_6F_5)]_4$ electrolyte.

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Supporting Information Available: Complete details of the crystallographic study (CIF and PDF) for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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