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Control of Ligand Substitution and Addition Reactions of (Arene)$Cr(CO)_3$ Complexes by Attachment of a Self-Closing Redox Switch

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The ferrocenyl group attached to the benzene ring in $(C_6H_5Fc)Cr(CO)_3$ (**3**) functions as a reversible redox switch by providing a mechanism for the chromium center to be oxidatively activated to ligand substitution and addition reactions. Because initial oxidation of **3** occurs at the ferrocenyl group, the potentials required for activation are far lower than would otherwise be the case, and this allows for controlled reactions without the unproductive decomposition that often accompanies oxidation of (arene)$Cr(CO)_3$ complexes. Although the chromium in $\mathbf{3}^+$ is predominantly an 18-electron center, it is sufficiently activated to undergo very rapid CO substitution by $P(OEt)_3$ to afford $(C_6H_5Fc)Cr(CO)_2P(OEt)_3^+$ ($\mathbf{4}^+$). Internal electron transfer from Cr to Fe accompanies this CO substitution, with the result that the ferrocenium group in $\mathbf{3}^+$ reverts to ferrocenyl in $\mathbf{4}^+$, thus closing the redox switch. Upon oxidation of $\mathbf{4}^+$ to $\mathbf{4}^{2+}$, the switch reopens and the chromium center is again activated, this time being attacked by $P(OEt)_3$ to give the purple addition complex, $(C_6H_5Fc)Cr(CO)_2[P(OEt)_3]_2^{2+}$ ($\mathbf{5}^{2+}$), which is readily isolated. The formation of $\mathbf{5}^{2+}$ from $\mathbf{4}^{2+}$ is also accompanied by internal electron transfer from Cr to Fe and automatic switch closing to afford a product with 18-electron centers. The degree of activation of **3** upon oxidation of the ferrocenyl switch is shown to be directly related to the difference in oxidation potentials of the chromium and iron centers. These results suggest that the attachment of a remote redox switch may be a useful general methodology for the quantitative control of the reactivity of a metal center.

Introduction

Organometallic compounds that undergo rapid chemically reversible oxidation or reduction may be able to function as effective redox switches that can be turned on or off by electron transfer. The objective is to modulate the chemical reactivity of a molecular system to which the redox active switch is attached. A well-known example of this is the control of cation binding to crown ethers and other macrocyclic receptor molecules by covalently attaching a ferrocenyl (Fc) group.[1,2] In this case, oxidation of the ferrocenyl moiety switches off the receptor site (due largely to simple electrostatic effects). In a similar vein, a cobaltocene group can be used to modulate anion binding.[1,3] Another example of control of Lewis acid/base strength is provided by the redox active ferrocenylboronic acid complex $CpFe[C_5H_4B(OH)_2]$. In this case the boron center is easily modulated electrochemically, resulting in selective recognition of fluoride in the presence of halides and other common anions.[4]

The chelating “hemilabile” ferrocenyl ligand $FcOCH_2CH_2PPh_2$ is particularly interesting because the weak bond formed between the ether oxygen and a metal is easily broken upon oxidation of the ferrocene center, thereby providing some control over the coordination environment (and reactivity) of the metal.[5] In another study, a ferrocenyl group was used as a redox switch to facilitate reductive elimination from a platinum(II) complex.[6] A chelating redox switch based on 1,1-bis(diphenylphosphino)cobaltocene ($L^{+/0}$) has been used[7] to control the electrophilicity of the carbonyl carbons in $(L^{+/0})Re(CO)_4^+$. Likewise, the reactivity of $(L^{+/0})Rh(acetone)_n^+$ as a hydrogenation and hydrosilation catalyst has been shown[8] to be very dependent on the oxidation state of L.

Herein we describe a system containing a self-closing redox switch that greatly facilitates ligand substitution and *addition* reactions of (arene)$Cr(CO)_3$ (**1**) (Chart 1). This was accomplished by the attachment of a ferrocenyl group, as shown in structure **3**. Complex **1** (R = H) is known[9] to undergo oxidation at the metal center to give

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[†] Brown University.
[‡] Seoul National University.
[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.
(1) Beer, P. D. *Chem. Soc. Rev.* **1989**, *18*, 409.
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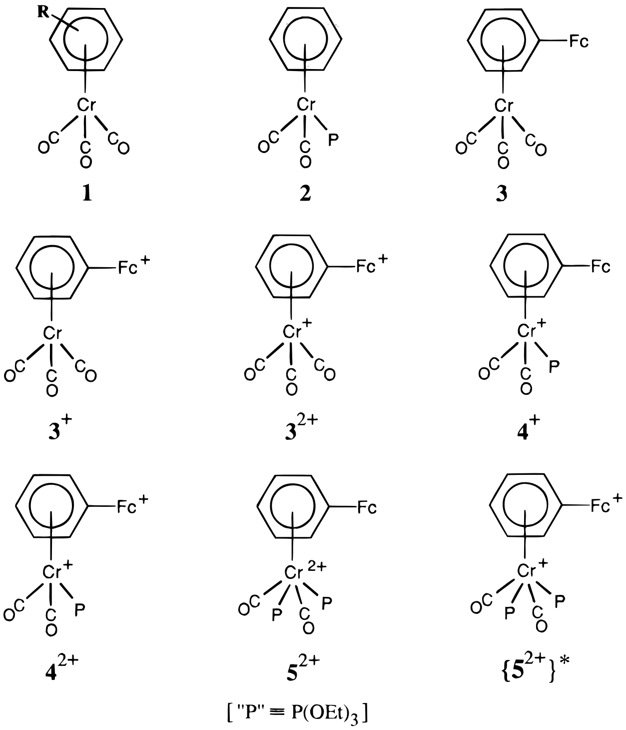
Chart 1



an extremely reactive radical that under most circumstances decomposes in an unproductive manner with liberation of benzene. That this occurs is not surprising since most 17-electron (and 19-electron) organometallic radicals are many orders of magnitude more reactive than their 18-electron precursors.[10] In **3**, however, oxidation occurs first (and reversibly) at the ferrocenyl center, with the result that $\mathbf{3}^+$ is much more stable than is $\mathbf{1}^+$. Nevertheless, it is demonstrated herein that the chromium in $\mathbf{3}^+$ acquires sufficient radical character to be activated to undergo rapid CO substitution by $P(OEt)_3$ (P) to afford $\mathbf{4}^+$. This CO substitution is accompanied by internal electron transfer from Cr to Fe, with the result that the ferrocenyl switch is automatically shut off in the product ($\mathbf{4}^+$), which becomes a 17-electron chromium(I) center. Upon oxidation to $\mathbf{4}^{2+}$, the switch reopens and the chromium is again attacked by $P(OEt)_3$, this time to give a purple *addition* complex ($\mathbf{5}^{2+}$). The formation of $\mathbf{5}^{2+}$ from $\mathbf{4}^{2+}$ is also accompanied by internal electron transfer from Cr to Fe and automatic switch closing to afford a product with 18-electron centers.

Experimental Section

$CpFe(C_5H_4C_6H_5)Cr(CO)_3$ (3). This complex was previously prepared in 13% yield.[11] A modified procedure was found to afford a higher yield: phenylferrocene (0.16 g, 0.60 mmol) and $Cr(CO)_6$ (0.20 g, 0.90 mmol) were dissolved in 40 mL of Bu_2O/THF (10:1), and the solution was refluxed for 3 days. After being cooled to room temperature, the solution was passed through a pad of Celite. The filtrate was concentrated and chromatographed on silica gel with hexane eluant. After evaporation of the solvent, the product was obtained in 83% yield (0.20 g) based on the phenylferrocene. IR (CH_2Cl_2): 1964 (s), 1889 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.52−5.41 (m, 4 H, Ph), 5.21 (t, J = 5.8, 1 H, Ph), 4.52 (s, 2 H, Cp), 4.36 (s, 2 H, Cp), 4.11 (s, 5 H, Cp).

$[CpFe(C_5H_4C_6H_5)Cr(CO)_2[P(OEt)_3]_2][BF_4]_2$ ($\mathbf{5}^{2+}$). Excess $P(OEt)_3$ (0.10 mL) was added to **3** (34.3 mg, 0.086 mol) in 6 mL of CH_2Cl_2. Acetylferrocenium tetrafluoroborate (53.4 mg, 0.170 mmol, 2.0 eq.) was then added and the mixture stirred for 30 min, after which the formation of $\mathbf{5}^{2+}$ was judged to be complete by IR spectroscopy. After filtration through Celite, the product was precipitated by addition of diethyl ether. The purple colored salt was repeatedly washed with diethyl ether and hexanes and dried in vacuo to afford 29.6 mg (40% yield) of $[\mathbf{5}^{2+}][BF_4]_2$. The small scale of the reaction accounts for the modest yield; IR spectra indicate that the formation of $\mathbf{5}^{2+}$ is, in fact, nearly quantitative. IR (CH_2Cl_2): 2025 (s), 1973 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 6.86 (m, 2 H, Ph), 6.72 (m, 2 H, Ph), 6.46 (m, 1 H, Ph), 5.08 (s, 2 H, Cp), 4.94 (s, 2 H, Cp), 4.27 (m, 12 H, OCH_2), 4.17 (s, 5 H, Cp), 1.42 (t, J = 6.9, 18 H, CH_3). Anal. Calcd for $C_{30}H_{44}O_4P_2CrFeB_2F_8$: C, 41.13; H, 5.06. Found: C, 40.38; H, 5.14.

$CpFe(C_5H_4C_6H_5)Cr(CO)_2P(OEt)_3$ (4). This complex was prepared by two methods. **Method A.** Complex $[\mathbf{5}^{2+}][BF_4]_2$ (29.6 mg, 0.034 mmol) in 6 mL of dry CH_2Cl_2 under N_2 was treated with cobaltocene (12.8 mg, 0.068 mmol, 2.0 equiv) and the reaction mixture stirred for 15 min. An IR spectrum at this point indicated nearly complete conversion to **4**. After filtration through Celite, diethyl ether was added to precipitate $[Cp_2Co][BF_4]$. The supernatant liquid was filtered through silica gel and the solvent stripped to give an oil that was purified using preparative TLC (5% diethyl ether in hexanes as eluant) to afford a 51% isolated yield (9.2 mg) of **4** as a yellow oil.

Method B. Photolysis of a THF solution of **3** and 1.6 equiv of $P(OEt)_3$ under N_2 with a Rayonet reactor for 1.5 h gave a solution of **4**, which was isolated as described above for method A. IR (CH_2Cl_2): 1892 (s), 1836 (s) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 5.39 (m, 2 H, Ph), 5.16 (m, 2 H, Ph), 5.06 (m, 1 H, Ph), 4.64 (2 H, Cp), 4.29 (2 H, Cp), 4.09 (s, 5 H, Cp), 3.79 (q, J = 7.0, 6 H, OCH_2), 1.16 (t, J = 7.0, 9 H, CH_3).

Electrochemistry. Voltammetric experiments were done under a blanket of nitrogen that was saturated with solvent. The electrolyte was 0.10 M Bu_4NPF_6, which was synthesized by metathesis of Bu_4Br and HPF_6, recrystallized from CH_2Cl_2/hexanes, and dried under vacuum. The solvent in all experiments was CH_2Cl_2, which was obtained in HPLC grade from Fisher Scientific Co. Additional purification was not necessary or desirable. Once opened, the solvent was kept under nitrogen or argon and contact with the atmosphere was minimized. Cyclic voltammetry was done with EG&G 173/175/179 potentiostatic instrumentation. The working electrode was a 1 mm diameter platinum or glassy carbon disk, and the counter electrode was a platinum wire. The reference was a Metrohm Ag/AgCl electrode filled with CH_2Cl_2/Bu_4NClO_4 and saturated with LiCl; this was separated from the test solution by a salt bridge containing 0.10 M Bu_4NPF_6 in CH_2Cl_2. IR spectroelectrochemistry was done with an optically transparent thin-layer electrode (OTTLE), the construction and use of which have been reported.[12] Digital simulations of proposed mechanisms was done with the program DigiSim.[13] Details of the simulations are provided in the Results and Discussion section.

Results and Discussion

Provided all reagents are completely free of basic impurities and a non-nucleophilic solvent (CH_2Cl_2) and

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[10] Sun, S.; Sweigart, D. A. *Adv. Organomet. Chem.*, in press.

[11] Gubin, S. P.; Khandkarova, V. S. *J. Organomet. Chem.* **1970**, *22*, 449.

[12] (a) Bullock, J. P.; Boyd, D. C.; Mann, K. R. *Inorg. Chem.* **1987**, *26*, 3086. (b) Pike, R. D.; Alavosus, T. J.; Camaioni-Neto, C. A.; Williams, J. C.; Sweigart, D. A. *Organometallics* **1989**, *8*, 2631.

[13] DigiSim 2.0 program: Bioanalytical Systems, Inc., West Lafayette, IN. Most of the simulations refer to data collected at a scan rate of 0.5 V/s. Some CV's at scan rates up to 2.0 V/s were collected and found to be consistent with data and simulations at 0.5 V/s.

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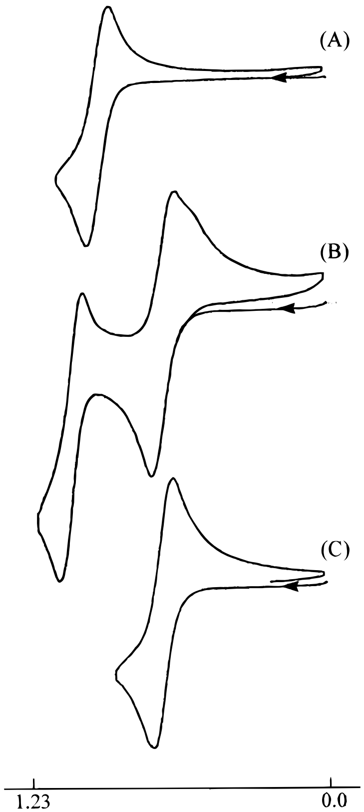

Figure 1. Cyclic voltammograms of (A) 1.2 mM (C_6H_6)-Cr(CO)$_3$ (**1**, R = H) and (B, C) CpFe($C_5H_4C_6H_5$)Cr(CO)$_3$ (**3**) in CH_2Cl_2/0.10 M Bu_4NPF_6 at 25 °C. The working electrode was a 1.0 mm diameter glassy carbon disk, and the scan rate was 0.50 V/s. Potentials are relative to ferrocene $E_{1/2}$ = 0.57 V.

Table 1. Reduction Potentials in Dichloromethane at Room Temperature[a]

couple	$E_{1/2}$ (V)[b]	couple	$E_{1/2}$ (V)[b]
$\mathbf{1}^+/\mathbf{1}$ (R = H)	0.98	$\mathbf{4}^+/\mathbf{4}$	0.39
$\mathbf{2}^+/\mathbf{2}$	0.47	$\mathbf{4}^{2+}/\mathbf{4}^+$	0.83
$\mathbf{3}^+/\mathbf{3}$	0.70	$\mathbf{5}^{3+}/\mathbf{5}^{2+}$	0.96
$\mathbf{3}^{2+}/\mathbf{3}^+$	1.09	$\mathbf{5}^{2+}/(\mathbf{4}^+ + \mathrm{P})$	−0.33[c]

[a] Electrolyte was 0.10 M Bu_4NPF_6. [b] All potentials relative to Fc^+/Fc = 0.57 V. [c] Peak potential at 0.50 V/s.

electrolyte (Bu_4NPF_6) are used, the voltammetric oxidation of **1** (R = H) occurs as a 1-electron chemically reversible process at a scan rate of 0.5 V/s (Figure 1A).[9,14] As illustrated in Figure 1B, the attachment of a ferrocenyl group to give **3** results in two oxidation processes, the first one ($\mathbf{3}^+/\mathbf{3}$) occurring at the iron center and the second one ($\mathbf{3}^{2+}/\mathbf{3}^+$) occurring at the chromium center.[15] Electrochemical data obtained for **3** and other compounds studied are summarized in Table 1. As expected, $E_{1/2}$ for $\mathbf{3}^+/\mathbf{3}$ is slightly higher than $E_{1/2}$ for Fc^+/Fc because of the electron-withdrawing nature of the (C_6H_5)Cr(CO)$_3$ moiety. Similarly, the positive charge in $\mathbf{3}^+$ results in the chromium being harder to oxidize than in **1** by 110 mV. It may be noted that the $\mathbf{3}^{2+}/\mathbf{3}^+$ couple in Figure 1B is only partly reversible (at 0.5 V/s) due to the highly electrophilic nature of $\mathbf{3}^{2+}$. The shoulder on the cathodic wave of the $\mathbf{3}^+/\mathbf{3}$ couple in Figure 1B is associated with the partial irreversibility of the $\mathbf{3}^+ \rightarrow \mathbf{3}^{2+}$ oxidation and is absent if the anodic sweep terminates short of the potential required to oxidize $\mathbf{3}^+$ (Figure 1C). Infrared spectral changes associated with the oxidation of **3** strongly support the indicated positive charge distributions in $\mathbf{3}^+$ and $\mathbf{3}^{2+}$. Table 2 gives IR data obtained by OTTLE experiments and/or by chemical oxidations with [Fc]-[BF_4] or [($C_5H_4C(O)Me$)(C_5H_5)Fe][BF_4]. Due to its short life time, the IR spectrum of $\mathbf{1}^+$ could not be recorded, but data for the sterically protected complex (C_6Et_6)-Cr(CO)$_3^+$ was easily obtained.[16] It can be seen in Figure 2 that oxidation of (C_6Et_6)Cr(CO)$_3$ is accompanied by increases of 111 and 107 cm^{-1} in the two ν_{CO} bands. By comparison, oxidation of **3** to $\mathbf{3}^+$ leads to increases in ν_{CO} of only 10 and 20 cm^{-1}, respectively. This confirms the expectation that oxidation of **3** to $\mathbf{3}^+$ is localized at the iron and not the chromium.

Table 2. Infrared Bands in the Carbonyl Region for Relevant Complexes[a]

complex	ν_{CO} (cm^{-1})
(C_6H_6)Cr(CO)$_3$ (**1**)	1971, 1891
(C_6H_6)Cr(CO)$_2$P(OEt)$_3$ (**2**)	1899, 1839
(C_6Et_6)Cr(CO)$_3$	1943, 1860
(C_6Et_6)Cr(CO)$_3^+$	2054, 1967
(C_6Et_6)Cr(CO)$_2$P(OBu)$_3$	1865, 1803
(C_6Et_6)Cr(CO)$_2$P(OBu)$_3^+$	1976, 1869
(C_6H_6)Cr(CO)$_2$PBu$_3$	1880, 1820[b]
(C_6H_6)Cr(CO)$_2$PBu$_3^+$	1989, 1881[b]
(1,3,5-$C_6H_3Me_3$)W(CO)$_2$P(OBu)$_3$	1882, 1821[b]
(1,3,5-$C_6H_3Me_3$)W(CO)$_2$[P(OBu)$_3$]$_2^{2+}$	2024, 1961[b]
CpFe(C_5H_4-C_6H_5)Cr(CO)$_3$ (**3**)	1964, 1887
CpFe(C_5H_4-C_6H_5)Cr(CO)$_3^+$ ($\mathbf{3}^+$)	1974, 1907
CpFe(C_5H_4-C_6H_5)Cr(CO)$_2$P(OEt)$_3$ (**4**)	1892, 1836
CpFe(C_5H_4-C_6H_5)Cr(CO)$_2$P(OEt)$_3^+$ ($\mathbf{4}^+$)	1990, 1892
CpFe(C_5H_4-C_6H_5)Cr(CO)$_2$[P(OEt)$_3$]$_2^{2+}$ ($\mathbf{5}^{2+}$)	2025, 1973

[a] All spectra recorded at room temperature in CH_2Cl_2. [b] Reference 18.

In previous studies it was shown that the organometallic chromium center in **3** is rapidly attacked and decomposed by donor solvents (MeCN, DMF) upon oxidation of the ferrocenyl group.[15b,c] The purpose of the present work was to determine if the neutral chromium in $\mathbf{3}^+$ is activated to CO substitution even though it is the iron and not the chromium center that is oxidized in the process $\mathbf{3} \rightarrow \mathbf{3}^+$. To establish the foundation for this question, it was first determined that oxidation of **1** (R = H) in the presence of P(OEt)$_3$ leads to rapid substitution of one CO according to the following simple scheme:

$$\mathbf{1} \underset{0.98\ \mathrm{V}}{\overset{-\,e^-}{\rightleftharpoons}} \mathbf{1}^+ \xrightarrow[k_{Cr}]{P(OEt)_3} \mathbf{2}^+ \underset{0.47\ \mathrm{V}}{\overset{+\,e^-}{\rightleftharpoons}} \mathbf{2}$$

Figure 3 shows the electrochemical behavior in this case. Assignment of the reversible couple at $E_{1/2}$ = 0.47 V to $\mathbf{2}^+/\mathbf{2}$ was verified by studying a genuine sample of **2**. The CV in Figure 3B shows a splitting of the initial oxidation wave, which occurs because the second-order reaction of $\mathbf{1}^+$ with P(OEt)$_3$ is very rapid and because there is a deficiency of nucleophile. In effect, the oxidation wave is kinetically shifted until all of the

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[14] Stone, N. J.; Sweigart, D. A.; Bond, A. M. *Organometallics* **1986**, *5*, 2553.

[15] The oxidation of complex **3** has been previously reported in DMF and MeCN, in which solvents the oxidation at the chromium center is chemically irreversible (see text): (a) Gubin, S. P.; Khandkarova, V. S. *J. Organomet. Chem.* **1970**, *22*, 449. (b) Degrand, C.; Besançon, J.; Radecki-Sudre, A. *J. Electroanal. Chem.* **1984**, *160*, 199. (c) Degrand, C.; Radecki-Sudre, A. *J. Organomet. Chem.* **1984**, *268*, 63.

[16] Meng, Q.; Huang, Y.; Ryan, W. J.; Sweigart, D. A. *Inorg. Chem.* **1992**, *31*, 4052.

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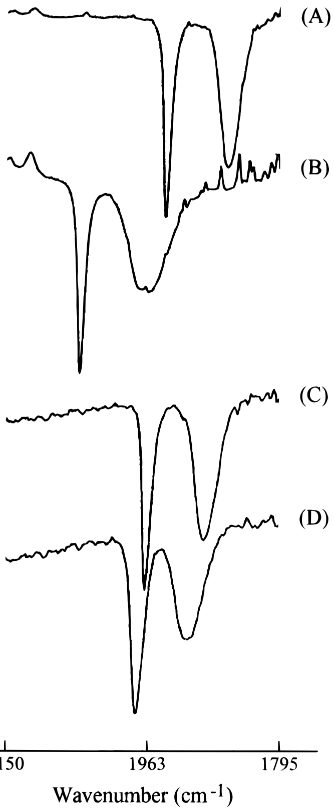

Figure 2. IR spectra in CH_2Cl_2/0.20 M Bu_4NPF_6 at 25 °C obtained with an OTTLE cell. (A) and (B) refer to 1.0 mM $C_6Et_6Cr(CO)_3$ before and after oxidation to the monocation. (C) and (D) refer to 1.0 mM $CpFe(C_5H_4C_6H_5)Cr(CO)_3$ (**3**) before and after oxidation to $\mathbf{3}^+$.

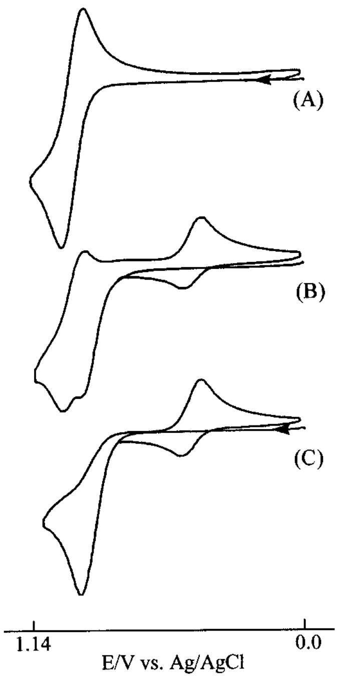

Figure 3. Cyclic voltammograms of 1.2 mM $(C_6H_6)Cr(CO)_3$ (**1**, R = H) in CH_2Cl_2/0.10 M Bu_4NPF_6 at 25 °C with $P(OEt)_3$ present at a concentration of (A) none, (B) 0.64 mM, and (C) 3.0 mM. The working electrode was a 1.0 mm diameter glassy carbon disk, and the scan rate was 0.50 V/s. Potentials are relative to ferrocene $E_{1/2}$ = 0.57 V.

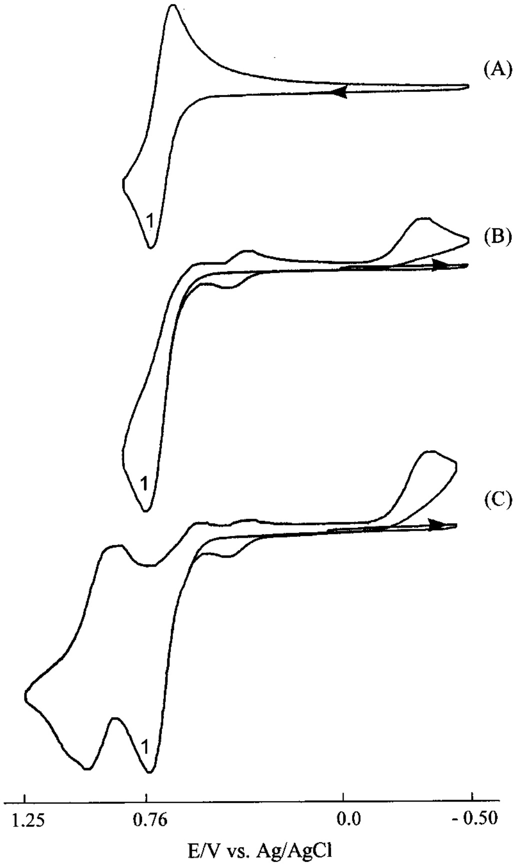

Figure 4. Cyclic voltammograms of 1.0 mM CpFe-$(C_5H_4C_6H_5)Cr(CO)_3$ (**3**) in CH_2Cl_2/0.10 M Bu_4NPF_6 at 25 °C with $P(OEt)_3$ present at a concentration of (A) none and (B, C) 0.030 M. The working electrode was a 1.0 mm diameter glassy carbon disk, and the scan rate was 0.50 V/s. Potentials are relative to ferrocene $E_{1/2}$ = 0.57 V.

nucleophile is consumed, and then oxidation continues at the unshifted potential, resulting in the appearence of a kinetic prewave. As elaborated by Parker et al.,[17] the separation of the two waves is a sensitive function of experimental parameters and can be used to determine second-order rate constants that are greater than 10^6 M^{-1} s^{-1}. Digital simulation of the CV in Figure 3B gave the rate constant (k_{Cr}) for the reaction of $\mathbf{1}^+$ (R = H) and $P(OEt)_3$ as 1.5 (±0.5) × 10^7 M^{-1} s^{-1}.

The oxidation of **3** with and without $P(OEt)_3$ present produced results shown in Figure 4. It is obvious from Figure 4B,C that $\mathbf{3}^+$ reacts rapidly with $P(OEt)_3$ and in a seemingly rather complicated manner. The prominant features of Figure 4B compared to 4A include (1) an apparent significant increase in the oxidation current due to the ferrocenyl group (wave 1), along with complete loss of chemical reversibility, (2) a small reduction wave at ca. 0.36 V, and (3) a chemically irreversible reduction wave at ca. −0.33 V. Extension of the potential range to 1.25 V with $P(OEt)_3$ present produced the CV in Figure 4C (cf. Figure 1B), which is somewhat muted on the return (cathodic) sweep from 1.25 V due to partial electrode coating.

The voltammograms in Figure 4B,C suggest that $P(OEt)_3$ attacks the chromium center in $\mathbf{3}^+$, possibly to effect CO substitution. To examine this possibility, $CpFe(C_5H_4C_6H_5)Cr(CO)_2P(OEt)_3$ (**4**) was synthesized and studied. Figure 5 shows pertinent CV's for the

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[17] Jensen, B. S.; Parker, V. D. *Electrochim. Acta* **1973**, *18*, 665. Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1987**, *109*, 2521. Huang, Y.; Carpenter, G. B.; Sweigart, D. A.; Chung, Y. K.; Lee, B. Y. *Organometallics* **1995**, *14*, 1423.

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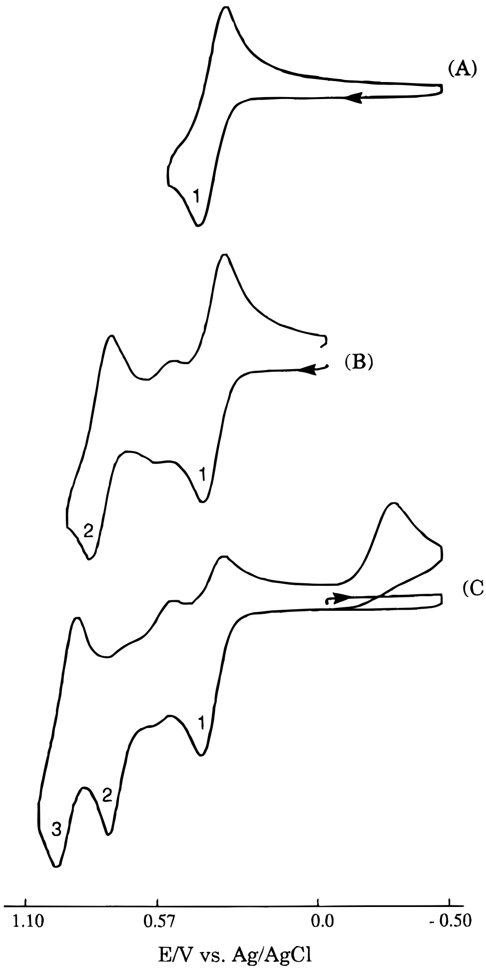

Figure 5. Cyclic voltammograms of 0.50 mM CpFe($C_5H_4C_6H_5$)Cr(CO)$_2$P(OEt)$_3$ (**4**) in CH_2Cl_2/0.10 M Bu_4NPF_6 at 25 °C with P(OEt)$_3$ present at a concentration of (A) none *or* 5.0 mM, (B) none, and (C) 5.0 mM. The working electrode was a 1.0 mm diameter glassy carbon disk, and the scan rate was 0.50 V/s. Potentials are relative to ferrocene $E_{1/2} = 0.57$ V.

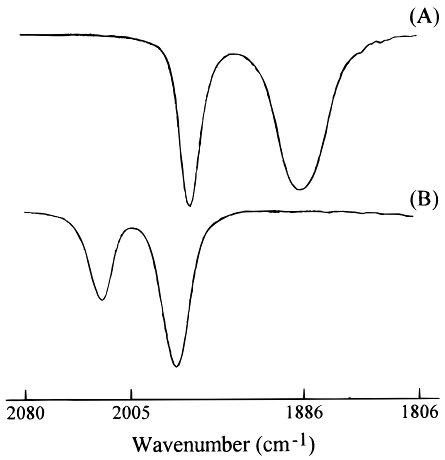

Figure 6. IR spectra of a CH_2Cl_2 solution containing 1.0 mM CpFe($C_5H_4C_6H_5$)Cr(CO)$_3$ (**3**) and 4.0 mM P(OEt)$_3$ (A) before and (B) after the addition of 4 equiv of the oxidizing agent [(C_5H_4C(O)Me)(C_5H_5)Fe][BF_4]. Spectrum B corresponds to $\mathbf{5}^{2+}$.

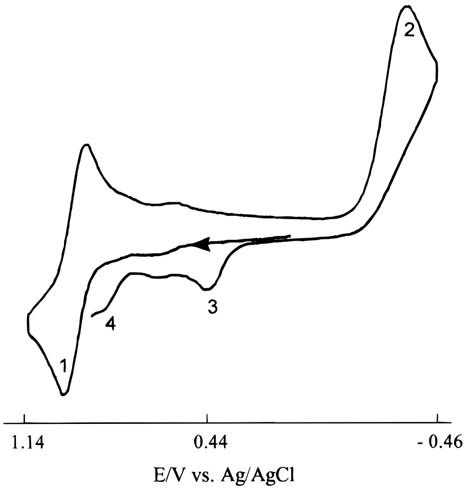

Figure 7. Cyclic voltammogram of 0.35 mM [CpFe($C_5H_4C_6H_5$)Cr(CO)$_2$[P(OEt)$_3$]$_2$][BF_4]$_2$ ($\mathbf{5}^{2+}$) in CH_2Cl_2/0.10 M Bu_4NPF_6 at 25 °C. The working electrode was a 1.0 mm diameter glassy carbon disk, and the scan rate was 0.50 V/s. Potentials are relative to ferrocene $E_{1/2} = 0.57$ V.

oxidation of **4** with and without P(OEt)$_3$ present. The first oxidation is reversible and occurs at $E_{1/2} = 0.39$ V to give a cation that does not react with P(OEt)$_3$ (Figure 5A). This information immediately identifies the oxidation to $\mathbf{4}^+$ as being chromium centered. This follows from a comparison to **2**, which oxidizes at a slightly higher potential (0.47 V) and similarly gives a radical cation that does not react with P(OEt)$_3$; the electron-donating character of the ferrocenyl group in **4** accounts for the lower $E_{1/2}$. IR spectra (Table 2) confirm the above assignment. Thus, oxidation of **4** to $\mathbf{4}^+$ results in increases in ν_{CO} of 98 and 56 cm^{-1}, which is about the same as that seen with the chromium-centered oxidation in (C_6Et_6)Cr(CO)$_2$P(OBu)$_3$ and (C_6H_6)Cr(CO)$_2$PBu$_3$. The second oxidation in Figure 5B (wave 2) occurs with $E_{1/2} = 0.83$ V and is identified with ferrocenyl oxidation in $\mathbf{4}^+$ to give $\mathbf{4}^{2+}$. (Note: the redox couple at 0.57 V in Figure 5B,C is due to ferrocene impurity.) The higher $E_{1/2}$ for ferrocenyl oxidation in $\mathbf{4}^+$ compared to **3** (0.70 V) is due to the positive charge of the former. The behavior shown in Figure 5C indicates the $\mathbf{4}^{2+}$ reacts with P(OEt)$_3$, which causes oxidation wave 2 to shift negatively by ca. 70 mV and become chemically irreversible while a new reversible oxidation appears at $E_{1/2} = 0.96$ V (wave 3). There is also a new irreversible reduction at -0.33 V. Whatever the identity of the product of the reaction of $\mathbf{4}^{2+}$ and P(OEt)$_3$, it seems reasonable to conclude that it contains at least two molecules of P(OEt)$_3$. Furthermore, a comparison of Figures 5C and 4B,C shows a number of common features, suggesting that the initial product of the reaction of $\mathbf{3}^+$ with P(OEt)$_3$ is $\mathbf{4}^+$.

The *chemical* oxidation of **3** (or **4**) in the presence of P(OEt)$_3$ resulted in the formation of a purple species with ν_{CO} bands at 2025 and 1973 cm^{-1} (Figure 6). The positions of these IR bands are quite similar to those reported[18] for (arene)W(CO)$_2$[P(OBu)$_3$]$_2^{2+}$, suggestive of structure $\mathbf{5}^{2+}$ in the present case. The purple complex was easily isolated as the BF_4^- salt (see Experimental Section), and its ^{1}H NMR spectrum was found to be completely consistent with the structure indicated for $\mathbf{5}^{2+}$. The relative intensities of the IR bands of $\mathbf{5}^{2+}$ imply a *trans* rather than *cis* arrangement of the CO's.[19] The cyclic voltammogram of [**5**][BF_4]$_2$ (Figure 7) shows

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(18) (a) Zhang, Y.; Gosser, D. K.; Rieger, P. H.; Sweigart, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 4062. (b) Huang, Y.; Meng, Q.; Ryan, W. J.; Sun, S.; Sweigart, D. A. To be submitted for publication.

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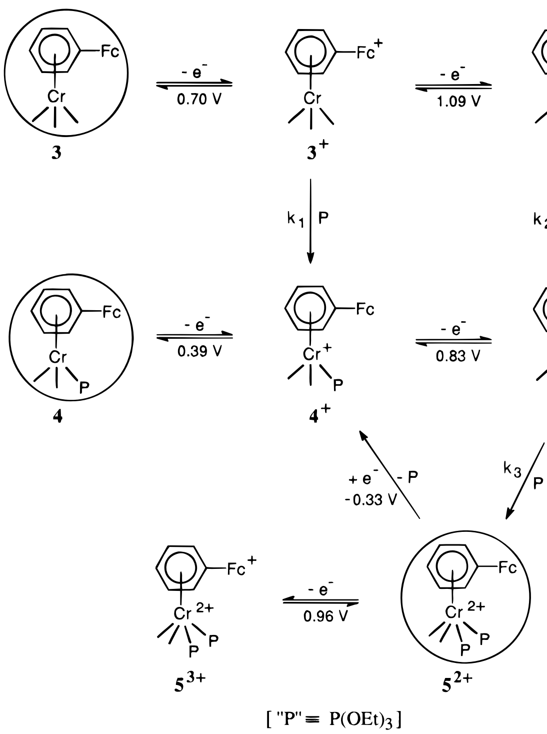
Scheme 1



reversible oxidation of the ferrocenyl group at wave **1** with $E_{1/2} = 0.96$ V. Reduction of $\mathbf{5}^{2+}$ occurs irreversibly at a potential of −0.33 V (wave 2); after sweeping through this reduction, the forward anodic scan shows two waves (3 and 4) that are assigned to the oxidation of **4** to $\mathbf{4}^{+}$ and $\mathbf{4}^{+}$ and $\mathbf{4}^{2+}$, respectively. The conclusion is that reduction of $\mathbf{5}^{2+}$ is a 2-electron process, generating **4** and free $P(OEt)_3$. In accordance with this, it was found that the chemical reduction of a solution of $\mathbf{5}^{2+}$ with cobaltocene ($E_{1/2} \approx -0.8$ V) gives a high yield of complex **4**. Indeed, this constitutes the most convenient way to synthesize **4** (*vide supra*).

All of the IR, electrochemical, and NMR results can be accommodated by Scheme 1. The complexes isolated and studied independently are encircled. Digital simulations of the voltammetric response predicted by Scheme 1 were performed with "DigiSim" software.[13] The procedure followed was to first simulate the CV's of intermediates **4** and $\mathbf{5}^{2+}$ and then use these results as input for the simulation of the behavior of **3**. Figure 8 gives the calculated CV's for **3** and **4** in the presence of $P(OEt)_3$ as well as for $\mathbf{5}^{2+}$; these can be seen to closely resemble the experimental results in Figures 4B, 5C, and 7. For the simulations, all redox couples were assumed to be Nernstian. The rate constants for the homogeneous reactions 1−3 could be estimated or at least bounded by requiring that the experimental voltammograms of **3**, **4**, and $\mathbf{5}^{2+}$ be simulated with a single set of rate parameters.

$$\mathbf{3}^{+} + \mathrm{P} \xrightarrow{k_1} \mathbf{4}^{+} \tag{1}$$

$$\mathbf{3}^{2+} + \mathrm{P} \xrightarrow{k_2} \mathbf{4}^{2+} \tag{2}$$

$$\mathbf{4}^{2+} + \mathrm{P} \xrightarrow{k_3} \mathbf{5}^{2+} \tag{3}$$

Consideration of Scheme 1 shows that the apparent increase in oxidation current for the ferrocenyl group in **3** when $P(OEt)_3$ is added to the solution (Figure 4, wave 1) occurs because $\mathbf{3}^{+}$ rapidly substitutes a CO to give $\mathbf{4}^{+}$, which oxidizes at a potential only slightly greater than that for **3** (0.83 and 0.70 V, respectively). These two anodic processes are not resolved in the overall 2-electron process $\mathbf{3} \rightarrow \mathbf{4}^{2+}$ because of differential kinetic shifts of the respective oxidation waves. In particular, the behavior of wave 1 in Figure 4 and wave 2 in Figure 5 implies a much larger kinetic shift associated with reaction 3 than reaction 1; the conclusion is that k_3 must be larger than k_1 by several orders of magnitude. Consideration of the oxidation wave for $\mathbf{4}^{+}$ in Figure 5C (wave 2) and Figure 7 (wave 4) allowed an estimate of rate constant k_3. The rate constant for reaction 2 could not be determined, except to place a lower limit. A summary of the conclusions regarding the homogeneous rate constants at 25 °C is as follows: $k_1 \approx 3 \times 10^3$ M^{-1} s^{-1}; $k_2 > 10^4$ M^{-1} s^{-1}; $k_3 \approx 10^6$ M^{-1} s^{-1}. Reactions 2 and 3 involve substitutions at 17-electron centers and would be expected to be rapid. Considering the coordination about the chromium in $\mathbf{3}^{2+}$ and $\mathbf{4}^{2+}$, it seems likely that k_2 is larger than k_3 and almost certainly exceeds the lower limit of 10^4 M^{-1} s^{-1} implied by the simulations.

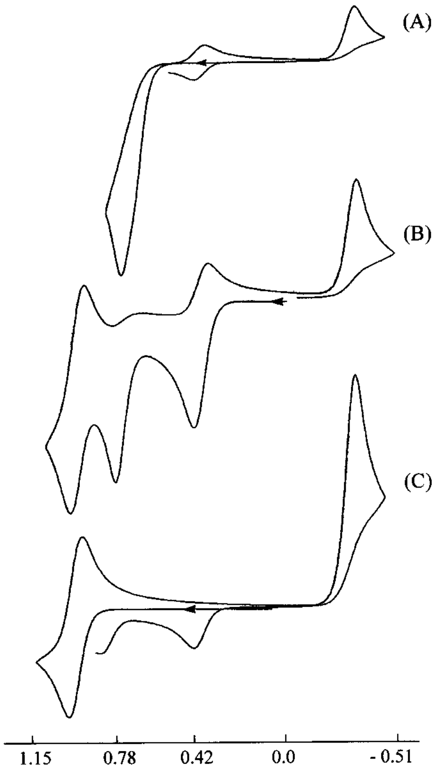


Figure 8. Simulated cyclic voltammograms based on Scheme 1 at 25 °C and 0.50 V/s. CV A corresponds to complex **3** (1.0 mM) and P (0.030 M); compare to Figure 4B. CV B corresponds to complex **4** (0.50 mM) and P (5.0 mM); compare to Figure 5C. CV C corresponds to complex **3** (0.35 mM); compare to Figure 7. The current scales of (A)−(C) are normalized.

One of the most important results to be gleaned from Scheme 1 concerns the role of the ferrocenyl group in reactivity modulation at the chromium center according to reaction 1. Thus, **3** does not react thermally with $P(OEt)_3$ over a period of several hours. "Turning on"

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(19) King, R. B.; Reimann, R. H.; Darensbourg, D. J. *J. Organomet. Chem.* **1975**, *93*, C23.

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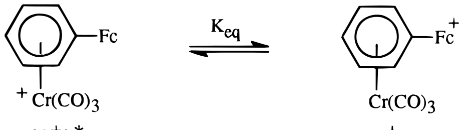
the ferrocenyl switch by oxidation leads to rapid CO substitution in **3**$^+$ even though IR spectra (Figure 2) clearly establish that the charge is localized at the iron center. This apparent paradox is easily rationalized. It is important to note that CO substitution in **3**$^+$ would appear rapid even if it were orders of magnitude slower than it is in the chromium centered radical **1**$^+$. Oxidation of **3** is predominantly at the iron, and this means that the equilibrium in eq 4 lies far to the right. The



{**3**$^+$}* **3**$^+$ (4)

equilibrium constant K_{eq} can be calculated from the potential data in Table 1. Thus, the difference in reduction potentials for **1**$^+$ and **3**$^+$ implies that the chromium to iron charge transfer **1**$^+$ → **3**$^+$ has an equilibrium constant of 5×10^4. This is not the same as "K_{eq}" in eq 4 because of the ferrocenyl substituent effect on the $E_{1/2}$ for {**3**$^+$}* relative to **1**$^+$. This substituent effect can be reasonably approximated as 80 mV by comparing the reduction potentials of the chromium centered radicals **2**$^+$ and **4**$^+$, which differ only by a ferrocenyl substituent. It is concluded that the $E_{1/2}$'s for {**3**$^+$}* and **3**$^+$ differ by 0.20 V, so that K_{eq} in eq 4 is 2.4×10^3. Assuming that the equilibrium in eq 4 is very rapid, the apparent rate of reaction of **3** with P(OEt)$_3$ upon oxidation is determined by the fraction of oxidized **3** present as the chromium-centered radical {**3**$^+$}*. This fraction is just $1/K_{eq}$. It was shown above that **1**$^+$ (R = H) reacts with P(OEt)$_3$ with a rate constant of 1.5×10^7 M^{-1} s^{-1}. Since **1**$^+$ and {**3**$^+$}* differ only by a neutral ferrocenyl substituent, their reactivity should be similar and one then predicts that the equilibrium mixture [**3**$^+$ + {**3**$^+$}*] should have an apparent rate constant (k_1) of ca. $1.5 \times 10^7/K_{eq} = 6 \times 10^3$ s^{-1}. This is gratifyingly close to the determined value of ca. 3×10^3 M^{-1} s^{-1} (*vide supra*). A corollary to the analysis just presented is that the reactivity of the chromium center in compounds such as **3** can be quantitatively tuned by appropriate variation of substituents on the cyclopentadienyl rings of the ferrocenyl switch. The conclusion is that oxidative activation at a metal is possible at potentials far short of that required to directly oxidize the metal. This methodology for reactivity control at a metal should be advantageous when the metal of interest can not be directly oxidized without suffering decomposition (a fairly common occurrence). The redox switch allows for controlled activation without self-destruction.

The chemistry in Scheme 1 contains some novel features. Perhaps most interesting is the self-closing nature of the ferrocenyl switch. Thus, oxidation of **3** to **3**$^+$ opens the switch, activating the chromium to CO substitution to afford **4**$^+$. The reaction **3**$^+$ → **4**$^+$ is accompanied by internal electron transfer from Cr to Fe, thereby closing the switch. That this should happen is easily predicted from the known $E_{1/2}$ values of Fc$^+$/Fc and **2**$^+$/**2**, which show that the chromium in **2** is more electron rich or more easily oxidized than is the iron in Fc. From a practical point of view, this automatic shut off of the switch as **4**$^+$ forms means that it can be reopened by further oxidation, thereby allowing successive activations at a single center. For example, oxidation of **4**$^+$ at 0.83 V is a clean (reversible) process that activates the chromium to further reaction with P(OEt)$_3$. In this case the reaction is ligand addition, **4**$^{2+}$ → **5**$^{2+}$, and once again is accompanied by switch closing. Oxidation of the ferrocenyl moiety in **3**, **4**$^+$, and **5**$^{2+}$ is reversible in each case with $E_{1/2}$ following a simple anticipated positive trend (0.70, 0.83, 0.96 V).

The driving force for the addition reaction **4**$^{2+}$ → **5**$^{2+}$ is the internal electron transfer, which allows the product to attain an 18-electron count at the chromium. Addition does not occur with **4**$^+$ (or **2**$^+$) because the chromium would then be a 19-electron center. In principle, **2**$^{2+}$ could react with P(OEt)$_3$ to give an analogue to **5**$^{2+}$. However, it was found that **2**$^{2+}$ is formed in a completely irreversible manner and that addition of P(OEt)$_3$ to the solution prior to oxidation of **2**$^+$ does not result in a species identifiable from IR or voltammetric behavior as being an addition product. In contrast, **4**$^{2+}$ is formed at a potential ca. 0.5 V lower than that required to generate **2**$^{2+}$ and is quite stable (**4**$^{2+}$/**4**$^+$ reversible) because it is the ferrocenyl group that is oxidized. Thus, it is the presence of the ferrocenium switch in **4**$^{2+}$ that makes it possible to generate **5**$^{2+}$. The intense purple color of **5**$^{2+}$ (λ_{max} = 548 nm; ϵ = 1930 M^{-1} cm^{-1} in CH$_2$Cl$_2$) is unusual in organometallic chemistry and arises from intervalence charge transfer to give the 19-electron complex {**5**$^{2+}$}*.

In summary, it was found that the ferrocenyl group in CpFe(C$_5$H$_4$C$_6$H$_5$)Cr(CO)$_3$ (**3**) functions as a reversible redox switch and provides a mechanism for the chromium center to be oxidatively activated to ligand substitution and addition reactions. Because initial oxidation occurs at the ferrocenyl group, the potentials required for activation are far lower than would otherwise be the case. In effect, the chromium center is "tickled" and this allows for controlled reactions without unproductive decomposition. The degree of activation is shown to be directly related to the difference in oxidation potentials of the chromium and iron centers, which suggests the possibility that the attachment of a remote redox switch may be a useful general methodology for the quantitative control of the reactivity of a metal center. It was found that the ligand substitution **3**$^+$ → **4**$^+$ is accompanied by internal electron transfer with the ferrocenium switch in **3**$^+$ closing to ferrocenyl in **4**$^+$. This provides a pathway for a second activation and subsequent ligand addition to afford the novel purple complex **5**$^{2+}$, the formation of which is concomitant with a second self-closing of the redox switch.

It can be anticipated that the attachment of a cobaltocenium switch to **1** would permit chromium activation by reduction. While oxidatively-promoted substitution of CO by P(OEt)$_3$ is a stoichiometric process, the reductively-promoted reaction would be expected to be electron transfer chain (ETC) catalyzed because the product is more easily oxidized than is the reactant. This chemistry is currently under investigation.

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