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Characterization and Reactions of Previously Elusive 17-Electron Cations: Electrochemical Oxidations of $(C_6H_6)Cr(CO)_3$ and $(C_5H_5)Co(CO)_2$ in the Presence of $[B(C_6F_5)_4]^-$

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We report the electrochemical generation of the 17-electron radicals $[(C_6H_6)Cr(CO)_3]^+$, **1**$^+$, and $[(C_5H_5)Co(CO)_2]^+$, **2**$^+$, under conditions of enhanced stability which allow the systematic study of their reactions. The key modification of earlier attempts[1] to generate persistent solutions of these cations is the use of $[B(C_6F_5)_4]^-$, an ion of limited nucleophilicity, as the supporting electrolyte anion.

Half-sandwich complexes of the type (π-ArL)M(CO)$_n$, where (π-ArL) is a planar aromatic ligand and n is the number of carbonyl groups required to achieve an 18-electron configuration,[2] are of both historical and practical importance in organometallic chemistry.[3] The considerable efforts to generate corresponding 17-electron cations on synthetically useful time scales have failed except for derivatives either having substituted π ligands or in which at least one CO has been replaced by an electron-donating ligand such as PR_3.[4] It is generally understood that the electrophilicity of the 17-electron cations leaves them susceptible to cleavage reactions with either donor solvents or other weak nucleophiles, including the supporting electrolyte anions. Perhaps the best understood of these processes involves **1**$^+$, which decomposes with loss of benzene after attack by anions such as $[ClO_4]^-$, $[BF_4]^-$, or, more slowly, $[PF_6]^-$ [1b,5] The recent emergence[6] of large fluoroaryl borate anions to implement the stabilization of reactive cations[7] raises the possibility of their utility in improving anodic reaction chemistry. Very promising results have already been reported using either $[B(C_6H_3(CF_3)_2)_4]^-$[8] or the closely related and even less nucleophilic[6b,9] anion $[B(C_6F_5)_4]^-$, TFAB.[10,11] We now show that the TFAB anion succeeds in stabilizing **1**$^+$, permitting an electrochemical switch mechanism for synthetic-level CO-substitution reactions of (benzene)Cr(CO)$_3$. The same electrolyte also allows the characterization of the **2**/**2**$^+$ couple by cyclic voltammetry (CV) and permits the study of dimerization processes and CO-substitution reactions of **2**$^+$.

The one-electron oxidation of **1** to **1**$^+$ ($E_{1/2} = 0.44$ V vs Fc) is chemically reversible by CV at room temperature in CH_2Cl_2/ 0.1 M $[NBu_4]$[TFAB]. Exhaustive one-electron oxidation (1.00 ± 0.04 F/equiv) at 273 K of 1−2 mM **1** at $E_{appl} = 0.8$ V gave dark yellow solutions of the monocation **1**$^+$. After more than 1 h, cathodic electrolysis at $E_{appl} = 0.2$ V regenerated 80−85% **1**. Solutions of **1**$^+$ were removed for EPR analysis ($g_{\parallel} = 2.017$, $g_{\perp} = 1.979$ at 149 K, silent in fluid solution[12]) and for IR spectroscopy (Figure 1). The increase in ν_{CO} (1971 and 1891 cm^{-1} in **1**; 2079 and 2009 cm^{-1} in **1**$^+$) is as expected for a one-electron oxidation. Consistent with previous literature,[1]anodic electrolysis of **1** in the presence of $[PF_6]^-$ gives decomposition of the complex, judging by the absence of products which show either electroactivity or ν_{CO} bands.

Treatment of solutions of **1**$^+$ with PPh_3, or oxidation of **1** in the presence of PPh_3, gave the substitution product $[(C_6H_6)Cr(CO)_2PPh_3]^+$, **3**$^+$ ($E_{1/2} = -0.22$ V, matching that of an authentic sample of **3**). Cathodic re-electrolysis of the dark orange solutions of **3**$^+$-gave neutral **3** in yields of up to 80%. By taking advantage of the increase in CO substitution rate[13] in **1**$^+$over **1**, the combined forward and back electrolyses provide isolable[14] **3** through an "electrochemical switch" mechanism (Scheme 1) which may be useful in promoting the substitution chemistry of the important class[15] of (arene)Cr(CO)$_3$ compounds.

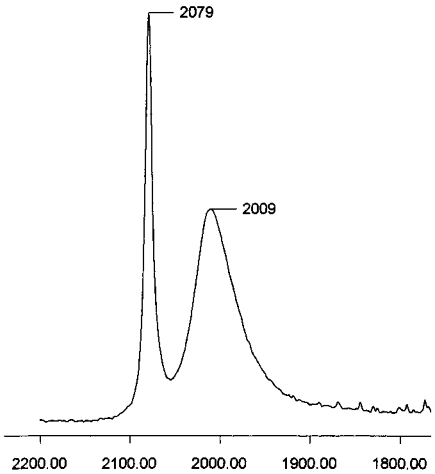
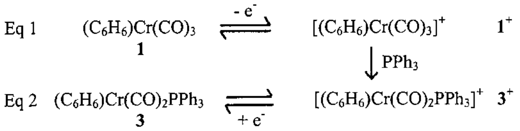


Figure 1. IR spectrum at room temperature in CO region for **1**$^+$ in CH_2Cl_2/$[NBu_4]$[TFAB] after bulk anodic electrolysis of 2 mM **1**.

Scheme 1



In contrast to the extensive previous CV evidence for transient **1**$^+$, the conceptually related complex **2**$^+$ has avoided detection. The cation **2**$^+$ forms a mercurous complex when anodized at a Hg electrode[16] and loses CO when generated by Ag(I).[17] The CV scans of some derivatized products such as $CpCo(CO)(PPh_3)$[4(b)] and $(C_5Me_5)Co(CO)_2$[16] have displayed reversible one-electron oxidations.

The voltammetric behavior of **2** in CH_2Cl_2/ 0.05 M $[NBu_4]$[TFAB] depends on scan rate, temperature and, most dramatically, on the concentration of **2**. Whereas low concentrations (≤0.3 mM) give CV wave shapes resembling those of a reversible one-electron oxidation, as the concentration of **2** is increased the wave broadens and resolves into two features (Figure 2). Since IR spectra obtained after bulk electrolysis ($E_{appl} = 0.7$ V, 298 K, 1.0 F/equiv) of 2 mM **2** show only terminal CO bands ($\nu_{CO} = 2135$ and 2104 cm^{-1}), the net product of the two waves is likely to be the previously unreported metal−metal bonded dimeric dication $[Cp_2Co_2(CO)_4]^{2+}$,

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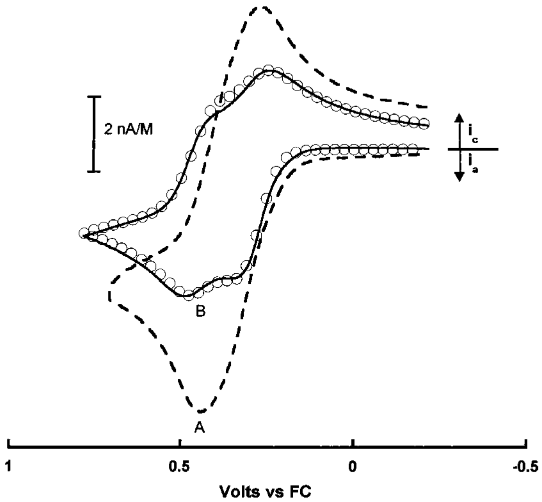
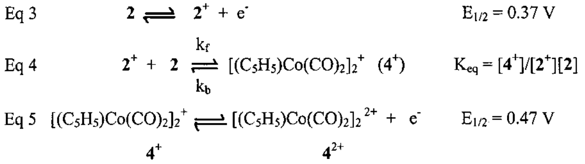


Figure 2. Experimental (dashed and solid lines) and simulated (circles) CV scans of **2** in CH_2Cl_2/[NBu_4][TFAB] at 1 mm GC disk, scan rate 0.5 V/s. Scan A: [**2**] = 0.3 mM; scan B: [**2**] = 2.3 mM; *y*-axis is concentration-normalized current. Simulation uses the mechanism of Scheme 2 with $K_{eq} = 3 \times 10^4\ M^{-1}$ and $k_f = 4 \times 10^6\ M^{-1}\ s^{-1}$.

Scheme 2. Proposed Mechanism for Formation of $\mathbf{4}^{2+}$



$$\text{Eq 3}\quad \mathbf{2} \rightleftharpoons \mathbf{2}^+ + e^- \qquad E_{1/2} = 0.37\ V$$

$$\text{Eq 4}\quad \mathbf{2}^+ + \mathbf{2} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [(C_5H_5)Co(CO)_2]_2^+\ (\mathbf{4}^+) \qquad K_{eq} = [\mathbf{4}^+]/[\mathbf{2}^+][\mathbf{2}]$$

$$\text{Eq 5}\quad \underset{\mathbf{4}^+}{[(C_5H_5)Co(CO)_2]_2^+} \rightleftharpoons \underset{\mathbf{4}^{2+}}{[(C_5H_5)Co(CO)_2]_2^{2+}} + e^- \qquad E_{1/2} = 0.47\ V$$

$\mathbf{4}^{2+}$. Cathodic back-electrolysis at $E_{appl} = 0$ V regenerated neutral **2** ($\nu_{CO} = 2024$ and $1958\ cm^{-1}$), with a small amount of Cp_2Co^+ as a side product. Although the SOMO of $\mathbf{2}^+$ has some cyclopentadienyl character,[18] the fact that we observe similar CV behavior for $(C_5Me_5)Co(CO)_2$ in this electrolyte[19] argues against dimerization through the five-membered ring.

The most common redox dimerization mechanisms are the radical−radical ($\mathbf{2}^+ + \mathbf{2}^+$) and radical−substrate ($\mathbf{2}^+ + \mathbf{2}$) processes.[20] Digital simulations[21] (Figure 2 and Scheme 2) favor the latter and suggest that the oxidation of $\mathbf{4}^+$ ($E_{1/2} = 0.47$ V) is thermodynamically slightly more difficult than the initial oxidation of **2** ($E_{1/2} = 0.37$ V).[22] Parallel to the behavior of $\mathbf{1}^+$, CV scans of **2** in the presence of 1 equiv of PPh_3 give the monosubstituted product $[CpCo(CO)(PPh_3)]^+$, identified by its $E_{1/2}$ value (−0.38 V).[4b]

Addition of a few equivalents of a “traditional” anion such as $[PF_6]^-$ eliminates the features ascribed to the $\mathbf{4}^+/\mathbf{4}^{2+}$ couple, resulting in a reversible one-electron oxidation wave for $\mathbf{2}/\mathbf{2}^+$.[23] With about 10 equiv of $[PF_6]^-$ present, adsorption effects are noted, stemming from the poor solubility of $\mathbf{2}[PF_6]$ in CH_2Cl_2. Taken together with the effects of added PPh_3 (vide supra), it appears that reagents of modest nucleophilicity, including $[PF_6]^-$, may limit or eliminate the dimerization reaction of $\mathbf{2}^+$.

The solubility and stability enhancements acquired with $[B(C_6F_5)_4]^-$-containing electrolytes should be applicable to a wide range of organic, inorganic, and organometallic anodic processes. Recent synthetic advances[6,24] in the preparation of large anions show that it is increasingly possible to tailor supporting electrolytes to specific electrochemical objectives. These aims include not only the presently addressed goals of kinetic stabilization and dissolution of highly electrophilic cations but also the desires to effect electrosynthesis in very low-polarity solvents and to control comproportionation equilibria [25] in multielectron processes.

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