Communication

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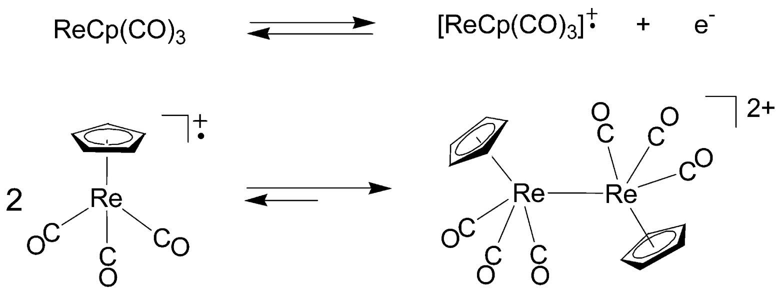

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Anodic Preparation of $[Re_2Cp_2(CO)_6]^{2+}$: A Dimeric Dication that Provides the Powerful One-Electron Oxidant $[ReCp(CO)_3]^+$

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As highly symmetric and structurally unencumbered parents of the ubiquitous family of half-sandwich organometallics, dileptic metal compounds containing only carbonyl groups along with cyclopentadienyl (Cp) or arene ligands play a central role in organometallic chemistry.[1] The anodic chemistry of these compounds is significantly broadened when electrochemistry is carried out in low-donor solvents having a weakly coordinating electrolyte anion (WCA).[2] We now report that anodic oxidation of $Re(\eta^5\text{-}C_5R_5)(CO)_3$ (**1**, R = H; or **2**, R = Me) in the presence of a WCA gives the unusual dimeric dication $[Re_2(C_5R_5)_2(CO)_6]^{2+}$ after first forming the radical cation, $\mathbf{1}^+$ or $\mathbf{2}^+$. Although the dimers are thermodynamically favored over the monomer radicals, the latter are present in solution in sufficient quantities to act as useful oxidizing agents. The very positive $E°$ value of $\mathbf{1}/\mathbf{1}^+$ (1.16 V vs $FeCp_2^{0/+}$) makes this system the strongest isolable organometallic oxidizing agent yet reported.[3]

The dominant feature of cyclic voltammetry (CV) scans of **1** at concentrations below about 0.6 mM in CH_2Cl_2/0.1 M $[NBu_4]$-[TFAB] (TFAB = $[B(C_6F_5)_4]^-$) is a one-electron oxidation wave, $E_{1/2}$ = 1.16 V vs $FeCp_2^{0/+}$, that is quasi-Nernstian but of only modest chemical reversibility[4] at scan rates below about 1 V s^{-1} (Figure 1). At slower scan rates or in higher concentrations, the oxidation of **1** is chemically irreversible and a broad cathodic product wave appears (irreversible, $E_{pc} \approx 0.55$ V), assigned to reduction of the dimer dication formed by radical−radical coupling of $\mathbf{1}^+$ (see eqs 1−3).

$$ReCp(CO)_3 \rightleftharpoons [ReCp(CO)_3]^+ + e^- \qquad E_{1/2} = 1.16\text{ V} \quad (1)$$

$$2[ReCp(CO)_3]^+ \rightleftharpoons [Re_2Cp_2(CO)_6]^{2+} \qquad K_{dim} \approx 10^5\text{ M}^{-1} \quad (2)$$

$$[Re_2Cp_2(CO)_6]^{2+} + 2\,e^- \rightarrow 2\,ReCp(CO)_3 \qquad E_{pc} \approx 0.55\text{ V} \quad (3)$$

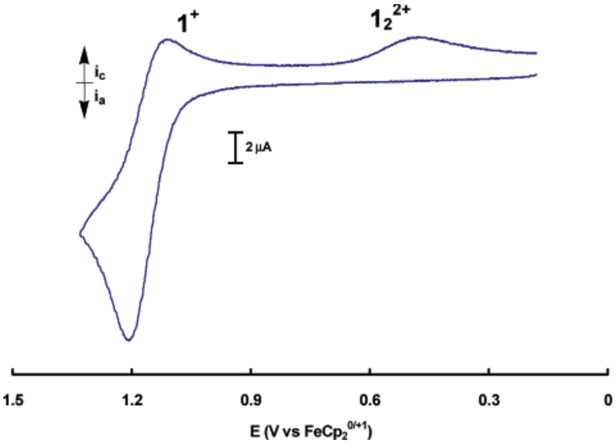
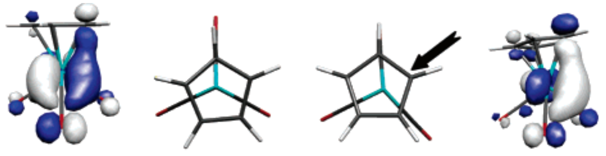


Figure 1. Cyclic voltammogram of 0.6 mM **1** in CH_2Cl_2/0.1 M $[NBu_4]$-[TFAB] at 0 °C; 2 mm glassy carbon electrode, scan rate = 0.3 V s^{-1}.



1 $\mathbf{1}^+$

Figure 2. Top view of complexes **1** and $\mathbf{1}^+$, HOMO of **1** on left and SOMO of $\mathbf{1}^+$(ADF) on right.

Bulk electrolysis of **1** passes 1 ± 0.1 F/equiv and gives an orange solution at room temperature with the major product peak being at E_{pc} = 0.55 V. Cathodic re-electrolysis at E_{appl} = 0.3 V regenerates **1**.[5] Conducting the anodic electrolysis at 243 K affords $[Re_2Cp_2(CO)_6][TFAB]_2$, $\mathbf{1}_2^{2+}$, in good yield as a precipitate from the electrolysis solution.[6] IR spectra of the solid in Nujol gave two pairs of ν_{CO} peaks, one at 2113 cm^{-1}, 2046 cm^{-1} and another at 2098 cm^{-1}, 2037 cm^{-1}. In CH_2Cl_2, a single set was observed at 2104 cm^{-1}, 2031 cm^{-1} (for **1**, ν_{sym} = 2024 cm^{-1}, ν_{asym} = 1926 cm^{-1}). The two sets of carbonyl peaks in the solid-state spectrum are attributed to the *cis* and *trans* isomers, respectively, of the dimer dication, with the more stable *trans* isomer (vide infra) being responsible for the solution spectrum.

Qualitatively similar results have been obtained on the oxidation of the permethylated Cp analogue $ReCp^*(CO)_3$, **2**. In this case, $E_{1/2}$ = 0.91 V for $\mathbf{2}/\mathbf{2}^+$ and $E_{pc} \approx 0.15$ V for reduction of the corresponding dimer dication. Bulk electrolyses gave very persistent solutions of the dication, which was isolated in 90% yield as analytically pure $[Re_2Cp^*_2(CO)_6][TFAB]_2$ by anodic electrolysis of **2** at low temperatures to facilitate its precipitation.[6]

DFT calculations[7] (ADF[8] and Gaussian98[9] programs) were carried out in which all the geometries were optimized without symmetry restraints. Whereas complex **1** is almost a perfect octahedron, with OC−Re−CO angles very close to 90° and cent−Re−CO of 125.4 ° (cent is the centroid of the Cp ring), the Re(II) radical $\mathbf{1}^+$ is distorted, with one wider (99.8°) and two narrower (85.3 and 87.7°) OC−Re−CO angles. One of the cent−Re−CO angles decreases significantly to 117.2°, while the others increase by only 1−2°. This distortion is accompanied by the opening of one CO−Re−cent−CO torsion angle (see top view in Figure 2).

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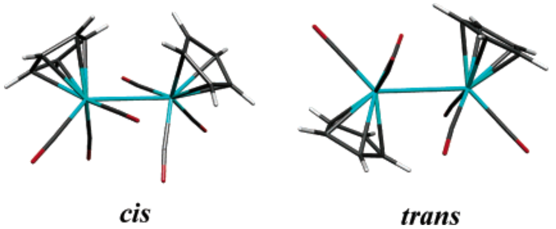

Figure 3. Optimized geometries of complexes *cis* and *trans* $\mathbf{1}_2^{2+}$ (ADF).

Compared to the HOMO of **1**, the SOMO of $\mathbf{1}^+$ is more hybridized away from Re, facilitating the metal−metal bonded dimerization of the latter. Two dimers, *cis* and *trans*, were optimized, the *trans* isomer being more stable by 3.7 kcal mol^{-1} (Figure 3). The Re−Re distances are long (3.285 Å for *cis* and 3.271 Å for *trans*), and the coordination geometry around each Re is in both cases a piano stool, with the three carbonyls and the other Re atom forming the legs. Calculated Wiberg indices,[10] obtained from a NPA analysis,[11] are 0.242 and 0.231, for *cis* and *trans*, respectively, indicating a Re−Re bond in both isomers.

Preliminary digital simulations (Digisim 3.0) of the CVs of **1** are consistent with a dimerization equilibrium constant, K_{dim}, of ca. 10^5 M^{-1} and a dimerization rate constant of the order of 10^3 M^{-1} s^{-1} for $\mathbf{1}^+$. We expect to refine these values by fitting a wider set of scans under different experimental conditions.

Once isolated, $[\mathrm{Re_2Cp_2(CO)_6}][\mathrm{TFAB}]_2$ is stable and may be stored and used as a source of $\mathbf{1}^+$ for the preparation of desired oxidized compounds[3] as their $[\mathrm{TFAB}]^-$ salts. Thus, we have prepared the 17-electron cations of ferrocene ($E° = 0$ V), 1,1′-diacetylferrocene ($E° = 0.49$ V), and MnCp*(CO)$_3$ ($E° = 0.64$ V) in essentially quantitative yields by this method, as well as the organic radical cation [thianthrene][TFAB] ($E° = 0.80$ V).[12] [MnCp*(CO)$_3$][TFAB] is the first isolated cymantrene-type radical cation[13] and will be described in due course. $\mathbf{1}^+$ also appears to electrocatalyze the oxidation of olefins and aromatic hydrocarbons, such as cyclopentene and 9,10-dihydroanthracene. These processes are under active investigation.

The dication $[\mathrm{Re_2Cp_2(CO)_6}]^{2+}$ may be considered to be the first *charged* analogue of the group of weakly metal−metal bonded dimers of piano-stool organometallic radicals, which has to now been confined to neutral complexes of first-row metals.[14,15] Aside from this point, $[\mathrm{Re_2Cp_2(CO)_6}]^{2+}$ is important for its ability to store and release the powerful one-electron oxidant $[\mathrm{ReCp(CO)_3}]^+$. Owing to the well-documented control of $E°$ potentials by cyclopentadienyl substituent effects,[16] this class of compounds offers promise as a precisely tunable group of very strong cationic organometallic oxidants accompanied by weakly coordinating anions.

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Supporting Information Available: Complete ref 9a. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Thirty-seven milligrams of **1** (Strem) in 0.05 M [NBu$_4$][TFAB] was electrolyzed in 10 mL of CH$_2$Cl$_2$ (243 K, $E_{\mathrm{appl}} = 1.4$ V) under drybox (N$_2$) conditions. The electrolysis mixture was kept cold and filtered to remove the precipitated $[\mathrm{Re_2Cp_2(CO)_6}][\mathrm{TFAB}]_2$, which was then washed with cold CH$_2$Cl$_2$ to remove any supporting electrolyte. Vacuum evaporation gave 78 mg (70%) of analytically pure $[\mathrm{Re_2Cp_2(CO)_6}][\mathrm{TFAB}]_2$. A similar procedure for **2** at 225 K gave 90% $[\mathrm{Re_2Cp^*{}_2(CO)_6}][\mathrm{TFAB}]_2$, ν_{CO} (CH$_2Cl_2$) = 2062 cm^{-1}, 2015 cm^{-1} (cf. 2005 cm^{-1}, 1906 cm^{-1} for **2**); C, 40.76 (calcd 40.97), H 1.28 (calcd 1.38).
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