Organometallics 1987, *6*, 611–616

Pentamethylcyclopentadienyl Cobalt and Rhodium Complexes of Octafluorocyclooctatetraene. Photochemical and Thermal Interconversion of 1,2,5,6-η- and 1,2,3,6-η-C_8F_8 Isomers. Electrochemical and ESR Characterization of the 19-Electron Radical Anion $[Co(\eta\text{-}C_5Me_5)(1,2,5,6\text{-}\eta\text{-}C_8F_8)]^-$

Richard T. Carl,[1a] Stephen J. Doig,[1a] William E. Geiger,*[1b] Richard C. Hemond,[1a]
Russell P. Hughes,*[1a,2] Richard S. Kelly,[1b] and Deborah E. Samkoff[1a]

Departments of Chemistry, Dartmouth College, Hanover, New Hampshire 03755, and University of Vermont, Burlington, Vermont 05405

Received September 4, 1986

Thermal reaction of a hexane solution of octafluorocyclooctatetraene (OFCOT) with either $[Co(Cp^*)(CO)_2]$ or $[Rh(Cp^*)(C_2H_4)_2]$ ($Cp^* = \eta\text{-}C_5Me_5$) in the dark afforded good yields of the complexes $[M(\eta\text{-}C_5Me_5)(1,2,5,6\text{-}\eta\text{-}C_8F_8)]$ (**11a**, M = Co; **11b**, M = Rh). Photolysis of solutions of **11a**,**b** at different temperatures afforded a photostationary 2.3:1.0 mixture of the starting complexes and the isomeric compounds $[M(\eta\text{-}C_5Me_5)(1,2,3,6\text{-}\eta\text{-}C_8F_8)]$ (**12a**, M = Co; **12b**, M = Rh). The ratio of isomers is independent of M and the photolysis temperature. Heating each mixture in the dark results in quantitative conversion to pure isomer **11**. One-electron reduction of **11a** results in an ECE mechanism. The first electron-transfer step produces the radical anion **11a**$^-$, in which the mode of ligation of OFCOT to cobalt is maintained and in which ESR studies show the half-filled orbital to be located primarily on the metal. Subsequent reaction of this radical anion occurs to give an electrochemically active product that was too unstable to characterize. This result stands in contrast to that obtained previously for the hydrocarbon analogue $[Co(\eta\text{-}C_5Me_5)(1,2,5,6\text{-}\eta\text{-}C_8H_8)]$, which after reduction rapidly isomerizes to the radical anion $[Co(\eta\text{-}C_5Me_5)(1,2,3,4\text{-}\eta\text{-}C_8H_8)]^-$, in which the half-filled orbital is located on the uncoordinated part of the C_8H_8 ligand.

Introduction

Cyclooctatetraene (COT) has been an historically important ligand in the development of the organometallic chemistry of the d-block and f-block elements. The coordination chemistry of COT and many of its hydrocarbon relatives has been thoroughly studied and has resulted in the synthesis of molecules that have provided an increased understanding of bonding and dynamic behavior of coordinated hydrocarbons.[3] We have been studying the transition-metal chemistry of the fluorocarbon analogue octafluorocyclooctatetraene (OFCOT), 1, whose synthesis[4] and molecular structure[5] have already been reported. In many respects the transition-metal chemistry of OFCOT has proven to be significantly different from that of COT. For example, OFCOT has been shown to react with $Fe_2(CO)_9$ to give initially an η^2-OFCOT derivative, 2, which then undergoes a facile decarbonylation reaction to afford the crystallographically characterized oxidative addition product 3.[6,7] In contrast, the corresponding $Fe(CO)_3$ complex of hydrocarbon COT has the well-known structure 4 (M = Fe).[8] While 4 is fluxional on the NMR time scale with respect to migration of the $Fe(CO)_3$ group around the periphery of the C_8H_8 ring,[8b] the fluorocarbon complexes 2 and 3 are stereochemically rigid at room temperature. Interestingly, the photochemical reaction of $[Os_3(CO)_{12}]$ with COT has been reported to produce 5, a direct hydrocarbon analogue of 3, as the kinetically formed product, which then undergoes subsequent thermal rearrangement to the thermodynamically stable isomer 4 (M = Os).[9]

The $M(C_5R_5)$ fragment (M = Co, Rh, Ir, R = H, Me) is isolobal[10] with $Fe(CO)_3$ but usually binds to COT in a different manner in 18-electron compounds. The thermodynamically more stable structure is the 1,2,5,6-η isomer 6 (containing the boat conformation of the COT ligand) in all cases, but the 1–4-η isomer 7 (containing the chair form of the ligand) has been shown to be present in equilibrium with 6 for M = Co and R = H or Me.[11] Isomer 7 (M = Rh, Ir; R = Me) is the kinetically favored product in the reaction of $[MCl_2(\eta\text{-}C_5Me_5)]_2$ with the COT dianion but rearranges slowly in solution to generate the more stable isomer 6[12]. A discussion of theoretical aspects of binding preferences between the $Fe(CO)_3$ and $Co(C_5H_5)$ fragments has appeared.[13]

In a previous paper the syntheses of OFCOT complexes containing the $M(C_5H_5)$ fragment (M = Co, Rh) and an

---

[1] (a) Dartmouth College. (b) University of Vermont.

[2] Alfred P. Sloan Research Fellow 1980–1984.

[3] For reviews of the organic and organometallic chemistry of cyclooctatetraene see: Fray, G. I.; Saxton, R. G. *The Chemistry of Cyclooctatetraene and Its Derivatives*; Cambridge University: Cambridge, 1978. Deganello, G. *Transition Metal Complexes of Cyclic Polyolefins*; Academic: New York, 1979. For reviews on the organometallic chemistry of Cobalt and Rhodium see: *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982: cobalt (Kemmitt, R. D. W.; Russell, D. R., Vol. 5, Chapter 34), rhodium (Hughes, R. P., Vol. 5, Chapter 35).

[4] Lemal, D. M.; Buzby, J. M.; Barefoot, A. C., III; Grayston, M. W.; Laganis, E. D. *J. Org. Chem.* **1980**, *45*, 3118–3120.

[5] Laird, B. B.; Davis, R. E. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 678–680.

[6] The structure of complex 2 has now been verified crystallographically: Davis, R. E., unpublished results.

[7] Barefoot, A. C., III; Corcoran, E. W., Jr.; Hughes, R. P.; Lemal, D. M.; Saunders, W. D.; Laird, B. B.; Davis, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 970.

[8] (a) Dickens, B.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1961**, *83*, 4862; *J. Chem. Phys.* **1962**, *37*, 2084. (b) Cotton, F. A. *Acc. Chem. Res.* **1968**, *1*, 257.

[9] (a) Bruce, M. I.; Cooke, M.; Green, M. *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 639. (b) Bruce, M. I.; Cooke, M.; Green, M.; Westlake, D. J. *J. Chem. Soc. A* **1969**, 987.

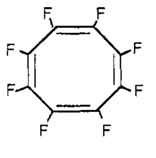
[10] Hoffman, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711–800.

[11] Moraczewski, J. E.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 3407–3408.

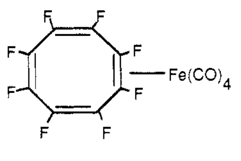
[12] Smith, A. K.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1976**, 1773.

[13] Green, J. C.; Powell, P.; van Tilborg, J. E. *Organometallics* **1984**, *3*, 211–217.

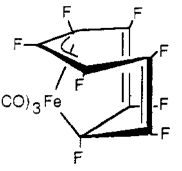
0276-7333/87/2306-0611$01.50/0



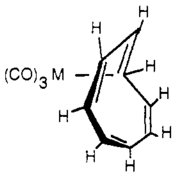
1



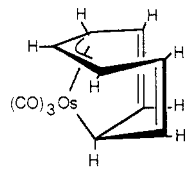
2



3



4

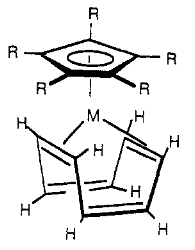


5

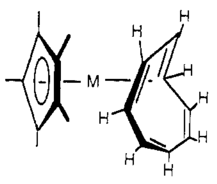
η^5-indenyl analogue were described.[14] In each case the ground-state structure was found to be **8**, and no other ligation or valence isomers could be detected under conditions of thermal or photochemical activation. Isomers **9** and **10**, containing the bicyclo[4.2.0]octatriene valence isomer of OFCOT, could be generated by an alternative route but showed no proclivity for thermal or photochemical isomerization to complexes containing monocyclic OFCOT.[14]

In 19-electron COT compounds of cobalt the preferred ligation of the COT ligand is different. It has been demonstrated that the equilibrium mixture of cobalt complexes **6** and **7** (R = H, Me) undergoes reversible electrochemical reduction to give a single radical anion.[15] This has been shown by ESR studies to have structure 7^- (R = H, Me), in which the unpaired electron occupies an orbital located on the uncoordinated diene portion of the COT ligand. Of particular interest is the observation that one-electron reduction of isomer **6** results in an extremely rapid hapticity change of the coordinated COT ligand to give 7^-. Extended Hückel MO calculations have provided a theoretical rationale for these observations.[16]

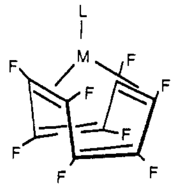
In contrast to the facility with which COT is reduced to both its radical anion and dianion,[17] reduction of OFCOT to give stable perfluorinated analogues of these species has been thwarted by the apparent ease by which elimination of fluoride ion occurs;[18] no organic products have been isolated from attempted chemical or electrochemical reductions of OFCOT.[18] The radical anion of OFCOT has been generated by γ-irradiation and its iso-



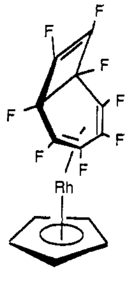
6



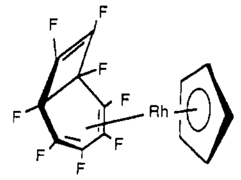
7



8
a. M = Co; L = η-C_5H_5
b. M = Rh; L = η-C_5H_5
c. M = Rh; L = η-C_9H_7



9



10

tropic ESR spectrum recorded at low temperatures;[19] the spectrum suggests that the radical anion adopts a planar delocalized structure of D_{8h} symmetry, similar to that of the hydrocarbon analogue.

In view of the difficulties encountered in generating the free OFCOT radical anion and of the fascinating ligation rearrangements encountered on reduction of metal complexes containing COT, it seemed appropriate to investigate corresponding reductions of metal complexes containing coordinated OFCOT. Since the cobalt complex **8a** could be prepared only in low yields,[14] we turned our attention to the synthesis of the pentamethylcyclopentadienyl (Cp*) derivative in the hope of being able to investigate its electrochemical behavior. A preliminary account of the synthetic part of this work has appeared.[20]

Results and Discussion

Preparation and Thermal and Photochemical Transformations of OFCOT Complexes. Reaction of OFCOT with either [Co(Cp*)$(CO)_2$] or [Rh(Cp*)$(C_2H_4)_2$] in refluxing hexane in the dark afforded good yields of the 1,2,5,6-η complexes **11a,b** after chromatography. The ^{1}H NMR spectra of these compounds showed a single Cp* resonance. Their ^{19}F NMR spectra exhibited two resonances, at 117.1 and 188.3 ppm for **11a** and at 118.1 and 187.3 ppm for **11b** (shifts upfield from internal $CFCl_3$). The lower field peaks are in the region for uncoordinated fluoroolefins, so the high-field resonances are assigned to the fluorines on the coordinated double bonds, demonstrating a significant upfield coordination shift. By way

---

[14] Doherty, N. M.; Ewels, B. E.; Hughes, R. P.; Samkoff, D. E.; Saunders, W. D.; Davis, R. E.; Laird, B. B. *Organometallics* **1985**, *4*, 1606–1611.

[15] Moraczewski, J. E.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 4779–4787.

[16] Albright, T. A.; Moraczewski, J. E.; Geiger, W. E., Jr.; Tulyathan, B. *J. Am. Chem. Soc.* **1981**, *103*, 4787–4794.

[17] Katz, T. J.; Reinmuth, W. H.; Smith, D. E. *J. Am. Chem. Soc.* **1962**, *84*, 802. Strauss, H. L.; Katz, T. J.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1963**, *85*, 2360.

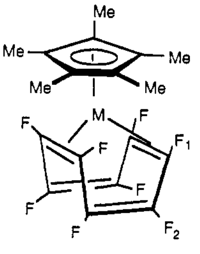
[18] McDade, C. Senior Fellowship Thesis, Dartmouth College, 1980.

[19] Walther, B. W.; Williams, F.; Lemal, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 548–551.

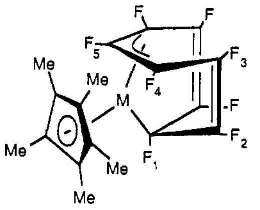
[20] Hughes, R. P.; Samkoff, D. E.; Davis, R. E.; Laird, B. B. *Organometallics* **1983**, *2*, 195–197.

of comparison, the fluorine nuclei of free OFCOT resonate at 123 ppm.[4] This upfield coordination shift is virtually independent of the metal but does depend significantly on the other ligand as shown by comparison with the Cp compounds **8a** [δ 114.0 (uncoordinated F), 163.9 (coordinated F)], **8b** [δ 116.4 (uncoordinated F), 163.8 (coordinated F)], and the indenyl analogue **8c** (δ 115.9 (uncoordinated F), 165.1 (coordinated F)].[14] Compound **8c** has been unambiguously characterized by a single-crystal X-ray diffraction study,[21] placing the structures of this class of compound on a firm footing. Curiously, while no ^{19}F coupling to either the ^{1}H or ^{13}C ring resonances was observed for the Cp or Cp* ligands of compounds **8a,b** or **11a,b**, the methyl carbon resonance of the Cp* ring of **11a** appeared as a binomial quintet in the ^{13}C{^{1}H} spectrum, illustrating coupling of 2.5 Hz to four equivalent fluorines.

When the syntheses and workup of compounds **11a,b** were carried out under ambient light conditions, the resultant material was invariably contaminated with a second isomeric product, assigned as **12a,b** on the basis of comparison of ^{19}F NMR spectral parameters with those of the crystallographically characterized compound **3**.[7] Coupling of the Cp* methyl carbon to ^{19}F was also observed in the ^{13}C{^{1}H} NMR spectrum of **12a**; the resonance appeared as an overlapping doublet of quartets, due to a 4-Hz coupling to a single fluorine and 1.5-Hz coupling to three other fluorines. Crystallization of the mixture resulted in pure **11a,b**, but the second isomer could not be isolated in the pure form. When the synthesis was carried out thermally in the dark, only isomer **11** was produced. Ultraviolet irradiation of solutions of **11** resulted in formation of a photostationary 2.3:1.0 mixture of **11** and **12**. The ratio **11**:**12** did not vary on changing the metal from cobalt to rhodium or with changes in the photolysis temperature over the range −78 to +25 °C. When solutions containing mixtures of **11** and **12** were heated in the dark, clean conversion of **12** back to **11** was observed. No such isomerization behavior was observed for the Cp or indenyl analogues **8**.[14]



11 a. M = Co
b. M = Rh



12 a. M = Co
b. M = Rh

The thermal conversion of **12** to **11** clearly defines **11** as the thermodynamically preferred isomer for both cobalt and rhodium coordination. Our irradiation studies indicate that a photochemically generated excited state of **11** must decay by two competitive pathways to give a photostationary mixture of **11** and **12**. This mixture was erroneously referred to as an equilibrium mixture in our preliminary communication.[20] The ratio of the two components of this photostationary mixture does not depend on the metal or on the temperature at which the photolysis is carried out, implying that the ratio of the rate constants for the two decay processes from the excited state is temperature-independent. It is currently unclear why the Cp* ligand but not the Cp or indenyl ligands give rise to this photochemical behavior. Further studies of multiphoton excitation of these compounds are currently underway.

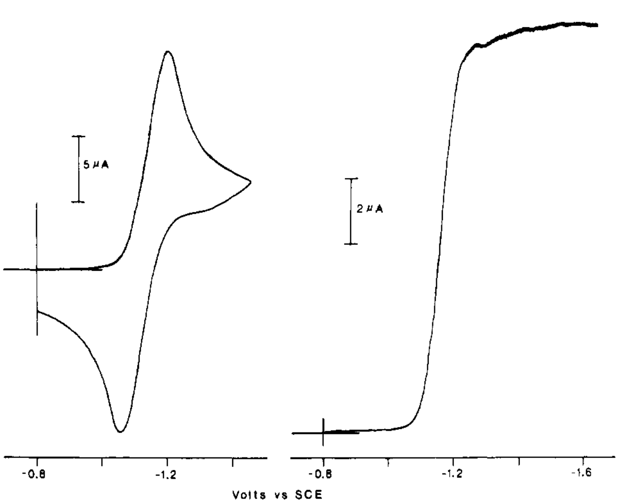


Figure 1. Cyclic voltammetry scan at v = 0.2 V s^{-1} (left) and rotating platinum electrode scan (right) of ca. 1 × 10^{-3} M **11a** in DMF at 228 K.

Electrochemical and ESR Studies on OFCOT Complexes. The electrochemical reduction of cobalt complexes **11a** and **12a** were studied at both mercury and platinum electrodes in a series of solvents, including DMF, THF, CH_2Cl_2, and CH_3CN, with the greatest amount of attention being given to the first two of these. The electrochemical response was essentially independent of the electrode material and the solvent employed.

Two questions were of particular interest from an electrochemical point of view. First, do the isomers **11a** and **12a** have different $E°$ potentials? Second, when **11a** is reduced, does it isomerize to the conformation in which the C_8F_8 ring attains the chair form, as found for the radical anion **7**$^-$ of the analogous C_8H_8 complex? Surprisingly, we found no evidence that isomer **12a** exhibits a separate wave within the range of potentials available (ca. +2.0 to −2.8 V vs. SCE). Furthermore, isomer **11a**, when reduced to its monoanion, showed no tendency to isomerize to an analogue of **7**$^-$. Rather, **11a** reduces through an apparent ECE mechanism (two one-electron transfers interspersed by a chemical reaction) to give an air-sensitive material that could not be isolated successfully.

Room-temperature cyclic voltammetry (CV) scans of **11a** negative of zero volts in DMF or THF show two waves, the relative heights of which were dependent on scan rate. At high sweep rates or low temperatures the first of these waves is chemically reversible ($E°$ = −1.16 V, Figure 1), and is assigned to the process **11a** + e$^-$ = **11a**$^-$. The second wave is also chemically reversible ($E°$ = −1.34 V) and is more prevalent under longer electrochemical experiment times. For example, repetitive CV scanning (Figure 2) showed that as the original complex **11a** was electrolyzed in successive scans (see decreasing first cathodic wave), the new product having $E°$ = −1.34 V was formed. This is referred to as X in the following discussion. Bulk electrolysis confirmed this, for coulometry at −1.25 V (between the first and second waves) consumed two electrons (n = 2.02 e in DMF and 2.00 e in THF) and resulted in efficient conversion to X. The current height of the wave at −1.34 V after electrolysis was about 80% of that of the original cathodic wave at −1.16 V, and the solution turned deep red, in contrast with the original orange color of **11a**.

The electrolysis product could not be isolated in pure form. After electrolysis in THF and removal of solvent,

---

[21] Marder, T. B.; Taylor, N. J., unpublished results (communicated to R. P. Hughes).

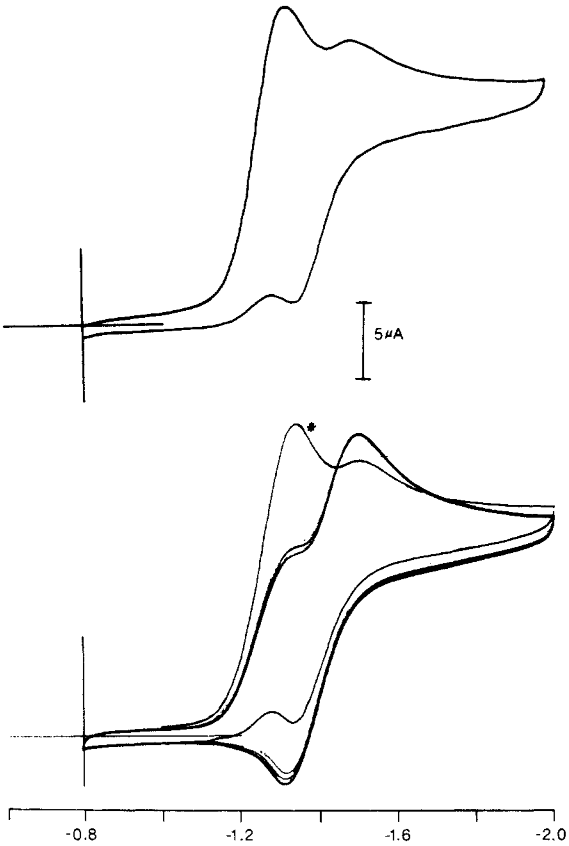


Figure 2. Cyclic voltammetry of 9×10^{-4} M **11a** in THF at 0.2 V s^{-1}: top, single scan; bottom, continuous scans, demonstrating enrichment of reaction product near electrode surface. The first scan is indicated by an asterisk.

extraction with heptane gave a very air-sensitive sample that exhibited the wave at $E° = -1.34$ V, but whose ^{19}F NMR spectrum showed it to be a mixture of at least two components. Attempts at chromatographic separation on silica or alumina led to decomposition. Product X may well result from loss of fluoride ion since the red solid showed an appreciable peak in its mass spectrum corresponding to $[CoCp^*(C_8F_7H)]^+$. Loss of fluoride is observed in attempts to reduce free OFCOT.[18]

Even though the product X remains unidentified, the fact that it is related to **11a** by two electrons in an apparent ECE process (eq 1–3) leads to two useful conclusions: (1)

$$\mathbf{11a} + e^- \rightleftharpoons \mathbf{11a}^- \tag{1}$$

$$\mathbf{11a}^- \text{ -> intermediate} \tag{2}$$

$$\text{intermediate} + e^- \rightleftharpoons X \tag{3}$$

the two observed cathodic waves of Figure 2 do *not* arise from two different isomers and (2) we can use the theory for the ECE mechanism to obtain a rate constant for reaction 2 if first-order kinetics are assumed. The method of Nicholson and Shain[22] was used to obtain this rate constant.

In this approach the current function (peak cathodic current, i_{pc}, divided by the square root of the scan rate, $v^{1/2}$, is measured over a range of scan rates and the values are compared to that expected for a pure diffusion-controlled one-electron change, $(i_{pc}/v^{1/2})_d$. In a kinetic regime in which the reaction leading to the ECE process is active, the current function is larger than $(i_{pc}/v^{1/2})_d$ because of the current flowing from the second reduction, and the amount of enhancement can be used to calculate the rate constant of the intervening chemical reaction. We observed a cathodic current function for the **11a** wave at $E_{peak} = -1.18$ V that increased smoothly from a constant value above $v = 1$ V s^{-1} to a value about 15% higher at $v = 0.05$ V s^{-1}. A 12-point analysis over this range gave a reasonable fit for the ECE mechanism with a rate constant of 0.22 s^{-1} at ambient temperature for reaction 2. The significance of this number is that it represents the upper limit for the rate of any isomerization of radical anion **11a**$^-$ to the chair form analogue of **7**$^-$, since the reaction to form X is much faster than any other reaction of **11a**$^-$.

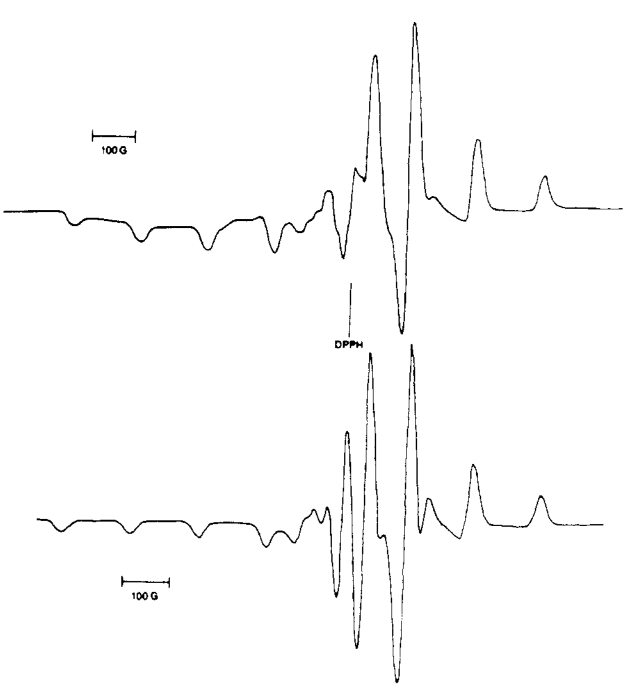


Figure 3. Top: ESR spectrum of **11a**$^-$ in frozen DMF ($T = 77$ K). Bottom; computer-simulated spectrum using $g\| = 2.170$, $g_\perp = 2.080$; $a\|(Co) = 142$ G, and $a_\perp$ (Co) = 33 G.

Therefore it can be concluded that the 1,2,5,6-η to 1,2,3,4-η isomerization of the C_8R_8 ring bound to the CoCp* fragment is enormously slowed when R = F compared to R = H. In the latter case, the first-order rate constant[23] for isomerization of the radical anion is 2000 s^{-1}, at least 4 orders of magnitude faster than for R = F. Clearly the 1,2,5,6-η form of the C_8R_8 complex is stabilized by the substitution of fluorine for hydrogen. We note also that the $E°$ value for **11a** is very much higher than that for its hydrocarbon analogue **6**, shifting positive by about 1200 mV. This may well reflect a higher degree of electron acceptor ability in the fluorinated ligand. The first cathodic wave (irreversible) for free OFCOT was found to be −1.50 V in DMF (Pt electrode), consistent with the value previously reported for CH_3CN solutions.[18] This represents a positive shift of less than 200 mV from the value of the first cathodic wave of free COT, but the significance of the measured shift in potential is uncertain due to the irreversibility of the OFCOT reduction.

Electrolysis at low temperatures was used to generate samples of the radical anion **11a**$^-$ for electron spin resonance (ESR) analysis. CV scans in DMF at 228 K showed only one reversible wave at $E° = 1.16$ V, suggesting that

---

[22] Nicholson, R. S.; Shain, I. *Anal. Chem.* **1965**, *37*, 190. Details of the voltammetric procedure may be found in: Kelly, R. S. Ph.D. Thesis, University of Vermont, 1985. A precision of ±0.04 s^{-1} is indicated for the chemical rate constant.

[23] Grezeszcuk, M.; Smith, D. E.; Geiger, W. E. *J. Chem. Soc.* **1983**, *105*, 1772.

the radical anion is relatively stable under these conditions. Bulk electrolysis (228 K, −1.50 V, Pt electrode) gave a red solution after consumption of 1.29 e (95% complete electrolysis). Rotating platinum electrode scans of the electrolysis solution showed that about 60% of the residue in solution was due to the original complex **11a**, equally split between the neutral compound and its monoanion.[24] This solution was sampled, with the sample being frozen for ESR analysis (Figure 3). Warming the electrolyzed solution to room temperature produced the expected new complex with $E°$ = −1.34 V and caused the ESR signal to disappear. Consequently the ESR signal is assigned to the radical anion **11a**$^-$.

The frozen solution ESR spectrum (Figure 3) is typical of d^9 cobalt π-complexes. The spectrum was successfully simulated to acceptable agreement using an axial tensor for the g values and for the cobalt hyperfine splittings: $a_\parallel(\text{Co}) = 142$ G, $a_\perp(\text{Co}) = 33$ G; $g_\parallel = 2.170$, $g_\perp = 2.080$. Similar spectra have been observed previously for Co(0) complexes such as $[\text{CoCp}(\eta^4\text{-C}_5\text{R}_4\text{O})]^-$ [24] and $[\text{CoCp}(1,2,5,6\text{-}\eta\text{-C}_8\text{H}_{12})]^-$[15,16] and are strongly indicative of the half-filled orbital in **11a**$^-$ being localized predominantly on the *metal*. In the hydrocarbon complex **7**$^-$, which has the chair conformation, the cobalt hyperfine splitting displayed very little anisotropy, consistent with a *ligand*-base half-filled orbital.[15,16]

Samples of **11a** known to contain the isomer **12a** did not show additional voltammetric waves over the range +2.0 to −2.8 V. Irradiation of pure **11a** for 20 min in CD_2Cl_2 gave the photostationary state mixture containing **12a** as confirmed by ^{19}F NMR spectroscopy. Addition of this mixture to DMF or CH_2Cl_2 solutions resulted in no new voltammetric waves. No broadening of the differential pulse polarographic wave at −1.14 V was observed (ca. 100-mV width at half-height) so that either isomer **12a** is not electroactive in the range scanned, or it has an $E°$ within a few millivolts of **11a**. A third, mechanistically more complex, possibility should be considered to account for the absence of a separate wave for isomer **12a** by considering what might be observed in CV scans if the $E°$ of **12a** is positive of **11a** *and* if the anion **12a**$^-$ were to isomerize very rapidly to **11a**$^-$. In this case only the reduction wave of **11a** would be observed, according to the following argument. As a negative-going scan is initiated, **11a**$^-$ would be produced at a potential positive of its $E°$, through isomerization of **12a**$^-$ to **11a**$^-$. This would result in rapid reoxidation of **11a**$^-$ to **11a**. No net current would be passed in converting **12a** to **11a** at the electrode surface, and continuing to scan more negative potentials would show only the usual cathodic wave of **11a**$^-$. Such electrocatalytic isomerization mechanisms have ample precedent.[26] Diagnosis of this mechanism would require scan rates sufficient to freeze out the isomerization of **12a**$^-$ to **11a**$^-$, so that the cathodic "prewave" of **12a**/**12a**$^-$ would be observed. These conditions could not be attained in this study. We can only conclude, therefore, that isomer **12a** does not show its own voltammetric wave under these conditions, and we cannot exclude the possibility that its electroactivity is masked either by the wave for isomer **11a** or by its electrocatalytic conversion to **11a** at the electrode surface.

Complex **11a** may also be oxidized electrochemically. CV scans in CH_3CN or CH_2Cl_2 showed the anodic wave to be irreversible up to $v = 1$ V s^{-1} ($E_{pa} = +1.26$ V in CH_3CN and +1.55 V in CH_2Cl_2). Bulk coulometry in CH_2Cl_2 at +1.65 V (Pt electrode, 298 K) resulted in release of about two electrons (n = 2.25 e) and formation of an unstable green solution. The oxidation was not studied further.

The rhodium compounds **8b** and **8c** are also reduced in THF at either Hg or Pt electrodes, but the reductions are irreversible. The most stringent conditions employed in the attempt to observe chemical reversibility of the reduction were temperatures of 258 K and scan rates of 1 V s^{-1}. Each compound had a primary cathodic wave followed by three or four other irreversible cathodic waves, and these systems were not studied in detail. The peak potentials of the first reduction (v = 0.2 V s^{-1}) were −1.79 V for **8b** and −1.41 V for **8c**.

Conclusion

Although both COT and OFCOT form stable complexes with the CoCp* fragment, interesting differences exist in the favored structural forms of both the neutral 18-electron complexes and in the related 19-electron monoanions. While the major thermodynamic isomer for both the 18-electron COT and OFCOT complexes is the 1,2,5,6-η form **6** or **11a**, respectively, a minor isomer in the COT system is **7** and that in the OFCOT system is **12a**. In the 19-electron manifold **6**$^-$ isomerizes to **7**$^-$ within a millisecond, whereas the fluorinated analogue **11a**$^-$ retains its structure for ca. 5 s before it reacts by a different route, probably involving loss of fluoride ion.

Experimental Section

General Synthetic Procedures. Unless otherwise noted all reactions were carried out in oven-dried glassware using conventional Schlenk techniques, under an atmosphere of dinitrogen which was deoxygenated over BASF catalyst and dried over Aquasorb or in a Vacuum Atmospheres drybox using a HE-493 drying train. Ether and hydrocarbon solvents were purified by distillation from Na/K alloy or sodium benzophenone ketyl and were stored and transferred under dinitrogen. Dichloromethane was dried by distillation from P_4O_{10}. Photolyses were performed by using the Pyrex-filtered output of a Hanovia 450-W Hg arc lamp.

^{1}H (300 MHz), ^{13}C{^{1}H} (75 MHz), and ^{19}F NMR (282 MHz) spectra were recorded on a Varian XL-300 FT spectrometer; ^{1}H and ^{13}C chemical shifts are downfield from the appropriate resonances of internal tetramethylsilane, and ^{19}F shifts are upfield from internal $CFCl_3$. IR spectra were recorded on Perkin-Elmer 599 dispersive or Digilab FTS-40 FT spectrometers. ESR spectra were run on a modified Varian E-3 instrument. Mass spectra were obtained on a Finnegan 4023 instrument at Dartmouth or at the Regional Mass Spectroscopy Facilities at M.I.T. and Johns Hopkins University. Microanalyses were performed by Spang, Eagle Harbor, MI.

Starting Materials. Literature procedures were used to prepare $[\text{Co}(\eta\text{-C}_5\text{Me}_5)(\text{CO})_2]$,[27] $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{C}_2\text{H}_4)_2]$,[28] and octafluorocyclooctatetraene (OFCOT).[4]

Reaction of $[\text{Co}(\eta\text{-C}_5\text{Me}_5)(\text{CO})_2]$ with OFCOT. $[\text{Co}(\eta\text{-C}_5\text{Me}_5)(\text{CO})_2]$ (1.47 g, 5.87 mmol) and OFCOT (2.56 g, 10.3 mmol) were dissolved in hexane (20 mL), and the solution was refluxed in the dark for 88 h, until the green color characteristic of the dinuclear complex $[\text{Co}(\eta\text{-C}_5\text{Me}_5)(\text{CO})]_2$ disappeared. The solution was evaporated to small volume and chromatographed on silica

---

[24] There was always evidence for some regeneration of starting material from reaction of the monoanion with adventitious impurities in these electrolyses. Coulomb counts were always slightly higher than that expected for a one-electron change, and solutions of the monoanion slowly regenerated starting material on standing. This behavior is not atypical of anions with quite negative E° values generated under these experimental conditions.

[25] van Willigen, H.; Geiger, W. E.; Rausch, M. D. *Inorg. Chem.* **1977**, *16*, 581.

[26] For example, see: Rieke, R. D.; Kojima, H.; Öfele, K. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 538.

[27] Frith, S. A.; Spencer, J. L. *Inorg. Synth.* **1985**, *23*, 15.

[28] Moseley, K.; Kang, J. W.; Maitlis, P. M. *J. Chem. Soc. A* **1970**, 2875.

gel. Elution with hexane afforded an orange band which on evaporation yielded spectroscopically pure [Co(η-C_5Me_5)(1,2,5,6-η-C_8F_8)] (**11a**) as an air-stable, orange, crystalline solid (1.43 g, 3.22 mmol, 55%), which was soluble in most common organic solvents to give air-stable solutions. Crystallization from hexane afforded analytically pure material [IR (CH_2Cl_2) $\nu_{C=C}$ 1736 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80 (s, Me); ^{19}F NMR ($CDCl_3$; see text for numbering) δ 117.1 (F_2, the peak appears as an apparent triplet, line spacing 18 Hz), 188.3 (F_1, the peak appears as an apparent triplet, line spacing 18 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 10.0 (quintet, J_{C-F} = 2.5 Hz, C_5Me_5), 105.7 (s, C_5Me_5), resonances due to the fluorinated carbons were not observed under these conditions); MS, *m/e* 442 (M^+)]. Anal. Calcd for $C_{18}H_{15}CoF_8$: C, 48.89; H, 3.42. Found: C, 48.74; H, 3.36%.

Reaction of [Rh(η-C_5Me_5)(C_2H_4)$_2$] with OFCOT. A solution of [Rh(η-C_5Me_5)(C_2H_4)$_2$] (1.37 g, 4.66 mmol) and OFCOT (2.36 g, 9.51 mmol) in hexane (30 mL) was refluxed for 102 h in the dark, cooled, and evaporated to small volume. Chromatography on silica gel afforded a yellow band that on evaporation afforded spectroscopically pure [Rh(η-C_5Me_5)(1,2,5,6-η-C_8F_8)] (**11b**) as an air-stable, yellow, crystalline solid. Crystallization from hexane afforded analytically pure material [IR (CH_2Cl_2) $\nu_{C=C}$ 1727 cm^{-1}; ^1H NMR (C_6D_6) δ 1.45 (s, Me); ^{19}F NMR ($CDCl_3$) δ 118.3 (F_2, the peak appears as an apparent 16-Hz triplet with additional J_{RH-F} = 4 Hz), 187.3 (F_1, the peak appears as an apparent 16-Hz triplet with additional J_{Rh-F} = 14 Hz); MS, *m/e* 486 (M^+)]. Anal. Calcd for $C_{18}H_{15}F_8Rh$: C, 44.47; H, 3.11. Found: C, 44.28; H, 3.10%.

Photochemical Isomerization of [M(η-C_5Me_5)(1,2,5,6-η-C_8F_8)] (M = Co, Rh). A sample of pure **11a** (0.020 g) in acetone-d_6 (0.5 mL) was placed in an NMR tube. The tube was immersed in a Pyrex Dewar flask at a distance of 2 in. from a 450-W Hanovia Hg arc lamp. The Dewar and the lamp jacket were cooled to −78 °C by using a cold circulating bath, and the contents of the tube were irradiated for 190 min. The tube was quickly removed from the Dewar and placed into the precooled probe of the NMR spectrometer, and the ^{19}F NMR spectrum was recorded. In addition to the resonances of **11a** new peaks due to isomer **12a** were observed (see text for numbering): δ 112.4 (m, F_2), 130.3 (m, F_3), 168.9 (m, F_5), 182.4 (m, F_4), 216.8 (m, F_1). Selective ^{19}F–^{19}F decoupling afforded the following coupling constants (Hz): $J_{1,2}$ = 18, $J_{1,3}$ = 7, $J_{3,5}$ = 6, $J_{3,4}$ = 34, $J_{4,5}$ = 36. Warming the sample to ambient temperature did not result in any change, and the ^1H and $^{13}C\{^1H\}$ NMR spectra of **12a** were recorded at room temperature. ^1H NMR ($CDCl_3$): δ 1.70 (s, Cp*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.2 (doublet of quartets, J_{C-F} = 4, 1.5 Hz, C_5Me_5), 102.5 (s, C_5Me_5). The integrated ratio of **11a**:**12a** in the ^1H and ^{19}F nmr spectra was found to be 2.3:1.0. Similar experiments were performed at −23 and 25 °C, giving identical ratios.

The mixture of **11a** and **12a** obtained by evaporation of the NMR sample was dissolved in hexane (10 mL) and refluxed for 1 h in the dark. The ^{19}F NMR spectrum of the resultant solution showed only the resonances of **11a**; no decomposition was observed.

Similar experiments were performed by using the rhodium analogue **12a**. The photostationary mixture of **12a**:**12b** was also found to be 2.3:1.0 over the temperature range −78 to 25 °C. **12b**: ^{19}F NMR (acetone-d_6) δ 113.7 (m, F_2), 130.0 (m, F_3), 163.8 (m, F_5), 174.5 (m, F_4), 211.2 (m, F_1). Selective ^{19}F–^{19}F decoupling afforded the following coupling constants (Hz): $J_{1,2}$ = 18, $J_{1,3}$ = 7, $J_{3,5}$ = 7, $J_{3,4}$ = 37, $J_{4,5}$ = 40. J_{Rh-F} (Hz): F_1, 8; F_2, 5; F_3, F_4, 7; F_5, 4. ^1H NMR (C_6D_6): δ 1.35 (s, Cp*). Refluxing a hexane solution in the dark rapidly transformed **12b** back to **12a**.

Electrochemical and ESR Studies. All potentials are referred to the saturated calomel electrode (SCE), which was separated from the solution by an aqueous salt bridge containing KCl and a fine frit. The tip of the reference electrode was terminated in a luggin probe,[29] which was placed 1–2 mm from the working electrode to minimize resistance effects. In most cases the working electrode was a platinum disk or bead sealed in soft glass, but cyclic voltammetry scans at a hanging mercury drop electrode produced identical results. The platinum electrodes were prepared either by polishing with 1 μm diamond polishing compound or by a chemical oxidation/reduction cycle involving refluxing concentrated HNO_3 followed by ferrous ammonium sulfate. No change in voltammetric behavior was noted.

The electrochemistry was done with Princeton Applied Research potentiostats, the PARC 174A or 173. Coulometry was performed with the PARC Model 179 digital coulometer, and current–time curves were followed independently on an X-Y recorder (Hewlett-Packard 7046B). Electrolyses were typically taken to 95–99% completion. Fast scan cyclic voltammograms were recorded on a Bascom-Turner Model 4120 digital recorder. Bulk electrolysis experiments were carried out in a Vacuum Atmospheres Drilab under dinitrogen. A platinum gauze basket was used as the working electrode, with the auxiliary compartment placed inside the basket and separated from it by a fine frit. Low-temperature electrolyses were accomplished by placing the cell in a heptane bath that was cooled by an FTS Systems Flexi-Cool refrigeration system. The precision of temperature control was ±1 °C.

The supporting electrolyte was in all cases tetrabutylammonium hexafluorophosphate (0.1 M), prepared by metathesis of *n*-Bu_4NI and NH_4PF_6 and recrystallized from 95% ethanol. Tetrahydrofuran (Aldrich Gold Label) was vacuum distilled from sodium benzophenone ketyl. Other solvents were purchased from Burdick and Jackson and used after being dried with molecular sieves, except for methylene chloride, which was distilled from CaH_2.

Polarographic measurements were consistent with the reduction of **11a** being a one-electron process at short drop times. The measured diffusion current constant for that molecule in DMF solution was 1.90 $\mu A\ s^{1/2}\ mg^{-2/3}\ mM^{-1}$ at a drop time of 0.5 s; it increased to 2.21 $\mu A\ s^{1/2}\ mg^{-2/3}\ mM^{-1}$ at a 5.0-s drop time, consistent with the ECE process seen under longer electrochemical observation times (see Results and Discussion).

Samples of **11a**$^-$ for ESR study were generated by bulk coulometric reduction of **11a** at reduced temperatures. Red solutions of **11a**$^-$ at 228 K were transferred under dinitrogen to an ESR sample tube by using a precooled syringe. The sample tube was capped and frozen in liquid nitrogen within a few seconds and was subsequently removed from the drybox for analysis as a frozen solution.

Acknowledgment. R.P.H. is grateful to the Air Force Office of Scientific Research (Grant AFOSR-86-0075), the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, and the Alfred P. Sloan Foundation for generous support of this work. W.E.G. gratefully acknowledges the support of the National Science Foundation (CHE83-08974) and the donors of the Petroleum Research Fund, administered by the American Chemical Society. Dartmouth's Varian XL-300 NMR spectrometer was purchased with funds from the National Science Foundation. We are grateful to Dr. Hans van Willigen for simulation of the ESR spectra and to Professor J. L. Spencer for a preprint of ref 27.

---

(29) Sawyer, D.; Roberts, J. *Experimental Electrochemistry for Chemists*; Wiley: New York, 1974; p 118.