h for millimolar solutions), and the product can be produced cleanly under the appropriate conditions. By using other ruthenium(II) nitrosyl complexes, the photoreaction should be adaptable for the synthesis of a variety of Ru(III) complexes.

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Registry No. $[(bpy)_2Ru(NO)N_3](PF_6)_2$, 61278-44-2; $[(bpy)_2Ru(NO)Cl](PF_6)_2$, 29102-12-3; $[(bpy)_2Ru(NO)Cl]I$, 54866-03-4; $[(bpy)_2Ru(NO)NO_2](PF_6)_2$, 29240-99-1; $[(bpy)_2Ru(NO)NH_3](PF_6)_3$, 61278-45-3; $[(bpy)_2Ru(NO)py](PF_6)_3$, 29241-00-7; $[(bpy)_2Ru(NO)(CH_3CN)](PF_6)_3$, 61303-15-9; $[(bpy)_2Ru(NO)(CH_3CN)](PF_6)_2$, 61303-16-0; $(bpy)_2RuCl_2$, 15746-57-3.

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Paramagnetic Complexes Produced in the Electrochemical and Chemical Reduction of Cyclopentadienyl-Cobalt- and -Rhodium-Cyclopentadienone Complexes

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The reduction of π-tetraphenylcyclopentadienone–π-cyclopentadienyl complexes of cobalt and rhodium has been studied by electrochemical methods and by electron spin resonance spectroscopy. All of the compounds studied undergo a reversible one-electron reduction, but only the cobalt compounds gave anions stable enough to allow ESR studies. Frozen solutions of $CpCo(tpc)^-$ and the anion radical of π-tetrakis(pentafluorophenyl)cyclopentadienone(π-cyclopentadienyl)cobalt, $[(f\text{-}tpc)CoCp]^-$, show highly anisotropic nonaxial ESR spectra. The ESR data as well as the electrochemical potentials are consistent with a high degree of metal character in the orbital involved in the reduction, leading to the designation of the reduced complexes as having the d^9 electron configuration, Co(0) and Rh(0). All of the complexes studied undergo further electrochemical reductions to uncharacterized products.

Introduction

Redox properties of organometallic π complexes have been increasingly investigated in recent years, and one of the major questions to be answered in such studies concerns the relative contributions of the metal and ligand moieties to the redox orbital.[1-3] Complexes involving ligands which can be isolated and hence be subjected to separate redox studies are especially attractive, and considerable efforts have been made to judge the metal vs. ligand contributions in molecules of this type.[4-6]

A group of complexes which seemed nicely amenable to such a study involved tetraphenylcyclopentadienone (Ph_4C_5O, I, tpc) and tetrakis(pentafluorophenyl)cyclopentadienone ($(Ph_F)_4C_5O$,

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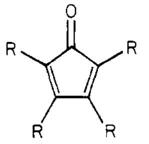
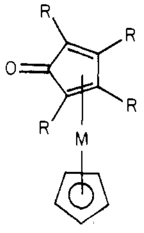
II, f-tpc) and the metal complexes π-tetraphenylcyclopentadienone(π-cyclopentadienyl)cobalt ((Ph_4C_5O)CoCp, III) and -rhodium ((Ph_4C_5O)RhCp, IV and π-tetrakis(pentafluorophenyl)cyclopentadienone(π-cyclopentadienyl)cobalt (($(Ph_F)_4C_5OCoCp$, V) and -rhodium (($(Ph_F)_4C_5OCoCp$, VI).



I, R = C_6H_5
II, R = C_6F_5



III, M = Co, R = C_6H_5
IV, M = Rh, R = C_6H_5
V, M = Co, R = C_6F_5
VI, M = Rh, R = C_6F_5

Metal complexes III–VI exist formally in the M(I) oxidation state, having a d^8 configuration for the neutral complex. Reduction of these complexes at the ligand would result in an ESR spectrum for the anion similar to that observed by Broser et al.[7] after the one-electron reduction of the free ligand I. On the other hand, reduction at the metal would result in a spectrum characteristic of d^9 metal complexes. This paper reports electrochemical and ESR data on the reduction of the free ligand I and complexes III–VI which establish that these complexes undergo reduction in a largely metal-based orbital.

Experimental Section

The ligand Ph_4C_5O was provided by D. W. Slocum. The cobalt and rhodium complexes were prepared according to the literature methods.[8]

Electrochemical measurements were made under nitrogen in the manner previously described.[9] Tetrahydrofuran (THF) and 1,2-dimethoxyethane (glyme) were prepared by stirring reagent grade solvent with lithium aluminum hydride followed by vacuum (bulb-to-bulb) distillation just prior to use. Spectrograde acetonitrile was used without further purification. Tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6), prepared by mixing tetrabutylammonium iodide with ammonium hexafluorophosphate, was recrystallized three times from ethanol and vacuum-dried. Electrolyte solutions were made 0.1 M in Bu_4NPF_6 and approximately 5×10^{-4} M in electroactive compound. Potentials are reported vs. the aqueous saturated calomel electrode.

Electron spin resonance (ESR) spectra were obtained with Varian E-line X- and Q-band spectrometers equipped with variable-temperature accessories. Q-band ESR spectra were obtained through the courtesy of Dr. D. Chasteen of the Chemistry Department of the University of New Hampshire. We thank Dr. L. White for recording the Q-band ESR spectra. Magnetic field measurements were performed with an AEG proton resonance field meter. The *g*-value measurements employed DPPH as a standard. Spectra were obtained on the cobalt and rhodium complexes after they had been reduced in vacuo with either sodium or potassium by the method described previously.[10] The solvent used for the ESR studies was methyltetrahydrofuran (MTHF).

Results and Discussion

Only the cobalt complexes III and V gave anion radicals stable enough for study by ESR. The limited stability of the rhodium complex anions was established both by ESR and by electrochemical measurements.

Electrochemical Data. All of the compounds studied showed at least one reversible reduction wave, ranging over about a 1-V change in potential (Table I). The reversibility of these reductions was checked by variable sweep rate cyclic voltammetry (CV). Potential separations between the cathodic and anodic peaks were about 100 mV for THF electrolyte solutions, reflecting the effect of uncompensated resistance on the voltammetry. Not all of the anions were stable on the CV time scale. Current ratios, i_a/i_c, were less than 1 for several complexes (Table I) showing the presence of follow-up reactions complicating the electron-transfer step. The anions derived from the tpc ligand itself, CpCo(tpc), and CpRh(f-tpc) were stable in THF, but slow follow-up reactions were noted for CpRh(tpc) in THF and CpCo(f-tpc) in acetonitrile, as manifested by i_a/i_c values less than unity at slow scan rates.

Table I. Electrochemical Data

Compd	Solvent	$E_{1/2}$,[a] V	i_a/i_c[b]	Scan rate mV/s
Tetraphenylcyclopentadienone (I)[c]	Glyme	−0.87	0.99	50
		−1.53	0.62	50
			1.00	300
CpCo(tpc) (III)	THF	−1.46	1.00	50
		−2.42	0.71	150
CpRh(tpc) (IV)	THF	−1.83	0.84	140
		−2.14	Irreversible	
CpCo(f-tpc) (V)	CH_3CN	−1.02	0.83	40
			0.97	140
		−1.82	Irreversible, multielectron	
		−2.45	Irreversible	
CpRh(f-tpc) (VI)	THF	−1.36	1.00	80
		−1.93	Peak potential of 1st of several irreversible waves	

[a] Potential vs. aqueous saturated calomel electrode. Data taken at dropping mercury electrode. [b] Ratio of anodic-to-cathodic peak current from cyclic voltammetry at a hanging mercury drop electrode. [c] Voltammetry on this compound had been previously reported in DMF: P. H. Given and M. E. Peover, *J. Chem. Soc.*, 465 (1960).

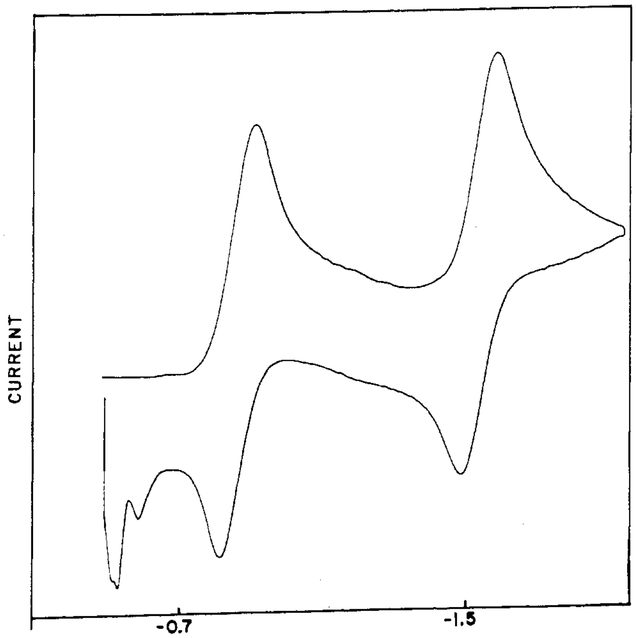


Figure 1. Cyclic voltammogram (300 mV/s) of 5.0×10^{-4} M tetraphenylcyclopentadienone in glyme at a hanging mercury drop. Anodic waves near −0.5 V are due to solution stirring effects.

Tetraphenylcyclopentadienone and its complexes III and IV each showed one more reduction of greatly varying reversibility. Cyclic voltammetry on the tpc ligand shows reversible formation of tpc^{2-} at scan rates in excess of 300 mV/s (Figure 1), and similar stability of $CpCo(tpc)^{2-}$ is observed, but CpRh(tpc) gives irreversible reduction of the monoanion (Figure 2).

The electrochemical data on the tpc complexes thus suggested that the anion derived from the cobalt complex III would be accessible by alkali metal reduction and stable once formed under anaerobic conditions, whereas similar attempts

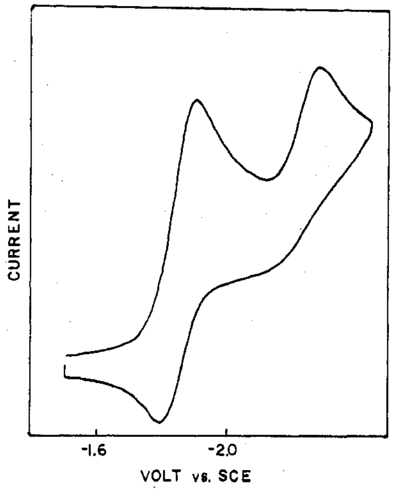


Figure 2. Cyclic voltammogram (200 mV/s) of 4.0 × 10^{-4} M CpRh(tpc) in THF at a mercury drop.

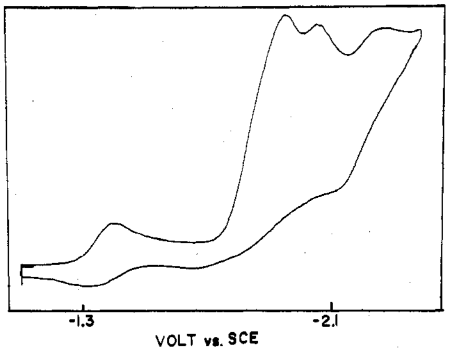


Figure 3. Cyclic voltammogram (30 mV/s) of ~5 × 10^{-4} M CpRh(f-tpc) in THF at a mercury drop.

at reduction of the rhodium complex IV would result in only fleeting existence for IV·⁻. With regard to the latter point, two factors weigh against obtaining stable solutions of IV·⁻: (a) the electrochemically demonstrated instability of IV·⁻ in THF solution and (b) the ease with which IV·⁻ is further, irreversibly, reduced. These conclusions are substantiated by our ESR data (vide infra).

Compounds V and VI, containing the perfluorotetraphenylcyclopentadienone ligand, can also be reduced past the monoanion stage. In each case, however, cyclic voltammetry shows the reduction of the monoanion to be a highly irreversible, multielectron process (e.g., Figure 3). Although these additional reductions were not of sufficient interest to these investigators to justify a mechanistic study, it is noted that highly irreversible reductions have been frequently found for polyhalogenated aromatics.[11]

In principle, the potentials observed for the various reductions hold information on the relative contributions of the metal and ligand to the redox orbital (LUMO) of the neutral complexes.[1-6] As the ligand is changed from tpc to f-tpc, the first reduction of both the cobalt and rhodium complexes shifts positive by slightly more than 0.4 V, indicating substantial covalency in the complex as a whole. Differences in potential between the first and second reductions should be more informative, however, because these measurements focus on the energetics of the LUMO itself. Unfortunately, no theory has been formulated which successfully relates these measurements to quantitative determinations of metal and ligand contributions to the redox orbital. It is clear, however, that the differences in $E_{1/2}$'s in the first and second reductions of CpCo(tpc) (Δ = 0.96 V) and CpRh(tpc) (Δ = 0.31 V) argue strongly for substantial metal involvement in the redox orbital.

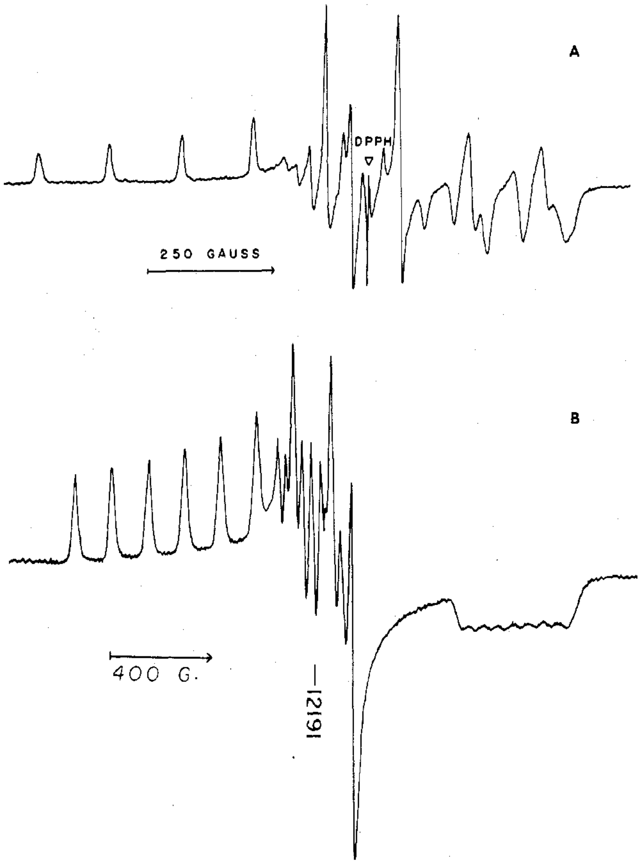


Figure 4. ESR spectra of π-cyclopentadienone(π-cyclopentadienyl)cobalt reduced with alkali metal; solvent MTHF, temperature 100 K: (A) X-band spectrum, reducing agent potassium, DPPH reference signal at 3261.9 G; (B) Q-band spectrum, reducing agent sodium.

Although such an analysis should use only reversible $E_{1/2}$ potentials, we have employed one chemically irreversible reduction potential in this analysis (reduction of IV⁻) because the potential shift from the reversible $E_{1/2}$ can normally be expected to be small.

ESR Data. Brown-orange solutions of the cobalt complexes in MTHF gradually turned dark brown upon treatment with alkali metal. Rigid matrix solutions (100 K) of these samples exhibited ESR spectra that initially increased in intensity with increasing reduction time, but prolonged reduction led to the disappearance of the signal. Reduced solutions of CpCo(tpc) were stable in the absence of moisture and air for days at room temperature, but introduction of air into the sample led to instantaneous disappearance of the ESR signal. Fluid solutions of the reduction products did not give rise to an observable ESR signal.

Reduction of the rhodium complexes was also attempted, but, as discussed above, the close spacing between the reduction waves and limited stability of the monoanion prevented the preparation of a solution of the paramagnetic anion in concentrations suitable for ESR studies. A brief treatment of the Rh complex dissolved in MTHF with alkali metal resulted in the appearance of a very weak structureless rigid-matrix ESR spectrum. Further reduction resulted in loss of the ESR signal.

The rigid matrix X- and Q-band ESR spectra obtained from the anion of CpCo(tpc) are shown in Figure 4. Spectra were independent of the identity of the metal counterion and showed a series of ^{59}Co ($I = {}^{7}/_{2}$) hyperfine lines. Metal hyperfine splittings (hfs) and g values derived from the spectrum are A_x = 41 G, A_y = 57 G, A_z = 144 G, g_x = 2.025, g_y = 1.906, and g_z = 2.103. The parameters derived from the ESR spectrum of (f-tpc)CoCp⁻ are essentially the same.

Depending on the relative signs of the hyperfine components the isotropic component of the Co hfs can be about 15 G (A_z opposite sign of A_x and A_y) or about 81 G (all three components same sign). A determination of the Fermi contact term and the relative signs of the hyperfine components is unfortunately precluded by the fact that no fluid-solution spectrum has been observed.

At the present time the reason for the absence of the fluid solution spectrum is not fully understood. The rigid-matrix spectrum at 100 K showed the onset of saturation at a microwave power level of about 5 mW. Hence, the spin–lattice relaxation time (T_1) is fairly long under these conditions. However, it is recognized that fluctuations in the geometry of the complex in fluid solution could lead to a significant decrease in T_1 and broadening of the spectrum.

Electronic Structure of the Cobalt Anions. In the absence of information on the value of the isotropic Co hfs constant it is not possible to give a quantitative interpretation of the data in terms of the electronic structure of the complex. Some qualitative observations can be made however. According to calculations by Freeman and Watson and Clementi the axial dipolar component of the Co hfs can vary from about 120 to 150 G depending on the oxidation state of the atom.[12,13] Hence, irrespective of the relative signs of the hyperfine components, the data show that the molecular orbital of the unpaired electron contains a large 3d contribution. The reduction definitely cannot be called ligand based.

It is worthwhile to compare the observed g values with those obtained for cobaltocene, Cp_2Co. In the latter case[14,15] the **g**-tensor components are well below the free-electron value (g_e). Furthermore, the deviations of g_z and $^1/_2(g_x + g_y)$ from g_e are significantly greater than the anisotropy in $g(g_x - g_y)$ in the plane parallel to the Cp rings. In the Co–tpc complexes, on the other hand, the g values are close to g_e and $g_x - g_y$ is of a magnitude comparable to the deviations from g_e.

Let us consider these differences in the light of the generally accepted qualitative energy level scheme for the metallocenes. The one-electron energy level scheme that satisfactorily accounts for the properties of all metallocenes shows the following ordering of 3d orbitals according to increasing energy:[14] $3d_{\pm 2}(e_{2g})$, $3d_0(a_{1g})$, $3d_{\pm 1}(e_{1g})$.[16] In cobaltocene (d^7) the e_{1g} level is occupied by a single electron. The orbital degeneracy is removed by the combined action of an orthorombic crystal field perturbation and a dynamic Jahn–Teller effect.[14] The splitting leaves the lowest of the two orbitals occupied by the unpaired electron. Mixing of the two e_{1g} orbitals by spin–orbital coupling accounts for the observation that $g_e > g_z > {}^1/_2(g_x + g_y)$.[14,15] The difference in magnitude of g_x and g_y is induced by spin–orbit admixture of the a_{1g} and e_{2g} orbitals. In Cp_2Co the energy level difference between the two e_{1g} orbitals is much smaller than that between the half-occupied e_{1g} orbital and the a_{1g}, e_{2g} orbitals. As a result, the deviations of the g factors from g_e are much larger than $g_x - g_y$.[14]

The g values of Co–tpc complexes qualitatively fit the metallocene energy level scheme, assuming that g_z represents the principal g-value component perpendicular to the aromatic planes. We note that the axial symmetry is now perturbed by the introduction of the cyclopentadienone ligand. As a result, it is reasonable to expect that the splitting of the e_{1g} orbitals will be much larger than in Cp_2Co. The deviations of the g values from g_e can be attributed again to spin–orbit admixture of the e_{1g} orbitals. However, the fact that now the highest of the two orbitals contains the unpaired electron results in sign changes in the formulas for the g-value components presented by Ammeter and Swalen.[14] As a consequence, theory predicts that e_{1g} admixture leads to $g_z > g_e$ and $^1/_2(g_x + g_y) < g_e$. Moreover, since the e_{1g} splitting is expected to be much larger than in Cp_2Co, the g-value deviations from g_e must be smaller than in Cp_2Co. The experimental observations clearly are in accordance with these qualitative theoretical arguments. From the fact that $g_x - g_y$ is about equal in magnitude to $g_z - g_e$ one can conclude that the energy separation between the e_{1g} orbitals is of a magnitude comparable to the splitting between the half-filled orbital and the e_{2g}, a_{1g} orbitals.

Summary

π-Cyclopentadienyl–cobalt and –rhodium π complexes of substituted cyclopentadienones undergo several successive electrochemical or chemical reductions, the first being reversible in each case. Potential separations between successive reductions argue strongly for a high degree of metal character in the molecular orbital involved in the first reduction. EPR data in frozen solutions of the anions derived from the cobalt complexes are consistent with formulation of the reduced species as a d^9, Co(0), complex.

Note Added in Proof. Successful computer simulation of the Q-band spectrum has yielded parameters close to those quoted above: $g_x = 2.027$, $g_y = 1.900$, $g_z = 2.100$ (all ±0.001) and hyperfine splittings (in units of cm^{-1}) of $A_x = 32.8 \times 10^{-4}$, $A_y = 52.0 \times 10^{-4}$, $A_z = 141.0 \times 10^{-4}$. A highly anisotropic linewidth was confirmed by this method, $W_x = 6.0$ G, $W_y = 25.0$ G, and $W_z = 10.0$ G. We again thank Dr. White for obtaining the simulation.

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Registry No. I, 479-33-4; III, 12119-11-8; IV, 31851-08-8; V, 31760-82-4; VI, 31760-84-6.

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(16) It should be emphasized that the orbital designation is not strictly correct since it ignores ligand contributions.