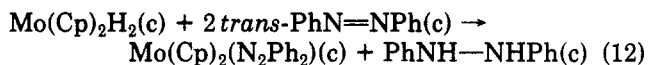


genation of azobenzene by dihydrogen or by metal hydrides.¹⁰ Comparison between the enthalpies of reactions 11 and 12, $\Delta H(11) = -99.9 \pm 4.3 \text{ kJ mol}^{-1}$ and $\Delta H(12) =$ $\text{trans-PhN=NPh(c)} + \text{H}_2(\text{g}) \rightarrow \text{PhNH-NHPh(c)}$ (11)



$-67.0 \pm 11.6 \text{ kJ mol}^{-1}$, indicates that the process is enthalpically less favorable for the metallic system. A crude estimate of the respective entropy changes (i.e., $\Delta S(11) = -S^\circ(\text{H}_2, \text{g}) = -130.57 \text{ J mol}^{-1} \text{ K}^{-1}$ ⁴² and $\Delta S(12) \approx 0$) yields similar ΔG for both reactions. Since reaction 11 requires drastic pressure and temperature conditions^{10b} while reaction 12 occurs in solution at ambient pressure and $\sim 65^\circ \text{C}$,^{11a} this shows the importance of the metallic system in lowering the H_2 activation barrier.

Conclusions

The transferability of titanium-nitrogen bond enthalpy terms seems to be a reasonable assumption, provided that the ligands involved are not too different in their bonding

modes. $E(\text{Ti-N})$ is in the range of $320\text{--}350 \text{ kJ mol}^{-1}$ for several σ -bonded nitrogen ligands but is considerably lower for azobenzene. Analysis of the bond enthalpy terms and bond lengths in the titanium-azobenzene and the titanium-azide complexes stresses the fact that stronger bonds do not necessarily imply shorter bonds, particularly if different types of bonding are involved.

$E(\text{Ti-I})$ in $\text{Ti(Cp)}_2\text{I}_2$ and in TiI_4 are in good agreement, thus supporting the assumption of identical $E(\text{Ti-Cl})$ in $\text{Ti(Cp)}_2\text{Cl}_2$ and TiCl_4 . Titanium-carbonyl bond enthalpy is substantially lower than titanium-methyl bond enthalpy in $\text{Ti(Cp)}_2\text{L}_2$ complexes.

Acknowledgment. We thank Dr. Maria João Ramos and Miss Natália Cordeiro (University of Porto, Portugal) for their help in the MNDO and MINDO/3 calculations. This project was financed by Instituto Nacional de Investigação Científica, Portugal.

Registry No. $\text{Ti(Cp)}_2(\text{PhN=NPh})$, 51159-65-0; $\text{Mo(Cp)}_2(\text{PhN=NPh})$, 53417-82-6; $\text{Ti(Cp)}_2\text{I}_2$, 12152-92-0; $\text{Ti(Cp)}_2(\text{CO})_2$, 12129-51-0; $\text{Mo(Cp)}_2\text{I}_2$, 12184-29-1; $\text{TiCl}_2(\text{CH}_3\text{N=NCH}_3)$, 88667-79-2; $\text{Ti(Cp)}_2(\text{N}_3)_2$, 1298-37-9; $\text{Ti(Cp)}_2(\text{NC}_8\text{H}_8)_2$, 84934-81-6.

Cobaltacycles in Three Oxidation States: Redox Properties and Reaction Routes

Richard S. Kelly and William E. Geiger*

Department of Chemistry, University of Vermont, Burlington, Vermont 05405

Received February 17, 1987

The electrochemical reduction and oxidation of the Co(III) metallacycle $\text{Cp(PPh}_3\text{)CoC}_4\text{Ph}_4$ (1) and its analogues have been studied. Oxidation is reversible ($E^\circ = +0.35 \text{ V vs. SCE}$) in dichloromethane to give a persistent cation radical which was characterized by ESR spectroscopy. A second oxidation ($E^\circ = +1.17 \text{ V}$) gives a more reactive dication which ultimately decomposes by disruption of the metallacycle. Reduction goes by fast one-electron transfer to a 19-electron complex which rapidly loses phosphine to give a transient 17-electron coordinatively unsaturated anion. In the presence of phosphines PR_3 which are more basic than PPh_3 , efficient substitution of PPh_3 by PR_3 accompanies the reduction, in a partially electrocatalytic process. In the absence of added ligands, the 17-electron anion undergoes protonation and subsequent reduction via a ECEC mechanism to give a π -butadiene complex. The electrochemical results are interpreted in terms of previously published molecular orbital calculations on this class of molecules.

Introduction

Since metallacycles exhibit an extensive chemistry and are postulated or demonstrated intermediates in a number of stoichiometric and catalytic reactions, they have been under intense investigation.¹ This class of compounds has been shown to have interesting redox properties, but the literature in this area is still sparse.²⁻¹¹ Because the

chemistry of 18-electron and 16-electron metallacycles is so rich, we thought it would be of interest to prepare a series of metallacyclic 17- or 19-electron radical ions for the purpose of comparing their physical and chemical properties with those of their even-electron counterparts.

This paper reports our first set of results, on the oxidation and reduction of cobaltacyclopentadienes of the type 1-3.

This class of compounds has received considerable attention,¹²⁻¹⁴ due in part to the fact that thermal dissociation

(1) Leading references may be found in recent reviews and theoretical papers: (a) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952. (b) Thorn, D. L.; Hoffmann, R. *Nouv. J. Chem.* **1979**, *3*, 39. (c) McKinney, R. J.; Thorn, D. L.; Hoffmann, R.; Stockis, A. *J. Am. Chem. Soc.* **1981**, *103*, 2595. (d) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149. (e) Moss, J. R.; Scott, L. G. *Coord. Chem. Rev.* **1984**, *60*, 171. (f) Wilke, G. *Pure Appl. Chem.* **1978**, *50*, 677.

(2) Zotti, G.; Rieke, R. D.; McKennis, J. S. *J. Organomet. Chem.* **1982**, *228*, 281 and references therein to earlier work on $(\text{CO})_3\text{Fe}$ metallacycles.

(3) King, M.; Holt, E. M.; Radnia, P.; McKennis, J. S. *Organometallics* **1982**, *1*, 1718.

(4) Klingler, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 2146.

(5) Chong, K. S.; Green, M. L. H. *Organometallics* **1982**, *1*, 1586.

(6) Koelle, U., University of Aachen, unpublished results on dicobaltacycles. Personal communication to W.E.G., 1984.

(7) Lau, W.; Huffman, J. C.; Kochi, J. K. *Organometallics* **1982**, *1*, 155.

(8) Although not metallacyclobutadiene complexes are viewed as metallacycle analogues and their redox chemistry is relevant: Maroney, M. J.; Troglor, W. C. *J. Am. Chem. Soc.* **1984**, *106*, 4144.

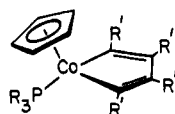
(9) Lappert, M. F.; Martin, T. R.; Milne, C. R. C.; Atwood, J. L.; Hunter, W. E.; Pentilla, R. E. *J. Organomet. Chem.* **1980**, *192*, C35.

(10) Kotz, J. C.; Getty, E. E.; Lin, L. *Organometallics* **1985**, *4*, 610.

(11) Lappert, M. F.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1980**, 1284.

(12) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1.

(13) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1666.



- 1, $R = R' = \text{Ph}$
 2, $R = \text{Ph}, R' = \text{Me}$
 3, $R = \text{Et}, R' = \text{Ph}$

tion of the phosphine (requiring temperatures above 340 K)^{13,15,16} leads to a 16-electron intermediate of general synthetic utility. The present electrochemical data show that phosphine labilization occurs rapidly even at subambient temperatures when the cobaltacycle is reduced by one electron to a transient Co(II) complex.

On the other hand, one-electron oxidation gives an intact formal Co(IV) monocation with an electronic structure that is apparently delocalized throughout the five-membered Co-C₄ ring. Thus, reduction gives a 17-electron coordinatively unsaturated anion, and oxidation gives a 17-electron coordinatively saturated cation. The post-electron-transfer reaction pathways are consistent both with these simple electronic descriptions and with the more sophisticated results of molecular orbital calculations.

Experimental Section

Electrochemical Procedures. The electrochemical techniques employed included direct current (dc) and differential pulse polarography, cyclic voltammetry, potential step and double potential step chronoamperometry, and controlled potential coulometry.

Potentials are referred to the aqueous saturated calomel electrode (SCE), and all solutions were 0.1 M in Bu₄NPF₆ as supporting electrolyte. Princeton Applied Research (PARC) instrumentation was employed as the potentiostat (Model 173 or 174A series), and peripheral equipment was as described earlier.¹⁷ Voltammetric curves from low or moderate sweep rates were recorded on a Hewlett-Packard Model 7046B X-Y recorder, and faster experiments (above ca. 0.5 V s⁻¹) utilized a Bascom-Turner Model 4120 digital recorder. All experiments employed a conventional three-electrode configuration with a platinum wire auxiliary electrode and a reference SCE separated from the solution by an agar bridge and a fine frit. A luggin capillary probe¹⁸ for the SCE and positive-feedback *iR* compensation were used routinely. The working electrode for voltammetry was either a platinum disk or bead sealed in soft glass, a dropping mercury electrode, or a hanging mercury drop electrode (HMDE). The area of the Pt disk (0.035 cm²) was calculated from the Randles-Sevcik equation¹⁹ using ferrocene in tetrahydrofuran (THF). The diffusion coefficient of ferrocene in THF/0.1 M Bu₄NPF₆ was found to be 2.1×10^{-5} cm² s⁻¹ by dc polarography. For minimization of resistance errors in reporting of cyclic voltammetry (CV) peak potentials, the measurements were frequently referenced to a Nernstian internal standard such as ferrocene(+/-0) or cobaltocene(+/-0).

For rotating platinum electrode (RPE) measurements, a Sargent synchronous rotator (1800 rpm) was employed. The platinum bead electrode was pretreated by refluxing it in nitric acid for 10 min, washing with distilled water, and then soaking it in a saturated ferrous ammonium sulfate solution in 1 M sulfuric acid for an equivalent amount of time. The platinum disk electrode was polished on emery cloth by using diamond polishing compound (1 μm) and then washed in a 1:1 mixture of concentrated sulfuric and nitric acids. Before being inserted into solution, electrodes of both types were rinsed with distilled water and dried with a tissue.

(14) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1984**, *272*, 251 and earlier papers in the series.

(15) Wakatsuki, Y.; Nomura, O.; Tone, H.; Yamazaki, H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1344.

(16) Yasufuku, K.; Hamada, A.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1980**, *102*, 4363.

(17) Moraczewski, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1981**, *103*, 4779.

(18) Sawyer, D.; Roberts, J. L. *Experimental Electrochemistry for Chemists*; Wiley: 1974; p 118.

(19) (a) Adams, R. *Electrochemistry at Solid Electrodes*; Marcel Dekker: New York, 1969; p 124. (b) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 218.

Table I. Summary of Electrochemical Potentials (vs. SCE) for Cobaltacycles^a

compd	solv	reductns	oxidatns
1	THF	-1.70, ^{b,c} -2.19	+0.52, +1.28 ^b
1	CH ₂ Cl ₂		+0.35, +1.22
2	THF	-2.18, ^b -2.56	+0.12, +0.82 ^b
3	THF	-1.97, ^b -2.19	+0.42, +1.2 ^b
3	CH ₂ Cl ₂		+0.31, +1.24
4	THF	-2.02	+0.61 ^b
4	CH ₂ Cl ₂		+0.54
5 ^d	THF	-2.26	+1.07 ^b
	CH ₂ Cl ₂		+0.90

^a *E*^o potentials (computed from average of *E*_{pc} and *E*_{pa} in CV experiments) given for reversible couples. ^b Irreversible; peak potential given (*v* = 200 mV s⁻¹). ^c Data on Hg electrode. *E*_p for first reduction is -1.83 V on Pt. ^d These results are consistent with earlier literature reports. See: ref 46a and Dessy, R. E.; Pohl, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 1995.

Bulk electrolysis experiments were carried out under nitrogen inside a Vacuum Atmospheres drybox. A flat-bottomed cell of approximately 200-mL volume was used with the anodic and cathodic half-cells separated by a fine frit. Solution volume was 50 ml. A platinum gauze basket was used as the working electrode in a co-cylindrical arrangement with the auxiliary electrode compartment.

Low-temperature electrochemical experiments done inside the drybox were accomplished either by passing nitrogen gas through a copper coil cooled in liquid nitrogen outside the box and then through a jacketed cell inside the box or by immersing the cell in a heptane bath inside the box cooled with a FTS Systems Flexi-Cool refrigeration system. The former method allowed temperature control of ca. ±3°, while the latter allowed control to ±1°. Low-temperature bench-top experiments were performed by cooling the voltammetry cell with liquid nitrogen-solvent slushes at various temperatures. Temperature control for bench-top work was on the order of ±5°.

Analytical Methods. Starting materials and electrolysis products were characterized by using appropriate instrumental methods, including electronic (UV-vis), infrared (IR), electron spin resonance (ESR), and ¹H and ³¹P nuclear magnetic resonance (NMR) spectroscopies and electron-impact (EI) and chemical-ionization (CI) mass spectrometry (MS).

UV-vis measurements were made on a Perkin-Elmer Model 552 spectrometer. Infrared spectra were recorded by using a Nicolet Series 600 FT-IR. Electron spin resonance measurements were performed on a modified Varian E-3 spectrometer with an external DPPH standard. ¹H and ³¹P NMR data were acquired with a 250-MHz Bruker WM-250 spectrometer, using an internal Me₄Si or an external H₃PO₄ standard, respectively. Mass spectral data were acquired by using a Finnigan MAT 4500 Series GC/MS system.

Reagents. Cp(PPh₃)CoC₄Ph₄ (1) was prepared as described by Yamazaki and Wakatsuki²⁰ from Cp(PPh₃)₂Co²¹ and diphenylacetylene, and 2 was similarly obtained by using 2-butyne.¹⁵ 3 was prepared by reaction of 1 with Et₃P in toluene at 373 K.²² The butadiene complex 4, CpCo(η⁴-C₄Ph₄H₂), and the cyclobutadiene complex 5, CpCo(η⁴-C₄Ph₄) were also prepared as previously reported.^{23,24} All reactions were carried out under nitrogen by using Schlenk-type apparatus or inside the drybox. The compounds were then recrystallized from the appropriate solvents. The purity of each was ascertained by using thin-layer chromatography and by comparing the IR and NMR spectra with those in the literature. TLC was performed on precoated silica plates (Whatman LK5F) using 5-10% benzene in hexanes.

Tetrabutylammonium hexafluorophosphate was prepared by the metathesis of Bu₄NI (Eastman) and ammonium hexafluorophosphate (Ozark Mahoning) in acetone. The Bu₄NPF₆

(20) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1977**, *139*, 157.

(21) Aresta, M.; Rossi, M.; Sacco, A. *Inorg. Chim. Acta* **1969**, *35*, 227.

(22) Yasufuku, K.; Hamada, A.; Aoki, K.; Yamazaki, H. *J. Amer. Chem. Soc.*, *102*, 4363.

(23) Yamazaki, H.; Yasufuku, K.; Wakatsuki, Y. *Organometallics* **1983**, *2*, 726.

(24) Rausch, M. D.; Genetti, R. A. *J. Org. Chem.* **1970**, *35*, 3888.

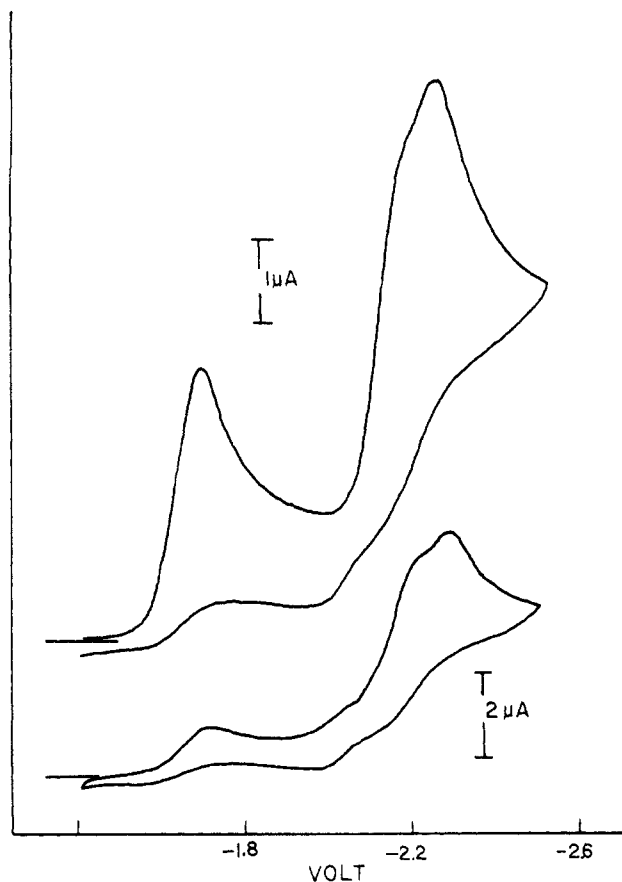


Figure 1. CV scans of 5.6×10^{-4} M **1** in THF at a mercury electrode: top, single scan with $\nu = 0.2$ V s^{-1} ; bottom, steady-state voltammogram after ca. five scans with $\nu = 0.5$ V s^{-1} . The new feature at $E^\circ = -2.07$ V in the bottom scan is due to the reduction of **4**, the ultimate electrolysis product.

precipitated by the addition of water and was then recrystallized from 95% ethanol and vacuum dried. Tetrahydrofuran (Aldrich Gold Label) was distilled from Na/benzophenone and stored over that mixture in vacuo to be distilled as needed. Methylene chloride (Burdick and Jackson Spectrograde) was similarly prepared by using CaH_2 as the drying agent. Acetonitrile, dimethylformamide, and ethylene dichloride (Burdick and Jackson Spectrograde) were used without further purification, except for storage over 4A molecular sieves.

Results

I. Reduction of Cobaltacycles. The cathodic behavior of these compounds was studied in THF and CH_3CN , the overall behavior being similar in the two solvents (Table I). Unless otherwise noted, the data discussed in this section was obtained by using thf as the solvent.

I.1. The Overall Mechanism. Figure 1 displays CV scans of **1** under two conditions. On top is the initial (single) scan at a scan rate of 200 mV s^{-1} . The bottom curve results from the steady-state (continuous cycle) scan using $\nu = 500$ mV s^{-1} , the last trace being recorded about 45 s after initiation of the first triangular waveform. Thus, the top curve is the CV of a fresh solution identical with that in the bulk of solution (assuming no adsorption), while the bottom curve is a composite scan of the electrolysis products in the electrochemical reaction layer and fresh reactant diffusing in from the bulk of solution. Four cathodic waves are to be explained, three of which ($E_{pc} = -1.70, -2.19, -2.26$ V) are present in the (top) scan of the fresh reaction layer, with one (-2.07 V) arising only after the potential is cycled through a second time. We have established (vide infra) that the first wave (-1.70 V) is the one-electron irreversible reduction of **1** and the second

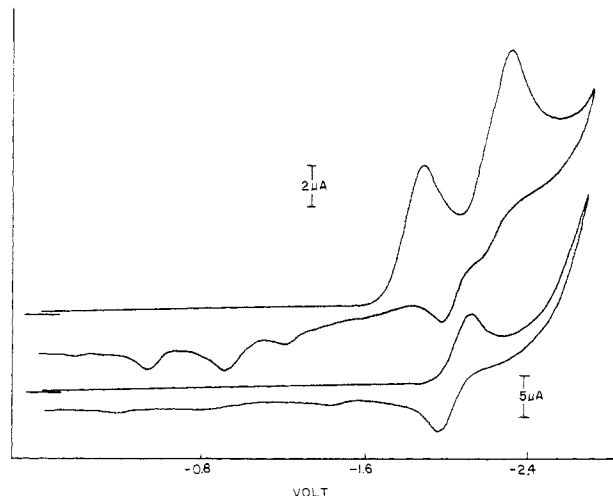
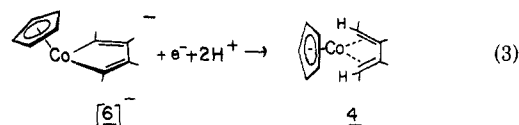
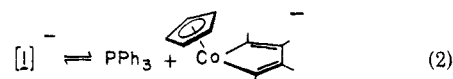


Figure 2. CV scans of 6.7×10^{-4} M **1** at Pt electrode in THF: top, prior to bulk electrolysis; bottom, after bulk electrolysis at -1.9 V (scan rate = 0.22 V s^{-1} , showing clean conversion of **1** to **4**).

wave (-2.19 V) arises from the reduction of $[CpCoC_4Ph_4]^-$, the anion of the original metallacycle minus the phosphine ligand. The small peak at -2.26 V is due to a minor product that does not appear after exhaustive electrolysis. The fourth cathodic wave is part of a reversible couple with $E^\circ = -2.02$ V, due to the final electrolysis product, the open-chain tetraphenylbutadiene complex **4**. Thus, the overall reduction mechanism of **1** includes the three identifiable reactions of eq 1–3.



I.2. Conversion of 1 to 4. The first cathodic wave of **1** is an irreversible one-electron process on the CV time scale but a 2-electron process on a preparative (coulometric) time scale. From the dc polarogram of **1**, a diffusion current constant of $1.94 \mu A \text{ mM}^{-1} \text{ mg}^{-2/3} \text{ s}^{1/2}$ compares well with the value of 2.26 we measure for $Cp_2Co^{+/0}$ in THF. Rotating platinum electrode (RPE) scans gave a cathodic plateau current equal to the oxidation of **1**, which is also a one-electron process (see section II). Finally, CV scans gave a cathodic current function²⁵ about 0.8 times that of the first oxidation wave. This is consistent with the reversible nature of $1^{0/+}$ and irreversible nature of $1^{0/-}$.²⁶

Bulk electrolysis of **1** at -1.95 V (negative of the first reduction) required 1.96 faraday ($n_{\text{total}} = 2$) as the solution changed from orange to red. Figure 2 shows CV scans before (top) and after (bottom) the bulk electrolysis, which demonstrate that the solution is converted cleanly to a single product with $E^\circ = -2.02$ V. Judging from the

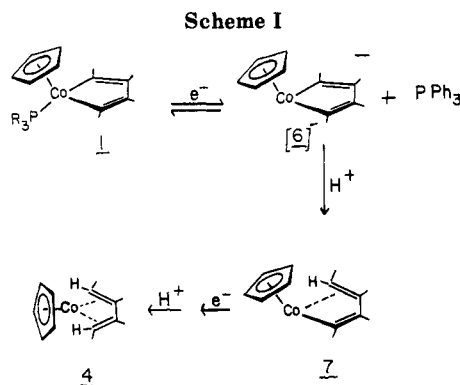
(25) The cathodic current function is the cathodic peak current divided by the square root of the scan rate.

(26) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706. Also ref 19b, p 222.

Table II. Voltammetric Criteria for Diagnosis of Several Electrode Mechanisms by dc Polarography or Linear Scan Voltammetry (LSV): E = Electron Transfer and C = Coupled Chemical Reaction

diagnostic	E_{REV}	E_{IRREV}^a	$E_{\text{REV}C_{\text{REV}}}$	$E_{\text{REV}C_{\text{IRREV}}}$	found ^b
LSV: E_p vs. $\log v$, mV	no shift ^c	$30/\alpha^c$	30^c	30^c	29
LSV: $E_p - E_{p/2}$, mV	57^c	$48/\alpha^c$	(depends on $k_f k_b$)	$57-48/\alpha^c$ (depends on k_f)	92
dc polgy: E_{app} vs. $\log [(i_d - i)/i]$, mV	59^d	$59/\alpha^e$	59^f	g	59

^a α is the symmetry parameter of the electron-transfer reaction and is about 0.5 in most reactions. ^b For the reduction of 1 in THF at a platinum electrode; potential measurements referenced to an internal standard to eliminate resistance effects. ^c Reference 34. ^d Reference 35, p 129. ^e Reference 35, p 213. ^f Reference 35, p 395, and ref 36-38. ^g It is generally believed that an irreversible reaction after reversible charge transfer will leave the polarographic wave with a reversible shape. However, we could find no explicit theoretical treatment of this case.



current heights, the conversion is essentially quantitative.²⁷ Following evaporation of the solvent and extraction with benzene, the sample was chromatographed on a short (3 cm \times 5 cm) alumina column with benzene as the eluent. The resulting red material displayed ¹H and ³¹P nmr spectra consistent with it being a mixture of 4 and free PPh₃.²⁸ This was confirmed by measuring the electrochemistry of an authentic sample²³ of 4, which has a reversible reduction at -2.02 V.

The data are strongly suggestive that the radical anion [1]⁻ formed upon initial reduction of the metallacycle rapidly ejects the phosphine ligand, leaving a coordinatively unsaturated 17-electron radical anion [6]⁻ (eq 2). Other data (vide infra) suggest that the phosphine dissociation is reversible. This anion, which we found to be too unstable for detection by ESR spectroscopy, could react with adventitious protons to give the final product by a ECEC process similar to that proposed in Scheme I.

This scheme invokes an intermediate, 7, in which the metal is σ, π -bonded to a C₄ butadienyl ring, formation of which could be preceded by attack of H⁺ at the metal. It is necessary that 7 be more easily reduced than 1 in order to complete the scheme.^{29,30}

(27) Use of current peaks or plateaus to imply a "percent yield" in bulk electrolytic experiments requires knowledge of the number of electrons transferred on a wave and the diffusion coefficient of the reactant and product. In the present case, the reduction of reactant 1 and product 4 both proceed by one electron in voltammetric scans, and their diffusion coefficients should be similar.

(28) ¹H NMR (CD₂Cl₂ vs. tetramethylsilane): δ 4.56 (5 H, Cp), 1.55 (2 H, olefinic hydrogens), 6.8-7.2 (20 H, phenyl), ascribed to 4²³, and ca. δ 7.3, assigned to free PPh₃. ³¹P NMR (CD₂Cl₂): -4.36 ppm vs. H₃PO₄, due to free PPh₃.

(29) The mechanism of Scheme I assumes that both electron transfers are heterogeneous, i.e., involving transfer from the electrode. An alternate mechanism involves homogeneous electron transfer from [6]⁻ to 7 in place of the second heterogeneous electron transfer, in a disproportionation mechanism. In either case, 4 is the predicted product by overall transfer of 2 electrons and 2 protons to 1: For leading references see: Amatore, C.; Saveant, J. M. *J. Electroanal. Chem.* 1978, 86, 227.

(30) The 18-electron complexes of structures analogous to 7 are known. Crocker, M.; Froom, S. F.; Green, M.; Morton, C. E. *Abstracts of Papers*, 191st National Meeting of the American Chemical Society, New York; American Chemical Society: Washington, DC, 1986; INOR 270.

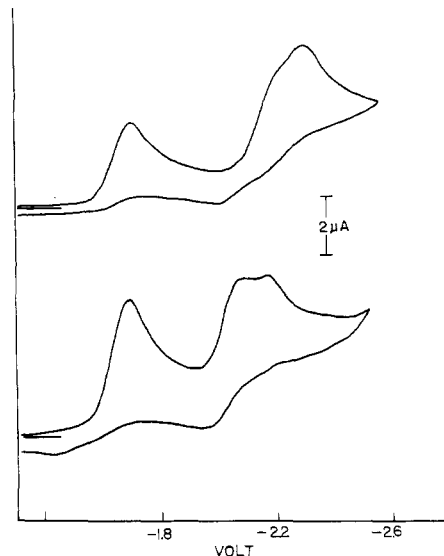


Figure 3. CV scans of 3.3×10^{-4} M 1 at Hg in THF: top, pure solution identical with that in Figure 1 (top); bottom, after addition of 6.6×10^{-4} M phenol (scan rate = 0.10 V s^{-1}). The increased current at -2.1 V is due to production of 4 in the electrode reaction layer.

Consistent with the proposed mechanism, addition of phenol to solutions of 1 resulted in nearly a doubling of the cathodic peak current at -1.70 and appearance of the wave for 4 in CV scans (Figure 3). The deliberate addition of acid therefore increases the rate of protonation of [6]⁻ and subsequent formation of 4.

1.3. The Question of Reversibility of Phosphine Loss from [1]⁻. Having established the overall stoichiometry of the reduction, it is of interest to focus on the key step, eq 1, involving loss of PPh₃ and formation of the unusual 17-electron radical anion [6]⁻. In order to shed light on the lifetime of [1]⁻ and on the reversibility of eq 2, we took two approaches. One was to see if voltammetric techniques could distinguish whether the initial wave was irreversible (A) because of slow charge transfer (implying phosphine loss concomitant with electron transfer³¹) or (B) because of a chemical reaction following fast charge transfer (implying a short but finite lifetime of a radical anion with an intact Co-P bond). The second approach was to use the possible reversibility of eq 2 to probe the substitution of PPh₃ by more basic phosphines.

Table II displays three key diagnostic experimental criteria for linear scan voltammetry (LSV)³² and dc polarography for a completely reversible redox couple (E_{REV})

(31) A well-studied example of apparently concerted electron transfer and bond cleavage is the reduction of alkyl halides; see: Baizer, M. M.; Lund, H., Eds. *Organic Electrochemistry*, 2nd ed.; Marcel Dekker: New York, 1983; p 259.

(32) Linear scan voltammetry, in this context, refers to the forward (negative-going) part of the CV sweep.

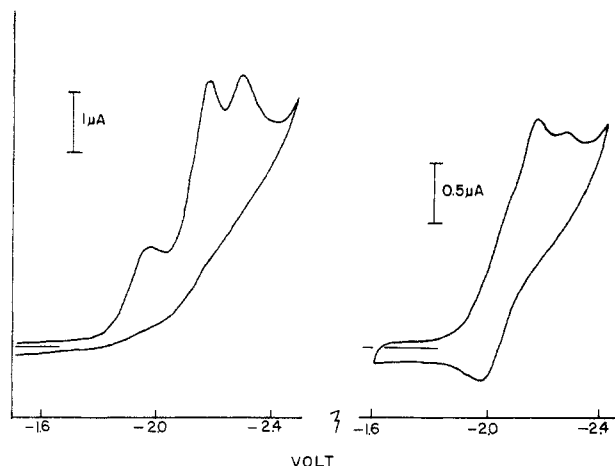
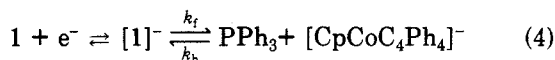


Figure 4. CV scans of 2.1×10^{-4} M **3** in THF at Hg: left, single scan with $\nu = 0.20$ V s^{-1} ; right, steady-state voltammogram with $\nu = 0.50$ V s^{-1} , which shows formation of **4** by the cathodic shoulder at -2.1 V and the coupled anodic wave.

and for the three mechanisms³³ possibly describing the one-electron irreversible reduction of **1** (assuming in each case $n = 1$). The measured values were 29 mV for E_p vs. $\log \nu$, 92 mV for $E_p - E_{p/2}$, and 59 mV for the polarographic log slope. The broadness of the cathodic portion of the CV wave, as measured by $E_p - E_{p/2}$, is not a good diagnostic for choosing among these mechanisms because the value of this quantity depends on the forward and backward rate constants of the coupled chemical reaction. However, the E_p dependence on scan rate and the 59 mV polarographic slope eliminate slow charge-transfer kinetics as the reason for the irreversible reduction of **1**, leaving us with a choice between the $E_{REV}C_{REV}$ and $E_{REV}C_{IRREV}$ mechanisms. Without considerable extension of previous work,³⁶⁻³⁸ theory of the polarographic wave shape is insufficient to diagnose the reversibility of the coupled chemical reaction. Thus the voltammetry is therefore consistent with either the $E_{REV}C_{REV}$ or $E_{REV}C_{IRREV}$ mechanisms. The lack of an anodic wave coupled to the cathodic wave of **1** establishes that the loss of phosphine from $[1]^-$ is very rapid, so that k_f in eq 4 is probably $10^8 s^{-1} > k_f > 10^2 s^{-1}$ and k_b is unknown. With this in mind, the irreversible shape of the



CV wave of **1** may be understood. The rapid removal of $[1]^-$ from the electrode by the phosphine dissociation facilitates the reduction of **1** and moves the cathodic wave positive of the potential at which a reversible wave would occur. Consequently, the more positive electrode potential is insufficient to drive the charge transfer at a sufficiently high rate.

1.4. Electrocatalytic Phosphine Substitution. The reversibility of eq 1 and 2 suggest that reduction of **1** in the presence of ligands, L, more basic than PPh_3 should lead to replacement of PPh_3 by L in a reaction catalytic in the number of electrons consumed. This is observed.

The triethylphosphine complex $Cp(PEt_3)CoC_4Ph_4$ (**3**) displays the expected voltammetry (Figure 4), with the first

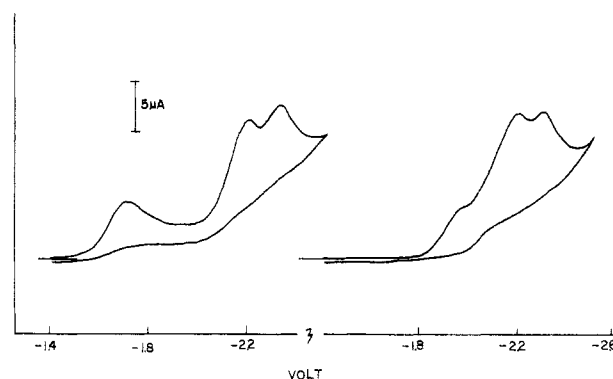


Figure 5. CV scans with $\nu = 0.22$ V s^{-1} of 8.6×10^{-4} M **1** at Hg in THF solution containing ca. 8×10^{-3} M PEt_3 : left, before electrolysis; right, after electrolysis at -1.7 V. The scans on the left are the same as those observed for pure solutions of **1**, that on the right being identical with those observed for solutions of **3** (refer to left side of Figure 4).

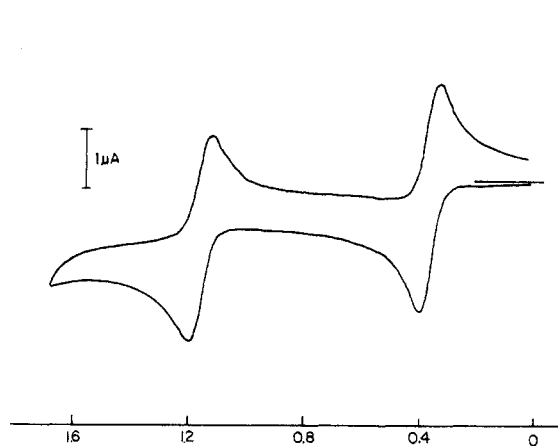
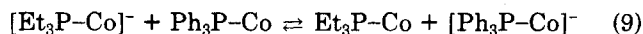
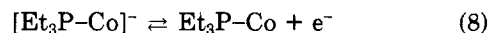
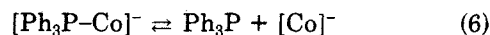
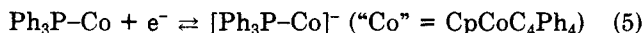


Figure 6. CV scans of oxidation of 3.0×10^{-4} M **1** in CH_2Cl_2 at Pt electrode ($\nu = 0.25$ V s^{-1} ; $T = 229$ K).

wave pushed to a more negative potential (-1.97 V) than that of **1**, but the other waves, of course from species no longer containing the phosphine, remaining at the same potentials. The continuous scan (steady-state) CV again indicated conversion in the reaction layer of **3** to **4**.

If a 10-fold excess of PEt_3 is added to solutions of **1** in thf, no reaction is observed over the period of several hours. But electrolysis of this solution at -1.9 V (negative of the first reduction of **1**) resulted in rapid and nearly quantitative formation of neutral $Cp(PEt_3)CoC_4Ph_4$. The electrolysis proceeded extremely rapidly, going to 97% completion in 210 s. The electricity consumed amounted to 0.38 faraday,³⁹ and CV scans before and after electrolysis demonstrated the efficiency of the phosphine replacement (Figure 5). RPE scans of the oxidation waves (vide infra) before and after electrolysis indicated about 90% conversion to the PEt_3 complex. Equations 5-9 account for the reaction sequence.



(33) Since these complexes have no reported tendency toward dissociation at room temperature, CE mechanisms requiring dissociation prior to electron transfer were not included in the analysis.

(34) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

(35) Heyrovsky, J.; Kuta, J. *Principles of Polarography*; Academic Press: New York, 1965.

(36) Kern, D. M. H. *J. Am. Chem. Soc.* **1954**, *76*, 1011.

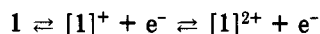
(37) Koutecky, J. *Collect. Czech. Chem. Commun.* **1955**, *20*, 116.

(38) Matsuda, H. *J. Electroanal. Chem.* **1974**, *56*, 165.

(39) At subambient temperatures, somewhat longer catalytic chains were observed.

Note that formation of neutral $\text{Cp}(\text{PET}_3)\text{CoC}_4\text{Ph}_4$ may occur in principle by electron transfer from $[\text{Cp}(\text{PET}_3)\text{CoC}_4\text{Ph}_4]^+$ either to the electrode (eq 8) or to neutral **1** (eq 9). The mechanistic details of these substitution reactions are under study.⁴⁰

II. Oxidation of Cobaltacycles. II.1. $\text{Cp}(\text{PPh}_3)\text{CoC}_4\text{Ph}_4$. Oxidation of **1** proceeded in two steps, both of which were reversible under appropriate conditions. CV scans in CH_2Cl_2 at 229 K showed two reversible one-electron waves (Figure 6) corresponding to formation of a metallacyclic mono- and dication:



Except for showing some effects from uncompensated resistance, these waves both correspond to diffusion-controlled reversible one-electron processes under these conditions. At higher temperatures or when THF was the solvent, the cations were less stable, as judged from the lower chemical reversibility of the couples. At ambient temperature in CH_2Cl_2 , the first oxidation ($E^\circ = +0.35$ V) displays complete chemical reversibility at CV scan rates $\nu > 0.5$ V s^{-1} and the second oxidation ($E^\circ = 1.17$ V) is reversible when $\nu > 5$ V s^{-1} .

The anodic current function of the first oxidation increased with decreasing scan rate, suggesting that an ECE mechanism was operative at the potential of the first wave. Bulk coulometry at +0.5 V at a Pt basket electrode in either CH_2Cl_2 or THF resulted in release of two electrons, consistent with a ECE process. Further indications of this mechanism came from chronoamperometry experiments (CH_2Cl_2), in which n_{app} increased from 1.2 (at a step time of 0.2 s) to 1.9 (4 s), and from the dc polarographic diffusion current constant (in THF), which increased from 1.7 when the drop time was 0.5 s to 4.0 at 5 s. Half-lives of the cations at 298 K were estimated from cyclic voltammetric data. The anodic current function for the first wave followed closely the scan rate dependence for a ECE process in which the rate of the intervening chemical reaction is 0.2 s^{-1} .⁴¹ The cathodic-to-anodic current ratios for the second oxidation wave were consistent with a first-order decomposition rate constant of 1.2 s^{-1} . Thus, the estimated half-lives of $[1]^+$ and $[1]^{2+}$ in CH_2Cl_2 at 298 K are ca. 3 and 0.6 s, respectively.

Electrolysis at 238 K in CH_2Cl_2 positive of the first oxidation wave ($E_{\text{app}} = +0.7$ V) released 1.08 faraday as the solution went from the orange of **1** to the purple of $[1]^+$. RPE scans indicated ca. 75% conversion to the monocation, and re-reduction gave back the original metallacycle in overall 60% yield. Attempts at electrolysis at the second wave were unsuccessful because of electrode passivation, apparently because of a highly insoluble dication. Addition of a few drops of CH_3CN to the cell solubilized the products but resulted in release of over three additional electrons and several unidentified electrolysis products.

The deep purple solutions of $[1]^+$ exhibited strong ESR signals. Frozen CH_2Cl_2 solutions gave only one line, apparently due to an exchange-narrowed resonance, which can arise from microcrystallization of $[1]^+$ as the solution is rapidly cooled to freezing. This interpretation was confirmed by electrolysis in a 1:1 dichloromethane–1,2-dichloroethane mixture, which forms a glass upon freezing. Cobalt hyperfine splittings are seen (Figure 7) in the CH_2Cl_2 – $\text{C}_2\text{H}_4\text{Cl}_2$ glass. The largest cobalt splitting is along the low-field g component [$g_1 = 2.075$, $A_{\text{Co}}(1) = 57$ G]. Pending a complete simulation of the spectrum, we cannot

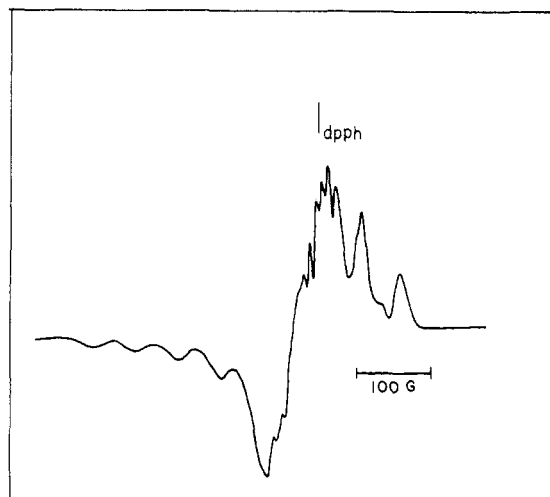


Figure 7. ESR spectra of $[1]^+$ at $T = 77$ K in frozen 1:1 $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_4\text{Cl}_2$.

rule out the possibility that ^{31}P splittings might be present in the g_2 or g_3 components, but it can be stated with confidence that there is an appreciable cobalt contribution to the half-filled orbital of the monocation.

When the monocation is generated in THF, complete disruption of the complex, including fragmentation of the metallacycle, is observed. Bulk electrolysis at $E_{\text{app}} = +0.8$ V in THF gave a yellow solution after passage of 2.2 faraday. CV, polarography, and UV-vis spectroscopy of the electrolysis solution indicated formation of solvated Co^{2+} as the major metal-containing product, with a smaller amount (<20%) of the cyclobutadiene complex $\text{CpCo}(\eta^4\text{-C}_4\text{Ph}_4)$ (**5**) also being formed. The mechanism whereby **1** is oxidatively converted to **5** is obscure, but the latter is frequently found as a side product when cobaltacycles undergo decomposition.^{42–45}

II.2. Oxidation of Other Cobaltacycles. Changing the phosphine ligand from PPh_3 to PET_3 resulted in a metallacycle cation with improved kinetic stability. However, the E° potential of the metallacycle(0/+) couple was shifted negative only by 40 mV (cf. **1** with **3**, Table I). In contrast, **2**, which has a PPh_3 ligand but has methyl groups replacing phenyls in the metallacyclic ring, exhibits a 400-mV shift (in THF) to more negative potentials for its first oxidation. We take this as an indication that the HOMO of these complexes contains a major contribution from the five-membered metallacyclic ring. CV studies of the radical cation $[2]^+$ indicated that it is quite stable in CH_2Cl_2 .

III. Electrochemistry of 4. Since electrochemical studies of the open-chain butadiene complex **4** have not been previously reported, we make mention of our brief studies on this complex (Table I). In THF a reversible one-electron reduction is observed with $E^\circ = -2.02$ V, and an oxidation wave is also seen ($E_p = 0.6$ V) which becomes chemically reversible at reduced temperatures (260 K) or higher scan rates. The cathodic to anodic current ratio for this wave was 0.7 at $\nu = 200$ mV s^{-1} and $T = 262$ K. Thus, there is evidence of the electron-transfer series: $[\text{CpCo}(\eta^4\text{-C}_4\text{Ph}_4\text{H}_2)]^+ \rightleftharpoons \text{CpCo}(\eta^4\text{-C}_4\text{Ph}_4\text{H}_2) \rightleftharpoons [\text{CpCo}(\eta^4\text{-C}_4\text{Ph}_4\text{H}_2)]^-$. Reversible electrochemistry has been re-

(40) Donovan, B. T., work in progress at University of Vermont.

(41) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1965**, *37*, 178.

(42) Compound **5** is clearly produced by photolysis of **1** in dry solvents [Trogler, W. C.; Ibers, J. A. *Organometallics* **1982**, *1*, 536] or by thermal decomposition (ref 43–45).

(43) Ville, G.; Vollhardt, K. P. C.; Winter, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 5267.

(44) McDonnell-Bushnell, L. P.; Evitt, E. R.; Bergman, R. G. *J. Organomet. Chem.* **1978**, *157*, 445.

(45) Yamazaki, H.; Hagihara, N. *J. Organomet. Chem.* **1967**, *7*, P22.

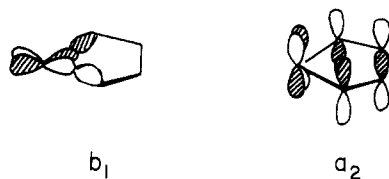
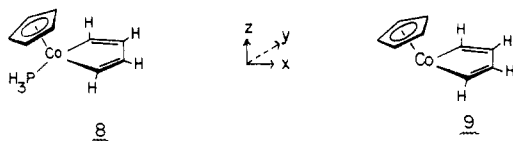


Figure 8. Representations of possible HOMO orbitals of 1, based on results of ref 1b.

ported previously for Co(III)/Co(II)/Co(I) couples involving CpCo(η^4 -polyolefin) complexes in which the polyolefin is cyclic,^{17,46} but the present data show that these oxidation states are accessible for open-chain polyolefin compounds as well.

Co(IV) Cation: Electronic Structure and Decomposition Pathway. The electronic structure of Cp(PH₃)CoC₄H₄ (8) has been probed by extended Hückel calculations,^{1b,15} and our results on the oxidation of 1–3, close analogues of 8, are pertinent to the conclusions drawn from those theoretical studies. Two orbitals are shown



to be the best candidates for the HOMO of 8 and, by inference, of 1. The one actually calculated to be of higher energy^{1b} (b_1 in pseudo- C_{2v} symmetry) is an in-plane σ -type orbital containing a d_{xy} cobalt contribution (Figure 8). However, the a_2 orbital of Figure 8 is calculated to be close in energy to the b_1 .⁴⁷ This orbital is comprised mostly of a ligand π -contribution, with an unspecified amount of Co d_{yz} .

An important difference between the b_1 and a_2 orbitals is that the former is bonding between the metal and the rest of the ring, whereas the latter is antibonding with respect to this interaction. Our observation that 1–3 may be oxidized in two successive one-electron steps to dications suggests that the b_1 orbital is not the HOMO, since removal of two, or even one, electron(s) from a Co–C σ -bonding orbital should lead to rapid rupture of the Co–C bond. Expulsion of the metal from the metallacyclic ring is in fact observed in our systems, but only after longer bulk electrolysis experiments. An additional problem with a b_1 HOMO is that unless the system undergoes orbital relaxation after the first one-electron oxidation, a Co(V) oxidation state would have to be assigned to the twice-oxidized dication.

On the other hand, our results are quite compatible with a a_2 HOMO. Removal of electrons from this orbital will not weaken the Co–ring interaction and may remove some of the localized double-bond ring character, leading to a metallacycle cation with considerable electronic delocalization. This would help to account for the fact that even the dication of the metallacycle is observed in CV experiments.

Comparison of our ESR spectra with those of Co(IV) radicals lends further support to this assignment of electronic structure. Halpern and co-workers have studied octahedral dimethylglyoxime (dmg) complexes which can

be oxidized from Co(III) to Co(IV).⁴⁸ The half-filled orbital was assigned as being in the equatorial plane, mostly Co $3d_{x^2-y^2}$, but with considerable Co 4p character mixed in.

The 4p admixture was necessary to explain g values close to the free spin value ($g_{\parallel} \approx g_{\perp} \approx 2.02 \pm 0.015$) and the small (<35 G) cobalt hyperfine splittings. A metallacycle cation with a b_1 half-filled orbital would be expected to have a similar ESR spectrum. Even though our spectrum (Figure 7) is not fully interpreted, it shows considerably larger g value anisotropy and higher Co hyperfine splittings than observed for the Co^{IV}(dmg) radicals. A similar conclusion is reached when comparing the ESR data of (1)⁺ with those of another octahedral Co(IV) complex which gave a virtually isotropic spectrum with $g = 2.011$ and $a(\text{Co}) = 16$ G.⁴⁹ Thus, electrochemical and ESR studies are consistent with the formulation of the metallacyclic cations as π -delocalized systems having significant mixing of Co d_{yz} and the ring π -MO's.

Reactions of the 19-Electron and 17-Electron Co(II)

Anions. Our results show that the loss of phosphine from the 19-electron Co(II) anion [1][−] is extremely rapid. Molecular orbital calculations have concluded that the LUMO of 1 is antibonding between cobalt and the phosphine,^{15,50} and rapid rupture of the Co–P bond in [1][−] is consistent with this suggestion. When electron density at the metal has been increased by using a more basic phosphine, weakening of the M–P bond has been observed, with an increase in catalytic activity of the metallacycle.¹⁴ Electron transfer into an orbital with Co–P character may therefore be viewed as an extreme example of this electronic effect. Enhancement of the rate of phosphine loss in the monoanion is remarkable. The rate constant for dissociation of PPh₃ in the complex Cp(PPh₃)CoC₄Me₄ is $1 \times 10^{-4} \text{ s}^{-1}$ at 347 K,⁵¹ whereas the lower limit of the dissociation rate in [1][−] is 10^2 s^{-1} at 298 K. Therefore, the dissociated complex is accessible under much milder conditions when produced by reductive rather than thermal dissociation. Of course, the former (reductive) route produces a Co(II) species, [6][−], whereas the latter produces a Co(III) species, [6]. However, the facile replacement of PPh₃ by PEt₃ through electrolysis at room temperature suggests that reactions of the unsaturated Co(II) species may in some cases parallel those of the Co(III) analogues and lead to extensions of the chemistry of these metallacycles. Although we have evidence that phosphine replacement reactions are catalytic in the quantity of electrons passed, the turnover number is low (<3 under our conditions) and the mechanism is not well-understood.⁵² Part of the difficulty in studying this system is that the 17-electron Co(II) anion [6][−] is subject to a competing reaction which produces 4, presumably after the anion is protonated.

(48) (a) Halpern, J.; Topich, J.; Zamaraeu, K. I. *Inorg. Chim. Acta* 1976, 20, L21. (b) Topich, J.; Halpern, J. *Inorg. Chem.* 1979, 18, 1339. (c) Halpern, J.; Chan, M. S.; Hanson, J.; Roche, T. S. Topich, J. A. *J. Am. Chem. Soc.* 1975, 97, 1606.

(49) Anson, F. C.; Collins, T. J.; Coots, R. J.; Gipson, S. L.; Richmond, T. G. *J. Am. Chem. Soc.* 1984, 106, 5037.

(50) The MO calculations of ref 1b did not explicitly consider the LUMO.

(51) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* 1977, 99, 1666.

(52) Electrode-catalyzed substitution reactions usually involve a reversible electrochemical process in which a relatively stable ion radical is initially formed. See: Bezems, J. W.; Rieger, P. H.; Visco, S. *J. Chem. Soc., Chem. Commun.* 1981, 265. Bruce, M. I.; Kehoe, D. C.; Matison, J. G.; Nicholson, B. K.; Rieger, P. H.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* 1982, 442. Bruce, M. I.; Matison, J. G.; Nicholson, B. K. *J. Organomet. Chem.* 1983, 247, 321. Kochi, J. K. *J. Organomet. Chem.* 1986, 300, 139 and references therein. However, catalytic substitution for irreversible electrochemical systems have precedent: Mihalova, D.; Vlcek, A. A. *J. Organomet. Chem.* 1982, 240, 413.

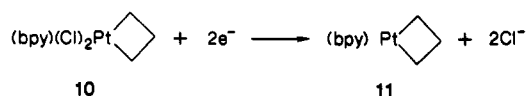
(46) (a) Koelle, U. *Inorg. Chim. Acta* 1981, 47, 13. (b) Moraczewski, J.; Geiger, W. E. *Organometallics* 1982, 1, 1385. (c) Van Willigen, H.; Geiger, W. E.; Rausch, M. D. *Inorg. Chem.* 1977, 16, 581. (d) Gubin, S. P.; Khandkarova, V. S. *J. Organomet. Chem.* 1968, 12, 523.

(47) The calculated difference in energy levels of the a_2 and b_1 orbitals is only about $1/2$ eV, within the error limits of the calculations of ref 1b; Thorn, D., personal communication.

(Scheme I). Efforts are underway to produce electronically similar 17-electron anions which are not prone to such side reactions.⁴⁰

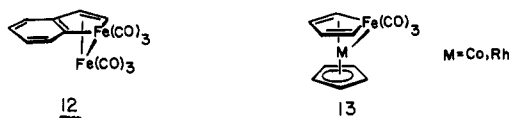
Opening of the metallacycle in the reaction of $[1]^-$ to give 4 is also consistent with molecular orbital predictions. Calculations⁵³ suggest that the LUMO of the 16-electron species 9, a model for 6, is similar to the b_1 orbital of Figure 8 and hence antibonding with respect to the metallacyclic Co-C σ -bond. Hence, $[6]^-$ is expected to exhibit a greater tendency than [6] toward rupture of the metallacycle, as is observed. Slow opening of the metallacycle to form π -complexes has previously been observed²³ in thermal reactions of 1 so that loss of phosphine is generally thought to weaken the metallacyclic unit.

Comparison with Other Metallacycle Redox Chemistry. 19-Electron Co complexes which do not have an easily dissociable 2-electron ligand may give far more stable anions⁸ than what we observe for $[1]^-$. However, the electrochemical study most pertinent to our work is that of Klingler, Huffman, and Kochi, who obtained the 16-electron platinacyclobutane 11 by reduction of the 18-electron complex 10 accompanied by rapid double loss of chloride⁴ (bpy = α, α' -bipyridine). The Pt(II) complex 11



displayed reactions typical of a coordinatively unsaturated complex. Furthermore, it was reducible in a reversible one-electron step to $[11]^-$, isoelectronic with $[6]^-$. Interestingly, though, the formal Pt(I) anion was more stable than our Co(II) analogue, and ESR spectra of solutions of $[11]^-$ were reported. It is not known whether delocalization of the unpaired electron into the bipyridyl ligand plays a role in this stabilization.

The only other examples of metallacyclic radical anions appear to be those derived from the dimetallic ferroles 12² and 13,³ but characterization of their reaction routes has not been reported.



Conclusions

1. Oxidation of the Co(III) metallacycles of the type 1 proceeds in two reversible one-electron processes. This behavior is consistent with an electronic structure of 1 in which the HOMO is π -delocalized throughout the metallacyclic fragment. Slow fragmentation of the metallacyclic unit leads ultimately to expulsion of the metal and complete disruption of the complex.

2. Reduction of 1 proceeds by reversible heterogeneous electron transfer followed by rapid loss of phosphine to give the coordinatively unsaturated anion $[6]^-$.

3. The 17-electron anion $[6]^-$ appears to be an intermediate in reductively induced phosphine exchange reactions of 1, the mechanism of which involves a catalytic route.

4. In the absence of other phosphines, $[6]^-$ is subject to protonation reactions which ultimately lead to formation of an open-chain butadiene complex in good yield.

5. Reductively induced expulsion of phosphine from 1 proceeds rapidly under milder conditions than needed for thermal dissociation of phosphine.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (CHE 83-08974) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We wish to thank Dr. D. Thorn for helpful correspondence about the molecular orbital description of these molecules.

Registry No. 1, 12124-09-3; 1^+ , 108452-84-2; 2, 62745-35-1; 2^+ , 108452-85-3; 3, 74658-23-4; 4, 12119-03-8; 5, 1278-02-0.

(53) Wakatsuki, Y.; Nomura, O.; Kitaura, K.; Morokuna, K.; Yamazaki, H. *J. Amer. Chem. Soc.* **1983**, *105*, 1907.