$N')_3I_2$ were investigated by Mössbauer spectroscopy[10a] and found to have even larger line widths than those of the spectra of **8** or **9**. It is not possible to compare the Mössbauer parameters of **8** and **9** with other suitable gold(I) compounds having a similar arrangement of ligands because such Mössbauer data have not been reported in the literature. The best candidate for such a comparison may be the linear $(Au—C\equiv N)_n$ (IS = 2.30 and QS = 7.95 mm/s) since in this compound the gold has one unsaturated carbon and one unsaturated nitrogen as donor ligands.

Gold(III) Derivatives. An X-ray crystal structure determination established that a trans square-planar coordination about the gold center is present in the cation $\{[(ArNH)_2C]_2AuI_2\}^+$ (no. 10 in Table I). The bonding involves $5d6s6p^2$ hybridization, and the Au–C bonds have been reported to be almost pure σ bonds.[33] Similar assumptions can be made by analogy for cation **11**.

The Mössbauer parameters of cations **10** and **11** are typical of covalent compounds containing gold(III). The parameters are close to those of another covalent species having two unsaturated C ligands and two iodine atoms around the gold(III) coordination center, namely, $[Au(C-N)_2I_2]^-$.[34] The EFG, which would be negative for a d_z^2 electron configuration, changes sign from negative to positive owing to the population of the Au p_x and p_y orbitals[24] in covalent Au(III) complexes. So a positive sign for the quadrupole coupling constant is expected for complexes **10** and **11**.

On complex formation not only the quadrupole coupling increases but also the isomer shift becomes more positive. Its value increases with the σ donor properties of the ligands. On comparing cations **10** and **11** it may be observed from the Mössbauer parameters that (Ar–NH)(EtO)C is a better σ donor than $(ArNH)_2C$, in agreement with the behavior of these ligands in the gold(I) complexes.

(25) Parish, R. V.; Parry, O.; McAuliffe, C. A. *J. Chem. Soc., Dalton Trans.* **1981**, 2098.

(26) Esperas, S. *Acta Chem. Scand. Ser. A* **1976**, *30A*, 527.

(27) Sham, T. K.; Watson, R. E.; Perlman, M. L. In *Mössbauer Spectroscopy and its Chemical Applications*; Stevens, J. G., Shenoy, G. K. Eds.; Adv. Chem. Ser. 194, American Chemical Society: Washington, DC, 1981; Chapter 2.

(28) Tiripicchio, A.; Camellini, M. T.; Minghetti, G. *J. Organomet. Chem.* **1979**, *171*, 399.

(29) Vaughan, L. G. *J. Organomet. Chem.* **1980**, *190*, C56; *J. Am. Chem. Soc.* **1970**, *92*, 730. U.S. Patent 3 755 329 (*Chem. Abstr.* **1973**, *79*, 115732).

(30) Jutzi, P.; Heusler, H. *J. Organomet. Chem.* **1976**, *114*, 265. Reference 8, p 294.

(31) Bovio, B.; Bonati, F.; Banditelli, G. *Inorg. Chim. Acta* **1984**, *87*, 25.

(32) Minghetti, G.; Banditelli, G.; Bonati, F. *Inorg. Chem.* **1979**, *18*, 658. Bonati, F.; Minghetti, G.; Banditelli, G. *J. Chem. Soc., Chem. Commun.* **1974**, 88.

(33) Manojlovic-Muir, L. *J. Organomet. Chem.* **1974**, *73*, C45.

(34) Faltens, M. O.; Shirley, D. A. *J. Chem. Phys.* **1970**, *53*, 4249.

Radicals of C7-Polyolefin Cobalt Complexes: Electrochemistry, Reaction Routes, and Structure of a Resulting Dimer

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The reduction and oxidation of several cyclopentadienyl (Cp) cobalt complexes with π-bonded C7-polyolefin ligands have been studied by electrochemical methods. The cycloheptadienyl complex $CpCo(\eta^5\text{-}C_7H_9)^+$ is reversibly reduced to a neutral radical which undergoes a slow dimerization reaction with a rate constant of $k = 1.35 \pm 0.23$ M^{-1} s^{-1} as measured by cyclic voltammetry. X-ray crystallographic studies of the dimer confirmed that coupling took place at the C7 ligand. The dimer crystallizes in the space group $P\bar{1}$ with $a = 6.577$ (1) Å, $b = 12.152$ (2) Å, $c = 12.693$ (2) Å, $\beta = 100.90$ (1)°, and $Z = 2$. $CpCo(\eta^4\text{-}C_7H_8)$ is reduced to a reactive monoanion that undergoes protonation and further reduction to yield $CpCo(\eta^4\text{-}C_7H_{10})$. $CpCo(\eta^4\text{-}C_7H_{10})$ is also reduced electrochemically, but its radical anion is very unstable and no product analysis was performed. However, $CpCo(\eta^4\text{-}C_7H_{10})$ gives a cation radical upon one-electron oxidation that is stable enough to be characterized by electron spin resonance spectroscopy.

Introduction

The (η^5-cyclopentadienyl)cobalt (CpCo) moiety has been useful as a template to facilitate the study of reactions of coordinated polyolefins with electrophiles and nucleophiles.[1-4] Since CpCo (polyolefin) complexes often display reversible electron-transfer reactions,[5] we sought to use electrochemistry to prepare CpCo (polyolefin) radicals in

(1) Green, M. L. H.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3753.

(2) Lewis, J.; Parkins, A. W. *J. Chem. Soc. A* **1967**, 1150.

Table I. Reduction Processes Observed for Cobalt Complexes in this Study

compd	solv	$E°(+/0)^b$	$E°(0/-)^{a,b}$	other waves^{a,b}
$[CpCo(\eta^5\text{-}C_7H_9)]$- $[PF_6]$ (1⁺)	THF	−0.75	−1.94	−2.29, −2.53
	CH₂Cl₂	−0.75	−2.0	c
	CH₃CN	−0.86	−1.91	−2.39, −2.63
	DMF	−0.82	−1.88	−2.29, −2.51
CpCo(η^4-C₇H₈) (2)	THF		−2.28	−2.50
	CH₃CN		−2.30^a	−2.65^a
CpCo(η^4-C₇H₁₀) (3)	THF		−2.48	
	CH₃CN		−2.65^a	

^{a} Cathodic peak potential given at v = 0.1 V/s. Electrode reaction is irreversible. ^{b} Electrolyte breakdown occurs at ca. −2 V. Potentials in volts referenced to aqueous saturated calomel electrode.

which the charge on the complex is plus one, zero, or minus one, in order to compare the stability and reaction pathways of radical cations, neutral radicals, and radical anions, respectively, of these complexes. In this work the polyolefins are cyclic C₇-hydrocarbons. They were chosen because studies of the addition and elimination of proton or hydride ion from these complexes[6] provide a useful basis on which to compare the reactivity of 17-, 18-, and 19-electron metal complexes.

Thus, we report electrochemical studies of the reduction of the cycloheptadienyl complex CpCo(η^5-C₇H₉)⁺ (1⁺) and the oxidation and reduction of the cycloheptatriene and cycloheptadiene complexes CpCo(η^4-C₇H₈) (2) and CpCo-(η^4-C₇H₁₀) (3), respectively. Electrochemically detectable
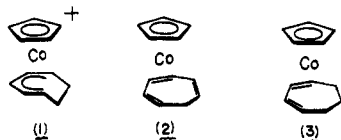
radicals were found in the one electron reduction of 1⁺, 2, and 3, and in the one-electron oxidation of 3. The radical anion 2⁻ undergoes protonation reactions, eventually forming 3, whereas the neutral radical 1° dimerizes in an efficient radical–radical coupling reaction.

Experimental Section

The cobalt compounds were prepared as previously described.[6,7] Tetra-n-butylammonium hexafluorophosphate (Bu₄NPF₆) was prepared from metathesis of Bu₄NI (Eastman) and NH₄PF₆ (Ozark-Mahoning) and recrystallized from absolute ethanol. Tetrahydrofuran (THF) (Aldrich) was distilled first from LiAlH₄ and then from the benzophenone ketyl. Acetonitrile (Burdick and Jackson) and methylene chloride (Aldrich) were distilled from CaH₂, and N,N-dimethylformamide (DMF) (Burdick and Jackson) was dried with type 4A molecular sieves.

Experiments with air-sensitive compounds 2 and 3 and all bulk coulometry experiments were performed inside a Vacuum Atmospheres Corp. drybox. Low-temperature experiments utilized precooled nitrogen gas, which circulated through a jacket around the electrochemical cell and gave a precision of ±2 °C. Electrochemical and spectroscopic procedures were as previously given.[8] Electrochemical potentials are referenced to the aqueous
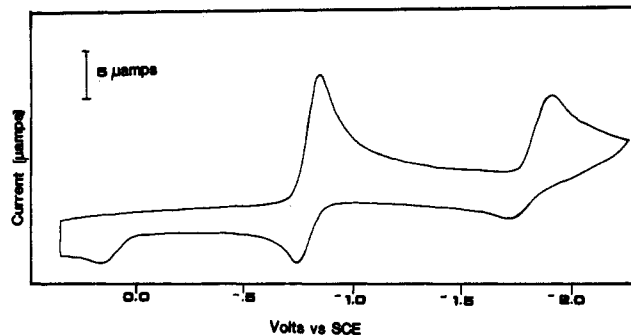
(3) Evans, J.; Johnson, B. F. G.; Lewis, J.; Yarrow, D. *J. Chem. Soc., Dalton Trans.* 2375.

(4) El Murr, N.; Laviron, E. *Can. J. Chem.* 1976, *54*, 3350, 3357.

(5) Leading references may be found in a recent review; Connelly, W.; Geiger, W. E. *Adv. Organomet. Chem.* 1984, *23*, 1.

(6) Salzer, A.; Bigler, P. *Inorg. Chim. Acta* 1981, *48*, 199.

(7) Jones, K.; Deffense, E.; Haberman, D. *Angew. Chem.* 1983, *95*, 729; *Angew. Chem., Int. Ed. Engl.* 1983, *22*, 716; *Angew. Chem. Suppl.* 1983, 1005.

(8) Moraczewski, J.; Geiger, W. E. *Organometallics* 1982, *1*, 1385.

Figure 1. Cyclic voltammogram of 4.0 × 10⁻⁴ M [CpCo(η^5-C₇H₉)][PF₆] in DMF/0.1 M Bu₄NPF₆ at a electrode at scan rate of 460 mV/s (T = 248 K).

saturated calomel electrode (SCE) and all electrochemical solutions contained 0.1 M Bu₄NPF₆ as supporting electrolyte. In many cases, voltammetry was performed at both mercury and platinum electrodes and in no case was there observed any dependence of the electrochemistry on the nature of the working electrode.

Crystallographic Structural Determination: Crystals of [CpCo(C₇H₉)]₂ were obtained by recrystallization from hexane at 250 K. Crystal parameters along with the details of data collection and the results of refinement are presented in Table II. The centrosymmetric space group, P$\bar{1}$, was suggested by the statistical distribution of E values and was confirmed by the chemically reasonable solution and well-behaved refinement of the structure. Corrections to the intensity data were made for Lp effects, but none for absorption was required; relative transmission (max/min = 1.00/0.91). The structure was solved by direct methods and completed by a series of difference Fourier syntheses. While a majority of the hydrogen atoms were eventually located, refinement was completed with calculated, idealized contributions to maintain a reasonable parameter/data ratio; d(C–H) = 0.96 Å, and U(H) = 1.2U(C). All non-hydrogen atoms were refined anisotropically. Programs used are contained in the Nicolet Corp. program libraries P3 (data collection) and SHELXTL, version 4.1 (data reduction and refinement).

Atomic coordinates are provided in Table III, and selected bond distances and angles in Table IV. Additional crystallographic data (a complete list of distances and angles, anisotropic temperature factors, and hydrogen atom coordinates) are available as supplementary material.

Results

I.a. Reduction of CpCo(η^5-C₇H₉)⁺ (1⁺). The reduction of this cation was studied in four nonaqueous solvents. Except for some small shifts in $E°$ value, similar behavior was observed. As indicated in Table I, two waves were observed, one at ca. −0.8 V and the other at ca. −1.9 V. Extensive electrochemical data establish that the first wave (Figure 1) corresponds to a simple one-electron reduction forming the 19-electron radical 1° which reacts to give a product that is identified as the dinuclear complex [CpCo(η^4-C₇H₉)]₂ (see below).

$$CpCo(\eta^5\text{-}C_7H_9)^+ + e^- \rightleftharpoons CpCo(\eta^5\text{-}C_7H_9) \quad E° = -0.8 \text{ V}$$

The lifetime of the radical, as judged by comparison of i_a/i_c values at a particular CV scan rate, appeared to be independent of solvent composition. This electrode process was studied by dc polarography, reverse-pulse polarogra-

(9) Abbreviations and symbols used in this paper: i_a/i_c = ratio of anodic to cathodic currents measured in a cyclic voltammetry scan; CV = cyclic voltammetry; v = CV scan rate; I = polarographic diffusion current constant; $E_{1/2}$ = polarographic half-wave potential; $E°$ = standard reduction potential; SCE = aqueous saturated calomel electrode; i_d = diffusion current on plateau of polarographic wave; ΔE_p = $|E_{Pc} - E_{Pa}|$ (separation of peak potentials in CV); k_s = standard heterogeneous electron-transfer rate; E = electron transfer; C = homogeneous chemical reaction; i_{Pc} = cathodic peak current; i_{Pa} = anodic peak current; $C°$ = bulk concentration of electrochemical reactant.

Table II. Crystal Data, Data Collection, and Refinement Parameters for [(C₇H₉)CoC₅H₅]₂

Crystal Data

formula	$C_{24}H_{28}Co_2$	V, Å³	970.9 (2)
cryst system	triclinic	Z	2
space group	$P1$	D(calcd), g cm⁻³	1.49
a, Å	6.577 (1)[a]	color	deep red
b, Å	12.152 (2)	size, mm	0.22 × 0.22 × 0.31
c, Å	12.693 (2)	shape	rect. prism
α, deg	92.39 (1)	μ, cm⁻¹	17.8
β, deg	100.90 (1)	$F(000)$	452
γ, deg	102.01 (1)		

Data Collection

diffractometer	Nicolet R3	scan technique	Wyckoft
radiation	Mo Kα (λ = 0.710 73 Å)	temperature	22 °C
monochromator	graphite	std reflns	3 stds/97 rflns
scan range, deg	4 ≤ 2θ ≤ 50	decay	<1%
scan speed, deg/min⁻¹	var 4–20		

Structure Refinement

rflns collected	3585	g^c	0.0007
unique data	3417	GOF[d]	1.524
$F_0 \geq 2.5\sigma(F_0)$ data	2827	highest peak, e/Å³, final diff map	0.46
R_T, %	1.28		
R_F,[b] %	4.93	mean (Δ/σ), final cycle	0.051
R_{wF}	5.04		

[a] Unit-cell dimensions from the least-squares refinement of the angular settings of 25 reflections (20° ≤ 2θ ≤ 30°). [b] $R_F = \sum|\Delta|/|\sum|F_o|$; $R_{wF} = \sum(|\Delta| w^{1/2})/\sum(|F_o|w^{1/2})$; $\Delta = |F_o| - |F_c|$. [c] $w^{-1} = \sigma^2(F_o) + gF_o^2$. [d] GOF = $[\sum w(\Delta^2)/(N_o - N_v)]^{1/2}$, $N_v = 182$.

Table III. Atom Coordinates (×10⁴) and Temperature Factors (Å² × 10³)

atom	x	y	z	$U_{iso}{}^a$
Co(1)	1189 (1)	3115 (1)	4174 (1)	38 (1)
Co(2)	−3280 (1)	1499 (1)	−1622 (1)	40 (1)
C(1)	2596 (11)	1841 (5)	4692 (5)	79 (3)
C(2)	429 (12)	1501 (5)	4549 (5)	101 (3)
C(3)	−328 (11)	2181 (7)	5254 (6)	102 (4)
C(4)	1455 (10)	2912 (5)	5827 (4)	73 (3)
C(5)	3200 (9)	2731 (5)	5484 (4)	64 (2)
C(6)	−778 (6)	3017 (4)	2708 (3)	34 (1)
C(7)	−521 (7)	4045 (4)	3344 (3)	40 (2)
C(8)	1517 (7)	4679 (4)	3790 (3)	42 (2)
C(9)	3304 (7)	4263 (4)	3596 (3)	42 (2)
C(10)	3757 (7)	3986 (4)	2501 (4)	47 (2)
C(11)	1845 (7)	3840 (4)	1584 (3)	41 (2)
C(12)	75 (6)	2862 (4)	1701 (3)	33 (1)
C(13)	−4163 (12)	444 (5)	−3048 (4)	83 (3)
C(14)	−5936 (11)	561 (5)	−2660 (5)	88 (3)
C(15)	−5763 (11)	161 (5)	−1673 (6)	86 (3)
C(16)	−3918 (11)	−186 (4)	−1410 (5)	81 (3)
C(17)	−2847 (14)	−9 (5)	−2271 (7)	97 (4)
C(18)	−1077 (7)	2139 (4)	−267 (3)	43 (2)
C(19)	−672 (7)	2667 (4)	−1204 (4)	46 (2)
C(20)	−2290 (8)	3083 (4)	−1840 (4)	45 (2)
C(21)	−4249 (7)	2960 (4)	−1523 (4)	44 (2)
C(22)	−4634 (7)	3377 (4)	−467 (4)	48 (2)
C(23)	−2674 (7)	3657 (4)	432 (3)	37 (2)
C(24)	−1773 (7)	2627 (3)	688 (3)	35 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthosonalized U_{ij} tensor.

Table IV. Selected Bond Distances and Angles for [(C₇H₉)CoC₅H₅]₂.[a]

(a) Bond Distances (Å)

Co(1)–C(1)	2.034 (7)	Co(2)–C(15)	2.040 (6)
Co(1)–C(2)	2.021 (6)	Co(2)–C(16)	2.043 (5)
Co(1)–C(3)	2.084 (8)	Co(2)–C(17)	2.073 (7)
Co(1)–C(4)	2.102 (5)	Co(2)–C(13)	2.087 (5)
Co(1)–C(5)	2.056 (5)	Co(2)–C(14)	2.064 (6)
Co(1)–C(6)	2.039 (4)	Co(2)–C(18)	2.035 (4)
Co(1)–C(7)	1.957 (5)	Co(2)–C(19)	1.954 (4)
Co(1)–C(8)	1.960 (5)	Co(2)–C(20)	1.948 (4)
Co(1)–C(9)	2.021 (4)	Co(2)–C(21)	2.013 (5)
C(6)–C(7)	1.420 (6)	C(18)–C(19)	1.418 (7)
C(7)–C(8)	1.399 (6)	C(19)–C(20)	1.404 (7)
C(8)–C(9)	1.429 (7)	C(20)–C(21)	1.402 (7)
C(9)–C(10)	1.514 (7)	C(21)–C(22)	1.498 (7)
C(10)–C(11)	1.518 (6)	C(22)–C(23)	1.519 (6)
C(11)–C(12)	1.515 (6)	C(23)–C(24)	1.514 (7)
C(6)–C(12)	1.509 (6)	C(18)–C(24)	1.514 (7)
		C(12)–C(24)	1.564 (5)

(b) Bond Angles (deg)

C(6)–Co(1)–C(7)	41.6 (2)	C(18)–C(2)–C(19)	41.6 (2)
C(6)–Co(1)–C(8)	75.2 (2)	C(18)–Co(2)–C(20)	75.2 (2)
C(6)–Co(1)–C(9)	86.9 (2)	C(18)–Co(2)–C(21)	86.0 (2)
C(7)–Co(1)–C(8)	41.9 (2)	C(19)–Co(2)–C(20)	42.2 (2)
C(7)–Co(1)–C(9)	75.3 (2)	C(19)–Co(2)–C(21)	74.9 (2)
C(8)–Co(1)–C(9)	42.0 (2)	C(20)–Co(2)–C(21)	41.4 (2)
C(6)–C(7)–C(8)	120.0 (4)	C(18)–C(19)–C(20)	118.9 (5)
C(7)–C(8)–C(9)	118.6 (4)	C(19)–C(20)–C(21)	118.7 (4)
C(8)–C(9)–C(10)	125.8 (4)	C(20)–C(21)–C(22)	127.0 (4)
C(9)–C(10)–C(11)	114.0 (4)	C(21)–C(22)–C(23)	114.4 (4)
C(10)–C(11)–C(12)	112.2 (4)	C(22)–C(23)–C(24)	111.7 (3)
C(11)–C(12)–C(6)	112.8 (3)	C(23)–C(24)–C(18)	112.2 (4)
C(6)–C(12)–C(24)	110.3 (3)	C(18)–C(24)–C(12)	110.7 (4)
C(11)–C(12)–C(24)	111.9 (3)	C(23)–C(24)–C(12)	112.5 (3)

[a] The related bond parameters for the two nearly identical halves of this molecule are compared on horizontal lines.

phy, differential pulse polarography, cyclic voltammetry, and bulk coulometry. In each experiment the data were consistent with a diffusion-controlled, reversible (Nernstian) one-electron charge-transfer reaction.

Consider typical voltammetric data in CH_3CN. Direct current polarography gave a diffusion-controlled wave with $E_{1/2}$ = −0.86 V, a diffusion current constant of I = 3.23 μA mM⁻¹ mg⁻²/³ s¹/² (cf. 3.33 for Cp₂Co⁺/Cp₂Co under the same conditions), and a slope in the plot of applied potential versus log $[i/(i_d - i)]$ of −59 mV, as expected for a Nernstian one-electron wave. Cyclic voltammetry (CV) measurements corroborated these conclusions. Scans at platinum or mercury electrodes over the range v = 0.05–0.5 V/s gave constant values of $i_{p_c}/v^{1/2}$ and peak separations

close to the Nernstian value. At the same time, certain deviations from complete reversibility were noted in the CV behavior. At the higher end of the scan rate range the peak separation rose to 70 mV, whereas Cp₂Co⁺/Cp₂Co showed a 60-mV separation, meaning that the ΔE_p increase of $1^{+/0}$ was real and not an artifact of solution resistance.[10]

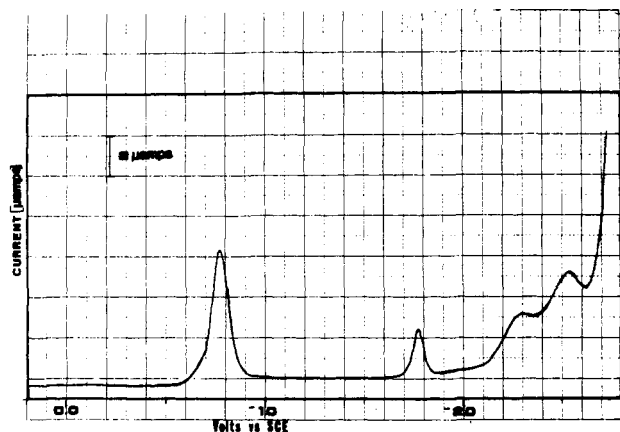(10) An electron-transfer rate in the quasi-reversible range is indicated by these results.

Figure 2. Differential pulse polarogram of 5×10^{-4} M [CpCo-(η^5-C₇H₉)][PF₆] in THF/0.1 M Bu₄NPF₆ (drop time = 0.5 s; pulse amplitude = 25 mV).

Figure 3. Molecular structure and labeling scheme for [CpCo-(η^4-C₇H₉)]₂. Thermal ellipsoids are depicted at the 40% probability level.

Figure 4. Unit cell stereo packing diagram for [CpCo(η^4-C₇H₉)]₂.

More importantly, the ratio of the reverse (anodic) current to the forward (cathodic) current, i_a/i_c, fell below unity when the scan rate was lower than about 0.5 V/s. This suggested that neutral 1^0 was subject to a chemical follow-up reaction, making the electrode process a $E_{rev}C$ mechanism. This was supported by reverse-pulse polarographic data. In this technique,[11] instead of applying a series of increasingly negative pulses (normal pulse polarography), the rest (initial) potential is held negative of the reduction wave (<-1.1 V in our case) and a series of positive-going pulses is applied to the electrode, becoming increasingly positive with each successive drop from the dropping mercury electrode. A value of unity for the ratio of the plateau current from the positive-going pulse to that from the negative-going pulse establishes a totally chemically reversible redox process. Consistent with the instability of 1^0, we obtained a value of only 0.55 for this ratio by using a pulse time of 56 ms. The chemical fate of 1^0 is described below.

The second wave ($E_{1/2} \approx -1.9$ V) is irreversible. The peak current of the cathodic wave was considerably smaller than that of the wave at −0.8 V, although the ratio of $i_{p_c}(2)/i_{p_c}(1)$ increased from about 0.3 to 0.6 as the CV scan rate was increased from $v = 0.10$ to 0.75 V/s. This wave likely represents the one-electron reduction of 1 to 1^-. Under the assumption that the second cathodic peak potential approximates E° for $1^0/1^-$, the potentials for the two reductions $1^+/1^0/1^-$ are seen to be very close to those of their isoelectronic metallocene analogues Cp₂Co⁺/Cp₂Co⁰/Cp₂Co⁻, which are $E^\circ_1 = -0.90$ V and $E^\circ_2 = -1.88$ V under these conditions.[12]

I.b. Dimerization of the Radical CpCo(η^5-C₇H₉). When a solvent with a sufficiently negative window was used (DMF, CH₃CN, THF), additional waves were seen close to the potential of electrolyte breakdown. A differential pulse polarogram is shown in Figure 2. These waves were chemically irreversible at CV sweep rates of 0.2 V/s and fell at ca. −2.3 and −2.55 V (see Table 1). It seemed clear that these waves arose from reactions of the electrolysis products of 1^0 and/or 1^- produced in the first two reduction waves. The above potentials are very close to those for reduction of CpCo(η^4-C₇H₈) and CpCo(η^4-C₇H₁₀) (Table I) which first led us to suspect that 1 and/or 1^- might react via H atom or proton abstraction to yield the partially saturated derivatives 2 and 3, respectively. However, isolation of the electrolysis product showed it to be a dimer of 1^0 having reduction waves at potentials

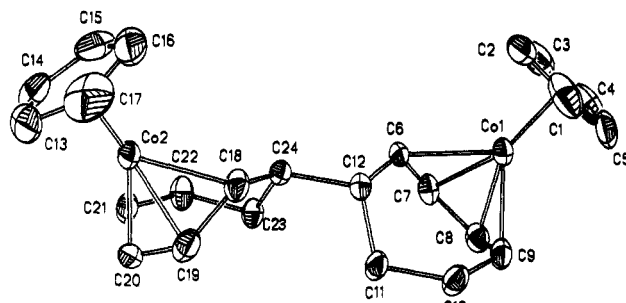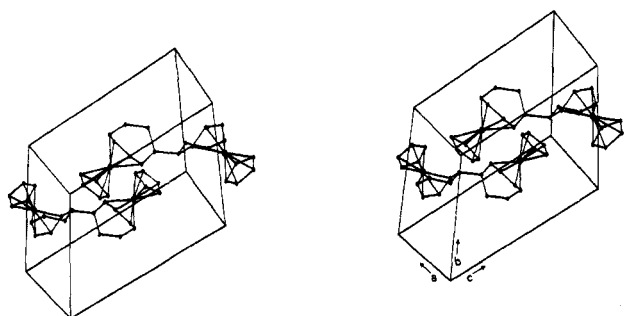very close to those of 2 and 3.

Bulk electrolysis of 1^+ in CH₃CN at −1.0 V using a Pt basket electrode required 1.0 F as the solution went from light orange to red. When the electrolysis was performed at 233 K, red microcrystals precipitated from solution and were filtered off. This crude product gave an NMR spectrum with fairly broad lines which obscured the spin–spin splittings, but, when recrystallized from hexane at 250 K (under N₂), pure needles were produced that analyzed for [CpCo(C₇H₉)]ₙ.[13] Electron-impact mass spectrometry gave a base peak of m/e 217 [CpCo(C₇H₉)], but a small peak at twice that value. A field desorption spectrum[14] gave m/e 434 as the base peak, establishing a dimeric formulation for the electrolysis product. ¹H NMR (C₆D₆) was also consistent with a dimer (4) bridging through the seven-membered ring [δ 4.57 (5 H, s, Cp); 4.69 (1 H, m, H₍ₐ₎); 4.61 (1 H, m, H₍ᵦ₎); 2.96 (1 H, m, H₍c₎); 2.64 (1 H, d, H₍d₎); 1.96–1.70 (3 H, m, H₍ₑ₎, H₍f₎, H₍g₎); 1.36 (1 H, m, H₍ₕ₎); 1.27 (1 H, m, H₍ᵢ₎): assignments given by lettering legend below were aided by decoupling experiments].

(4)   (5)
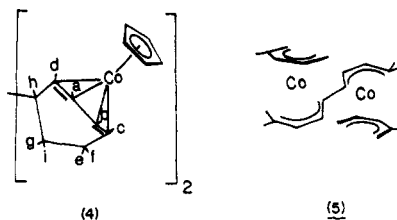
I.c. Structure of the Dimer [CpCo(η^4-C₇H₉)]₂. 4 consists of two CpCo(C₇H₉) moieties linked through the C₇ polyolefin (Figures 3 and 4). Each half has a 18-electron cobalt which achieves that electronic configuration by coordination to a η^5-cyclopentadienyl ligand and a planar η^5-diolefin portion of the C₇H₉ ring. Selected bond distances and angles are given in Table IV. The Co–C

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(11) Osteryoung, J.; Kirowa-Eisner, E. *Anal. Chem.* **1980**, *52*, 62.

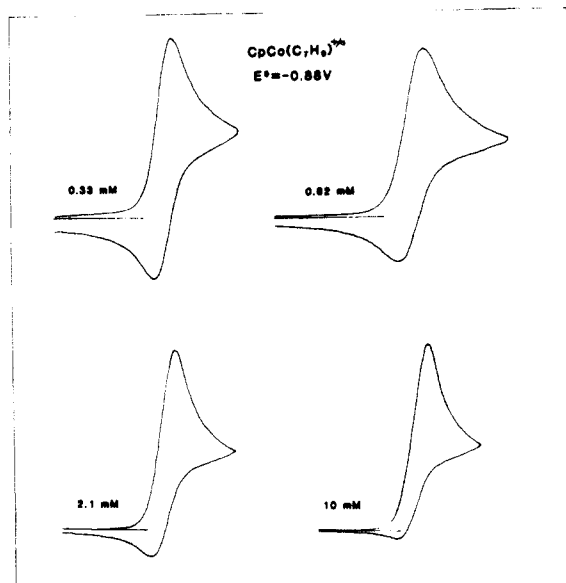(12) Geiger, W. E. *J. Am. Chem. Soc.* **1974**, *96*, 2632.

(13) Calcd for C₂₄H₂₈Co₂: C, 66.37; H, 6.65. Found (Schwarzkopf): C, 66.04; H, 6.43.

(14) The field desorption spectrum was obtained at the NSF regional mass spectrometry facility at MIT. We thank Dr. Catherine Costello for obtaining the spectrum.

Figure 5. Cyclic voltammograms of various concentrations of [CpCo(η^5-C$_7$H$_9$)][PF$_6$] in CH$_3$CN/0.1 M Bu$_4$NPF$_6$ at a Pt electrode (scan rate = 100 mV/s, at 300 K). Scans shown are from -0.44 to -1.16 V vs. SCE, and x and y scales were adjusted to give similar peak currents. The horizontal line gives zero current for each scan. Concentrations of [CpCo(η^5-C$_7$H$_9$)][PF$_6$] as given next to each CV curve.

distances to the outer carbons of the butadiene-like fragments of the C$_7$H$_9$ ring (e.g., Co$_1$-C$_6$ and Co$_1$-C$_9$) are somewhat longer than the distances to the inner carbons (e.g., Co$_1$-C$_7$ and Co$_1$-C$_8$), averaging 2.028 vs. 1.955 Å. The inner C-C bond in the butadiene-like fragment averages shorter than the outer C-C bonds, 1.402 vs. 1.416 Å. These effects are similar to those observed previously for the related dimer[15] of bis(2,4-dimethylpentadienyl)cobalt (5) and for isoelectronic (η^4-diolefin)iron tricarbonyl complexes.[16] Other pertinent data are given in Tables II and III.

I.d. Dimerization Kinetics of CpCo(η^5-C$_7$H$_9$). Cyclic voltammetry can be used to diagnose and to measure the rate of a dimerization reaction. The response of the CV wave to changes in experimental conditions depends on the kinetics and equilibrium constant of the dimerization process.[17-20] If the dimer is favored at equilibrium (the present case), the situation is simplified and the CV wave response depends on the kinetic parameter λ_{DIM} = ($k_{DIM}C^0/v$)(RT/F), in which C^0 is the bulk concentration of the electrochemical reactant, v is the scan rate, and k_{DIM} is the rate constant for the dimerization reaction. If λ_{DIM} is large (fast reaction, slow scan limit), the wave appears irreversible and the peak potential is a linear function both of log C^0 and log v. However, if λ_{DIM} is relatively small, the wave will appear at least partially chemically reversible, and the cathodic peak potential will be virtually independent of concentration and scan rate. In the latter case (slow dimerization, referring to the kinetic zone KO of ref 18) the rate of the dimerization reaction is measured from the ratio of the anodic and cathodic CV currents.[21,22] The

(15) Wilson, D. R.; Ernst, R. D.; Kralik, M. S. *Organometallics* **1984**, *3*, 1442.

(16) Cotton, F. A.; Day, V. W.; Frenk, B. A.; Hardcastle, K. I.; Troup, J. M. *J. Am. Chem. Soc.* **95**, 4522 (1973).

(17) Saveant, J. M.; Vianello, E. *Electrochim. Acta* **1967**, *12*, 1545.

(18) Andrieux, C. P.; Nadjo, L.; Saveant, J. M. *J. Electroanal. Chem.* **1970**, *26*, 147.

(19) Mastragostino, M.; Nadjo, L.; Saveant, J. M. *Electrochim. Acta* **1968**, *13*, 721.

(20) Andrieux, C. P.; Nadjo, L.; Saveant, J. M. *J. Electroanal. Chem.* **1973**, *42*, 223.

Table V. CV Data at Different Concentrations of 1$^+$ Used To Calculate the Dimerization Rate of the Radical CpCo(C$_7$H$_9$)^e

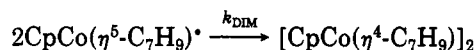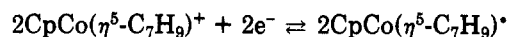| concn of (1$^+$, mM)	v,^{a} V/S	$(i_{p_a})_0/i_{p_c}$^{b}	k_{DIM},^{c} M^{-1} s^{-1}
0.33	0.050	0.25	1.55
0.62	0.050	0.18	1.30
0.62	0.10	0.27	1.41
0.62	0.50	0.50	1.57
2.08	0.10	0.15	1.11
2.08	0.50	0.34	1.36
5.00	0.10	0.09	d
5.00	0.50	0.23	1.14
9.96	0.50	0.15	1.21

^{a} Cyclic voltammetry scan rate. ^{b} $(i_{p_a})_0$ and i_{p_c} are the anodic and cathodic currents, respectively, measured from the zero current line. ^{c} Rate constant for dimerization, calculated by the method of Lasia,[22] using a switching potential 250 mV past the cathodic peak potential for the 1$^+$/1^0 wave. A total of 16 measurements at different concentrations and scan rates averaged a value of k_{DIM} = 1.35 (±0.23) M^{-1} s^{-1}. ^{d} Value of $(i_{p_a})_0/i_{p_c}$ too low to yield reliable value of k_{DIM}. ^{e} Data taken at a platinum electrode in CH$_2$Cl$_2$/0.1 M Bu$_4$NPF$_6$.

Table VI. E° Potentials vs. SCE of Some CpCo(η^4-diolefin) Complexes Having Cyclic Polyolefins

polyolefin	E° of Co(I)/Co(0) couple, V	ref
1,3-C$_8$H$_8$	-1.82	23, 45
1,5-C$_8$H$_8$	-2.05	23, 45
C$_8$H$_{10}$	-2.28	23
C$_7$H$_8$	-2.28	this work
C$_8$H$_{12}$	-2.45	23
C$_7$H$_{10}$	-2.48	this work

dimerization of 1^0 falls in this category.

In this treatment we assume that the dimerization involves coupling of two neutral radicals

$$2CpCo(\eta^5\text{-}C_7H_9)^+ + 2e^- \rightleftharpoons 2CpCo(\eta^5\text{-}C_7H_9)^\bullet$$

$$2CpCo(\eta^5\text{-}C_7H_9)^\bullet \xrightarrow{k_{DIM}} [CpCo(\eta^4\text{-}C_7H_9)]_2$$

(DIM 1 mechanism in ref 18 and 20), and we use the method of Lasia,[22] in which the anodic current $(i_{p_a})_0$ is measured from the zero current line (Figure 5). The CV switching potential was 250 mV past the cathodic peak potential. As expected, values of $(i_{p_a})_0/i_{p_c}$ decreased with either decreasing scan rate at a single concentration or with higher concentrations at the same scan rate (Figure 5). Typical values are given in Table V. From each value of $(i_{p_a})_0/i_{p_c}$ a value of λ_{DIM} was obtained from a working curve constructed from Table II of ref 22. Knowing C^0 and v enables the calculation of k_{DIM}, with typical values given in Table V. At each scan rate an independent value of k_{DIM} is obtained. We used a minimum of four scan rates at five concentrations varying from 0.33 to 9.96 mM to obtain the value

$$k_{DIM} = 1.35 \pm 0.23 \text{ M}^{-1} \text{ s}^{-1}$$

The error limit is a relative standard deviation.

Additional confirmation of this mechanism arises from the observed lack of shift of E_{p_c} as a function of scan rate, which is predicted if λ_{DIM} is small.[18,20] E_{p_c} was measured at three concentrations over the range of scan rates v = 0.02 to 0.50 V/s. In DMF at a mercury drop electrode, a shift of -13 mV in d(E_{p_c})/d(log v) was observed for both 1$^+$ and the reversible one-electron standard Cp$_2$Co$^+$/Cp$_2$Co, showing that, after correction for small iR losses, the peak

(21) Olmstead, M. L.; Hamilton, R. G.; Nicholson, R. S. *Anal. Chem.* **1969**, *41*, 260.

(22) Lasia, A.; *J. Electroanal. Chem.* **1983**, *146*, 413.

**Table VII. Oxidation Process Observed for Cobalt Complexes in This Study[b]**

compd	solv	$E°(0/+)$	$E°(+/2+)$	other waves
1⁺		none		
CpCo(η^4-C$_7$H$_8$) (2)	CH$_2$Cl$_2$	+0.08[a]		+0.56 ($E°$)
	THF	+0.20[a]		+0.54 ($E°$)
CpCo(η^4-C$_7$H$_{10}$) (3)	CH$_2$Cl$_2$	+0.23	+1.13	
	THF	+0.33[a]		+0.71 ($E°$)
[CpCo(C$_7$H$_9$)]$_2$ (4)	CH$_2$Cl$_2$	+0.16	+0.28	

[a] Anodic peak potential given at v = 0.1 V/s. Electrode reaction is irreversible. [b] Potentials in volts referenced to aqueous saturated calomel electrode.

potential of **1⁺** is independent of scan rate.

II. Reduction of CpCo(η^4-C$_7$H$_8$) and CpCo(η^4-C$_7$H$_{10}$). Briefer investigations were conducted of the reduction of the cycloheptatriene and cycloheptadiene complexes **2** and **3**, respectively. Both compounds show chemically reversible one-electron reductions at very low potentials. In THF, $E°$ for **2** is -2.28 V and $E°$ for **3** is -2.48 V. In Table VI these potentials are compared to those of other CpCo(polyolefin) compounds, the $E°$ potentials becoming more negative as the degree of unsaturation of the polyolefin decreases.

Red **2** reduces in a one-electron (coulometry, 253 K) process to a green monoanion which apparently undergoes protonation and subsequent reduction to yield **3** in the overall reaction

$$CpCo(\eta^4\text{-}C_7H_8) + 2e^- + 2H^+ \rightarrow CpCo(\eta^4\text{-}C_7H_{10})$$
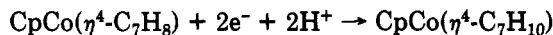
Evidence for this comes from CV scans of **2**, in which at slower scan rates (ca. 0.50 V/s) a product wave occurs at $E°$ = -2.50 V, within experimental error of that measured independently for **3**. The free ligand C$_7$H$_8$ also reduces at this potential, but its reduction is irreversible, unlike that of **3**, aiding our diagnosis that the second wave of **2** arises from **3** formed near the electrode surface. Thus, the reductive behavior of CpCo(η^4-C$_7$H$_8$) is seen to be similar to that of cyclooctatetraene complexes of both CpCo[23] and Fe(CO)$_3$,[24] in that electron addition ultimately leads to addition of dihydrogen to the cyclic polyolefin.

The reduction wave for **3** became completely chemically reversible (i_a/i_c = 1) at scan rates in excess of 1 V/s. The height of the wave was equal to that of the one-electron oxidation of the same compound, which was established as a n = 1 process by voltammetry and coulometry (vide infra).

III. Oxidation of CpCo(η^4-C$_7$C$_8$) and CpCo(η^4-C$_7$H$_{10}$). Oxidation of CpCo(η^4-polyolefin) complexes has been reported to yield a reactive cation radical in mild solvents such as dichloromethane.[8,25] The process appears to involve an uncomplicated one-electron transfer provided that the η^4-polyolefin has no additional uncoordinated double bonds.[8] Not surprisingly, therefore, oxidation of **3** gives a one-electron oxidation arising from the reaction

$$CpCo(\eta^4\text{-}C_7H_{10}) \rightleftharpoons CpCo(\eta^4\text{-}C_7H_{10})^+ + e^-$$
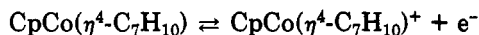
to give a radical cation (**3⁺**) which is reasonably stable in CH$_2$Cl$_2$ ($E°$ = +0.23 V, Table VII). The i_c/i_a ratio was unity when v > 0.25 V/s and the wave was diffusion-controlled (constant value of $i_{p_a}/v^{1/2}$ over the range 0.05 V/s < v < 0.5 V/s). The cation oxidizes in another one-electron step at $E°$ = +1.13 V (Figure 6) which is only chemically reversible at v > 5 V/s.

Bulk coulometry of **3** in CH$_2$Cl$_2$ (Pt basket electrode, E_{app} = +0.46 V, T = 298 K) resulted in release of 1.0 F of electricity (n = 1 electron) as the color went from red-
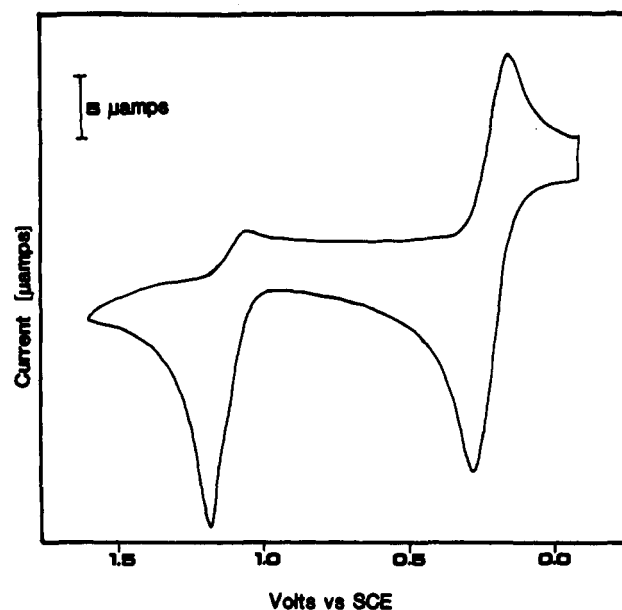

Figure 6. Cyclic voltammogram of 6.9 × 10⁻⁴ M CpCo(η^4-C$_7$H$_{10}$) in CH$_2$Cl$_2$/0.1 M Bu$_4$NPF$_6$ at a Pt electrode (scan rate = 160 mV/s).

orange to yellow. Since voltammograms of the resulting solution showed only the waves attributable to Cp$_2$Co⁺ (-0.81 and -1.9 V), the cation radical is apparently unstable and yields Cp$_2$Co⁺, as previously observed for other Co(d⁷) analogues:[8,25]

$$CpCo(C_7H_{10})^+ \rightarrow {}^1/_2\ Cp_2Co^+ + {}^1/_2\ Co^+ + C_7H_{10}$$
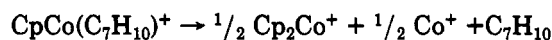
A weak ESR spectrum tentatively attributed to the transient cation radical **3⁺** was observed in these coulometry experiments, and its identity was confirmed by ESR studies on the oxidation of **3** by ferrocenium ion. If CH$_2$Cl$_2$ solutions of **3** and [Cp$_2$Fe][PF$_6$] were mixed at a temperature just warm enough to melt the solvent (mp 178 K), the solution became a deep green and a frozen solution ESR spectrum displayed a strong signal due to **3⁺**. The X-band spectra are strongly overlapped, and we can only report with certainty that the dominant Co hyperfine splitting is from the high-field **g** tensor component, with A(Co) ≈ 80 G. These radicals are of interest because of the rarity of Co(II) π-complexes, so their ESR spectra are being studied in greater detail.

Cyclic voltammetry or bulk electrolysis of the oxidation of **3** in stronger donor solvents like THF or CH$_3$CN yielded Cp$_2$Co⁺ without any indication of **3⁺**, consistent with results on other CpCo(polyolefin) compounds.[8,25]

Oxidation of the cycloheptatriene complex **2** in CH$_2$Cl$_2$ does not give a reversible wave. Rather, the apparent one-electron wave is irreversible up to at least v = 1 V/s, with E_{p_a} = +0.08 V at v = 0.25 V/s. CV scans and bulk coulometry experiments again indicate that the oxidation yields Cp$_2$Co⁺, mostly likely after rapid decomposition of **2⁺**. The instability of **2⁺** is similar to that noted for the cation radical of [CpCo(η^4-C$_8$H$_8$)]⁺.[8]

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

(24) El Murr, N.; Riveccie, M.; Laviron, E. *Tetrahedron Lett.* **1976**, 3339.
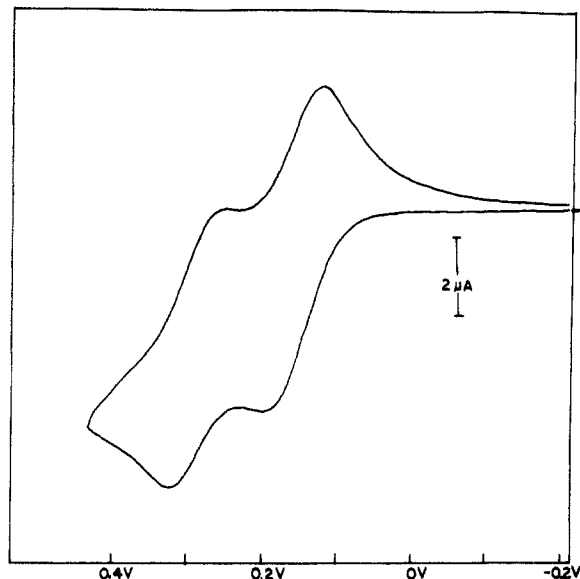
(25) Koelle, U. *Inorg. Chim. Acta* **1981**, *47*, 13.

Figure 7. Cyclic voltammogram of ca. 5 × 10⁻⁴ M [CpCo(η^4-C₇H₉)]₂ in CH₂Cl₂/0.1 M Bu₄NPF₆ (scan rate = 120 mV/s; T = 233 K; Pt electrode).

IV. Oxidation of the Dimer [CpCo(η^4-C₇H₉)]₂ (4).

Each half of the dimer consists of a CpCo(η^4-polyolefin) with no further unsaturation in the polyolefin. Thus, the dimer might be expected to undergo reversible oxidations. Indeed, this is observed. At low temperatures (below ca. 250 K) two closely spaced chemically reversible waves are observed (Figure 7) with $E°$ values of approximately +0.16 and +0.25 V. Both waves were diffusion-controlled, and ΔE_p values of ca. 120 mV were observed when T = 233 K, similar to values of Cp₂Fe at this same concentration and temperature. Thus, the dimer appears to oxidize in two one-electron steps with only limited electronic communication between the two halves of the complex. If the two oxidation sites were rigorously isolated electronically from each other, only a single wave would be found.

Bulk coulometry past the second oxidation wave at 233 K in CH₂Cl₂ gave a well-behaved exponential current/time curve and indicated release of 2.1 F (n = 2 overall). The products of the oxidation were monitored by CV scans after electrolysis. Two closely spaced reduction waves, both reversible, were seen, with apparent $E°$ values of −0.86 and −0.93 V, but the identity of the oxidation products was not established. These results and CV results at ambient temperatures indicate that the dication of the dimer has about the same stability as the monocation of its mononuclear analogue 3.

Discussion

Analogy of Reduction of 1⁺ to That of Cp₂Co⁺. The formal potentials of the Co^{III}/Co^{II} and Co^{II}/Co^{I} couples are very similar for 1⁺ and for Cp₂Co⁺. This implies that the electronic structures of the two compounds are similar in spite of the fact that the second η^5-polyolefin ring of 1⁺ has an interrupted conjugation. A similar comparison is found in the redox potentials of CpFe(η^5-C₆H₇) and Cp₂Fe,[26] which are isoelectronic with the cobalt systems. However, the post-electrode reactions are different for 1⁰ and for Cp₂Co, since the latter shows no tendency to dimerize.

Reports concerning the dimerization of organometallic π-complex radicals produced through electrochemical (or other redox) methods have appeared. Although the num-

ber of systems studied is not large, some trends may be noted. *Neutral* radicals having *17-electron metals* favor dimerization through metal–metal bond formation, reliable examples being the dimerization of (η^3-allyl)Fe(CO)₃[27,28] (6) and CpM(CO)₃ (M = Cr, Mo, W) (7).[29-31] It is interesting to note that both 6 and 7 have analogues in which stable 17-electron monomers are isolated. Thus, (η^3-C₈H₁₃)Fe[P(OMe₃)₃][32,33] and TpMo(CO)₃[34] (Tp = hydridotris(pyrazolyl)borate) show no tendency to dimerize, perhaps because of the greater steric requirements of the ligands.

Coupling reactions at the *ligand* have been observed for 17-electron compounds which are *radical cations*, examples being CpFe[(η^5-C₆Me₅(CH₂)]⁺,[35] (η^4-C₈H₈)Fe(CO)₃⁺,[36] CpFe(CO)₂[CH₂C(R)=CR₂]⁺,[37] and CpFe(CO)₂SR⁺.[38]

On the other hand, when *19-electron radicals* undergo coupling reactions, the dimerization site appears to be restricted to the ligands. Cp₂Rh couples through the polyolefin,[39,40] as does (η^5-C₈H₉)Fe(CO)₃.[41] The transient radicals (η^7-C₇H₇)M(CO)₃ (M = Cr, Mo, W) dimerize through the cycloheptatrienyl ring[42,43] and (η^6-C₆R₆)FeCp dimerizes through the arene.[44] In each case this results in lowering of the hapticity of the polyolefin and reestablishment of the 18-electron structure for the metal: It
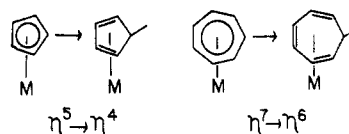
is unclear why CpCo(η^5-C₇H₉) dimerizes while Cp₂Co does not, but there may be a greater contribution of the C₇H₉ ligand to the half-filled orbital of 1⁰, resulting in higher spin density on the cycloheptadienyl ligand.

The greater tendency of the non-Cp η^5-ligand to dimerize is also consistent with the observations of Ernst et al.,[15] who tried to prepare the acyclic analogue of Cp₂Co, bis-(2,4-dimethylpentadienyl)cobalt but instead isolated the dimer 5 in which coupling through one dimethylpentadienyl unit had occurred.

Although some attempts have been made to measure the equilibrium constants for dimerization of the above radicals,[27,29] the present work appears to be the first mea-

(26) El Murr, N.; *J. Chem. Soc., Chem. Commun.* **1981**, 251.

(27) Murdoch, H. D.; Lucken, E. A. C. *Helv. Chim. Acta* **1964**, *47*, 1517.

(28) Gubin, S. P.; Denisovich, L. I. *J. Organomet. Chem.* **1968**, *15*, 471.

(29) Madach, T.; Vahrenkamp, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1301.

(30) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 1258.

(31) Fischer, E. O.; Hafner, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1955**, *10B*, 140.

(32) Ittel, S. D.; Krusic, P. J. Meakin, P. *J. Am. Chem. Soc.* **1978**, *100*, 3264.

(33) Harlow, R. L.; McKinney, R. J.; Ittel, S. D. *J. Am. Chem. Soc.* **1979**, *101*, 7496.

(34) Shiu, K.-B.; Curtis, M. D.; Huffman, J. C. *Organometallics* **1983**, *2*, 936.

(35) Hamon, J.-R.; Astruc, D.; Roman, E.; Batail, P.; Mayerle, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 2431.

(36) Connelly, N. G.; Kitchen, M. D.; Stansfield, R. F. D.; Whiting, S. M.; Woodward, P. *J. Organomet. Chem.* **1978**, *155*, C34.

(37) Waterman, P. S.; Giering, W. P. *J. Organomet. Chem.* **1978**, *155*, C47.

(38) Triechel, P. M.; Rosenheim, L. D. *J. Am. Chem. Soc.* **1981**, *103*, 691.

(39) Fischer, E. O.; Wawersik, H. *J. Organomet. Chem.* **1966**, *5*, 559.

(40) El Murr, N.; Sheats, J. E.; Geiger, W. E.; Holloway, J. D. L. *Inorg. Chem.* **1979**, *18*, 1443.

(41) McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1963**, 2162.

(42) Zahedi, F.; Ziegler, M. L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 918.

(43) Olgemöller, B.; Beck, W. *Chem. Ber.* **1981**, *114*, 867.

(44) Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 758.
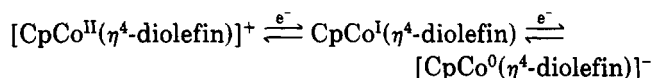
(45) Grzeszczuk, M.; Smith, D. E.; Geiger, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 1772.

surement of the rate of a ligand-based coupling reaction of a metal π-radical.

Oxidation and Reduction of CpCo(η^4-diolefins) (2 and 3). Although less intensively studied than the reduction of 1^+, the results on the η^4-diolefins generally are consistent with earlier observations about the redox pathways of CpCo(η^4-diolefin) compounds:

1. Cation radicals of the type [CpCo(η^4-diolefin)]$^+$ are stable enough in dry CH_2Cl_2 to be observed by cyclic voltammetry and by ESR spectroscopy. Examples now include η^4-diolefin = cyclobutadienes[25] and the cyclodienes C_5H_6,[25] C_6H_8,[25] C_7H_{10} (present work), and C_8H_{12}.[8,25] Exceptions seem to involve η^4-diolefins that retain unsaturation because of unattached double bonds, such as cyclooctatetraene[8] and cycloheptatriene (present work). It is postulated that rapid rearrangement pathways exist for the latter π-ligands leading, at least initially, to isomerized metal π-complexes similar to those observed by Connelly et al. for Fe(CO)$_3$ analogues.[36]

2. Anion radicals of the type [CpCo(η^4-diolefin)]$^-$ are also stable enough to be observed by cyclic voltammetry and, in some cases,[23] by ESR. Thus, an electron-transfer series involving d^7, d^8, and d^9 cobalt complexes exists:

$$[\text{CpCo}^{II}(\eta^4\text{-diolefin})]^+ \overset{e^-}{\rightleftharpoons} \text{CpCo}^I(\eta^4\text{-diolefin}) \overset{e^-}{\rightleftharpoons}$$
$$[\text{CpCo}^0(\eta^4\text{-diolefin})]^-$$

E° values for the d$^7 \rightleftharpoons$ d^8 couple (Co^{II}/Co^I) show a smaller dependence on the nature of the diolefin (a range of +0.08 to +0.35 V is found) compared to the d$^8 \rightleftharpoons$ d^9 process (Co^I/Co^0) (range –1.8 to –2.6 V). Detailed ESR studies of

the two series of ion radicals would be of interest to address the origin of this difference.

3. The favored reaction pathway for formally Co^0 π-anion radicals appears to be protonation of the polyolefin, followed by further reduction and protonation. The product is a more highly reduced polyolefin and implies an overall ECEC process:[23]

$$\text{CpCo}(\eta^4\text{-diolefin}) + 2e^- + 2H^+ \rightleftharpoons \text{CpCo}(\eta^4\text{-H}_2\text{diolefin})$$
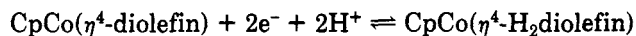
This is only possible, of course, when the diolefin has unattached carbon–carbon double bonds (e.g., C_8H_8, C_8H_{10}, or C_7H_8) and is also found for Fe(CO)$_3$ analogues.[24] If all double bonds of the η^4-diolefin are already employed in coordination to the metal, as in C_8H_{12} or C_7H_{10}, E° for the Co^I/Co^0 couple is very negative, and the ultimate fate of the anion radical is still unknown. The Co^0 anions usually undergo simple regeneration to the beginning Co^I complex by reaction with adventitious oxygen or other weak oxidizing agents.

Supplementary Material Available: Complete listings of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, hydrogen atom coordinates, and structure factor tables (22 pages). Ordering information is given on any current masthead page.

Structures and the Reversible Interconversion of Closo Rhodium–Triiron M₄(μ₄-E) Clusters. Oxidation Reduction and ESR Spectra of Organometallic Anion and Cation Radicals

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The bicapped rhodium–triiron cluster $(C_5Me_5)RhFe_3(CO)_8(PPh)_2$ (I) is synthesized from the dianion of the triiron cluster $Fe_3(CO)_9(PPh)_2^{2-}$ and the dimeric rhodium complex $[(C_5Me_5)RhCl_2]_2$. The unsaturated cluster I reversibly binds CO to form the saturated cluster II. The interconversion I ⇌ II occurs with minimal alteration of the closo six-vertex framework which is characteristic of the bicapped tetranuclear clusters of the general formulation $M_4(\mu_4\text{-E})_2$, where E is a phosphinidene bridge. The unsaturated cluster undergoes a pair of one-electron reversible reductions to afford successively the anion I⁻· and the dianion I²⁻·. Similarly the saturated cluster II undergoes a pair of one-electron reversible oxidations to afford successively the cation II⁺· and the dication II²⁺. These facile redox changes in the unsaturated and saturated clusters together with the ESR spectra of the ion radicals I⁻· and II⁺· confirm the theoretical predictions of Halet, Hoffmann, and Saillard for the bonding in closo six-vertex clusters. The rapid dissociative loss of CO in the anion radical of the saturated cluster (II⁻· → I⁻· + CO) is also considered. The unsaturated cluster I ($RhFe_3P_2O_8C_{30}H_{25}$) crystallized in the monoclinic space group $P2_1/c$ with lattice constants $a = 16.367$ (3) Å, $b = 10.684$ (3) Å, $c = 19.648$ (5) Å, $\beta = 110.37$ (1)°, and $Z = 4$, and the saturated cluster II ($RhFe_3P_2O_9C_{31}H_{25}$) crystallized in the monoclinic space group $P2_1$ with lattice constants $a = 9.260$ (1) Å, $b = 18.307$ (3) Å, $c = 19.562$ (3) Å, $\beta = 90.51$ (1)°, and $Z = 4$.

Introduction

Active interest in transition-metal clusters continues in their syntheses, chemical reactions, catalytic properties, and novel structures.[1] Among these polynuclear systems,

the capped organometallic clusters consisting of a planar array of four transition-metal atoms has attracted theoretical analysis. Thus following the discovery of the bicapped tetracobalt cluster $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$ by Ryan and Dahl,[2] there has been developed various procedures for the

(1) Johnson, B. F. G., Ed. *Transition Metal Clusters*; Wiley: New York, 1980. Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169. Sappa, E.; Tiripicchio, A.; Braunstein, P. *Coord. Chem. Rev.* **1985**, *65*, 219.

(2) Ryan, R. C.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6904.