to the narrow component is present as spatially isolated monohydrides and molecular H_2. The remaining hydrogen, which consists of between 4 and 16 atom % H in device quality films, is attributed to clusters of monohydrides.

We have used multiple-quantum NMR to determine the size and extent of clustering in a-Si:H thin films.[3] Shown in Figure 14 are plots of the number of correlated spins vs. time for a number of samples containing different concentrations of hydrogen. In Figure 14a, two extremes are presented: a 50 atom % sample for which the effective system size grows rapidly and continuously, and an 8 atom % sample for which $N(\tau)$ remains essentially constant over time. The trends in these plots indicate that the polymeric sample consists of a continuous network of atoms, whereas the 8 atom % sample is composed of clusters of approximately six atoms. A plot of the number of correlated spins for an a-Si:H sample containing 16 atom % H is shown in Figure 14b: values of $N(\tau)$ increase over time, whereas $N_c(\tau)$ levels off at 6. Similarly to the 8 atom % sample, the size of the clusters in the 16 atom % sample is approximately six, but now they exist in higher concentrations, as evidenced by the more rapid growth of $N(\tau)$. The values in these plots are very similar to those of 1,8-DMN in perdeuterated DMN shown in Figure 8.

Summary

Multiple-quantum NMR, a technique which induces spins to act collectively through their dipolar couplings, is used to determine the spatial distribution of atoms in materials lacking long-range order; in particular, the size and extent of clustering is probed. Based on the proximity of spins to one another, correlations between them will develop more or less rapidly. A time-resolved multiple-quantum experiment measures both the number of correlated spins and the rate at which these develop. The key feature in the time-dependent experiments is that in clustered materials, where groups are physically isolated from one another, the number of absorbed quanta and correlated spins is essentially bounded, on the experimental time scale, by the size of the cluster. In a uniform distribution, however, the interacting network of spins increases monotonically with time. These events are displayed in the multiple-quantum spectra by changes in the overall intensity distribution across the multiple-quantum orders. The intensity envelope is quantified by two time-dependent parameters, the effective system size $N(\tau)$ and the effective cluster size $N_c(\tau)$. Thus by studying the trends in $N(\tau)$ and $N_c(\tau)$, i.e., whether they level off or grow with time, we can ascertain the size and extent of clustering in solids.

Model systems containing different hydrogen environments were investigated by this technique: a liquid crystal in which intercluster couplings were zero; solid solutions consisting of protonated samples mixed with perdeuterated counterparts in which intercluster distances were varied by manipulating the level of dilution; neat protonated polycrystalline solids where inter- and intracluster dipolar couplings were roughly comparable; and hydrogenated amorphous silicon thin films containing different concentrations of hydrogen atoms. The atomic distributions in these materials ranged from truly isolated clusters to uniformly distributed arrangements, with emphasis on the intermediate cases where concentrations of clusters were addressed. These techniques are presently being used to study clustering of molecules adsorbed on zeolites and trapped in silicate glasses.

Acknowledgment. We gratefully acknowledge helpful discussions and assistance from Dr. M. Munowitz, Dr. A. N. Garroway, Professor J. Reimer, and Karen Gleason throughout the course of this work. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy and by the Director's Program Development Funds of the Lawrence Berkeley Laboratory under Contract No. DE-AC03-76SF00098.

Registry No. 1,2,3,4-Tetrachloronapthalene-bis(hexachloropentadiene) adduct, 80789-64-6; *p*-hexyl-*p*′-cyanobiphenyl, 78322-94-8; 1,8-dimethylnaphthalene-d_6, 104489-28-3; 1,8-dimethylnaphthalene-d_{12}, 104489-29-4.

Interconversion of Conjugated and Nonconjugated Polyolefin–Cobalt Complexes in Two Oxidation States: An Electrochemical and NMR Study

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Abstract: The kinetics of interconversion between the conjugated (1,3) and nonconjugated (1,5) isomers of cyclooctatetraene (cot) complexes of CpCo [Cp = C_5H_5] **1** and *CpCo [*Cp = C_5Me_5] **2** have been studied. Dynamic NMR studies were employed for neutral CpCo(cot) and gave a rate of 3 s^{-1} at 370 K, extrapolated to 4×10^{-3} s^{-1} at 298 K. The permethylated complex isomerizes more slowly, $k = 3 \times 10^{-4}$ s^{-1} at 370 K. However, fast fourier transform ac polarography results show that the *monoanions* of CpCo(cot) and *CpCo(cot) isomerize at the same fast rate, 2×10^3 s^{-1} at 298 K. An explanation is offered in terms of the lifting of symmetry restrictions to the simplest molecular isomerization motion in the anion radicals. The dibenzocyclooctatetraene complex CpCo(1,5-dbcot) (**3**) reduces to a stable anion which shows no tendency to isomerize. This is explained by a likely change in electronic ground states of $[CpCo(cot)]^-$ and $[CpCo(dbcot)]^-$, a conclusion supported by ESR results.

The geometrical preferences of diolefins bonded to metals are in many cases poorly understood, in spite of a voluminous literature.[1] The problem is obvious when considering that coordination to conjugated double bonds is strongly favored in complexes of

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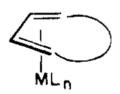
[§] University of Zürich.

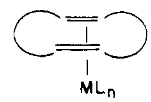
[⊥] Northwestern University. Deceased January 9, 1985.

(1) For leading references on the preparation, structures, and properties of metal–diolefin complexes, see: Rybinskaya, N. I.; Krivykh, V. V. *Russ. Chem. Revs.* **1984**, *53*, 476 as well as other papers cited in the present manuscript.

$M(CO)_3$[2,3] M = Fe, Ru, Os, and CoL_3^+, L = phosphine,[4,5] structure A, but that coordination to *non*conjugated double bonds is favored[1,2,6-8] in complexes of CpM, M = Co, Rh, Ir, Cp = η^5-C_5H_5, structure B. Elian and Hoffmann have explained the preference for isomer A in terms of the symmetries and energies of the π-donor and -acceptor orbitals of the conjugated ligand.[3] Since the CpM fragment is isolobal with $M(CO)_3$,[9] the preference of the former for nonconjugated dienes is unexplained.[8] Since understanding preferred metal-polyolefin geometries would seem to be crucial to understanding metal-polyolefin reaction routes,[10] a closer look at some aspects of this problem appears to be justified.

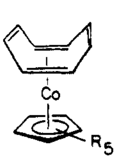


A

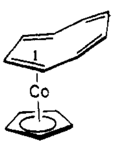


B

A set of metal complexes favorable for studying the preferred geometry of cycloocta-polyene complexes is that containing CpM, M = Co, Rh, Ir. Cyclooctadiene (cod) forms exclusively the nonconjugated, η^4-1,2,5,6-isomer with these metal fragments.[11] Hereafter, we refer to this structure as the 1,5-isomer. The 1,5-isomer C is also favored when the ligand is cyclooctatetraene (cot).[11,12] However, the conjugated η^4-1,2,3,4-isomer D is detected in the preparation of the Rh and Ir complexes[12] and exists in equilibrium with the 1,5-isomer when the metal is cobalt.[13] Henceforth, D is called the 1,3-isomer. One-electron reduction of the cobalt complexes shifts the equilibrium in favor of the 1,3-isomer.[13-16] Hence, this group of complexes seems well-suited to systematic study of the effect of electronic or steric changes on the relative stabilities of the conjugatively and nonconjugatively bound ligands.

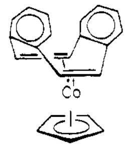


C R=H, (1,5-1)
R=Me, (1,5-2)



D

In this paper we report the kinetics of the 1,5 ⇄ 1,3 isomerization reaction, both for the neutral cobalt cot complexes and their radical anions. Electronic effects are explored by comparing the behavior of the analogous η^5-C_5H_5(Cp) and η^5-C_5Me_5 (*Cp) complexes. The results allow some insight into the mechanism of the 1,3 ⇄ 1,5 isomerization process. Furthermore, it is shown that when dibenzocyclooctatetraene (dbcot) is the η^4-polyene, the complex remains locked in the 1,5-isomeric form upon reduction. The complexes studied were CpCo(cot) (**1**), *CpCo(cot) (**2**), and CpCo(dbcot) (**3**). The related cyclononatetraene complex, CpCo(η^4-1,2,5,6-C_9H_{10}) (**4**), was also investigated.



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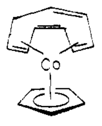

4

Experimental Section

Compounds. Literature procedures were employed to prepare **1**,[11] **2**,[17] and **4**.[18] CpCo(dbcot) (**3**) was prepared by reflux of $CpCo(CO)_2$[19] with dibenzocyclooctatetraene[20] and recrystallized from CH_2Cl_2/hexane to yield orange crystals. The identity of **3** was confirmed by ^1H NMR spectroscopy in CD_2Cl_2 [δ 4.21 (s, 4 H, olefinic H of dbcot), δ 4.87 (s, 5 H, Cp), δ 6.81 (m, 8 H, phenyl)].

Electrochemistry. ac polarography was used to obtain the rate constant for isomerization of $(1,5\text{-}\mathbf{2})^-$ to $(1,3\text{-}\mathbf{2})^-$, by using the fast Fourier transform (FFT) method previously described.[21,22] These studies utilized a homemade Ag,AgI/(0.1 M Et_4NI, DMF) reference electrode, which had a potential ca. 0.4 V positive of the aqueous saturated calomel electrode (SCE). Reported potentials are, however, referenced to the SCE. Since the FFT procedure allows for efficient resistance compensation[23,24] concentrations of 1-5 mM of **2** were used. Corrections for charging current were made by comparing the response of cells with and without electroactive species. Other voltammetric procedures (dc polarography, cyclic voltammetry, pulse polarography) utilized methods and solvent purifications described in separate papers.[14,16]

Dimethylformamide (Burdick and Jackson) was dried with activated alumina. The supporting electrolyte was 0.1 M Bu_4NPF_6, except for ac polarography studies, which utilized 0.1 M Bu_4NBF_4 in DMF. Solutions of the neutral compounds were stable enough to be handled under a blanket of nitrogen or argon. Bulk reduction to the anions required more stringent conditions. 3^- was generated by bulk coulometric reduction inside a Vacuum Atmospheres drybox. 4^- was prepared by using Na/K reducing alloy (MSA Research Corp.) under vacuum.

Magnetic Resonance. ESR data were recorded on a modified Varian E-3 spectrometer by using DPPH as a field calibrant. Two fourier transform NMR spectrometers were employed in variable temperature studies. 250-MHz data were obtained at Vermont with a Bruker 250 instrument that employed a Bruker VT 1000 temperature control. 90-MHz data were obtained at the University of New Hampshire on a Varian FX90 instrument. The line shaping analysis was accomplished by using programs loaned to us by Dr. C. H. Bushweller, on a DEC 2060 computer by using TOPS 20 graphics.

Results

1. Background. It had been previously shown[14,16] that (a) the (1,5 ⇄ 1,3) isomerization is much faster for 1^- than for 1°, although the rate constant for the latter was too slow to be

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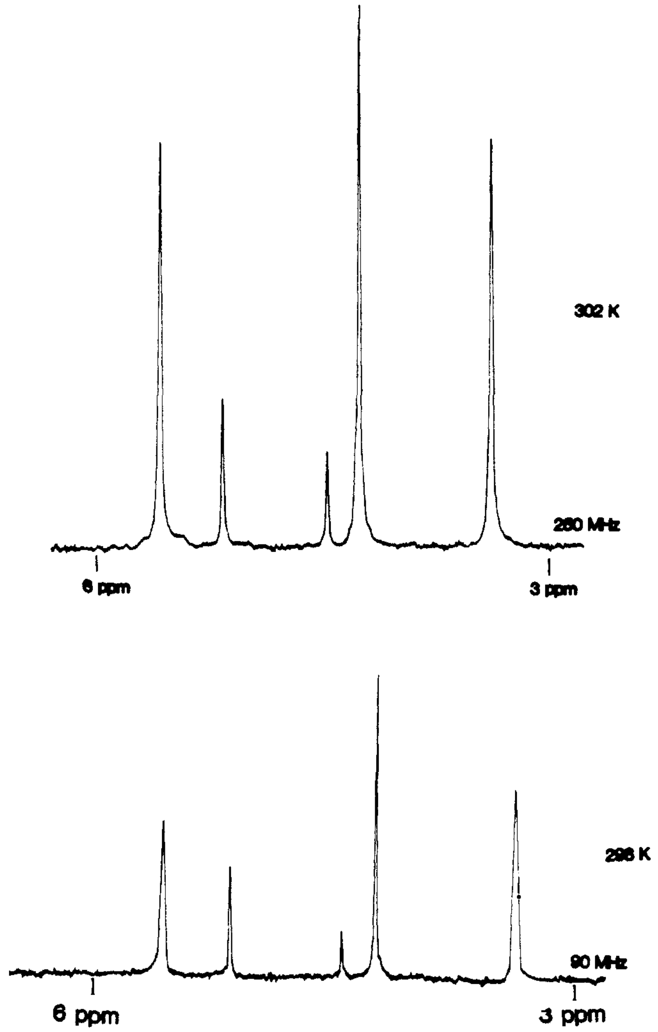

Figure 1. 250-MHz (top) and 90-MHz (bottom) ^{1}H spectra of CpCo(cot) in *o*-xylene-d_{10} at ambient temperature. The three largest peaks are assigned to the 1,5-isomer and the two smallest peaks to the 1,3-isomer.

measured by moderate sweep rate (v = <200 V/s) cyclic voltammetry and that (b) the same situation appeared to be true for **2** and **2**$^-$, although measurements on that system were much more briefly reported.

2. 1,5 ⇄ 1,3 Isomerization Rates for Neutral 1 and 2. NMR Studies. That the ^{1}H NMR spectrum of the 1,5-cot isomer **1** is temperature dependent was recognized two decades ago.[25] At elevated temperatures the two COT resonances undergo line broadening, almost disappearing at ca. 380 K (60-MHz spectra).[25] A transition state involving a 1,3-cot structure was considered, along with other possibilities, including a solvent-coordinated intermediate.[25,26] Assignment of the two peaks originating from the 1,3-isomer is key to analysis of the spectra. Figure 1 displays the room temperature spectrum. The 1,5-isomer has resonances assigned to the cyclopentadienyl protons (δ = 4.26) and cyclooctatetraene protons (δ = 3.39 and 5.59). The lowest field resonance is assigned to the protons on the carbons bonded to the metal. The two smaller resonances at δ = 4.47 and 5.17 are assigned to the Cp and cot resonances, respectively, of the 1,3-cot isomer. A singlet for the 1,3-cot resonance is consistent with the expected fluxionality of the metal-1,3-cot structure.[27] The 1,5-isomer is thermodynamically favored.

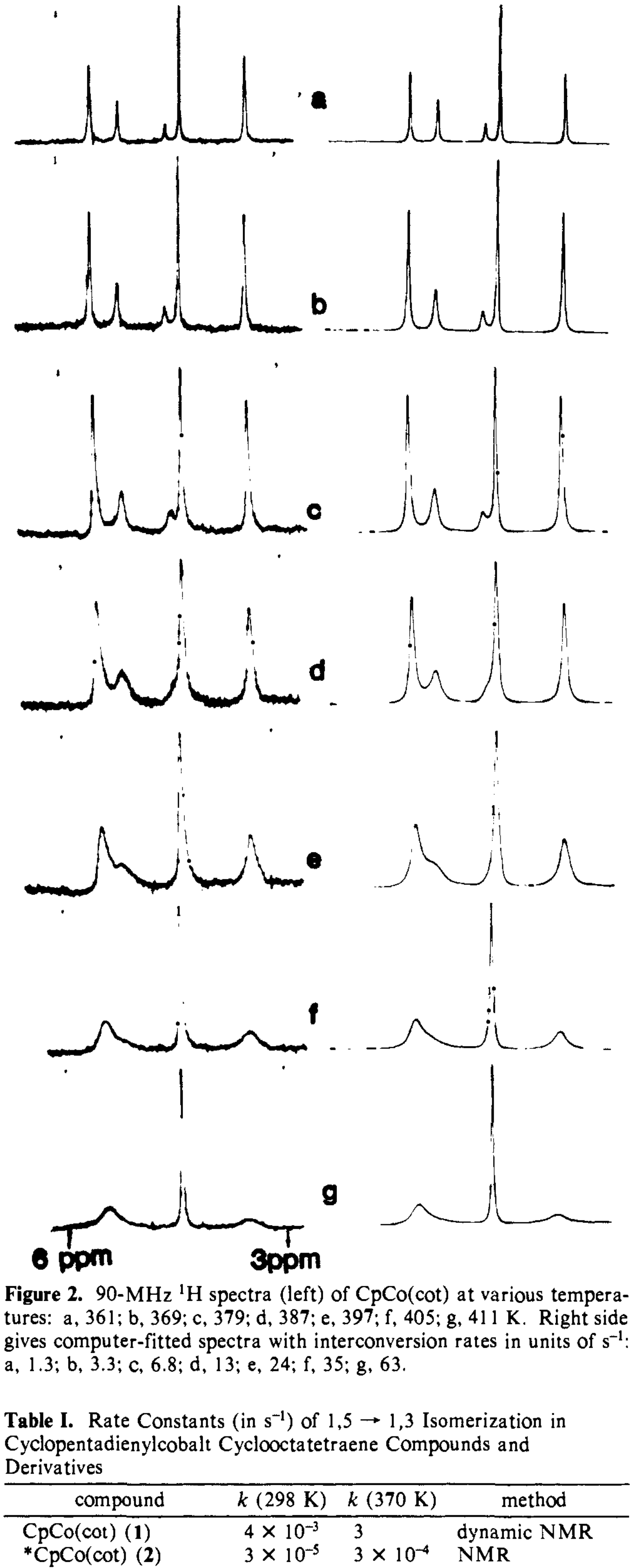

Figure 2. 90-MHz ^{1}H spectra (left) of CpCo(cot) at various temperatures: a, 361; b, 369; c, 379; d, 387; e, 397; f, 405; g, 411 K. Right side gives computer-fitted spectra with interconversion rates in units of s^{-1}: a, 1.3; b, 3.3; c, 6.8; d, 13; e, 24; f, 35; g, 63.

Table I. Rate Constants (in s^{-1}) of 1,5 → 1,3 Isomerization in Cyclopentadienylcobalt Cyclooctatetraene Compounds and Derivatives

compound	*k* (298 K)	*k* (370 K)	method
CpCo(cot) (**1**)	4×10^{-3}	3	dynamic NMR
*CpCo(cot) (**2**)	3×10^{-5}	3×10^{-4}	NMR
[CpCo(cot)]$^-$ (**1**)$^-$	2×10^3		ac polgy (ref 16)
[*CpCo(cot)]$^-$ (**2**)$^-$	2×10^3		ac polgy
CpCo(dbcot)$^{0,-}$ (**3**)$^{0,-}$	*a*	*a*	
CpCo(C_9H_{10})$^{0,-}$ (**4**)$^{0,-}$	*a*	*a*	

[a] Too slow t_ detect.

At elevated temperatures the peaks for both isomers broaden (Figure 2) as interconversion between the two forms accelerates. When a 90-MHz instrument is used, the Cp resonances undergo coalescence at ca. 390 K (420 K at 250 MHz). Although we noticed no appreciable decomposition of the sample up to ca. 420

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Table II. Potentials of Reductions of $CpCoC_8$ or $CpCoC_9$ Compounds

compound	E^0 (1,3-isomer)[a]	E^0 (1,5-isomer)[a]
CpCo(cot) (**1**)	−1.82[b]	−2.05[b,c]
*CpCo(cot) (**2**)	−2.03	−2.34
CpCo(dbcot) (**3**)		−1.96
$CpCo(C_9H_{10})$ (**4**)		−2.23

[a] Volt vs. SCE. [b] Data from ref 14. [c] Data from ref 16.

K, the temperature range was insufficient to allow observation of the cot coalescence, since the two resonances are separated by a greater difference in chemical shift than are the Cp resonances. The cot resonances are calculated[28] to undergo coalescence above 480 K when a 250-MHz instrument is used.

Simple two-site exchange (1,5- and 1,3-isomers) accounts for the observed spectral changes, as indicated in Figure 2 by the agreement between observed (90 MHz) and calculated spectra. Very similar results were obtained by using a 250-MHz resonance frequency, a rate constant of 3 s^{-1} being observed at 370 K for both sets of experiments (Table I).

Rate constants from Figure 2 were used to construct an Eyring plot (ln k/T vs. 1/T) which was linear (correlation coefficient 0.997). A free energy of activation, $\Delta G^{\ddagger}$, of 21.0 ± 0.1 kcal/mol was calculated from this data. A similar treatment of the 250-MHz data yielded $\Delta G^{\ddagger}$ = 21.3 ± 0.1 kcal/mol. The slope of the Eyring plot allows an estimate of the isomerization rate at 298 K, a value of 4 × 10^{-3} s^{-1} being obtained from this calculation (Table I). Electrochemical experiments had previously characterized isomerization of the neutral isomers as slow at room temperature.[14]

The room temperature spectrum of the permethylated cyclopentadienyl derivative **2** *CpCo(cot), was quite similar to that of its Cp analogue taking into account the replacement of the C–H Cp resonance by that of the $C-CH_3$ *Cp resonance. The 1,5-isomer is again thermodynamically favored in the neutral complex. Assignments are as follows (90-MHz data): δ = 1.72 (5 CH_3, 1,3-isomer), 4.88 (8 H, fluxional 1,3-cot), δ = 1.45 (5 CH_3, 1,5-isomer), 2.59 (4 H, free olefin of 1,5-isomer), 5.59 (4 H, metal-bonded olefin of 1,5-isomer).

No line broadening was observed when solutions of *CpCo(cot) were heated as high as 411 K, showing that the 1,5 ⇄ 1,3 interconversion in **2** is much slower than in **1**. Equilibrium shifts *were* observed, as evidenced by the greater relative intensities of 1,3-isomer peaks at elevated temperatures (Figure 3, compare scans at 288 and 408 K).[29] Since line-broadening was insufficient to measure the isomerization rate, we turned to a different kinetic probe. First, the sample was heated (external to the NMR probe) at 500 K for 2 h to increase the amount of the 1,3-isomer. The sample was then transferred to the NMR probe thermostated at 298 or 370 K, and the decrease of the *Cp resonance of the 1,3-isomer was monitored against time. A plot was made of ln $[I_0 - I_E/(I - I_E)]$ vs. time, where I_0 is the initial concentration (peak height) of the 1,3-isomer, I_E is its equilibrium concentration (peak height), and I is the concentration (peak height) at any time. The slope gives the sum of the forward and backward rate constants for the equilibration. When combined with the equilibrium constant,[29] the rate of the 1,5 → 1,3 isomerization can be calculated. Values of ca. × 10^{-4} s^{-1} (370 K) and 3 × 10^{-5} s^{-1} (298 K were obtained for **2**. Although these values are considerably less accurate than those obtained from the line-broadening experiments on CpCo(cot), they allow a semiquantitative comparison of the isomerization rates of neutral **1** and **2** (Table I). Isomerization of the *Cp derivative is over 2 orders of magnitude slower at room temperature and over 4 orders of magnitude slower at 370 K. A $\Delta G^{\ddagger}$ of 29.4 ± 1.0 kcal/mol is calculated for isomerization of *CpCo(cot), about 8 kcal higher than the Cp derivative.

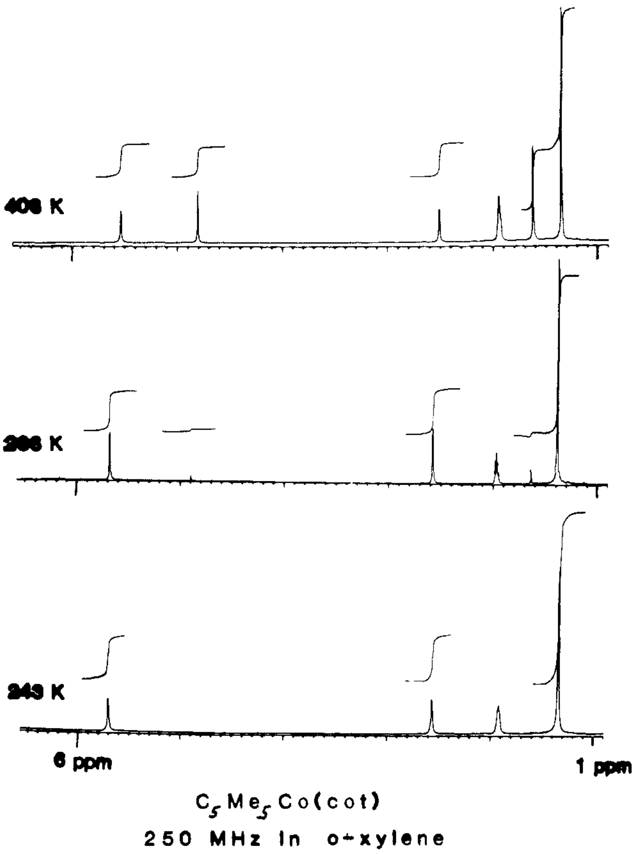

Figure 3. 250-MHz ^1H spectra of *CpCo(cot) in *o*-xylene-d_{10} at three temperatures. The three integral peaks in the 243 K spectrum are assigned to the 1,5-isomer. At higher temperatures two additional bands appear due to the 1,3-isomer.

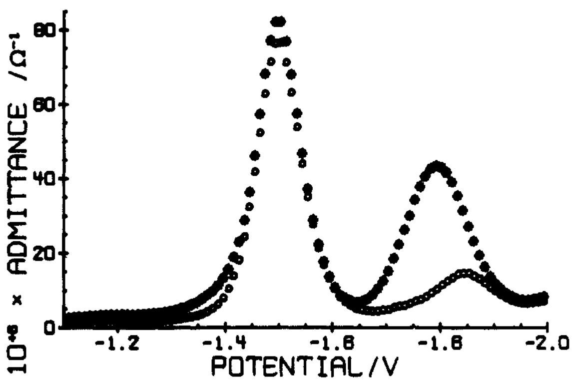

Figure 4. ac polarogram of 5 × 10^{-3} M *CpCo(cot) in DMF 0.1 M Bu_4NBF_4, T = 298 K, frequency = 48.8 Hz, droptime = 1 s, 15 domain averages, * = inphase component, o = quadratic component, potentials vs. Ag/AgI.

When freshly prepared samples of *CpCo(cot) were monitored at low temperatures, only the peaks due to the 1,5-isomer were observed. Figure 3 demonstrates this for T = 243 K, but similar observations were also made at short times by using T = 288 K. These experiments suggest that crystals of *CpCo(cot) are conformationally pure, containing only the 1,5-isomer.

3. 1,5 ⇄ 1,3 Isomerization Rate for the Radical Anion 2^-. ac Polarography. CV scans of *CpCo(cot) showed two reductions of **2** pertinent to this study:[14] a reversible wave with E^0 = −2.03 V (in CH_3CN) and a larger irreversible wave having E_p = −2.40 V. The former was assigned to the 1,3-isomer, the latter to the 1,5-isomer. Scans in excess of 100 V/s failed to reveal any chemical reversibility for the second wave, thereby excluding an estimate of the lifetime of $(1,5\text{-}2)^-$. Fast Fourier transform faradaic admittance measurements (FFT-FAM) were undertaken to allow examination of the 1,5 ⇄ 1,3 isomerization of 2^- on a

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[28] This estimate was obtained by computer-generated spectra at elevated temperatures.

[29] The equilibrium constant of **2**, $K_{eq} = [1,5]/[1,3]$, was ca. 4.6 at 298 K and 2.1 at 370 K.

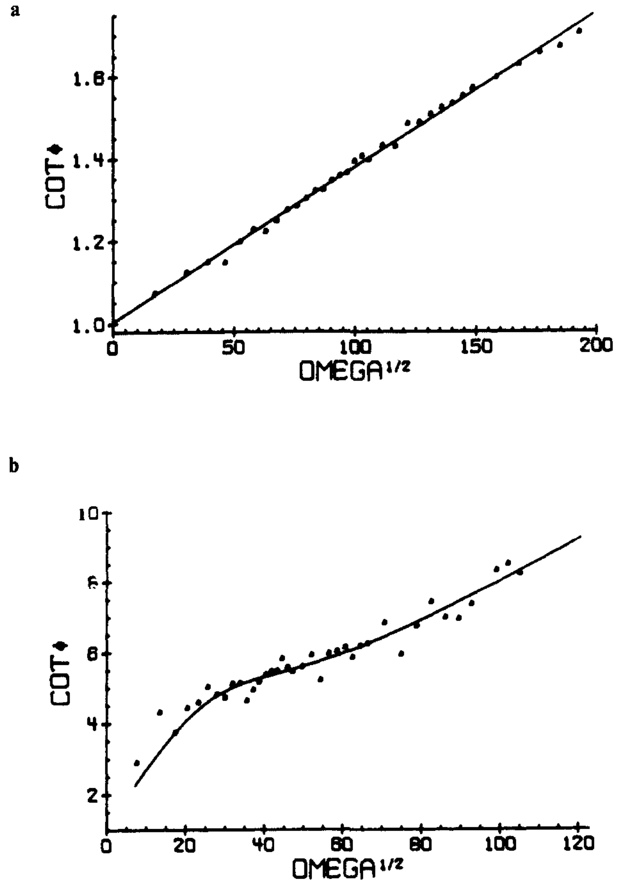

Figure 5. (a) Plot of cot ϕ $\omega^{1/2}$ for the isomer *CpCo(1,3-cot), drop time 1 s, T = 298 K, DMF/0.1 M Bu_4NBF_4, formal concentration of **2** = 5 × 10^{-3} M. (b) Comparison of theory and experiment for cot ϕ vs. $\omega^{1/2}$ plots for the isomer *CpCo(1,5-cot), line = theoretical, points = experimental. Parameters used in calculation; EC mechanism, n = 1, T = 298 K, D_0 = 3.0 × 10^{-6} cm^2 s^{-1}, k_s = 0.019 cm s^{-1}, α = 0.040, k_{isom} = 2 × 10^3 s^{-1}.

shorter time scale than available by cyclic voltammetry.

ac polarograms of *CpCo(cot) are as expected (Figure 4), with two waves separated by ca. 0.3 V. The small peak height of the second wave is consistent with its irreversibility.[30] Accurate measurements of this component required care in reducing charging currents and electronic noise, especially at higher frequencies.

The ac response of the 1,3-isomer (first wave) was analyzed according to a simple quasireversible heterogeneous charge-transfer process (E_{QR} mechanism).[31,32] The heterogeneous charge-transfer rate, k_s,[33] was calculated from the response of the system over a wide frequency range[34] (Figure 5a). A value of 0.32 (±0.005) cm/s was obtained, close to that reported earlier[16] for the Cp analogue, **1**. These results confirm that the 1,3-isomer undergoes rapid reduction to a stable anion.

Table III. Charge-Transfer Parameters for the (η-C_5R_5)*CpCo(cot)$^{0/-}$ Couple[a]

redox couple	E^0	α	k_s (app)[b]	k_s (corr)[c]
CpCo(1,3-cot)$^{0/-}$[d]	−1.82	0.61	0.28	2.9
*CpCo(1,3-cot)$^{0/-}$	−2.03	0.50	0.32	2.4
CpCo(1,5-cot)$^{0/-}$[d]	−2.05	0.4	0.06	0.3
*CpCo(1,5-cot)$^{0/-}$	−2.34	0.40	0.019	0.11

[a] From ac polarography data at 298 K in DMF/0.1 M Bu_4NBF_4. [b] Apparent standard heterogeneous rate constant. [c] Rate constant corrected for double-layer effects. [d] From ref 16.

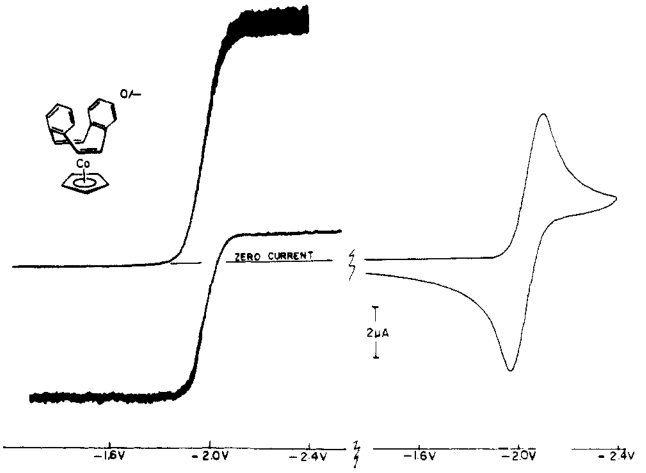

Figure 6. Voltammetry of CpCo(dbcot). Left side: voltammograms at the rotating platinum electrode (RPE) before (top) and after (bottom) electrolysis at −2.4 V. Conditions: THF/0.1 M Bu_4NPF_6, T = 263 K, electrolysis at Pt basket electrode, RPE scan rate 10 mV s^{-1}. Right side: CV scan after electrolysis, v = 200 mV s^{-1}, Pt bead electrode.

Analysis of the response of the 1,5-isomer of **2** is more involved. Plots of cot ϕ vs. $\omega^{1/2}$ (ϕ is the phase angle between the output current and the in phase peak potential; ω is 2π times the ac frequency) are influenced both by quasireversible charge-transfer kinetics and by the isomerization reaction (E_{QR}C mechanism)

$$(1,5\text{-}\mathbf{2}) + e^- \overset{k_s}{\rightleftharpoons} (1,5\text{-}\mathbf{2})^- \quad E_{QR}$$

$$(1,5\text{-}\mathbf{2})^- \xrightarrow{k_{isom}} (1,3\text{-}\mathbf{2})^- \quad C$$

In order to obtain a value for k_{isom}, k_s first had to be evaluated. This was done in two ways. It can be shown[16] that at potentials ca. 60 mV or more negative of the E^0 value, the effects of the chemical reaction on the ac wave are minimal. Under these conditions, eq 1 holds

$$\frac{\ln \partial \cot \phi}{\partial \omega^{1/2}} = \frac{\ln(2D)^{1/2}}{k_s} + \frac{\alpha n F \left(E_{dc} - E_{1/2}^{r}\right)}{RT} \qquad (1)$$

$$E_{dc} << E_{1/2}^{r}$$

In this equation, D is the diffusion coefficient, α is the charge-transfer symmetry parameter, $E_{1/2}^{r}$ is the reversible half-wave potential, and the other parameters have their usual significance. A plot of the parameter on the left side of eq 1 vs. ($E_{dc} - E_{1/2}^{r}$) allowed determination of k_s from the intercept and α from the slope.

k_s may also be obtained from the slope of cot ϕ vs. $\omega^{1/2}$ plots at frequencies high enough not to be influenced by the chemical reaction.[32] The reduction wave of [1,5-*CpCo(cot)] behaved like a simple E_{QR} system at ac frequencies above ca. 1 kHz. The k_s values obtained by these two different procedures are in complete agreement, k_s = 0.019 ± 0.006 cm/s (Table III). Once k_s was in hand, the isomerization rate constant, k_{isom}, could be obtained by fitting the cot ϕ vs. $\omega^{1/2}$ plots over the entire range of ac frequencies. The best fit (Figure 5b) was obtained by using k_{isom} = 2 × 10^3 s^{-1} (Table I). Remarkably, this is the *same* value obtained[16] for the isomerization rate of the Cp analogue [1,5-

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(30) McCord, T. G.; Hung, H. C.; Smith, D. E. *J. Electroanal. Chem.* **1969**, *21*, 5.

(31) In this context, "quasireversible" does not refer to a particular range of heterogeneous rate constants. Rather, it refers to an electron transfer process which displays non-Nerstian behavior under the experimental conditions employed. Reference 32, pp 26–42, discusses the ac polarographic response of such systems.

(32) Smith, D. E. In *Electroanalytical* Chemistry; Bard, A. J.; Ed.; Marcel Dekker: New York, 1966; Vol. 1.

(33) The apparent standard heterogeneous electron-transfer rate is calculated from this procedure. This is the k_s value uncorrected for double-layer effects. The corrected value, obtained by using the Frumkin procedure [Frumkin, A. N., *Z. Phys. Chem.* **1933**, *164*, 121], is also reported in Table III.

(34) A linear response of cot ϕ vs. $\omega^{1/2}$ was found for ac frequencies over the range 35–6000 Hz.

CpCo(cot)]$^-$ → [1,3-CpCo(cot)]$^-$.

4. Reduction of Complexes Having Interrupted Polyolefin Conjugation. Compounds **3** and **4** were investigated to see if CpCo(polyolefin) anions could be locked into the 1,5-coordination mode by changing the electronic requirements of the polyolefin. **3** is particularly appropriate for this purpose. Isomerization from 1,5- to 1,3-coordination would require the metal to bond to one double bond in the arene substituent and result in loss of resonance stabilization energy. Consequently, only the 1,5-isomer is detected in solutions of CpCo(dbcot). Furthermore, reduction by one electron gives only [1,5-CpCo(dbcot)]$^-$.

Reduction of CpCo(dbcot) (**3**) gave one diffusion-controlled wave at Hg or Pt electrodes in DMF or THF. $E_{1/2}$ was −1.96 V in DMF (dc polarography). The reverse anodic current in CV experiments was exactly as expected for a stable reduction product, down to scan rates 0.05 V/s (Figure 6). Peak separations were 65–80 mV on Hg (0.02 V/s $< v <$ 0.2 V/s) but were larger on Pt (80–120 mV) over the same scan rate range. The charge-transfer process is apparently quasireversible. The CV cathodic peak current was confirmed as being appropriate for a one-electron process by comparison of its value with that of the one-electron reduction[35] of the structurally related complex [(η^5-C_5Ph_5)Pd(dbcot)]$^+$.

Electrodic details aside, it is the fate of the 1,5-CpCo(dbcot) anion which is of interest. When bulk electrolyzed in THF at 263 K (−2.3 V, Pt electrode), the yellow solution turned the deep brown of the monoanion. Voltammograms with a rotating Pt electrode monitored the solution for 3 h after electrolysis. During this time the anodic wave of **3**$^-$ gradually became a mixed anodic/cathodic wave as neutral **3** was regenerated, most likely due to adventitious oxidants. No new waves of more than 5% of the original wave height were observed. At potentials positive of the (1,5-**3**)$^{0/-}$ wave, where a 1,3-isomer wave would be expected to appear, there was none. Hence, the dibenzocot derivative **3** exists exclusively as the 1,5-isomer in both its neutral and anionic forms.

ESR of [CpCo(dbcot)]$^-$ was recorded on frozen solutions of the anion generated after electrolysis in THF. Identical spectra were observed after Na/K reduction of **3** in THF. A rhombic spectrum typical[36,37] of a Co^0 polyolefin was observed. The cobalt hyperfine splitting for the highest g value (low field) was 170 G, typical of other predominantly metal-based radicals such as [CpCo(1,5-cyclooctadiene)]$^-$.[15]

The cyclononatetraene complex CpCo(η^4-C_9H_{10}) (**4**) also exists as the 1,5-isomer and shows only one reduction wave. Although the evidence is not unequivocal as in **3**$^-$, indications are very strong that **4**$^-$ retains the 1,5-isomeric form.

CV of **4** in THF, DMF, or CH_3CN shows a diffusion-controlled reduction wave at E^0 = −2.23 V. The ratio of the reverse to forward current is 1.0 down to scan rates of 0.07 V/s, indicating considerable stability of the monoanion. The charge-transfer kinetics are quasireversible, with ΔE_p values of 90–120 mV (Pt electrode, DMF) when v is increased from 0.07 to 0.40 V/s. dc polarography gives a diffusion current constant (3.33 μA mM^{-1} $mg^{-2/3}$ $s^{1/2}$) in CH_3CN consistent with a one-electron process, but the slope of the plot of E_{app} vs. log [$(i_d - i)/i$], 77 mV, is greater than the 59 mV predicted for a nernstian process. Again, quasireversible electrode kinetics are indicated.

Bulk reduction of **4** at 238 K in DMF changed the solution color from the yellow of neutral **4** to the green of **4**$^-$. ESR samples taken at this point gave frozen spectra with the characteristic Co^0 appearance. At 270 K or higher the green color fades to a murky brown, the ESR signals are no longer present, and a product with an irreversible reduction wave at −2.49 V appears. Although this final product is unidentified, the fact that its E^0 is negative of **4** makes it very unlikely to be the 1,3-isomer.[14,15] CpCo(1,5-C_9H_{10}) therefore appears to exhibit strong preference for the nonconjugated isomer in both its neutral (Co^1) and anionic (Co°) forms.

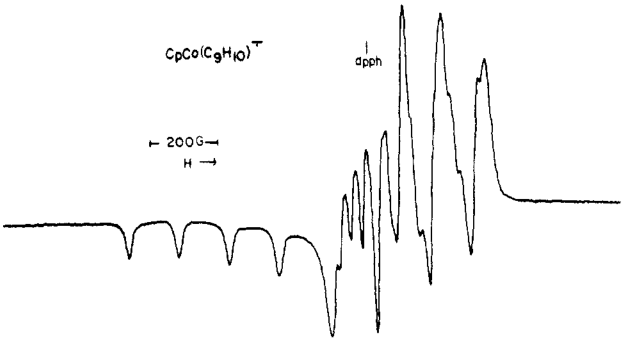

Figure 7. Frozen solution X-band ESR spectrum of CpCo (C_9C_{10})$^-$ produced by reduction with Na/K alloy. Conditions: THF, T = 153 K, modulation amplitude = 7 G. The resonance field of dpph (g = 2.0036) is indicated.

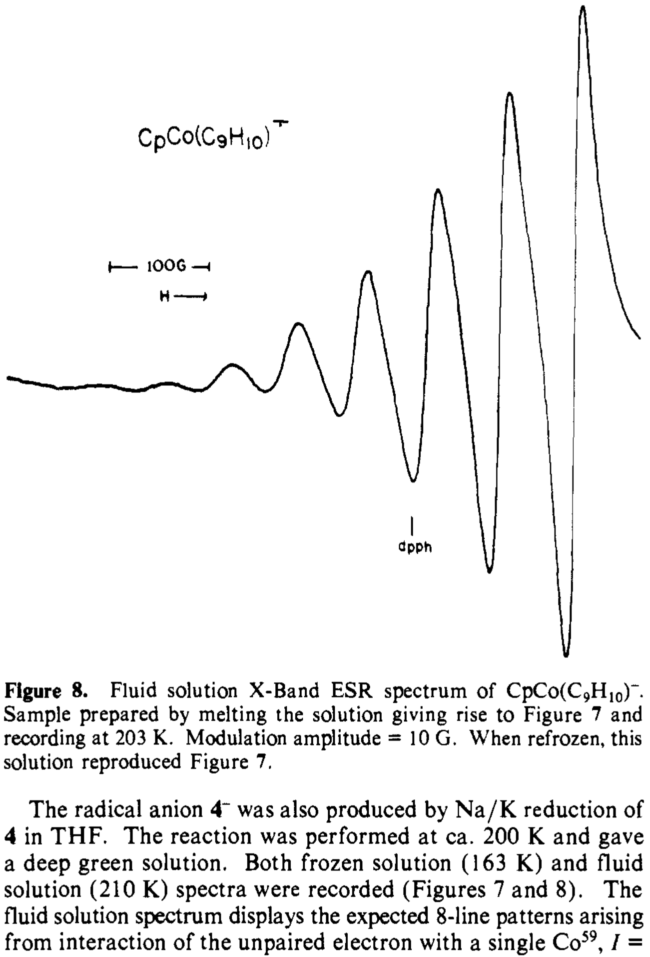

Figure 8. Fluid solution X-Band ESR spectrum of CpCo(C_9H_{10})$^-$. Sample prepared by melting the solution giving rise to Figure 7 and recording at 203 K. Modulation amplitude = 10 G. When refrozen, this solution reproduced Figure 7.

The radical anion **4**$^-$ was also produced by Na/K reduction of **4** in THF. The reaction was performed at ca. 200 K and gave a deep green solution. Both frozen solution (163 K) and fluid solution (210 K) spectra were recorded (Figures 7 and 8). The fluid solution spectrum displays the expected 8-line patterns arising from interaction of the unpaired electron with a single Co^{59}, I = $^7/_2$ (a_{Co} = 73 G). An interesting line width variation occurs, with lower field lines being selectively broadened. This apparently arises from incomplete averaging of the g tensor.[38]

Discussion

The most noteworthy kinetic effects may be summarized as follows: (1) The nonconjugated → conjugated diolefin isomerization is many orders of magnitude faster in the 19-electron Co° anions than in the 18-electron Co^1 neutrals. The rate increase is $>10^5$ for the Cp complex **1** and $>10^7$ for the *Cp complex **2**; (2) In going from the Co^1 neutral Cp complex to the neutral *Cp complex, the isomerization rate decreases by ca. 10^2 at 298 K; (3) However, the isomerization rate of the 19-electron Co° anions *does not change* in going from Cp to *Cp. The reason why permethylation of the C_5 ring has a pronounced effect on the rate of the Co^1 isomerization but not on the Co° isomerization may

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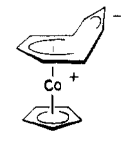
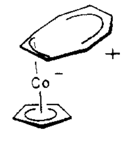
be explicable in terms of different mechanisms in the two metal oxidation states.

Albright has considered mechanistic possibilities for interconversion of the 1,5- and 1,3-isomers.[15] Two of the transition states considered for the neutral complexes have the charge-separated structures E and F, in which the C_8 ligand bonds in a η^5- or η^3-fashion, respectively. Permethylation of the C_5 ring would have the effect of destabilizing structure F due to increased electron density on the metal. The observed rate decrease in the neutral *Cp complex is therefore consistent with transition-state structure F but not E. However, there are other possible transition states[15] for which the methyl substituent effect is more difficult to predict.

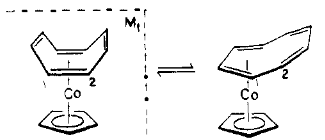


E



F

A more definitive conclusion can be made about the isomerization mechanism for the Co^0 anions. Albright showed that the simplest molecular motion leading to interconversion of the two isomers involves slippage along the mirror plane M_1 bisecting the cot in the plane of the paper. However, this motion requires correlation of the symmetric (b_1) HOMO of G with the symmetric ($4a'$) LUMO of H. Hence, it is symmetry forbidden and would have a high activation barrier.



G H

In a radical ion this symmetry restriction is expected to be lifted[39] and the pathway M_1 becomes allowed. By comparing the isomerization rates of the neutral and anionic complexes, it can be concluded that the energy barrier for the G $\rightleftarrows$ H interconversion along M_1 is lowered by at least 8 kcal/mol in the anions. Intuitively, we expect the activation barrier to slippage along M_1 to be relatively insensitive to a rather subtle electronic effect like substitution of CH_3 for H in the Cp ring. The identical isomerization rate of $\mathbf{1}^-$ and $\mathbf{2}^-$ is therefore consistent with the mechanism G $\rightleftarrows$ H in the radical anions.

Permethylation of the Cp ring has only a minor effect on the thermodynamic balance between the two isomers in the neutral complexes, a slight shift in favor of the 1,5-isomer bring observed.[29,40] The *CpCo moiety is expected to have larger metal orbitals and provide a more covalent M–cot bond, a factor that Green et al.[8] have suggested as favoring formation of a 1,5-isomer. Certainly, the isomeric preferences in cobalt-group polyolefins might be better understood if more crystallographic information were available. This point was recently made in an excellent discussion of polyolefin bonding preferences of palladium complexes.[41]

Let us turn now to consideration of the dibenzocyclooctatetraene complex **3**. The free ligand, *sym*-dbcot, has a reduction potential over 300 mV *negative* of free cot.[42,43] The electron affinity of dbcot is apparently lower than that of cot. In spite of this, the cobalt complex CpCo(dbcot) has a reduction potential ca. 90 mV *positive* of (the 1,5-isomer of) CpCo(cot). This effect appears to arise from inversion of the ground electronic states for $[CpCo(1,5\text{-cot})]^-$ and $[CpCo(dbcot)]^-$.

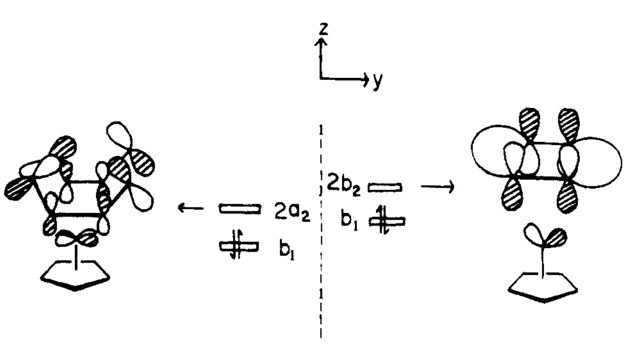
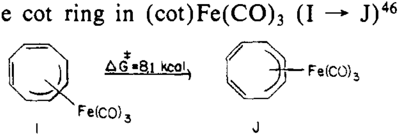


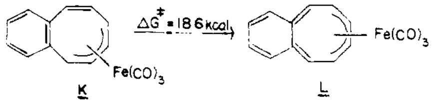
Figure 9. Representations of the LUMO of CpCo(1,5-cot) (left) and CpCo(dbcot) (right). Based on EHMO calculations of Albright on **1** and $CpCo(C_2H_4)_2$, respectively, ref 15.

Consider Figure 9, in which the HOMO and two lowest lying unfilled orbitals of **1** are displayed.[16] The semioccupied orbital (SOMO) of $\mathbf{1}^-$ is predicted to be of $2a_2$ type (in C_{2v} idealized symmetry). This orbital has some cobalt d_{xy} character, but it is mostly ligand-based, arising from a combination of π-orbitals on cot. If the C_8 ligand is nondelocalized, as is cod or dbcot, the $2a_2$ orbital drops out of the picture, and the SOMO of $[CpCo(cod)]^-$ or $[CpCo(dbcot)]^-$ is predicted to be $2b_2$ (Figure 9, right side). The metal contribution, Co $3d_{yz}$ in this case, is expected to be substantially larger than for $[CpCo(cot)]^-$. The ESR data are completely consistent with this scenario and establish the $3d_{yz}$ ground state for $\mathbf{3}^-$. Thus, rather than viewing **3** as a substituted cyclooctatetraene complex, it should be viewed as a substituted cyclooctadiene complex, since the alternate double bonds are tied up by the phenyl rings. Thus, it is more appropriate to compare the E^0 value of **3** with that of CpCo(1,5-cod). Then, a shift to more positive potentials (by 440 mV) not surprising, since free dbcot has a reduction potential at least 800 mV positive of free cod.[45]

By setting a lower limit on the rate of 1,5 → 1,3 isomerization of **3** and comparing it to the isomerization rate of **1**, one can calculate the minimum raising of the free energy barrier to isomerization in the dbcot vs. cot complexes. Since $\mathbf{3}^-$ survives for several hours without isomerization, we employ $k_{isom} < 10^{-4}$ s^{-1} to describe its isomerization rate. When compared with $k_{isom} > 10^3$ s^{-1} for $\mathbf{1}^-$, it can be shown that $\Delta G^‡$ is at least 9.4 kcal/mol higher for isomerization of the Co^0 dbcot complex. That this is reasonable can be seen by comparison with data on fluxionality of $(CO)_3Fe(cot)$ complexes. The 1,2-shift which leads to fluxionality of the cot ring in $(cot)Fe(CO)_3$ (I → J)[46] is slowed considerably with benzo-cot is the ligand.[47] An increase of 10.5 kcal/mol in activation energy arises from the loss of aromatic stabilization in the transition state in going from K to L.[27] This is basically the same process that would have to occur in going from 1,5- to 1,3-dbcot in $\mathbf{3}^-$. Hence, the raising of the energy barrier to isomerization of $\mathbf{3}^-$ by >9.4 kcal/mol is seen to be consistent with earlier estimates.



I J



K L

Conclusions

1. Permethylation of the cyclopentadienyl ring in $(\eta^5\text{-}C_5R_5)$-Co(cot) has a significant effect on the 1,5 → 1,3 isomerization

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(39) Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378.

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(44) E^0 of CpCo(1,5-cod) was reported as −2.35 V in DMF in ref 14.

(45) The reduction of 1,5-cyclooctadiene is not observed within the potential range extending down to −2.8 V.

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rate in the Co^{I} neutral complexes but not in the Co^{0} anion radicals. This argues that the isomerization mechanism is different in the two different metal oxidation states.

2. The rapid isomerization of the Co^{0} complexes may arise from lifting of symmetry restrictions to the simplest molecular isomerization mechanism in the 19-electron monoanions.

3. When dibenzocyclooctatetraene is used as the ligand, the Co^{0} monoanion has a different ground state than [CpCo(cot)]$^{-}$, and CpCo(dbcot) behaves more like a cod complex with electron-withdrawing substituents. The activation barrier to isomerization in [CpCo(dbcot)]$^{-}$ is raised at least 9.4 kcal/mol over that of [CpCo(cot)]$^{-}$, a value consistent with the necessity to break up aromatic resonance in a 1,3-isomer of CpCo(dbcot).

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Electrocatalytic Reduction of CO_2 by Ni Cyclam^{2+} in Water: Study of the Factors Affecting the Efficiency and the Selectivity of the Process

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Abstract: The electrocatalytic properties of Ni cyclam^{2+} in CO_2 reduction have been studied. The influence of various experimental factors on the course of the reaction has been investigated. Under given conditions, Ni cyclam^{2+} is remarkably efficient and selective for electroreduction of CO_2 into CO, even in water. The stability of the system has been tested in long range electrolysis, showing that even after thousands of catalytic cycles no deactivation occurs. The mechanistic investigation presently described points to the importance of molecular species adsorbed on the cathode surface. The contribution of reduced species in the bulk is marginal. In addition, during the electrocatalytic process, a nickel(I) carbonyl complex is present: [Ni(cyclam)(CO)]$^{+}$. The latter complex may be involved in the catalytic reaction leading to CO evolution. Surprisingly, the behavior of Ni cyclam^{2+} as electrocatalyst is unique. Among the numerous complexes investigated, only Ni cyclam^{2+} shows such a large selectivity for the electroreduction of CO_2 over the electroreduction of water. The size of the cyclam ligand and the presence of secondary amine groups (NH) might account for the very special properties of the electrocatalyst.

The transformation of CO_2 into organic substances is a promising long term objective. It could allow the preparation of fuels or chemicals from a cheap and abundent carbon source. Among various possible approaches, the electrochemical reduction of CO_2 appears to be an attractive method. Indeed, studies on the electrochemical reduction of CO_2 on a metallic cathode were begun as early as the nineteenth century[1] or very early this century.[2] The main product was found to be formic acid. Early studies on CO_2 electroreduction in aqueous media are discussed in an excellent review and references cited therein.[3]

The electrochemical reduction of CO_2 on mercury or on lead in low protic medium was also performed.[4] More recent investigations have been carried out with various cathodic materials.[5] In particular, indium was claimed to be an interesting material, allowing CO_2 electroreduction with a very low overvoltage.[6] Electroanalytical studies on tin and indium have recently been carried out.[7] Unfortunately, indium does not seem to display the catalytic properties previously postulated, as shown by further investigations.[8,9] Use of rhodium[10] and ruthenium[11] cathodes gave low overpotentials, but with such materials, whose catalytic properties for H_2O reduction to H_2 are excellent, the selectivity of CO_2 electroreduction in aqueous medium is expected to be low. In addition, the catalytic nature of the process using ruthenium cathodes[11] remains to be proven, although highly reduced products (CH_4 and CH_3OH) are found, making the ruthenium cathode a promising system. Semiconductors have also been used as cathodic materials, either in the dark[12-14] or under light irradiation. In the latter case, semiconductor suspensions have been used,[15-19] or the reaction has been performed in a photoelectrochemical cell

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