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(5) The spectrum does not show a clear quartet since the spin–spin coupling constants $^3J_{P(1)-H}$, $^3J_{P(2)-H}$, and $^3J_{P(3)-H}$ (see Figure 1) are slightly different. Interpretation on the fine structures observed in each peaks must await further investigations.
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(8) The complex crystallized in the monoclinic space group $P2_1/c$ with cell dimensions a = 15.40 (1) Å, b = 20.65 (2) Å, c = 9.72 (1) Å, and β = 97.16 (2)°. Diffraction data were collected on a Rigaku automatic four-circle diffractometer; 1850 reflections ($|F_o| \geqq 3\sigma|F_o|$) were used in the structure solution and refinement. The structure was solved by the heavy-atom method. The programs used for this analysis were the UNICS and X-RAY system, and all calculations were done by a HITAC 8700/8800 computer. Since the crystal was not good, the final residuals were R = 0.13 and R_w = 0.17 using full-matrix least-squares with isotropic thermal parameters for N and C, respectively.
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(10) Anal. Calcd for $C_{48}H_{56}N_2BrClBP_3W$: C, 54.19; H, 5.31; N, 2.63; Br, 7.51; Cl, 3.33. Found: C, 54.36; H, 5.80; N, 2.86; Br, 7.53; Cl, 3.34.

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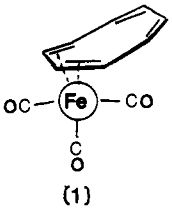
Structural Consequences of Electron-Transfer Reactions. 3.[1] Electrochemical Isomerization of a Metal–Hydrocarbon Bond in the Reduction of Cyclopentadienylcobalt Cyclooctatetraene

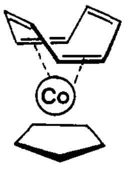
Sir:

Geometrical preferences of polyolefins bonded to metals are of importance to catalytic processes involving organometallic compounds and intermediates. We report electrochemical and NMR data showing that cyclooctatetraene (COT) may bond either as a 1,3 diolefin or 1,5 diolefin to cobalt in the π compound (COT)CoCp (Cp = η^5-C_5H_5), in an equilibrium mixture. Furthermore, the thermodynamically favored 1,5 compound rapidly and quantitatively isomerizes to the 1,3 compound when it is reduced by one electron. This appears to be the first known example of a *reversible electrochemical isomerization* of a metal–hydrocarbon bond.

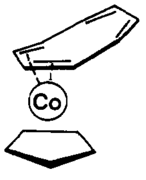
The ways in which the polyolefin cyclooctatetraene may bond to a metal are manifold and have been the subject of much discussion.[2-5] Interestingly, the ligand bonds as a conjugated 1,3 diolefin to tricarbonyliron (**1**),[6] but has been reported to bond as a nonconjugated 1,5 diolefin to η^5-cyclopentadienylcobalt (**2**).[3,7] However, our electrochemical experiments indicated the presence of two species, in equilibrium, in solutions of samples of carefully purified (**2**).[8] Cyclic voltammetry (CV) measurements of the reduction of nominal **2** in nonaqueous solvents such as THF or CH_3CN[9] showed two reduction waves (A, e_{p_c} = −1.84; B, e_{p_c} = −2.07 V) and one oxidation wave (C, e_{p_a} = −1.78 V) in the region of interest (Figure 1). Waves A and C form a reversible couple, as scans reversed at the foot of wave B demonstrate (Figure 1). When the scan is negative enough to include reduction B, oxidation wave C is greatly enhanced. As the temperature was lowered, the height of wave B increased at the expense of wave A, but the oxidation current C remained the same (corrected, of course, for changes in diffusion rate). The temperature effects were completely reversible, and the total reduction current corresponded to passage of one electron. Thus, species A and B are in equilibrium, with B being the thermodynamically more stable isomer. However, the anion of B is very unstable, and rapidly forms the radical anion of A, which is reoxidized at −1.78 V.



(1)



(2)



(3)

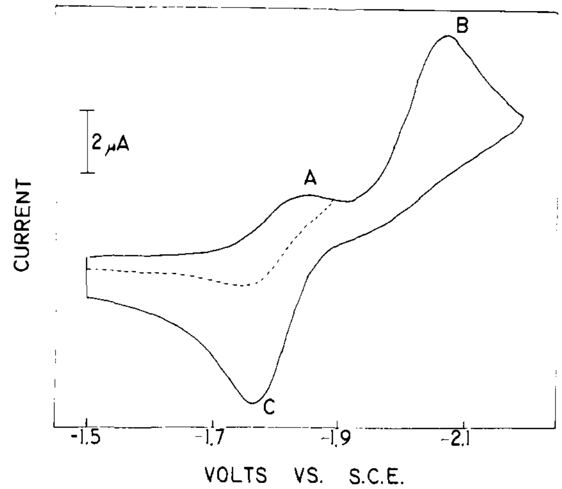


Figure 1. Cyclic voltammogram of (COT)CoCp in THF–0.1 M Bu_4NPF_6 at a hanging mercury drop electrode. Dotted line shows result of scan in which potential was reversed prior to onset of wave B. Scan rate = 500 mV/s.

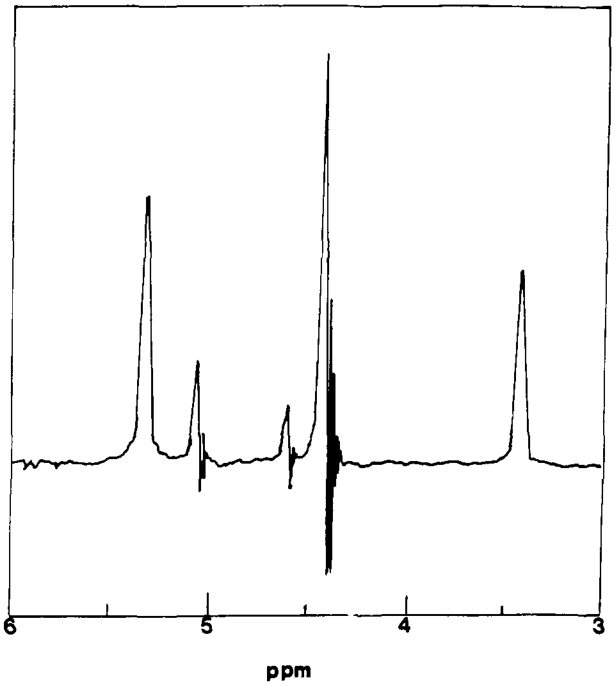


Figure 2. 60-MHz ^{1}H NMR spectrum of (COT)CoCp in hexane at 20 °C. Chemical shifts are reported as δ values.

NMR spectroscopy allows identification of B as the 1,5-bonded diene **2**, as previously reported by several groups[3,7,10] (4:5:4 pattern at δ 3.5, 4.5, and 5.4 for the COT protons on the metal-bonded carbons, the Cp protons, and the COT protons on the nonmetal-bonded carbons, respectively). Furthermore, careful inspection of the spectrum (Figure 2) reveals that the singlets[11] at δ 5.1 and 4.7 may be ascribed to species A, with integrated intensities of 1.6-1 (8 COT protons:5 Cp protons) allowing identification of the δ 5.1 ppm resonance as being due to the cyclooctatetraene protons. Excluding the unlikely possibility that species A contains a planar COT ring, we must conclude that it is a fluxional compound. Based on the known fluxional compounds $(COT)M(CO)_3$ (M = Fe, Ru, Os),[13,14] we assign a structure to this species in which the COT ring is bonded as a 1,3 diene to the cobalt (**3**). Although a reversible isomerization of a 1,3- and 1,5-bonded metal diene seems to be without precedent, we note that Smith and Maitlis have recently isolated thermally unstable 1,3-bonded COT complexes $(COT)M(\eta^5\text{-}C_5Me_5)$ (M = Rh, Ir) which rearrange irreversibly to the 1,5-bonded isomers at 20 °C. Significantly, the 1,3-COT resonances are singlets.[15]

At higher temperatures *each* resonance in the (COT)CoCp spectrum broadens, showing that the temperature dependence to the spectrum observed previously[10,12] is due to the kinetics of the isomerization process, rather than to fluxionality of the 1,5-bonded compound. Quantitative aspects of the NMR temperature dependence are being studied.[16]

Bulk electrochemical reduction at −2.2 V produced a solution containing only the 1,3-bonded anion (3^-). A frozen solution of the anion displayed an intense electron spin resonance spectrum with cobalt hyperfine splittings. The original mixture of **2** and **3** was regenerated by electrolytic reoxidation of the solution.

All of these data are consistent with the following chemistry of (COT) CoCp:

$$\begin{tikzcd}
(1,3\text{-}\eta^4\text{-COT})\text{CoCp} \arrow[r, shift left] \arrow[d, shift left, "e^-(-1.8\text{V})"] & (1,5\text{-}\eta^4\text{-COT})\text{CoCp} \arrow[l, shift left] \arrow[d, "e^-(-2.0\text{V})"] \\
(1,3\text{-}\eta^4\text{-COT})\text{CoCp}^- \arrow[u, shift left] & (1,5\text{-}\eta^4\text{-COT})\text{CoCp}^- \arrow[l]
\end{tikzcd}$$

Clearly, the 1,5 isomer is the more stable of the neutral compounds, but the 1,3 isomer is favored in the anion. The shift in stability may be due to the ability of the 1,3 isomer to delocalize the extra electron of the anion among the four metal-bound olefinic carbons. It is apparent from these results that the nature of a metal-polyolefin bond may be sensitive to the formal oxidation state of the metal, and that electrochemical methods may prove useful in designing ways to reversibly alter the nature of the metal-olefin bond.

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(9) The starting compound is air stable and simple nitrogen-blanketing techniques were sufficient for most voltammetric experiments. Some bulk electrolyses have been carried out in a glove box under nitrogen. Supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. Solvents were prepared and equipment was employed as described previously: W. L. Bowden, J. D. L. Holloway, and W. E. Geiger, Jr., *Inorg. Chem.*, **17,** 256 (1978). Potentials are referred to the aqueous saturated calomel electrode.
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(16) These studies are being pursued in conjunction with Dr. C. H. Bushweller of our department.

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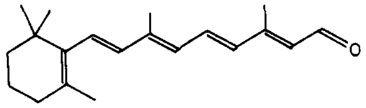
Fluorescence Lifetime of *all-trans*-Retinal at 77 K[1]

Sir:

all-trans-Retinal (**1**) shows spectroscopic anomalies such as diffuseness of the absorption spectrum at 14-300 K,[2] excitation wavelength (λ_{ex}) dependence of ϕ_F,[3-9] temperature dependence of radiative lifetime,[5] τ_F^0, calculated from the relation $\tau_F/\phi_F = \tau_F^0$, an unusually large "Stokes" shift,[2-7] and a large disparity between τ_F^0 from the integrated absorption band (Bu ← Ag) and τ_F^0 from the measured quantity, τ_F/ϕ_F.[2-5,7]



(1)

Of these anomalies, the λ_{ex} dependence of ϕ_F is most intriguing. Recently, it has been shown that the λ_{ex} dependence can be largely accounted for in terms of a hydrogen-bonded *all-trans*-retinal as the emitting species.[4] Thus, an intrinsic fluorescence quantum yield of *all-trans*-retinal has been shown to be independent of λ_{ex} within 25%.[4b] An equilibrium involving a dimeric *all-trans*-retinal (fluorescent) has also been suggested as an additional contributor to the wavelength dependence.[4c,6]

Since the λ_{ex} dependence of ϕ_F has not been examined in terms of fluorescence lifetime which can be used to discriminate contributions of the ground-state and excited-state properties of retinal to the wavelength-dependent fluorescence, we have measured τ_F of *all-trans*-retinal in ethanol as a function of λ_{ex}. We have chosen ethanol as the solvent for the following reason: the λ_{ex} dependence of ϕ_F persists in ethanol, even though (a) nearly all of the retinal should be hydrogen bonded to the solvent molecules during freezing to and at 77 K[5,6] and (b) a rapid proton tunneling within the retinal-ethanol H-bonding pair, RC=O···HOtE, may occur along the H-bonding potential curve in the excited state. If the latter occurs prior to fluorescence emission, the expected λ_{ex} dependence of ϕ_F due to the H-bonding of retinal can be minimized because of the inequality between equilibrium constants, K and K^*, in the ground and excited states, respectively:

$$K = \frac{(\mathrm{RC{=}O})(\mathrm{EtOH})}{(\mathrm{RC{=}O\cdots HOtE})} > K^* = \frac{(\mathrm{RC{=}O^*})(\mathrm{EtOH})}{(\mathrm{RC{=}O^*\cdots HOtE})}$$

The above inequality is predicted from the increase in π-elec-

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