Figure 3. Ir spectra (hexane solution; $\nu(M)$—C≡O) absorptions in cm^{-1}) of compounds III and V (a), III (b), III and IV (c) and IV (d).

stable at 25° for several hours in hexane solution saturated with CO but decomposes by loss of CO at 25° within 1 hr if isolated in crystalline form to give 1,3,4,5-η-pent-4-ene-3,1-yliron tricarbonyl (IV). Flash distillation (15°; 0.001 Torr) of III gives IV (almost quantitative; yellow oil; m/e 208; ir (hexane) $\nu((M)$—C≡O) 2053, 1994, 1989 cm^{-1}; nmr[4] (Figure 2, CS$_2$; −20°) δ 3.9 (m, H-4), 3.7 (m, H-3), 3.50 (d, H-5 syn), 2.6–2.2 (m, H-5 anti, H-1, H-2). *Anal.* Calcd for C$_8$H$_8$FeO$_3$: C, 46.20; H, 3.88. Found: C, 46.37; H, 3.99.)

Interconversion of III and IV can be followed by ir (Figure 3). The two carbonyl absorptions at 2064 and 2005 cm^{-1} typical[2b] of III disappear within seconds, if nitrogen is bubbled through a hexane solution of III at 25°, while three new absorptions appear at 2053, 1994, and 1989 cm^{-1} typical [2b] of IV (Figure 3, spectra b → c → d). If CO is bubbled through the hexane solution of IV for a few seconds, the original spectrum of III can be observed again. Solutions of III treated for at least 20 sec with a stream of CO show absorptions at 2066 and 2008 cm^{-1} in addition to those of III. These absorptions are due to a new compound, for which structure V is assumed. V may be formed by the equilibrium III + CO ⇌ V suggesting, that an Fe–olefin bond in III is replaced by an Fe–CO bond in V. Attempts to isolate this compound have been unsuccessful so far.

Solutions of III decompose to 2-cyclohexenone[2b,5] (80%) under the influence of air or if a positive pressure of CO (20 atm) is applied. II on warming in a sealed ampoule (benzene, 50°, 24 hr) gives a 3:1 mixture (nmr analysis) of pentadi-1,3-ene–iron tricarbonyl complexes[6] VIa and VIb in 76% yield.

(5) Cyclohexenones have been obtained also by Sarel on the light induced reaction of vinylcyclopropanes with Fe(CO)$_5$: R. Victor, R. Ben-Shoshan, and S. Sarel, *Tetrahedron Lett.*, 4253 (1970).

(6) G. F. Emerson, J. E. Mahler, R. Kochhar, and R. Pettit, *J. Org. Chem.*, 29, 3620 (1964); 1,3-diene–Fe(CO)$_3$ complexes have been isolated by Sarel, *et al.*, on reaction of vinylcyclopropane with Fe(CO)$_5$ (ref 5).

$$\text{II} \xrightarrow{50°} \text{VIa} + \text{VIb}$$

Fe(CO)$_3$ Fe(CO)$_3$

VIa   VIb
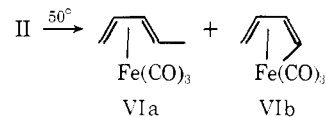
II does not rearrange to III on low temperature photolysis. We suggest[3] that II and III are formed by competing reactions of I with different iron carbonyl species generated on photolysis of Fe(CO)$_5$[7] in ether.

(7) E. Koerner von Gustorf and F.-W. Grevels, *Fortschr. Chem. Forsch.*, 13, 379 (1969); E. Koerner von Gustorf, private communication.

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Electroreduction of Cobaltocene. Evidence for a Metallocene Anion

Sir:

Except for the report of a Ni(IV) species formed by dioxidation of nickelocene,[1,2] no unusual redox properties have been reported for di-π-cyclopentadienyl-metal complexes[3,4] (the "metallocenes," $(\pi\text{-Cp})_2M$). In particular, no claims of unusually highly reduced metallocenes or metallocene anions have appeared.[5,6] Indeed, attempts to reduce neutral ferrocene, nickelocene, and chromocene with potassium in liquid ammonia have led to complete disruption of the organometallic species.[7] Since complexes in lower metal oxidation states in this class would be of interest as possible model systems for electrophilic attack at metallocenes, we wish to report the results of experiments in which we have successfully generated by electrochemical methods stable dimethoxyethane solutions of the cobaltocene anion, Cp_2Co^-. This species, the first reported metallocene anion, is the third member of the electron-transfer series consisting of Cp_2Co^+, Cp_2Co, and Cp_2Co^-. These compounds possess respectively the formal d^6, d^7, and d^8 electron configurations, iso-

(1) R. J. Wilson, L. F. Warren, Jr., and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 91, 758 (1969).

(2) R. P. Van Duyne and C. N. Reilly, *Anal. Chem.*, 44, 158 (1972).

(3) For a recent review see E. G. Perevalova and T. V. Nikitina, *Organometal. React.*, 4, 163 (1972).

(4) Representative papers concerned with metallocene redox processes are (a) T. Kuwana, D. E. Bublitz, and G. Hoh, *J. Amer. Chem. Soc.*, 82, 5811 (1960); S. P. Gubin, S. A. Smirnova, L. I. Denisovich, and A. A. Lubovich, *J. Organometal. Chem.*, 30, 243 (1971) (Fe, Ru, Os); (b) A. A. Vlcek, *Collect. Czech. Chem. Commun.*, 30, 952 (1965); S. P. Gubin, S. A. Smirnova, and L. I. Denisovich, *J. Organometal. Chem.*, 30, 257 (1971) (Co); (c) F. A. Cotton, R. O. Whipple, and G. Wilkinson, *J. Amer. Chem. Soc.*, 75, 3586 (1953) (Rh, Ir); (d) G. Wilkinson and J. M. Birmingham, *ibid.*, 76, 4281 (1954) (V, Nb).
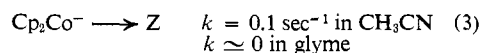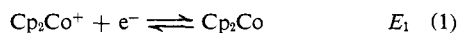
(5) Several papers have appeared in which the reduction of substituted (*e.g.*, nitrophenyl) ferrocenes have yielded stable anions. However, esr studies have shown that these species should be considered as organic anion radicals with a ferrocenyl substituent: (a) Ch. Elschenbroich and M. Cais, *J. Organometal. Chem.*, 18, 135 (1969); (b) G. R. Underwood, D. Jurkowitz, and S. C. Dickerman, *J. Phys. Chem.*, 74, 544 (1970); (c) G. Bigam, J. Hooz, S. Linke, R. E. D. McClung, M. W. Mosher, and D. D. Tanner, *Can. J. Chem.*, 50, 1825 (1972). Ferrocene itself is not reduced electrochemically.

(6) Recently some excellent work has been reported on the reduction of mixed π-sandwich complexes of chromium; see Ch. Elschenbroich and F. Gerson, *J. Organometal. Chem.*, 49, 445 (1973); Ch. Elschenbroich, F. Gerson, and F. Stohler, *J. Amer. Chem. Soc.*, 95, 6956 (1973).

(7) G. W. Watt and L. J. Baye, *J. Inorg. Nucl. Chem.*, 26, 2099 (1964); L. J. Baye, *Diss. Abstr.*, 24, 3968 (1964).

electronic to the Cp_2Ni^{2+}, Cp_2Ni^+, Cp_2Ni series.[1,2] Consistent with the highly reduced character of the Co(I) anion, solutions of it were extremely air sensitive and could be generated only with rigorous exclusion of oxygen, using vacuum line electrolytic procedures.[8]

Solutions of $Cp_2Co^+PF_6^-$ in either acetonitrile (MeCN) or 1,2-dimethoxyethane (glyme) were reduced in two successive steps (Figure 1); the first wave (-0.94 V in MeCN, -0.80 V in glyme)[9] represented the well-

$$Cp_2Co^+ + e^- \rightleftharpoons Cp_2Co \qquad E_1 \quad (1)$$

$$Cp_2Co + e^- \rightleftharpoons Cp_2Co^- \qquad E_2 \quad (2)$$

$$Cp_2Co^- \longrightarrow Z \quad k = 0.1 \text{ sec}^{-1} \text{ in } CH_3CN \quad (3)$$
$$k \simeq 0 \text{ in glyme}$$

$$Z + e^- \rightleftharpoons Z^- \qquad E_3 \quad (4)$$

known, one-electron reversible reduction to cobaltocene (step 1)[4b] and the second wave (-1.88 V in MeCN, -1.89 V in glyme) involved reduction of the neutral compound to the cobaltocene anion (2). It was convenient to begin with the cation in order to avoid problems associated with the air sensitivity of cobaltocene. The presence of the $Cp_2Co^+ \rightleftharpoons Cp_2Co$ redox couple (1) provided a one-electron internal "calibrant" against which to measure currents passed on the second wave.

The $Cp_2Co \rightleftharpoons Cp_2Co^-$ couple (2) was highly reversible in either MeCN or glyme, as judged from its ac polarographic[10] and cyclic voltammetric response.[11] Very slow cyclic voltammetry experiments indicated that the anion was stable in glyme over a time scale of at least 30 sec but that significant decomposition of the anion occurred in MeCN during a similar period. In agreement with these observations, stable solutions of the anion could be generated in glyme but not in MeCN. Thus, after a light yellow 0.30 mM solution of $Cp_2Co^+PF_6^-$ in glyme was exhaustively electrolyzed under vacuum at a mercury pool at -2.1 V, the bright brown-orange color of Cp_2Co^- appeared in the cathode compartment. A polarogram of the resulting solution indicated oxidation waves of equal height[12] at -1.88 and -0.80 V, corresponding to the oxidation of Cp_2Co^- and Cp_2Co. The heights of these waves showed no dimunition over the period of 1 hr, indicating a high degree of stability of the anion in this solvent.[13] An exhaustive reoxidation of this solution at -0.50 V regenerated over 90% of the original Cp_2Co^+. Coulometry confirmed that a total of

Figure 1. Dc polarogram of a 6.30×10^{-4} M solution of cobalticinium hexafluorophosphate in acetonitrile containing 0.15 M tetrabutylammonium hexafluorophosphate.

two electrons was consumed in going from the cation to the anion.

When the cation was reduced at -2.1 V in acetonitrile, however, coulometry indicated consumption of *three* electrons. Since one electron is utilized in formation of Cp_2Co (1), this means that the overall, long-term reduction mechanism of neutral Cp_2Co requires *two* electrons in MeCN in contrast to the earlier report of one electron by Gubin, *et al.*[4b] Polarographic and cyclic voltammetric experiments have confirmed that neutral Cp_2Co is reduced by an ECE mechanism[14-16] (steps 2–4) in acetonitrile wherein $E_3 > E_2$; that is, the intermediate, Z, must be more easily reduced than cobaltocene itself. The mechanism was diagnosed on the basis of cyclic voltammetric measurements of the anodic-to-cathodic current ratio and the cathodic current function (ratio of cathodic peak current to square root of scan rate) as a function of scan rate.[14,16] The rate of the intermediate chemical reaction (3) was found to be 0.1 sec^{-1} by these methods. Polarographic measurement of the rate constant was effected by comparison of the diffusion current constants of the first and second polarographic waves and yielded a similar value.[15] Details of the electrochemical measurements will be published at a later date.

The identity of the intermediate in acetonitrile, Z, has not yet been determined, but the possibility that it is π-cyclopentadienylcobaltcyclopentadiene, $CpCoC_5H_6$, in accord with earlier suggestions of other workers,[4b,17] has been ruled out because the reduction potential of $CpCoC_5H_6$ is too negative[18,19] to fulfill the condition $E_3 > E_2$ required of the true intermediate. Consequently we can say unambiguously that $CpCoC_5H_6$ *is not formed in this reduction*. In spite of this, we found the

(8) In full-scale electrolytic preparations of the anion, an electrolysis cell was employed which operates under the solvent vapor pressure, without use of an inert gas (detailed description to be published). Other polarographic or cyclic voltammetric data were obtained using a standard cell arrangement with an argon purge.

(9) Potentials are referred to the aqueous saturated calomel electrode. Electrochemical experiments were performed with Princeton Applied Research Model 173 potentiostat and Model 170 electrochemistry system. Tetrabutylammonium hexafluorophosphate was the supporting electrolyte (0.15 M in glyme, 0.3 M in MeCN).

(10) W. E. Geiger, Jr., and D. E. Smith, *J. Electroanal. Chem.*, **50**, 31 (1974).

(11) A standard apparent rate constant of 0.3 cm sec^{-1} for the heterogeneous electron transfer step (2) was calculated from the cathodic-anodic peak separation following the procedure of R. S. Nicholson, *Anal. Chem.*, **37**, 1351 (1965).

(12) The wave at -0.80 V has a maximum typical of polarograms of oxidation waves at very negative potentials; see K. Santhanam and A. J. Bard, *J. Amer. Chem. Soc.*, **88**, 2669 (1966).

(13) Preliminary experiments suggest that the cobaltocene anion can also be generated by reduction of dimethoxyethane solutions of cobaltocene with sodium-potassium alloy, in which the solution changes color from purple to brown. Thus far we have not been able to isolate the anion from these solutions, but further experiments are being conducted.
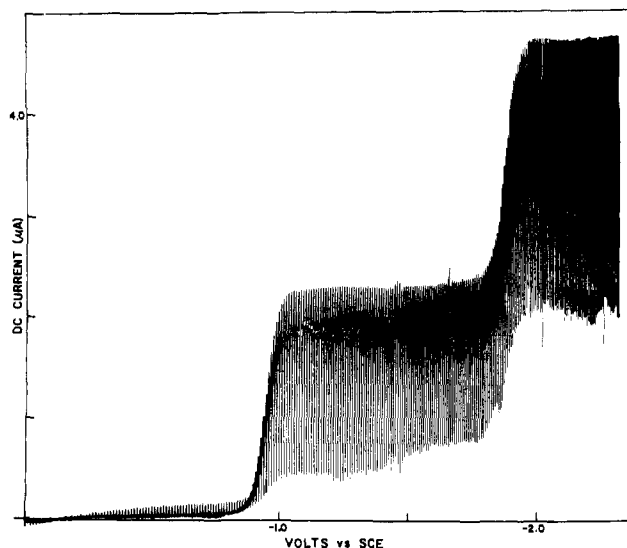
(14) R. S. Nicholson and I. Shain, *Anal. Chem.*, **37**, 178 (1965).

(15) R. S. Nicholson, J. M. Wilson, and M. L. Olmstead, *Anal. Chem.*, **38**, 542 (1966).

(16) R. S. Nicholson and I. Shain, *Anal. Chem.*, **37**, 190 (1965).

(17) N. El Murr, R. Dabard, and E. Laviron, *J. Organometal. Chem.*, **47**, C13 (1973).

(18) The half-wave potential of an authentic sample[19] of $CpCoC_5H_6$ in CH_3CN was -2.28 V.

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

rate of the chemical reaction to be greatly enhanced by the addition to the MeCN solution of small amounts of a strong proton donor such as phenol. It seems likely, then, that the proton-assisted reaction (3) may be resulting in protonation at the *metal* rather than at the ligand, although we have not yet obtained direct evidence to support this hypothesis. In view of the expected highly basic character of the metal in Cp_2Co^-, such a reaction would not seem anomalous and would signal the investigation of a series of reactions between electrophiles and the Co(I) atom.

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Reactions of Coordinated Nucleophiles.
## Intramolecular Imine Formation

Sir:

The facility with which coordinated nucleophiles can attack reactive centers within a metal complex has been suspected for a long time. Usually the complexes have been too labile for the assertion to be proved although a few examples are known[1] where neither the coordinated nucleophile nor the ligand which is attacked actually ever leave the metal ion. Processes of this kind are commonly assumed to be involved in so-called "metal template" synthesis[2] though unequivocal proof that the reaction does occur while the reactants are fully coordinated appears to be lacking. A common and important process in "template" syntheses is the formation of the carbon–nitrogen double bond (imine), and we are currently investigating several kinetically inert complexes wherein this is observed as a rapid-intramolecular process. This is part of a program designed to evaluate the efficiency and potentiality of such intramolecular reactions, and we describe here such a condensation.

When the pH of a dilute[3] aqueous solution of pyruvatopentaamminecobalt(III) ion, $[(NH_3)_5CoO_2C-COCH_3]^{2+}$ (A), was raised to ≥ 12, an intense brown-red color rapidly developed. Acidification with $HClO_4$ immediately produced a clear orange solution from which a crystalline perchlorate salt was isolated. Dissolution of this solid in aqueous NaOH (0.05 M)

(1) (a) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 91, 3451 (1969); (b) *ibid.*, 91, 4102 (1969); (c) D. A. Buckingham, D. M. Foster, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 9, 11 (1970); (d) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 92, 6151 (1970); (e) D. A. Buckingham, C. E. Davis, and A. M. Sargeson, *ibid.*, 92, 6159 (1970).

(2) For reviews of this extensive area of chemistry see N. F. Curtis *Coord. Chem. Rev.*, 3, 3 (1968); D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Advan. Chem. Ser.*, No. 100, 44 (1971); L. F. Lindoy and D. H. Busch "Preparative Inorganic Reactions," Vol. 6, W. L. Jolly, Ed., Interscience, New York, N. Y., 1971, p 1.

(3) In concentrated solutions another reaction, leading to polymeric complex products, is observed. While of interest, this reaction is not relevant to the present report and may readily be made insignificant by appropriate choice of conditions.

A

B (orange)

(red)
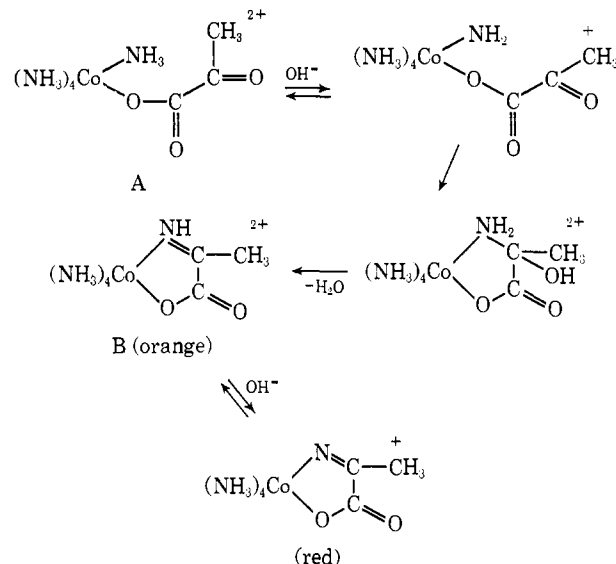
immediately regenerated the intense red color indicating it was simply due to a product deprotonation reaction ($pK_a = 10.5$ at 25°, $\mu = 1.0$, $NaClO_4$). The red species slowly decomposed in the basic medium. At lower pH (≈ 10) the reaction proceeded more slowly (~ 5 min) and directly to the orange product which appeared to be indefinitely stable in quite concentrated acid (3 M HCl). Analysis of the perchlorate salt was consistent with loss of 1 mol of water from the reactant. *Anal.* Calcd for $CoC_3H_{16}N_5O_{10}Cl_2$: Co, 14.30; C, 8.75; H, 3.91; N, 17.00; Cl, 17.21. Found: Co, 14.48; C, 8.81; H, 4.08; N, 16.75; Cl, 16.84. Infrared and pmr spectra provide convincing evidence that the orange product is the pyruvilidene–imine chelate complex of tetraamminecobalt(III) (B). Thus, the process results in replacement of the >C=O stretching absorption at 1720 cm^{-1} in the reactant by a strong product band at 1680 cm^{-1} ($\nu_{C=N}$), just resolved from carboxylate absorption (in the N-deuterated complexes). In DMSO-d_6 proton magnetic resonances appear at δ (ppm) -12.1 (=NH), -3.92 (NH$_3$), -3.33 (2 NH$_3$), -2.94 (NH$_3$), and -2.36 (N=CCH$_3$) relative to internal tetramethylsilane. The reaction is assumed to occur by attack of the deprotonated ammonia cis to the carboxylate ligand at the carbonyl center of the keto form of coordinated pyruvate although it is known that the gem-diol form is present in significant amounts.[4] Preliminary kinetic measurements indicate that the carbinolamine intermediate does not attain significant concentrations, the reaction appearing as a single rate process first order in reactant complex concentration. The dependence of the rate on hydroxide ion concentration is not simple, being close to first order between pH 8 and 11, but declining to zero order for [OH$^-$] $\geq$ 0.5 M. In 1 M NaOH the half-life of reaction is ~ 0.2 sec at 25°. At lower pH values proton exchange at the ammonias cis to the pyruvate ligand exceeds the reaction rate by a factor $\sim 2 \times 10^2$ only. Clearly the coordinated amide ion is fairly efficient at capturing the >C=O center. The specific rate of chelation of the deprotonated reactant is estimated at ≥ 7000 sec^{-1} at 25° using the esti-

(4) (a) H. J. Price and H. Taube, *J. Amer. Chem. Soc.*, 89, 269 (1967); (b) *Inorg. Chem.*, 7, 1 (1968); (c) L. Pratt and G. Occupati, *J. Chem. Soc., Dalton Trans.*, 1699 (1973).