Reduction of η^5-Cyclopentadienyldicarbonylcobalt. Formation of Tetracarbonylcobaltate and $[\eta^5\text{-}C_5H_5CoCO]_2{\cdot}^-$. A Binuclear Cobalt Radical Anion

Sir:

The reduction of transition metal carbonyl complexes provides synthetic access to a number of interesting anionic organometallic species.[1] Typically, binuclear carbonyls (e.g., **1** and **3**) are reduced to mononuclear anions (**2** and **4**), and certain mononuclear carbonyls (e.g., **5**) can be used to prepare both bi- and mononuclear dianions (**6** and **7**). In certain cases (e.g., $Fe(CO)_4{}^{2-}$), these derivatives have been shown to possess sufficient nucleophilicity to serve as useful stoichiometric reagents in organic synthesis.[2]

$$\underset{\mathbf{1}}{Mn_2(CO)_{10}} \xrightarrow{+2e^-} \underset{\mathbf{2}}{2Mn(CO)_5{}^-}$$

$$\underset{\mathbf{3}}{(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4} \xrightarrow{+2e^-} \underset{\mathbf{4}}{2(\eta^5\text{-}C_5H_5)Fe(CO)_2{}^-}$$

$$\underset{\mathbf{5}}{2Cr(CO)_6} \xrightarrow[-2CO]{+2e^-} \underset{\mathbf{6}}{Cr_2(CO)_{10}{}^{2-}} \xrightarrow{+2e^-} \underset{\mathbf{7}}{2Cr(CO)_5{}^{2-}}$$

Although mononuclear η^5-cyclopentadienyl metal carbonyls might be expected to mimic this reduction behavior (at least one appears to[3]), we wish to report that reduction of η^5-cyclopentadienyldicarbonylcobalt (**8**) follows a more complicated, and in some ways more intriguing, reaction course.

Treatment of 0.02-2.0 *M* solutions of **8** in tetrahydrofuran with 0.7% sodium amalgam, under scrupulously air- and water-free conditions, resulted in the formation of a heterogeneous mixture containing a greenish solid and yellow-green supernatant solution. Infrared analysis of the solution showed new bands at 1897, 1889, 1855, 1740, 1690, and 1660 cm^{-1} in the metal carbonyl region of the spectrum. When the reduction was carried out by adding small amounts of sodium in hexamethylphosphoric triamide (HMPT) to a solution of **8** in HMPT, the solution remained homogeneous and as the bands due to **8** (2020 and 1955 cm^{-1}) disappeared (Figure 1) only two new bands (1890 and 1690 cm^{-1}) grew in. Less than 1 equiv of Na was required to completely convert **8** to this new mixture.

That the reduced THF solution contained two new complexes was demonstrated as follows. (i) Addition of petroleum ether to the supernatant precipitated the rest of the green solid and eliminated the three low-frequency solution ir absorptions. The resulting yellowish solution was concentrated in vacuo, yielding an off-white material which exhibited ir absorptions at 1897, 1889, and 1855 cm^{-1}, identical with those reported[4] for $NaCo(CO)_4$ (**9**). Addition of 18-crown-6 to the yellow solution produced a single ir band in THF at 1889 cm^{-1}, and preparation of the known[5,6] derivatives $Hg[Co(CO)_4]_2$ (mp 80-81°) and $[(C_6H_5)_3P]_2NCo(CO)_4$ (mp 186-188°) confirmed the assignment of $NaCo(CO)_4$ as the identity of the more THF-soluble component. (ii) Exhaustive extraction of the less soluble green complex with THF gave rise to a second yellow solution which, upon either retreatment with petroleum ether or concentration in vacuo, yielded a green microcrystalline material (**10**). This complex exhibited only the 1660, 1690, and 1740 cm^{-1} ir bands upon redissolution.

The green complex, which was obtained in yields up to 70%, ignited immediately upon contact with air but could be stored indefinitely at room temperature under an atmosphere of purified nitrogen. Complexation studies using 18-crown-6 indicated that it was a sodium salt; addition of successive amounts of the crown ether gradually converted the CO region of the ir spectrum in THF to a single band at 1690 cm^{-1} (identical with the frequency observed in the highly polar medium HMPT). Apparently both 18-crown-6 and HMPT convert one or more ion-paired species (bands at 1660 and 1740 cm^{-1}) to the free ion, which has only a single band at 1690 cm^{-1}.

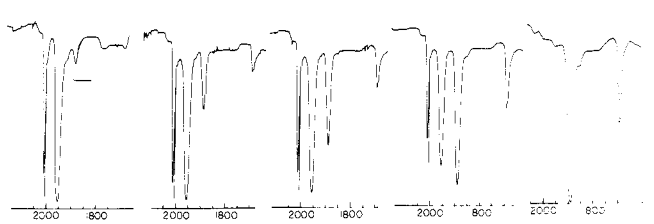
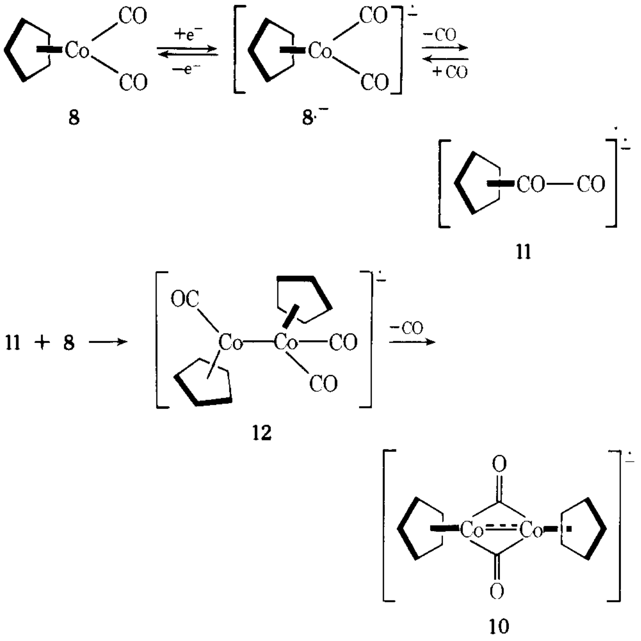


Figure 1. Ir spectra taken during reduction of $\eta^5\text{-}C_5H_5Co(CO)_2$ (**8**) by addition of successive amounts of sodium in HMPT to a solution of **8** in HMPT. In the sequence of spectra shown, reading from left to right, the mole ratio of sodium to **8** is 0.06, 0.2, 0.3, 0.4, 0.6.

Scheme I



Treatment of a saturated solution of **10** in THF with bis(triphenylphosphine)iminium chloride (PPN^+Cl^-)[6,7] deposited NaCl and also converted the carbonyl ir spectrum to a single band at 1690 cm^{-1}. After concentration in vacuo, this solution slowly deposited the PPN^+ salt as paramagnetic,[8,9] deep orange-red crystals which analyzed correctly for $[\eta^5\text{-}C_5H_5CoCO]_2{}^-PPN^+$. The molecular structure of this material has been solved using x-ray diffraction techniques (see accompanying communication[10]) and shown to be the binuclear "radical anion" complex illustrated as **10** in Scheme I.[11]

With regard to the mechanism of formation of **10**, the first step presumably involves formation of **8**$\cdot^-$ (the radical anion of **8**), followed by loss of one molecule of carbon monoxide (cf. Scheme I). Preliminary results on the electrochemistry[12] of **8** indicate that this is a two-step (rather than synchronous) process. Cyclic voltammetry showed a reduction wave at −2.14 V relative to $Ag|AgClO_4$, which is cleanly reversible even at relatively slow scan rates (20 mV/s). We assume that following CO loss, the radical anion **11** attacks a molecule of neutral **8**, giving intermediate **12**, which loses a second molecule of CO to form the anionic binuclear complex **10**. The isolated ratio of **10** to $NaCo(CO)_4$ depends on the initial concentration of **8**; it can be raised from about 2:1 to 0.5 M to about 5:1 at 2.0 M.

The mechanism of formation of $NaCo(CO)_4$ (**9**) from **8**, a reaction which involves loss of the carbocyclic ring, is less clear.[13] However, some indication that interceptible, highly unsaturated (or THF-solvated) metal species are involved is provided by the following experiment. Slow addition of **8** to a mixture of Na-Hg in THF containing 1.2 M $(C_6H_5)_3P$ gave a solution which contained only small amounts of **9** and **10**, but much larger quantities of $NaCo(CO)_2(P(C_6H_5)_3)_2$ (**13**)[14] and $NaCo(CO)_3(P(C_6H_5)_3)$ (**14**).[15] Control experiments showed that (a) **9** is inert to substitution[16] by $P(C_6H_5)_3$ under these reaction conditions; (b) η^5-$C_5H_5Co(CO)((C_6H_5)_3P)$ is formed only slowly from **8** and $(C_6H_5)_3P$ at these temperatures, and in any case gives neither **13** nor **14** when reduced with Na-Hg in THF in the presence of excess phosphine.[17,18]

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References and Notes

(1) For reviews, see (a) J. E. Ellis, *J. Organomet. Chem.*, **86**, 1 (1975); (b) R. B. King, *Acc. Chem. Res.*, **3**, 417 (1970).
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(4) (a) W. F. Edgell, J. Lyford, A. Barbetta, and C. I. Jose, *J. Am. Chem. Soc.*, **93**, 6403 (1971); (b) W. F. Edgell and J. Lyford, *ibid.*, **93**, 6407 (1971).
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(6) J. K. Ruff, *Inorg. Chem.*, **7**, 1818 (1968).
(7) (a) J. K. Ruff, *Inorg. Chem.*, **7**, 1821, 1499 (1968); (b) J. K. Ruff and W. J. Schlientz, *Inorg. Syn.*, **15**, 84 (1974).
(8) The magnetic moment of **10**, measured using either the Gouy balance method or the procedure of Evans,[9] is 1.70 ± 0.10 μ_B (corrected for ligand diamagnetism).
(9) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(10) N. E. Schore, C. S. Ilenda, and R. G. Bergman, *J. Am. Chem. Soc.*, following paper in this issue.
(11) We have obtained preliminary results on both the reduction of **10** and its reaction with alkylating agents. Although it is stable to 1% Na-Hg in THF, under more severe reducing conditions (Na dispersion in THF or Na in HMPT over a period of 24 h) **10** is converted in high yield to sodium cyclopentadienide and unidentified metallic products. Methyl iodide and *n*-propyl bromide react at least an order of magnitude more rapidly with **10** than with $Co(CO)_4^-$; characterization of the products of these reactions is in progress and will be reported in a full paper.
(12) Electrochemical experiments were carried out in acetonitrile under a nitrogen atmosphere at a mercury-drop electrode. Tetraethylammonium perchlorate was the supporting electrolyte and silver-silver perchlorate reference was used.
(13) Control experiments have demonstrated that under the conditions of the reduction of **8** in THF or HMPT, the sodium cyclopentadienide NMR resonance is severely broadened and is therefore difficult to observe. Apparently electron exchange between Na^+Cp^- and **10** (or some other paramagnetic species) occurs rapidly on the NMR time scale in these solvents. In acetonitrile, however, the Na^+Cp^- signal (only slightly broadened) may be observed in the NMR during reduction; Na^+Cp^- is therefore a product of the initial reduction reaction and is apparently produced in yields comparable to $NaCo(CO)_4$. We assume that the ring is extruded as cyclopentadienide in THF and HMPT as well. We have considered the possible intermediacy of cobaltocene in this reaction; however, although there is precedent for the formation of cobaltocene from **8** under certain conditions,[13a] it apparently is not converted to Cp^- by reduction;[13b] (a) D. Sellmann, *Z. Naturforsch. B*, **25**, 1482 (1970); (b) W. E. Geiger, Jr., *J. Am. Chem. Soc.*, **96**, 2632 (1974).
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(16) This is consistent with other observations on the substitution inertness of metal carbonyl anions; see, for example, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1967, p 541.
(17) η^5-$C_5H_5Co(CO)[P(C_6H_5)_3]$ is reduced more slowly than **8** to give $(C_6H_5)_3P$ and a dark, insoluble (probably polymeric) complex. Interestingly, however, exposure of this material to carbon monoxide in THF immediately forms **9** and **10** in a ratio similar to that observed on direct reduction of **8**.
(18) (a) Reduction of η^5-$C_5H_5Rh(CO)_2$ with Na-Hg in THF has been reported[18b] to also produce a product having an ir band near 1890 cm^{-1}. However, this material is apparently not the known[18c] $NaRh(CO)_4$, since it has been assigned the rhodium hydride structure $Na^+[\eta^5$-$C_5H_5Rh(H)(CO)]^-$; (b) R. Hill and S. A. R. Knox, *J. Organomet. Chem.*, **84**, C31 (1975); (c) P. Chini and S. Martinengo, *Inorg. Chim. Acta*, **3**, 21 (1969).
(19) National Institutes of Health Postdoctoral Fellow, 1975-present.
(20) National Institutes of Health Postdoctoral Fellow, 1974-present.
(21) Camille and Henry Dreyfus Teacher-Scholar Grant Awardee, 1970-1975.

Casmir S. Ilenda,[19] Neil E. Schore,[20] Robert G. Bergman*[21]
Contribution No. 5157, Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91125

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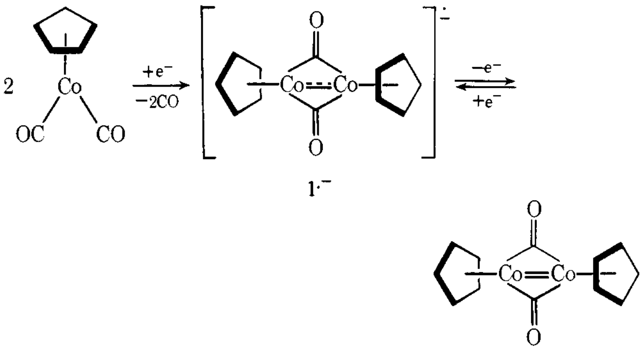
Crystal and Molecular Structure, Spectroscopic Properties, and Redox Behavior of $[\eta^5\text{-}C_5H_5CoCO]_2{\cdot}^-$, a "Mixed-Valence" Organometallic Radical Anion Having a High Degree of Intramolecular Delocalization and Cobalt in Formal Oxidation State +0.5

Sir:

We wish to report the structure, ESR and electronic spectra, and redox behavior of the paramagnetic title compound (**1**·⁻). This material can be considered a formal cobalt(I)-cobalt(0) "mixed-valence" transition metal complex[1] having a high degree of interaction or delocalization between the two intramolecular metal atoms; each cobalt is in formal oxidation state +0.5. It is one of the very few examples of a complex having cobalt-cobalt multiple bond character (in this case a bond order of ca. 1,5), and it is easily oxidized to a neutral complex which presumably has a complete cobalt-cobalt double bond.

The bis(triphenylphosphine)iminium salt of radical anion **1**·⁻, prepared by Na-Hg reduction of η^5-$C_5H_5Co(CO)_2$ as described in the accompanying communication,[2] crystallizes in the triclinic system with the following crystal data: a = 11.279 (3), b = 17.593 (5), c = 10.428 (1) Å; α = 101.59 (3), β = 93.52 (6), γ = 91.69 (2)°; space group $P\bar{1}$; Z = 2. The density, 1.37 (2) g cm^{-3} at 23°, measured by flotation in aqueous KBr, corresponds to ρ_{calcd} = 1.385 g cm^{-3}. Single-crystal x-ray diffraction data were collected on a Datex-automated General Electric diffractometer using monochromatic Mo Kα radiation at room temperature; the structure was determined using 2871 reflections with intensities $I \geq 3\sigma(I)$, and phased by both heavy atom techniques and direct methods (MULTAN). A three-dimensional electron density map revealed the locations of all 55 nonhydrogen atoms in the asymmetric unit. Refinement was carried out using group parameters for the phenyl rings of the PPN^+ cation (rigid body approximation); positions of the 40 hydrogen atoms were calculated and were not refined. Anisotropic full-matrix least-squares refinement



1·⁻

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