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Chemical and Electrochemical Reduction of η^5-Cyclopentadienyldicarbonylcobalt(I) and η^5-Cyclopentadienyl(triphenylphosphine)carbonylcobalt(I). Synthesis, Crystal and Molecular Structure, and Chemistry of Sodium and Bis(triphenylphosphine)iminium Bis(η^5-cyclopentadienyl)di-μ-carbonyl-dicobaltate, a Binuclear Cobalt Radical Anion

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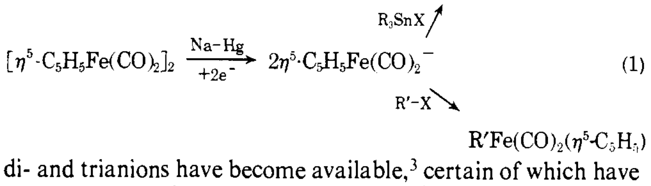
Abstract: Reduction of η^5-$C_5H_5Co(CO)_2$ (**1**) in THF at room temperature under air- and water-free conditions gave $NaCo(CO)_4$ and a new pyrophoric binuclear paramagnetic complex, $Na^+[(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2]\cdot^-$ (Na^+**3**$\cdot^-$). IR studies show that the new material is contact ion-paired in THF, but exists as dissociated ions (or perhaps solvent-separated pairs) in HMPT or THF containing 18-crown-6. An air-stable crystalline salt of **3**$\cdot^-$ was obtained by exchanging Na^+ for $(PPh_3)_2N^+$, and its structure was determined by x-ray diffraction methods. This revealed an unusually short Co-Co bond in **3**$\cdot^-$, consistent with both MO and valence bond predictions of partial double bond character. In agreement with this picture, it was found that **3**$\cdot^-$ could be oxidized to $[(\eta^5\text{-}C_5H_5)Co(CO)]_2$, which presumably has a full Co-Co double bond. Reduction of $(\eta^5\text{-}C_5H_5)$-$Co(CO)PPh_3$ (**8**) occurred more slowly than did reduction of **1**, giving a dark (presumably oligomeric) cobalt complex. This material also led to $NaCo(CO)_4$ and **3**$\cdot^-$ upon carbonylation.

The reduction of transition metal carbonyl complexes provides access to a number of interesting anionic organometallic species.[2] Monoanions such as $Co(CO)_4^-$ and η^5-$C_5H_5Fe(CO)_2^-$ have shown considerable utility in the preparation of compounds with metal–metal and metal–carbon bonds (e.g., eq 1). More recently, synthetic routes to a few organometallic di- and trianions have become available,[3] certain of which have proven very useful in organic synthesis.[4]



$$\begin{tikzcd}[column sep=small] & & R_3SnFe(CO)_2(\eta^5\text{-}C_5H_5) \\ {[\eta^5\text{-}C_5H_5Fe(CO)_2]_2} \arrow[r, "Na-Hg", "+2e^-"'] & 2\eta^5\text{-}C_5H_5Fe(CO)_2^- \arrow[ur, "R_3SnX"] \arrow[dr, "R'-X"'] & \\ & & R'Fe(CO)_2(\eta^5\text{-}C_5H_5) \end{tikzcd} \quad (1)$$

Singly charged anionic metal carbonyl complexes are generally prepared by reduction of neutral binuclear complexes (e.g., $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$). The few low-valent polyanionic metal carbonyls known have been obtained by reduction of neutral mononuclear precursors (e.g., $Fe(CO)_5 \rightarrow Fe(CO)_4^{2-}$). Little information is available, however, on the reduction chemistry of mononuclear organometallic carbonyl complexes which are relatively CO deficient. One might expect that in such cases either (a) reduction itself will be very slow, (b) reduction will occur at a reasonable rate but the reduced species will undergo chemical reaction before the dianionic stage is reached, or (c) an extremely reactive dianion might be formed. In order to determine which of these possibilities was most likely in a specific case, we investigated the chemical reduction of η^5-$C_5H_5Co(CO)_2$ and η^5-$C_5H_5Co(CO)PPh_3$. This paper reports the details of our experiments.[5]

Results and Discussion

Reduction of η^5-Cyclopentadienyldicarbonylcobalt (1). The reduction of η^5-cyclopentadienyldicarbonylcobalt (**1**) may be effected using sodium metal or sodium amalgam in a variety of solvents. Treatment of an 0.019 M solution of **1** in hexamethylphosphoric triamide (HMPT) with aliquots of a freshly prepared 0.031 M solution of Na in HMPT causes a decrease in the intensity of the carbonyl IR bands of **1** at 1955 and 2020 cm^{-1}, and the appearance of two new bands at 1690 and 1890 cm^{-1} (Figure 1). The reaction is over within minutes, and the starting material is completely consumed by approximately 0.6 equiv of Na. A similar transformation takes place in acetonitrile, using 0.74% sodium amalgam (Na–Hg) as the reductant.

Reduction of a 2.2 M solution of **1** in tetrahydrofuran (THF) with 0.74% Na–Hg leads to a heterogeneous mixture

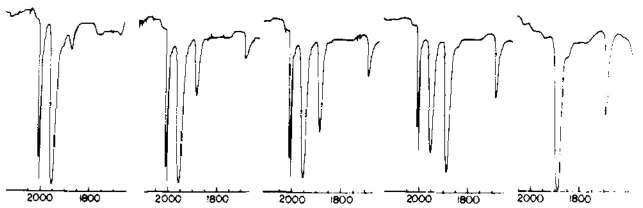


Figure 1. IR spectra taken during reduction of η^5-$C_5H_5Co(CO)_2$ (1) by addition of successive amounts of sodium in HMPT to a solution of 1 in HMPT. In the sequence of spectra shown, reading from left to right, the mole ratio of sodium to the initial amount of 1 is 0.06, 0.2, 0.3, 0.4, and 0.6.

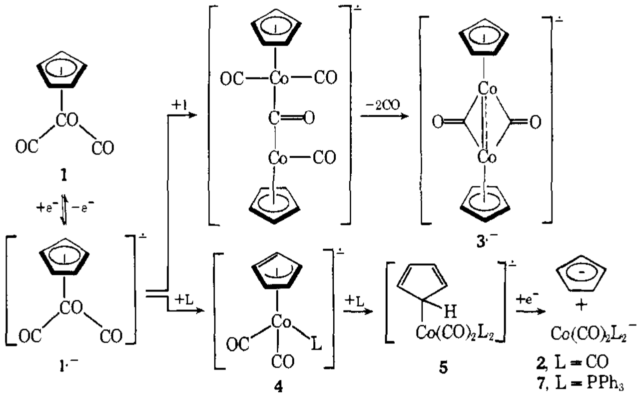
displaying IR bands at 1897 (vs), 1889 (vs), 1855 (s), 1740 (m), 1690 (m), and 1660 (s) cm^{-1}. From this mixture is obtained one fraction, soluble in 3:2 petroleum ether–THF, possessing only the 1897, 1889, and 1855 cm^{-1} IR absorptions (see Experimental Section). Removal of solvent yields an off-white solid which, when dissolved in either HMPT or THF containing a small amount of 18-crown-6, displays only a single carbonyl absorption at 1890 cm^{-1}, behavior identical with that reported[6] for $NaCo(CO)_4$ (**2**). Derivatization to form the known[7] compounds $Hg[Co(CO)_4]_2$ and $[(PPh_3)_2N]Co(CO)_4$ confirmed this assignment.

The remaining material from the reduction of **1** in THF consists of small amount of black, THF-insoluble residue, and a moderately soluble greenish yellow solid exhibiting carbonyl absorptions at 1740, 1690, and 1660 cm^{-1} in THF, and 1690 cm^{-1} alone in HMPT. This green complex, which is isolated as a THF solvate contaminated with substantial amounts of sodium cyclopentadienide, has been characterized as the sodium salt of the binuclear radical anion $Cp_2Co_2(CO)_2\cdot^-$ [**3**$\cdot^-$] (vide infra). The yields of **2** and **3**$\cdot^-$ are 23 and 65%, respectively.

Because **2** has no proton NMR spectrum and **3**$\cdot^-$ is paramagnetic, attempts to follow the reduction reaction by proton NMR were not very useful. It was interesting, however, that although the formation of **2** requires loss of the cyclopentadienyl ligand from **1**, the usual sharp cyclopentadienyl anion (Cp^-) resonance[8] was not observed in the THF reduction. A simple control experiment was run by preparing Cp^- independently from cyclopentadiene and sodium in THF; this demonstrated that the sharp Cp^- line[8] was clearly observable at the concentration expected in the reduction experiment. However, when this pure Cp^-/THF solution was *mixed* with a solution of freshly reduced $CpCo(CO)_2$ in THF, the sharp line disappeared. Careful examination of the NMR spectrum revealed a very broad absorption centered at a position 1.2 ppm upfield from the sharp resonance of benzene (added as internal standard). Addition of further aliquots of Cp^-/THF to the reduction solution caused this absorption to gradually sharpen and move toward the chemical shift of pure Cp^- in THF; at very high ratios of Cp^- to reduction products, the line was clearly observed but was still not as sharp as that for pure Cp^-. We assume from these observations that Cp^- undergoes rapid and reversible electron transfer with some paramagnetic component of the reduction mixture (perhaps **3**$\cdot^-$), and this results in paramagnetic broadening of the normally sharp Cp^- NMR resonance. In acetonitrile this electron transfer reaction is apparently not quite so rapid, and a somewhat broadened line due to Cp^- may be observed in modest yield as the reduction reaction proceeds.

Cyclic voltammetric measurements on solutions of **1** in CH_3CN show reversible waves at −0.06 and −2.14 V, relative to Ag|AgClO$_4$ (rest potential −0.33 V), corresponding to oxidation to **1**$^+$, and reduction to **1**$\cdot^-$, respectively. We therefore feel that a likely first step in the chemical reduction of **1** is formation of the formal 19-electron complex **1**$\cdot^-$ which possesses a highly nucleophilic cobalt center capable of attacking another molecule of **1**, but which is also ultimately unstable toward loss of the weakly π acidic cyclopentadienyl ring. Scheme I summarizes our hypotheses regarding the two pathways leading to **2** and **3**. Attack of **1**$\cdot^-$ on a carbonyl ligand of **1** seems more reasonable than initial cobalt–cobalt bond formation, by analogy with known reactivity patterns of nucleophiles with metal carbonyls;[9] the details of the subsequent steps that lead to **3**$\cdot^-$ are speculative, but quite reasonable in requiring dissociation of CO from only *neutral*, and not *anionic* cobalt centers.[10]

Scheme I



The loss of the η^5-ring may be viewed as proceeding via stepwise loss of the ring from formal 19-electron cobalt centers like **1**$\cdot^-$ to give formal 17-electron species capable of being trapped by external ligands (Scheme I). In support of this hypothesis, we have found that slow addition of **1** to a mixture of 0.74% Na–Hg in THF containing a large excess of $(C_6H_5)_3P$ results predominantly in the formation of $NaCo(CO)_3PPh_3$ (**6**) and $NaCo(CO)_2(PPh_3)_2$ (**7**); i.e., the formation of both **2** and **3**$\cdot^-$ is strongly suppressed by addition of the external ligand. In control experiments we have found that **3**$\cdot^-$ is completely unreactive toward $(C_6H_5)_3P$ either in the presence or absence of 0.74% Na–Hg, and **1** reacts only slowly with $(C_6H_5)_3P$ under these conditions giving η^5-$C_5H_5Co(CO)(C_6H_5)_3P$, whose reduction by 0.74% Na–Hg is very slow and gives very little **7** and no **6**. The latter experiments have, in addition, demonstrated that species like η^5-$C_5H_5CoCO\cdot^-$ are unlikely to be involved in the reduction of **1** (vide infra); i.e., the loss of CO from anion **1**$\cdot^-$ is strongly disfavored relative to loss of the ring.

Characterization of $Cp_2Co_2(CO)_2\cdot^-$ (3$\cdot^-$). The major product from the reduction of **1** is a greenish yellow microcrystalline solid, pyrophoric upon exposure to air, but indefinitely stable at room temperature under an atmosphere of purified nitrogen. Solutions of **3**$\cdot^-$ in THF display IR bands at 1740 (m, broad), 1690 (m, sharp), and 1660 (s, broad) cm^{-1}; addition of small amounts of petroleum ether causes the band at 1690 cm^{-1} to diminish in intensity, while treatment of the THF solution with 18-crown-6 has the opposite effect, enhancing the 1690 cm^{-1} absorption relative to the other two (Figure 2). This behavior, together with the observation of only a single carbonyl band at 1690 cm^{-1} in HMPT, supports the contention that the bands at 1740 and 1660 cm^{-1} are due to a sodium-ion paired species,[6] while the free anion is responsible for the single, sharp peak at 1690 cm^{-1}. This anion has been crystallized as an air stable salt by addition[7b] of excess solid $[P(C_6H_5)_3]_2NCl(PPN^+Cl^-)$ to a saturated solution of the sodium salt in THF. The IR spectrum of the solution shows rapid conversion to a single carbonyl band at 1690 cm^{-1} as granular NaCl precipitates. Filtration of this solution followed by removal of ca. 90% of the solvent in vacuo produces a supersaturated solution from which the PPN^+ salt of **3**$\cdot^-$ is slowly deposited as large, well-formed, prismatic crystals, deep orange-red in color, and indefinitely stable in the air at room temperature.

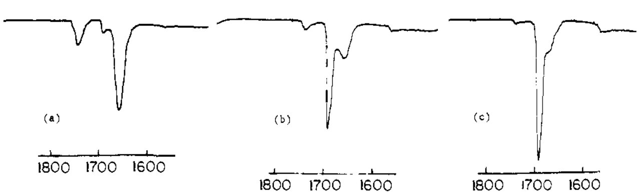


Figure 2. IR spectra of $Na^+[(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2]^{\cdot -}$ in THF in the presence of varying amounts of 18-crown-6: (a) 0.0 equiv of crown ether added; (b) 0.5 equiv; (c) 0.75 equiv.

Table I. Cobalt-Cobalt Bond Distances[a] in Selected Organometallic Compounds

Compound	Co-Co distance, Å
$Co_2(CO)_8$	2.52
$Co_3(CO)_9CCH_3$	2.47
$Co_4(CO)_{12}$	2.49
$Cp_3Co_3(CO)_3$	2.44, 2.46
$Cp_4Co_4H_4$	2.47

[a] Data taken from ref 13.

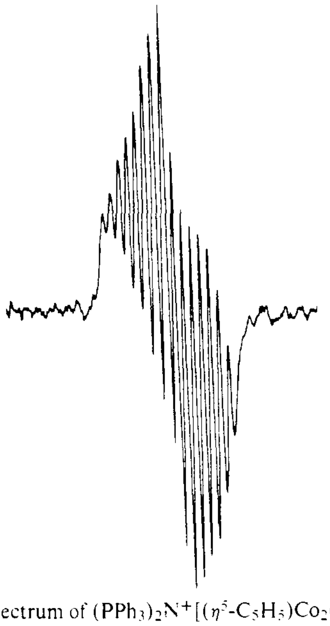


Figure 3. ESR spectrum of $(PPh_3)_2N^+[(\eta^5\text{-}C_5H_5)Co_2(CO)_2]^{\cdot -}$ in THF solution at room temperature.

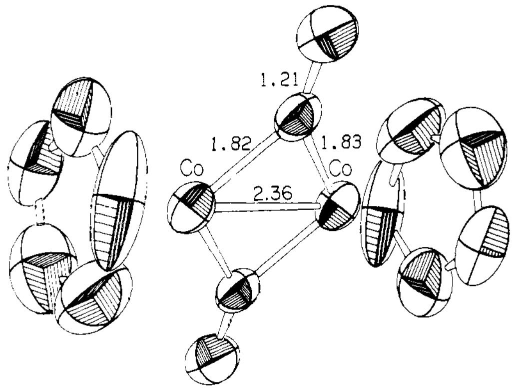


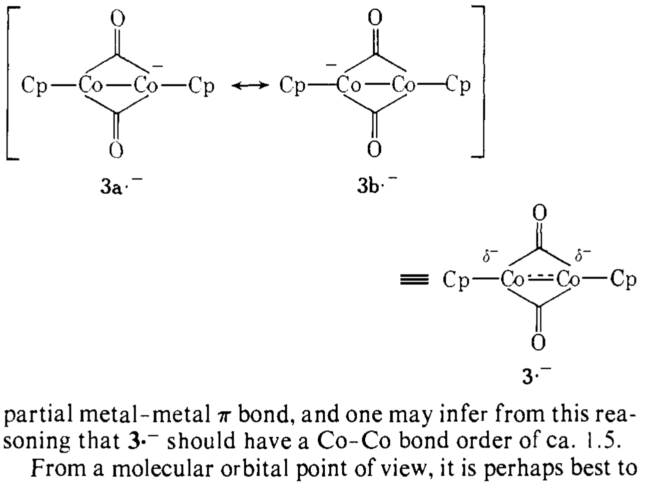
Figure 4. ORTEP drawing of the molecular structure of $[\eta^5\text{-}C_5H_5Co\text{-}CO]_2^{\cdot -}$, determined by x-ray diffraction on the bis(triphenylphosphineiminium) salt.

NMR analysis of this salt shows only a broad absorption centered about δ 7.55 ppm due to the hydrogens of the PPN+ cation. Inasmuch as oxidative decomposition of the sodium salt of **3**·− is always accompanied by an intense odor characteristic of **1**, the lack of any NMR signal due to cyclopentadienyl hydrogens suggested to us the possibility that the anion was paramagnetic. Indeed, magnetic susceptibility measurements using both the Gouy balance method and the NMR shift method of Evans[11] confirmed the paramagnetic nature of **3**·−, and gave values of $\mu_{\text{eff}} = 1.69 \pm 0.1\ \mu_B$, corresponding to 0.98 ± 0.08 unpaired electrons per unit of 842 molecular weight (corresponding to the formula $PPN^+Cp_2Co_2(CO)_2^{\cdot -}$). Solutions of either the sodium or PPN+ salts of **3**·− in THF at room temperature display symmetrical 15-line ESR spectra (Figure 3) centered at roughly 3100 G with $a_0 = 50$ G, indicative of an unpaired electron delocalized over two cobalt atoms ($I = \frac{7}{2}$).

The molecular structure of **3**·−, was determined by x-ray crystallography on the PPN+ salt (Figure 4); details of the structure determination are presented in the Experimental Section. The structure shows two crystallographically distinct anions, located at centers of inversion (½, 0, 0) and (½, ½, ½). The cobalt atoms and bridging carbonyl groups are coplanar to better than ±0.01 Å in each anion, and the Co–Co distances are 2.372 (2) and 2.359 (2) Å in the two distinct **3**·− units. Other important dimensions are a range of 1.80–1.84 (2) Å for the Co- - -carbonyl carbon distances, and 2.05–2.12 (2) Å for the Co- - -cyclopentadienyl carbon distances. All the PPN+ cations are crystallographically identical, with unremarkable geometries (in particular, the P–N–P angle is 142.1 (7)°, in accord with all but one[12] of the reported structures for PPN+ salts).

Perhaps the most interesting feature of the structure of **3**·− is its very short metal-metal bond distance, relative to other di-, tri-, and tetranuclear cobalt complexes (Table I) whose structures have been determined.[13] This suggests strongly that there is significant multiple-bond character in this interaction, and a number of ways of thinking about the structure of **3**·− support this inference. A simple valence-bond picture of **3**·− is shown in Scheme II. Structure **3a**·− contains one 18- and 17-electron cobalt atom. However, it is clear from both x-ray structure and ESR spectrum that the unpaired electron is shared equally by both cobalt atoms, and so **3b**·− must contribute equally to the total structure of **3**·−. This delocalization of the extra electron is clearly just another way of writing a partial metal-metal π bond, and one may infer from this reasoning that **3**·− should have a Co-Co bond order of ca. 1.5.

Scheme II



3a·− **3b**·− **3**·−

From a molecular orbital point of view, it is perhaps best to look at the structure in relation to its oxidized relative **3**, which should in principle be obtainable by removal of one electron from **3**·− (see below for experiments designed to carry out this transformation). In order to make the neutral complex fit the 18-electron rule, a metal-metal double bond is needed. Support for this picture may be obtained from a qualitative molecular

Scheme III

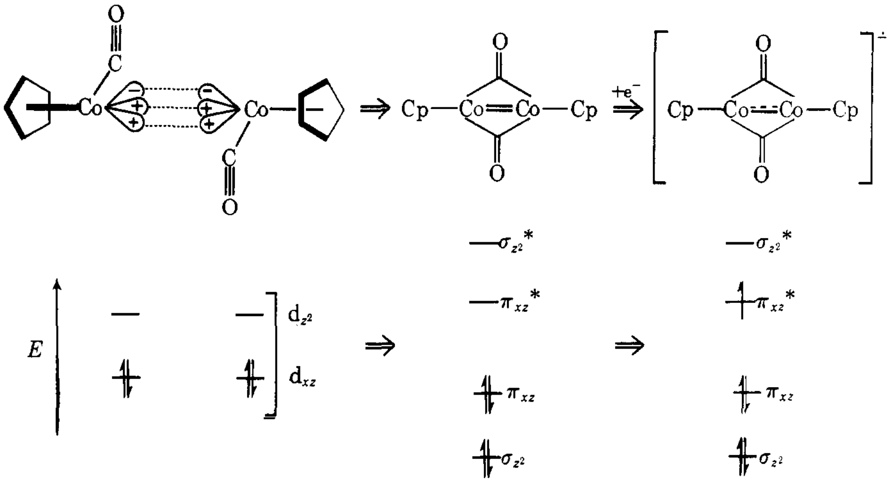


Table II. Electronic Absorption Spectroscopy of PPN$^+$**3**·$^-$ in THF

λ_{max} (±5 nm)	ε (±20%)
325	4000
375	6000
720	50
850	(shoulder)
1195	50

orbital analysis by examining the interaction of two 16-electron CpCoCO "fragments"[14] in such a way as to form the neutral complex **3** (Scheme III; for clarity, only cobalt-directed lobes of d orbitals are illustrated). Inspection of the types of orbital energy changes involved in this process reveals that the d orbitals interacting most strongly with the organic ligands should be the d_{yz}. This leaves one lobe of each d_{z^2} orbital free to form a σ-type metal-metal bond and the two d_{xz} orbitals may interact to form π and π* d-d molecular orbitals, with two electrons placed in the π orbital. The radical anion **3**·$^-$ may then be formed by adding another electron to the *delocalized* d-d π* molecular orbital.

Valence bond formulas such as **3a**·$^-$ and **3b**·$^-$ may be thought of as "mixed valence" structures, since each has one cobalt atom in a formal + 1 and the other in a formal zero oxidation state. The x-ray and ESR data clearly place **3**·$^-$ in the "class III" or completely delocalized category of mixed valence complexes,[15] and thus it is probably most reasonable to think of each metal atom as formally "Co (+½)". A variety of electronic transitions in the visible and near-infrared is observed in THF solutions of **3**·$^-$ (Table II), including a long-wavelength band at 1195 nm. Although the presence of bands in this region in class II mixed valence organometallic complexes has in several cases been assigned to optically induced electron transfer processes,[15b] strong near-IR bands have also been observed in other class III complexes.[15d] In any case, we have found that crystals of **3**·$^-$ are semiconductors; the large distance between anionic units in the crystal would probably make this complex a poor candidate for conductivity even if it were in the class II category.

We have also probed the solid-state electronic distribution of **3**·$^-$ using the ESCA (x-ray photoelectron spectroscopy) technique. A film of PPN$^+$ **3**·$^-$ adsorbed on gold, evaporated from a THF solution, displays signals at binding energies listed in Table III. For comparison, ESCA data for two other cobalt compounds and several related organometallic species are also listed. The most significant findings in this study are (a) that the cobalt atoms display only one set of signals and therefore appear to be electronically equivalent in this system, and (b) the oxygen and, to a smaller extent, cobalt binding energies are somewhat lower in **3**·$^-$ than in the model compounds, indicative of excess negative charge density on these atoms.

Chemistry of $Cp_2Co_2(CO)_2\cdot^-$. As mentioned previously, **3**·$^-$, either in solution or as the solid sodium salt, is exceptionally sensitive toward attack by atmospheric oxygen. Careful monitoring of this oxidation by IR shows **1** to be the sole carbonyl-containing product formed upon extended exposure of solutions of **3**·$^-$ to air. However, a weak transient absorption at 1790 cm^{-1} may be observed upon brief exposure of **3**·$^-$ to small amounts of air. The material responsible for this peak is itself air-sensitive and decomposes to **1** upon further air oxidation.

Lee and Brintzinger have found neutral **3** to be one of the products of the photolysis of **1** at low temperature under nitrogen sweep.[17] We find that oxidation of **3**·$^-$ to **3** may be effected under a wide variety of conditions. Cyclic voltametric measurements on solutions of **3**·$^-$ in CH_3CN display a reversible oxidation wave at −1.05 V (vs. Ag|AgClO$_4$, rest potential −1.20 V). Preparative experiments were attempted at a potential of −0.50 V; initially, the yellow solution of **3**·$^-$ acquired a turquoise color characteristic of neutral **3**, but the color gradually faded before the theoretical amount of current was absorbed, indicating decomposition had taken place.

Preparative chemical oxidation is more successful. A number of reagents readily oxidize **3**·$^-$ to **3**, but the reaction is always accompanied by formation of some **1**, and the isolation of completely pure **3** has not yet been accomplished on a large scale. Of the reagents tried, chloranil, CuCl, and elemental sulfur give poor yields of **3**, contaminated by other materials. Other metal ion oxidants, like $FeCl_3$ and Tl_2SO_4, give higher yields of **3**, but still present problems with regard to separation from other materials. Oxidation of the sodium salt of **3**·$^-$ with $FeCl_3$ in THF gives a high yield of **3**, but a simultaneous reaction of $FeCl_3$ with the sodium cyclopentadienide contaminant in crude **3**·$^-$ yields ferrocene, which has proven to be difficult to remove under conditions that do not decompose the cobalt dimer. However, samples of **3** containing relatively small amounts of impurities, pure enough to allow examination of the chemical behavior of this complex, have been obtained.

Neutral **3**, being a highly unsaturated, formally multiply bonded species, is attacked rapidly by CO and triphenylphosphine, yielding $CpCo(CO)_2$ and $CpCo(CO)(PPh_3)$, respectively. Curiously, it possesses considerable stability in the presence of such potential ligands as 1-hexene, acetonitrile, THF, and water. A slow reaction takes place between **3** and acetylenes, but the products have not as yet been identified.

Complex **3**$^-$ is stable indefinitely towards further reduction

Table III. ESCA Signals for Several Organometallic and Inorganic Materials[a] All Calibrated to Organic C_{1s} = 284.9 eV

Compound	C_{1s} (C_5H_5)	C_{1s} (CO)	O_{1s}	$M_{2p1/2}$	$M_{2p3/2}$
CO		290.5 (290.6)	536.7 (535.8)		
$Ni(CO)_4$		288.8	536.4	876.4	859.2
$(C_5H_5)_2Ni$	285.5			874.9	857.7
$(C_5H_5)Mn(CO)_3$	286.4 (285.2)	288.4 (287.0)	535.6 (532.9)	654.4	643.4 (640.8)
$(C_5H_5)_2Co$	285.7 (284.6)			797.5	782.2 (779.3)
PPN^+**3**$\cdot^-$	*b*	291.8	530.5	795.6	779.9
$CoCl_2$				800.0	784.0

[a] Data taken from references in footnote 16. Where values from two sources do not precisely agree, the second value is listed in parentheses in the table. [b] Presumably hidden under signal for PPN^+ phenyl groups at 284.9 eV. Error limits ±0.2 eV except for O_{1s} and $M_{2p1/2}$, ±0.6 eV.

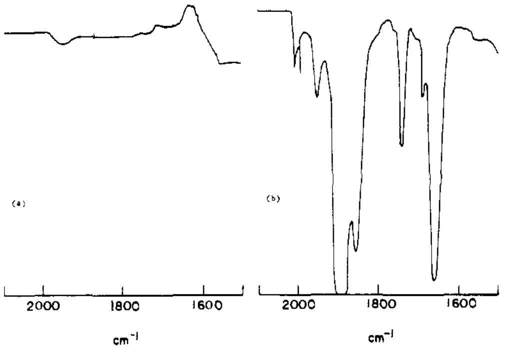


Figure 5. (a) IR spectrum of a suspension of the black, insoluble product of the reduction of **8** in THF; (b) same solution, after 5 min of treatment with gaseous CO.

by 0.7% Na-Hg, but is destroyed rapidly by 40% Na-Hg, yielding NaC_5H_5 as the only identifiable product. At early stages of the reaction, a transient IR band at 1630 cm^{-1} appears, consistent with what one might expect from a dianion such as 3^{2-}. Supporting this hypothesis is the observation that brief exposure of this partly reduced solution to air regenerates bands due to **3**$\cdot^-$ while causing the 1630-cm^{-1} band to disappear.

Reduction of η^5-Cyclopentadienyltriphenylphosphinecarbonylcobalt (8). Treatment of a THF solution 0.04 M in **8** with excess 0.74% Na-Hg leads to very slow disappearance of the infrared carbonyl band of the starting material at 1930 cm^{-1}; a qualitatively similar but more rapid reaction takes place when 40% Na-Hg is used as the reducing agent. Complete disappearance of IR and NMR signals due to starting material requires approximately 12 h at room temperature and is accompanied by the precipitation of a substantial amount of black solid. The only new NMR signal observed is that of free triphenylphosphine, formed in essentially quantitative yield. Infrared spectroscopy indicates the formation of radical anion **3**$\cdot^-$ in low yield as well as the presence of very small amounts of unidentified materials having carbonyl absorptions at 1840 and 1875 cm^{-1}. Reduction with Na/HMPT proceeds similarly, but at a more rapid rate, again yielding a material with an IR absorption at 1875 cm^{-1}, as well as **3**$\cdot^-$

Partial characterization of these cobalt-containing products has been achieved. The black precipitate obtained in greater than 80% yield from the reduction of **8** by 40% Na-Hg in THF shows no IR absorptions above 1590 cm^{-1} (Nujol) and is not soluble enough in any common solvents for NMR analysis. It contains mostly carbon, hydrogen, cobalt, and sodium by elemental analysis (small amounts of mercury, phosphorus, and, presumably, oxygen, are also present), but the ratios do not correspond to any simple stoichiometry. Remarkably, however, a suspension of this material in THF becomes nearly homogeneous upon exposure to gaseous CO; the resultant solution shows weak IR bands characteristic of **1**, and intense bands due to the presence of *both* **2** and **3**$\cdot^-$ (Figure 5).

The remaining cobalt-containing product from the reduction of **8** is a THF-soluble material with a broad carbonyl IR band at 1875 cm^{-1}, isolated in very low yield, contaminated with triphenylphosphine. This material is also highly reactive toward CO, being converted to a mixture containing predominantly **6**, mixed with small amounts of **1**, **2**, and **8**. This mixture may contain the sodium salt of $Co(CO)_2[P(C_6H_5)_3]_2^-$ (**7**), which we have also found to be converted readily to **6** and **2** by CO. The small quantities isolated in these experiments were insufficient for unequivocal characterization.

Conclusion

The results of this study show that although the ease of reduction of a cobalt(I) metal carbonyl complex depends upon the number of carbonyls bound to the metal, two bound CO molecules are sufficient to promote relatively rapid electron transfer from sodium amalgam to the cobalt atom at room temperature. Unlike systems containing additional CO molecules, however, subsequent chemical reaction of the singly reduced species is rapid enough (or addition of a second electron is slow enough) that the dianionic stage is not reached, and the products we observe are all adequately rationalized as arising from one-electron reduction processes.

It is interesting that the intermolecular reaction which in the case discussed here leads to **3**$\cdot^-$ has an interesting analogy in even-electron systems. That is, it is often possible to generate a reactive (although electron-deficient) species by dissociation of a ligand from an 18-electron substrate (e.g., eq 2),

$$Fe(CO)_5 \xrightarrow{h\nu} Fe(CO)_4 \xrightarrow{Fe(CO)_5} Fe_2(CO)_9 \qquad (2)$$

which forms a dimer by attacking a second molecule of starting material. Our results demonstrate that it is possible, using reduction techniques, to generate a paramagnetic electron-*rich* species which also finds a way to stabilize itself chemically via attack upon starting material. In addition, we have found that the paramagnetic binuclear species so produced (**3**$\cdot^-$) may partake of partial double bonding to reach an effective 18-electron (and therefore relatively stable) configuration about each metal.

Experimental Section

General Techniques. All manipulations were carried out in a Vacuum Atmospheres inert atmosphere box under N_2, prescrubbed and continuously circulated through a purifier to maintain an atmosphere containing less than 1 ppm O_2 and H_2O. For use in the drybox, THF was vacuum transferred from sodium-benzophenone. η^5-Cyclopentadienyldicarbonylcobalt (**1**) was obtained from Strem Chemical Co., filtered before use, and shown by NMR to contain no detectable impurities. Petroleum ether and benzene were washed several times with concentrated H_2SO_4 and several times with water, dried over $CaSO_4$, and treated with a solution of sodium-benzophenone in tetraglyme prior to vacuum transfer. HMPT and Me$_2$SO were distilled from CaH$_2$ at reduced pressure and thoroughly degassed. Bis(triphenylphosphine)iminium chloride and 18-crown-6 were used as received. Deuterated solvents for NMR (Varian A-60-A instrument) were obtained in vials, sealed under N$_2$, and used without further purification. NMR samples of air-sensitive materials were prepared in the drybox using standard sample tubes with tight-fitting plastic caps. IR samples (Perkin-Elmer 257 instrument) were similarly prepared using solution cells with Teflon stoppers. Air-oxidation due to leakage was not found to be a problem during the measurement of either NMR or IR spectra. Elemental analyses were performed by Caltech and/or Galbraith microanalytical laboratories.

Reduction of η^5-Cyclopentadienyldicarbonylcobalt (1) with Na in HMPT. A solution of 17 mg (0.094 mmol) of **1** in 5 mL of HMPT was treated with 0.1-mL aliquots of a solution of 6.5 mg (0.282 mmol) of Na in 5 mL of HMPT. The reaction was monitored by IR spectroscopy (1600-2100 cm^{-1}), and was complete upon addition of 1.0 mL (0.056 mmol) of Na-HMPT. Only two carbonyl bands, at 1690 and 1890 cm^{-1}, in an intensity ratio of ~1:3, were present.

Reduction of 1 with Dilute Na-Hg in CH$_3$CN. A solution containing 130 mg of **1**, 30 μL of C$_6$H$_6$, and 1.5 mL of CH$_3$CN was prepared in an NMR tube and spectra were recorded before and after addition of 0.74% Na-Hg. The initial spectrum displayed absorptions at δ 5.05 due to **1** and δ 1.85 due to CH$_3$CN, relative to C$_6$H$_6$ at δ 7.27 ppm. Subsequent spectra, taken after addition of amalgam with shaking, showed a new peak at δ 5.68 appearing as **1** was consumed. The intensity of this new signal, later shown to be due to cyclopentadienide anion by addition of authentic sodium cyclopentadienide to the solution, was estimated to be 25% relative to consumed **1**.

Preparative-Scale Reduction of 1 with Dilute Na-Hg in THF. Under scrupulously air- and water-free conditions (Vacuum Atmospheres inert atmosphere box, N$_2$ atmosphere), 10.0 g (56 mmol) of **1** was added all at once to a rapidly stirred mixture of 50 mL of 0.74% Na-Hg (217 mmol of Na) and 25 mL of THF. The mixture, originally deep red in color, began to froth and within 0.5 h had deposited a substantial amount of very dark green solid. Infrared analysis at this point showed complete absence of **1** (carbonyl bands at 1955 and 2020 cm^{-1}), and a number of new bands spanning the 1650-1900-cm^{-1} region (see Results and Discussion). The soluble products from this reaction were isolated by stirring the mixture with 12 150-mL portions of THF, each for 2 h. Each of these THF solutions was decanted away from undissolved solid and filtered under suction through a coarse fritted funnel and then through a medium fritted funnel. Eventually only a small amount of insoluble black solid remained, along with the unreacted Na-Hg. The combined filtrates were removed from the drybox in round-bottom flasks fitted with vacuum stopcocks, and solvent was removed by vacuum transfer such that the total volume of THF remaining was roughly 150 mL. (It is convenient to do these vacuum transfers on several portions of the filtered extracts as they are obtained rather than on the entire volume at once; in addition, these solutions must be protected from any exposure to oxygen as the materials they contain are pyrophoric.)

A large amount of green solid was isolated by filtration after the material obtained from vacuum transfer was returned to the drybox. This solid was washed with 2 × 100-mL 3:2 petroleum ether:THF mixture. The filtrates were combined for subsequent workup and isolation of NaCo(CO)$_4$. The green solid amounted to 10.7 g and displayed IR bands in THF at 1660 (s, broad), 1690 (m, sharp), and 1740 (m, broad) cm^{-1}. NMR analysis of a weighed sample in CH$_3$CN (benzene as internal quantitative standard) showed that the solid contained approximately 10% NaC$_5$H$_5$ and 35% THF, by weight. The remaining 55% corresponds to 5.9 g, or 65% yield, of Na[(C$_5$H$_5$)$_2$Co$_2$(CO)$_2$], **3**$^{\cdot-}$.

Isolation and Identification of NaCo(CO)$_4$ (2). The combined filtrates from the purification of **3**$^{\cdot-}$ were refiltered to remove additional precipitated **3**$^{\cdot-}$. Removal of solvent by vacuum transfer left a black oily semisolid from which the remaining **3**$^{\cdot-}$ could be removed by trituration with 2:1 petroleum ether:THF, filtration, and removal of solvent. The product slowly solidified upon storage under nitrogen to yield 2.4 g (23% yield) of an off-white solid, IR (THF) 2005 (v wk), 1897 (vs), 1889 (vs), and 1855 (m) cm^{-1}, identical with the spectrum reported[6] for NaCo(CO)$_4$. Addition of either 18-crown-6 or [(C$_6$H$_5$)$_3$P]$_2$NCl to a THF solution of **2** or dissolution of the solid in HMPT gave solutions displaying a single carbonyl stretch at 1890 cm^{-1}.

The structure of **2** was confirmed by derivatization. A 100-mg sample of **2** was treated with 0.5 mL of water, 0.5 mL of NH$_4$Cl, and 2 mL of 3.5% (w/v) aqueous HgCl$_2$ under an argon blanket. The dark yellow precipitate was filtered off, washed with 2 × 2 mL of water, 2 mL of 5% aqueous HCl, and 2 mL of water, and dried in a desiccator for 30 min. Recrystallization at 0 °C from aqueous acetone yielded golden-yellow needles (mp 80-81 °C; IR (CCl$_4$) 1962 (w), 2008 (vs), 2025 (m), 2074 (vs) cm^{-1}) identical with that reported[7a] for Hg[Co(CO)$_4$]$_2$.

A second sample of **2** weighing 185 mg was dissolved in 10 mL of THF and treated with enough PPNCl to completely convert the carbonyl region of the IR to a single band at 1890 cm^{-1}. Removal of half the solvent in vacuo and layering of the resultant solution with petroleum ether yielded 670 mg (97% yield) of PPNCo(CO)$_4$, mp 186-188 °C (lit.[7b] mp 185-187 °C).

Bis(triphenylphosphine)iminium Bis(η^5-cyclopentadienyl)di-μ-carbonyl-dicobaltate, PPN$^+$3$^{\cdot-}$. A mixture of 155 mg of crude solid Na[(C$_5$H$_5$)$_2$Co$_2$(CO)$_2$] and 326 mg of PPNCl[18] was treated with 15 mL of THF and stirred for 2 h. IR of the solution showed 1660 (wk, shoulder), 1690 (vs), and 1740 (v wk) cm^{-1}; addition of additional PPNCl caused no further change. The solution was filtered through a coarse fritted funnel to remove precipitated NaCl and excess PPNCl. Careful concentration to a volume of 1.5 mL produced a supersaturated solution from which deep orange-red crystals of PPN[(C$_5$H$_5$)$_2$Co$_2$(CO)$_2$] spontaneously separated over a period of hours in the drybox under N$_2$. The crystals were quickly washed with several small portions of THF and separated from the solvent by decantation. Recrystallization by dissolution in 15 mL of THF (dissolves very slowly), filtration, concentration in vacuo, and storage under N$_2$ gave crystalline material suitable for all spectroscopic and analytical characterization.

Anal. Calcd for C$_{48}$H$_{40}$Co$_2$P$_2$NO$_2$: C, 68.42; H, 4.75; Co, 13.99; P, 7.37; N, 1.66. Found: C, 66.92; H, 4.80; Co, 13.58; P, 7.38; N, 1.83.

Solutions of this material are rapidly air oxidized; the crystalline solid, however, appears to be stable indefinitely in air at room temperature; mp >200 °C w/dec.

Oxidation of PPN$^+$3$^{\cdot-}$. To a solution of 0.76 g (0.9 mmol) of PPN$^+$**3**$^{\cdot-}$ in 250 mL of THF was added a solution of 0.15 g (0.9 mmol) of anhydrous FeCl$_3$ in 60 mL of THF, dropwise, over a period of 6 h. The extremely slow addition was necessary to minimize overoxidation to **1**. At the conclusion of the addition, IR analysis showed an absorption at 1790 cm^{-1}, corresponding to neutral, dimeric **3**, with an intensity approximately four times that of the peaks at 1955 and 2020 cm^{-1}, due to **1**. All but 25 mL of solvent was removed from this solution by vacuum transfer; treatment with 75 mL of petroleum ether and filtration gave a solution containing only **1** and **3** by IR. Removal of volatile material in vacuo left deep blue **3** as a slightly gummy solid, IR 1790 cm^{-1} in THF and 1805 cm^{-1} in petroleum ether. This material may be sublimed under high vacuum, but the sublimation does not substantially improve the purity.

Reduction of η^5-Cyclopentadienyltriphenylphosphinecarbonylcobalt (8) with 40% Na-Hg in THF. A mixture of 0.285 g (0.69 mmol) of **8** in 10 mL of THF was treated with 20 μL of 40% Na-Hg (0.85 mmol of Na). The carbonyl band of **8** at 1930 cm^{-1} slowly disappeared over a period of 12 h as a black precipitate formed and weak carbonyl absorptions appeared at 1875, 1840, 1740, 1690, and 1660 cm^{-1} (the latter three matching the spectrum of Na$^+$**3**$^{\cdot-}$). About 100 mg of black solid was collected by filtration and showed no carbonyl absorptions above 1600 cm^{-1} (Nujol) although a broad absorption below 1580 cm^{-1} was noted. Some of the chemical behavior of this material is described in the Results and Discussion section. Its elemental analysis was C, 25.95; H, 2.98; P, 0.95; Co, 40.86; Na, 21.40; and Hg, 6.31.

The filtrate from the reduction of **8** was treated with 15 mL of petroleum ether; 20 mg of crude Na$^+$**3**$^{\cdot-}$ precipitated. The remaining solution was reddish in color and possessed a weak IR band at 1870 cm^{-1} as well as an intense series of bands characteristic of free (C$_6$H$_5$)$_3$P.

Electrochemical Experiments. All experiments were carried out using acetonitrile as the solvent and tetraethylammonium perchlorate as supporting electrolyte. The solvent was purified by reflux and distillation from, first AlCl$_3$, then KMnO$_4$-Li$_2$CO$_3$, KHSO$_4$, and finally CaH$_2$. The latter distillation was carried out under N$_2$ using a 4 ft glass-helix-packed column with Teflon sleeves at all points. The material collected had a bp 81.6 °C. Cyclic voltammetry of **1** was carried out at a Hg-drop electrode, using an Ar-purged 0.002 M solution of **1** in CH$_3$CN and a Ag-AgClO$_4$ reference. The rest potential of the solution was −0.33 V and reversible waves were observed at −0.06 V (net oxidation) and −2.14 V (net reduction). In each case the potential difference between the forward and reverse scans was 60 ± 5 mV, indicative of one-electron processes. Similar experiments on $PPN^+\mathbf{3}\cdot^-$ were carried out, with the exception that the solvent was degassed and the experiment conducted in the drybox under purified N_2. An 0.005 M solution displayed a rest potential of −1.2 eV, again vs. $Ag-AgClO_4$, and a net oxidation at −1.05 V. Waves characteristic of **1** were also seen.

Magnetic Susceptibility Measurements on $PPN^+\mathbf{3}\cdot^-$. (a) Gouy Balance Method. A cell was calibrated using a known amount of $HgCo(SCN)_4$. The diamagnetic correction term was calculated from the empirical formula and adjusted for the presence of the unsaturated carbocyclic rings. Measurements were carried out at 24 °C, and gave $\chi_m^{corr} = 1.20 \times 10^{-3}$; $\mu_{eff} = 1.70 \pm 0.09\ \mu_B$.

(b) NMR Shift Method.[11] Dimethyl sulfoxide was used as the solvent; the displacement of the NMR resonance of the pure solvent (in a capillary) was measured relative to the Me_2SO resonance of a solution containing a known amount of paramagnetic material. The technique was calibrated using $HgCo(SCN)_4$. The measurement was made on a solution of 19.5 mg of $PPN^+\mathbf{3}\cdot^-$ in 320 μL of Me_2SO, in the probe of an A-60A spectrometer at 35 °C, and gave $\chi_m^{corr} = 1.15 \times 10^{-3}$; $\mu_{eff} = 1.69 \pm 0.10\ \mu_B$.

Crystal Data. Crystals of $C_{48}H_{40}Co_2O_2P_2N$ [$PPN^+\mathbf{3}\cdot^-$], M = 842.62, are triclinic with $a = 11.279$ (3), $b = 17.593$ (5), $c = 10.428$ (1) Å; $\alpha = 101.59$ (3), $\beta = 93.52$ (6), $\gamma = 91.69$ (2)°; space group $P\bar{1}$; $Z = 2$. The density, 1.37 (2) g cm^{-3} at 23 °C was determined by placing a crystal into pure water and adding concentrated aqueous KBr until the crystal began to rise from the bottom. The density of the solution was then measured directly; $\rho_{calcd} = 1.385$ g cm^{-3}.

X-ray diffraction data were collected on a crystal 0.1 × 0.3 × 0.6 mm using a Datex-automated General Electric diffractometer. Graphite-filtered $MoK\alpha$ radiation (λ 0.709 Å) was used to measure 3752 reflections through a range $6° \leq 2\theta \leq 40°$. The θ–2θ technique was used to scan each reflection at a speed set to vary continuously from 2°/min at $2\theta = 5°$ to 4°/min at $2\theta = 80°$. Backgrounds (20 s) were measured before and after each scan. Data were corrected for a decline in intensity of three check reflections with time (maximum correction = 15% in F_o). The structure was determined using 2871 reflections for which $I \geq 3\sigma$ (±).

Solution and Refinement of the Structure. The structure was solved using heavy-atom techniques to locate the four Co atoms in the unit cell. The R value $(\sum \| F_o| - |F_c\| / \sum |F_o|)$ was 0.358 for a model including 2 Co atoms and 25 more atoms in the asymmetric unit identified by MULTAN (direct methods). A three-dimensional electron density map revealed the Co location of all 55 non-hydrogen atoms in the asymmetric unit, giving an R of 0.211 before refinement. Refinement was carried out using group parameters for the phenyl rings of the PPN^+ cation (rigid body approximation). Full-matrix least-squares refinement was carried out in two parts: (a) the scale factor, and positions and isotropic temperature factors for 19 heavy atoms and 6 phenyl rings, reducing R to 0.113; (b) calculation of hydrogen atom positions (not refined) and anisotropic temperature factors for 19 heavy atoms, giving a final $R = 0.073$. The maximum electron density unaccounted for on a difference Fourier is 0.8 e/$Å^3$.

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Supplementary Material Available: Five tables, listing interatomic distances and angles, fractional coordinates, and intensity data (22 pages), are provided in ref 5b.

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