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REDUCTION CHEMISTRY OF SUBSTITUTED DERIVATIVES OF CYCLOPENTADIENYLDICARBONYLCOBALT. ESR AND INFRARED SPECTROSCOPY AND THEIR RELATIONSHIP TO ELECTRONIC STRUCTURE OF THE DINUCLEAR REDUCTION PRODUCTS

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Summary

The reductions of five substituted cyclopentadienyl dicarbonyl cobalt complexes have been carried out. Mixtures of dinuclear radical anions, $\text{Ring}_2\text{Co}_2(\text{CO})_2^{-\cdot}$, and ring loss products are obtained with the former predominating except in the case of $(C_5H_4CO_2CH_3)Co(CO)_2$ where 85% ring loss is observed. Infrared and electron spin resonance measurements on the radical anions yield the following data: $g_{\text{iso}} = 2.08 \pm 0.01$ and $g_{\parallel} = 2.18 \pm 0.01$ for all systems; a_{iso} and $a_{\parallel}$ vary over a 10% range, thereby revealing variations in spin density on cobalt over the series. A qualitative electronic picture of the system is presented.

Introduction

The chemical reduction of simple mononuclear metal carbonyls has been a subject of intensive study, resulting in the discovery of a large number of examples of the process described in eq. 1, loss of CO from an 18-electron metal accompanied by addition of 2 electrons from a suitable reducing agent e.g.

$$M(CO)_n^{-m} \xrightarrow[-CO]{+2e^-} M(CO)_{n-1}^{-m-2} \qquad (1)$$

$m = 0, 1, 2$; $n = 4, 5, 6$; various M

$Cr(CO)_5^{2-}$ [1a], $Fe(CO)_4^{2-}$ [1b] and $Mn(CO)_4^{3-}$ [1c]. In contrast, more complex, ring substituted mononuclear metal carbonyls have been much less studied, and only one case to date has been found to follow the general pattern described above (eq. 2) [2]. The major process that occurs in a number of such systems involves instead partial or complete loss of the ring in preference to dissocia-

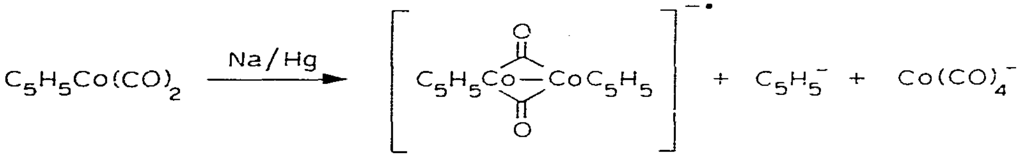
$$C_5H_5V(CO)_4 \xrightarrow[THF]{Na/Hg} C_5H_5V(CO)_3^{2-} \qquad (2)$$

tion of the more strongly π-acidic CO ligand (eq. 3, 4) [1c,3].

$$\eta^6\text{-}C_6H_6Cr(CO)_3 \rightarrow \eta^4\text{-}C_6H_6Cr(CO)_3^{2-} \qquad (3)$$

$$C_5H_5Mn(CO)_3 \xrightarrow{Na/Hg} C_5H_5^- + Mn(CO)_3^- + \text{other products} \qquad (4)$$

Intermediate behavior is observed in the cyclopentadienylcobalt system, with products resulting from loss of CO predominating over those obtained via ring dissociation (eq. 5) [4].



$$C_5H_5Co(CO)_2 \xrightarrow{Na/Hg} \left[C_5H_5Co(\mu\text{-}CO)_2CoC_5H_5 \right]^{-\bullet} + C_5H_5^- + Co(CO)_4^- \qquad (5)$$

(Ia) (IIa)

The first step in both processes appears to be addition of one electron to the lowest unoccupied orbital of Ia. The opportunity therefore exists to investigate relative effects of ring substitution on ring—metal bonding in both the 18-electron analogues of I, and their 19-electron counterparts, $I^{-\bullet}$. For example, electron-withdrawing substituents may stabilize $I^{-\bullet}$ by increasing the π-acidity and back-bonding capacity of the ring; if so, this approach might succeed in yielding derivatives of the as yet inaccessible dianion $C_5H_5CoCO^{2-}$. On the other hand, stabilization of the ring anion itself by such substitution may simply lower the barrier towards its dissociation from the metal.

The possibility that relatively minor alterations in the electronic nature of the ring might lead to substantial changes in the properties and chemistry of these compounds has led us to prepare a number of ring-substituted compounds I, carry out their chemical reduction, and investigate the properties of their paramagnetic analogues of IIa thus formed.

Results and discussion

Preparation and properties of substituted cyclopentadienyldicarbonylcobalt complexes

Compounds Ib—f were prepared via thermal reaction of octacarbonyldicobalt and the corresponding cyclopentadiene (eq. 6). Of these, Ib [5], Id [6], and If [7] are known compounds although only the first had been prepared in this manner previously; Ic and Ie have not been reported. Compounds were obtained as deep red liquids or solids in yields of 10—60%. Relevant spectroscopic data for these materials are presented in Table 1. As expected, the carbonyl stretching frequencies increase as substituents on the ring become rela-

$$\text{Ring—H} + Co_2(CO)_8 \xrightarrow[\text{ether}]{\Delta} \underset{(I)}{\text{Ring—Co}(CO)_2} + CO + H_2 \qquad (6)$$

Ring = $C_5H_4Si(CH_3)_3$ (b), $C_5H_4SiCH_3(C_6H_5)_2$ (c), $C_5H_4CO_2CH_3$ (d), $C_5H_4CH_2CO_2CH_3$ (e), $C_5(CH_3)_5$ (f)

TABLE 1

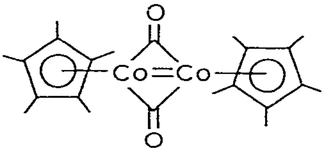
IR AND NMR DATA FOR SUBSTITUTED CYCLOPENTADIENYLCOBALT DICARBONYLS

Compound	IR [a] (ν(CO), cm^{-1})	NMR (δ, ppm)
$C_5H_5Co(CO)_2$ (Ia)	1954, 2019	5.17 (THF-d_8) 4.50 (benzene-d_6)
$[C_5H_4Si(CH_3)_3]Co(CO)_2$ (Ib)	1957, 2030	0.27 (s), 5.10 (t, $J \sim 2$ Hz), 5.36 (t, $J \sim 2$ Hz) (acetonitrile-d_3) 0.23 (s), 4.56 (t, $J \sim 2$ Hz), 4.83 (t, $J \sim 2$ Hz) (benzene-d_6)
$[C_5H_4SiCH_3(C_6H_5)_2]Co(CO)_2$ (Ic)	1960, 2030	0.80 (s), 5.00 (m), 5.45 (m), ~7.5 (m) (acetonitrile-d_3) 0.66 (s), 4.37 (m), 4.68 (m), 7.20 (m, 6 H), 7.55 (m, 4 H) (benzene-d_6)
$(C_5H_4CO_2CH_3)Co(CO)_2$ (Id)	1971, 2038 (ester, 1730)	3.75 (s), 5.58 (m), 5.70 (m) (DMSO-d_6) 3.46 (s), 4.53 (t, $J \sim 2$ Hz), 5.21 (t, $J \sim 2$ Hz) (benzene-d_6)
$(C_5H_4CH_2CO_2CH_3)Co(CO)_2$ (Ie)	1956, 2019 (ester, 1741)	3.43 (s, 2 H), 3.70 (s, 3 H), 5.31 (m), 5.46 (m) (DMSO-d_6) 2.83 (s, 2 H), 3.30 (s, 3 H), 4.37 (t, $J \sim 2$ Hz), 4.71 (t, $J \sim 2$ Hz) (benzene-d_6)
$[C_5(CH_3)_5]Co(CO)_2$ (If)	1936, 1999	2.15 (s) (acetonitrile-d_3)

[a] THF solution, values ± 1 cm^{-1}.

tively more electron-withdrawing (relative to hydrogen, the trimethylsilyl and diphenylmethylsilyl substituents have been found to be electron-withdrawing on the cyclopentadienyl ring [8]).

Accompanying the formation of If was a green solid exhibiting a single IR band at 1752 cm^{-1} which, on the basis of these properties and its chemical behavior (vide infra), appears to be the neutral dimeric compound III, possessing a formal cobalt—cobalt double bond. Separation of III and If is readily affected by chromatography on silica gel, petroleum ether eluting If and benzene, III.



(III)

The analogous compound possessing unsubstituted C_5H_5 rings has been described earlier [4b]. We are currently investigating the properties and chemistry of III and will report fully on it at a later date.

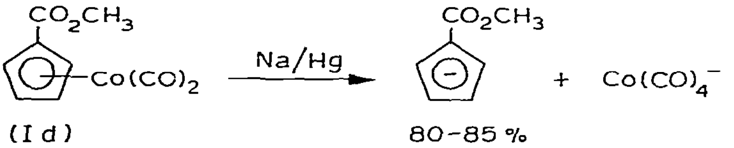
Reductions of silyl-substituted cyclopentadienyldicarbonylcobalt complexes Ib and Ic

Compounds Ib and Ic, possessing mildly electron-withdrawing substituents on the carbocyclic ring, were reduced with 0.8% sodium amalgam in tetrahydrofuran, conditions essentially identical to the previous reported reduction of unsubstituted Ia [4]. The courses of these reductions were found to be virtually identical to that of Ia itself. In each case the reduction was complete in minutes, and the major product was the corresponding dinuclear radical anion (IIb or IIc) in ca. 65% yield. These compounds were somewhat more difficult to isolate than the corresponding unsubstituted salt IIa, being considerably more soluble in THF or THF/petroleum ether mixture; however, after isolation of the crude products by treatment of the reduction mixtures with excess petroleum ether, IIb and IIc could be obtained as olive green and brilliant green crystalline solids respectively, as by dissolution in THF and careful addition of sufficient petroleum ether to just induce crystallization (see Experimental). These salts are thermally quite stable in the solid state as well as in solution, but are rapidly oxidized by atmospheric oxygen. Both materials displayed infrared and ESR spectroscopic characteristics very similar to those of the parent system. As in the case of IIa, THF was found by NMR and elemental analysis to comprise 20—30 wt.% of the solid compounds as isolated corresponding roughly to 1.5—2.7 molecules of THF per molecule of sodium salt.

The remaining products were the $Co(CO)_4^-$ anion, in about 20% yield, and $C_5H_4Si(CH_3)_3^-$ or $C_5H_4SiCH_3(C_6H_5)_2^-$, respectively. Although effects of the silyl substituents are observable in the properties of the starting materials and products (vide infra), they are not clearly observable in the course of the reaction itself.

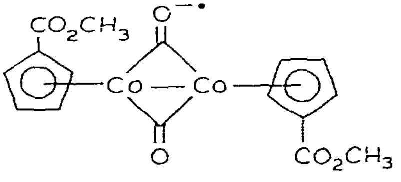
Reductions of ester substituted complexes Id and Ie

Substitution of an ester group for a hydrogen on the cyclopentadienyl ring of Ia would be expected to greatly facilitate the reduction of the complex, and indeed, (carbomethoxycyclopentadienyl)dicarbonylcobalt, Id, is reduced virtually instantaneously by dilute sodium amalgam. In THF solution, only infrared absorption due to $Co(CO)_4^-$ is observed after the disappearance of starting material. When the reaction is carried out in deuterated dimethylsulfoxide, NMR signals characteristic of the $C_5H_4CO_2CH_3^-$ anion (δ 6.10(m), 5.48(m), and 3.44 (s) ppm) rapidly replace those of the initial complex (δ 5.70 (m), 5.58 (m), 3.75 (s) ppm); their intensity reveals that some 80—85% of the starting material is reacting via the ring loss pathway (eq. 7).



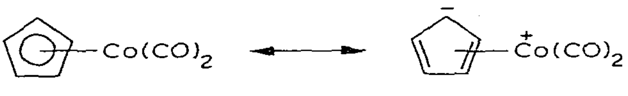
(7)

Obviously the maximum possible yield of $Co(CO)_4^-$ can be only 50% relative to the initial amount of cobalt available and these data provide no indication as to the fate of the remaining cobalt-containing material. However, examination of the crude supernatant THF solution obtained from the reduction of Id reveals a 15-line ESR signal quite similar to those characteristic of the dinuclear radical anions IIa—c. Further analysis of these solutions (vide infra) has confirmed that IId is indeed a product of this reduction albeit a very minor one. We have attempted to increase the amount of IId formed in this process by increasing the concentration of Id in the initial reduction. We find however that even reaction of sodium amalgam with *neat liquid* Id gives rise to no more than 5—10% IId. Thus the presence of the carbomethoxy substituent on the ring has lowered the barrier to loss of the ring anion to the extent that the bimolecular processes evident in the reductions of Ia—c compete only slightly.



(IId)

As early as 1961, the bimolecular pathway of ligand substitution in $C_5H_5Co(CO)_2$ (Ia) was recognized by Wojcicki and Basolo [9], and in subsequent work mechanistic suggestions were made implying the importance of the resonance contribution IV in determining the behavior of Ia. Comparative calculations on



(Ia) (IV)

Ia and $C_3H_5Co(CO)_3$ (V) have been reported [10], however, indicating that the ring in Ia is a net electron *donor*, resulting in significantly greater electron density in the π^* orbitals of the carbonyl ligands relative to V, in which the allyl ligand is a net electron acceptor. A brief comparison of infrared data and chemical behavior for Ia, Id, and V is presented in Table 2.

According to the basic mechanism set out by us earlier (Scheme 1), the branch point between the ring loss pathway and the pathway leading to binuclear products occurs at 19-electron intermediate I, which may either attack an unreduced molecule of Ia, or undergo attack by another ligand on cobalt to initiate ring loss. The presence of an electron-withdrawing ring substituent apparently reduces the nucleophilicity of the metal in $I^{-\cdot}$ and simultaneously renders it more susceptible to attack by an external neutral ligand (note alternate ring-charged formulations in Scheme 1), the result being suppression of the second order process leading to radical anion in favor of pseudo-first order chemistry resulting in ring loss *. Referring to the data in Table 2, one might therefore expect suitable calculations to show that the $C_5H_4CO_2CH_3$ ring in Id is a net electron acceptor, similar to the allyl ligand in V, and in contrast to the cyclopentadienyl fragment of Ia.

Complex Ie, the dicarbonylcobalt derivative of the methyl ester of cyclopentadienylacetic acid, was synthesized and observed under reduction conditions in order to identify any effect on the reaction due merely to the proximity of an ester group, which might bear on our observations and conclusions regarding complex Id. Compound Ie is sensitive thermally, apparently losing CO when exposed to either high vacuum or a current of N_2 at temperatures slightly above room temperature. The process is accompanied by a change in color from deep red to bright green, but little change in the IR except for the appearance

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* The presence of excess triphenylphosphine in solutions of Ia undergoing reduction also favors ring loss and suppresses radical anion formation, as expected by this mechanism [4].

TABLE 2

REDUCTION PRODUCTS OF SELECTED COBALT CARBONYL DERIVATIVES

Compound	IR (ν(CO), cm^{-1})	Major products upon Na/Hg redn.
Ia	1954, 2019	$(C_5H_5)_2Co_2(CO)_2^-$ (IIa)
Id	1971, 2038	$Co(CO)_4^-$ and $C_5H_4CO_2CH_3^-$
V	1980, 2062	$Co(CO)_4^-$ and $CH_2{=}CHCH_2^-$

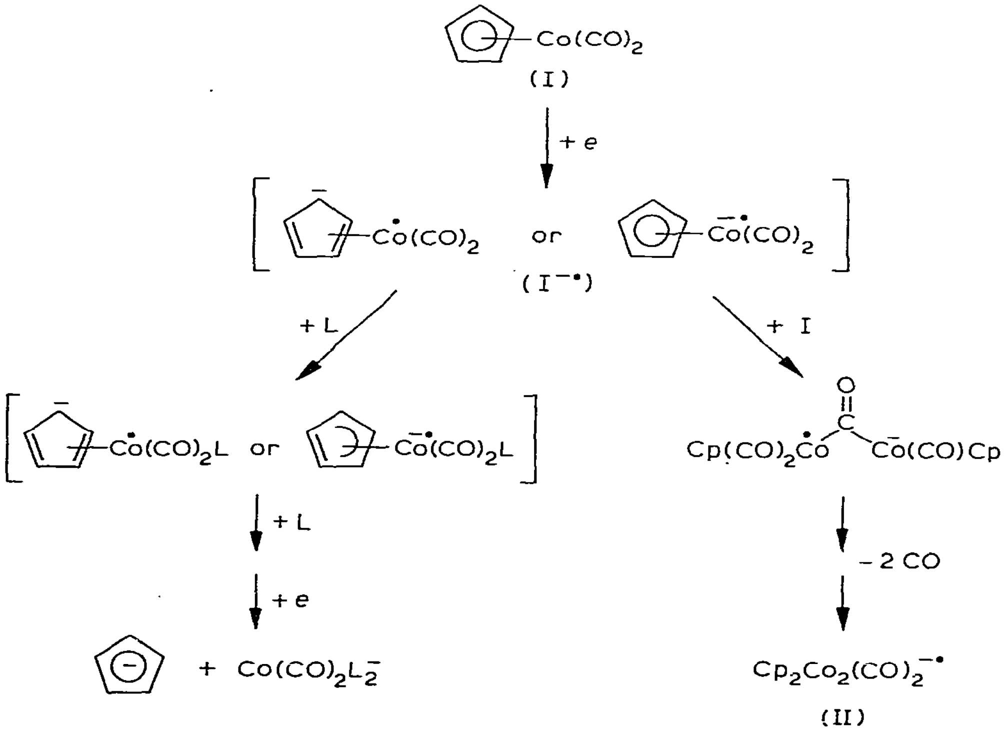
of a new, weak absorption at 1777 cm^{-1} (THF solution). Exposure of this material to CO regenerates the red color of Ie, behavior one would expect of a dimeric neutral dicarbonyl of the form $(C_5H_4CH_2CO_2CH_3)_2Co_2(CO)_2$ [4]. Our experience with the corresponding pentamethylcyclopentadienyl compounds (vide infra) suggests that only small amounts of the intensely colored dimer are necessary to impart a green color to material that is predominantly composed of mononuclear dicarbonyl. We have, however, been unable to completely free the green material produced by Ie from its precursor, or obtain quantities sufficient for further characterization.

The reduction of Ie is rather similar to that of complexes Ia—c: radical

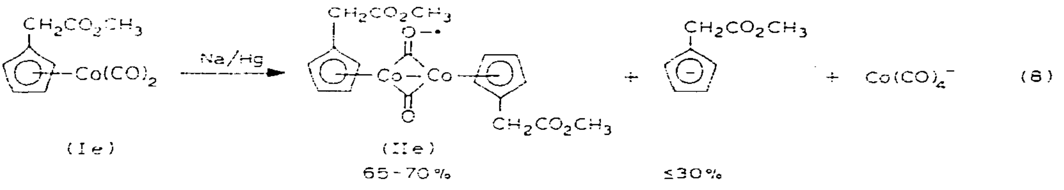
SCHEME 1

PROPOSED REDUCTION MECHANISM FOR COMPOUNDS I

Likely alternative electronic distributions for reduction intermediates are indicated by structures in brackets.



anion IIe is the major product. Estimates of the relative yields of IIe and —$CH_2CO_2CH_3$ by IR and NMR indicate approximately 65—70% of the former vs. 30% as an upper limit for ring loss product (eq. 8). Thus no unusual chemistry is brought about by the isolated ester function itself in this system.



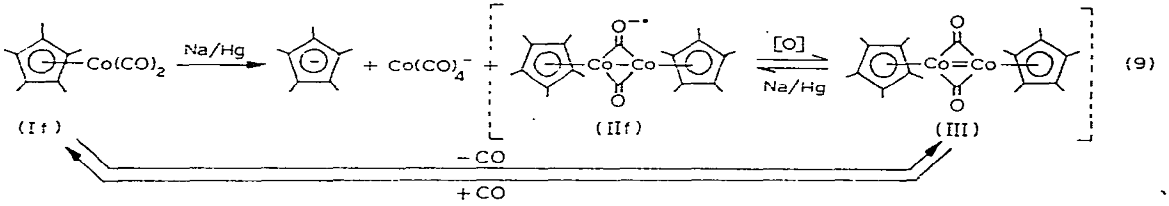
Reductions of pentamethylcyclopentadienylcobalt complexes

Replacement of a cyclopentadienyl ligand by a pentamethylcyclopentadienyl ring is known in several cases to substantially affect the chemistry of the attached transition metal [11]. We therefore sought to compare reduction of the cobalt derivative possessing this extreme electron donor ligand with the other systems already described.

Reduction of (pentamethylcyclopentadienyl)dicarbonylcobalt If is quite slow in THF, requiring days for complete consumption of starting material. The reduction mixture displays, in addition to the intense $Co(CO)_4^-$ IR bands at 1855 and ~1890 cm^{-1}, three bands in the bridging carbonyl region, qualitatively similar to those characteristic of radical anion IIa, but appearing at ca. 1630s, 1665vwk, and 1715wk cm^{-1}, considerably lower in energy than those of the unsubstituted system. The yield of this material is 70—75%, with ring loss products accounting for most of the remaining material.

Compound If is considerably less stable than Ia. Loss of CO and conversion of the dark red If to green III occurs at room temperature either in vacuo or upon standing under the nitrogen atmosphere of a dry box. Carbon monoxide reconverts III to If; thus, the highest yields of If are obtained upon reaction of $Co_2(CO)_8$ and $HC_5(CH_3)_5$ under CO, while use of a nitrogen atmosphere gives rise to a significant amount of III.

Neutral dimer III, IR 1752 cm^{-1}, may be reduced with sodium amalgam in THF to give yellow-brown solutions displaying the same three low energy IR bands that are seen in the reduction of If, but totally free of $Co(CO)_4^-$. These results and the ESR data described below are consistent with the formation of radical anion IIf as the major product from the reduction of If and the sole product from the reduction of III (eq. 9).



Radical anion IIf is extraordinarily prone to oxidation; under a nitrogen atmosphere scrubbed to a purity of <10 ppm water and oxygen, solutions of

IIf removed from contact with sodium amalgam slowly become green (formation of small amounts of III) whereas solutions of the corresponding IIa show no visible signs of oxidation over extended periods of time under the same circumstances.

Comparative spectroscopy of radical anions IIa—IIf: infrared, room-temperature, and low-temperature ESR

The detailed nature of systems containing multiple metal—metal bonds is a topic of great interest, and in this regard the radical anion IIa poses a number of questions. Formally, it possesses a cobalt—cobalt bond order of 1.5 based on the 18-electron rule, but Bernal and co-workers have demonstrated the lack of dependence of bond length on formal bond order in several compounds of this type [12], thus calling into question the applicability of such commonly used bonding conventions in these systems. By their very nature, as stable radical anions, compounds IIa—f as a series provide an unusual opportunity to study electronic structure by ESR in systems where dispersal of excess charge is important, and to some extent controllable by substitution, and is readily monitored by IR.

We have measured the infrared and ESR spectra of IIa—f in THF solutions at room temperature. In the compounds possessing electron-withdrawing ring substituents we observe a modest relationship between the increasing carbonyl stretching frequencies and the decreasing isotropic cobalt hyperfine coupling constants as the electron-withdrawing capability of the ring is strengthened. This simple qualitative relationship does not hold, however, for the permethyl complex IIf, whose cobalt hyperfine coupling might naively be expected to be the largest in the series. In fact, the isotropic a value for IIf is significantly smaller than that displayed by any of the other compounds studied and must therefore be reflecting several effects besides simple metal—ring distribution of odd-electron density.

ESR measurements on glassy solutions of radical anions IIa—f have been taken (2-methyltetrahydrofuran, —196°C) in order to begin to answer the questions raised concerning these materials. The broad, 15-line patterns observed at room temperature are replaced by sharp, highly structured, complex spectra from which useful comparative data may be extracted. These low-temperature spectra exhibit a well-defined pattern of lines with a spacing of ca. 85 G, clearly a portion of a 15-line multiplet the remainder of which is obscured by a much more complex spectral pattern (Fig. 1). Approximate evaluation of one of the components, a_1, of the anisotropic hyperfine tensor is possible using the relationship $a_1 = A_1 - a_{iso}$ where A_1 is the measured line-to-line spacing and a_{iso} is the room-temperature isotropic hyperfine value. IR data and values for a_{iso}, A_1, and a_1 are presented in Table 3. The assumption is made that A_1 and a_{iso} (and therefore a_1) are all negative. This is required by the fact that A_1 is clearly the spacing with the largest magnitude and that the three values A_1, A_2, and A_3 must average to the experimental a_{iso} which is almost certainly negative [13].

It is found that the component of the anisotropic hyperfine tensor derived from the major splitting of the low-temperature spectrum is in fact related to the ring substitution in a reasonable way. The lack of a good frequency and mag-

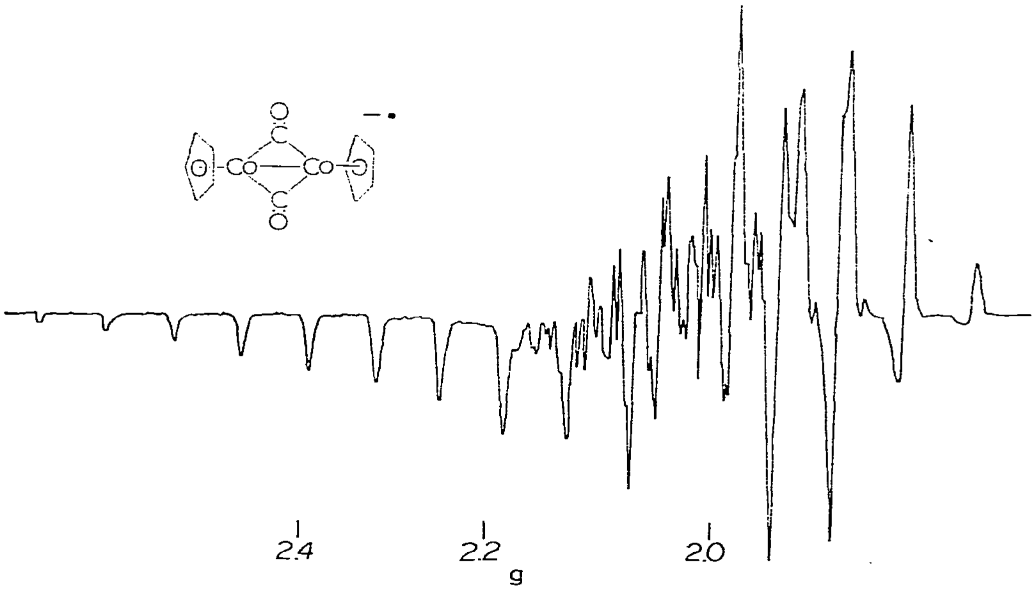


Fig. 1. ESR of IIa in 2-methyltetrahydrofuran at 77 K. Microwave frequency 9.032 × 10^9 Hz.

netic field measurement capability in the Varian E-4 spectrometer limits the accuracy of the data. We have therefore chosen not to carry out a treatment on any sort of sophisticated level. Nevertheless, one can generate an approximate interpretation of this information by (1) dropping the indirect dipolar contribution to the total hyperfine interaction and (2) equating the measured a_1 with the direct dipolar term $4\alpha^2 P/7$ where $P = g\beta g_N\beta_N \langle r^{-3}\rangle$ and α is the coefficient of the d orbital on each cobalt contained in the molecular orbital responsible for this interaction.

Compounds II may be considered as either mixed-valence Co^0—Co^+ complexes or complexes of "$Co^{+0.5}$" (that the electron is distributed equally over the two metals is evident from the solution ESR, however.) We therefore use for P the average of the values for $Co^0(d^9)$ and $Co^+(d^8)$ [14]: $P = 0.215\ cm^{-1}$. The α^2 values obtained are presented in Table 4. The fraction of the odd electron residing on

TABLE 3

IR AND ESR DATA FOR DINUCLEAR RADICAL ANIONS IIa—f

Compound, $(Ring)_2Co_2(CO)_2^{-\cdot}$	IR [a] (ν(CO), cm^{-1})	ESR ($\|a_{iso}\|$ [b], G)	$\|A_1\|$ [c] (G)	$\|a_1\|$ [d] (G)
IId, Ring = $C_5H_4CO_2CH_3$		46.15	84.7	38.5
IIc, Ring = $C_5H_4Si(C_6H_5)_2CH_3$	1663, 1697, 1748	46.20	85.8	39.6
IIb, Ring = $C_5H_4Si(CH_3)_3$	1657, 1693, 1745	46.78	86.6	39.8
IIe, Ring = $C_5H_4CH_2CO_2CH_3$	1656	47.45	87.0	39.5
IIa, Ring = C_5H_5	1656, 1691, 1744	47.34	87.1	39.7
IIf, Ring = $C_5(CH_3)_5$	1630, 1668, 1719	43.95	87.0	43.0

[a] THF soln., ±1 cm^{-1}. Absorptions for IId and IIe obscured by ester peaks. [b] THF soln., ±0.1 G, 25°C. [c] 2-Methyltetrahydrofuran soln., ±0.1 G, 77 K. [d] ±0.2 G.

TABLE 4

ESR-DERIVED PARAMETERS FOR IIa—f

Compound	$\lvert a_1 \rvert$ (cm^{-1})	α^2
IId	0.0063	0.29
IIa, b, c, e	0.0065	0.30
IIf	0.0070	0.33

the two cobalts, $2\alpha^2$, ranges from 0.58 to 0.66 over the series and, assuming that the neglected terms are very similar for all these compounds *, indicates a reasonable relationship between unpaired electron density on the metals and electron donor ability of the rings to the extent that IIf and IId, representing the extremes of ring electron donation and withdrawal, respectively, fall at either end of the series while the remaining four compounds show no significant differences by this experimental criterion. Further study will be necessary in order to reveal the full nature of the hyperfine interaction in these compounds and thereby understand the unusual variations in a_{iso} observed throughout this series.

Finally, approximate g values for these complexes have been extracted from these spectra from the position of the eighth line of each 15-line pattern. For all compounds we find $g_{\text{iso}} \approx 2.08 \pm 0.01$ and g_1, again derived from the major pattern of the low-temperature spectrum, 2.18 ± 0.01, with only minor variation throughout the series. This allows estimation of an average value for g_2 and g_3, $(g_2 + g_3)/2 \simeq 2.03$.

These values are consistent with the simple molecular orbital picture of the system described earlier [4b] wherein the odd electron occupies a $\pi^{\star}_{xz}$-type orbital derived from the (+) combination of the d_{xz} orbitals on each cobalt atom (Fig. 2). Applying a simple spin—orbit coupling argument [16], mixing of this $\pi^{\star}$ orbital with the filled σ_{z^2} orbital brought about by a field in the y direction should give rise to a $\Delta g_y >> 0$ (and hence $g_y >> 2$) due to the energetic proximity of the orbitals involved. Note that symmetry considerations in two-centered systems restrict spin—orbit interactions such that (+) algebraic combinations couple only with other (+) combinations, and (—) only with (—); therefore no spin—orbit contribution between $\pi^{\star}_{xz}(+)$ and the empty $\sigma^{\star}_{z^2}$ (—) is to be expected. Spin—orbit coupling about the remaining axes mixes $\pi^{\star}_{xz}$ with lower-lying filled d combinations heavily involved in ring—metal and carbonyl—metal bonding: therefore both $\Delta g_x > 0$ and $\Delta g_z > 0$. Neither of the Δg values in the latter two cases will be as large as Δg_y, thus this formalism is consistent with $g_y \sim 2.18$ and $(g_x + g_z)/2 \sim 2.03$.

A qualitative treatment of the system along the lines of Hoffmann's fragment analyses of dinuclear complexes [17] demonstrates, however, that the actual orbital arrangement may be quite different than the picture described above. In particular, the d_{z^2} combinations are shown to be much lower in energy than the

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* Although these terms are certainly not negligible and may be as large as 10—30% of the direct dipolar term, they are functions of the spin orbit coupling parameter, which varies little among compounds of a metal in the same oxidation state, and the components of the g tensor, which are shown to be virtually identical for all these compounds (vide supra) [15].

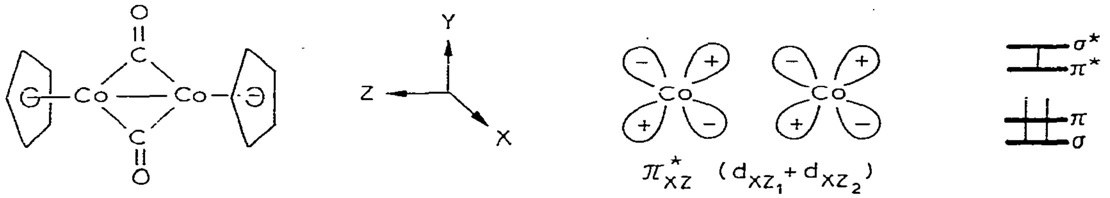

Fig. 2. Antibonding orbital derived from overlap of d_{xz} orbitals on cobalt atoms of II. Note that orbitals are located in the plane perpendicular to the molecule as illustrated.

frontier orbitals, and combinations derived from metal d_{yz} orbitals, involved in carbonyl—metal bonding, are likely to be quite close in energy to the d_{xz} combinations under consideration.

The four orbitals involved are derived as shown in Fig. 3. We have utilized Hoffmann's description of the Cp_2Ni_2 and $Fe_2(CO)_6$ systems [17a] with minor modifications as the basis for our diagram for the Cp_2Co_2 fragment. Allowing two CO molecules to interact in the manner depicted in Fig. 2 should result in

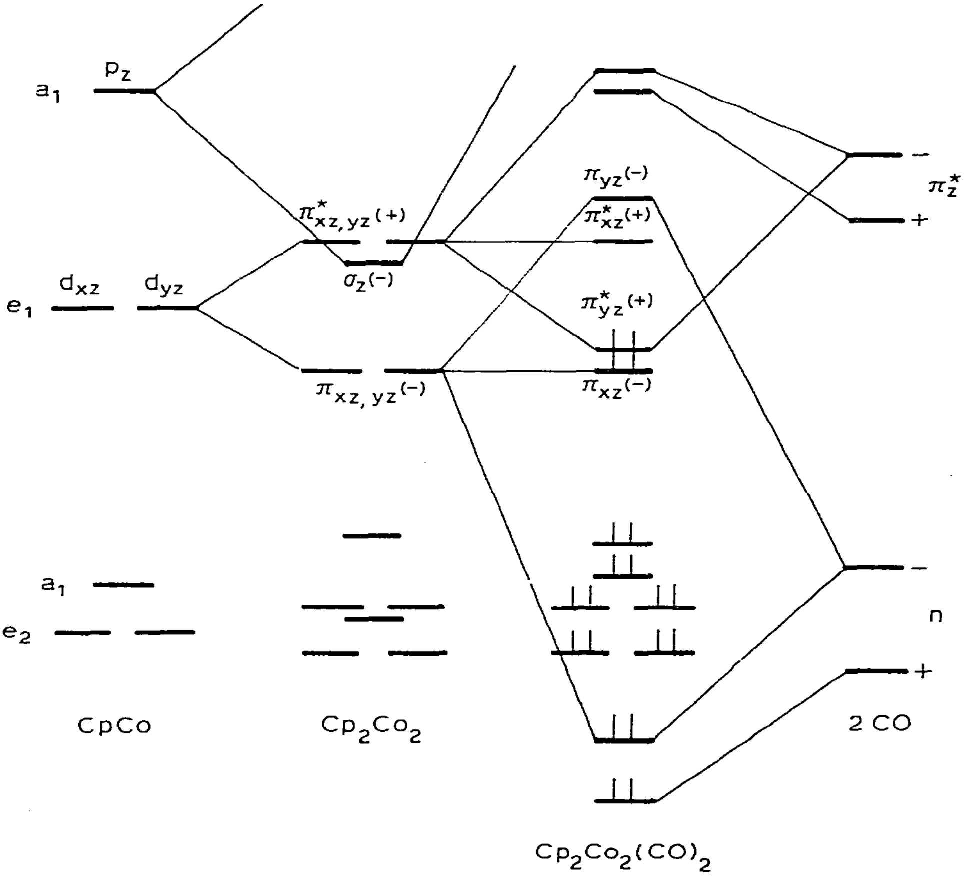

Fig. 3. Qualitative interaction diagram for the frontier orbitals of $Cp_2Co_2(CO)_2$ (neutral molecule). Order of four π orbitals is only one of several possibilities (see text).

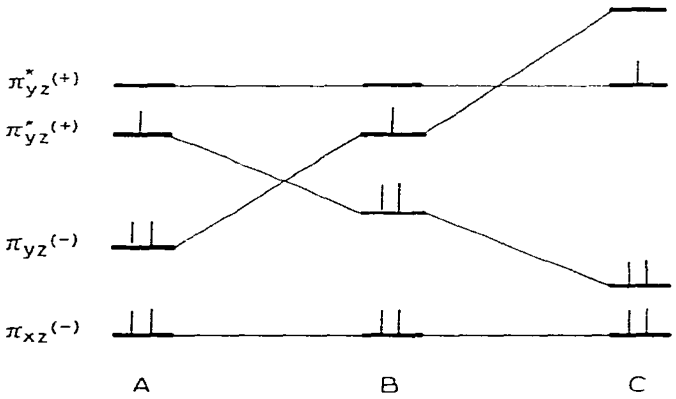

Fig. 4. Three possible arrangements of the π orbitals of IIa. Case A results from a relatively small interaction of the π_{yz} and π^*_{yz} orbitals with the carbonyl n and π^* orbitals, respectively. The splitting is largest in case C (used in Fig. 3).

substantial splitting of the metal d_{yz} combinations (formation of metal—CO carbon σ bonds), one of the effects of which is the likelihood of the inversion of the order of the $\pi_{yz}(-)$ and $\pi^*_{yz}(+)$ orbitals, formally bonding and antibonding between the metals, respectively (Fig. 3). The actual order of these orbitals and, obviously, the identity of the singly occupied orbital in II, will depend on the relative magnitudes of the two metal—carbonyl interactions in the yz plane. Three possibilities are shown in Fig. 4. In case A, the major spin—orbit interaction would involve $\pi^*_{yz}(+)$ with the nearby, vacant, $\pi^*_{xz}(+)$, predicting $g_z << 2$, in conflict with the data; therefore this orbital arrangement may immediately be ruled out. Cases B and C are both consistent with the spectroscopy, requiring all three components of g be >2. In case B, the major interaction couples $\pi_{yz}(-)$ with the filled $\pi_{xz}(-)$ leading to $g_z >> 2$ while case C predicts the same result, this time via the coupling of $\pi^*_{xz}(+)$ with the nearby filled $\pi^*_{yz}(+)$ orbital. In each case the remaining components of g will be >2 since the orbitals involved in these interactions, the d_{xy} and d_{z^2} combinations, are all filled and lie quite low in energy (Fig. 3). The odd electron, therefore, either occupies the metal—metal antibonding π^*_{xz} orbital, or the metal—CO σ^* antibonding combination of one of the non-bonding CO orbitals and the metal—metal bonding π_{yz} orbital. The question of the involvement of the $\pi^*_{xz}(+)$ orbital is not answered by the IR data for IIa—f since the π^* carbonyl orbitals are located at a node of this orbital, and interact chiefly with the filled $\pi_{xz}(-)$. On the basis of the experimental evidence available at present a distinction between these two situations does not appear possible.

Experimental

General techniques

Standard vacuum line and drybox techniques were employed. Diethyl ether, THF, 2-methyltetrahydrofuran, and benzene were vacuum transferred from sodium/benzophenone solutions for all work described. Petroleum ether was distilled from a tetraglyme solution of sodium/benzophenone. Cyclopentadienyldicarbonylcobalt (Ia) and octacarbonyldicobalt were obtained from Strem Chemical Co. Compounds Ib, c, d, and f were prepared in the manner described for Ic, below. Spectroscopic data were obtained with the following instruments: Perkin—Elmer 180 (IR), Varian EM-360 and A-60A (NMR), Varian E-4 (ESR). Microanalyses were carried out by Galbraith and U.C. Berkeley Microanalytical Laboratories.

[(Methyldiphenylsilyl)cyclopentadienyl]dicarbonylcobalt(Ic)

A mixture of 7.1 g (methyldiphenylsilyl)cyclopentadiene (mixture of isomers) [8] (27 mmol) and 4.8 g octacarbonyldicobalt (14 mmol) in 70 ml diethyl ether was refluxed under nitrogen for 4 h, cooled to room temperature, and then stripped of solvent under high vacuum. Repeated trituration of the solid residue with petroleum ether enabled separation of the desired complex from the less soluble octacarbonyl cobalt. Pure Ic was eventually obtained (1.4 g, 14% yield) as red-brown crystals from petroleum ether at —40°C, m.p. 100—103°C. Anal.: found: C, 63.89; H, 4.72; Si, 7.74. Calcd. for $C_{20}H_{17}SiCoO_2$: C, 63.82: H, 4.55; Si, 7.46%. Spectral data are presented in Table 1.

[(Carbomethoxymethyl)cyclopentadienyl]dicarbonylcobalt(Ie)

To a stirred suspension of sodium dispersion (50%, 1.2 g, 25 mmol, washed with 2 × 10 ml petroleum ether) under nitrogen in 12 ml THF was added, dropwise, 2.0 g (30 mmol) cyclopentadiene at 25°C. The mixture was cooled to —78°C and 3.8 g (25 mmol) methyl bromoacetate was added dropwise, followed by 15 min of stirring at —40°C. Then 10.0 g (29 mmol) octacarbonyldicobalt was added all at once, and the reaction mixture heated to 40°C for 1 h. Solvent was removed (vacuum line) and a portion of the semi-solid residue chromatographed on silica gel in the dry box. Three fractions were obtained: petroleum ether eluted a small amount of unsubstituted Ia; benzene eluted desired complex Ie in sufficient purity for the experiments described. The remainder, consisting of uncomplexed organic esters, was removed in an ether fraction. Further purification of the Ie thus obtained was achieved by rechromatography on silica gel using pet. ether/benzene (3/1) as eluant. Removal of solvent at 20°C and high vacuum left deep red Ie as a moderately viscous oil. Anal.: found: C, 48.75; H, 3.79; Co, 22.3. Calcd. for $C_{10}H_9CoO_4$: C, 47.64; H, 3.60; Co, 23.38%. MS, *m/e* (24 eV) (%, likely identity of fragment): 252 (0.5, *M*), 237 (1, $M - CH_3$), 224 (10, $M - CO$), 196 (29, $M - 2\ CO$), 193 (5, $M - CO_2CH_3$), 179 (18, $C_5H_4Co(CO)_2$), 151 (27, C_5H_4CoCO), 138 (98, $C_5H_4CH_2CO_2CH_3$), 91 (100), 79 (96, $C_5H_4CH_2$). Other spectral data are presented in Table 1.

General procedure for reduction experiments

The procedure described for Ia was employed. Solutions of Ib—f, ca. 2 *M* in THF, were treated with excess 0.7—0.8% sodium amalgam all at once under nitrogen and monitored by IR until starting material had been completely consumed. The time required varied from a few seconds for Id to several days for If. Reductions in all cases were followed by IR and NMR spectroscopy. In all cases IR absorptions characteristic of $Co(CO)_4^-$ and the appropriate radical anion species (see Table 3) replaced those of starting material. As described earlier for

IIa, the IR spectra of these anions in THF are indicative of ion pairing in solution, with the middle of the three bands to one characteristic of the free ion, and the only one seen in more polar solvents, e.g. CH_3CN or DMSO. Reductions in the latter solvents (deuterated) result in the appearance of the peaks characteristic of the substituted cyclopentadienyl anion. Yields of IIb, c, e and f were estimated by comparing the intensities of their IR absorptions in the reduced solutions with those of IIa, for which isolated as well as spectroscopic yield data is available. Ring loss yields were obtained similarly by comparison of the intensities of the $Co(CO)_4^-$ IR absorptions in the reductions of Ib—f with that of Ia; these were in agreement with ring anion yields calculated from the NMR spectra (integration of starting material and product signals vs. solvent signals).

Partial purifications of IIb and IIc were achieved in spite of the tendencies of compounds like this to co-crystallize with solvent and other ionic materials, e.g. $Na(RC_5H_4)$ and $NaCo(CO)_4$, the major impurities in these product mixtures. The following sections describe these procedures.

Sodium bis(trimethylsilylcyclopentadienyl)dicarbonyldicobaltate(—1) (IIb)

Utilizing the general procedure 1.0 g (4 mmol) trimethylsilylcyclopentadienyldicarbonylcobalt (Ib) was reduced with 3.5 ml 0.74% Na/Hg in 1.8 ml THF. Dilution of the reaction mixture with 5 ml THF, filtration, and treatment with ca. 25 ml petroleum ether caused separation of a dark oil from which a modest yield (~ 0.3 g) of dark solid material was eventually obtained by repeated dissolution with THF/pet. ether mixtures of varying composition and cooling to —40°C. Although the IR spectra of the crude reduction mixture indicated a yield of some 65% IIb, and much IIb was shown still to be present in the liquid fractions of the product mixture, the isolation was discontinued at this point and efforts to further purify the isolated solid material begun. The solid was dissolved in 6 ml THF and treated slowly with 18 ml pet. ether with stirring until a persistent cloudiness appeared. This colloidal mixture soon deposited fine crystalline material which was washed with 2 × 12 ml pet. ether/THF (5/1) and dried. Yield 0.29 g olive green crystalline solid. Both NMR and elemental analysis confirm the presence of ca. 2 mol of THF per mol of IIb. Anal.: found C, 46.15; H, 5.82, Co, 18.6. Calcd. for $NaC_{18}H_{26}Co_2Si_2O_2 \cdot 1.5\ C_4H_8O$: C, 49.74; H, 6.61; Co, 20.34%. (Calcd. for $NaC_{18}H_{26}Co_2Si_2O_2$: C, 45.86; H, 5.56; Co, 25.00%).

Sodium bis(methyldiphenylsilylcyclopentadienyl)dicarbonyldicobaltate(—1) (IIc)

Methyldiphenylsilylcyclopentadienyldicarbonylcobalt (Ic), 0.5 g (1.3 mmol) was reduced with 2.5 ml 0.74% Na/Hg in 0.9 ml THF. Dilution with THF, treatment with pet. ether, and cooling as for IIb afforded a semisolid mixture from which 0.33 g solid, crude IIc was obtained after removal by decantation of a $NaCo(CO)_4$-containing oil. The crude IIc was taken up in 8 ml THF and treated with 12 ml pet. ether, depositing a small amount of dark brown residue which was removed by filtration and discarded. To the filtrate was added an additional 15 ml pet. ether slowly, inducing crystallization of the desired material, which was washed with 2 × 10 ml pet. ether/THF (5/1) and dried. Yield 0.31 g brilliant green crystalline solid. Again, 2.5—3 moles THF appear to be present in the material as isolated (NMR and elemental analysis). Anal.: found: C, 61.10; H, 6.04; Co, 13.0. Calcd. for $NaC_{38}H_{34}Co_2Si_2O_2 \cdot 2.7\ C_4H_8O$: C, 64.10; H, 6.13; Co, 12.89%. (Calcd. for $NaC_{38}H_{34}Co_2Si_2O_2$: C, 63.42; H, 4.76; Co, 16.38%.)

Sodium salts of anions IId, IIe, IIf

Solutions of these anions were obtained as described and used directly for all spectroscopic studies. Anion IId was characterized only by its room- and low-temperature ESR spectra in solution; IIe likewise was obtained only in solution and identified by ESR and IR. Anion IIf was obtained as a dark solid contaminated by its oxidation product III. Solutions of IIf could routinely be freed of the green III by brief stirring over dilute sodium amalgam. The brownish-yellow solutions thus obtained displayed only the three IR absorptions of IIf. No indication of thermal instability of these materials was obtained in any instance. The ESR spectra of anions IIa—f appear to be totally insensitive to variations in purity or counterion, and only somewhat affected by changes in concentration to the extent that some line broadeneing in the low temperature ESR is observed at concentrations of IIf exceeding ca. 10^{-2} *M*.

Conclusion

Substituent effects on the couse of the reduction of cyclopentadienylcarbonylcobalt complexes may be explained in terms of variations in the reactivity of the cobalt atom towards available donor ligands versus its nucleophilicity towards another molecule of complex. Whether this concept will be of predictive value in very different sorts of compounds has yet to be established. (Could, for instance, heavy electron-donor substitution on the allyl ligand of allyltricarbonylcobalt divert its chemical reduction from 100% anion loss over to dinuclear complex formation?).

Both magnetic and electronic spectroscopy of dinuclear radical anions II show transmission of the electronic effects of the ring substituents into the cobalt—carbonyl core of the molecule. ESR data from glassy solutions at low temperature reveal some information concerning the electronic structural details of these species, and partly resolve anomalous trends in room temperature isotropic hyperfine data. We anticipate that future work, e.g. single crystal ESR studies, will help clarify the questions still remaining on these points.

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