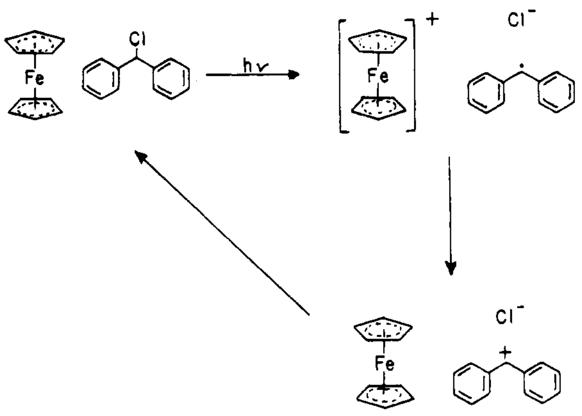
Scheme I



oxidant. Thus, the slowest rate of radical oxidation being observed in cyclohexane is consistent with the preponderance of contact ion pairs in this solvent. In ethanol, hydrogen bonding effects must be considered. We have previously found that ethanol is superior to acetonitrile in supporting solvent separated ion pairs,[1] and, on the basis of this observation, we would have expected to observe a faster rate of radical oxidation in ethanol. It is possible that the observed decrease in rate in changing the solvent from acetonitrile to ethanol is due to hydrogen bonding effects on the oxidation potential diphenylmethyl radical.

Summary

The mechanism for the reaction of ferrocene and diphenylmethylchloride is given in Scheme I. Electron transfer from a ground-state complex results in rapid carbon–chlorine bond cleavage relative to electron transfer, forming ferricenium, Cl^-, and the diphenylmethyl radical. The radical is then oxidized by ferricenium forming ferrocene and the diphenylmethyl cation, chloride anion ion pair. Work is currently underway to examine the ensuing ion-pair dynamics as well as other ion-pair-induced reactions using metallocenes as catalysts.

Acknowledgment. This work is supported by a grant from the National Science Foundation. No. CHE-8117519. K.S.P. also wishes to thank the Camille and Henry Dreyfus Foundation and the Alfred P. Sloan Foundation.

Registry No. $FeCp_2$, 102-54-5; diphenylmethyl cation chloride anion, 87263-01-2; ferricenium, 12125-80-3; diphenylmethyl radical, 4471-17-4; diphenylchloromethane, 90-99-3.

Cobalt Carbonyl Cluster Radicals in Irradiated $HCo(CO)_4$/Kr Mixtures[†]

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Received June 27, 1983

The EPR spectra of two binuclear cobalt carbonyl cluster radicals have been detected at 77 K in γ- and UV-irradiated solid solutions of $HCo(CO)_4$ in Kr. Partial analyses of the powder spectra suggest assignments to a hydrogen-bridged dimer, $HCo_2(CO)_8$, of C_{2v} symmetry for one species and to a nonbridged anion, $Co_2(CO)_8^-$, of D_{3d} or D_{2d} symmetry for the other.

Introduction

A natural extension of our spectroscopic studies of mononuclear metal carbonyl radicals[1-4] is the investigation of polynuclear species, i.e., metal carbonyl cluster radicals. With one notable exception,[5] however, our attempts to incorporate such species into single-crystal hosts have been unsuccessful. We have therefore resorted to the examination of irradiated polycrystalline samples in the hope of generating and characterizing paramagnetic metal carbonyl clusters. Research in this particular area is already being pursued in several laboratories.[6-8] Unfortunately, in many instances the spectral line widths of species detected in organic or metal carbonyl hosts are large and assignments are accordingly uncertain. In our experience, krypton is a superlative host[9] for the examination of powder EPR spectra. It is totally inert, a surprisingly good solvent, and is stable toward ionizing radiation and exhibits narrow-line EPR spectra in many cases. Moreover, small molecules become mobile in krypton above 90 K, suggesting a method of generating cluster species. In the case of irradiated solutions of $HCo(CO)_4$ in Kr this possibility has been realized: the initial free radical products of irradiation disappear on annealing and are replaced by binuclear cobalt carbonyl radicals. The EPR spectra and structure of these species are described in this article.

Experimental Section

Hydridocobalt tetracarbonyl, $HCo(CO)_4$, was synthesized[10] by the acidification of the complex formed from dicobalt octacarbonyl and dry pyridine. ^{13}C-enriched $HCo(CO)_4$ was produced from the complex which had been exchanged with 99% ^{13}C-enriched CO,

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[†] NRCC No. 22738.

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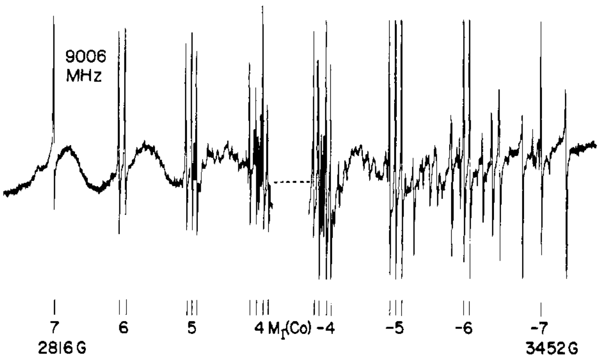

Figure 1. First-derivative EPR spectrum of γ-irradiated $HCo(CO)_4/Kr$ recorded at 77 K after annealing at 100 K. Perpendicular transitions of the spectrum of radical A are labeled with M_I values for the combined spins ($^7/_2$) of two ^{59}Co nuclei.

and the deuterium-containing product was obtained by using D_2SO_4 in the acidification step.

Samples of dry krypton containing ~1 mol % of $HCo(CO)_4$ were sealed in 4-mm diameter Suprasil tubes and immersed in a slush bath of *n*-pentane (140 K) to encourage dissolution of the carbonyl in the matrix. The samples were subsequently irradiated at 77 K either in a 19 000 Ci ^{60}Co γ source or with the full light of a 1000-W high-pressure Hg–Xe arc. EPR spectra were obtained and recorded with a Varian E-12 spectrometer and accessories. Samples were annealed while under observation in the cavity of the spectrometer using a cold N_2-flow cryostat. All spectra were recorded and measured at 77 K.

Results

Examination of the EPR spectra of freshly γ- or UV-irradiated $Kr/HCo(CO)_4$ mixtures at 77 K shows[11] the presence of $Co(CO)_4$, $H_2Co(CO)_3$, and $HCo(CO)_4^-$ among the products of the irradiation. Annealing to 100 K results in the loss of EPR signals due to these radicals and the emergence of new spectra characteristic of free radicals containing two ^{59}Co ($I = {}^7/_2$) nuclei. Two such cobalt carbonyl clusters were identified, one of them (A) being most intense (Figure 1) in γ-irradiated samples and the other (B) being the dominant free radical in UV-irradiated samples (Figure 2). The powder spectra of both species show a very clear hyperfine manifold (Figures 1 and 2) due to interactions of a single unpaired electron with two equivalent ^{59}Co nuclei. In addition, the spectrum of B showed a further doublet splitting (Figure 2) characteristic of coupling of the unpaired electron with a single proton ($I = {}^1/_2$). Replacement of the doublets by 1:1:1 triplets in a spectrum derived from "heavy" hydrido cobalt tetracarbonyl, i.e., $DCo(CO)_4$, confirmed the presence of a spin-bearing proton in dimer B (Figure 2).

Certain of the 15 possible transitions of the wide manifold were obscured in both spectra by regions of great spectral complexity that have defied analysis. Our assignments will therefore be somewhat tentative since they will be based on analysis of one set of features, the wide manifold, for each radical.

With the exception of the two outside lines ($M_I = \pm 7$), each of the transitions for radical A consisted of a multiplet of equally intense lines whose number and separation were appropriate for "second-order" splitting[12] in a radical having two equivalent nuclear spins $^7/_2$. In the first-derivative spectrum of A, all the observed lines of the manifold crossed the base line, indicating that they were "perpendicular" features of an axially symmetric free radical. Although features corresponding to H_0 parallel to the molecular axis were not discernible, the magnitude of the second-order splitting in the perpendicular features suggests $a_\parallel \approx 40$ G, somewhat less than $a_\perp$.

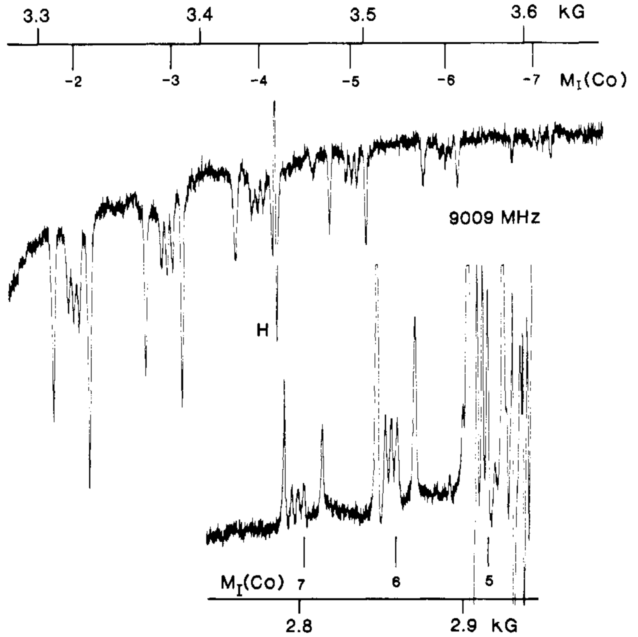

Figure 2. High- and low-field portions of the first-derivative spectrum of UV-photolyzed Kr containing a mixture of $HCo(CO)_4$ and $DCo(CO)_4$ recorded at 77 K after annealing at 100 K. Transition centers for radical B ($H_0//x$) are labeled with M_I values for two equivalent nuclear spins of $^7/_2$.

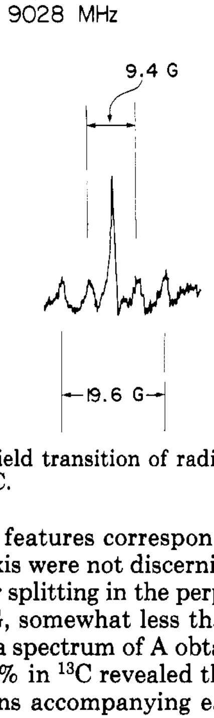

Figure 3. Lowest field transition of radical A containing approximately 20% ^{13}C.

Examination of a spectrum of A obtained from $HCo(CO)_4$ enriched to 20% in ^{13}C revealed the presence of four satellite absorptions accompanying each line of the ^{12}C spectrum (Figure 3). Two distinct groups of ^{13}C nuclei exhibit hyperfine interactions of 9.4 and 19.6 G when H_0 lies perpendicular to the molecular axis in A. The satellite intensities relative to the ^{12}C line suggest that two carbons belong to each group, but we are inclined not to accept this result as definitive since it is based on a rather weak powder spectrum. Unfortunately, we have been unsuccessful in our attempts to generate a pure ^{13}C spectrum of A.

In contrast with the spectrum of A, the spectral lines of species B (Figure 2) were "absorption" type; i.e., they did not cross the base line. The manifold in this case represents the spectrum when H_0 lies along a unique di-

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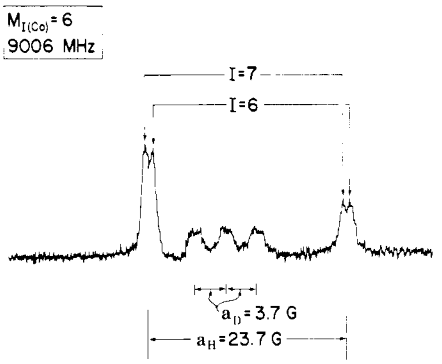


Figure 4. M_I equals 6 transitions of $HCo_2(CO)_8$ and $DCo_2(CO)_8$ in Kr at 77 K.

Table I. EPR Parameters for One[a] Canonical Direction in Radicals A and B

parameter	A	B
g	2.051	2.008
$a_{Co}(2)$, G	45.45	57.4 for H 58.1 for D
$a_C(2)$, G	9.4, 19.6	23.7
$a_C(6)$, G		3.2
$a_H(1)$, G		23.7
$a_D(1)$, G		3.7

[a] Perpendicular direction for A; unique (x) direction for B.

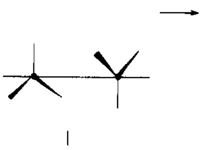
rection (x) in the molecule. The absence of clearly defined "perpendicular" features in the spectrum of B leads us to conclude that the free radical does not possess axial symmetry. Second-order splittings were only just resolved (Figure 4), and to a good approximation the manifold was a first-order spectrum of two equivalent cobalt nuclei and a proton. The magnitude of the observed second-order splittings suggests that the root-mean-square ^{59}Co hyperfine coupling for the y, z directions is ~20 G.

Substitution of ^{13}C ($I = {}^1/_2$) for ^{12}C in the substrate resulted in a spectrum of B in which each of the original lines was replaced by a 1:2:1 24-G triplet of 3-G septets having binomial distributions of intensity. Thus for the particular direction x in this molecule the constituent carbon nuclei consist of a set of two and a set of six equivalent nuclei.

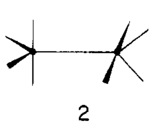
Spectral parameters estimated from the manifolds for the two radicals are summarized in Table I.

Discussion

(i) Species A. The absence of detectable proton hyperfine interactions in the EPR spectrum of this species strongly suggests that it is a charged binuclear cobalt carbonyl. Likely candidates for the carrier of the spectrum are $Co_2(CO)_8^+$ and $Co_2(CO)_8^-$. Two axially symmetric structures compatible with such formulations and with the existence of two distinct groups of ^{13}C nuclei are the D_{3d}- and D_{2d}-nonbridged isomers of $Co_2(CO)_8$:



1



2

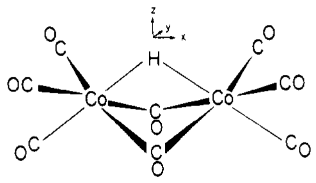
There is good infrared evidence[13] for the presence of both of these isomers in matrix-isolated $Co_2(CO)_8$. An alternative D_{3h} isomer, the eclipsed version of structure 1, is considered to be an unlikely possibility.

Combination of the frontier orbitals[14] for either (1) two $Co(CO)_4$ fragments having C_{3v} symmetry or (2) two such units having C_{2v} symmetry leads us to anticipate LUMO's (lowest unoccupied molecular orbitals) of similar composition for both D_{3d} and D_{2d} isomers of $Co_2(CO)_8$, namely, antibonding σ^* orbitals composed principally of equal, out-of-phase contributions from $Co(3d_{z^2})$ orbitals. Semioccupation of either of these orbitals would result in a negative radical ion with a ground-state electronic configuration ($^2A_{2u}$ in D_{3d} or $^2B_2$ in D_{2d}) consistent with the limited spectroscopic data for radical A. We are thus inclined to favor the assignment $Co_2(CO)_8^-$ with one of the nonbridged structures 1 or 2 for this species.

Dealing firstly with the ^{59}Co hyperfine interactions, we note that the sign choice (40, −45, −45 G) suggests[15] an unpaired spin population of ~33% in each $Co(3d_{z^2})$. Contributions from ligand orbitals could easily account for the remaining 34% unpaired spin density. The positive displacement of $g_\perp$ from free spin arises through spin–orbit interaction with a low-lying degenerate ^2E_u (D_{3d}) or ^2E (D_{2d}) excited state. Doubly occupied e_u or e levels arise naturally from the combination of $Co(CO)_4$ frontier orbitals; they are nonbonding or weakly antibonding in the Co–Co distance and may well lie close to the SOMO (semioccupied molecular orbital). On the other hand, $g_\parallel$ is expected to be close to the free spin value for the radical since the requisite a_{1u} (D_{3d}) and b_1 (D_{2d}) levels are remote from the SOMO in the orbital schemes. Although the parallel features were not analyzed, it was clear that $g_\parallel$ was closer to free spin than $g_\perp$.

Experimentally we were unable to distinguish between structures 1 and 2 for $Co_2(CO)_8^-$. However, the similarity of its spectroscopic parameters to those of the recently reported[8] anion radicals $Co_2(CO)_6L_2^-$, which have D_{3d} geometry, leads us to suspect that 1 is the more likely structure. We do not regard the equality of ^{13}C satellite intensities of Figure 3 as compelling evidence favoring structure 2. Anisotropy of the equatorial ^{13}C hyperfine interaction in the perpendicular plane of 1 could well reduce the intensity of the equatorial satellites relative to that of the axial features; a 1:1 intensity ratio in the first-derivative spectrum of 1 might then arise accidentally.

(ii) Species B. Although the spectral information for species B is limited to one direction (Table I), it provides important clues in determining the molecular geometry. The magnetic equivalence of the cobalt nuclei and of two groups of carbon nuclei leaves little doubt that the radical is a hydrogen-bridged cluster with a structure similar to that[16] of the $HFe_2(CO)_8^-$ anion:



Krusic[17] has obtained isotropic EPR parameters for the neutral radical $HFe_2(CO)_8$ which suggest that it too has a structure similar to the diiron carbonyl hydride anion. We are inclined to believe that species B is also a neutral radical, $HCo_2(CO)_8$, having two more electrons than $HFe_2(CO)_8$. The generation of a doubly charged cation $HCo_2(CO)_8^{2+}$ by UV photolysis with wavelengths longer than 2537 Å is considered rather unlikely in view of the

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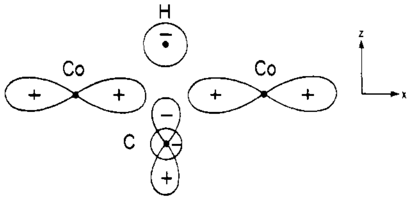
high[18] (8.9 eV) ionization potential of $HCo(CO)_4$.

Speculation regarding the composition of the semioccupied orbital (SOMO) in $HCo_2(CO)_8$ is perhaps somewhat premature in view of the meagre data for the **g** and hyperfine tensors. One telling piece of information, however, is the magnitude of the proton hyperfine interaction (23.7 G along x). This undoubtedly contains a large isotropic component since we estimate a maximum dipolar contribution to the proton hyperfine interaction of ~6 G in a molecule having geometry[16] identical with that of $HFe_2(CO)_8^-$. A large proton hyperfine interaction suggests direct participation of H(1s) in the SOMO and, hence, a ground state of the totally symmetric representation A_1 in C_{2v} symmetry. Cobalt atomic orbital contributions (d_{x^2}) would necessarily be in phase in an a_1 orbital, and significant contributions from bridging carbon 2s and $2p_z$ orbitals might be anticipated:



With equal, small, direct contributions from the remaining six terminal carbon nuclei, such a molecular orbital provides a good explanation of the experimental spectrum ($H_0//x$).

The theoretical calculations of Thorn and Hoffmann[19] and of Teo et al.[20] on $Fe_2(CO)_8^{2-}$ and related molecules lend some support for our proposed SOMO: The three highest filled orbitals in $Fe_2(CO)_8^{2-}$ would appear to be a_2, a_1, and b_2, the latter being the HOMO. Of these, the a_1 orbital is essentially an in-phase combination of $Co(3d_{x^2})$ atomic orbitals, destabilized by antibonding with bridging CO π donor orbitals. Further destabilization of this a_1 orbital would be expected with the inclusion of an additional H(1s) level, leading to an orbital of composition similar to that proposed above and of higher energy than the b_2 level. In other words, this a_1 orbital would become the SOMO for radicals such as $HFe_2(CO)_8^{2-}$ and $HCo_2(CO)_8$. Furthermore, the proximity of the filled a_2 and b_2 orbitals would result in positive g shifts for $H_0//z$ and $H_0//y$; the absence of nearby b_1 levels would result in a g_{xx} value near that of free spin, as observed experimentally (Table I).

An alternative description of the a_1 SOMO places more unpaired spin density on two of the terminal carbons (lying in xz) than on the remaining carbon nuclei. The latter, consisting of two bridging and four terminal carbon nuclei, could be magnetically equivalent by accident for $H_0//x$. Krusic[17] has in fact adduced indirect evidence that a terminal pair of ^{13}C nuclei is responsible for the triplet splitting in the spectrum of $HFe_2(^{13}CO)_8$. Our data unfortunately do not permit us to make such a distinction in the case of $HCo_2(CO)_8$.

The possibility that two species differing by two valence electrons should have the same $^2A_1$ ground state does not worry us unduly, especially in view of the calculations of Teo et al.[20] In the series of molecules $Fe_2(CO)_6(PH_2)_2^{n-}$, $n = 0–2$, the computed $4b_2$ level rapidly approached the doubly occupied $6a_1$ level with increasing negative charge, an indication that $HFe_2(CO)_8$ and $HCo_2(CO)_8$ might well have $^2A_1$ ground states of similar composition.

A reviewer of this article has criticized our assignment of the wide manifold to a direction (x, i.e., Co–Co) for which g and a_{Co} are not required by symmetry to be parallel. The spectrum (Figure 2) certainly indicates that the tensors are colinear, or nearly so, and thus suggests an assignment to y, the only direction for which g and a_{Co} are necessarily parallel. However, overlap considerations lead us to expect Co ($3d_{xz}$) contributions to the a_1 SOMO in such a case. An appreciably larger g shift than observed might then be anticipated. We concede, however, that the alternative assignment is a distinct possibility; our preference for x relies rather heavily on the theoretical arguments advanced above.

A striking feature of the spectrum of the hydride cluster was the marked difference (Figure 4) in field positions of the transition centers for light and heavy hydrogen-containing species. This was due to the significantly larger ~1%) ^{59}Co hyperfine coupling of the deuterium-containing radical. There can be little doubt that this effect arises through modulation of the ^{59}Co hyperfine interaction by a low-frequency vibration of the molecule. Such effects are well documented[21-23] and should, furthermore, be anticipated for highly fluxional species such as metal carbonyl free radicals. For an effect as large as we have observed in $HCo_2(CO)_8$, the low-frequency mode must belong to a representation other than that (A_1) of the ground-state electronic wave function. A normal mode of the B_1 or B_2 representations involving motion of the bridging hydrogen atom may well be responsible. This would result in admixture of Co 3d orbitals other than d_{x^2} into the ground state and a lowering of the ^{59}Co hyperfine coupling along x.

Registry No. $HCo(CO)_4$, 16842-03-8; $HCo_2(CO)_8$, 87249-39-6; $Co_2(CO)_8^-$, 87249-40-9.

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