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Paramagnetic Organometallic Molecules. 2. Electrochemical Investigation of the Tricobalt Carbon Cluster

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Detailed aspects of the redox behavior of the cobalt clusters $YCCo_3(CO)_9$ have been studied using the techniques of dc and ac polarography at mercury electrodes and dc and ac cyclic voltammetry. One-electron reduction at both mercury and platinum electrodes is both electrochemically and chemically reversible. The $E^r_{1/2}$ values for the $YCCo_3(CO)_9/YCCo_3(CO)_9\cdot^-$ couple vary with Y and in acetone fall within the range $-0.2 \rightarrow -0.5$ V vs. Ag/AgCl. The $E^r_{1/2}$ value can be correlated with the charge density on the cobalt atoms in the neutral cluster, but when Y is a halogen, it is necessary to invoke a mesomeric as well as an inductive component in bonding to the apical substituent. Further reduction to the dianions $YCCo_3(CO)_9^{2-}$ causes rapid disintegration of the cluster unit. No evidence was found for an electrochemical oxidation step and it would therefore seem that the cluster cannot accommodate an extensive electron-transfer series.

Introduction

Reduction potentials for a wide range of carbonyl derivatives have been reported by Dessy and co-workers[2-5] and in some instances[3-5] the systems were studied in depth by ESR and NMR techniques. Vlček[6] studied the iron carbonyl series and other workers have investigated the redox behavior of binary carbonyls[7,8] and halocarbonyls,[9] species containing the $[(\eta^5\text{-Cp})M(CO)]$ grouping[10-15] and various substituted carbonyl derivatives.[16-18] In contrast, electrochemical data for carbonyl clusters is lacking, apart from a detailed study[19,20] of the redox series $[(\eta^5\text{-Cp})Fe(CO)]_4^{2+,+,0,-}$. In this series the iron–iron bond remained intact in all oxidation states and well-defined salts of the monocation were isolated and structurally characterized.[19,20] More recently, a dicobalt radical anion species $[(\eta^5\text{-Cp})Co(CO)]_2\cdot^-$ has been prepared[21] by the chemical or electrochemical reduction of $(\eta^5\text{-Cp})Co(CO)_2$. Crystallographic and ESR data for the radical anion salt are consistent with considerable delocalization of the unpaired electron over both cobalt atoms.[21]

Radical anion formation from metal carbonyl clusters, exemplified by the tricobalt carbon system discussed in the preceding paper,[22] offers an excellent opportunity to investigate the physicochemical and structural consequences of departing from the usual 18-electron configuration. It was suggested[23] that the "electron reservoir" concept can be applied to carbonyl clusters and, if this description is correct, there exists the possibility of reduction or oxidation with retention of the cluster moiety. The preparative and spectroscopic work[22] has shown this to be true for the tricobalt carbon cluster but the full extent of its redox behavior was still open to question. Accordingly we undertook a detailed electrochemical investigation using the techniques of ac and dc polarography and cyclic voltammetry at mercury and platinum electrodes. Considerable thermodynamic and kinetic data became available from these measurements which provide confirmation of the ideas developed from the spectroscopic work.

Experimental Section

The tricobalt carbon derivatives were prepared by published procedures[23] and purified by vacuum sublimation and/or recrystallization. Dicobalt octacarbonyl (Strem) was recrystallized from methanol.

The electrochemistry of the $Co(CO)_4^-$ anion was undertaken using the $[(Ph_3P)_2N]^+[Co(CO)_4]^-$ salt prepared by the method of Ruff.[24] Anion radicals were prepared by reducing the parent clusters with a sodium mirror.[22]

Electrochemical Instrumentation. Ac and dc polarograms and voltammograms, from which data in this paper are reported, were recorded with a PAR electrochemistry system, Model 170. Acetone or dichloromethane was used as the solvent with 0.1 mol dm^{-3} $Et_4N^+ClO_4^-$ as the supporting electrolyte at a concentration of 0.10 (acetone) or 0.05 mol dm^{-3} (dichloromethane). All solutions were

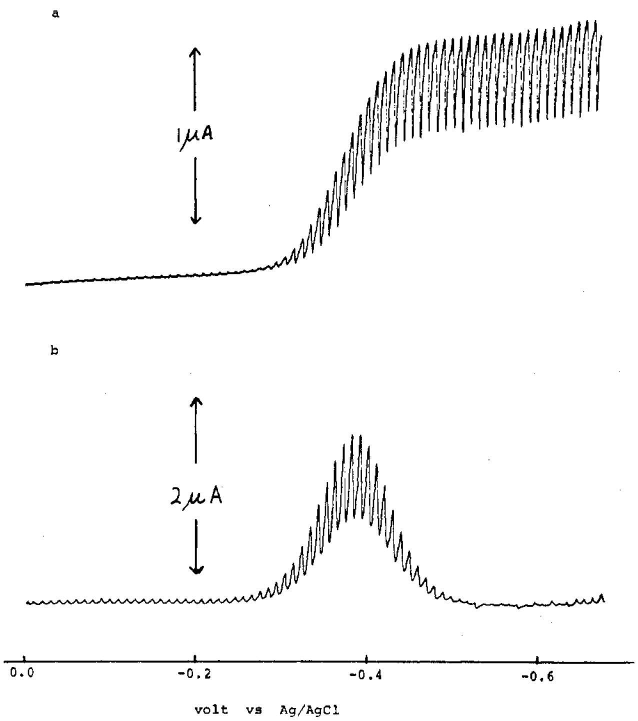

Figure 1. (a) Ac and (b) dc polarograms for the reduction of $C_6H_5CCo_3(CO)_9$ to the anion radical in acetone (0.1 M Et_4NClO_4); drop time 0.5 s; applied ac signal 10 mV p–p at 200 Hz.

thermostated at 293 ± 1 K and degassed with argon for 10 min prior to undertaking measurements. A three-electrode system coupled with positive feedback circuitry was employed to minimize *IR* drop losses. The working electrode was either a dropping mercury electrode (controlled drop time) or a platinum-disk electrode. The reference electrode was Ag/AgCl [0.1 mol dm^{-3} LiCl (acetone)] and the third electrode was platinum wire. Modifications to the Model 170 electrochemistry system enabling ac cyclic voltammetry etc. to be performed are described in the literature.[25–27]

Some of the preliminary polarograms were recorded in dichloromethane on a Radiometer 404 G polarographic analyzer and with the use of an $Ag/AgClO_4$ reference electrode.

Results and Discussion

The $YCCo_3(CO)_9/YCCo_3(CO)_9{\cdot}^-$ Couple. Voltammetric measurements on the tricobalt carbon clusters in acetone and dichloromethane, at both mercury and platinum electrodes, indicated the existence of several electrode processes. Figure 1 shows typical dc and ac polarograms for the first reduction wave of these clusters. Analysis of the wave shapes and positions (Table I) and the *n* values (number of electrons) obtained from a dc polarographic plot of log $[(I_d - I)/I]$ against applied potential were consistent with a reversible one-electron reduction

$$YCCo_3(CO)_9 + e^- \rightleftharpoons YCCo_3(CO)_9{\cdot}^- \qquad (1)$$

Reduction of an acetone solution of $C_6H_5CCo_3(CO)_9$ by a sodium mirror gave rise to a species whose polarographic behavior in the potential range where cluster reduction occurs is displayed in Figure 2. A reversible one-electron oxidation wave is seen with $E^r_{1/2}$ (reversible half-wave potential) the same as that for reduction of $C_6H_5CCo_3(CO)_9$. This fact, combined with the spectroscopic evidence, unambiguously establishes the identity of the radical anion produced by sodium reduction and confirms electrode process (1). Quantitative polarographic measurements showed that, for the phenyl cluster, about 50% yield of radical anion is obtained using sodium reduction in acetone, although yields are higher in other solvents. Lower yields were found for other derivatives particularly those that had been shown to be unstable at ambient temperature (see ref 22).

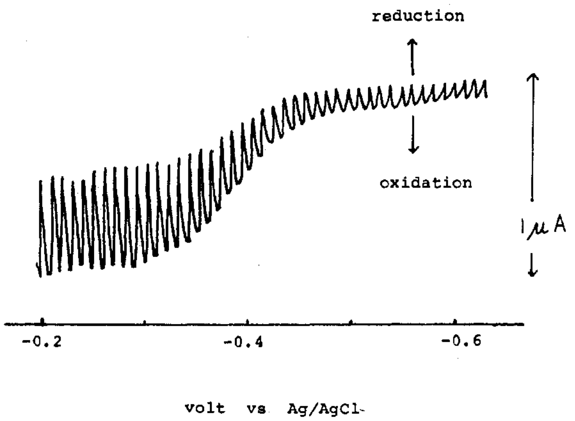

Figure 2. Polarogram of an acetone (0.1 M Et_4NClO_4) solution of $C_6H_5CCo_3(CO)_9$ after reduction with sodium; drop time 0.5 s.

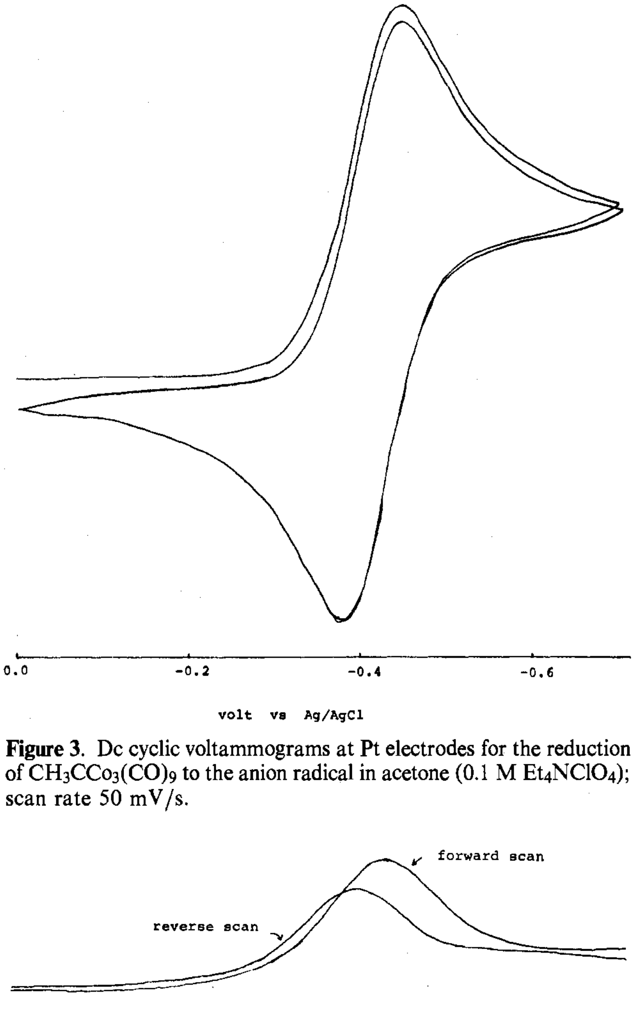

Figure 3. Dc cyclic voltammograms at Pt electrodes for the reduction of $CH_3CCo_3(CO)_9$ to the anion radical in acetone (0.1 M Et_4NClO_4); scan rate 50 mV/s.

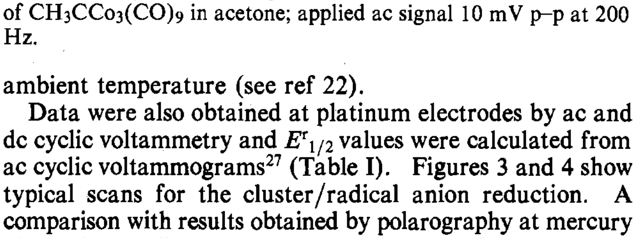

Figure 4. Ac cyclic voltammogram at the Pt electrode for the reduction of $CH_3CCo_3(CO)_9$ in acetone; applied ac signal 10 mV p–p at 200 Hz.

Data were also obtained at platinum electrodes by ac and dc cyclic voltammetry and $E^r_{1/2}$ values were calculated from ac cyclic voltammograms[27] (Table I). Figures 3 and 4 show typical scans for the cluster/radical anion reduction. A comparison with results obtained by polarography at mercury electrodes confirms that chemical aspects of the electrode

Table I. Data Obtained at Mercury and Platinum Electrodes for the Electrode Process $YCCo_3(CO)_9 + e^- \rightleftharpoons YCCo_3(CO)_9\cdot^-$ in Acetone[a]

	Mercury electrode				Platinum electrode			
	Dc polarography		Ac polarography[b]		Dc cyclic voltammetry[c]			Ac cyclic voltammetry[d]
Cluster	$E_{1/2}$	$E_{1/4}-E_{3/4}$[e]	E_p	Half-width[e]	E_p(Red)	E_p(Ox)	$E_{1/2}$	$E^r_{1/2}$ calcd assuming $\alpha = 0.5$
F	−0.280	56	−0.282	90	−0.348	−0.250	−0.302	−0.276
Cl	−0.286	58	−0.290	90	−0.364	−0.264	−0.310	−0.284
Br	−0.274	58	−0.276	90	−0.350	−0.242	−0.298	−0.276
CF_3	−0.270	56	−0.270	90	−0.275	−0.180	−0.240	−0.270
H	−0.372	56	−0.376	90	−0.440	−0.320	−0.404	−0.366
Ph[f]	−0.384	58	−0.388	90	−0.450	−0.370	−0.410	−0.378
Me_3Si	−0.406	58	−0.408	90	−0.450	−0.368	−0.420	−0.400
Me	−0.428	56	−0.428	90	−0.486	−0.384	−0.444	−0.424

[a] Supporting electrolyte 0.1 M Et_4NClO_4; concentration of cluster 2×10^{-3} M; $E_{1/2}$, $E^r_{1/2}$, and E_p in V vs. Ag/AgCl. [b] Amplitude 10 mV p-p at 200 Hz. [c] Scan rate 200 mV s^{-1}. Results vary depending on treatment of platinum electrode. [d] α is the charge transfer coefficient (see ref 27); amplitude 10 mV p-p at 400 Hz; scan rate 50 mV s^{-1}. [e] Units mV. [f] Substituted aryl derivatives give essentially the same electrochemical parameters as $PhCCo_3(CO)_9$.

Table II. Summary of Electrochemical and Spectroscopic Data for $YCCo_3(CO)_9$

Y	$E°$,[a] V	A^{Co},[b] G	g[b]	ν(CO),[c] cm^{-1}
F	−0.28	36.7	2.024	2110
Cl	−0.29	36.2	2.020	2109
Br	−0.27	37.1	2.023	2109
CF_3	−0.27	34.5	2.020	2115
H	−0.37	34.4	1.978	2106
Ph	−0.38	35.6	2.019	2102
Me	−0.43	36.6	2.017	2101
Me_3Si	−0.41	34.2	2.017	2101

[a] Vs. Ag/AgCl for the couple $YCCo_3(CO)_9 + e^- \rightleftharpoons YCCo_3(CO)_9\cdot^-$, $T = 293$ K, acetone solution. [b] Reference 22. [c] A_1 in-phase symmetrical stretching mode for the neutral cluster in hexane.

process are the same at both electrode surfaces. For all clusters the heterogeneous charge-transfer rate constants, k_s, at platinum are of the order 10^{-2} to 10^{-3} cm s^{-1}, the exact value depending on the history of the electrode. At mercury electrodes in acetone the electron-transfer step is essentially diffusion controlled under dc and ac polarographic conditions ($k_s > 0.1$ cm s^{-1}). In the sense that the cluster is structurally complex and the metal centers are sterically protected it is surprising that k_s is so high for these clusters. Intuitively, direct electron transfer onto a metal site should be a slow process, although it is interesting that fast electron transfer was also noted[19] in the electrochemical reduction of $[(\eta^5\text{-Cp})Fe(CO)]_4$. The considerable difference between k_s values at platinum and mercury further confuses the issue but, to accommodate these observations, we suggest that electron transfer at the electrode could be via bridging of the electrode to an unhindered carbonyl group rather than directly to the Co_3C moiety, a suggestion not without precedent.[2,18]

Tables I and II summarize polarographic data obtained in acetone. The $E_{1/2}$ values and ac peak potentials E_p obtained at mercury electrodes are equal to, or close to, the reversible $E^r_1/_2$ value for the cluster/radical anion couple calculated from data at platinum electrodes. In marked contrast to systems involving the cleavage of metal–metal bonds[10,11] these $E_{1/2}$ values are insensitive to the nature of the solvent.

The reduction potential is sensitive to small variations in the electronic nature of the apical substituent and this adds strong support to the concept[22,28,29] of delocalized bonding in a $YCCo_3$ moiety that is an inefficient charge sink. As expected, the clusters most difficult to reduce are those with electron-donating apical substituents. $E_{1/2}$ becomes more positive as the electronegativity of Y increases and is the most positive for a trifluoromethyl substituent. Nonetheless, the big difference between the $E_{1/2}$ values for nonhalogen and halogen apical substituents is surprising and the similar $E_{1/2}$ values of ~0.28 V for the halo clusters are not compatible with these simple inductive arguments. $E_{1/2}$ values measure the free energy difference between the neutral and reduced species, and thus variations in $E_{1/2}$ reflect the relative stabilities of either the parent clusters or the radical anions. An increase in charge will increase the separation between the HOMO and LUMO of the neutral cluster, making reduction more difficult. It is therefore significant that there is a correlation (Table II) between $E_{1/2}$ and a ground-state parameter, the frequency of the symmetrical in-phase A_1 ν(CO) mode, a mode which is sensitive to changes in electron density on the cluster.[28] Many facets of tricobalt carbon chemistry, including changes in A_1 ν(CO), high ν(C–X) frequencies,[23,28] the stability of compounds with a positively charged center at the apical substituent,[28-32] and Hammett functions,[33] indicate that the cluster can participate in "push–pull" electron interactions in either direction. In the case of the apical substituent these may involve a π component.[28,29] We suggest that the electron-withdrawing capability of the fluorine substituent is compensated by an opposing mesomeric effect using filled p orbitals of the fluorine atom. The $+M$ effect will be negligible for bromine and the ultimate result is the more or less identical $E_{1/2}$ values for the halo clusters. The well-documented[34] inductive and mesomeric interaction of the CF_3 group will account, in a like manner, for the ease of reduction of the $CF_3CCo_3(CO)_9$ cluster.

In view of the paucity of data for other carbonyl clusters it is difficult to judge what effect these interactions have on the absolute magnitude of $E_{1/2}$ but the tricobalt carbon clusters are certainly easier to reduce than $[(\eta^5\text{-Cp})Fe(CO)]_4$,[13] $[(\eta^5\text{-Cp})Co(CO)]_3$,[3] $[(\eta^5\text{-Cp})Ni(CO)]_3$,[3] and the trinuclear iron group derivatives.[35] A more rigorous comparison is not possible as the nature of the redox orbitals for those structurally different clusters is still open to question.

A Comparison of $E_{1/2}$ and ESR Data. Within a series of isostructural clusters there is an opportunity to examine the relationship between $E^r_{1/2}$ ($E°$), hyperfine coupling constants, and g values, parameters which reflect the electronic characteristics of the neutral and paramagnetic species (Table II). In fact for most paramagnetic systems[2,36,37] there is rarely a correlation between charge and spin distribution and the tricobalt carbon clusters are no exception. Standard electrode potentials are a measure of the difference in free energy between the initial and final states of the redox couple which in turn is related to the separation between the HOMO and LUMO of the neutral cluster. This parameter was found to be sensitive to the nature of the apical substituent Y. Hyperfine coupling constants, on the other hand, relate to the spin distribution in the radical anions and their magnitude is a function of the unpaired electron density at the cobalt nuclei;

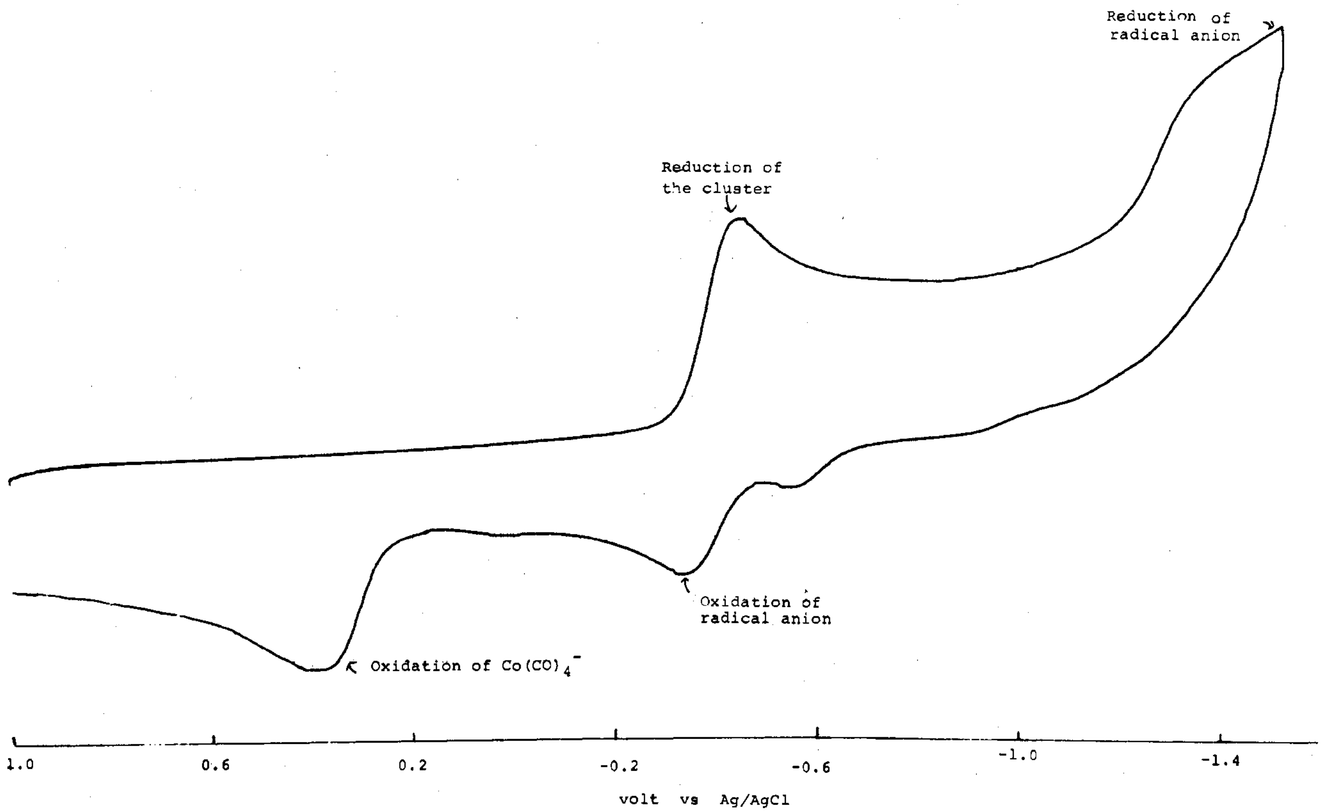

Figure 5. Dc cyclic voltammograms of $(CH_3)_3SiCCo_3(CO)_9$ over an extended potential range at platinum in acetone (0.1 M Et_4NClO_4); scan rate 200 mV/s.

A^{Co} does not significantly vary with Y.

Dahl[20,38] has given persuasive evidence that the extra electron in trinuclear clusters enters a singly degenerate orbital that is antibonding and predominantly metal in character. This would seem to hold for the tricobalt carbon radical anion.[22] From the invariant A^{Co} values it appears that the spin density and energy of this singly degenerate level are relatively constant throughout the series. It follows that the free energy for the redox process is then a function of the charge distribution in the HOMO. If the HOMO is a delocalized orbital with contributions from the basal cobalt atoms, the apical carbon atom, and, possibly, the apical substituent, then the sensitivity to the nature of Y is understandable. Photoelectron spectral and theoretical studies currently under way should shed further light on the validity of these proposals.[35]

Reduction of the Radical Anion. Figure 5 shows a typical cyclic voltammogram obtained at a Pt electrode over an extended potential range. A radical anion generated at a potential around −0.3 V (vs. Ag/AgCl) can itself be reduced at potentials near the solvent limit; data are summarized in Table III.

Table III. Electrochemical Data Obtained at Mercury and Platinum Electrodes in Acetone[a] for the Second Reduction Step, $YCCo_3(CO)_9^{\cdot -} \rightarrow YCCo_3(CO)_9^{2-} \rightarrow Co(CO)_4^- +$ products

	Dc polarography (dropping Hg electrode)[b]	Cyclic voltammetry (Pt electrode)[c]	
Cluster	$E_{1/2}$	E_p(Red)	E_p(Ox)[d]
F	−1.15	−1.40	0.38
Cl	−1.16	−1.36	0.38
Br	−1.17	−1.38	0.38
CF_3	−1.21	−1.32	0.38
H	−1.23	−1.44	0.38
Ph	−1.16	−1.48	0.38
Me_3Si	−1.28	−1.42	0.38
Me	−1.26	−1.49	0.38

[a] Supporting electrolyte 0.1 M Et_4NClO_4; 2×10^{-3} M cluster; $E_{1/2}$ and E_p in V vs. Ag/AgCl. [b] Other waves also seen at more negative potentials. [c] Scan rate 200 mV s^{-1}; peak potentials dependent on the history of the Pt electrode. [d] Other weak peaks also observed for most compounds on the reverse scan at about −0.90, −0.65, and 0.05 V.

Even at scan rates of 100 V s^{-1} and temperatures down to 193 K, the reduction of the radical anion is chemically irreversible and apparently the dianion, $YCCo_3(CO)_9^{2-}$, has no inherent stability. Disintegration of the cluster unit on the addition of two electrons is demonstrated by the extra waves on the reverse scan of the cyclic voltammogram and the complexity of the polarograms (Figure 6). Furthermore, the products of this disintegration themselves cause a substantial modification of the radical anion oxidation pathway. Thus the voltammogram with the switching potential at more negative potentials than the second reduction step (Figure 5) is considerably different from that when the potential scan direction is reversed prior to the onset of the second wave (Figure 3). A cross redox reaction must occur between a highly reactive species generated from the dianion and the cluster (or radical anion). An oxidation wave at 0.4 V vs. Ag/AgCl was considered to correspond to a possible fragmentation product, $Co(CO)_4^-$, and this was confirmed by reference to a cyclic voltammogram of the anion (Figure 7). Whether $Co(CO)_4^-$ is obtained directly or via a secondary reduction of $Co_2(CO)_8$ is immaterial as reduction of $Co_2(CO)_8$ would occur immediately at the negative potentials associated with the second electrode process. The complete electrode process at platinum can now be written as (with Y = Ph for example)

$$PhCCo_3(CO)_9 \xrightleftharpoons{-0.45\ V} PhCCo_3(CO)_9^{\cdot -} \xrightleftharpoons{-1.48\ V} PhCCo_3(CO)_9^{2-}$$
$$\xrightarrow{\text{fast}} Co(CO)_4^- + ?$$

At mercury electrodes, the *n* value ≥1 for the second reduction

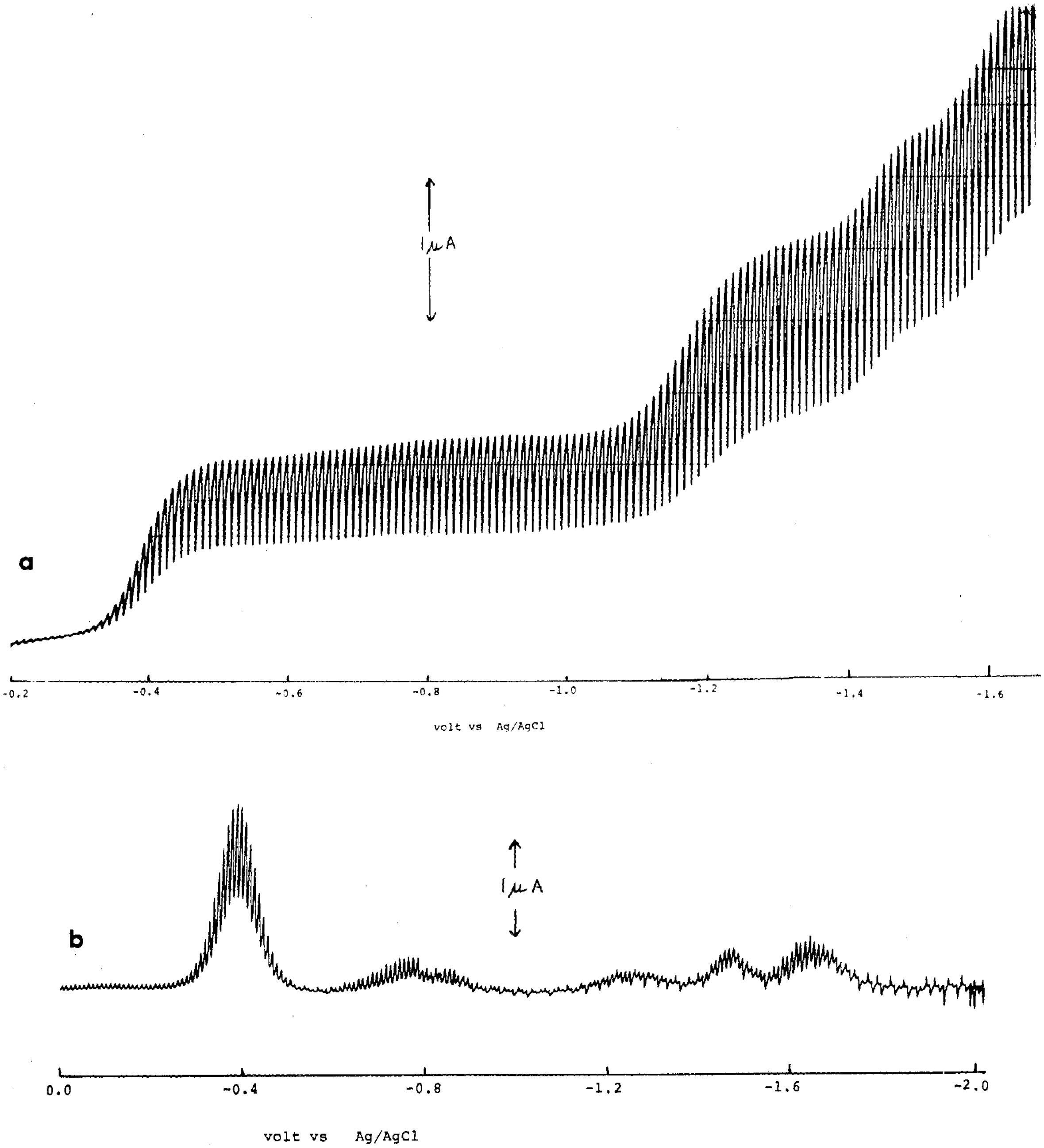

Figure 6. (a) Dc and (b) ac polarograms for reduction of $C_6H_5CCo_3(CO)_9$ in acetone (0.1 M Et_4NClO_4); drop time 0.5 s; ac potential 10 mV p–p at 200 Hz.

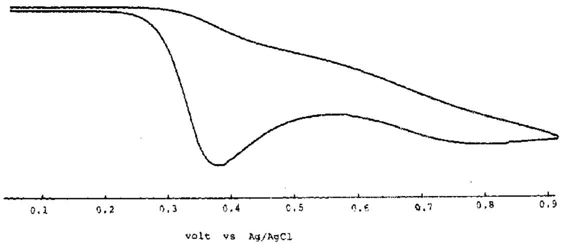

Figure 7. Cyclic voltammogram at platinum for the oxidation of $Co(CO)_4^-$ in acetone (0.1 M Et_4NClO_4); scan rate 200 mV/s.

step indicates that further electron transfer can be coupled with the rearrangement or decomposition of $YCCo_3(CO)_9^{2-}$.

The instability of a dianion is explicable in terms of Wade's[39] simple ideas of cluster bonding. According to these ideas two-electron reduction would produce polyhedral expansion from the nido neutral tetrahedral cluster to an arachno square-planar or cis-divacant Co_3C moiety. It is unlikely that the stereochemical requirements of the arachno geometry would engender stability in the dianion. Furthermore, its instability is understandable if the two electrons enter an antibonding molecular energy level.

Finally, it is important to remember that chemical reduction of $PhCCo_3(CO)_9$ or $CH_3CCo_3(CO)_9$ with sodium amalgam, although ultimately giving $Co(CO)_4^-$, proceeds via a red-brown intermediate stage, from which crystalline unstable salts of composition $Hg[YCCo_3(CO)_x]_2^{2-}$ could be isolated.[40] It is believed that these salts may well be mercury-stabilized salts of the dianion and an effort is currently being made to characterize these products by x-ray crystallographic methods.

Oxidation of Tricobalt Carbon Derivatives. In acetone, at both platinum and mercury electrodes, no oxidation waves were detected and it is therefore understandable that all attempts to chemically oxidize the clusters with retention of the metal–metal framework failed (e.g., with $AgPF_6$, halogens). We conclude that the redox behavior of the tricobalt carbon clusters is limited because of the particular delocalized bonding structure of these clusters.

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Registry No. $FCCo_3(CO)_9$, 18433-91-5; $ClCCo_3(CO)_9$, 19512-60-8; $BrCCo_3(CO)_9$, 19512-61-9; $CF_3CCo_3(CO)_9$, 22043-50-1; $HCCo_3(CO)_9$, 15664-75-2; $PhCCo_3(CO)_9$, 20756-47-2; $Me_3SiCCo_3(CO)_9$, 41620-07-9; $MeCCo_3(CO)_9$, 13682-04-7; $FCCo_3(CO)_9{}^{\cdot-}$, 51900-19-7; $ClCCo_3(CO)_9{}^{\cdot-}$, 61024-77-9; $BrCCo_3(CO)_9{}^{\cdot-}$, 61024-76-8; $CF_3CCo_3(CO)_9{}^{\cdot-}$, 61024-78-0; $HCCo_3(CO)_9{}^{\cdot-}$, 51900-20-0; $PhCCo_3(CO)_9{}^{\cdot-}$, 61024-80-4; $Me_3SiCCo_3(CO)_9{}^{\cdot-}$, 61024-69-9; $MeCCo_3(CO)_9{}^{\cdot-}$, 61024-79-1; $FCCo_3(CO)_9{}^{2-}$, 61024-61-1; $ClCCo_3(CO)_9{}^{2-}$, 61024-60-0; $BrCCo_3(CO)_9{}^{2-}$, 61024-59-7; $CF_3CCo_3(CO)_9{}^{2-}$, 61024-64-4; $HCCo_3(CO)_9{}^{2-}$, 61024-63-3; $PhCCo_3(CO)_9{}^{2-}$, 61024-74-6; $Me_3SiCCo_3(CO)_9{}^{2-}$, 61024-70-2; $MeCCo_3(CO)_9{}^{2-}$, 61024-66-6.

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Infrared Spectra of Matrix-Isolated Dicobalt Octacarbonyl. Evidence for the Third Isomer[1]

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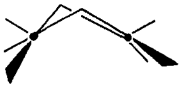
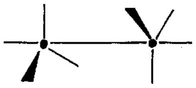
The infrared spectra of dicobalt octacarbonyl matrix-isolated in Ar, hexane, and several other matrices have been examined. From the IR spectra of photolyzed matrices and of matrices subjected to visible radiation following photolysis, it is possible to assign absorptions to three isomeric forms of $Co_2(CO)_8$. Two of these are the accepted isomeric forms. The third has no bridging CO groups. The IR spectrum is in best accord with a structure of D_{2d} symmetry, in which the Co–Co bond axis lies in the plane of the trigonal-bipyramidal arrangement at each metal. The isomers are observed to interconvert rapidly. Conversion of the nonbridged D_{3d} isomeric form to the bridged form occurs in hexane matrices with $\Delta G^{\ddagger} = 6.4 \pm 0.4$ kcal/mol at 84 K.

Dicobalt octacarbonyl, $Co_2(CO)_8$, exhibits interesting and unusually complex structural characteristics. In the solid state the structure is of C_{2v} point group symmetry, **1**, involving a pair of bridging CO groups.[3] In solutions, the presence of a second form involving no bridging CO groups is evident in the IR spectra. The nonbridged form has been assigned a D_{3d} symmetry structure, **2**.[4,5] More recently, Bor and Noack have suggested the presence of still a third isomer,[6] on the basis of two bands in the CO stretching region in solution IR spectra, not assignable to either **1** or **2**.


1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Dicobalt octacarbonyl is of considerable interest because it is a precursor to substances of importance as catalysts, notably $HCo(CO)_4$, and because under reaction conditions $Co_2(CO)_8$ may be involved in equilibria with active catalytic species.[7] However, there is very little information in the literature regarding the kinetics of $Co_2(CO)_8$ reactions.