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Paramagnetic Organometallic Molecules. 1. Radical Anions Based on the Tricobalt Carbon Cluster

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Methinyltricobalt enneacarbonyls, $YCCo_3(CO)_9$, compounds having as their structural core the tricobalt carbon cluster, undergo facile alkali metal and electrochemical one-electron reduction to produce stable radical anions. Their ESR, IR, and visible–ultraviolet spectra have been examined and analyzed in relation to the electronic nature of the apical substituent Y. The cluster unit is retained on reduction and hyperfine coupling to the three cobalt nuclei is observed; A^{Co} does not vary significantly with the nature of the apical substituent. Hyperfine interactions with bound CO, the apical carbon nucleus, or apical substituent nuclei are absent and it is suggested that the unpaired electron occupies a nondegenerate level, largely metal in character. These observations are shown to be compatible with other facets of tricobalt carbon cluster chemistry. The unusual line shape of the ESR spectra is attributed to g value anisotropy.

Introduction

A fundamental tenet of organometallic chemistry is that the most "stable" compounds have a spherical electronic charge distribution about the metal atom. The stoichiometry and reactivity of these compounds can be successfully rationalized by an ad hoc 18- (or 16-) electron rule[1-3] and the VSEPR model[3,4] used to account for the observed geometry. Matrix techniques have been extensively employed to isolate binary carbonyl species that do not obey the 18-electron formalism[5-8] and the more varied geometries observed for such species have been discussed in terms of "holes" in the spherical charge distribution.[9,10] Nonetheless, these species are formally diamagnetic and there have been few attempts to isolate and study paramagnetic organometallic molecules even though they have been implicated in many photochemical, redox, and catalytic organometallic processes. Homolytic photochemical cleavage of metal–metal or metal–ligand bonds is an obvious route to organometallic radicals[11,12] but their tenuous existence under normal conditions and propensity to disproportionate or react with the solvent make characterization difficult. Furthermore, homolysis may be induced or enhanced by the spin-trap used to identify the radical, rather than being the primary photoprocess.[13] Chemical or electrochemical redox reactions, particularly of metal–metal bonded molecules, are probably the most satisfactory route to paramagnetic species[14] and have been exploited by several investigators.[14,15] It is the objective of our research program to isolate stable paramagnetic organometallic species, investigate their involvement in organometallic reactions, and elucidate their electronic structure from spectral measurements and theoretical calculations. To date, radicals and radical anions have been produced by chemical,[16-18] electrochemical,[16-18] and high-[16] and low-energy[16,19] photon reactions including dissociative electron capture.[20]

Metal carbonyl clusters can be regarded as a special class of organometallic molecule as chemically significant cooperative interactions may lead to an electronic structure analogous to that of a metal; these clusters then become soluble analogues of the metal catalysts. Our comprehensive study of the tricobalt carbon cluster, Co_3C, core of the methinyltricobalt enneacarbonyls has brought to light the way in which cooperative interactions can operate in a polynuclear system.[21-24] It is clear that the concept of a delocalized Co_3C core with the ability to participate in a "push–pull" electronic interaction, that is, to function as an electron reservoir, is necessary in order to explain the physicochemical data.[21,22] This concept should apply equally well to homonuclear clusters and recent kinetic studies[25] on $Ir_4(CO)_{12}$ bear out this suggestion. Because of the cooperative interactions, clusters can more effectively buffer changes in spin and/or charge density at a metal atom than a mononuclear compound, and redox reactions should be more efficient for cluster species. The efficiency of a cluster as a spin or charge sink is reflected in the spectral and electrochemical parameters for the paramagnetic derivatives and, providing crystalline compounds can be isolated, by subtle changes in structural parameters for an isoelectronic series,[14] such as those studied by Dahl and coworkers.[26-28] Another interesting possibility is that polyhedral expansion or contraction may occur on two-electron reduction or oxidation.[29] These ideas were substantiated by an investigation of a remarkably stable series of radical anions derived from the tricobalt carbon cluster. This paper is concerned with the preparation and spectral study of the radical anions $YCCo_3(CO)_9\cdot^-$; the following paper[30] deals with the detailed electrochemical behavior of tricobalt carbon compounds.

Experimental Section

Literature methods[23-31] were used to prepare the tricobalt carbon derivatives; $CF_3CH_2CCo_3(CO)_9$ was kindly provided by Dr. R. Dickson, Monash University, Melbourne. $Cl^{13}CCo_3(CO)_9$ was prepared from $^{13}CCl_4$ (99% isotopic purity) and $^{13}CH_3{}^{13}CCo_3(CO)_9$ by acidification of $(^{13}CH{=}^{13}CH)Co_2(CO)_6$. Up to 60% substitution by ^{13}CO could be achieved by cycling ^{13}CO through dichloromethane solutions of a cluster for 24 h. The tricobalt carbon derivatives were recrystallized from either hexane or pentane and, where appropriate, further purified by vacuum sublimation; they were stored under vacuum.

Ether solvents were purified by the methods of Bolton and Fraenkel[32] and stored, in vacuo, over potassium anthracenide. Dichloromethane was washed with 10% K_2CO_3, twice distilled from $CaCl_2$, and stored over molecular sieves (4A).[33]

Preparation of the Radical Anions by Alkali Metal Reduction. Reduction of the neutral clusters was carried out in an evacuated vessel which allowed ESR and electronic spectra to be run on the same reduced solution. The reaction vessel was a simple T design, one arm being connected to a Suprasil quartz ESR tube and one connected to a reservoir, volume 5 cm^3. Another arm contained a silica 1-cm path optical cell while the fourth arm had constrictions and a joint for connection to a vacuum system. A weighed sample of the neutral cluster was placed in the reservoir and the reservoir stoppered. A small piece of freshly cut alkali metal was placed at the beginning of the constricted side arm, the vessel evacuated, and a metal mirror formed further along the side arm by gentle heating of the crude metal; this procedure was repeated to give a highly reactive mirror. Solvent was distilled into the reservoir and the side arm was then sealed so as to isolate the crude metal.

Judicious tipping of the solution in the reservoir brought it into contact with the mirror. The initial reaction was rapid but the extent of conversion to the radical anion depended on the purity of the metal mirror. The solution could then be tipped into the ESR tube or silica cell and spectra recorded. If the radical anion was unstable, the whole apparatus could be cooled by liquid nitrogen or the appropriate slush

Table I. A^{Co} and g Values of the Cluster Anions, $YCCo_3(CO)_9\cdot^-$

Y	g^a	A^{Co},[b] G	Y	g^a	A^{Co},[b] G
Me	2.017	36.6	Ph[e]	2.019	35.6
Et	2.017	35.7	$2\text{-}FC_6H_4$[d]	2.018	35.4
H[c]	1.98	34.4	$3\text{-}FC_6H_4$	2.021	35.5
F	2.024	36.7	$\alpha\text{-}C_{10}H_7$	2.021	35.3
CF_3	2.014	34.5	HOOC-	2.021	34.5
CF_3CH_2	2.017	35.6	$3\text{-}OHC_6H_4$	2.019	35.6
Cl	2.020	36.2	Me_3Si[d]	2.017	34.2
Br[d]	2.023	37.1			

[a] Calculated assuming an isotropic spectrum. [b] Derived from the separation of the central lines corresponding to components of nuclear angular momentum with $M_I = -{}^1/_2$ and $+{}^1/_2$. [c] Recorded at 213 K. [d] Recorded at 253 K. [e] A number of other aryl-substituted derivatives were investigated but are not included in this table as the g and A^{Co} values were very similar to the values for the phenyl derivative.

bath. A more effective procedure for cesium reductions was to produce the metal by the reaction of CsCl and Ca turnings; a mirror was subsequently formed as described above for the other alkali metals.

Preparative Electrolytic Reduction. Two methods were employed: either in situ radical anion generation in the cavity of the ESR spectrometer or external generation using an apparatus similar to that described for alkali metal reduction. In the latter case the constricted side arm was replaced by a simple electrochemical cell with platinum electrodes. Electrolysis was performed in THF or CH_2Cl_2 solutions approximately 10^{-3} mol dm^{-3} in the cluster compound with 0.1 mol dm^{-3} $Bu_4N^+ClO_4^-$ as supporting electrolyte at an applied potential of 1.5 V.

ESR Measurements. All spectra were recorded on a Varian E-4 X-band electron spin resonance spectrometer with a 100-kHz modulation and the Varian V-2507 variable-temperature accessory. Estimated error in the g values was ±0.004.

The cobalt hyperfine coupling constants A^{Co} given in Table I were, for reasons given in the text, derived from the separation of the central lines corresponding to components of nuclear angular momentum with $M_I = -{}^1/_2$ and $+{}^1/_2$; thus A^{Co} is not the average of all of the coupling constants. The computer-simulated spectra were calculated using a program SIMESR written by B. M. Peake to simulate first-order ESR spectra.

Electronic and IR Spectral Measurements. The electronic spectra were recorded on a Beckman DK-2A recording spectrophotometer; wavelength accuracy was estimated to be ±3 nm. Infrared spectra were recorded on a JASCO IR-2 spectrometer; accuracy was ±2 cm^{-1} with matched pairs of cells. Solutions (in THF) for the infrared measurements were produced externally by sodium reduction and samples of the reduced solutions rapidly transferred in an inert atmosphere to appropriate IR cells. In all cases reproducible spectra were obtained.

Attempted Preparations of Crystalline Salts of $YCCo_3(CO)_9\cdot^-$. A solution containing the $YCCo_3(CO)_9\cdot^-$ radical anion in THF was generated by alkali metal reduction as outlined above. The solution was then transferred under vacuum to a Schlenk vessel charged with a solution of the heavy cations $(Ph_3P)_2N^+$ or $PhCH_2NMe_3^+$. The THF was removed and the resulting product washed with hexane to extract the neutral cluster. Although a small amount of precipitate always remained, all efforts to crystallize the salt gave only the neutral cluster.

Quantitative Analysis of the Oxidation of $YCCo_3(CO)_9\cdot^-$. For these experiments the $YCCo_3(CO)_9\cdot^-$ radical anion was prepared from a known amount of the parent cluster. The anion was then quenched either by aerial oxidation or by the addition of methyl iodide. The solvent was removed from the quenched solution at 273 K; hexane was then added and the solution filtered. The hexane was removed in vacuo and the remaining oil sublimed in vacuo to give, in all cases except Y = H, Br, COOH, and Me_3Si, at least 99% recovery of the crystalline neutral cluster.

Results and Discussion

Radical anion formation from the parent clusters can be accomplished by alkali metal or electrolytic reduction.

$$M + YCCo_3(CO)_9 \rightarrow M^+ + YCCo_3(CO)_9\cdot^- \quad (M = Na, Cs)$$

$$YCCo_3(CO)_9 + e^- \xrightarrow{Pt} YCCo_3(CO)_9\cdot^-$$

Formation of the radical anion is accompanied by a color change from purple to yellow-brown and is accomplished in several minutes.

The majority of the radical anions had lifetimes of several hours irrespective of the mode of preparation; aryl derivatives were the most stable and persisted in ether solvents or dichloromethane for more than 36 h. The stability of these species raised the possibility that crystalline salts could be isolated but all our attempts resulted in a solid contaminated with the neutral cluster. Certain radical anions (Y = Br, HO_2C, Me_3Si), rapidly decomposed above 273 K while $HCCo_3(CO)_9\cdot^-$ could only be detected below 223 K. There is no obvious explanation for this order of stability. Alkali metals are known[34,35] to encourage intramolecular carbonyl-migration reactions in neutral Co_3C derivatives with reactive apical substituents and could well be the reason for their instability in alkali metal reduction but this behavior was also found when they were prepared by electrolytic reduction. Aerial oxidation or reaction of $YCCo_3(CO)_9\cdot^-$ with an alkyl halide regenerated the parent cluster as evidenced, not only by a rapid color change but also by the IR and mass spectrum of the oxidation product. This provided strong evidence that no structural change or disproportionation reaction occurred on reduction, a fact confirmed by the spectral data.

A variety of ether solvents were suitable media for chemical reduction while electrolytic reductions could be carried out in dichloromethane or acetone. The nonspecificity of solvent stabilization indicates that the radical anion is not strongly solvated; this is not surprising when the molecular volume of the cluster is considered. Both sodium and cesium could be employed with equal facility but solutions of the cesium salt were less stable at ambient temperature. Comparable observations with alkali-reduced organic systems have been ascribed[36] to poor solvation of the cesium ion in ether solvents, but another factor may be important in the Co_3C system. The equatorial and axial carbonyl groups will hinder the approach of the bulky cesium to the $YCCo_3$ species with consequent loss in Coulombic energy. However, the small solvated sodium ion should fit into the "hole" provided by the conformation of the axial carbonyl groups.

ESR Spectra. The ESR spectrum of $EtCCo_3(CO)_9\cdot^-$ in dimethoxyethane (Figure 1a) typifies those of the $YCCo_3(CO)_9\cdot^-$ radical anions, with the exception of Y = F or $2\text{-}FC_6H_4$ (Figure 2a). The line shape and line width were as shown in these figures, irrespective of whether chemical or electrochemical methods were used to generate the anions, and were also invariant within the temperature range 203–313 K. Hyperfine interaction of the unpaired electron with three equivalent cobalt nuclei ($I = {}^7/_2$ for ^{59}Co) gives rise to well-resolved hyperfine structure consisting of 22 lines whose general features could be successfully calculated to first order using a single hyperfine coupling constant and g value. It must be emphasized that spectra were obtained for solutions of the tricobalt carbon radical anions and, yet, the hyperfine structure closely resembles that reported[37] for the anisotropic spectrum of the isoelectronic $SeCo_3(CO)_9$ doped in a host lattice of the diamagnetic cluster, $SeFeCo_2(CO)_9$. Moreover, Strouse and Dahl found[37,38] that little or no cobalt hyperfine structure could be resolved in the ESR spectra of either $SCo_3(CO)_9$ or $SeCo_3(CO)_9$ recorded in ether solvents. These differences in the spectra of the CCo_3 and chalcogen derivatives may be directly relevant to the problem of why $FCCo_3(CO)_9\cdot^-$ has a more complex hyperfine structure (vide infra). Because there is some uncertainty in accounting for this line shape, the hyperfine coupling constants listed in Table I were calculated from the separation of the central lines corresponding to components of nuclear angular momentum with $M_I = +{}^1/_2$ and $-{}^1/_2$. Within the limits of accuracy, there was no obvious

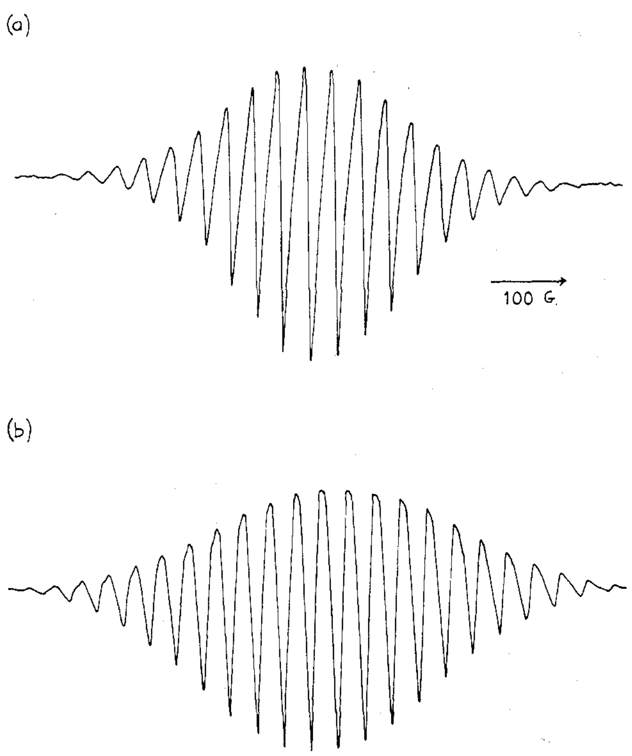

Figure 1. ESR spectra for $EtCCo_3(CO)_9\cdot^-$: (a) spectrum observed at 298 K (anion prepared by Na reduction in dimethoxyethane); (b) simulated spectrum; see text.

trend in the magnitude of A^{Co} and it is clear that the spin densities at the three cobalt nuclei do not vary significantly with the electronic nuances of the apical substituents. The cluster is therefore an efficient spin sink and we conclude that the unpaired electron occupies a level largely metal in character. Hyperfine interaction of the nuclei of transition metal complexes containing an unpaired electron in a d orbital is attributed to spin polarization of the inner s electrons and gives rise[39] to a negative A^{Co}. Because we are dealing with an electron in a molecular orbital comprised of a linear combination of three cobalt metal orbitals, a valid comparison with mononuclear cobalt complexes is $3A^{Co}$. This is approximately −107 G for the tricobalt carbon radical anions which is significantly higher than −94.7 G for Co(I) doped in a MgO host lattice[40] and −93 G for $SCo_3(CO)_9$ in hexane solution.[38] If the unpaired electron resides in a molecular orbital of correct symmetry (for example, an a_1 orbital) to allow a contribution from the 4s metal orbitals, there will be a Fermi contact contribution to the measured hyperfine interaction. The calculated[41] hyperfine coupling constants for unit population of 3d and 4s orbitals are respectively 152 and 1320 G and thus the maximum spin densities in the two orbitals are approximately 71% and 8%. Thus there is a significant 4s and 4p contribution to the lowest unoccupied level and an expanded basis set is required in order to construct satisfactory energy levels for the tricobalt carbon clusters. Molecular orbital calculations[42] also indicate that the 4s and 4p orbitals have a significant role in metal–metal bonding in first-row transition metal clusters. It is not surprising that there is a different set of energy levels for the chalcogen clusters (Strouse and Dahl[37,38] suggest that the odd electron occupies an a_2 orbital) and we are currently investigating their redox behavior with this possibility in mind.

All of the g values listed in Table I (calculated assuming no g value anisotropy) are close to the free-electron value, from which it can be inferred that the orbital angular momentum in the ground state is almost quenched and that the electron resides in a nondegenerate orbital. Exactly the same conclusion was reached by Strouse and Dahl for the chalcogen clusters.[37,38]

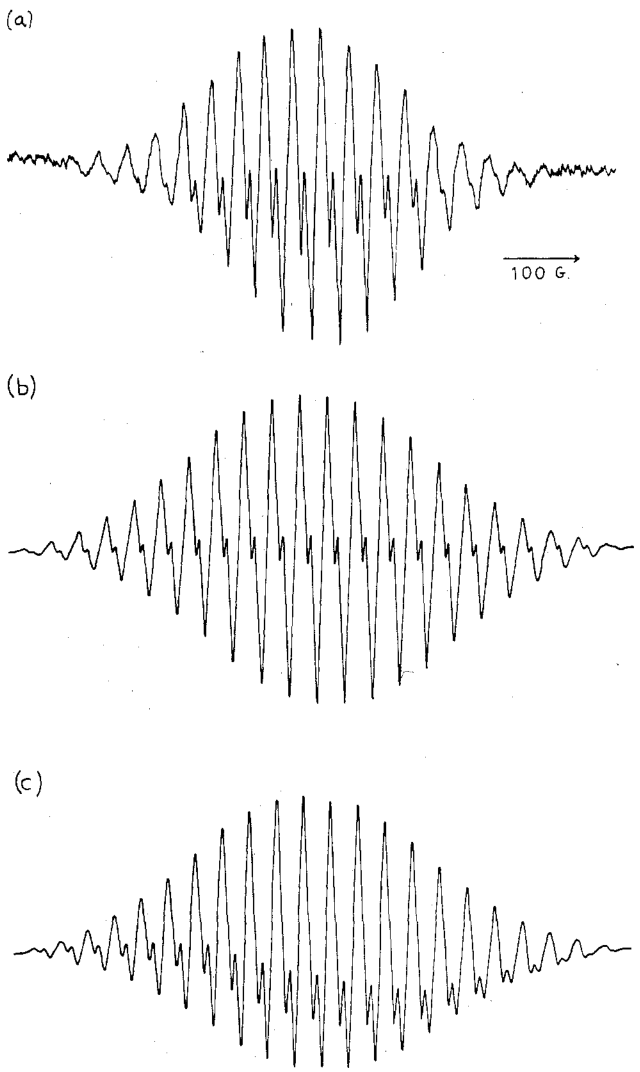

Figure 2. ESR spectra for $FCCo_3(CO)_9\cdot^-$: (a) spectrum observed at 298 K (anion prepared by Na reduction in dimethoxyethane); (b) simulated spectrum assuming fluorine hyperfine coupling, $A^F = 10.8$ G; (c) simulated spectrum assuming g value anisotropy.

An intriguing feature of the ESR spectra of the radical anions was the unusual line shape, in particular, the apparent splitting of each cobalt hyperfine component in the spectra of $FCCo_3(CO)_9\cdot^-$ (Figure 2a) and $2\text{-}FC_6H_4CCo_3(CO)_9\cdot^-$. In a preliminary communication[17] we attributed this splitting to hyperfine coupling to the fluorine nucleus. A simulated spectrum, with a seemingly reasonable value of $A^F = 10.8$ G, qualitatively reproduced the $FCCo_3(CO)_9\cdot^-$ spectrum (Figure 2b). Nonetheless, we now believe this explanation to be untenable, for several reasons, as follow.

(a) For coupling to a nucleus of spin $^1/_2$ the hyperfine components should have equal intensity; instead, the actual ratio of intensities of the low-field to high-field line in each doublet is approximately 1.0:0.7, respectively.

(b) There is no resolvable hydrogen hyperfine interaction seen in the spectrum of $HCCo_3(CO)_9\cdot^-$. Although this hydrogen bound to the apical carbon atom is acidic,[43] there is no reason a priori that a hydrogen hyperfine coupling constant should be less than the line width of approximately 10 G.

(c) If there was sufficient delocalization of the unpaired electron density onto the apical substituent to give an observable fluorine hyperfine interaction, then it is reasonable to expect a more definitive hyperfine interaction with the apical carbon nucleus. However, no difference was apparent, in either the line width or hyperfine pattern, between the spectra of $ClCCo_3(CO)_9$ and $Cl^{13}CCo_3(CO)_9$ (99% isotopic purity). Likewise, there was no hyperfine interaction with more distant apical nuclei or the carbon nucleus of a carbonyl group; for example, the spectra of $CH_3CCo_3(CO)_9$, $CD_3CCo_3(CO)_9$, $^{13}CH_3CCo_3(CO)_9$, and $CH_3CCo_3(^{13}CO)_9$ (60% isotopic purity) were identical. These results demonstrate the unpaired electron is in a nondegenerate orbital centered on the three cobalt atoms.

(d) No fluorine interaction was observed in the spectra of the 4-FC_6H_4, 3-FC_6H_4, or CF_3 derivatives.

We suggest that the splitting observed in Figure 2a and the asymmetric line shape of the cobalt hyperfine components (see Figure 1a) arise from a common phenomenon. That this might be ion pairing can be discounted on the grounds that neither the line shape nor line width was altered by the presence of a crown ether or by a change in solvent or cation. Similarly, nuclear quadrupole and/or spin–orbit coupling could contribute to the comparatively large line widths of the 22 hyperfine components but are unlikely to drastically alter the line shape. It is known[44] that where nuclear quadrupole relaxation effects are operative, linewidths decrease with increase in temperature but there was no change in this respect in the spectra of the tricobalt carbon derivatives. The absence of any temperature dependence would also tend to eliminate the possibility of spin–orbit coupling effects.[45] Therefore, we propose that the phenomenon arises from g value anisotropy and in this context it is important to reiterate that the line shape in Figure 1a is the same as that reported[37] for the ESR spectra of the doped $SeCo_3(CO)_9$ cluster. To test this hypothesis, spectra were simulated using a variety of hypothetical $g_\parallel$ and $g_\perp$ values. It appears that the essential features of the spectra as shown in Figure 1a can be reproduced (Figure 2b) using the values $g_\parallel = 2.030$ and $g_\perp = 2.013$. These values are compatible with those obtained by Strouse and Dahl[38] from single-crystal studies on $SCo_3(CO)_9$ ($g_\parallel = 2.04$, $g_\perp = 2.02$). In contrast, Figure 2a is reproduced (Figure 2c) using a *smaller* difference in $g_\parallel$ and $g_\perp$ (2.037 and 2.022, respectively). At present we are unable to give a satisfactory explanation as to why this g value anisotropy should be observed for radical species in solution, particularly as the line shape and hyperfine pattern are independent of temperature, or why only the $FCCo_3(CO)_9\cdot^-$ and 2-$FC_6H_4CCo_3(CO)_9\cdot^-$ anions display a different degree of anisotropy. In view of the close proximity of the equatorial carbonyl groups to the apical substituent[21] it is possible to envisage an intramolecular through-space interaction which results in a perturbation of the three cobalt atoms. The magnitude of this effect will depend on the polarity of the apical substituent, and a combination of steric factors and polarity may account for differences in spectral properties between the 2-FC_6H_4 and F derivatives and those of the 3-FC_6H_4 and 4-FC_6H_4 derivatives.

Infrared and Visible Spectra. Because reduction of the tricobalt carbon clusters is both chemically and electrochemically reversible it was implicit in our analysis of the ESR spectra that no gross structural modification of the clusters occurred upon reduction. An analysis of the infrared and visible spectra substantiated this conclusion.

Four of the five predicted carbonyl stretching frequencies are observed in the infrared spectra of most neutral $YCCo_3(CO)_9$ compounds and the "missing" E mode, calculated[46] to be approximately 2010 cm^{-1}, is seen in clusters with asymmetrical apical substituents. The symmetrical in-phase A ν(CO) mode between 2120 and 2095 cm^{-1} is a sensitive guide to the charge density on the cobalt atoms[21] and this mode systematically decreases in frequency in the order F > Cl > Br > Ph ~ H > Me; this order holds as well for substituted Co_3C derivatives.[47] Transmission of charge between the apical substituent and cobalt atoms would appear from this order to be primarily via a σ effect. The addition of an electron to an orbital having a high degree of metal character should not severely alter the electronic structure of the molecule and the trend in the frequency of the ν(CO) A_1 mode should be retained.

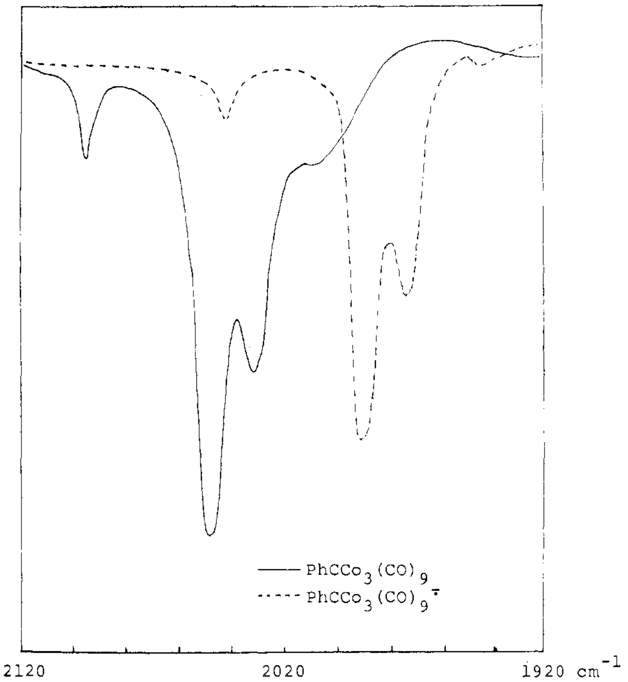

Figure 3. Infrared spectra (2120–1920 cm^{-1}) of $PhCCo_3(CO)_9$ and $PhCCo_3(CO)_9\cdot^-$ in tetrahydrofuran at 293 K. The radical anion was prepared by Na reduction in THF.

A typical infrared spectrum of neutral and radical anion clusters is shown in Figure 3. The spectral profile is exactly the same in the two species for all derivatives confirming that the molecular symmetry does not change on reduction; band assignments are therefore as given by Bor[46] for the neutral species. All bands, however, shift ~60 cm^{-1} to lower frequency upon reduction. There is no directly related system with which to compare the magnitude of this shift, except perhaps binuclear chromium and iron phosphine carbonyls, since the comprehensive series of redox species studied by Dessy and Wieczorek[48] mainly involved compounds where the additional electron occupied a π^* level primarily ligand in character. When an electron is added to a metallic LUMO, the cobalt 3d orbitals will be destabilized such that they become closer to the carbonyl π orbitals which will lead to a decrease in the carbonyl stretching frequencies, as is observed. Recent calculations[49] on dimeric bridged-metal systems bear out this argument. The extent of d-orbital destabilization will depend however on whether the LUMO is antibonding or nonbonding although a shift of 60 cm^{-1} is similar to that found in the binuclear series $[Cr_2(CO)_8(\mu\text{-}PR_2)_2]^{n-2}$ where the LUMO is believed[49] to be a σ^* level. It is worth noting at this point that the ν(CO) frequencies of the $YCCo_3(CO)_9$ clusters and the isoelectronic but paramagnetic $SCo_3(CO)_9$ cluster[50] are virtually the same, even though the odd electron also appears to occupy an antibonding metal cluster orbital.[26] A possible rationale is that there is more efficient cobalt–nonmetal overlap in the sulfur derivative which consequently reduces the electron density on the cobalt atoms relative to the carbon clusters and, in turn, reduces the back-donation to the carbonyl groups.

The 60-cm^{-1} shift on reduction is in fact equivalent to that found for the substitution of two carbonyl groups in the neutral clusters by two basic phosphine ligands. With the phosphine

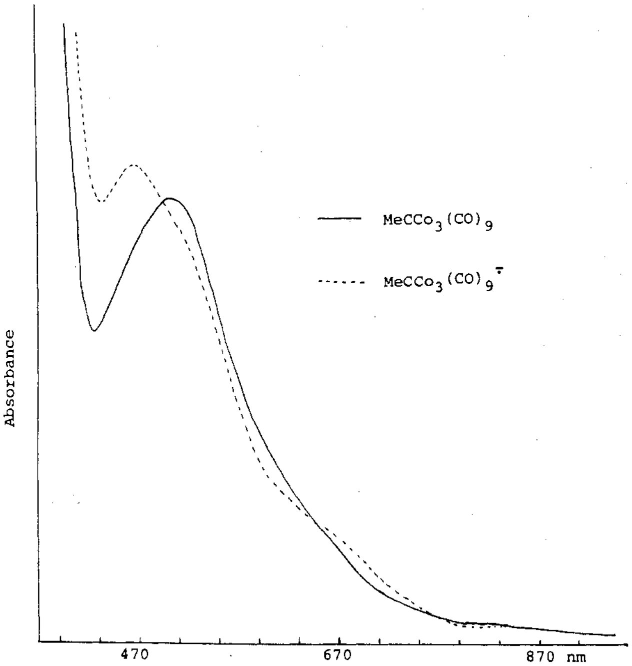

Figure 4. Electronic spectra (910–390 nm) of $MeCCo_3(CO)_9$ and $MeCCo_3(CO)_9\cdot^-$ in dimethoxyethane at 293 K. The radical anion was generated by Na reduction.

derivatives however there is an associated structural reorganization to a bridged-carbonyl configuration and this is thought to be an attempt by the cluster to dissipate the excess charge on the cobalt atoms.[47] There was no evidence for a bridged radical anion species, which is again compatible with the idea that the extra electron is in a level which is more or less entirely metal in character.

In general, there is a paucity of detailed information on the electronic spectra of neutral metal carbonyl clusters and this is certainly true for the tricobalt carbon clusters. Spectra have been recorded for a number of Co_3C derivatives[16] but detailed assignments were not attempted because a satisfactory description of the energy levels in these molecules is not available. Nonetheless a qualitative discussion, suitable for the purposes of this paper, is presented. All neutral $YCCo_3(CO)_9$ compounds give electronic spectra with the following features: an intense charge-transfer envelope above 28 500 cm^{-1} and a weaker band around 19 600 cm^{-1} ($\epsilon \sim 2000$ dm^3 mol^{-1} cm^{-1}) (Figure 3). The energy of the latter transition only decreases by some 400 cm^{-1} on going from a methyl group to the most electronegative substituent, fluorine.

As the energy is relatively constant within the series and the extinction coefficient is consistent with an absorption involving delocalized molecular levels, the low-energy band is assigned to a transition within energy levels associated with the Co_3C core. On reduction, there is a general increase in energy of this transition but the spectral profiles of the neutral and paramagnetic species are very similar (Figure 4). This further substantiates the conclusion that no structural reorganization occurs on reduction and that there is no significant reordering of molecular energy levels. An increase in energy is expected as the energy of the reduced species will be greater by an amount proportional to the average Coulombic repulsion between an electron in the σ level and the one in the σ^* level. Of interest is the appearance, upon reduction, of a very weak band at about 675 nm (it is most pronounced when Y is an aromatic substituent); this is tentatively assigned to a transition from the highest occupied level (probably a nondegenerate antibonding level; see below) to the first excited level. More rigorous assignments of the observed spectra must await the results of our theoretical calculations and information from the photoelectron spectra at present being recorded.[16]

Conclusion

Tricobalt carbon clusters readily undergo a chemically reversible one-electron reduction to produce some exceptionally stable radical anions.[51] Reduction does not lead to a gross change in molecular geometry or to a significant change in the energy levels of the $CCo_3(CO)_9$ moiety. The spectral data allow an assignment of the unpaired electron to a nondegenerate, delocalized, metal-centered orbital and there is evidence that this is an antibonding level of a_1 symmetry. It is clear that the remarkable stability of the radical anions is a consequence of the geometrical configuration of these clusters and the particular cooperative bonding interactions that have already been documented for the neutral clusters.[21,22] None of the spectral or electrochemical data invalidate the model of an electron reservoir that can participate in cooperative interactions with both the apical substituent and the coordinated ligands. A theoretical interpretation of this model will be difficult as a complete basis set of metal 3d, 4s, and 4p orbitals will be needed for the calculations to be meaningful.[52]

The long lifetimes of certain of the radical anions, for example $PhCCo_3(CO)_9\cdot^-$ and $MeCCo_3(CO)_9\cdot^-$, opens up a new area of tricobalt carbon cluster chemistry which is currently being explored. Preliminary experiments show that the radical anions are excellent electron-transfer reagents (cf. $Ta_6Cl_{12}^{n+}$ clusters[53]) but that the rate of electron transfer is very dependent on the nature of the substrate Thus, electron transfer to 1,4,5,8-tetranitronaphthalene (TNN) is virtually instantaneous, the product being the $TNN\cdot^-$ radical anion, whereas electron transfer to alkyl halides results in cleavage of the R–X bond but the parent cluster is not quantitatively regenerated for, in some cases, up to 40 min. Finally, the studies reported in this paper are complemented by the electrochemical work[30] which shows that $YCCo_3(CO)_9$ complexes have limited redox behavior. However, radical cations can be detected when carbonyl groups are substituted by basic phosphine ligands.[16]

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Registry No. $MeCCo_3(CO)_9\cdot^-$, 61024-79-1; $EtCCo_3(CO)_9\cdot^-$, 61024-68-8; $HCCo_3(CO)_9\cdot^-$, 61024-62-2; $FCCo_3(CO)_9\cdot^-$, 51900-19-7; $CF_3CCo_3(CO)_9\cdot^-$, 61024-78-0; $CF_3CH_2CCo_3(CO)_9\cdot^-$, 61024-67-7; $ClCCo_3(CO)_9\cdot^-$, 61024-77-9; $BrCCo_3(CO)_9\cdot^-$, 61024-76-8; $PhCCo_3(CO)_9\cdot^-$, 61024-80-4; 2-$FC_6H_4CCo_3(CO)_9\cdot^-$, 61024-71-3; 3-$FC_6H_4CCo_3(CO)_9\cdot^-$, 61024-72-4; α-$C_{10}H_7CCo_3(CO)_9\cdot^-$, 61024-75-7; $HOOCCCo_3(CO)_9\cdot^-$, 61024-65-5; 3-$OHC_6H_4CCo_3(CO)_9\cdot^-$, 61024-73-5; $Me_3SiCCo_3(CO)_9\cdot^-$, 51900-28-8; $PhCoCo_3(CO)_9$, 20756-47-2; $MeCCo_3(CO)_9$, 13682-04-7.

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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 → −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. Vlčeck[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