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Paramagnetic Organometallic Molecules. 5. Tricobalt–Carbon Lewis Base Derivatives

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A detailed study of the redox behavior of Lewis base derivatives of tricobalt–carbon clusters, $YCCo_3(CO)_{9-n}L_n$ (n = 1–3; L = R_3P, $(RO)_3P$, RNC), using the techniques of dc polarography at mercury electrodes and dc cyclic voltammetry at mercury or platinum, revealed that an electron-transfer series consisting of $YCCo_3(CO)_{9-n}L_n^{+/0/-}$ does exist providing the right ligands are used. Monosubstituted derivatives undergo chemically reversible one-electron reduction at platinum or mercury electrodes in dichloromethane and acetone at 203 K. Reduction becomes progressively more difficult and oxidation easier as CO groups are replaced by Lewis bases. Thus, irreversible oxidations are seen when n = 2, but when n = 3, the derivatives show both reversible reduction and oxidation at platinum and mercury electrodes. Attempts to obtain the isotropic ESR spectra of the radical anions were thwarted by facile ligand dissociation, coupled with decomposition, such that only spectra of the $YCCo_3(CO)_9^{-}\cdot$ species were observed. Frozen-solution spectra were obtained and these show that the a_2 antibonding orbital of the Co_3C clusters is only slightly perturbed by substitution of a CO group by a Lewis base. The electrochemical and ESR data are related to the electronic structure of these clusters.

Introduction

Previous electrochemical[2a] and spectroscopic studies[2b] of tricobalt–carbon clusters showed that they undergo chemically and electrochemically reversible one-electron reductions to the unusually stable radical anions $YCCo_3(CO)_9^{-}\cdot$. A considerable amount of information on the electronic structure of the $YCCo_3$ moiety was gleaned from these studies. The HOMO orbital is believed to be a delocalized orbital encompassing the whole Co_3CY cluster unit; it is variations in the energy of this orbital that largely determine the reduction potential. In contrast, the a_2 LUMO orbital is largely metal in character and probably antibonding with respect to the metal–metal framework. From these observations it was clear that the electron-transfer series could be extended to include an oxidized species, that is, a cation, if the electron density on the cobalt atoms was increased. Lewis base derivatives of the cluster are well-known[3] and the phosphine complexes have the added attraction that a dynamic equilibrium exists in solution between carbonyl-nonbridged and -bridged forms[3,4] affording the opportunity to examine the influence of the ligand configuration on redox behavior. This paper deals with phosphine,[3] phosphite, and isocyanide[5] derivatives of the type $YCCo_3(CO)_{9-n}L_n$ (n = 1–3).

Experimental Section

The tricobalt–carbon clusters were prepared by published procedures.[6] Phosphite, phosphine, and isocyanide derivatives were prepared by boiling the appropriate cluster and ligand in hexane. The compounds were isolated as described in the literature.[3,5] The phosphite derivatives are all new compounds and were characterized by analyses and infrared spectra; details will be published elsewhere.[7] In contrast to the phosphine derivatives, the phosphite complexes have a carbonyl-nonbridged structure irrespective of the degree of substitution.

The electrochemical instrumentation, sodium reduction, and solvent purification procedures have been described previously.[2] Potentials were measured with respect to a Ag/AgCl reference electrode (acetone, 0.1 mol dm^{-3} LiCl). Unless otherwise specified, data refer to 293 K. The drop time of the mercury electrode and the scan rate for cyclic voltammetry were usually 0.5 s and 200 mV s^{-1}, respectively. The complex concentration was approximately 10^{-3} mol dm^{-3}. The supporting electrolyte was Et_4NClO_4 at a concentration of 0.1 mol dm^{-3} in acetone and 0.07 mol dm^{-3} in dichloromethane.

Results

Electrochemistry—Reduction. A well-defined reduction step was characterized for all compounds studied in dichloromethane and acetone, at both platinum and mercury electrodes. The half-wave potentials in acetone were in the range −0.42 to −0.81 V for $YCCo_3(CO)_8L$, −0.67 to −0.98 V for $YCCo_3(CO)_7L_2$, and −0.84 to −1.45 V for $YCCo_3(CO)_6L_3$ (Tables I and II). Similar half-wave potentials and electrode responses were obtained in dichloromethane. Figures 1 and 2 show a typical dc polarogram and cyclic voltammogram of this reduction step. In contrast to the parent clusters $YCCo_3(CO)_9$, the electrode process is not completely chemically reversible at 293 K as shown by the unequal peak heights of the cathodic and anodic scans of the cyclic voltammograms and the appearance of additional waves on the anodic and subsequent cycles (Figure 3(a)). Chemical reversibility is approached at faster potential scan rates and is achieved by lowering the temperature to 203 K, where the radical anion is stable on the cyclic voltammetry time scale (Figure 3).

Values of $E_{1/4} - E_{3/4}$ for the dc polarograms were often somewhat less than 56 mV, suggesting that, over the life of a mercury drop, more than one electron is transferred per diffusing cluster molecule. Similarly, analysis of ac polarograms and ac and dc cyclic voltammograms using the method of digital simulation[8] suggests that a chemical step followed by further reduction of a product occurs after an initially reversible one-electron reduction. The anodic peak at ~0.37 V can be attributed[2a] to oxidation of $Co(CO)_4^-$ while peaks can be discerned on subsequent cycles which correspond to the reduction of the parent cluster $YCCo_3(CO)_9$ to the radical anion $YCCo_3(CO)_9^{-}\cdot$ and its reoxidation. Thus fragmentation

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Table I. Electrochemical Data for the First Reduction and Selected Other Electrode Processes in Acetone (0.1 M Et_4NClO_4) at 293 K[a]

	dc polarography[c]		cyclic voltammetry at Pt[b]		
	$E_{1/2}{}^r$	$E_{1/4} - E_{3/4}$	$E_p{}^{Red}$	$E_p{}^{Ox}$	peak potentls for main waves on rev scan
$PhCCo_3(CO)_8PPh_3$	−0.61	50	−0.65	−0.60	−0.42, 0.36
$MeCCo_3(CO)_8PPh_3$	−0.64	60	−0.68	−0.63	−0.42, 0.37
$FCCo_3(CO)_8PPh_3$	−0.56	50	−0.58	−0.52	−0.26, 0.34
$MeCCo_3(CO)_8P(C_6H_{11})_3$[d]	−0.54	60			
$FCCo_3(CO)_8P(C_6H_{11})_3$	−0.57	50	−0.63	−0.57	−0.26, 0.36
$FCCo_3(CO)_8CNPh$	−0.52	50	−0.59	−0.52	−0.32, 0.30
$FCCo_3(CO)_8P(OEt)_3$	−0.59	55	−0.66	−0.58	−0.24, 0.36
$FCCo_3(CO)_8P(OMe)_3$	−0.55	65	−0.62	−0.53	−0.22, 0.40
$FCCo_3(CO)_8P(OPh)_3$	−0.42	50	−0.52		
$MeCCo_3(CO)_8P(OMe)_3$	−0.67	50	−0.74	−0.66	−0.36, 0.40
$MeCCo_3(CO)_8CNPh$	−0.67	65	−0.72	−0.67	0.66, 0.32
$MeCCo_3(CO)_8PEt_2Ph$	−0.77	45	−0.81	−0.70	−0.43, 0.34
$MeCCo_3(CO)_8P$-*n*-Bu_3	−0.81	42	−0.85	−0.71	0.12, 0.50
$HCCo_3(CO)_8PMePh_2$	−0.68	70	−0.73	−0.68	−0.41, 0.36
m-$MePhCCo_3(CO)_7C_7H_8$	−0.67	60	−0.72	−0.62	0.34

[a] V vs. Ag/AgCl, except $E_{1/4} - E_{3/4}$ in mV. [b] Scan rate 200 mV s^{-1}. Switching potential −1.4 V vs. Ag/AgCl; initial potential 1.0 V vs. Ag/AgCl. [c] Drop time 0.5 s; scan rate 10 mV s^{-1}. [d] Results time dependent; results given for freshly prepared solutions.

Table II. Electrochemical Data for $YCCo_3(CO)_{9-n}L_n$ (n = 2, 3) in Acetone (0.1 M Et_4NClO_4) at 293 K[a]

	cyclic voltammetry at Pt[b,c]						dc polarography[d]			
	reduction			oxidation			reduction		oxidation	
	$E_p{}^{Red}$	$E_p{}^{Ox}$	$E_{1/2}$	$E_p{}^{Ox}$	$E_p{}^{Red}$	$E_{1/2}$	$E_{1/2}$	$E_{1/4} - E_{3/4}$	$E_{1/2}$	$E_{1/4} - E_{3/4}$
				$YCCo_3(CO)_7L_2$						
Me/$P(OMe)_3$	−1.00	−0.84	−0.98	1.00		0.97	−0.96	50		
Me/$P(OPh)_3$	−0.82	−0.74	−0.80	1.09		1.06	−0.78	50		
F/$P(OMe)_3$	−0.89	−0.72	−0.86	1.22		1.19	−0.82	65		
F/$P(OPh)_3$	−0.73	−0.61	−0.70	1.17		1.14	−0.67	60		
				$YCCo_3(CO)_6L_3$						
Me/$P(OMe)_3$	−1.30	−1.10	1.26	0.73	0.66	0.70	−1.20	40	0.68	40
Me/$P(OPh)_3$	−1.03			1.06			−0.95	40		
Me/PEt_2Ph	−1.5			0.48	0.39		−1.45	55	0.43	58
F/$P(OMe)_3$	−1.18	−0.98	−1.16	0.88	0.75	0.83	−1.07	40	0.76	40
F/$P(OPh)_3$	−0.90		−1.07	1.07	0.98	1.05	−0.84	60		

[a] V vs. Ag/AgCl, except $E_{1/4} - E_{3/4}$ in mV. [b] Scan rate 200 mV s^{-1}. Switching potential −1.4 V vs. Ag/AgCl; initial potential 1.0 V vs. Ag/AgCl. [c] Other waves seen but are not tabulated as they are meaningless without a complete description of the processes. [d] Drop time 0.5 s; scan rate 10 mV s^{-1}.

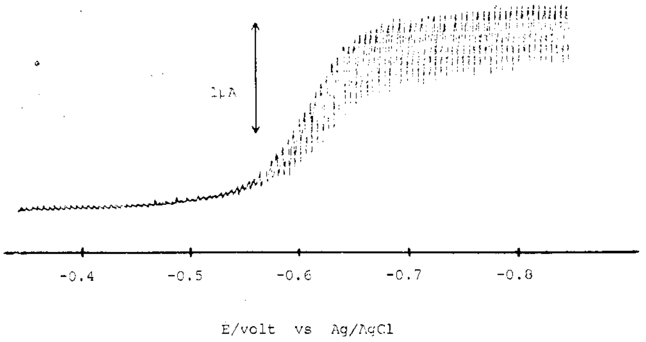

Figure 1. Dc polarogram for the reduction of $PhCCo_3(CO)_8PPh_3$ in acetone (T = 298 K; drop time 0.5 s; scan rate 10 mV s^{-1}).

of the substituted tricobalt–carbon derivatives occurs after the addition of the first electron whereas the parent $YCCo_3(CO)_9$ clusters fragment only after the formation of the dianion $YCCo_3(CO)_9{}^{2-}$. The electrode process may be represented by Scheme I.

Scheme I

$$YCCo_3(CO)_{9-n}L_n + e^- \rightleftharpoons YCCo_3(CO)_{9-n}L_n{}^{-}\cdot \quad (1)$$

$$YCCo_3(CO)_{9-n}L_n{}^{-}\cdot \rightarrow Co(CO)_4{}^- + YCCo_3(CO)_9{}^{-}\cdot + \text{other products} \quad (2)$$

Cyclic voltammograms on platinum showed separations of cathodic and anodic peaks of 50–60 mV for most of the monosubstituted tricobalt–carbon derivatives, $YCCo_3(CO)_8L$, consistent with an electrochemically reversible, one-electron transfer. The disubstituted derivatives, on the other hand, showed peak separations ranging from 80 to 170 mV, and the two trisubstituted derivatives for which anodic peaks were observed showed peak separations of 180 and 200 mV. These data suggest that electron transfer at platinum is slower for the more highly substituted derivatives, consistent with the notion that electron transfer occurs through the carbonyl ligands.

In the polarogram of an unsubstituted tricobalt–carbon cluster $YCCo_3(CO)_9$, a second one-electron reduction is seen which, although the step is chemically irreversible, implies at least the transient existence of the dianion. The monosubstituted derivatives exhibit ill-defined, chemically irreversible reduction waves at mercury and platinum between −0.9 and −1.90 V and another series at mercury near the solvent limit in acetone (−2.25 V vs. Ag/AgCl). These waves probably correspond to reduction of decomposition products but may indicate further reduction of the radical anion.

Electrochemistry—Oxidation. A consideration of the nature of the HOMO and LUMO orbitals of the $YCCo_3(CO)_9$ clusters convinced us that the cations $YCCo_3(CO)_{9-n}L_n{}^+$ should be accessible providing sufficient electron density could be placed on the cobalt atoms.[9] This is borne out by the electrochemistry of $YCCo_3(CO)_6L_3$ derivatives in acetone at platinum and mercury electrodes. A completely reversible oxidation step is observed at low temperature or fast scan rates

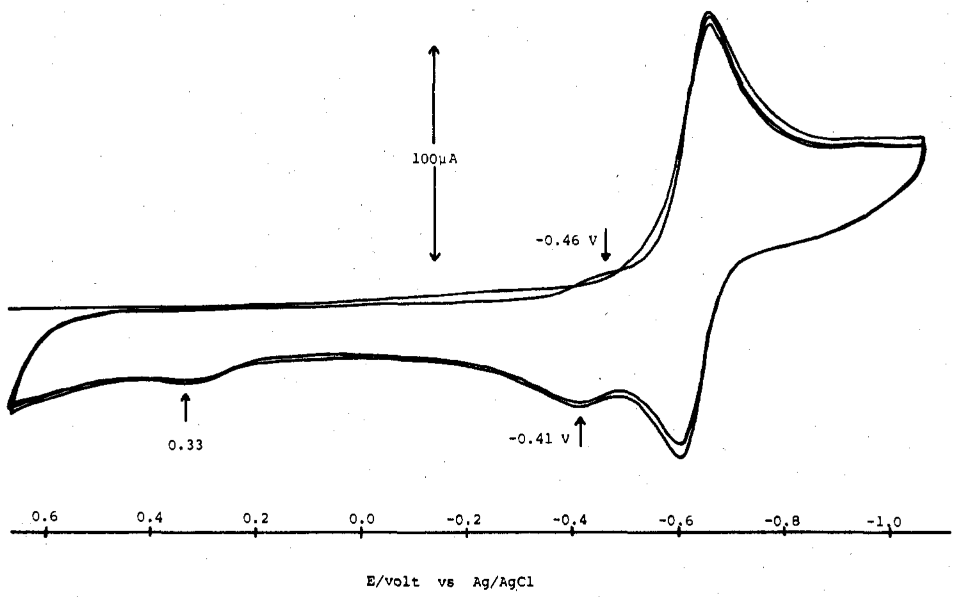

Figure 2. Dc cyclic voltammogram at platinum of $PhCCo_3(CO)_8PPh_3$ in acetone (T = 298 K; scan rate 200 mV s^{-1}).

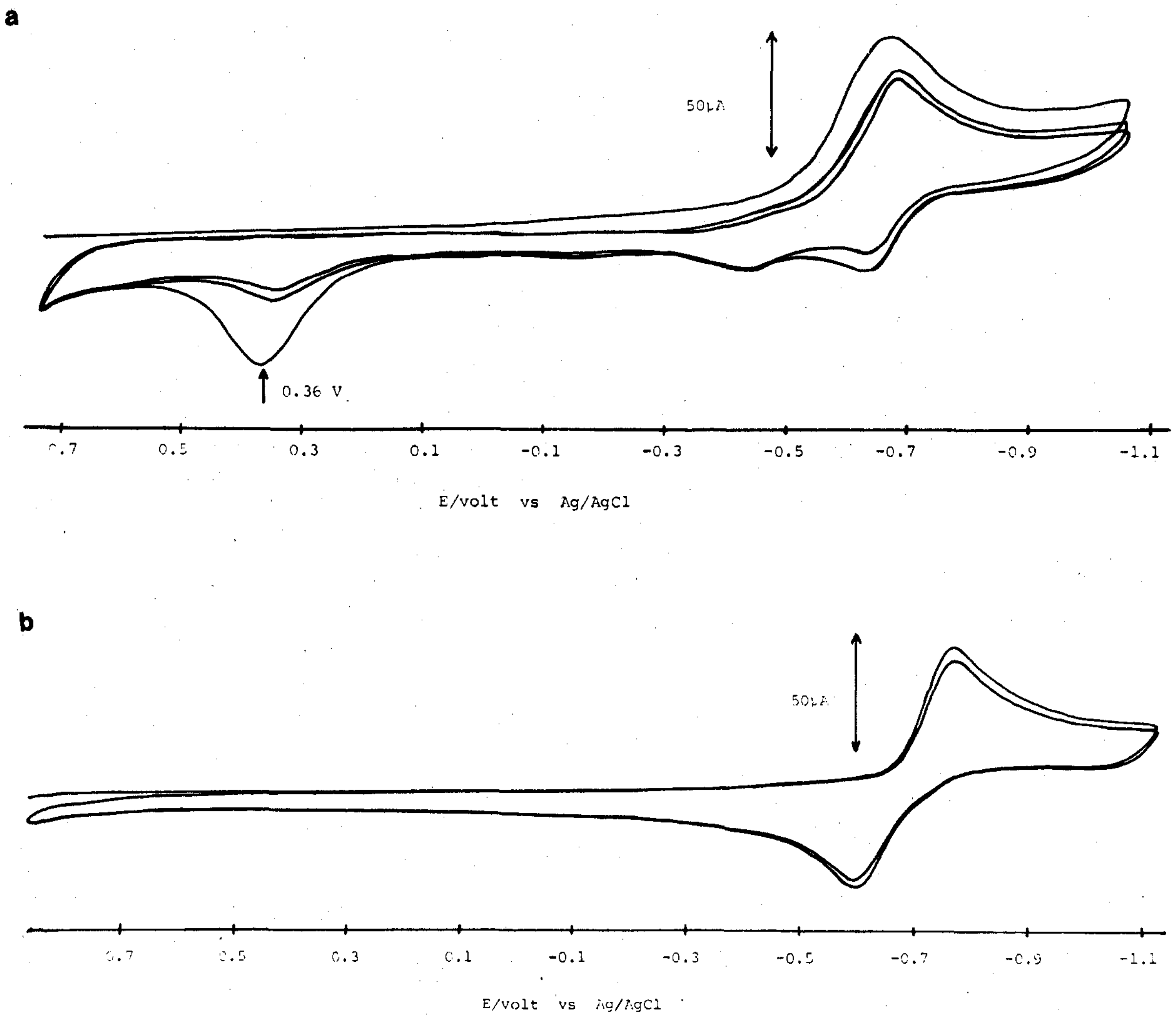

Figure 3. Dc cyclic voltammograms at platinum of $CH_3CCo_3(CO)_8PPh_3$ in acetone: (a) T = 298 K; scan rate 200 mV s^{-1}; (b) T = 200 K; scan rate 200 mV s^{-1}.

for L = $P(OMe)_3$, $P(OPh)_3$, or $PPhEt_2$ (Table II, Figures 4 and 5). With the exception of L = $PPhEt_2$, this step is only partially reversible at 293 K. Absorption phenomena such as pre-waves are seen at mercury, but the electrode processes are chemically reversible. When n = 2, there is a completely irreversible multielectron oxidation process which offers no evidence for a stable cation even at low temperatures or fast scan rates at platinum. Oxidation for the complexes with n = 1 or 0 must lie outside the solvent range in acetone and dichloromethane. Other workers[10] have recently described the

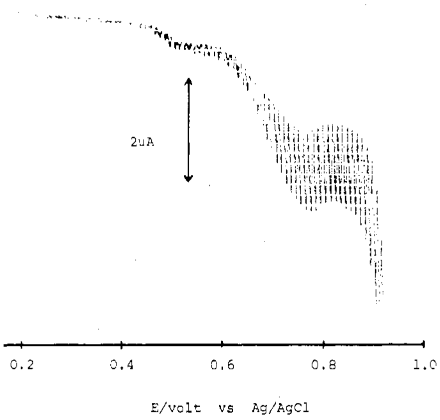

Figure 4. Dc polarogram for the oxidation of $MeCCo_3(CO)_6[P(OMe)_3]_3$ in acetone (T = 298 K; drop time 0.5 s; scan rate 20 mV s^{-1}).

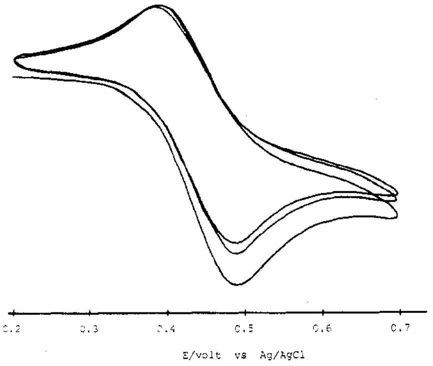

Figure 5. Dc cyclic voltammogram at platinum for the oxidation of $MeCCo_3(CO)_6[P(Et_2Ph)_3]_3$ in acetone (T = 293 K).

electrochemistry of some $YCCo_3(CO)_9$ complexes in dichloromethane. Despite extensive efforts to reproduce their results, we could find no evidence for the oxidation waves reported or the instability associated with $YCCo_3(CO)_9^-$. Certain reduction waves we have repeatedly observed were not mentioned.

Spectroscopic Studies. Electrolytic reduction of $YCCo_3(CO)_{9-n}L_n$ in THF or CH_2Cl_2 solutions in the ESR cavity at temperatures down to 203 K gave ESR spectra identical with those of the parent radical anions $YCCo_3(CO)_9^-\cdot$. The electrolytic reduction of $FCCo_3(CO)_8P(OMe)_3$ above 213 K, to take a specific example, gave the ESR spectrum of $FCCo_3(CO)_9^-\cdot$ which, under constant-current conditions, grew in amplitude linearly with time. At 203 K, on the other hand, an induction period of 10–15 min was found during which no ESR signal of any kind could be observed; following the induction period, growth of the ESR spectrum of $FCCo_3(CO)_9^-\cdot$ approached linear behavior after about 20 min. However, if the electrolysis current was turned off after the $FCCo_3(CO)_9^-\cdot$ signal was observed, the signal continued to increase in intensity for up to 45 min. The time dependence of the ESR signal amplitude could be analyzed quantitatively assuming initial formation of $FCCo_3(CO)_8P(OMe)_3^-\cdot$, which decayed to $FCCo_3(CO)_9^-\cdot$ with a half-life of 15 min.

If electrolysis at 203 K was discontinued after about 10 min, before the appearance of a detectable amount of $FCCo_3(CO)_9^-\cdot$, and the solution cooled to 113 K, a frozen-solution ESR spectrum was observed which was significantly different from that of $FCCo_3(CO)_9^-\cdot$. This is attributed to $FCCo_3(CO)_8P(OMe)_3^-\cdot$: $g_\parallel = 2.008 \pm 0.003$, $a_\parallel = -7.00 \pm 0.03$ mT (cf. $FCCo_3(CO)_9^-\cdot$: $g_\parallel = 2.005 \pm 0.003$, $a_\parallel = -7.63 \pm 0.02$ mT). There was no suggestion of phosphorus (or fluorine) hyperfine coupling so that a^P must be less than the line widths, ~2.0 mT. If the frozen solution was thawed, warmed to room temperature, and then recooled to 203 K without further electrolysis, the isotropic ESR spectrum of $FCCo_3(CO)_9^-\cdot$ was easily observed. Thus the radical anion $FCCo_3(CO)_8P(OMe)_3^-\cdot$ is certainly formed at 203 K and is reasonably stable, but the isotropic ESR spectrum is not detectable (vide infra). Other monosubstituted phosphite derivatives behave similarly, but, in contrast, $YCCo_3(CO)_8PR_3$ solutions gave the spectrum of the $YCCo_3(CO)_9^-\cdot$ radical anion immediately on commencing electrolysis even at 203 K.

Attempts to detect the paramagnetic cations $YCCo_3(CO)_6L_3^+$ have so far failed.

Discussion

Substitution of a carbonyl group of a tricobalt–carbon cluster by a Lewis base has significant kinetic and thermodynamic effects on the redox behavior. Reduction to the radical anion $YCCo_3(CO)_{9-n}L_n^-\cdot$ becomes progressively more difficult with an increase in n and, once produced, the anion is more labile than the parent species $YCCo_3(CO)_9^-\cdot$. Conversely, a point is reached at the $YCCo_3(CO)_6L_3$ derivatives where the increased electron density on the cluster allows a reversible one-electron oxidation to $YCCo_3(CO)_6L_3^+$. Thus, for the Co_3C compounds, we have identified an extended electron-transfer series $[YCCo_3(CO)_{9-n}L_n]^{+/0/-/2-}$.

Both the electrochemical and ESR results showed that $YCCo_3(CO)_9$ compounds, and the corresponding radical anions, were produced on reduction of the phosphine and phosphite derivatives. The mechanism for the formation of $YCCo_3(CO)_9^-\cdot$ ($YC^-\cdot$) outlined in Scheme II accommodates the experimental observations ($YCP^-\cdot \equiv YCCo_3(CO)_{9-n}L_n^-\cdot$) The formation of the unstable dianions $[YCCo_3(CO)_{9-n}L_n]^{2-}$, either by electrolysis or by disproportionation of the radical anion, immediately liberates CO which initiates the series of electron-transfer and ligand-replacement reactions. Previous work[3,4,12] has shown the phosphine and phosphite ligands to be labile and, specifically, the first-order rate constant for the reaction of CO with $[MeCCo_3(CO)_8PPh_3]$ is 2×10^{-5} s^{-1} at 323 K.[14] The cyclic voltammograms suggest that the formation of $YCCo_3(CO)_9^-\cdot$ from $[YCCo_3(CO)_{9-n}L_n]^-\cdot$ takes place with a first-order rate constant of ~1 s^{-1} at 293 K. Thus, the lability of the ligand is markedly increased when the charge on the cobalt atom is increased.

Scheme II

$$YCP + e^- \rightleftharpoons YCP^-\cdot$$

$$\left.\begin{array}{c} 2YCP^-\cdot \rightarrow YCP + YCP^{2-} \\ YCP^-\cdot + e^- \rightarrow YCP^{2-} \end{array}\right\} \text{either/or}$$

$$YCP^{2-} \rightarrow \text{decomposition products including CO}$$

$$YCP^-\cdot + CO \rightleftharpoons YC^-\cdot + P$$

$$\left.\begin{array}{c} YC + e^- \rightarrow YC^-\cdot \\ YC + YCP^-\cdot \rightarrow YC^-\cdot + YCP \end{array}\right\} \text{either/or}$$

Difficulties in the recording of ESR spectra, which arose in this work, may be partially a consequence of this ligand lability and serve to indicate that frozen-solution spectra of radical anions of this type should be recorded as a matter of course. The failure to detect the isotropic ESR spectra of $YCCo_3(CO)_8P(OR)_3^-\cdot$ at 203 K, despite strong evidence for the existence of these radicals at that temperature, must be due to the lines of the spectra being broader and/or being of lower amplitude than those in the spectra of the parent anions $YCCo_3(CO)_9^-\cdot$. If there is significant hyperfine coupling to phosphorus, then all lines would be doubled. Further, the three cobalt nuclei may not be equivalent in $YCCo_3(CO)_8P(OR)_3$, leading to further splitting in the spectra. Thus more lines would be expected than in the spectrum of $YCCo_3(CO)_9^-\cdot$ and, at equivalent radical concentration and spectrometer sensitivity, they would be more difficult to detect. In addition, the Lewis base derivatives are fluxional on the ^{13}C NMR time scale,[4,12] even at 203 K, and this fluxionality might modulate the cobalt coupling constants and lead to further line broadening. Under the conditions of the experiments, the ESR spectrometer is operated near the limits of detection for the parent radicals $YCCo_3(CO)_9^{-}\cdot$; it is not surprising that the $YCCo_3(CO)_8P(OMe)_3^{-}\cdot$ anion cannot be detected at 203 K.

The fact that frozen-solution spectra of the phosphite derivatives are so similar to those of $YCCo_3(CO)_9^{-}\cdot$ is an important observation as it reinforces the view[2b] that the orbital occupied by the odd electron in paramagnetic metal–carbonyl clusters is antibonding and largely metal in character (a_2 symmetry in Co_3C clusters). The small reduction in $a_{\parallel}$ relative to $YCCo_3(CO)_9^{-}\cdot$ could be attributed to a decrease in spin density on the cobalt atoms but this seems illogical as a CO group is replaced by a better donor ligand. On the other hand, admixture of a small amount of 4s character in the LUMO (which is permitted under the C_n symmetry of the derivatives) would give a positive contribution to $\langle a \rangle$ (and $a_{\parallel}$) and easily explain the observations. This might well be the only perturbation suffered by the a_2 level on coordination of a donor ligand.

For the reasons outlined in earlier papers[2] trends in half-wave potentials reflect changes in the electron density of the HOMO level, an orbital encompassing the whole Co_3C unit. Because of the short lifetimes of the substituted radical anions, $E_{1/2}$ values in the tables are slightly displaced from the thermodynamically significant reversible half-wave potentials $E_{1/2}^{r}$. Nonetheless, the gross trend to more negative potentials as the CO groups are progressively replaced by weaker π acceptors can be attributed to a lowering of energy of the HOMO level. Subtle changes in $E_{1/2}^{r}$ in a particular series of complexes are complicated by the possibility of structural isomers in solution but the following trends in $E_{1/2}^{r}$ are significant: (a) it is modified by the inductive effect of the apical substituent Y, and Y = F compounds are the easiest to reduce; (b) it is constantly more negative (by ~0.2 V) for $P(OMe)_3$ than for $P(OPh)_3$ derivatives (also found in $Fe_3(CO)_{12-n}L_n$ compounds);[11] (c) in an isostructural series it becomes more negative with increasing basicity of the ligand and also reflects the relative π-acceptor ability of the ligand.

Oxidation of the trisubstituted derivatives $YCCo_3(CO)_6L_3$ occurred most readily when $L = PPhEt_2$. It is significant that oxidation was observed for $L = P(OR)_3$ despite the fact that phosphites are much better π acceptors than phosphines. The substitution of three carbonyl groups by three ligands which are better σ donors apparently raises the energy of the HOMO level to an extent that permits the oxidation process to take place within solvent limits.

The oxidation of the $YCCo_3(CO)_6L_3$ derivatives occurred at potentials well within the range of common oxidizing agents such as $AgBF_4$ and $NOPF_6$. Although a vigorous reaction took place when $AgBF_4$ was added to the cluster derivative in CH_2Cl_2 and a Ag mirror formed, no ESR signals were detected even at 213 K. Spectroscopic investigation of the resulting solution showed that no tricobalt–carbon derivatives were present.[15] Further attempts are being made to control this reaction as the $YCCo_3(CO)_6L_3^{+}$ cations must be produced, at least as transient species.

The redox series established for the tricobalt–carbon complexes is remarkably similar to that of the triiron clusters $Fe_3(CO)_{12-n}L_n$.[11,12] For both clusters the cation is only produced when $n = 3$ while the dianions are not stable and can only be implicated as reactive intermediates in electrode processes. It seems likely that the HOMO and LUMO orbitals in both clusters are closely related although the reduction potentials for the triiron compounds are more positive.[11] This is to be expected as there is good evidence[1,6,13] for a net charge transfer to the Co_3 unit from the apical CY group. In contrast to the Co_3C derivatives, excellent ESR spectra of the triiron derivatives (showing ^{31}P hyperfine coupling) can be obtained at low temperatures.[12]

Further studies on other trinuclear and tetranuclear cluster systems to confirm the ideas outlined in this paper are currently underway.

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Registry No. $PhCCo_3(CO)_8PPh_3$, 13681-99-7; $MeCCo_3(CO)_8PPh_3$, 56694-17-8; $FCCo_3(CO)_8PPh_3$, 33395-77-6; $MeCCo_3(CO)_8P(C_6H_{11})_3$, 56694-14-5; $FCCo_3(CO)_8P(C_6H_{11})_3$, 33392-88-0; $FCCo_3(CO)_8CNPh$, 68389-05-9; $FCCo_3(CO)_8P(OEt)_3$, 68389-06-0; $FCCo_3(CO)_8P(OMe)_3$, 68389-07-1; $FCCo_3(CO)_8P(OPh)_3$, 68399-56-4; $MeCCo_3(CO)_8P(OMe)_3$, 68389-08-2; $MeCCo_3(CO)_8CNPh$, 68389-09-3; $MeCCo_3(CO)_8PEt_2Ph$, 68409-53-0; $MeCCo_3(CO)_8P$-*n*-Bu_3, 56694-15-6; $HCCo_3(CO)_8PMePh_2$, 68399-55-3; *m*-$MePhCCo_3(CO)_7C_7H_8$, 57812-76-7; $MeCCo_3(CO)_7[P(OMe)_3]_2$, 68389-11-7; $MeCCo_3(CO)_7[P(OPh)_3]_2$, 68389-12-8; $FCCo_3(CO)_7[P(OMe)_3]_2$, 68389-13-9; $FCCo_3(CO)_7[P(OPh)_3]_2$, 68389-14-0; $MeCCo_3(CO)_6[P(OMe)_3]_3$, 68389-15-1; $MeCCo_3(CO)_6[P(OPh)_3]_3$, 68389-16-2; $MeCCo_3(CO)_6[PEt_2Ph]_3$, 68389-17-3; $FCCo_3(CO)_6[P(OMe)_3]_3$, 68389-18-4; $FCCo_3(CO)_6[P(OPh)_3]_3$, 68389-19-5.

References and Notes

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