(15) K. Singh and D. V. Stynes, to be submitted for publication.

(16) The symbolism k_{+x} for addition of x to the five-coordinate intermediate and k_{-x} for dissociation of x from the six-coordinate complexes is used here in place of the more general but less descriptive than k_1, k_2, k_{-1}, and k_{-2} used previously.

(17) E. Wilhelm and R. Battino, *Chem. Rev.*, 73, 1 (1973).

(18) Details of the photochromic properties of these systems will be published elsewhere.

(19) I. W. Pang, K. Singh, and D. V. Stynes, *J. Chem. Soc., Chem. Commun.*, 132 (1976).

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Paramagnetic Organometallic Molecules. 4.[1] Electrochemical Investigation of the Iron Group Carbonyls and Their Phosphine-Substituted Derivatives

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The redox behavior of the iron carbonyl species $Fe_3(CO)_{12-n}L_n$ (n = 0–3) and $Fe(CO)_{5-n}L_n$ (n = 0–2) (L = PPh_3, $P(OMe)_3$, $P(OPh)_3$) has been studied in acetone and dichloromethane using the techniques of dc polarography at mercury electrodes and dc cyclic voltammetry at platinum electrodes. A chemically reversible one-electron reduction step was observed for the triiron species within the temperature range 203–293 K. The $E^r_{1/2}$ values for the reduction became increasingly negative with increasing phosphine substitution which correlates well with the charge density on the iron atoms in the parent complexes. The carbonyls $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ undergo an irreversible reduction within the temperature range of this investigation leading to rapid decomposition of the carbonyl moieties. Further reduction to the dianions $Fe_3(CO)_{12-n}L_n^{2-}$ occurred for the iron species and caused irreversible disintegration of the cluster unit. A one-electron oxidation step was observed for $Fe_3(CO)_9[P(OMe)_3]_3$. The mononuclear iron derivatives gave well-defined one-electron oxidation and two-electron reduction waves at mercury electrodes. The oxidation step was found to be chemically reversible. No evidence was found for the formation of the radical anion $Fe(CO)_5^-\cdot$ under the experimental conditions employed.

Introduction

Earlier papers in this series[3] described an investigation of the remarkably stable paramagnetic radical anions produced from the methinyltricobalt enneacarbonyls $YCCo_3(CO)_9$ and the somewhat less stable phosphine-substituted anions.[4] Electrochemical[3a] and spectral studies[3b] allowed a complete characterization of the redox behavior and provided kinetic and thermodynamic data for the cluster/radical anion couple. These studies also added to our understanding of the HOMO and LUMO levels in the neutral tricobalt carbon cluster and the kinetic and thermodynamic stability of the radical anions was attributed[3b] to an "electron-reservoir" mode of bonding and stereochemical protection afforded by the equatorial and axial carbonyl groups.[5] Whether these ideas have any validity when applied to metal–carbonyl clusters that do not include a nonmetal atom as an integral part of the cluster framework is open to question and thus we extended our investigations to tri- and tetrametallic cluster derivatives.

Trinuclear metal carbonyl clusters $M_3(CO)_{12}$ differ markedly in structure and properties[6] from the tricobalt carbon system but preliminary ESR studies[7] of the products from alkali metal reduction suggested that they might also be reduced to give radical anions. Unambiguous interpretation of the ESR data proved more difficult in this instance and the success achieved with electrochemical studies in the cobalt system[3a] prompted the electrochemical investigation of $M_3(CO)_{12}$ (M = Fe, Ru, Os) and the Lewis base substituted derivatives $Fe_3(CO)_{12-n}L_n$ (n = 0–3) reported herein. Further, since alkali metal reduction apparently produced monomeric and dimeric compounds, as well as trinuclear anions,[8] an electrochemical investigation of $Fe(CO)_5$ and the substituted derivatives $Fe(CO)_{5-n}L_n$ (n = 1, 2) was also undertaken. The electrochemistry of a limited range of iron carbonyl derivatives has been reported previously,[9–14] but this did not include a systematic examination of the redox behavior as the σ-donor and π-acceptor properties of the ligands are varied. Dessy et al.[9] found a reduction wave for $Fe(CO)_5$ at mercury in dimethoxyethane which they interpret as being due to the formation of the unstable radical species $Fe(CO)_5^-\cdot$. Picket and Pletcher[13] also described a one-electron reduction of $Fe(CO)_5$ at platinum in THF which they attribute to the overall process

$$Fe(CO)_5 + e^- = {}^1/_2[Fe_2(CO)_8]^{2-} + CO$$

Experimental Section

$Fe(CO)_5$, $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ were purified by distillation or sublimation in vacuo. Phosphine and phosphite derivatives were prepared from $Fe_3(CO)_{12}$ in hexane by published procedures.[15–18] Separation of the complexes from a particular reaction was most satisfactorily achieved using preparative TLC. The compounds $[Et_3NH][Fe_3(CO)_{11}H]$ and $[(Ph_3P)_2N][HFe(CO)_4]$ were prepared from $Fe(CO)_5$ using procedures based on the methods of McFarlane and Wilkinson[19] and Case and Whiting,[20] respectively.

Electrochemical Instrumentation. Dc polarograms, 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 $Et_4N^+ClO_4^-$ as the supporting electrolyte at a concentration of 0.10 (acetone) or 0.08 mol dm^{-3} (dichloromethane). All the solutions were thermostated at the appropriate temperature 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.[21–23]

Results

$Fe_3(CO)_{12}$. Figure 1 shows the dc polarographic behavior of $Fe_3(CO)_{12}$ in acetone. Two extremely well-defined reduction waves are observed in freshly prepared solutions, with $E_{1/2}$ values −0.21 and −0.76 V vs. Ag/AgCl, respectively. On standing in the electrochemical cell, some decomposition occurred and additional waves appeared near the anodic limit (+0.8 V vs. Ag/AgCl) and at potentials more negative than −1.2 V vs. Ag/AgCl. Little decomposition was observed in dichloromethane and, in this solvent, two well-defined waves were again found ($E_{1/2}$ = −0.30 and −0.64 V vs. Ag/AgCl) corresponding to the same electrode processes as seen in acetone. Analysis of the wave shapes and positions (Tables I and II) and the number of electrons, n, obtained from the limiting-current magnitude and applied potential, were consistent with an initial one-electron reduction followed by

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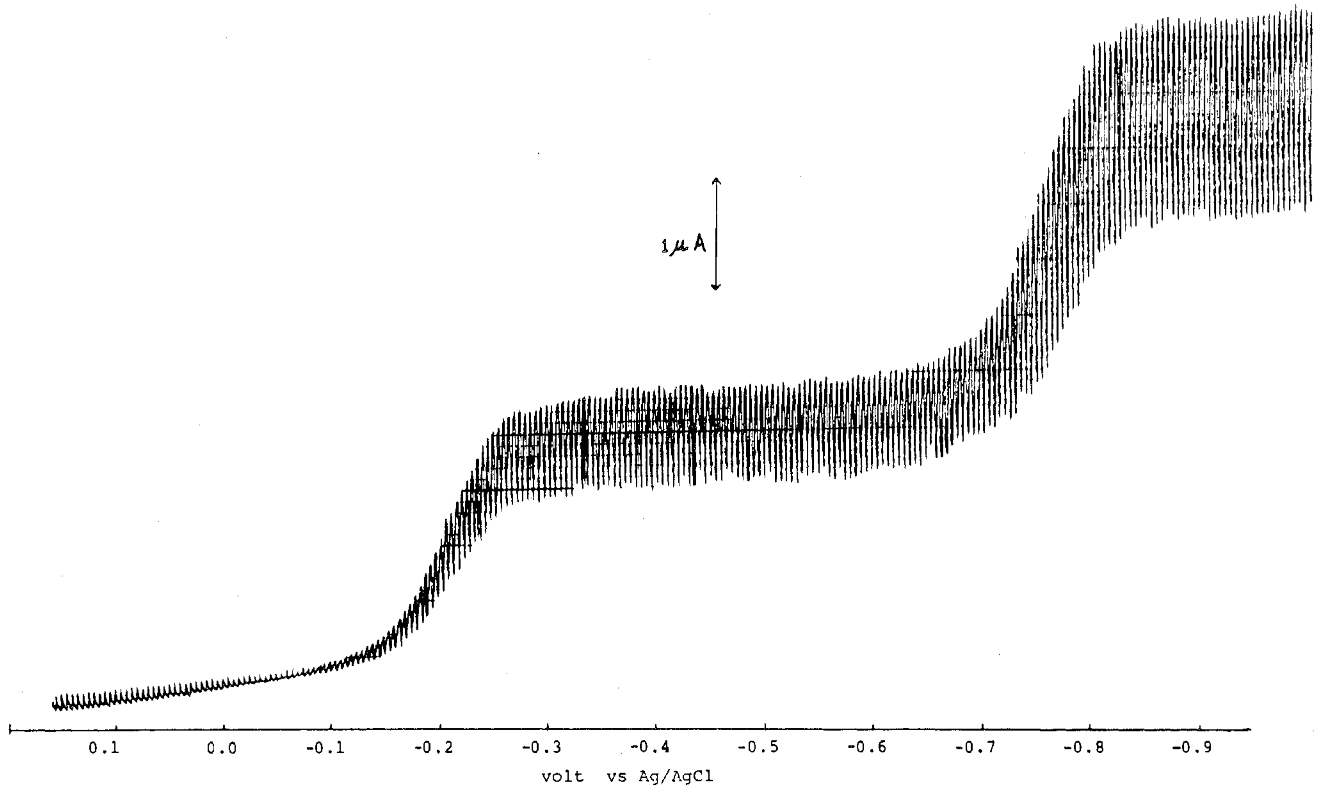

Figure 1. Dc polarogram of $Fe_3(CO)_{12}$ in acetone at 298 K; drop time 0.5 s; scan rate 10 mV s^{-1}.

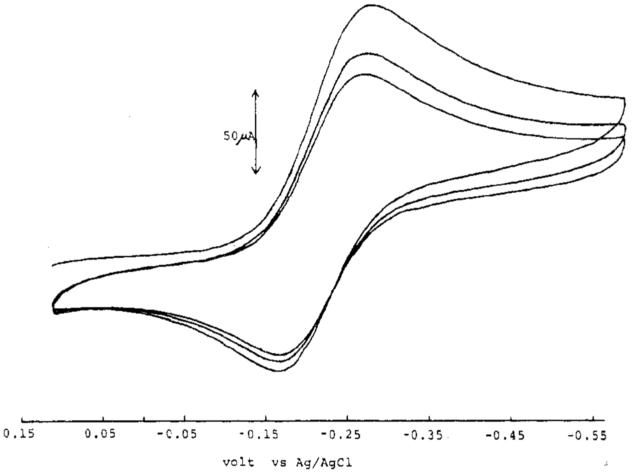

Figure 2. Dc cyclic voltammogram at platinum of $Fe_3(CO)_{12}$ in acetone at 268 K; scan rate 200 mV s^{-1}.

a second one-electron reduction step.

Figure 2 shows a cyclic voltammogram of the first reduction process in acetone at a platinum electrode at 268 K. It can be seen that, at this temperature, the electrode process is completely reversible in the chemical sense; above this temperature the process is not entirely reversible. This first reduction step can therefore be assigned to the formation of a radical anion

$$Fe_3(CO)_{12} + e^- \rightleftharpoons Fe_3(CO)_{12}^{-}\cdot$$

In dichloromethane, chemical reversibility for this electrode process was observed at room temperature under cyclic voltammetric conditions with a scan rate of 200 mV s^{-1}. Thus $Fe_3(CO)_{12}$ forms a radical anion that has reasonable stability on the electrochemical time scale.

Figure 3 shows cyclic voltammograms obtained at a platinum electrode over an extended potential range, in acetone at 203 K (Figure 3b) and in dichloromethane at 293 K. In all cases, the radical anion generated at approximately −0.26 V (acetone) or −0.39 V (dichloromethane) vs. Ag/AgCl undergoes a further one-electron reduction process at more negative potentials. Reduction of the radical anion is found

Table I. Polarographic Data[a,b]

	1-e redn		Oxidn		Further redn
Compd	$E_{1/2}{}^1$	$(E_{1/4} - E_{3/4})^1$	$E_{1/2}$	$E_{1/4} - E_{3/4}$	$E_{1/2}{}^2$
$Fe_3(CO)_{12}$	−0.208	56			−0.764
$Fe_3(CO)_{11}L^f$	−0.404	44			−1.12
$Fe_3(CO)_{11}L'$	−0.444	46			−1.10
$Fe_3(CO)_{11}L''$	−0.406	45			−0.99
$Fe_3(CO)_{10}L'_2$	−0.758	49			−1.12
$Fe_3(CO)_{10}L''_2$	−0.592	45			−0.95
$Fe_3(CO)_9L'_3$	−1.033	30	0.72[c]		
$Fe_3(CO)_9L''_3$	−0.92				−1.10
$[HFe_3(CO)_{11}]^-$	−1.13	42	0.484 (0.66)[d]	61	−1.90
$Fe(CO)_5$	−1.676	140	0.737 (0.594)[d]	30	
$Fe(CO)_4L$	−1.63	83	0.734	40	
$Fe(CO)_3L_2$	−2.2[e]		0.50 (0.53)[d]	45	
$Fe(CO)_4L'$	−2.1[e]		0.66	30	
$Fe(CO)_3L'_2$	*e*		0.42 −0.27	75	
$[HFe(CO)_4]^-$	−1.94	30	0.64	90	
$Ru_3(CO)_{12}$	−0.815	100			−2.0
$Os_3(CO)_{12}$	−1.16	94			

[a] In volts vs. Ag/AgCl [0.1 M LiCl, acetone] except $E_{1/4} - E_{3/4}$ values which are in mV. Solutions: 10^{-3} M in acetone, 0.1 M Et_4NClO_4, 298 K. Superscript 1 (as in $E_{1/2}{}^1$) refers to a first reduction process; superscript 2, to further processes. [b] DME; drop time 0.5 s; scan rate 10 mV s^{-1} (or 20 mV s^{-1} for monomeric derivatives). [c] 0.76 V at Pt, the process being reversible at lower temperatures. [d] Prewave associated with the oxidation wave. [e] Reduction wave merges with the solvent wave. [f] L = PPh_3; L′ = $P(OMe)_3$; L″ = $P(OPh)_3$.

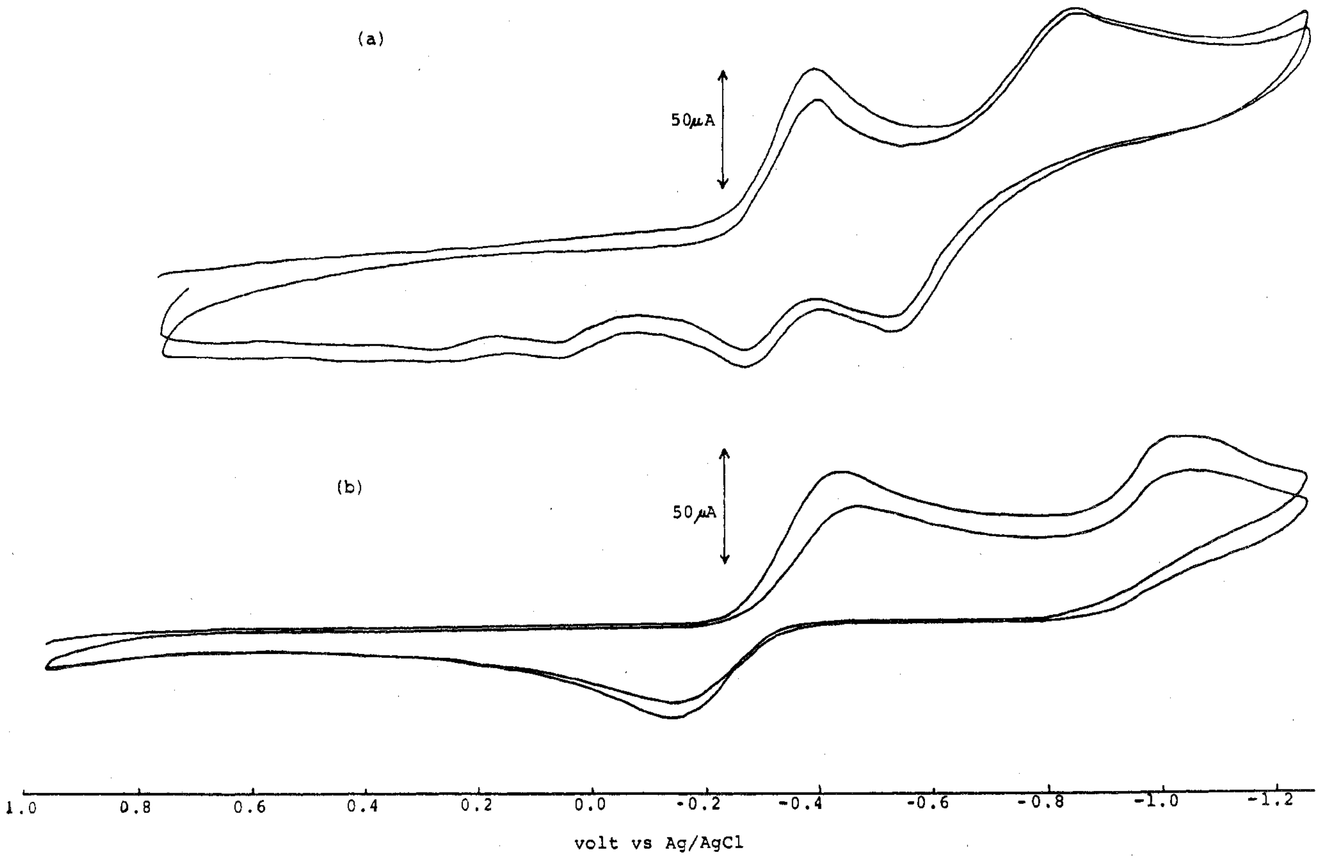

Figure 3. Dc cyclic voltammograms of $Fe_3(CO)_{12}$ over an extended range in (a) dichloromethane at 298 K and (b) acetone at 203 K; scan rate 200 mV s^{-1}.

to be chemically completely irreversible over the temperature range 313–203 K and a range of voltage scan rates. The presence of additional waves in the reverse scan of the voltammogram suggests that fragmentation of the $Fe_3(CO)_{12}$ unit accompanies the addition of a second electron. The reduction of the radical anion is therefore described by the equation

$$Fe_3(CO)_{12}^{-\cdot} + e^- \rightarrow Fe_3(CO)_{12}^{2-} \rightarrow \text{products}$$

The basic electrode processes are similar in both acetone and dichloromethane but the decomposition of the dianion species is faster in acetone. Comparison of voltammograms in acetone at 293 and 203 K shows the complete absence of waves corresponding to decomposition products at the lower temperature, although the reduction of the radical anion clearly remains irreversible. Voltammograms recorded in an atmosphere of carbon monoxide and in solutions that had been saturated with CO gas showed that both electrode processes were independent of CO concentration.

The $E_{1/2}$ values (Table I) found in this investigation for the reduction of $Fe_3(CO)_{12}$ are at variance with those of Dessy et al.[9] which suggested that the reduction of $Fe_3(CO)_{12}$ occurs at very negative potentials (~1.6 and 2.4 V vs. $Ag/AgClO_4$). The differences between the two sets of data may be explained by the observation that $Fe_3(CO)_{12}$ decomposed in the polar solvent, acetone, to give products which produced additional waves close to the cathodic limit. We suggest therefore that the values quoted by Dessy for solutions in dimethoxyethane refer to these, as yet, uncharacterized decomposition products.

$Fe_3(CO)_{12-n}L_n$ [L = Pr_3, $P(OR)_3$; n = 1–3]. Tables I and II summarize the electrochemical data for a range of phosphine-substituted triiron dodecacarbonyl derivatives. The electrochemistry at a dropping mercury electrode is characterized by a well-defined reduction step and a second, more diffuse, reduction step at more negative potentials. Additional electrode processes at very negative potentials also occur and these become increasingly complex as phosphine substitution at the metal cluster increases. Two corresponding reduction steps are observed in cyclic voltammograms at platinum electrodes. Figures 4 and 5 show representative polarograms and voltammograms obtained at 293 K. Considerable simplification of the electrode processes occurs at lower temperatures (Figure 6). In particular, the first reduction step is chemically reversible at 195 K and, at this temperature, decomposition of the radical anion species is arrested for all but the trisubstituted derivatives. The voltammograms at 195 K closely resemble the corresponding i–E curve for $Fe_3(CO)_{12}$ at ambient temperature (Figure 2). The complete electrode process at 195 K can therefore be written as

$$Fe_3(CO)_{12-n}L_n + e^- \overset{195\ K}{\rightleftharpoons} [Fe_3(CO)_{12-n}L_n]^{-\cdot}$$

$$[Fe_3(CO)_{12-n}L_n]^{-\cdot} + e^- \xrightarrow{195\ K} [Fe_3(CO)_{12-n}L_n]^{2-} \xrightarrow{\text{fast}} \text{products}$$

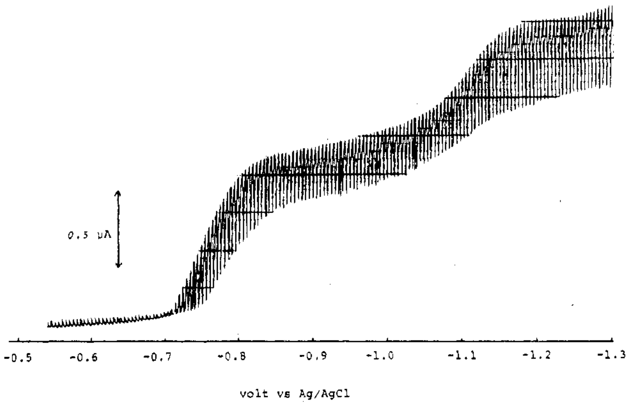

Figure 4. Dc polarogram of $Fe_3(CO)_{10}[P(OMe)_3]_2$ in acetone at 293 K; scan rate 10 mV s^{-1}.

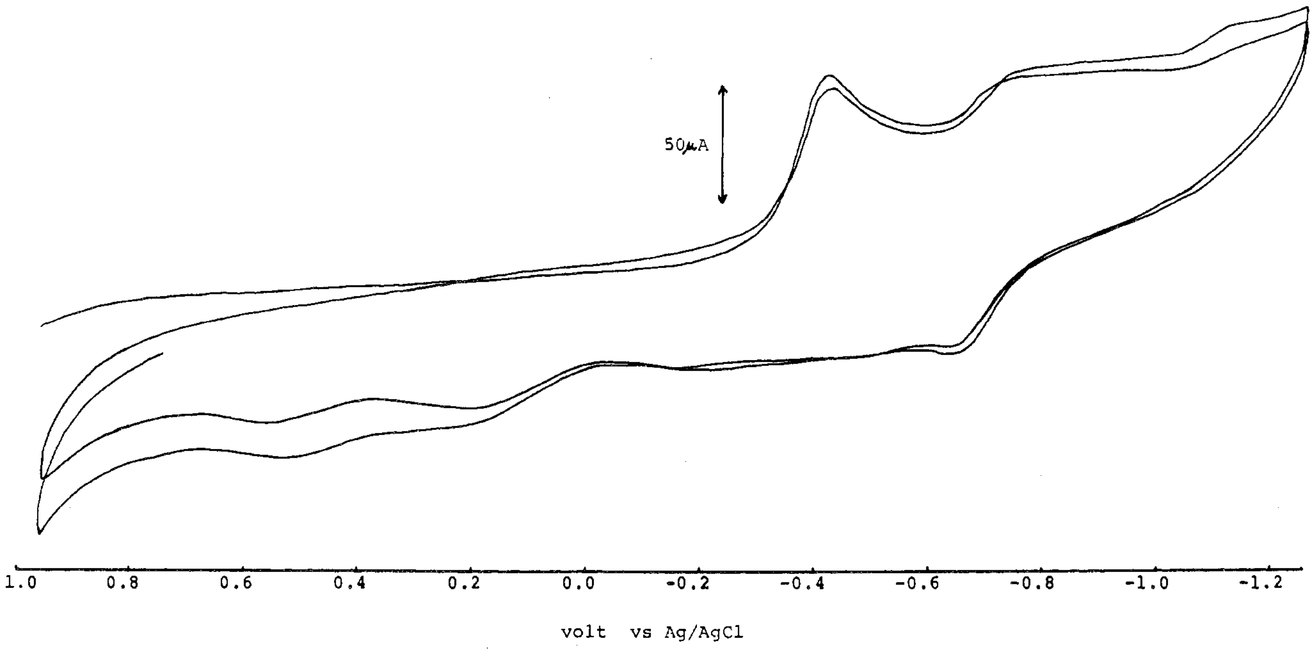

Figure 5. Dc cyclic voltammogram at platinum of $Fe_3(CO)_{11}[P(OPh)_3]$ in acetone at 293 K; scan rate 200 mV s^{-1}.

Table II. Cyclic Voltammetric Data[a, b]

Compd	1-e redn E_p^{r1}	Further redn E_p^{r2}	Oxidn			
			E_p^{ox2} [c]		E_p^{ox} [d]	E_p^{r} [d]
			−0.66	−0.50		
$Fe_3(CO)_{12}$	−0.26	−0.95	0.20	0.50		
		−0.74	−0.65	−0.20		
$Fe_3(CO)_{11}L$[e]	−0.48	−0.96	0.18			
			−0.62	−0.42		
$Fe_3(CO)_{11}L'$	−0.52	−1.15	0.16	0.52		
		−0.73	−0.65	−0.47		
$Fe_3(CO)_{11}L''$	−0.44	−1.1	0.18	0.50		
			−1.10	−0.96		
$Fe_3(CO)_{10}L'_2$	−0.84	−1.18	−0.40	0.27		
			−0.98	−0.89		
$Fe_3(CO)_{10}L''_2$	−0.66	−1.11	0.27	0.54		
			−1.2	−1.0		
$Fe_3(CO)_9L'_3$	−1.13	−1.32	−0.45		0.76	0.68
			0.09			
$Fe_3(CO)_9L''_3$	−0.90	−1.0	0.33			
			0.16	0.54		
$[HFe_3(CO)_{11}]^-$	−1.21		0.66	0.48	0.58	
$Fe(CO)_5$	−1.67		−1.37		0.64	0.58
					0.65	0.59
$Fe(CO)_4L$	−1.86		−1.31		0.76	0.72
$Fe(CO)_3L_2$					0.62	0.48
					0.57	
$Fe(CO)_4L'$	−1.73				0.75	0.52
					0.44	
$Fe(CO)_3L'_2$					0.61	0.30
$[HFe(CO)_4]^-$	−1.98				−0.11	−0.32

[a] In volts vs. Ag/AgCl [0.1 M LiCl, acetone]. Solutions: 10^{-3} M in acetone, 0.1 M Et_4NClO_4, 298 K. Superscript 1 (as in E_p^{r1}) refers to a first reduction process; superscript 2, to further processes. [b] Pt wire electrode, scan rate 200 mV s^{-1} for trimeric derivatives; hanging Hg drop electrode, scan rate 1 V s^{-1} for other derivatives. [c] E_p^{ox2} refers to fragmentation peaks on reverse and subsequent scans (switching potential −1.4 V). Reduction processes for the monomeric derivatives were not reversible under any conditions studied. [d] The oxidation processes showed some degree of reversibility. [e] L = PPh_3; L′ = $P(OMe)_3$; L″ = $P(OPh)_3$.

At higher temperatures, the electrochemistry is complicated by the concomitant decomposition of the radical anion and the first irreversible reduction step is

$$Fe_3(CO)_{12-n}L_n + e^- \xrightarrow{293\text{ K}} [Fe_3(CO)_{12-n}L_n]^{-\cdot} \xrightarrow{\text{fast}} \text{products}$$

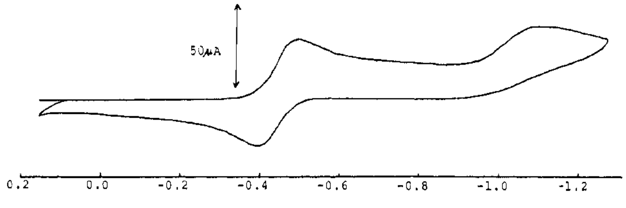

Figure 6. Dc cyclic voltammogram at platinum of $Fe_3(CO)_{11}[P(OPh)_3]$ in acetone at 195 K; scan rate 200 mV s^{-1}.

The ($E_{1/4} - E_{3/4}$) values and other data indicate that the products are electroactive to give an ECE type mechanism. The electrochemistry of the phosphine derivatives in dichloromethane is similar to that in acetone apart from slight kinetic differences in the decomposition steps. Saturation of the solvent with CO did not serve to stabilize either of the reduced species although some alteration of the relative heights of waves due to decomposition products was detected under these conditions.

Substitution of a phosphine ligand for carbon monoxide at $Fe_3(CO)_{12}$ has a number of significant effects on the electrochemistry of the system. The most striking is the clear trend to more negative $E_{1/2}$ values for the first reduction waves with increasing phosphine substitution, i.e., with increasing charge on the iron atoms. The first reduction potential is remarkably insensitive to the σ-donor/π-acceptor capabilities of the ligand for the $Fe_3(CO)_{11}L$ series but this is not true for the more highly substituted derivatives. In these cases the $P(OMe)_3$ derivatives have significantly more negative potentials than the comparable $P(OPh)_3$ compounds (Tables I and II) although, as will be discussed later, this difference probably arises from steric effects. Another consequence of increased phosphine substitution is to increase the rate of decomposition of both the radical anion and the dianion species. Decomposition is faster in acetone than in dichloromethane and this may be due to a solvent-assisted disproportionation of the reduction products. Attempts to characterize the decomposition products from both reduction steps are under way.

The $[Fe_3(CO)_{11}H]^-$ Anion. The $[Fe_3(CO)_{11}H]^-$ anion undergoes an irreversible one-electron reduction in acetone at a Pt electrode. However, this reduction is reversible at low temperatures at mercury electrodes and occurs at a more negative potential ($E_{1/2} = -1.13$ V vs Ag/AgCl) than those for $Fe_3(CO)_{11}L$ derivatives. A second irreversible reduction step occurred at −1.9 V vs. Ag/AgCl close to the solvent limit. Dessy et al.[9] also reported two reduction waves although it seems that they do not correspond to those we observed. The potential for the first reduction step is close to that for $Fe_3(CO)_9[P(OMe)_3]_3$ and, like this derivative, the anion undergoes a one-electron oxidation at both platinum and mercury electrodes. Presumably the hydride ion is retained in the oxidized product and it may be possible to isolate a neutral paramagnetic $Fe_3(CO)_{11}H$ species.

Oxidation of the $Fe_3(CO)_{12-n}L_n$ Derivatives. Attempts to electrochemically oxidize the phosphine-substituted triiron dodecacarbonyl derivatives at both mercury and platinum electrodes proved fruitless, within the range of solvent stability, with one exception. Polarograms and voltammograms for $Fe_3(CO)_9[P(OMe)_3]_3$, in acetone, revealed a reversible wave corresponding to a one-electron oxidation at approximately +0.7 V (vs. Ag/AgCl). The electrode process is therefore

$$Fe_3(CO)_9[P(OMe)_3]_3 \rightleftharpoons Fe_3(CO)_9[P(OMe)_3]_3^+ + e^-$$

A decrease in oxidation potential with increasing substitution of ligands which are good σ donors has been noted previously by a number of workers.[14,24,25] Presumably in this case, the replacement of three carbonyl by three $P(OMe)_3$ groups results in an increase in electron density on the iron atoms sufficient to raise the energy of the highest occupied level to a point where oxidation can occur within the potential range of the solvent.

$Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. The electrochemistry of both carbonyls is characterized by a well-defined reduction step that was both chemically and electrochemically irreversible at temperatures as low as 195 K. A second, ill-defined wave appeared in the polarograms of both species at very negative potentials (Table I). The electrode process corresponding to this second wave cannot be designated with certainty (in fact, it probably is an electrode process involving a fragmentation product of the clusters) but, by analogy with the iron system, the initial reduction can be written as

$$M_3(CO)_{12} + e^- \rightarrow M_3(CO)_{12}^{-\cdot} \rightarrow \text{products}$$
$$(M = Ru, Os)$$

The $E_{1/2}$ values, −0.82 V for $Ru_3(CO)_{12}$ and −1.16 V for $Os_3(CO)_{12}$ (vs. Ag/AgCl), show their reduction to be considerably more difficult than that of $Fe_3(CO)_{12}$.

$Fe(CO)_{5-n}L_n$ [L = PPh_3, $P(OMe)_3$, $P(OPh)_3$; n = 0, 1, 3]. Iron pentacarbonyl and its phosphine-substituted derivatives give well-defined reduction waves in acetone at mercury electrodes. These occur at very negative potentials (Tables I and II) and, for the disubstituted species, the waves merge with the solvent limit (∼−2.25 V vs. Ag/AgCl). Figure 7 shows the result of cyclic voltammetry at a mercury drop for $Fe(CO)_5$ from which it can be seen that the reduction step is not reversible. Lowering the temperature of the solution had little effect on the nature of the waves produced. No well-defined waves were found for the mononuclear iron derivatives at platinum electrodes in acetone.

The $Fe(CO)_{5-n}L_n$ derivatives also undergo a reversible one-electron oxidation at mercury electrodes, the reversibility being demonstrated by cyclic voltammetry

$$Fe(CO)_{5-n}L_n \rightleftharpoons Fe(CO)_{5-n}L_n^+ + e^-$$

Figure 8 shows a polarogram for $Fe(CO)_5$ over an extended potential range from which it can be seen that the height of the oxidation wave is approximately half that of the reduction step. A prewave is associated with the oxidation step. A similar oxidation process has been reported previously for $Fe(CO)_5$ in acetonitrile[13] and trifluoroacetic acid[26] and for $Fe(CO)_3L_2$ in dichloromethane.[43]

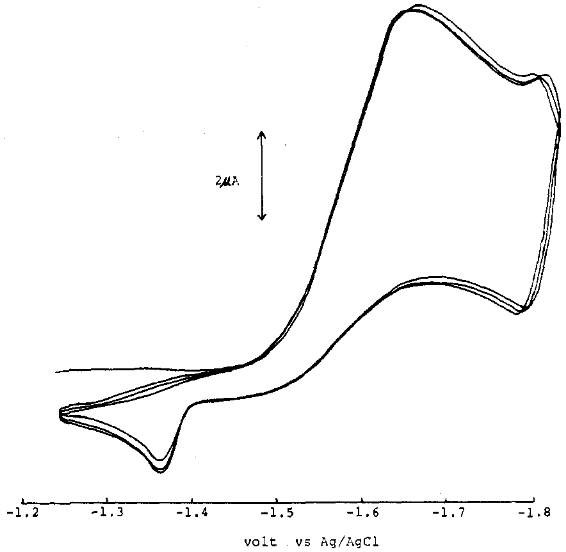

Figure 7. Dc cyclic voltammogram of $Fe(CO)_5$ in acetone at 293 K using a hanging Hg drop electrode; scan rate 1 V s^{-1}.

Our data do not support the suggestion of Dessy et al.[9] that the reduction wave for $Fe(CO)_5$ at mercury in dimethoxyethane is due to the formation of the unstable radical anion species $Fe(CO)_5^{-\cdot}$. In acetone at a mercury electrode the current per unit concentration for the reduction of $Fe(CO)_5$ was found to be almost exactly *twice* that for the known one-electron reductions of $ClCCo_3(CO)_9$[2], $Fe_3(CO)_{12}$, and $Fe_3(CO)_{11}P(OPh)_3$. This, together with the relative heights of the oxidation and reduction waves for $Fe(CO)_5$ mentioned previously, leads us to attribute the reduction at mercury to a two-electron step

$$Fe(CO)_5 + 2e^- \rightarrow Fe(CO)_4^{2-} + CO$$

The ultimate product under conditions of controlled-potential electrolysis could well be $Fe_2(CO)_8^{2-}$ or other polynuclear carbonyl anions as the electrochemical behavior of $Fe(CO)_4^{2-}$ is as yet unknown. In our hands, no electrochemical evidence could be found for a one-electron reduction step at a mercury electrode or for the formation of $Fe(CO)_5^{-\cdot}$ in the temperature range 233–298 K. It is surprising that reduction did not occur at platinum electrodes and this raises the question as to whether mercury derivatives of iron carbonyl anions are involved in the electrode processes.[40] Hopefully our IR and ESR studies[4] will answer this question but it is pertinent to note that Picket and Pletcher described[13] a one-electron reduction at platinum in THF. They concluded that $Fe_2(CO)_8^{2-}$ is the product and clearly the solvent and electrode material play an important role in the electrochemistry of $Fe(CO)_5$. The anion $HFe(CO)_4^-$ undergoes an irreversible oxidation at mercury electrodes and it is certainly not a product in electrochemical reactions of $Fe(CO)_5$ or $[HFe_3(CO)_{11}]^-$.

Discussion

In acetone or dichloromethane solution the trinuclear iron clusters $Fe_3(CO)_{12-n}L_n$ (n = 0–3) undergo a one-electron reduction to the radical anions $[Fe_3(CO)_{12-n}L_n]^{-\cdot}$. Substitution of a carbonyl group by a basic ligand progressively decreases the lifetime of the reduced product, concomitant with a cathodic shift in $E_{1/2}$. Examination of ac cyclic voltammograms and ac polarograms over a range of dc scan rates (voltammetry) and drop times (polarography) and frequencies

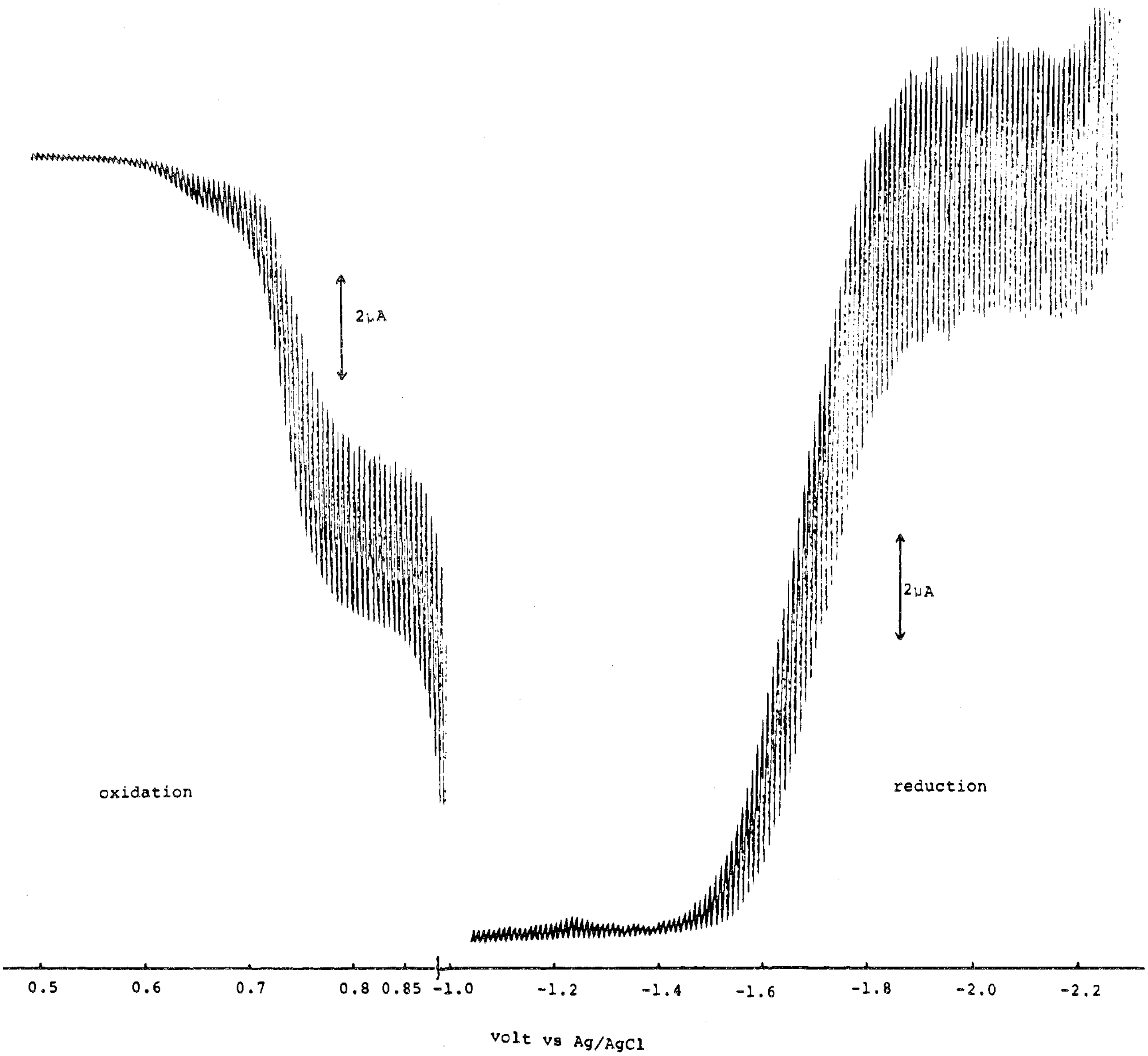

Figure 8. Dc polarogram of $Fe(CO)_5$ over an extended potential range at 293 K; scan rate 20 mV s^{-1}.

demonstrated that $E_{1/2}$ values were only slightly perturbed from $E^r{}_{1/2}$ by the follow-up chemical reaction and for discussion purposes $E_{1/2}$ values can be equated with the thermodynamic $E^\ominus$ values. Provided that the free energy of solvation during the reduction is constant for this series of compounds (a restriction which is probably met as the compounds have basically the same ligand conformation about the metal atoms) and that no gross structural change takes place on reduction, then one would expect a correlation between the electrode potentials and the difference in energy between the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO). Theoretical calculations[27-30] and arguments based on chemical and structural data[27,28,31] suggest that both the HOMO and LUMO (which is possibly an antibonding level) in metal carbonyl clusters are predominantly metal in character. Therefore, an increase in charge on the iron atoms brought about by substituting a basic ligand will increase the energy of the HOMO and reduction will become more difficult. This trend culminates at $Fe_3(CO)_9[P(OMe)_3]_3$ and in an anionic derivative $[Fe_3(CO)_{11}H]^-$ where the HOMO levels have been raised in energy to the extent that a one-electron oxidation is also observed. Within the limited $Fe_3(CO)_{11}L$ series [L = PPh_3, $P(OMe)_3$, $P(OPh)_3$] examined in this work there is no significant dependence of $E_{1/2}$ on the σ-donor/π-acceptor ability of the ligand. This is in direct contrast to the large variations in $E_{1/2}$ with ligand basicity found[14,24,25] for the oxidation potentials of a number of mononuclear carbonyl complexes. In this context, the nature of the redox orbitals is undoubtedly important. For mononuclear derivatives the redox orbitals appear to have contributions from both the carbonyl and phosphine ligands,[10,14] whereas for the clusters, these are largely metal in character and small variations in charge on the metal atoms are buffered through delocalization over the cluster unit. However, on this premise it is difficult to understand the marked difference in $E_{1/2}$ values for $Fe_3(CO)_{10}[P(OR)_3]_2$ (R = Me, Ph). Infrared and ^{13}C NMR studies[32] show that, in solution, the bis-substituted derivatives have a CO-bridged configuration at the temperatures used in our investigation and for this configuration space-filling models show that there are serious CO–CO and CO–ligand steric interactions (assuming an axial–equatorial ligand orientation). Because of an accentuated steric effect when the ligand is $P(OPh)_3$ there will be a barrier to metal–ligand interaction and the energy of the highest occupied level will be depressed relative to that in the $P(OMe)_3$ compound leading to a more positive $E^{\ominus}_{1/2}$. The same argument holds for the $Fe_3(CO)_9L_3$ compounds and it is significant that only the $P(OMe)_3$ derivative gave a well-defined reversible oxidation wave.

The potentials for the second reduction step, corresponding to the reduction of the radical anion species, mirror the trend discussed for the first reduction step. The instability of the two-electron reduction product of $YCCo_3(CO)_9$ clusters could be readily explained[3a] in terms of the Wade[32] theory of bonding in electron-deficient cluster systems. A similar treatment of $Fe_3(CO)_{12-n}L_n$ derivatives is not so successful as this theory would designate the neutral derivatives, with six available skeletal bonding pairs, to an *arachno* structure based on a trigonal bipyramid with two unoccupied vertices. There is no provision in this theory for the addition of two further electrons to give the $(n + 4)$ skeletal electron pairs of the dianion species. An alternative treatment of the $Fe(CO)_{12-n}L_n$ derivatives is to regard them as electron-precise polyhedra, having just the correct number of skeletal electron pairs to form two-center, two-electron bonds along the three edges of the metal triangle.[12] Provision for electron-precise and electron-rich polyhedra in skeletal electron accountancy has been made by Mingos,[34] who proposed that each electron pair over and above those required for an electron-precise system will result in the breaking of one edge bond in the polyhedron. On this approach, two-electron reduction of $Fe_3(CO)_{12}$ or its derivatives would give an electron-rich species. The concomitant loss of one edge bond would result in a V-shaped molecule and the stability engendered by the metal cluster system would be lost. Such an approach accommodates the belief that the added electrons enter antibonding molecular levels with consequent destabilization of the polyhedral framework.

Reduction of mononuclear iron carbonyl derivatives occurs at very negative potentials and this ill-defined two-electron process is irreversible. The electron density in the redox orbital of these compounds is clearly sufficient to raise the energy to the stage where one-electron oxidation is feasible and it is the paramagnetic oxidized species which should be most readily detected by ESR methods. The paramagnetic mononuclear iron compounds produced in the sodium reduction of the trinuclear derivatives[7] must arise from cleavage of the $Fe_3(CO)_{12-n}L_n$ radical anions or dianions rather than reduction of mononuclear impurities. This would explain why there is no correlation between the electrochemical behavior of these fragmentation products and that of the $Fe(CO)_{5-n}L_n$ derivatives. Preliminary ESR results indicate that the fragmentation products are solvated species of the type $Fe(CO)_{4-n}L_n(S)$ (S = THF etc.).[4] In the case of the $Fe(CO)_{5-n}L_n$ derivatives it is not possible to give a satisfactory description of the redox orbital except that it is unlikely to be largely metal in character. The ESR spectra of paramagnetic species generated from ^{13}CO-substituted species show hyperfine coupling to the ^{13}C nucleus,[4] and this suggests that the redox orbital has significant carbonyl contribution. If this is correct, then it is not surprising that only a high-energy two-electron reduction is observed and that oxidation is thermodynamically more feasible.

Reduction of the congeners of $Fe_3(CO)_{12}$ becomes progressively more difficult as the atomic number of the metal increases. The instability of the anion radicals has the effect of making $E_{1/2}$ more positive than $E^{\ominus}$ with the shift from $E^{\ominus}$ being in the order Os > Ru > Fe. Consequently the decomposition of the anion radical causes the $E_{1/2}$ values to converge and differences in $E^{\ominus}$ values are even greater than those for the tabulated $E_{1/2}$ values. Changes in the free energy of solvation or entropy during reduction should not account for the differences in $E^{\ominus}$ for these isostructural[35] clusters and they must arise from variations in the internal energy of the neutral/radical anion cluster system. In fact, the experimental results indicate that the energy gap between the HOMO and LUMO increases from $Fe_3(CO)_{12}$ to $Os_3(CO)_{12}$. Little attention has been given to the excited-state chemistry of these clusters but, simply on the basis of their color, it is anticipated that low-energy metal–metal transitions would be ordered energetically as Os > Ru > Fe.[38] This indeed is the case, and there is a good correlation with the $E_{1/2}$ values. A theoretical rationale of this trend is not simple as the symmetry and relative energies of metal-centered orbitals for these clusters is unknown. Nevertheless, the more efficient orbital overlap, decreased valence-shell repulsions, and intramolecular ligand interactions down the group would all contribute to a decrease in the energy of the HOMO. It is interesting that there is a much greater difference in $E_{1/2}$ values between $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ than between $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. Clearly, valence-shell repulsions and intramolecular carbonyl interactions are more important[39] in $Fe_3(CO)_{12}$ and this, combined with a lower effective nuclear charge, will additionally raise the energy of the HOMO. One consequence of the lower free energy of neutral $Fe_3(CO)_{12}$ is the increased lifetime of the reduced species relative to its congeners. In fact the lifetimes of $Ru_3(CO)_{12}^{-}\cdot$ and $Os_3(CO)_{12}^{-}\cdot$ are so short on the electrochemical time scale, even at low temperatures, as to preclude the observation of a second reduction step to the dianion. The reduction wave observed at potentials more negative than -1.7 V (vs. Ag/AgCl) must result from an electrode process involving a fragmentation product. Certainly, the differences in potential between the first and second waves for the ruthenium and osmium compounds are significantly greater than those of any triiron derivative.

The electrochemical work on $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ gives a lead to the systems which will be most profitable to investigate spectroscopically. With more extensive development of delocalized cluster bonding, as in hexanuclear clusters like $Os_6(CO)_{18}$, it should be possible to reach an energetic situation where one- or two-electron-reduced species can be generated electrochemically or chemically, with lifetimes suitable for spectroscopic investigation. On the other hand, phosphine-substituted ruthenium and osmium clusters should undergo facile one-electron oxidations. A comparison with the $YCCo_3(CO)_9$ clusters[2] shows that, although one-electron reduction is just as readily achieved for $Fe_3(CO)_{12}$ and its monosubstituted phosphine derivatives, the lifetime of the resulting radical anions is an order of magnitude shorter than that of $YCCo_3(CO)_9^{-}\cdot$ at ambient temperatures. Sodium reduction, which was a convenient means of generating the tricobalt carbon radical anions,[3] is therefore unlikely to give a clean reaction for the iron compounds. The assignments of ESR signals produced by sodium reduction[7] must be viewed with caution until comparable species have been generated by controlled electrochemical reduction, although there is no doubt that paramagnetic trinuclear iron compounds were detected. It is interesting to note that similar trinuclear and mononuclear radical anions can be formed by electron attachment to $Fe_3(CO)_{12-n}L_n$ or $Fe(CO)_{5-n}L_n$ utilizing the electrons obtained from the photodissociation of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine in organic glasses.[30]

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Registry No. $Fe_3(CO)_{12}$, 17685-52-8; $Fe_3(CO)_{11}PPh_3$, 12101-59-6; $Fe_3(CO)_{11}P(OMe)_3$, 63104-15-4; $Fe_3(CO)_{11}P(OPh)_3$, 55787-43-4; $Fe_3(CO)_{10}[P(OMe)_3]_2$, 63104-16-5; $Fe_3(CO)_{10}[P(OPh)_3]_2$, 63104-18-7; $Fe_3(CO)_9[P(OMe)_3]_3$, 63104-17-6; $Fe_3(CO)_9[P(OPh)_3]_3$, 63104-19-8; $[HFe_3(CO)_{11}]^-$, 25948-56-5; $Fe(CO)_5$, 13463-40-6; $Fe(CO)_4PPh_3$, 14649-69-5; $Fe(CO)_3(PPh_3)_2$, 14741-34-5; $Fe(CO)_4P(OMe)_3$, 14878-71-8; $Fe(CO)_3[P(OMe)_3]_2$, 14949-85-0;

$[HFe(CO)_4]^-$, 18716-80-8; $Ru_3(CO)_{12}$, 15243-33-1; $Os_3(CO)_{12}$, 15696-40-9.

References and Notes

(1) Part 3: A. S. Huffadine, B. M. Peake, B. H. Robinson, J. Simpson, and P. A. Dawson, *J. Organomet. Chem.*, **121**, 391 (1976).
(2) University of Melbourne.
(3) (a) A. M. Bond, B. M. Peake, B. H. Robinson, J. Simpson, and D. J. Watson, *Inorg. Chem.*, **16**, 410 (1977); (b) B. M. Peake, B. H. Robinson, J. Simpson, and D. J. Watson, *ibid.*, **16**, 405 (1977).
(4) P. Dawson, to be submitted for publication.
(5) B. Penfold and B. H. Robinson, *Acc. Chem. Res.*, **6**, 73 (1973).
(6) E. Abel and F. G. A. Stone, *Q. Rev., Chem. Soc.*, **23** 325 (1969).
(7) B. M. Peake, B. H. Robinson, J. Simpson, and D. J. Watson, *J. Chem. Soc., Chem. Commun.*, 945 (1974).
(8) The correlation between ESR signals and paramagnetic species in ether solutions is more complex than reported earlier[7] and the temperature variation in ESR signal is unlikely to be due to isomerism as suggested.
(9) R. E. Dessy, R. B. King, and M. Waldrop, *J. Am. Chem. Soc.*, **88** 471, 5112 (1966).
(10) R. E. Dessy and L. E. Bares, *Acc. Chem. Res.*, **5**, 415 (1972).
(11) J. A. Fergusson and T. J. Meyer, *J. Am. Chem. Soc.*, **94**, 3409 (1972).
(12) M. A. Neuman, Trinh-Toan, and L. F. Dahl, *J. Am. Chem. Soc.*, **94**, 3383 (1972).
(13) C. J. Pickett and D. Pletcher, *J. Chem. Soc., Dalton Trans.*, 879 (1975).
(14) C. J. Pickett and D. Pletcher, *J. Organomet. Chem.*, **102**, 327 (1975).
(15) R. J. Angelici and E. E. Siefert, *Inorg. Chem.*, **5**, 1457 (1966).
(16) A. F. Clifford and A. K. Mirkherjee, *Inorg. Synth.*, **8**, 185 (1966).
(17) P. J. Pollick and A. Wojcicki, *J. Organomet. Chem.*, **14**, 469 (1968).
(18) J. D. Colton and R. L. Heaglewood, *Aust. J. Chem.*, **22**, 2673 (1969).
(19) W. McFarlane and G. Wilkinson, *Inorg. Synth.*, **8** 181 (1966).
(20) J. R. Case and M. C. Whiting, *J. Chem. Soc.*, 4632 (1960).
(21) A. M. Bond, *J. Electroanal. Chem.*, **50**, 285 (1974).
(22) H. Blutstein and A. M. Bond, *Anal. Chem.*, **46**, 1934 (1974).
(23) A. M. Bond, R. J. O'Halloran, I. Ruzic, and D. E. Smith, *Anal. Chem.*, **48**, 872 (1976).
(24) J. A. Connor, E. M. Jones, G. K. McEwen, M. L. Lloyd, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1246 (1972).
(25) P. M. Triechel, G. E. Duncan, and H. J. Hauh, *J. Organomet. Chem.*, **44**, 339 (1972).
(26) C. J. Pickett and D. Pletcher, *J. Chem. Soc., Dalton Trans.*, 637 (1976).
(27) C. E. Strouse and L. F. Dahl, *J. Am. Chem. Soc.*, **93**, 6032 (1971), and references therein.
(28) Trinh-Troan, W. P. Fehlhammer, and L. F. Dahl, *J. Am. Chem. Soc.*, **94**, 3389 (1972).
(29) D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 133 (1974).
(30) Unpublished work, University of Otago.
(31) T. J. Meyer, *Prog. Inorg. Chem.*, **19**, 1 (1975).
(32) T. W. Matheson, B. H. Robinson, B. F. G. Johnson, and J. Lewis, to be submitted for publication.
(33) K. Wade, *Chem. Br.*, **11**, 177 (1975).
(34) D. M. P. Mingos, *Nature (London), Phys. Sci.*, **236**, 99 (1972).
(35) Although $Fe_3(CO)_{12}$ has an asymmetrically CO-bridged structure in the crystal[36] recent work[32,37] has shown that, in solution, it exists largely as molecule with essentially the same geometry as $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$.
(36) F. A. Cotton and D. L. Hunter, *Inorg. Chem.*, **13**, 2044 (1974).
(37) F. A. Cotton and D. L. Hunter, *Inorg. Chim. Acta*, **11**, L9 (1974).
(38) M. Wrighton, *Chem. Rev.*, **74**, 401 (1974).
(39) Models and calculations show that the nonbridged configuration of $Fe_3(CO)_{12}$ suffers from extensive CO–CO interactions because the CO groups are eclipsed; moreover the short unbridged Fe–Fe bond would lead to valence-shell repulsions. Both of these factors would provide a driving force for the molecule to adopt a partially bridged configuration.
(40) A reviewer has pointed out that electrode reactions at platinum are known[41] to be inhibited by chemisorption of carbon monoxide on the electrode surface. While this is a feasible explanation of the failure to observe reduction at platinum electrodes, the ease with which mercury derivatives of metal carbonyl anions are formed[42] makes our alternative explanation attractive.
(41) B. J. Piersma in "Electrosorption", E. Gileadi, Ed., Plenum Press, New York, N.Y., 1967, p 19.
(42) R. B. King, *Adv. Organomet. Chem.*, **2** 157 (1964).
(43) N. G. Connelly and K. R. Somers, *J. Organomet. Chem.*, **113**, C39 (1976).

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A Spectrochemical and Electrochemical Study of Complexes of Cobalt with Macrocyclic Ligands Having Various Degrees of Unsaturation

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Spectrochemical and electrochemical studies have been carried out on a series of macrocyclic complexes of cobalt, which vary in the nature and degree of ligand unsaturation. The complexes are of the type $[Co(MAC)(CH_3CN)_2]^{3+}$ where MAC represents a series of 14-membered macrocycles varying in their degree and position of ligand unsaturation and substitution. Spectral analysis of the cobalt(III) complexes provides an evaluation of the variation of the ligand field strength as a function of position and degree of ligand unsaturation for macrocycles of the same ring size and donor atoms. The half-wave potentials for the Co^{II}/Co^{I} couple vary in a predictable manner related to ligand unsaturation, while the Co^{III}/Co^{II} couple is insensitive to these structural variations.

Introduction

Macrocyclic complexes of cobalt(III) have been the subject of several studies concerning various aspects of stereochemistry, electrochemistry, and electronic structure.[1-4] Stereochemical considerations have led to a better understanding of such factors as ring size effects, steric interactions, the inflexibility of unsaturated structures toward folding, and the energetics and consequences of possible chelate ring conformations. In the case of cobalt, electronic relationships have received scant attention, so that the effect of varying the position and extent of ligand unsaturation in the macrocyclic ring on such parameters as ligand field strength and the oxidation state stability of the cobalt complexes is poorly documented. Electrochemical studies on macrocyclic complexes of nickel(II)[5-7] and iron(II)[8] have shed considerable light on the chemistry of such systems, including the stabilization of unusual metal oxidation states, the ease of oxidation or reduction of the central metal ion with respect to macrocyclic ring size and the degree and position of ligand unsaturation, and the reactivity of the ligand as a function of the site of electron donating or withdrawing substituents.

The availability of a substantial series of complexes of cobalt(III) with macrocyclic ligands (Figure 1) allows an extension of our studies to this metal system. The complexes present a unique opportunity to study and correlate the significant changes in spectroscopic and redox properties which occur as a result of changing ligand structural parameters. The complexes reported here all involve coordination of 14-membered tetradentate macrocyclic ligands in a square-planar fashion, with coordinating CH_3CN groups present in the axial sites. The use of acetonitrile in the coordination sphere, and as solvent in our investigations, overcomes the problems associated with solvolysis reactions when other coordinated species, such as Cl^- or Br^-, are used.

Results and Discussion

Synthesis of the New Complexes. The series of 14-membered macrocyclic cobalt(III) complexes containing coordi-