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Redox behaviour of anionic heterotetranuclear clusters $[MCo_3(CO)_{12-2n}(C_2Ph_2)_n]^-$ (M = Fe, Ru; $n = 0, 1$)

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Abstract

The anionic clusters $[MCo_3(CO)_{12-2n}(C_2Ph_2)_n]^-$ (M = Fe, Ru; $n = 0$, 1) undergo two consecutive one-electron reductions, and a single four electrons oxidation. In the absence of bridging ligand C_2Ph_2 ($n = 0$) the reductive electron transfer can involve either two distinct one electron steps or a single two electrons reaction. The two-step process was observed in the presence of poor electron acceptors and good electron donors (DMF as solvent or other solvents containing PPh_3), whereas the one-step process was favoured in solvents such as 1,2-$C_2H_4Cl_2$, CH_3CN, and propylene carbonate, which are better electron acceptors and poorer donors than DMF. Thus, the reduction of this cluster is "tunable" either as a two 1e steps process or as a unique 2e step process by appropriate choice of solvent.

Electrochemical studies of clusters involving a tetrahedral homonuclear metallic Co_4 core revealed [1,2,3] the operation of two one-electron reductions when the tetrametallic frame carried bis- and tri-dentate bridging ligands, for sample dppm (bis(diphenylphosphinomethane)) in $[Co_4(CO)_8(dppm)_2]$ and tripod (tris(diphenylphosphinomethane)) in $[Co_4(CO)_9\text{tripod}]$. Furthermore the species generated upon electrochemical reduction of these clusters were stable on the voltammetric time scale, in contrast with the reduced species $[Co_4(CO)_{12}]^-$ [2], which underwent fast decomposition. Thus, a direct link was established between the improved stabilities of reduced clusters (reversible redox couples $0/-1$ and $-1/-2$) and the metal–metal bridging by multidentate ligands. It was also observed that the reduction potentials were linearly related to the number of phosphorous atoms coordinated to the clusters.

Similar conclusions were reached from the analysis of oxidation processes: the observed one-electron oxidation steps were only reversible for Co_4 clusters bearing the bridging ligands dppm or tripod [1,2], thus leading to stabilization of oxidized $(+1)$ species.

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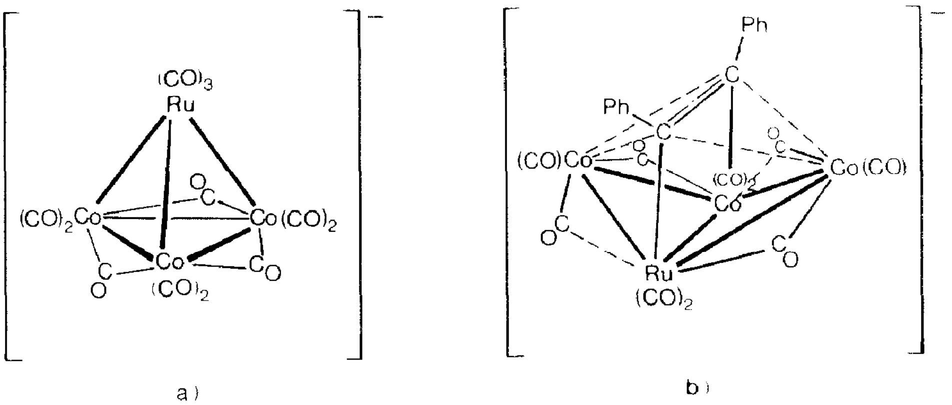

a) b)

Fig. 1. Structures [4,5,6] of the studied clusters $[MCo_3(CO)_{12}]^-$ (a) and $[MCo_3(CO)_{10}C_2Ph_2]^-$ (b) (M = Fe, Ru).

It was thus of interest to examine the behaviour of heteronuclear tetrametallic clusters under similar conditions, and so clusters $[MCo_3(CO)_{12-2n}(C_2Ph_2)_n]^-$ (M = Fe, Ru, $n = 0$ or 1) (Fig. 1) were studied. Electrochemical results [1] for clusters in which the tetrametallic core involved two rhodium and two cobalt atoms, have shown that the redox potentials undergo only minor changes on changing from the Co_4 to a Co_2Rh_2 core. The radical anion $[Co_2Rh_2(CO)_{12}]^{\cdot-}$ was, however, observed to be less stable than $[Co_4(CO)_{12}]^{\cdot-}$. When the central tetrametallic core consists of three cobalt and one Fe or one Ru, the resulting cluster is an ionic species $[MCo_3(CO)_{12}]^-$ (M = Fe, Ru) (Fig. 1a) [4,5]. Thermal, photochemical and catalytic properties of these anionic clusters had been studied [4], but electrochemical characteristics remained to be determined. When C_2Ph_2 was coordinated, thus replacing two CO in the cluster, the cluster changed from tetrahedral (Fig. 1a) to "butterfly" [6] (Fig. 1b) conformation.

Experimental

The clusters were synthesized by published procedures [7]. All experiments were carried out under argon with carefully deaerated solutions at 20 °C. The redox characteristics of the clusters $[MCo_3(CO)_{12}]^-$ and $[MCo_3(CO)_{10}(C_2Ph_2)]^-$ were determined on gold electrodes (disk of area 3.14 mm^2), in *N,N*-dimethylformamide (DMF) containing 0.1 *M* tetraethylammonium perchlorate (TEAP) as supporting electrolyte. Under these conditions, the ferrocene–ferricinium couple was characterized by $E_{1/2}$ +0.49 V/SCE (SCE = KCl saturated calomel electrode plus liquid junction potential between DMF + 0.1 *M* TEAP and KCl saturated water in the glass-frit junction). For stationary voltammetry, the disk electrode was rotated at 2000 rds/min. Experimental procedures were as previously described [8].

Results

The electrochemical data obtained are listed in Table 1.

Electrochemical reduction of clusters $[MCo_3(CO)_{12}]^-$

In DMF + 0.1 *M* TEAP, each of the two studied clusters $[MCo_3(CO)_{12}]^-$ NEt_4^+ (M = Fe, Ru) exhibited three distinct one-electron reductions whose respective half

Table 1

Reduction characteristics of clusters $[MCo_3(CO)_{12}]^-$ and $[MCo_3(CO)_{10}C_2Ph_2]^-$ (M = Fe, Ru) in DMF + 0.1 *M* TEAP. Cluster conc. $= 10^{-4}$ *M*; Electrode: Au. Coulometry: $n_1 = 1$; $n_2 = 1$

Cluster	$E_{1/2}$ (V/SCE)	$\log \frac{I}{I_d - I}$ (mV/log)	$n\,\Delta E_p$ [a] (mV)	$\frac{I_{pa}}{I_{pc}}$	$k_s \times 10^3$ [b] (cm s^{-1})
First reduction					
$[FeCo_3(CO)_{12}]^-$	−0.99	64	80	0.8	7
$[RuCo_3(CO)_{12}]^-$	−1.12	64	95	0.9	5
$[FeCo_3(CO)_{10}C_2Ph_2]^-$	−1.06	65	65	0.9	–
$[RuCo_3(CO)_{10}C_2Ph_2]^-$	−1.14	60	70	0.9	17
Second reduction					
$[FeCo_3(CO)_{12}]^-$	−1.24	70	110		4
$[RuCo_3(CO)_{12}]^-$	−1.32	61	irrev.		
$[FeCo_3(CO)_{10}C_2Ph_2]^-$	−1.66	74	irrev.		
$[RuCo_3(CO)_{10}C_2Ph_2]^-$	−1.68	60	irrev.		

[a] At scan rate v 0.1 V s^{-1}; $\Delta E_p = E_{pa} - E_{pc}$. [b] k_s calculated according to R.S. Nicholson, Anal. Chem., 37(11) (1965) 1351.

wave potentials were (in V/SCE). (M = Fe): −0.99, −1.24, −1.81; and (M = Ru): −1.12, −1.32; −2.03. For both clusters the third reduction was irreversible, and too close to the cathodic electroactivity limit of the medium to be analyzed in detail. The two first reduction steps were reversible for M = Fe, whereas only the first step was reversible for M = Ru. The limiting current was diffusion controlled, as indicated by the linear relationship between $1/I_{lim}$ and $1/\omega^{1/2}$ (crossing the origin of the axes) in stationary voltammetry on rotating disk electrode, and by the linear relationship between I_{lim} and the concentration of the cluster in the solution.

Cyclic voltammograms for the $FeCo_3$-containing cluster exhibited (Fig. 2) two pairs of peaks for the reduction, plus two small additional peaks corresponding to re-oxidations on the reverse scan at −0.45 and +0.25 V/SCE ($v = 0.1$ V s^{-1}) respectively. For the two first pairs of peaks, the peak currents were proportional to $v^{1/2}$ and the potential difference between conjugated peaks (ΔE_p) increased with the scan rate v. In both steps, the standard electron transfer rate constants corresponded (Table 1) to a quasi-reversible process.

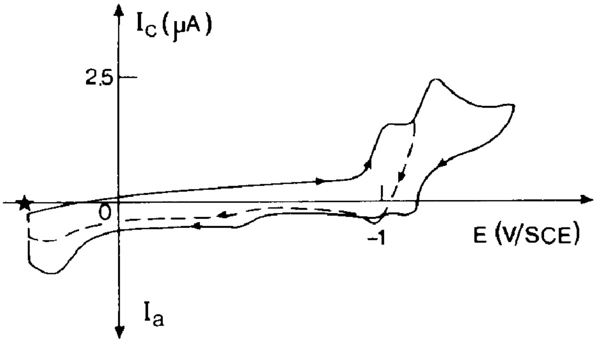

Fig. 2. Cyclic voltammetry of $[FeCo_3(CO)_{12}]^-$ NEt_4^+ (c 10^{-4} *M*) DMF + 0.1 *M* TEAP; v 0.1 V s^{-1}. ★ start of the scan.

Cyclic voltammograms for the $RuCo_3$ based cluster exhibited two reduction peaks, of which the second was ill-defined. On the reverse scan, one reoxidation peak corresponded to the first reduction step, and two additional small peaks were observed at ca. 0 and +0.25 V/SCE. For the first reduction step, analysis of the dependence on v of the reduction peak potential and of the potential difference between conjugated cathodic and anodic peaks led to a standard rate constant corresponding to a quasireversible electron transfer.

The reduced forms of both clusters were stable only on the voltammetric time-scale.

When the clusters were submitted to an exhaustive coulometric electrolysis corresponding to the first reduction ($n = 1e^-$), the stationary voltammograms of the resulting solution, as expected, exhibited a wave corresponding to the second reduction, but with a limiting current smaller than expected, whereas an oxidation wave appeared at ca. +0.2 V/SCE, as already observed for cyclic voltammograms. This oxidation wave, corresponding to the oxidation of $[Co(CO)_4]^-$ into $[Co(CO)_4]^{\cdot}$, was assigned by comparison with the electrochemical oxidation of the anion $[Co(CO)_4]^-$ introduced into the solution [9], and also by comparison of the IR spectra (ν(CO) 1866 cm^{-1} in DMF) of the electrolyzed and authentic solutions containing $[Co(CO)_4]^-$.

ESR spectra were recorded for the solution containing the species generated by exhaustive electrolysis corresponding to the first reduction step. A sample of the solution was removed under argon and immediately frozen in liquid nitrogen. Hyperfine structure was observed for both reduced clusters ($g = 2.036$ when M = Fe and $g = 2.085$ when M = Ru), and the spectra showed no significant change when Fe was replaced by Ru (Fig. 3a and 3b). The natural isotopic abundance of spins other than zero is small for Fe (2% with spin 1/2) and also for Ru (13% with spin 3/2 and 17% with spin 5/2). Thus the hyperfine structure of the spectra probably results from an interaction of the electron with the three cobalt atoms, each of which has a spin of 7/2, thus generating the observed spectra with 22 bands.

When the solution of each cluster was examined after exhaustive coulometric reduction corresponding to the second reduction step ($n = 1e^-$), the solution showed no ESR signal, and the observed electrochemical signal corresponded to the oxidation of $[Co(CO)_4]^-$, thus providing convincing evidence for cluster fragmentation.

Solvent effects on the reduction of $[MCo_3(CO)_{12}]^-$ *(Table 2)*

In poor electron accepting solvent such as DMF, two distinct one electron reduction steps were observed, separated by 200–250 mV. In contrast, a single two-electron irreversible reduction was observed in better acceptors (acetonitrile, propylene carbonate, 1,2-dichloroethane). In the latter solvents, analysis ($\log I = f(t)$) of the current response in potentiostatic coulometry indicated that there was coupling of a chemical step to the electron transfer.

When the single step, two-electron, reduction was examined in the presence of phosphine ($[PPh_3]$: 3.5×10^{-3} *M*) in 1,2-$C_2H_4Cl_2$, cyclic voltammetry revealed that when the electrode potential was held constant for 1 minute on the reductive scan at the potential value of the reduction peak, a new reduction step became observable at ca. −1.4 V/SCE, i.e. about 200 mV more negative than the reduction of the initial cluster. After this addition of PPh_3, the total of both limiting currents

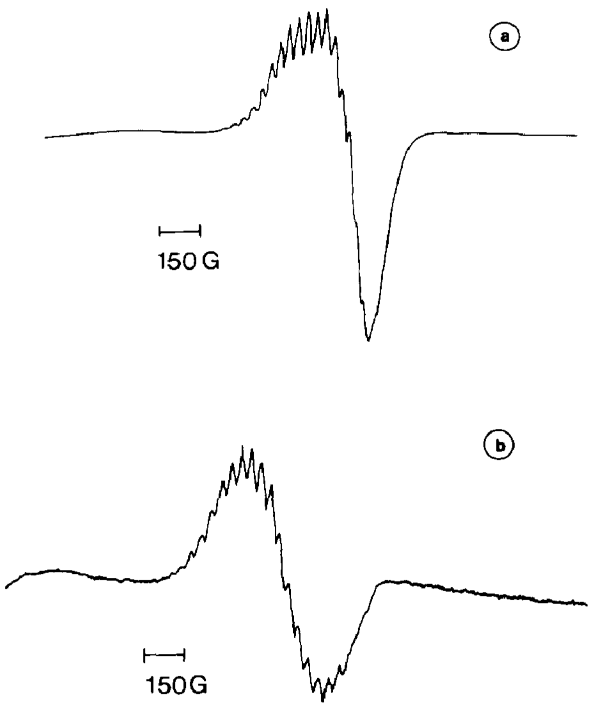

Fig. 3. ESR spectra of the clusters $[MCo_3(CO)_{12}]^-$ $[NEt_4]^+$ (a, M = Fe; b, M = Ru, c 10^{-3} M), after exhaustive coulometry corresponding to the first reduction. DMF + 0.1 M TEAP; T 100 K.

corresponding to the two reduction waves was equal to the limiting current initially observed for the single two-electron reduction wave in the absence of PPh_3. This result was consistent with the expectation that PPh_3 might react with the reduced cluster [1], and the observed shift in the reduction potential was consistent with the expected shift corresponding to one PPh_3 coordinated [2]. This hypothesis was confirmed by comparison with the electrochemical behaviour of the authentic cluster $[FeCo_3(CO)_{11}(PPh_3)]^-$, which was reduced at -1.4 V/SCE after generation by known procedures [10].

These results obtained in better accepting solvents than DMF and in the presence of PPh_3 were similar to those obtained in DMF in the absence of PPh_3, i.e. there were distinct reductive steps separated by about 200 mV. Thus, taking into account

Table 2

Solvent effects on the results of stationary voltammetry on $[FeCo_3(CO)_{12}]^-$ $[NEt_4]^+$

Solvent	AN [11]	$E_{1/2}^{red}$ (V/SCE)	$E/\log \frac{I}{I_d - I}$ (mV/log)	n (F/mole)
$C_2H_4Cl_2$	23.1	-1.22	91	2
CH_3CN	19.3	-1.14	77/125	2
Propylene carbonate	18.3	-1.08	114/133	2
DMF	16	$-0.99/-1.24$	64/70	1/1

the well known donor ability of DMF (donor number ~ 26), we are tempted to suggest that DMF, like PPh_3, replaces one CO ligand in the reduced form of the cluster through an electro-initiated nucleophilic substitution.

Electrochemical reduction of the clusters $[MCo_3(CO)_{10}C_2Ph_2]^-$

The experiments were carried out in *N,N*-dimethylformamide (DMF) containing 0.1 *M* tetraethylammonium perchlorate. In the other solvents (CH_3CN, propylene carbonate, $C_2H_4Cl_2$) no significantly different behaviour was observed.

Both clusters (M = Fe, Ru) exhibited two one-electron reductions, of which only the first was reversible. The polarographic half-wave potentials (Table 1) corresponding to the first reduction were close to those for $[MCo_3(CO)_{12}]^-$. In contrast, the potentials for the second reduction step were several hundreds of millivolts more negative than those corresponding to $[MCo_3(CO)_{12}]^-$. This potential shift, of about 400 mV, was consistent with two phosphines coordinated to the tetrametallic core [2], and clearly indicated that the cluster anion radical was stabilized towards further reduction by the bridging ligand C_2Ph_2.

Furthermore, for both clusters the limiting currents corresponding to the two reduction steps were diffusion controlled, as shown by the linear relationship of $1/I_{lim}$ with $1/\omega^{1/2}$ and of I_{lim} with the cluster concentration in stationary voltammetry on rotating disk electrode.

Cyclic voltammetry provided additional interesting information. For both clusters the voltammetric curves indicated that the first reduction was reversible (one pair of peaks, respectively reductive and oxidative, was observed), whereas the second reduction was irreversible (Fig. 4).

Further analysis of the characteristics of the first reduction step revealed that the reduction peak current (I_{pc1}) increased more than proportionally with $v^{1/2}$ (v = scan rate). Also, the ratio of the conjugated peaks currents I_{pa1}/I_{pc1}, equal to one at low scan rate, decreased with $v^{1/2}$. Both observations were consistent with a weak adsorption of the cluster on the electrode. This hypothesis was confirmed by analyzing the temperature effect on the ratio I_{pa1}/I_{pc1}; at 40 °C this ratio remained at unity over the whole range of scan rates used ($0.02\ V\ s^{-1} < v < 1\ V\ s^{-1}$). Furthermore, for the cluster $[FeCo_3(CO)_{10}C_2Ph_2]^-$, the reduction peak potential E_{pc1} was independent of v, while $\Delta E_{p1} = E_{pc1} - E_{pa1}$ also remained constant, equal to 70 mV. In contrast, the cluster $[RuCO_3(CO)_{10}C_2Ph_2]^-$ exhibited a first reduction peak potential E_{pc1} which became more negative when v was increased, while ΔE_{p1} simultaneously increased.

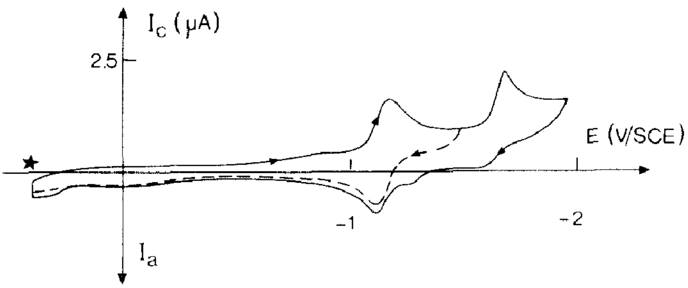

Fig. 4. Cyclic voltammetry of $[RuCo_3(CO)_{10}C_2Ph_2]^-$ $[NEt_4]^+$ (c 10^{-4} *M*) DMF + 0.1 *M* TEAP; v 0.1 V s^{-1}. ★ start of the scan.

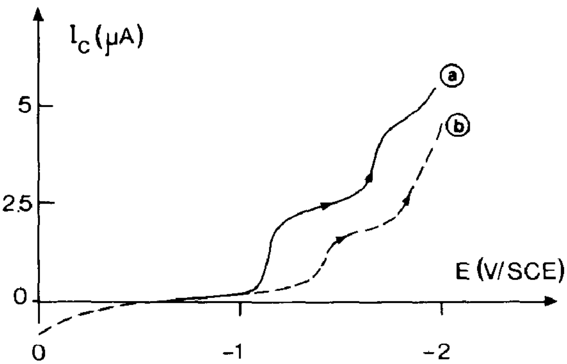

Fig. 5. Stationary voltammetry of $[RuCo_3(CO)_{10}C_2Ph_2]^-$ $[NEt_4]^+$ (c 10^{-4} M), DMF+0.1 M TEAP+3.5×10^{-3} M PPh_3; (a) reduction waves of the clusters, (b) reduction observed after exhaustive coulometry of the cluster at E -1.3 V/SCE.

Thus, the first reduction is a fast reversible process in the case of $[FeCo_3(CO)_{10}C_2Ph_2]^-$ but is slower and quasi-reversible for $[RuCo_3(CO)_{10}C_2Ph_2]^-$, for which the standard electron transfer rate constant was calculated as 1.7×10^{-2} cm s^{-1}.

In each of the two clusters, the second reduction was a slow irreversible reaction, as indicated by the fact that the reduction potential, E_{pc2} became more negative as v was increased ($E_{pc2}=f(\log v)$ linear). Further analysis of cyclic voltammograms revealed that a chemical reaction was associated to this reductive electron transfer. On the other hand, when CO was dissolved in the solution, this second reduction step became reversible on the cyclic voltammetry time scale, thus identifying the chemical step as the reversible coordination-decoordination of CO or of a CO-containing moiety. On the reverse scan in the cyclic voltammogram, two oxidative small peaks were detected, at -1.25 and $+0.30$ V/SCE.

When exhaustive coulometry was performed on each cluster at a potential corresponding to the first reduction, neither of the clusters exhibited electroactive species over the potential range $+1.5$ to -2.0 V/SCE. In contrast, when the electrolyses were performed in the presence of PPh_3 (3.5×10^{-3} M), each of the two electrolyzed clusters exhibited a new reduction signal at about 200 mV more cathodic than the potential for the first reduction (Fig. 5). This result illustrated the stabilizing effect of the PPh_3 coordination on the cluster dianion radical. These results are consistent with the known [1,2] substitution of CO by phosphine groups in tetranuclear clusters, paralleled by a shift of the reduction potential of about -200 mV per coordinated phosphine group.

Attempts to identify by NMR spectroscopy the site of replacement of CO by PPh_3 failed. However, previous work [10] has predicted that the chemical substitution of one CO by PPh_3 in the clusters $[MCo_3(CO)_{12}]^-$ should occur preferably at cobalt, and the topology of the clusters $[MCo_3(CO)_{10}C_2Ph_2]^-$ also favours this.

The possibility of obtaining $[MCo_3(CO)_{10}C_2Ph_2]^-$ by electrochemical reduction of $[MCo_3(CO)_{12}]^-$ in the presence of C_2Ph_2 was also successfully explored [14*] under the following conditions. In 1,2-$C_2H_4Cl_2$ as solvent (containing 0.1 M

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* Reference number with asterisk indicates a note in the list of references

Table 3

Oxidation polarographic half wave potentials of clusters $[MCo_3(CO)_{12}]^-$ and $[MCo_3(CO)_{10}C_2Ph_2]^-$ (M = Fe, Ru) in DMF + 0.1 *M* TEAP (Cluster conc. 10^{-4} *M*)

Cluster	$E_{1/2}^{ox}$ (V/SCE)	$E_{1/2}^{Ox} - E_{1/2}^{Red1}$ (V)
$[FeCo_3(CO)_{12}]^-$	+0.75	1.74
$[RuCo_3(CO)_{12}]^-$	+0.72	1.84
$[FeCo_3(CO)_{10}C_2Ph_2]^-$	+0.50	1.56
$[RuCo_3(CO)_{10}C_2Ph_2]^-$	+0.55	1.62

Bu_4NClO_4), on a Pt electrode, $[MCo_3(CO)_{12}]^-$ (concentration 3.8×10^{-4} *M*) was coulometrically reduced (at −1.3 V/SCE for M = Fe, and at −1.4 V/SCE for M = Ru) in the presence of an excess of C_2Ph_2 (concentration 3.3×10^{-3} *M*). After electrolysis the voltammetric signal became more reversible, since the reduction of $[MCo_3(CO)_{12}]^-$ was irreversible, whereas that of the authentic $[MCo_3(CO)_{10}C_2Ph_2]$ was reversible, this result was consistent with possible generation of $[MCo_3(CO)_{10}C_2Ph_2]^-$ in the solution. Secondly, comparisons of the absorption visible spectra of $[RuCo_3(CO)_{12}]^-$, $[RuCo_3(CO)_{10}C_2Ph_2]^-$, and of the electrolyzed ($[RuCo_3(CO)_{12}]^- + C_2Ph_2$) solution revealed that the electrolyzed solution exhibited a small peak at 520 nm which is unambiguously characteristic of $[RuCo_3(CO)_{10}C_2Ph_2]^-$ [7]. Of course, the net substitution yield is very low, owing to competition by fragmentation of the reduced cluster.

Electrochemical oxidation of the clusters $[MCo_3(CO)_{12}]^-$ and $[MCo_3(CO)_{10}C_2Ph_2]^-$ (M = Fe, Ru)

In DMF + 0.1 *M* TEAP, a single oxidation step was observed for each of the four clusters. Comparison of the oxidation polarographic limiting current with that of the first reduction step indicated that four electrons were transferred in the oxidation step. That was further confirmed by exhaustive potentiostatic coulometry.

The oxidation potentials (Table 3) showed that when the bridging ligand C_2Ph_2 replaced two CO ligands, and the oxidation was facilitated by 170–250 mV. No further information could be obtained for the oxidized clusters because the latter underwent fragmentation upon oxidation; the fully oxidized solution did not show any ESR signal. This behaviour was reminiscent of that observed previously for $[Co_4(CO)_{12}]$ [2].

Discussion

The electrochemical results obtained for the clusters $[MCo_3(CO)_{12}]^-$ and $[MCo_3(CO)_{10}C_2Ph_2]^-$ reveal the effects of M (Fe or Ru) and of the bridging ligand C_2Ph_2 on the redox characteristics.

The clusters $[MCo_3(CO)_{12}]^-$ with M = Fe or Ru, are reduced via three well defined reduction steps, of which the two first involve one-electron, semi-reversible, transfers. In keeping with the higher basicity of Ru than of Fe, the $RuCo_3$-based complex was more difficult to reduce than its $FeCo_3$ analogue. Solvents effects were large: whereas in DMF a good electron donor and poor electron acceptor, the two first electron transfers operated via two distinct reduction steps separated by about

200 mV, in a good acceptor solvent such as 1,2-$C_2H_4Cl_2$ these two steps merged into a single two-electron transfer. This contrast in behaviour may be ascribed to the high reactivity of the species $[MCo_3(CO)_{12}]^{2-}$ generated by the first reduction, which triggered the replacement of CO by the solvent S when the solvent S had the appropriate characteristics. The splitting of the two first one-electron transfers from a single two electron signal into two distinct one electron transfers can thus be rationalized in the following terms:

(i) After the first electron transfer and when S is a sufficiently strong electron donor, one CO is replaced by one molecule of solvent S to generate $[MCo_3(CO)_{11}S]^{2-}$.
(ii) This dianion radical is then oxidized by the starting cluster anion to generate $[MCo_3(CO)_{11}S]^-$.
(iii) This substituted species is more difficult to reduce than the unsubstituted one, and thereby the second electron transfer occurs at a more negative potential than the first electron transfer, on the macroscopic scale.

The ESR spectra of the dianion radical resulting from the first one-electron transfer exhibits a hyperfine structure arising from the anisotropic interaction of the Fe or Ru with the three Co atoms of the cluster frame. Thus the frontier orbital involved in the first reduction of the cluster appears to be metal-centered, and the tendences of the reduced forms to undergo fragmentation is indicative of antibonding character for this orbital.

On this basis, the following overall reaction scheme may be proposed for the reduction of the tetrahedral clusters $[MCo_3(CO)_{12}]^-$ (M = Fe, Ru).

(1) In a poor electron accepting and good electron donating solvent (S = DMF)

$$\text{(E)}\quad [MCO_3(CO)_{12}]^- + e \rightleftharpoons [MCo_3(CO)_{12}]^{2-}$$

$$\begin{tikzcd}
 & \text{fragments } [Co(CO)_4]^- \\
\text{(C)}\quad [MCo_3(CO)_{12}]^{2-} \arrow[ur, "\text{chem}"] \arrow[dr, "\text{chem}", "+S"'] & \\
 & {[MCo_3(CO)_{11}S]^{2-} + CO}
\end{tikzcd}$$

$$[MCo_3(CO)_{11}S]^{2-} + [MCo_3(CO)_{12}]^- \longrightarrow [MCo_3(CO)_{12}]^{2-} + [MCo_3(CO)_{11}S]^-$$

$$\text{(E)}\quad [MCo_3(CO)_{11}S]^- + e \underset{(1)}{\rightleftharpoons} [MCo_3(CO)_{11}S]^{2-}$$

(1) only when M = Fe.

(2) In a poor electron donating solvent which is a better acceptor than DMF (S = 1,2-$C_2H_4Cl_2$)

$$[MCo_3(CO)_{12}]^- + 2e \longrightarrow [MCo_3(CO)_{12}]^{3-} \xrightarrow{\text{chem}} \text{fragments}$$

The findings make possible the "tuning" of the electrochemical reduction of $[MCo_3(CO)_{12}]^-$ clusters to direct it either via two distinct one-electron steps or via a single two-electron step by appropriate choice of the solvent.

The clusters $[MCo_3(CO)_{10}C_2Ph_2]^-$, obtained from clusters $[MCo_3(CO)_{12}]^-$ by introducing one ligand C_2Ph_2 in place of two CO ligands undergo two distinct one-electron reductions, and this behaviour is unaffected by the solvent in which the electrochemical reductions are carried out (DMF, 1,2-$C_2H_4Cl_2$, propylene carbonate, CH_3CN). The bridging ligand C_2Ph_2 induces several changes in the redox behaviour of the clusters $[MCo_3(CO)_{10}C_2Ph_2]^-$ compared with that of $[MCo_3(CO)_{12}]^-$: the characteristics of the second, one-electron, reduction step clearly reveal that C_2Ph_2 stabilizes the dianion radical generated by the first reduction. This is also confirmed by the finding that no $[Co(CO)_4]^-$ fragment can be detected in the solution obtained after the first reduction of the cluster. Thus, the dianion radicals $[MCo_3(CO)_{10}C_2Ph_2]^{2\cdot -}$ are more stable than the analogous $[MCo_3(CO)_{12}]^{2\cdot -}$.On the basis of these findings, the following overall reduction scheme may be suggested for the $[MCo_3(CO)_{10}C_2Ph_2]^-$ clusters.

(1) In the absence of PPh_3

1st reduction step

$$[MCo_3(CO)_{10}C_2Ph_2]^- + e \rightleftharpoons [MCo_3(CO)_{10}C_2Ph_2]^{2\cdot -}$$

2nd reduction step

$$[MCo_3(CO)_{10}C_2Ph_2]^{2\cdot -} + e \rightleftharpoons [MCo_3(CO)_{10}C_2Ph_2]^{3-} \xrightarrow{\text{chem (1)}} \text{fragments}$$

(1) slow step with CO

(2) In the presence of PPh_3

1st reduction step

$$[MCo_3(CO)_{10}C_2Ph_2]^- + e \rightleftharpoons [MCo_3(CO)_{10}C_2Ph_2]^{2\cdot -}$$

$$[MCo_3(CO)_{10}C_2Ph_2]^{2\cdot -} + PPh_3 \xrightarrow{\text{chim}} [MCo_3(CO)_9C_2Ph_2(PPh_3)]^{2\cdot -} + CO$$

$$[MCo_3(CO)_9C_2Ph_2(PPh_3)]^{2\cdot -} + [MCo_3(CO)_{10}C_2Ph_2]^- \longrightarrow$$
$$[MCo_3(CO)_9C_2Ph_2(PPh_3)]^- + [MCo_3(CO)_{10}C_2Ph_2]^{2\cdot -}$$

2nd reduction step

$$[MCo_3(CO)_9C_2Ph_2(PPh_3)]^- + e \rightleftharpoons [MCo_3(CO)_9C_2Ph_2(PPh_3)]^{2\cdot -}$$

3rd reduction step

$$[MCo_3(CO)_9C_2Ph_2(PPh_3)]^{2\cdot -} + e \longrightarrow [MCo_3(CO)_9C_2Ph_2(PPh_3)]^{3-}$$

The observed behaviour of the clusters $[MCo_3(CO)_{12}]^-$ and $[MCo_3(CO)_{10}C_2Ph_2]^-$ provide additional confirmation of the direct relationship between the chemical composition and structure of tetrametallic clusters and their redox characteristics.

The parent tetrahedral clusters with a Co_4 tetrametallic frame were identified [1,2] years ago as delocalized electron sources and sinks in their oxidation or reduction, respectively. However, it became clear also that the corresponding redox potentials did not parallel the changes in the energy of HOMO and LUMO frontiers orbitals upon change in the ligands coordinated to the metallic core [3]. For a Co_4 core, these potentials were shown [3] to be shifted along with the cluster core charge as determined by the ligand environment. These findings were consistent with the previous analyses of the electronic structures of the clusters [12,13].

The clusters $[MCo_3(CO)_{12}]^-$, which may be regarded as derived from $[Co_4(CO)_{12}]$ by replacement of one Co by M (Fe or Ru) are more difficult to reduce than $[Co_4(CO)_{12}]$, as expected from their anionic character as well as from the characteristics of the metal M.

As well as showing that the coordination of a bridging ligand C_2Ph_2 to the MCo_3-based cluster stabilizes the reduced species, in line with the reduction potential increment of about -200 mV for introduction of each coordinated phosphine moiety, the behaviour of the clusters $[MCo_3(CO)_{12}]^-$ ($M = Fe$, Ru) shows that two consecutive one-electron transfers in clusters can be induced to take place in either simultaneous or distinct steps on the macroscopic time-scale simply by changing the solvent.

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