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ELECTROCHEMISTRY OF PLATINUM(II) COORDINATION COMPOUNDS

II *. ELECTROREDUCTION OF TRIMETALLIC DIMETALLIOBIS(ISOCYANIDE)PLATINUM(II) COMPLEXES

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Summary

Linear trimetallic M—$Pt^{II}L_2$—M complexes (M = $Cr(CO)_3(\eta\text{-}C_5H_5)$, $Mo(CO)_3$-$(\eta\text{-}C_5H_5)$, $W(CO)_3(\eta\text{-}C_5H_5)$, $Mn(CO)_5$, $Fe(CO)_3NO$, $Co(CO)_4$; L = t-BuNC, cyclo-$C_6H_{11}NC$) are reduced on platinum and gold electrodes in non-aqueous medium. All these complexes undergo irreversible one electron reductions, which result in the rupture of one Pt—metal bond and the liberation of one M^- ion per mole reduced. Coupled ESR spectroscopy and coulometry show that a radical is generated during the reduction of the trimetallic complexes. The several ESR signals obtained for these paramagnetic Pt^I species exhibit no hyperfine structure.

The electrochemical behaviour of M—PtL_2—M complexes is compared with that of the following linear trimetallic complexes: M—Hg—M and $(M—Au—M)^-$.

Introduction

The complexes whose electrochemical reduction properties are reported in this article are listed in Table 1 according to the identity of the central metallic atom: Pt, Au, Hg. Among these three homologous families, only the electrochemical reduction of mercury complexes, M—Hg—M, has previously been studied [1—5], and for these the overall reaction is described by equation 1.

$$\text{M—Hg—M} + 2\,e^- \rightarrow 2\,\text{M}^- + \text{Hg} \qquad (1)$$

M^- designates a mononuclear carbonyl metallate fragment, (e.g. $Co(CO)_4^-$).

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[*] For part I see ref. 25.

TABLE 1

COMPLEXES STUDIED IN THE PRESENT WORK

Studied complexes:	Complexes with electronic configuration $d^n{-}d^{10}{-}d^n$	Complexes with electronic configuration $(d^n{-}d^{10}{-}d^n)^-$	Complexes with electronic configuration $d^n{-}d^8{-}d^n$
	$\mathrm{M{-}Hg^0{-}M}$	$\mathrm{(M{-}Au^I{-}M)^-}$ $\mathrm{Et_4N^+}$	$\mathrm{M{-}\overset{L}{\underset{L}{Pt^{II}}}{-}M}$
	$\mathrm{M = Mn(CO)_5}$ $\mathrm{Co(CO)_4}$	$\mathrm{M = Cr(CO)_3(\eta\text{-}C_5H_5)}$ $\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}$ $\mathrm{W(CO)_3(\eta\text{-}C_5H_5)}$	L = tert-butylisocyanide cyclohexylisocyanide $\mathrm{M = Mn(CO)_5}$ $\mathrm{Fe(CO)_3NO}$ $\mathrm{Co(CO)_4}$ $\mathrm{Cr(CO)_3(\eta\text{-}C_5H_5)}$ $\mathrm{Mo(CO)_3(\eta\text{-}C_5H_5)}$ $\mathrm{W(CO)_3(\eta\text{-}C_5H_5)}$
Ref. for Synthesis:	22, 26	7, 8	9, 10

The compounds M—Hg—M are reduced at higher anodic potentials (between +0.2 and +0.4 V) than the corresponding dinuclear compounds M—M, for which the electrochemical reduction is known [11,12] to occur as in equation 2:

$$\mathrm{M{-}M} + 2\,e^- \rightarrow 2\ \mathrm{M}^- \tag{2}$$

It is also known that the M—M bimetallic compounds, irradiated by UV light, give radicals which may be trapped, by nitrosodurene for example, according to the equation (3) [13,14]:

$$\mathrm{LM{-}ML} + \mathrm{ArNO} \xrightarrow{h\nu(\mathrm{UV})} \mathrm{ArN(ML)O^{\cdot}} \tag{3}$$

(Ar = 2, 3, 5, 6-$\mathrm{Me_4C_6H}$),

while solutions of M—M′ dimers irradiated under the same conditions show no ESR signal. However, recent work has showed that $\mathrm{M^{\cdot}}$ radicals can be generated [6,17]; the existence of $\mathrm{M(O)_2^{\cdot}}$ was detected recently by ESR (15).

Regarding cobalt-mercury compounds, Vlcek [2,3] has presented the following electrochemical reaction scheme interconnecting the carbonyl complexes:

$$\begin{tikzcd}
\mathrm{Co_2(CO)_8} \arrow[r, bend left, "E_{1/2} = -0.35\ \mathrm{V/SCE(Hg)}"] & \mathrm{Co(CO)_4^-} \arrow[l, bend left, "E_{1/2} = +0.12\ \mathrm{V/SCE(Pt)}"] \arrow[d, leftrightarrow, "E_{1/2} = -0.35\ \mathrm{V/SCE(Hg)}"] \\
& \mathrm{(CO)_4Co{-}Hg{-}Co(CO)_4}
\end{tikzcd} \tag{4}$$

Understanding of the mechanisms of these reactions 4 is nevertheless incomplete, particularly if account is taken of the recent work by Paliani et al. [16] and by Vahrenkamp et al. [17]. Thus, the electrochemical reactions connecting the three iron compounds $\mathrm{Fe(CO)_3NO^-}$, $\mathrm{Fe(CO)_3NO^{\cdot}}$ and $\mathrm{NO(CO)_3Fe{-}Hg{-}Fe(CO)_3NO}$, take place on a Hg electrode according to the sequence 5 [16]:

$$\left.\begin{aligned}
&2\ \mathrm{Fe(CO)_3NO^-} + \mathrm{Hg} \rightleftharpoons \mathrm{Hg(Fe(CO)_3NO)_2} + 2\,e^- \\
&\mathrm{Hg(Fe(CO)_3NO)_2} \rightarrow \mathrm{Hg^{2+}} + 2\,e^- + 2\ \mathrm{Fe(CO)_3NO^{\cdot}}
\end{aligned}\right\} \tag{5}$$

and on a platinum electrode as:

$$Fe(CO)_3NO^- \rightarrow Fe(CO)_3NO^{\cdot} + e^-$$

For the three chromium compounds $Cr(CO)_3(\eta\text{-}C_5H_5)^{\cdot}$, $Cr(CO)_3(\eta\text{-}C_5H_5)^-$ and $(\eta\text{-}C_5H_5)(CO)_3Cr{-}Cr(CO)_3(\eta\text{-}C_5H_5)$, the equations 6 summarize the electrochemical interrelationships [17]:

$$\left.\begin{array}{l} Cr(CO)_3(\eta\text{-}C_5H_5)^- \rightarrow Cr(CO)_3(\eta\text{-}C_5H_5)^{\cdot} + e^- \\ 2\,Cr(CO)_3(\eta\text{-}C_5H_5)^{\cdot} \rightarrow (\eta\text{-}C_5H_5)(CO)_3Cr{-}Cr(CO)_3(\eta\text{-}C_5H_5) \end{array}\right\} \quad (6)$$

These two reports, together with results from the UV irradiation of carbonyl compounds containing a metal—metal bond, suggest the general existence of an $M^{\cdot}$ radical electrochemically intermediate between the M^- anion and the M—M dimer. Thus, transition from the anion to the dimer can take place only by way of an electrochemical-chemical [7] oxidation mechanism 7:

$$\begin{array}{l} M^- \rightarrow M^{\cdot} + e^- \\ 2\,M^{\cdot} \rightarrow M{-}M \end{array} \quad (7)$$

The aim of this work was to prove that the oxidation of M^- to M—M takes place through a radical intermediate when M = $Co(CO)_4$, $Mn(CO)_5$, $Fe(CO)_3NO$, $Cr(CO)_3(\eta\text{-}C_5H_5)$, $Mo(CO)_3(\eta\text{-}C_5H_5)$, $W(CO)_3(\eta\text{-}C_5H_5)$.

The results of previous studies [11,12—18] of carbonyl M—M and M^- complexes make it possible to identify, by their oxidation and reduction potentials, species produced upon the exhaustive reduction of trimetallic complexes; thus, this study of the cathodic behavior of $M{-}PtL_2{-}M$ or $(M{-}Au{-}M)^-$, is based upon known electrochemical characteristics of M—M and M^-. Further, a recent study [19] of symmetric dinuclear complexes of type $(\eta\text{-}C_5H_5)(CO)_3Mo{-}AsMe_2{-}Mo(\eta\text{-}C_5H_5)(CO)_3$, has shown that the chemical reduction of these compounds leads to the radical $(\eta\text{-}C_5H_5)(CO)_3Mo{-}AsMe_2^{\cdot}$ and the anion $Mo(\eta\text{-}C_5H_5)(CO)_3^-$. This result will be of use in our interpretation of the monoelectronic reduction of the complexes $M{-}Pt^{II}L_2{-}M$.

The compounds studied (Table 1) are for the most part soluble in non-aqueous solvents: two solvents were used, propylene carbonate (PC) and acetonitrile (CH_3CN). Only the compounds $M{-}PtL_2{-}M$ (M = $Cr(CO)_3(\eta\text{-}C_5H_5)$; $Mo(CO)_3(\eta\text{-}C_5H_5)$; $W(CO)_3(\eta\text{-}C_5H_5)$) are very weakly soluble in these and the usual organic solvents (less than 10^{-4} mole/l in PC and CH_3CN), and we were unable to obtain quantitative results using their saturated solutions. The other studied complexes, $(M{-}Au{-}M)^-$ and $M{-}PtL_2{-}M$ react chemically with mercury to give the corresponding M—Hg—M compounds, and so the mercury electrode had to be replaced by a platinum or gold electrode. It should be mentioned that the Pt complexes studied are weakly ionized in non-aqueous solution: even freshly prepared solutions of these compounds show an oxidation wave of the anion ($M^- \rightarrow M^{\cdot} + e^-$) in stationary voltammetry, identified by its half-wave potential. One can therefore assume chemical equilibria of type 8 in PC or CH_3CN solution, which lie strongly over towards the left, since the ratio of limiting currents for the reduction of $M{-}PtL_2{-}M$ and the oxidation of M^- reaches no higher than several percent (up to 8%) for concentrations of the order of 10^{-3} *M*.

$$\begin{aligned} &\mathrm{M{-}PtL_2{-}M} \rightleftharpoons \mathrm{M^-} + \mathrm{(PtL_2{-}M)^+} \\ &\mathrm{(PtL_2{-}M)^+} \rightleftharpoons \mathrm{M^-} + \mathrm{PtL_2^{2+}} \end{aligned} \qquad (8)$$

Further, conductimetry measurements carried out at 24°C on solutions of $(CO)_4Co{-}PtL_2{-}Co(CO)_4$ in CH_3CN show that the conductivity χ changes from $\chi = 0.3 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ to $\chi = 0.45 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ during the 10 min following formation of a solution 10^{-3} *M*. Previously, Vahrenkamp [19] observed that the preparation of a solution of $(Cr(CO)_3(\eta\text{-}C_5H_5))_2$ in C_6H_5CN leads to 1% formation of the radical $Cr(CO)_3(\eta\text{-}C_5H_5)^{\bullet}$. In the present work, devoted to $M{-}PtL_2{-}M$ complexes, ESR measurements carried out on saturated solutions of trimetallic complexes did not allow detection of the presence of radicals.

The difference in electronegativity between the metals participating in the metal—metal bond leads one to expect the presence of ions in solution. Thus, the infrared study of the complexes [9] implied for the metal carbonyl M group a much larger residual charge δ^- in the $M{-}PtL_2{-}M$ complexes than in the corresponding M—Hg—M compounds (—0.43 to —0.45 instead of —0.1, when M = $Co(CO)_4$. The covalent character of the metal—metal bond increases in the following order:

$$\mathrm{M{-}PtL_2{-}M} < \mathrm{(M{-}Au{-}M)^-} < \mathrm{M{-}Hg{-}M} < \mathrm{M{-}M}$$

Solutions of trimetallic compounds (Table 1) were studied by stationary voltammetry (SV), cyclic voltammetry (CV), by potentiostatic coulometry and by coulometry associated with ESR. Preliminary results of these measurements have been published [6].

Experimental

The employed experimental apparatus and techniques were described in part I of this series [25]. The compounds studied were air-sensitive and were handled under argon.

Results

(a) Electroreduction of M—Hg—M (M = $Co(CO)_4$, $Mn(CO)_5$)

Our study of the electrochemical reduction of M—Hg—M confirmed previously published results [2,4] and the reduction scheme 9 accepted up to then, namely:

$$2\,\mathrm{M^-} \rightarrow \mathrm{M_2} + 2\,e^- \qquad (9)$$

appears in the light of our results below, to be a general scheme corresponding mechanistically to the electrochemical-chemical sequence 7, and involving a paramagnetic intermediate species $M^{\bullet}$ between M^- and M_2.

(b) Electroreduction of $(M{-}Au{-}M)^-$ (M = $Cr(CO)_3(\eta\text{-}C_5H_5)$, $Mo(CO)_3(\eta\text{-}C_5H_5)$, $W(CO)_3(\eta\text{-}C_5H_5)$)

With stationary voltammetry (rotating disc electrode), these complexes give a poorly defined reduction wave near —1.9 V/SCE (Table 2). In cyclic voltammetry, the reduction peak is accompanied by an oxidation peak whose potential (near

TABLE 2

ELECTROREDUCTION OF [M—Au—M]$^-$ BY STATIONARY AND CYCLIC VOLTAMMETRY ON GO GOLD ELECTRODE, IN CP + TEAP (0.1 *M*)

Compounds [a]	$E_{1/2}$(V/SCE)	n(experiment.) [b]	E_{Pc} at 1 V/s	E_{Pa} at 1 V/s
$Bu_4N^+[L_3L'Cr—Au—CrL'L_3]^-$	—1.90	—	—2.02	—0.12
$Et_4N^+[L_3L'Mo—Au—MoL'L_3]^-$	—1.90	1.11	—2.05	—0.03
$Et_4N^+[L_3L'W—Au—WL'L_3]^-$	—1.93	1.19	—2.10	—0.01

[a] L = CO; L' = η-C_5H_5. [b] Values obtained by comparison of the limiting currents of [M—Au—M]$^-$ with those of corresponding M—M complexes in the same conditions.

0V) corresponds to the well known oxidation potential for M^- anions [6]. The reduction is irreversible, and potentiostatic coulometry results show that one electron is exchanged per electroactive molecule. The comparison of (M—Au—M)$^-$ reduction wave heights with those for M_2 obtained in the same conditions confirms this result (Table 2). In addition, the platinum electrode was covered with a deposit after cathodic polarization. Electron probe X-ray microanalysis showed the deposit to contain gold. After exhaustive coulometric reduction of (M—Au—M)$^-$, we determined the quantity of free M^- in solution by comparing the height of its oxidation wave with that of a calibrated solution: 2 M^- are liberated per reduced (M—Au—M)$^-$ anion. Also, when (M—Au—M)$^-$ is reduced in the cavity of the ESR spectrometer, and the M^- formed is oxidized to $M^\cdot$, this radical was identified from the known characteristics (g and ΔH) of its ESR signal (Table 2, ref. 6). Consequently, the overall reaction scheme for the reduction of the (M—Au—M)$^-$ complex is as follows:

$$(M—Au—M)^- + e^- \rightarrow 2\,M^- + Au^0 \qquad (10)$$

This mechanism is in agreement with the reduction mechanism previously reported by Sawyer et al. [29] on the similar $(Cl—Au^I—Cl)^-$ complex.

(c) M—PtL$_2$—M complexes

1. $(CO)_4Co—PtL_2—Co(CO)_4$

We used $(CO)_4Co—PtL_2—Co(CO)_4$ (L = *cyclo*-$C_6H_{11}NC$) in CH_3CN and PC as solvents, and the electrochemical measurements were carried out with a solid gold electrode. A reduction wave at $E_{1/2}$ = —1.25 V/SCE (Figure 1) was observed in the electrochemical reduction. The study of the relations between the limiting current, I_{lim}, and the concentration c or the rotation rate ω($I_{lim} = f(c)$, $1/I_{lim} = f(1/\omega^{1/2})$) shows that the reduction current is controlled by diffusion; and the Levitch relation [20] is therefore applicable. The appearance of a weak anodic wave (Figure 1) at the potential $E_{1/2}$ = +0.20 V/SCE corresponds to the oxidation of $Co(CO)_4^-$ and confirms the partial dissociation of $(CO)_4Co—PtL_2—Co(CO)_4$ in solution (see Introduction).

We have compared the reduction wave height for $(CO)_4Co—PtL_2—Co(CO)_4$ with that obtained with solutions containing the compounds $(CO)_4Co—Hg—Co(CO)_4$ and $Co_2(CO)_8$ at the same concentration; these latter complexes are known to reduce by a two electron process. The obtained wave heights were in the ratio

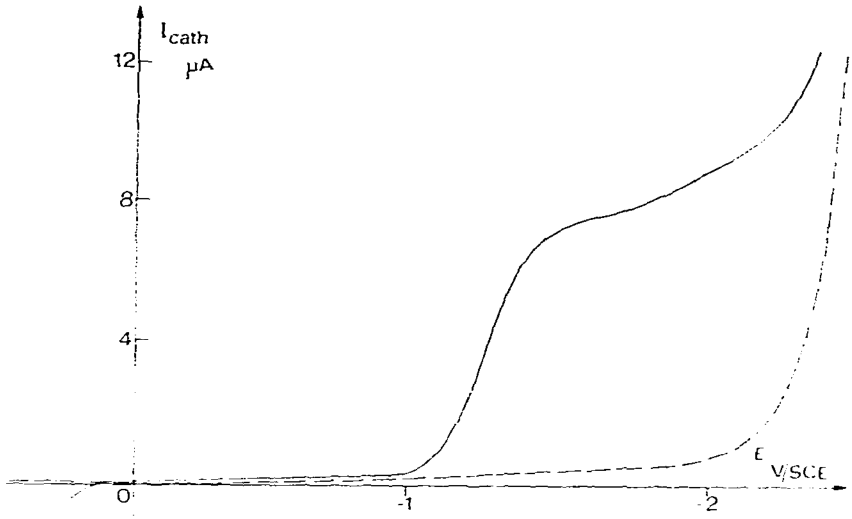

Fig. 1. Stationary voltammetry (solid line) of $(CO)_4Co—PtL_2—Co(CO)_4$; $c = 1.1 \times 10^{-3}$ mol l^{-1}; Au rotating disc electrode in CP + 0.1 M TEAP; (ω = 2000 rpm; scan rate 60 mV min^{-1}) Dashed line: supported electrolyte alone.

of 1 : 2 : 2. Assuming that the diffusion coefficients of these complexes are similar, this result indicates that the reduction of $(CO)_4Co—PtL_2—Co(CO)_4$ is monoelectronic.

We confirmed this result by coulometric reduction of $(CO)_4Co—PtL_2—Co(CO)_4$ in CH_3CN and in PC. Also, after exhaustive electrolysis of a solution, we identified $Co(CO)_4^-$ as one of the reduction products by its characteristic oxidation wave at $E_{1/2}$ = +0.20 V/SCE.

The reduction of $(CO)_4Co—PtL_2—Co(CO)_4$ was shown to be irreversible by

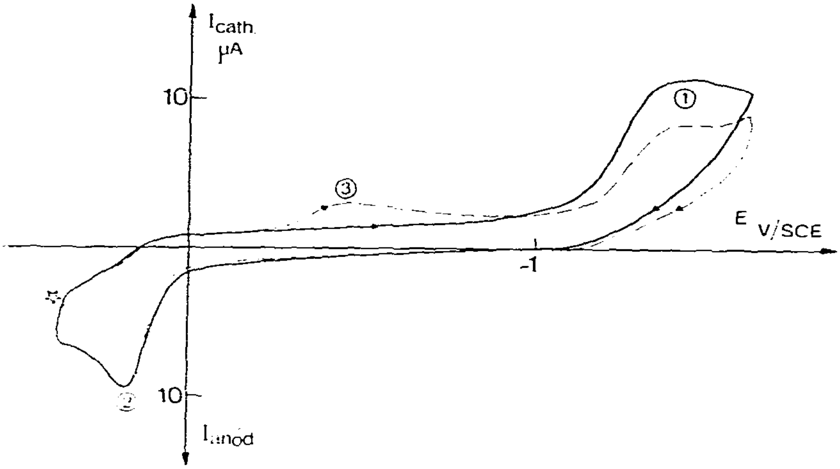

Fig. 2. Cyclic voltammetry curves of $(CO)_4Co—PtL_2—Co(CO)_4$; $c = 1.1 \times 10^{-3}$ mol l^{-1}; Au electrode in CP + 0.1 M TEAP; Scan rate 1 V s^{-1}. ———, single scan; - - - - —, multiple scans; *, start of the scan.

cyclic voltammetry (Figure 2, peak 1). During the anodic sweep, we observe an anodic peak (2) corresponding to the oxidation of the $Co(CO)_4^-$ reduction product. The cathodic peak 3 observed for multiple sweeps has been identified as corresponding to the reduction of the $Co_2(CO)_8$ dimer formed after step 2 (dimerization of the radical $Co(CO)_4^{\cdot}$ produced by oxidation of $Co(CO)_4^-$) *

ESR measurements at 25°C on a solution of $(CO)_4Co—PtL_2—Co(CO)_4$ electrolysed at —1.5 V/SCE in the spectrometric resonance cavity show the appearance of a signal whose characteristics are identical to those already reported (ref. 6, Table 2). This signal increases with electrolysis time, and rapidly disappears when the electrolysis is interrupted, indicating that the paramagnetic species formed is unstable. Further, when a solution of $(CO)_4Co—PtL_2—Co(CO)_4$, that was initially reduced at —1.5 V/SCE, is anodically polarized (+0.5 V/SCE), a new ESR signal appears while the previous signal reduces in intensity. We attribute the new signal to $Co(CO)_4^{\cdot}$, resulting from the oxidation of $Co(CO)_4^-$ (see ref. 6, Table 2).

These results lead to the following scheme (reactions 11—13) for the redox reactions of $(CO)_4Co—PtL_2—Co(CO)_4$:

(i) Reduction of $(CO)_4Co—PtL_2—Co(CO)_4$

$$(CO)_4Co—PtL_2—Co(CO)_4 + e^- \xrightarrow{E_{1/2} = —1.25\ V/SCE} (CO)_4Co—PtL_2^{\cdot} + Co(CO)_4^- \quad (11)$$

(ii) Oxido-reduction of the reduction products

$$Co(CO)_4^- \xrightarrow{E_{1/2} = +0.20\ V/SCE} Co(CO)_4^{\cdot} + e^- \quad (12)$$

$$2\ Co(CO)_4^{\cdot} \rightarrow Co_2(CO)_8$$

$$Co_2(CO)_8 + 2\ e^- \xrightarrow{E_{1/2} = —0.45\ V/SCE} 2\ Co(CO)_4^- \quad (13)$$

2. $(CO)_3NOFe—PtL_2—FeNO(CO)_3$

This complex represents a departure from the main series studied, the corresponding homobimetallic iron complex being unknown. The electrochemical behaviour of the anion $[Fe(CO)_3NO]^-$ has been studied previously [16]: $[Et_4N]^+$ $[Fe(CO)_3NO]^-$ is oxidized apparently to give the radical $Fe(CO)_3NO^{\cdot}$

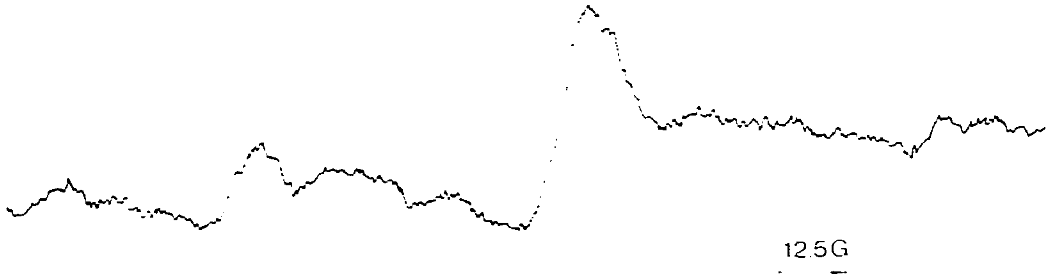

Fig. 3. ESR spectrum of saturated $(CO)_3NOFe—Pt(t\text{-}BuNC)_2—Fe(CO)_3NO$, reduced at —1.5 V/SCE on platinum, in CH_3CN + 0.1 *M* TEAP (77 K). When the electrolysis was stopped, the signal decreased by 50% in 10 min.

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* At faster potential scans (>10 V s^{-1}) an aniodic peak (*E*p = —1 V/SCE), corresponding to the cathiodic peak 1, was seen by CV.

according to equation 14 in CH_3CN + 0.1 *M* TEAP and on a platinum electrode:

$$[Fe(CO)_3NO]^- \xrightarrow{E_{1/2} = +0.18\ V/SCE} Fe(CO)_3NO^{\cdot} + e^- \qquad (14)$$

We repeated this study on the analogous compound $KFe(CO)_3NO$, which is reversibly oxidized on a gold electrode at $E_{1/2} = +0.20$ V/SCE in PC containing 0.1 *M* TEAP. In cyclic voltammetry at low potential scan rates, the current of the cathodic peak is weaker than that of the anodic peak, confirming the existence of a chemical reaction which consumes the formed radical, in competition with its own reduction. This is in accord with earlier results obtained in CH_3CN [16].

The trimetallic complex $(CO)_3NOFe{-}PtL_2{-}Fe(CO)_3NO$ (L = t-BuNC) is soluble in PC or CH_3CN, where it dissociates to the extent of 5%, as judged by the anodic wave height (oxidation of $Fe(CO)_3NO^-$), which is detected when the solution is freshly made. The complex shows an irreversible monoelectronic reduction wave at $E_{1/2} = -1.10$ V/SCE, of which the limiting current is proportional to the concentration (range 2×10^{-4} to 1.6×10^{-3} *M*). A plot of $1/I_{lim}$ vs. $f(\omega^{-1/2})$ (ω in rev./min) is a straight line with a correlation coefficient of 0.999; thus Levich's equation [20] applies. The potentiostatic coulometric reduction of the trimetallic complex shows that one electron is exchanged per mole of complex, while one gram ion of $[Fe(CO)_3NO]^-$ is liberated (as determined by oxidation limiting current compared with calibrated values from $KFe(CO)_3NO$ solutions). Consequently, the reduction scheme is as follows:

$$(CO)_3NOFe{-}PtL_2{-}Fe(CO)_3NO + 1\ e^- \xrightarrow{E_{1/2} = -1.10\ V/SCE} Fe(CO)_3NO^- + {}^{\cdot}PtL_2Fe(CO)_3NO \qquad (15)$$

The generation of $Fe(CO)_3NO^-$ in the irreversible reduction is confirmed by the reoxidation peak at +0.27 V/SCE (Fig. 4).

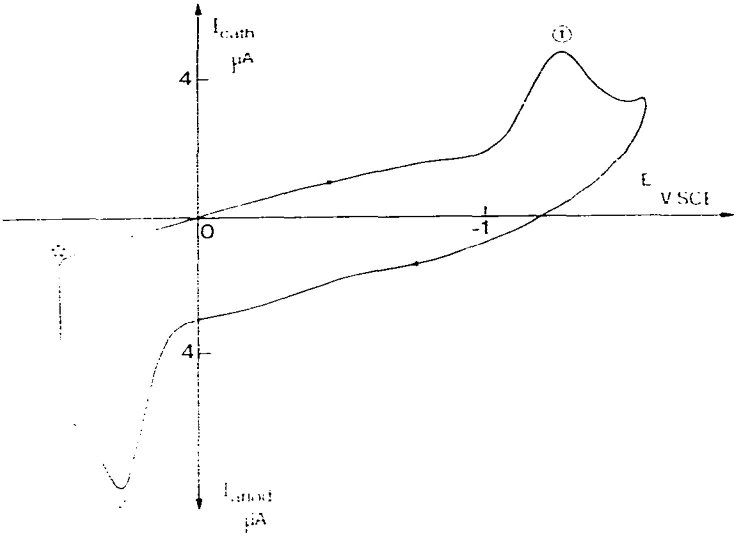

Fig. 4. Cyclic voltammetry of $(CO)_3NOFe{-}PtL_2{-}FeNO(CO)_3$, 10^{-3} *M*, in CP + 0.1 *M* TEAP at Au electrode; Scan rate 1 V s^{-1}. (1) reduction of the complex, (2) oxidation of $[Fe(CO)_3NO]^-$ generated in the step 1.

The radical $^{\cdot}PtL_2Fe(CO)_3NO$ produces an ESR signal (Figure 3) of which it is not possible to observe any hyperfine structure, even at 77 K. The characteristic of this radical have already been published (Table 2, ref. 6).

3. $(CO)_5Mn—PtL_2—Mn(CO)_5$

The studied compound (with L = *cyclo*-$C_6H_{11}NC$) shows, by stationary voltammetry (gold rotating disc electrode) in PC +0.1 *M* TEAP a cathodic wave at $E_{1/2} = -1.50$ V/SCE. The measured limiting current is proportional to the concentration of electroactive species over a limited concentration range of 10^{-4} to 5×10^{-4} *M* (this complex is only weakly soluble in PC), the current obeying the Levich equation [20]. In the same solution, the comparison of the reduction wave height for $Mn_2(CO)_{10}$ (the reduction of which is known to be bielectronic and, under our experimental conditions was found to lie at $E_{1/2} = -1.25$ V/SCE [12,18]) with that of $(CO)_5Mn—PtL_2—Mn(CO)_5$, permits calculation of the number of electrons exchanged in the reduction of the trimetallic complex, the diffusion coefficients for these complexes being assumed to be similar. The value was found to be $n = 1.02$, and this result was confirmed by exhaustive potentiostatic coulometry. The study of the complex by cyclic voltammetry (Figure 5) shows that the cathodic peak (1), corresponding to the reduction of the trimetallic complex, is associated with a reoxidation peak (2) ($E_p^a = -0.10$ V/SCE at 0.1 V/s) which corresponds to the oxidation of free $Mn(CO)_5^-$ to $Mn(CO)_5^{\cdot}$ [28]. This identification was made by cyclic voltammetry (Figure 5, curve B), and confirmed by ESR measurements described below. The electrochemical quantitative determination shows that one gram ion of $Mn(CO)_5^-$ is liberated per mole of reduced $Mn(CO)_5—PtL_2—Mn(CO)_5$. Figure 6 shows the change in the ESR signal of a trimetallic complex solution when exhaustive coulometry is carried out in

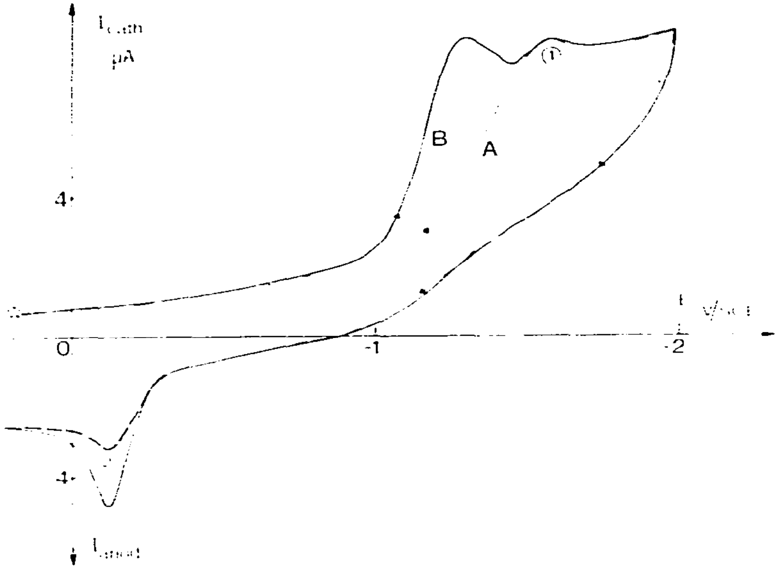

Fig. 5. Cyclic voltammetry on gold electrode, in PC + 0.1 *M* TEAP. Curve A, $Mn(CO)_5—Pt(t\text{-}BuNC)_2—Mn(CO)_5$ alone; Curve B, same as curve A, plus $Mn_2(CO)_{10}$. (Scan rate: 0.1 V s^{-1}). * Start of the scan.

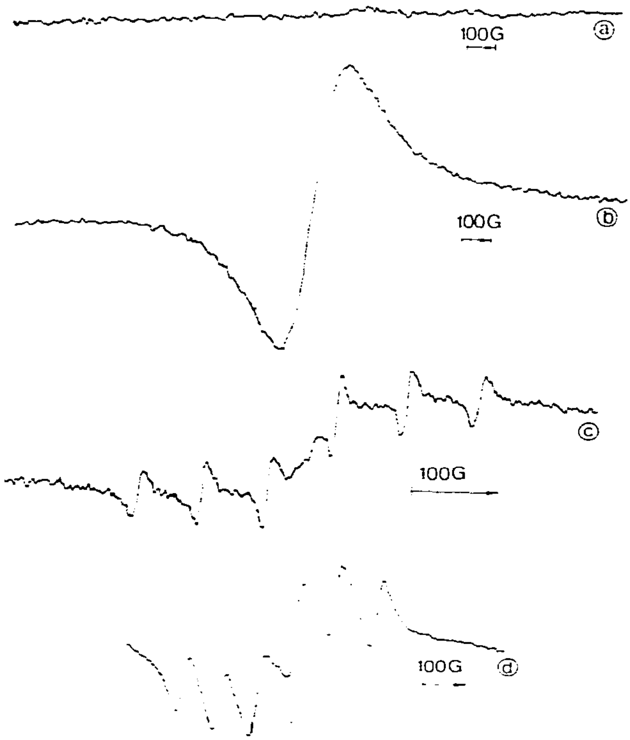

Fig. 6. ESR signals obtained on a saturated solution of $(CO)_5Mn—Pt$ (cyclo-$C_6H_{11}NC)_2—Mn(CO)_5$ in CH_3CN + 0.1 *M* TEAP, on platinum electrode at 298 K. (a) Before electrolysis; (b) After three hours polarization at —2 V/SCE (reduction of the trimetallic complex); (c) Same solution as b, after 3 hours polarization at +0.5 V/SCE (electrooxidation of $[Mn(CO)_5]^-$); (d) In the same medium, ESR signal obtained on a solution of $Mn(CO)_5^-$ electrolyzed at +0.1 V/SCE. $Mn(CO)_5^-$ was generated from electroreduction of $Mn_2(CO)_{10}$. Curve d is given for comparison with curve c.

the resonant cavity of an ESR spectrometer at 298°K. The signal due to $(CO)_5MnPtL_2^{\cdot}$ [6] is broad, while that due to $Mn(CO)_5^{\cdot}$, resulting from the oxidation of $Mn(CO)_5^-$, consists of the six manganese lines. The characteristics (g and ΔH) for these signals are given in Table 2, ref. 6. No hyperfine structure was obtained either at 298°K or at 77°K.

On the basis of these results, we propose the following reaction schemes:

(i) For the trimetallic complex reduction:

$$(CO)_5Mn—PtL_2—Mn(CO)_5 + e^- \xrightarrow{E_{1/2} = -1.50\text{ V/SCE}} Mn(CO)_5^- + {}^{\cdot}PtL_2—Mn(CO)_5$$

(ii) For the oxidation of the reduction products

$$Mn(CO)_5^- \xrightarrow{E_{1/2} = -0.10\text{ V/SCE}} Mn(CO)_5^{\cdot} + e^-$$

4. The electrochemical reduction of M—PtL$_2$—M (M = Cr(CO)$_3$(η-C$_5$H$_5$), Mo(CO)$_3$(η-C$_5$H$_5$), W(CO)$_3$(η-C$_5$H$_5$))

The lack of solubility of these complexes prevented analysis of their potentiostatic coulometric reduction. The complexes with L = t-BuNC are more soluble than those with L = *cyclo*-$C_6H_{11}NC$ ligands. The reduction potentials are little affected by the nature of L (thus, for the Cr—PtL_2—Cr complexes, with L = t-BuNC, $E_{1/2} = -1.48$ V/SCE, while with L = *cyclo*-$C_6H_{11}NC$, $E_{1/2} = -1.55$ V/SCE). The results below refer to complexes involving the ligand t-BuNC. These compounds show a well defined reduction wave whose potential undergoes cathodic shift from chromium to tungsten complex; such behaviour was observed with the corresponding dimers (Table 2, ref. 6). The reduction potentials of the trimetallic compounds are more cathodic than that of the corresponding M—M dimers, contrary to the M—Hg—M compounds.

The results obtained by cyclic voltammetry for the M—PtL_2—M compounds, are illustrated in Figure 7. Associated with the cathodic peak (1) corresponding to the reduction of the M—PtL_2—M complex is an anodic peak (2) due to the electrochemical oxidation of the M^- anion, product of reduction 1. This step 2 was identified by comparison with the curves (SV) [5] obtained under the same experimental conditions for the corresponding dimer M—M, the reduction product of which is the M^- anion. For multiple triangular potential sweeps, a new

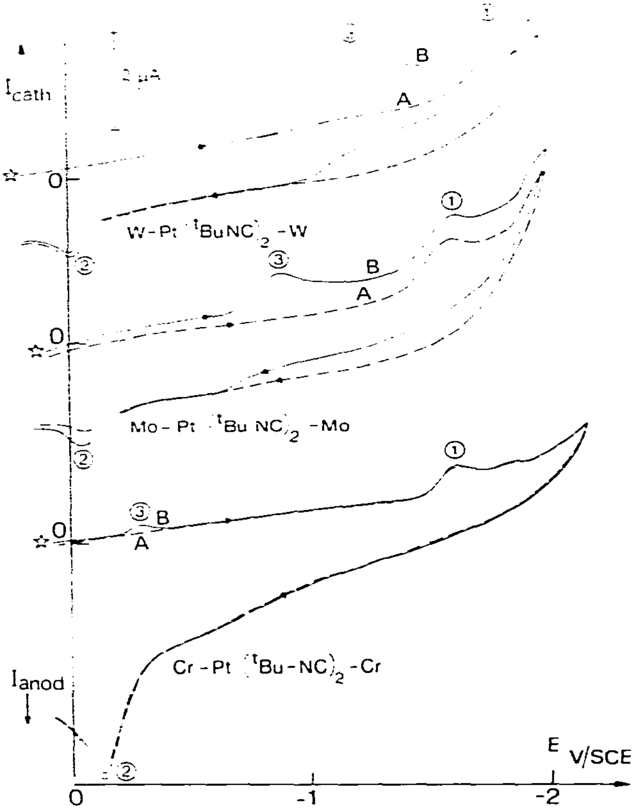

Fig. 7. Cyclic voltammetry (gold electrode) on saturated solutions of M—PtL_2—M, in propylene carbonate containing 0.1 *M* tetraethylammonium perchlorate. (L = t-BuNC) Potential scan; 0 to —2 V at 0.1 V/s, —2 V to 0 at 1 V/s; Potential start 0 V/SCE. Curves A, without M_2; Curves B, plus M_2. M = $Cr(CO)_3(\eta\text{-}C_5H_5)$, M = $Mo(CO)_3(\eta\text{-}C_5H_5)$, $W(CO)_3(\eta\text{-}C_5H_5)$.

TABLE 3

CYCLIC VOLTAMMETRY OF M-Pt^{II}L$_2$—M: PEAK POTENTIALS UNDER THE EXPERIMENTAL CONDITIONS OF FIGURE 7

M in M—Pt^{II}L$_2$—M	E_p^c (1) (V/SCE)	E_p^a (2) (V/SCE)	E_p^c (3) (V/SCE)
$Cr(CO)_3(\eta\text{-}C_5H_5)$	−1.60	−0.13	−0.29
$Mo(CO)_3(\eta\text{-}C_5H_5)$	−1.62	−0.03	−0.85
$W(CO)_3(\eta\text{-}C_5H_5)$	−1.75	−0.01	−1.18

reduction peak (3) is detected, which corresponds to the reduction of the dimer. This dimer reduction peak 3 is observed only for potential scan rates greater than 1 V/s, (under the experimental conditions of Figure 7). The potentials of the peaks in Figure 7 are given in Table 3.

With stationary voltammetry, comparison of reduction wave heights for M—M and M—PtL$_2$—M (the difference in their diffusion coefficients being neglected) permits the determination of the number of electrons exchanged in the reduction of the trimetallic complex. The values thus obtained lie between 0.8 and 1.1.

Reduction of M—PtL$_2$—M (M = $Cr(CO)_3(\eta\text{-}C_5H_5)$, $Mo(CO)_3(\eta\text{-}C_5H_5)$, $W(CO)_3(\eta\text{-}C_5H_5)$) on platinum electrode in an ESR cavity, and in a saturated solution of the complex, does not result in an ESR signal, probably due to insufficient concentration of M—PtL$_2^{\cdot}$. On the other hand, if after such a reduction, one returns to a positive potential, where M^- is oxidized to $M^{\cdot}$, for example with $Cr(CO)_3(\eta\text{-}C_5H_5)$—Pt(*cyclo*-$C_6H_{11}NC)_2$—$Cr(CO)_3(\eta\text{-}C_5H_5)$, the ESR signal is observed for the radical $Cr(CO)_3(\eta\text{-}C_5H_5)^{\cdot}$ (Figure 8), with $g = 2.023$ (line width $\Delta H = 13.56$ Gauss) in accordance with the value obtained by Vahrenkamp for $^{\cdot}Cr(CO)_3(\eta\text{-}C_5H_5)$ [19]. These g and ΔH values are listed in Table 2, ref. 6.

From these results, the redox reactions of these compounds may be described by the following reaction scheme:

(i) Trimetallic reduction:

M—PtL$_2$M + e^- → M—PtL$_2^{\cdot}$ + M^- (peak 1, Figure 7)

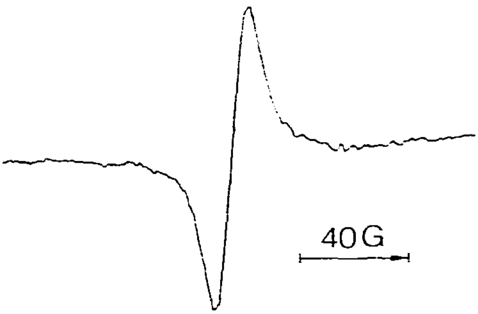

Fig. 8. ESR spectrum of $[Cr(CO)_3(\eta\text{-}C_5H_5)]^{\cdot}$ obtained in situ at 298°K as follows: A saturated solution of $Cr(CO)_3(\eta\text{-}C_5H_5)$—$Pt(C_6H_{11}NC)_2$—$Cr(CO)_3(\eta\text{-}C_5H_5)$ was electrolyzed 2 hours at −1.5 V/SCE in CH_3CN + 0.1 *M* TEAP. This was followed by the electrochemical oxidation of the reduction product ($[Cr(CO)_3(\eta\text{-}C_5H_5)]^-$ under pure argon atmosphere.

(ii) Oxidoreduction of above reaction products:

$M^- \rightarrow M^{\cdot} + e^-$ (peak 2, Figure 7)

$2\,M^{\cdot} \rightarrow M{-}M$

$M{-}M + 2e^- \rightarrow 2\,M^-$ (peak 3, Figure 7)

The electrochemical reduction mechanism for the trimetallic complexes of Pt^{II} with Cr, Mo, W is therefore very reminiscent of that for the Pt^{II} complexes with Mn, Fe, Co.

Discussion

It is difficult to find a systematic correlation of the reduction potential variations among the different families of complexes studied, M—M, M—Hg—M, $(M{-}Au{-}M)^-$, M—PtL_2—M, X—PtL_2—X (X = Cl, Br, I) because of the considerable variation in their properties. However, a number of conclusions can be drawn for a given family of complexes. Thus, for the family of trimetallic compounds M—PtL_2—M, Braunstein [9] has shown, from IR spectroscopy and chemical reactivity, that there is an increase in π back-donation from platinum to the ligand L according to the following sequence of the M moieties:

$Co(CO)_4 \sim Fe(CO)_3NO < Mo(CO)_3(\eta\text{-}C_5H_5) < W(CO)_3(\eta\text{-}C_5H_5) < Mn(CO)_5$

This is a consequence of the increased electron density on the Pt on going from the Co to the Mn complex. Further, he showed that $Co(CO)_4$ and $Fe(CO)_3NO$ were better leaving groups than the other carbonyl fragments. These observations agree with the half-wave reduction potential values which are more cathodic in going from Co to Mn. However, the results obtained previously for the analogous compounds X—PtL_2—X [25] (X = Cl, Br, I) cannot be interpreted in terms of this scheme, the electronic properties of X and M being very different.

In the series M—Hg—M, the half-wave potential values show similar trends. Indeed the half-wave potential of $(CO)_4Co{-}Hg{-}Co(CO)_4$, $E_{1/2} = -0.35$ V/SCE is more anodic than that of $(CO)_5Mn{-}Hg{-}Mn(CO)_5$, $E_{1/2} = -0.74$ V/SCE, and thus the manganese compound is again more difficult to reduce than the cobalt analogue.

Depending on the nature of the central metal in the trimetallic complexes, the observed reduction reactions may be represented in terms of the following schemes:

$M{-}Hg{-}M + 2\,e^- \rightarrow 2\,M^- + Hg$

$(M{-}Au{-}M)^- + e^- \rightarrow 2\,M^- + Au$

$M{-}Pt^{II}L_2{-}M + e^- \rightarrow M^- + {}^{\cdot}PtL_2M$

The ligands L (isocyanide ligands) introduce a strong π-acceptor character able to stabilize the otherwise unstable Pt^I radical. This is not surprising in view of the fact that the Pt^I complexes known to date are often compounds with isocyanide ligands [25]. The only known paramagnetic mononuclear Pt^I compounds are obtained either by electroreduction of dithiolene Pt^{II} complexes and of their amino analogs [23], or by γ-irradiation of $K_2(PtCl_6)$ [24].

The $\cdot Pt^I L_2M$ radicals obtained in our reductions are of low stability judging by the disappearance of the ESR signals when the electrolysis is interrupted. They probably undergo either dimerization or coordination with solvent (CH_3CN) molecules. Attempts to characterize these radicals by NMR or by mass spectrometry after exhaustive coulometric reduction of M—PtL_2—M failed. The absence of any hyperfine structure in the ESR at 298° K or at 77° K precluded their detailed analysis. In conclusion, the $E_{1/2}^{cath}$ of M—PtL_2—M varies little with R when L = RNC (L = t-BuNC, L = *cyclo*-C_6H_{11}NC-) but more so with the nature of M. On the other hand, the fact that L is a strong π-acceptor ligand (isocyanide) results in a relative stabilization of the Pt^I radical and affords the redox mechanism presented here.

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