Electroreduction of Linear Trimetallic Complexes: M–Hg–M, $(\text{M–Au–M})^-$, M–PtL_2–M [M = Co(CO)_4, $\text{Fe(CO)}_3\text{NO}$, Mn(CO)_5, $\text{Cr(CO)}_3(\eta\text{-C}_5\text{H}_5)$, $\text{Mo(CO)}_3(\eta\text{-C}_5\text{H}_5)$, or $\text{W(CO)}_3(\eta\text{-C}_5\text{H}_5)$; L = Bu^tNC or $\text{C}_6\text{H}_{11}\text{NC}$]; Unexpected Generation of Radicals[1]

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Summary Cathodic reduction of Pt^{II} isocyanide compounds M–$\text{Pt}^{\text{II}}\text{L}_2$–M on platinum and gold electrodes in an aprotic medium leads to unexpected paramagnetic Pt^{I} species, whereas under the same conditions M–Hg–M and $(\text{M–Au–M})^-$ exhibit predictable metal–metal bond cleavage.

EARLIER electrochemical results devoted to linear trimetallic compounds are summarized in Table 1. However we observed that, when electro-oxidation of M^- [M = Co(CO)_4, $\text{Fe(CO)}_3\text{NO}$, Mn(CO)_5, $\text{Cr(CO)}_3(\eta\text{-C}_5\text{H}_5)$, $\text{Mo(CO)}_3(\eta\text{-C}_5\text{H}_5)$, or $\text{W(CO)}_3(\eta\text{-C}_5\text{H}_5)$] is carried out in the cavity of an e.s.r. spectrometer, a signal is detected which may be ascribed to the radical M· or, according to recent work,[6] to the oxygenated radical $\text{M(O}_2)^\cdot$. Therefore, we assign the following scheme (equation 1) to the oxidation process for each of the above M^-.

$$\text{M}^- \rightarrow \text{M}^\cdot + \text{e}$$

$$\text{M}^\cdot \rightarrow \tfrac{1}{2}\,\text{M}_2 \qquad (1)$$

TABLE 1. Earlier electrochemical results devoted to linear trimetallic complexes

Compounds	Ref.	Redox mechanisms studied Electroreduction:	Electro-oxidation
$\text{Hg[Co(CO)}_4]_2$	2	$\text{Hg[Co(CO)}_4]_2 + 2\text{e} \rightarrow \text{Hg} + 2\ \text{Co(CO)}_4{}^-$	$2\ \text{Co(CO)}_4{}^- \rightarrow \text{Co}_2\text{(CO)}_8 + 2\text{e}$
$\text{Hg[Cr(CO)}_3(\eta\text{-C}_5\text{H}_5)]_2$	3	$\text{Hg[Cr(CO)}_3(\eta\text{-C}_5\text{H}_5)]_2 + 2\text{e} \rightarrow \text{Hg} + 2\ [\text{Cr(CO)}_3(\eta\text{-C}_5\text{H}_5)]^-$	
$\text{Hg[Mo(CO)}_3(\eta\text{-C}_5\text{H}_5)]_2$		$\text{Hg[Mo(CO)}_3(\eta\text{-C}_5\text{H}_5)]_2 + 2\text{e} \rightarrow \text{Hg} + 2\ [\text{Mo(CO)}_3(\eta\text{-C}_5\text{H}_5)]^-$	
$\text{Hg[W(CO)}_3(\eta\text{-C}_5\text{H}_5)]_2$	4	$\text{Hg[W(CO)}_3(\eta\text{-C}_5\text{H}_5)]_2 + 2\text{e} \rightarrow \text{Hg} + 2\ [\text{W(CO)}_3(\eta\text{-C}_5\text{H}_5)]^-$	
$\text{Hg[Mn(CO)}_5]_2$		$\text{Hg[Mn(CO)}_5]_2 + 2\text{e} \rightarrow \text{Hg} + 2\ [\text{Mn(CO)}_5]^-$	
$\text{Hg[Fe(CO)}_3\text{NO]}_2$	5	$\text{Hg[Fe(CO)}_3\text{NO]}_2 + 2\text{e} \rightarrow \text{Hg} + 2\ [\text{Fe(CO)}_3\text{NO}]^-$	$\text{Hg[Fe(CO)}_3\text{NO]}_2 \rightarrow \text{Hg}^{2+} + 2\ [\text{Fe(CO)}_3\text{NO}]^\cdot + 2\text{e}$
		General scheme for the electroreduction: $\text{M–Hg–M} + 2\text{e} \rightarrow \text{Hg} + 2\ \text{M}^-$	

Until this work, the only radicals of the type M· known, whose existence had been detected from the electrochemical oxidation of M^-, were $\text{Fe(CO)}_3\text{NO}^\cdot$[5] and $\text{Cr(CO)}_3(\eta\text{-C}_5\text{H}_5)^\cdot$.[7]

Complexes Et_4N^+ $(\text{M–Au–M})^-$ were synthesized recently, where M = $\text{Cr(CO)}_3(\eta\text{-C}_5\text{H}_5)$,[8a] $\text{Mo(CO)}_3(\eta\text{-C}_5\text{H}_5)$, or $\text{W(CO)}_3(\eta\text{-C}_5\text{H}_5)$.[8b] On a Pt electrode, in propylene carbonate containing 0·1 M Et_4NClO_4, these complexes exhibit an ill-defined irreversible wave near $E_{1/2} = -2{\cdot}0$ V *vs.* standard calomel electrode (stationary voltammetry). Exhaustive reduction at this potential ($n = 1$ by coulometry) leads to a gold deposit on the platinum electrode (identified by electron probe microanalysis) and to the release of two M^- per reduced $(\text{M–Au–M})^-$. A standard quantity of M^- produced from M_2 electroreduction was used to identify and to titrate the reduction products of $(\text{M–Au–M})^-$, by comparison of $E_{1/2}$ and of the wave heights. However, after reduction of the $(\text{M–Au–M})^-$ species, followed by reoxidation, in the e.s.r. cavity, of M^- so generated, M· was identified by its e.s.r. signal (see Table 2, column **). On the basis of these results, we propose the following reduction scheme for $(\text{M–Au–M})^-$ (equation 2).

$$(\text{M–Au–M})^- + \text{e} \rightarrow \text{Au} + 2\ \text{M}^- \qquad (2)$$

The isocyanide Pt^{II} complexes M–PtL_2–M (L = Bu^tNC or $\text{C}_6\text{H}_{11}\text{NC}$)[9,10] show surprising behaviour and are reduced in an irreversible monoelectronic step, on a gold electrode in propylene carbonate + 0·1 M Et_4NClO_4. The experimental results of stationary voltammetry and cyclic voltammetry are given in Table 2. The $E_{1/2}$ values measured by stationary voltammetry follow the order: $\text{PtL}_2[\text{Fe(CO)}_3\text{NO}]_2 > \text{PtL}_2[\text{Co(CO)}_4]_2 > \text{PtL}_2[\text{Cr(CO)}_3(\eta\text{-C}_5\text{H}_5)]_2 > \text{PtL}_2[\text{Mn(CO)}_5]_2 > \text{PtL}_2[\text{Mo(CO)}_3(\eta\text{-C}_5\text{H}_5)]_2 > \text{PtL}_2[\text{W(CO)}_3(\eta\text{-C}_5\text{H}_5)]_2$.

This sequence parallels roughly the order of increasing covalency estimated by i.r. spectroscopy.[9] After potentiostatic coulometry on the plateau of the reduction wave, one M^- is liberated per M–PtL_2–M reduced. Potentiostatic coulometry in a e.s.r. spectrometer cavity (Bruker *X*-band), causes a signal to appear whose intensity increases during the course of the reduction. When the reduction is interrupted, this signal (see Table 2, column *) has a lifetime of *ca.* 30 min at room temperature. No hyperfine structure was observed for the radicals at 298 and at 77 K. (The only effect of decreasing the temperature to 77 K was

TABLE 2. Electrochemical reduction of M–PtL_2–M on a gold electrode in propylene carbonate and 0·1 M Et_4NClO_4

Reduced compound M–PtL_2–M	$E_{1/2}$ (cathode)/V *vs.* s.c.e. Au, 2000 r.p.m. Stationary voltammetry	E_p (cathode) v = 0·1 V s^{-1} Cyclic voltammetry[d]	E_p (anode) v = 1 V s^{-1} Cyclic voltammetry[e]	n	(*) e.s.r. M–PtL_2• 25 °C		(**) e.s.r. M• 25 °C[b]	
					Linewidth ΔH/Gauss	g	Linewidth ΔH/Gauss	g
M = $Cr(CO)_3(\eta\text{-}C_5H_5)$ L = Bu^tNC	−1·48	−1·60	−0·13	[a]	[a]		13·5	2·023
M = $Mo(CO)_3(\eta\text{-}C_5H_5)$ L = Bu^tNC	−1·52	−1·62	−0·03	[a]	[a]		5	1·955
M = $W(CO)_3(\eta\text{-}C_5H_5)$ L = Bu^tNC	−1·62	−1·75	−0·01	[a]	[a]		33	1·925 2·002
M = $Fe(CO)_3NO$ L = Bu^tNC	−1·10	−1·18	+0·20	1	60	2·031	21	2·035
M = $Co(CO)_4$ L = cyclo-$C_6H_{11}NC$	−1·25[c]	−1·28	+0·20	1	1800	2·648	150	2·165
M = $Mn(CO)_5$ L = cyclo-$C_6H_{11}NC$	−1·50	−1·60	−0·08	1	200	2·001	14	2·006

[a] Unable to be determined (saturated solutions) owing to poor solubility in the solvent. [b] Recent work (ref. 6) reports the occurrence of the $M(O_2)$• species. [c] In benzonitrile + $Bu^n_4NClO_4$ (0·1 M) Vahrenkamp and Madach measured −1·25 V *vs.* s.c.e. and n = 1 (personal communication). [d] Values obtained on freshly polished electrodes before passivation. [e] Rate was chosen in order to observe the current peak in spite of rapid diffusion of the species.

to narrow the e.s.r. signal.) Attempts to isolate pure reduction complexes failed. The reduction scheme in equation (3) is consistent with the experimental data.

$$\text{M–PtL}_2\text{–M} + 1e \rightarrow \text{M}^- + \text{M–PtL}_2^{\bullet} \qquad (3)$$

The generation of a radical having been demonstrated by e.s.r. spectroscopy, its identity was established from electrochemical measurements (1 electron exchanged, and generation of one M^- per M–PtL_2–M reduced).

The stabilization of the radical is probably due to the π-acceptor properties of the isocyanide ligands. It is clear, from recent work, that most of the known (often isocyanide) Pt^I species are dimeric with direct Pt–Pt bonds.[11] The only paramagnetic, and hence presumably monomeric Pt^I species, known so far have been obtained (i) by electro-reduction of dithiolene Pt^{II} complexes and of their amino analogues,[12] (ii) by γ- and electron-irradiation of $K_2[PtCl_6]$ single crystals.[13]

Thus, the present results demonstrate that electro-reduction of trimetallic PtM_2L_2 leads to novel Pt^I heterobimetallic paramagnetic species, and that the reactions of these complexes in solution may very well involve radical pathways.

As a result of electrochemical and e.s.r. (77 K) experiments carried out in extension of this work, we have observed that PtL_2X_2 (X = Cl, I) complexes are also monoelectronically reduced leading to the loss of one X^- per PtL_2X_2 and to the generation of a Pt^I radical [$E_{1/2}$ = −1·18 V, g = 2·048, ΔH = 80 G for $Pt(\text{cyclo-}C_6H_{11}NC)_2I_2$, $E_{1/2}$ = −1·80 V, g = 2·005, ΔH = 7 G for $Pt(\text{cyclo-}C_6H_{11}NC)_2Cl_2$].

This behaviour appears to be typical for Pt^{II} complexes with appropriate ligands.

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