Electrochemical Behaviour of Mixed Tetrametallic Clusters with Pd_2M_2 and Pt_2M_2 Cores (M = Cr, Mo, W)

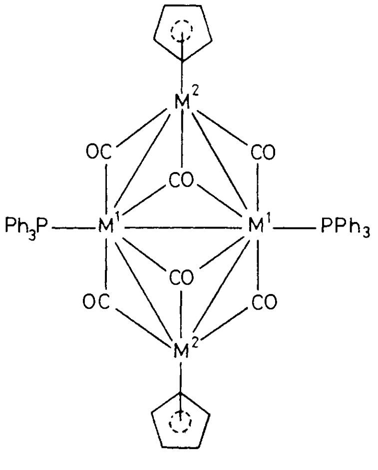
Rodolphe Jund,[a] Paul Lemoine,[a] Maurice Gross,[a] Robert Bender,[b] and Pierre Braunstein[b]

[a] *Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, E.R.A. au C.N.R.S. n° 468, Université Louis Pasteur, 4 rue Blaise Pascal, F-67000 Strasbourg, France*

[b] *Laboratoire de Chimie de Coordination, E.R.A. au C.N.R.S. n° 670, Université Louis Pasteur, 4 rue Blaise Pascal, F-67000 Strasbourg, France*

Tetrametallic clusters $[M^1M^2(\mu^3\text{-CO})(\mu^2\text{-CO})_2(C_5H_5)(PPh_3)]_2$ (M^1 = Pd, Pt; M^2 = Cr, Mo, W) exhibit an unexpected irreversible two-electron reduction leading to the rupture of the metallic core into identified fragments; in contrast, the first two oxidation waves of the clusters indicate that oxidation occurs in one-electron steps.

Several electrochemical studies have been carried out on homonuclear transition metal clusters but little is known about the electrochemistry of heteronuclear metal clusters.[1,2] As part of our studies on transition metal cluster electrochemistry,[1] we have examined the electrochemical properties of a new series of heterometallic clusters[3] of general formula $[M^1M^2(\mu^3\text{-CO})(\mu^2\text{-CO})_2(\eta^5\text{-}C_5H_5)(PPh_3)]_2$ (M^1 = Pd, Pt; M^2 = Cr, Mo, W) (**1**) which have recently been used as precursors of heterogeneous catalysts.[4] These compounds exhibit a planar metallic core in the solid state and remain unaltered in solution; this has been shown by i.r. and n.m.r. spectroscopy. The formal oxidation states of the metals have been described as +1 for M^1 and zero for M^2.[3] We now report the observation of a two-electron reduction process which is in contrast with the multiple one-electron reduction steps generally observed in clusters.[5]



(1)

The present clusters exhibit a single, well defined cathodic wave on a rotating platinum disc electrode (2000 r.p.m.; area 3.14 mm^2; $E_{1/2}$ in Table 1). Passivation of the Pt electrode was observed both in *N,N*-dimethylformamide (DMF) + 0.1M $[(C_6H_{13})_4N]ClO_4$ and in CH_2Cl_2 + $(Et_4N)ClO_4$: the limiting currents and the number *n* of electrons exchanged per mole of cluster (n = 1.4) were smaller than the calculated values for a two-electron process. After controlled-potential electrolysis of the Pd_2W_2 cluster, a metallic deposit on the Pt electrode was identified as Pd by scanning electron microscopy. Typical cyclic voltammetric curves are given in Figure 1.

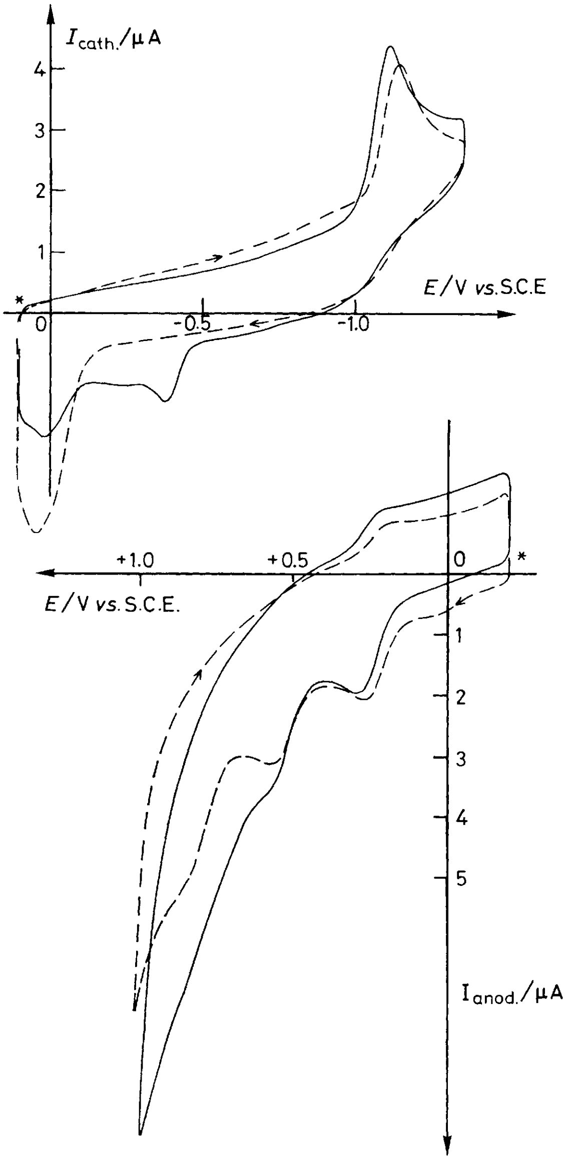
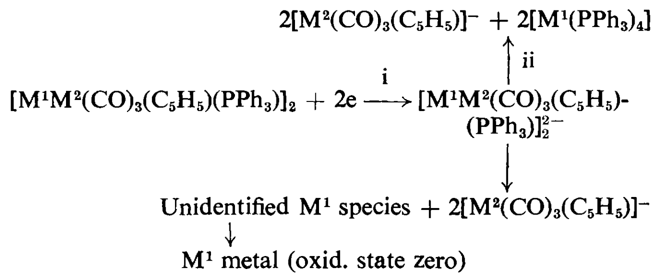


Figure 1. Cyclic voltammetry of $[PdW(CO)_3(C_5H_5)(PPh_3)]_2$ 10^{-4} M in DMF + 0.1 M Et_4NClO_4; Pt electrode, potential scan rate 0.5 V s^{-1}. Full line: without PPh_3; dashed line: in the presence of an excess of PPh_3 (3.74×10^{-3} M). An asterisk denotes the start of the scan.

One of the reoxidation peaks [at *ca.* 0 V *vs.* saturated calomel electrode (S.C.E.)] was identified as showing the oxidation of the anion $[M^2(CO)_3(C_5H_5)]^-$ which was also characterized by i.r. spectroscopy on totally reduced solutions.[1] The presence of a Pd^0 deposit on the electrode led us to infer that a second cluster-derived fragment might involve zero-valent Pd or Pt species which could not, however, be isolated or identified in solution. Addition to the electrolyte of an excess of PPh_3, which is electroinactive in reduction, allowed us to characterize, after exhaustive reduction, the complexes $M^1(PPh_3)_4$ by comparison with authentic samples. In addition, coulometric reduction of the clusters carried out with an excess of PPh_3 gave $n = 1.9 \pm 0.1$. In DMF, $Pt(PPh_3)_4$ and $Pd(PPh_3)_4$ are oxidized at $E_{1/2} = +0.03$ V *vs.* S.C.E. and $E_{1/2} = 0.05$ V *vs.* S.C.E., respectively (Figure 1). The irreversible two-electron† reduction of the studied clusters thus leads to their fragmentation (Scheme 1). The two Pt^I or Pd^I centres are formally electroreduced to Pt^0 or Pd^0 in one step. To our knowledge, this is the first example reported in which two metallic centres are simultaneously reduced in a single process within the electrochemical time scale.

Oxidation occurs in several steps, of which only the first two led to well defined signals (Figure 1). The clusters first undergo a one-electron oxidation step ($E_{1/2}$ in Table 1). In CH_2Cl_2 + 0.1 M $[(C_6H_{13})_4N]ClO_4$ the peak current ratio i_{pc}/i_{pa} from cyclic voltammetry experiments increases from 0.8 to 1.0 when the potential scan rate varies from 0.01 to 1 V s^{-1} whereas in DMF + 0.1M $(Et_4N)ClO_4$ i_{pc}/i_{pa} remains smaller than unity, even at 1 V s^{-1}, indicating the presence of chemical step(s) following the electron transfer. A second, ill defined one-electron oxidation step is observed at more anodic potentials (Table 1, Figure 1). This irreversible step is solvent- and



Scheme 1. Reduction of the mixed-metal clusters. i, Electrochemical step; ii, excess of PPh_3.

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† E.s.r. experiments (no radical), as well as the geometry of the curves obtained in differential and normal pulse polarography (current log transforms) and in cyclic voltammetry ($E_p - E_{p/2}$) also indicate that the reduction is a two-electron step within the time scale of the electrochemical experiments.

Table 1. Electrochemical results on $[M^1M^2(\mu^3\text{-}CO)(\mu^2\text{-}CO)_2(C_5H_5)(PPh_3)]_2$.[a]

					E_p (anod.) First step			
M^1	M^2	$E_{1/2}$ (cath.)	E_p (cath.)	$E_{1/2}$ (anod.) First step	Direct scan	Reverse scan	$E_{1/2}$ (anod.) Second step	E_p (anod.) Second step
Pd	Cr	−0.84	−0.85	+0.26	+0.30	+0.23	+1.15	+1.04
Pd	Mo	−0.99	−1.02	+0.29	+0.33	+0.26	+0.73	+0.73
Pd	W	−1.07	−1.09	+0.18	+0.22	+0.15	+0.66	+0.65
Pt	Cr	−1.17	−1.18	+0.21	+0.25	+0.18	+0.95	+0.98
Pt	Mo	−1.33	−1.34	+0.23	+0.27	+0.20	+0.61	+0.73
Pt	W	−1.42	−1.44	+0.08	+0.11	+0.04	+0.44	+0.40

[a] $E_{1/2}$ and E_p values in V *vs.* S.C.E.; E_p at 0.1 V s^{-1} for cathodic and anodic reactions. Conc. range = (0.90—2.02) $\times 10^{-4}$ M. Pt electrode. Cathodic reactions in DMF + 0.1 M Et_4NClO_4; anodic reactions in CH_2Cl_2 + 0.1 M $(C_6H_{13})_4NClO_4$.

$$\begin{tikzcd}
 & \text{Slow chemical step} \\
{[M^1M^2(CO)_3(C_5H_5)(PPh_3)]_2} \arrow[r, rightleftharpoons, "i"] & {[M^1M^2(CO)_3(C_5H_5)(PPh_3)]_2^{+} + 1e} \arrow[u] \arrow[d] \\
\text{Rapid fragmentation of the cluster} & {[M^1M^2(CO)_3(C_5H_5)(PPh_3)]_2^{2+} + 1e} \arrow[l]
\end{tikzcd}$$

Scheme 2. Oxidation of the mixed-metal clusters. i, Electrochemical step.

[PPh_3]-dependent (Figure 1). On the basis of these results, the oxidation process in CH_2Cl_2, shown in Scheme 2, may be proposed.

After exhaustive electrolysis of the Pd_2Mo_2 cluster in DMF + 0.1 M [$(C_6H_{13})_4N$]ClO_4 at potentials corresponding to the second oxidation step, two new cathodic signals were detected at *ca.* −0.45 V *vs.* S.C.E. and −0.95 V *vs.* S.C.E. These are identical to those obtained with the oxidation products of $[M^2(CO)_3(C_5H_5)]_2$ at +1.3 V *vs.* S.C.E. The cathodic signal at −0.45 V *vs.* S.C.E. was identified as the reduction of $[Mo(CO)_3 (C_5H_5) (DMF)]^+$ by comparison with an authentic sample.

The above results reveal that electrochemical oxidation of the clusters affects, as expected, the electron-rich M^2 centres, whereas electrochemical reduction involves the M^1 centres. Also, the results gathered in Table 1 clearly illustrate that the reduction potentials are cathodically shifted from Cr to W and from Pd to Pt, and thus parallel the basicity of the metals. On the other hand, the $M^1_2\,Cr_2$ and $M^1_2\,Mo_2$ clusters have very similar oxidation potentials, while $M^1_2\,W_2$ clusters are easier to oxidize.

Previous studies on metal–metal bonded carbonyl complexes have revealed metal–metal bond breaking induced by electroreduction.[6] This was explained by the involvement of a LUMO level with antibonding metallic character. It is therefore reasonable to suggest that an antibonding orbital of M^1–M^1 character is involved in the reduction of these clusters. Moreover, this explanation is fully consistent with the formal description of an oxidation state of +1 for M^1 and zero for M^2 centres.[3] In contrast, the HOMO level involved in the oxidation steps is probably of M^2 character.

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