Electrochemistry of Clusters. Part 4.* Redox Behaviour of Tetrametallic Clusters $[M^1{}_2M^2{}_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2(\mu\text{-}CO)_4(PR_3)_2]$ (M^1 = Pt or Pd; M^2 = Cr, Mo, or W; R = Me, Et, Bu^n, or Ph)

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Electrochemical characteristics of the planar tetrametallic clusters $[M^1{}_2M^2{}_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2\text{-}(\mu\text{-}CO)_4(PR_3)_2]$ (M^1 = Pt or Pd; M^2 = Cr, Mo, or W; R = Me, Et, Bu^n, or Ph) have been determined in the non-aqueous solvents dimethylformamide and 1,2-dichloroethane. The clusters undergo a two-electron reduction and two distinct one-electron oxidations. The reduction and the second oxidation steps are followed by chemical decomposition. Major species resulting from the sequence of reduction and chemical steps have been identified.

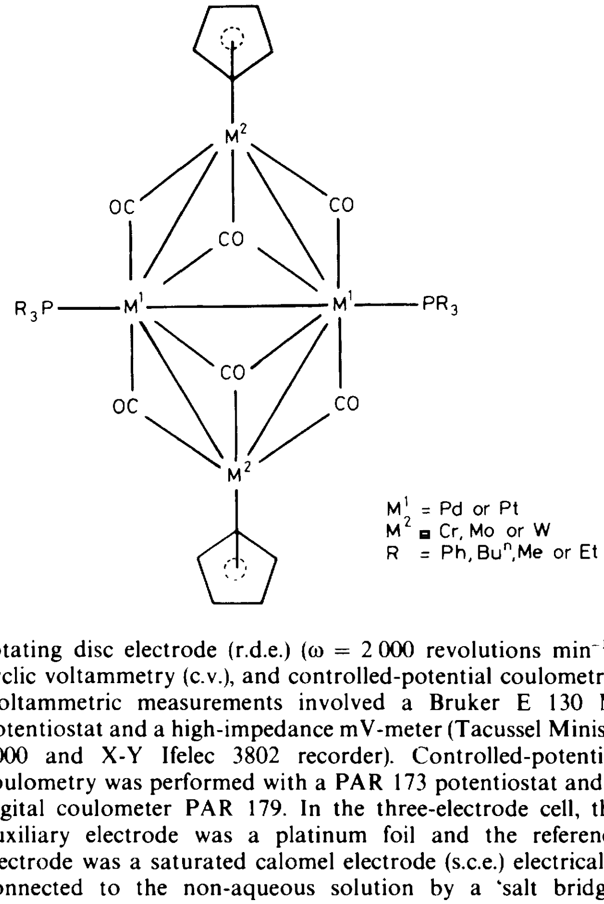
The electrochemical studies carried out up to now on tetrametallic clusters were mainly devoted to homometallic species involving a Fe_4,[1] Co_4,[2] or Ir_4[3] framework, and revealed that these clusters undergo several distinct one-electron steps in reduction as well as in oxidation. It was also observed that polydentate ligands like bis(diphenylphosphino)methane (dppm)[2] and tris(diphenylphosphino)methane $HC(PPh_2)_3$[4] increase the chemical stability of the electrogenerated cluster radical anions and cations. Less is known of the electrochemistry of mixed-metal clusters;[5] only those involving the metallic cores $PtCo_2$, Pt_2Co_2,[6] Co_2M^2 (M^2 = Cr, Mo, or W), CoM^3M^4 (M^3 = Fe, M^4 = Mo or Ni), $FeCo_2$,[7] and Ni_2Co[8] have been studied.

A preliminary communication[9] on the mixed tetrametallic clusters $[M^1{}_2M^2{}_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2(\mu\text{-}CO)_4(PR_3)_2]$ (M^1 = Pd or Pt; M^2 = Cr, Mo, or W; R = Ph) established that these clusters undergo a single two-electron irreversible reduction and two distinct one-electron oxidations. After exhaustive reduction, two types of fragments were identified: the anions $[M^2(\eta^5\text{-}C_5H_5)(CO)_3]^-$ and other zerovalent M^1-containing fragments. The crystal structure of these diamagnetic clusters is characterized by a planar metal framework[10] which remains unaltered in organic solvents, as indicated by i.r. and n.m.r. spectroscopy. An unprecedented feature of these clusters is the presence of two $M^2(\eta^5\text{-}C_5H_5)(CO)_3$ fragments interacting with *two* metal atoms, namely the M^1–M^1 unit. These interactions have been formally described as resulting from two four-electron donor $[M^2(\eta^5\text{-}C_5H_5)(CO)_3]^-$ anions bridging the d^9–d^9 $(L\rightarrow M^1\text{–}M^1\leftarrow L)^{2+}$ central unit.[11] The catalytic relevance of such clusters has been illustrated by the selective heterogeneous carbonylation of nitrobenzene to phenyl isocyanate.[12]

The present paper reports further investigations and new results on the electrochemical behaviour of these clusters and on the chemical reactions induced by electron transfer to and from the clusters. These chemical reactions were observed to be strongly dependent on the solution composition and major final products were identified. Also, significant substituent effects were detected in the reduction step, by changing R from Me to Et, Bu^n, and Ph.

Experimental

The electrochemical experiments were carried out with platinum electrodes (area 3.14 mm^2), by voltammetry at a rotating disc electrode (r.d.e.) (ω = 2 000 revolutions min^{-1}), cyclic voltammetry (c.v.), and controlled-potential coulometry. Voltammetric measurements involved a Bruker E 130 M potentiostat and a high-impedance mV-meter (Tacussel Minisis 6000 and X-Y Ifelec 3802 recorder). Controlled-potential coulometry was performed with a PAR 173 potentiostat and a digital coulometer PAR 179. In the three-electrode cell, the auxiliary electrode was a platinum foil and the reference electrode was a saturated calomel electrode (s.c.e.) electrically connected to the non-aqueous solution by a 'salt bridge' containing the same non-aqueous solvent and the supporting electrolyte.



Under the experimental conditions employed the ferrocene–ferrocenium couple exhibited $E_{\frac{1}{2}}$ = +0.54 V *vs.* s.c.e. in 1,2-dichloroethane + 0.1 mol dm^{-3} NBu_4ClO_4 and +0.49 V *vs.* s.c.e. in dimethylformamide (dmf) + 0.1 mol dm^{-3} NEt_4ClO_4.

The clusters were prepared according to published procedures.[11]

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* Part 3 is ref. 4.

The solvents used were anhydrous dmf and 1,2-dichloroethane to compare cluster (or cluster-derived fragments)–solvent co-ordinative interactions. Several tetra-alkylammonium salts were used as supporting electrolytes: tetraethylammonium perchlorate, tetrabutylammonium perchlorate, tetraoctylammonium perchlorate, tetrahexylammonium perchlorate, and tetrabutylammonium fluoride trihydrate, bromide, and hydrogensulphate.

It was verified that identical reduction potentials were measured at Pt (r.d.e.) and Hg (dropping mercury electrode). Therefore, only results obtained at platinum electrodes are reported, since Pt offers a wider anodic electroactivity range than Hg.

Infrared spectra in solutions were recorded on a Perkin-Elmer 398 spectrophotometer or after solvent removal and separation of the supporting electrolyte (KBr pellet). E.s.r. (*X*-band) spectra were recorded on a Bruker ER 200 D at 106 K.

Results

All clusters studied exhibit one reduction and two oxidation steps in dmf as solvent. Unless indicated otherwise, the R substituent in PR_3 was Ph.

Reduction of the Clusters.—The reduction of the tetranuclear clusters was studied under an argon atmosphere in carefully deaerated dmf solutions, and the effects of introducing the basic ligands PPh_3 and CO in the studied solutions were examined. In the presence of PPh_3 ligands (1—10 mmol dm^{-3}) all clusters are reducible at potentials not significantly different (Table 1) from those measured in the absence of PPh_3.[9] For a given constant metal (M^1 or M^2), the potentials were observed to shift as a function of the basicity of the second metal. For instance, a cathodic shift in reduction potentials was observed (Table 1) from Pd to Pt (310—350 mV for compounds $Pd_2M^2{}_2$ and $Pt_2M^2{}_2$), from Cr to Mo (140—160 mV for compounds $M^1{}_2Cr_2$ and $M^1{}_2Mo_2$), and from Mo to W (90—110 mV for compounds $M^1{}_2Mo_2$ and $M^1{}_2W_2$).

The two-electron reduction of the clusters[9] results in cleavage of the metal–metal bonds, at any time-scale of the electrochemical experiments. In addition, the following observations were made in stationary voltammetry at the r.d.e., in the absence of PPh_3 added to the solution: (*i*) the limiting current is smaller than expected for a two-electron process, suggesting electrode passivation; (*ii*) a Pd-containing deposit was identified by electron scanning microscopy of the platinum electrode after large-scale reduction of the cluster $[Pd_2W_2(\eta^5\text{-}C_5H_5)_2(CO)_6(PPh_3)_2]$; and (*iii*) in controlled-potential reductive coulometry, an average of 1.4—1.5 electrons were exchanged per mol of cluster, after which the current decreased to a residual value owing to electrode surface passivation.

Table 1. Oxidation/reduction characteristics of tetranuclear clusters in dmf. Stationary voltammetry at a platinum rotating disk electrode (2 000 revolutions min^{-1})

	Reduction[a]		Oxidation[b]	
Cluster	$E_{\frac{1}{2}}{}^{Red}$/ V *vs.* s.c.e.	log(I/ $I_{lim} - I$)	$E_{\frac{1}{2}}{}^{Ox_1}$ V *vs.* s.c.e.	$E_{\frac{1}{2}}{}^{Ox_2}$ V *vs.* s.c.e.
M^1 = Pd M^2 = Cr	−0.85	77	+0.31	+1.08
M^1 = Pd M^2 = Mo	−0.99	72	+0.32	+0.77
M^1 = Pd M^2 = W	−1.08	70	+0.25	+0.56
M^1 = Pt M^2 = Cr	−1.16	75	+0.23	+0.86
M^1 = Pt M^2 = Mo	−1.32	72	+0.24	+0.54
M^1 = Pt M^2 = W	−1.43	68	+0.14	+0.45

Concentration range: 0.9×10^{-4}—2.0×10^{-4} mol dm^{-3}.

[a] In dmf + 0.1 mol dm^{-3} NEt_4ClO_4 + 3.5×10^{-3} mol dm^{-3} PPh_3 ($E_{\frac{1}{2}}$ not affected by PPh_3) under Ar. Reductive coulometry: $n_{red} = 2$. [b] In dmf + 0.1 mol dm^{-3} NEt_4ClO_4.

In cyclic voltammetry, where the time-scale of the electrochemical measurements is smaller ($v \geqslant 0.1$ V s^{-1}) the return (oxidative) scan exhibits three re-oxidation peaks with Pt_2 [Figure 1(*a*)] and only two peaks with Pd_2 clusters [Figure 2(*a*)]. These peaks correspond to the oxidation of fragments generated by chemical decomposition of the reduced clusters. Among the fragments, $[M^2(\eta^5\text{-}C_5H_5)(CO)_3]^-$ was unambiguously identified for all studied clusters by (*a*) comparison with authentic samples obtained by electrochemical reduction of the dimers $[\{M^2(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$[13] and (*b*) observation of characteristic i.r. spectra,[11] ν(CO) at 1 895s and 1 770s, br cm^{-1} for M^2 = Mo and 1 888s and 1 772s, br cm^{-1} for M^2 = W.

Introduction of PPh_3 in the studied solutions did not modify the electron-transfer characteristics, but the following chemical interactions were identified between PPh_3 and dissolved species. First, none of the original clusters except Pd_2Cr_2 reacts spontaneously with PPh_3. Secondly, PPh_3 reacts with the reduced clusters (other than Pd_2Cr_2) or fragments therefrom as evidenced by the following observations. (*i*) Two oxidation peaks are present on the return scan of cyclic voltammograms for both $Pt_2M^2{}_2$ and $Pd_2M^2{}_2$ clusters [Figures 1(*b*) and 2(*b*)]. One of these peaks corresponds to the oxidation of $[M^2(\eta^5\text{-}C_5H_5)(CO)_3]^-$ already observed at the same potential in the absence of PPh_3,[9] E_{peak}(re-oxidation) at 0.2 V s^{-1}: −0.12

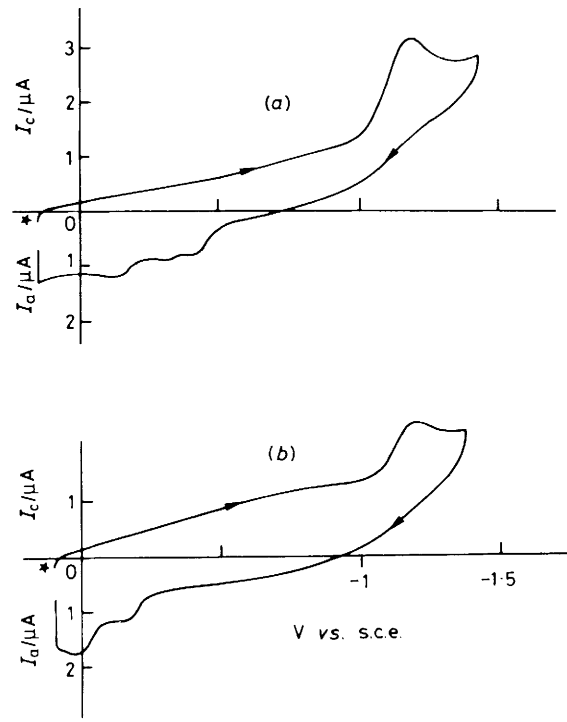

Figure 1. Cyclic voltammetry: reduction of the Pt_2Cr_2 cluster in dmf + 0.1 mol dm^{-3} NEt_4ClO_4 at a platinum electrode; 0.2 V s^{-1}. The asterisks indicate the start of the scans. (*a*) Cluster alone (1.7×10^{-4} mol dm^{-3}); (*b*) addition of free PPh_3 (3.5×10^{-3} mol dm^{-3})

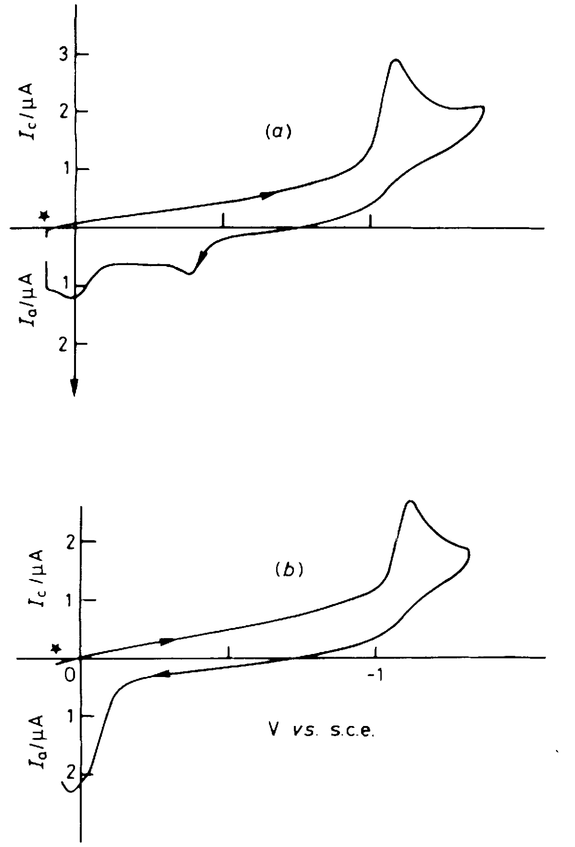

Figure 2. Cyclic voltammetry: reduction of the Pd_2W_2 cluster under the same conditions as in Figure 1: (a) cluster alone (1.5×10^{-4} mol dm^{-3}); (b) addition of free PPh_3 (3.5×10^{-3} mol dm^{-3})

for M^2 = Cr; −0.01 for M^2 = Mo; and +0.01 V *vs.* s.c.e. for M^2 = W. The second peak corresponds to the oxidation of $M^1(PPh_3)_4$ as shown in (*ii*). (*ii*) Authentic samples of $[Pt(PPh_3)_4]$ and of $[Pd(PPh_3)_4]$ were oxidized at $E_{\frac{1}{2}}$ = +0.03 and −0.02 V *vs.* s.c.e. respectively under comparable conditions (dmf + 0.1 mol dm^{-3} NEt_4ClO_4). These potentials were those measured on the second oxidation peak mentioned in (*i*) for Pt_2 and Pd_2 clusters respectively.* (*iii*) By comparison of limiting currents measured by stationary voltammetry at the r.d.e. with those of standard solutions of $[M^2(\eta^5\text{-}C_5H_5)(CO)_3]^-$ and of $[M^1(PPh_3)_4]$, it was established that each mol of reduced cluster generates 2 mol of $[M^1(PPh_3)_4]$ and 2 mol of $[M^2(\eta^5\text{-}C_5H_5)(CO)_3]^-$.

When reduced in CO-saturated 1,2-dichloroethane (+ about 0.05 mol dm^{-3} NEt_4ClO_4), Pt_2W_2 clusters† generate $[W(\eta^5\text{-}C_5H_5)(CO)_3]^-$ as above, plus oligomers $[Pt_3(CO)_3(PPh_3)_4]$ and $[Pt_5(CO)_6(PPh_3)_4]$. All these species were isolated and identified by i.r. spectroscopy: ν(CO) at 1 848w and 1 786s for Pt_3 cluster,[14] 1 995s, 1 887w, 1 852s, 1 810vs, and 1 785vs cm^{-1} for Pt_5 cluster.[15]

These results clearly demonstrate that electrochemical two-electron reduction of the studied tetranuclear clusters leads to rupture of the metal–metal bonds.

Table 2. Oxidation characteristics of the studied clusters in 1,2-dichloroethane + 0.05 mol dm^{-3} NBu_4ClO_4. Stationary voltammetry as in Table 1

	First oxidation		Second oxidation	
Cluster	$E_{\frac{1}{2}}^{Ox}$/ V *vs.* s.c.e.	log(I/ $I_{lim} - I$)	$E_{\frac{1}{2}}^{Ox}$/ V *vs.* s.c.e.	log(I/ $I_{lim} - I$)
M^1 = Pd M^2 = Cr	+0.25	60	+1.00	61
M^1 = Pd M^2 = Mo	+0.27	66	+0.70	58
M^1 = Pd M^2 = W	+0.19	62	+0.66	56
M^1 = Pt M^2 = Cr	+0.19	63	+0.88	54
M^1 = Pt M^2 = Mo	+0.20	63	+0.69	62
M^1 = Pt M^2 = W	+0.08	59	+0.54	59

Concentration: 10×10^{-4} to 1.6×10^{-4} mol dm^{-3}. Coulometry: $n_{ox_1} = 1$, $n_{ox_2} = 1$.

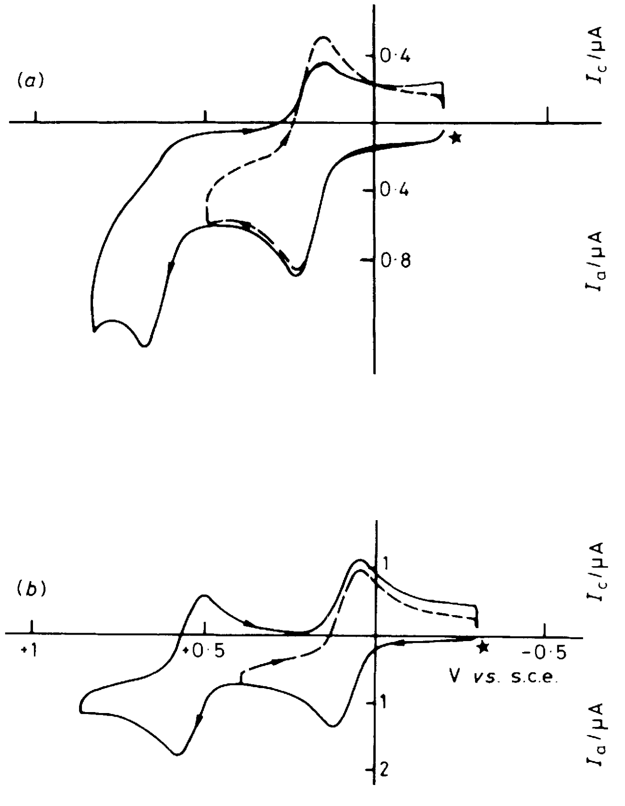

Figure 3. Oxidative cyclic voltammetry of clusters in 1,2-dichloroethane + 0.05 mol dm^{-3} NBu_4ClO_4 at a platinum electrode, 0.2 V s^{-1}: (a) Pd_2W_2 (1.0×10^{-4} mol dm^{-3}); (b) Pt_2W_2 (1.6×10^{-4} mol dm^{-3}); broken line indicates the first oxidation step only

Electrochemical Oxidation.—The studied clusters are oxidized in two steps, of which the potentials are solvent dependent as shown in Tables 1 and 2. In 1,2-dichloroethane both oxidation steps are almost reversible (Table 2). The first step near 0.2 V *vs.* s.c.e. is diffusion controlled (i_{lim} is proportional to concentration and $1/i_{lim}$ is linearly related to $1/\omega^{\frac{1}{2}}$ in stationary voltammetry at the r.d.e.) and no chemical step was detectable after this first oxidation, as evidenced by the following results: (a) I_{pa}/I_{pc} = 1

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* When 1 equiv. PPh_3 was added per mol of the Pt_2W_2 cluster, $[Pt(PPh_3)_3]$ ($E_{\frac{1}{2}}^{ox}$ = +0.67 V *vs.* s.c.e.) was identified in the solution instead of $[Pt(PPh_3)_4]$.

† $Pd_2M^2{}_2$ clusters decompose spontaneously in the presence of CO, generating dimers $[\{M^2(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$ and other species currently under investigation.

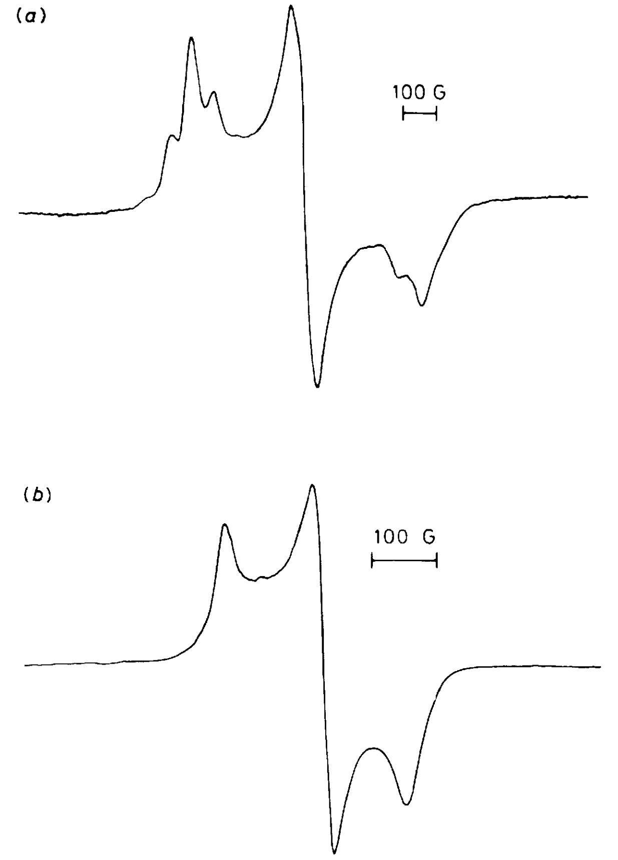


Figure 4. E.s.r. spectra at 106 K of frozen solutions (1,2-dichloroethane + 0.05 mol dm^{-3} NBu_4ClO_4) after one-electron oxidation of (*a*) Pt_2W_2 at +0.2 V *vs.* s.c.e. and (*b*) Pd_2W_2 at +0.4 V *vs.* s.c.e. G = 10^{-4} T

in cyclic voltammetry for v ranging from 0.02 to 1 V s^{-1} (Figure 3) and (*b*) exhaustive potentiostatic first oxidation of clusters ($n = 0.9 \pm 0.1$ electron per molecule), followed by one-electron reduction of the obtained solution, regenerated the starting cluster. On the other hand, in cyclic voltammetry the peak separation $E_p = E_{pa1} - E_{pc1}$ increases from 60 mV to higher values with increasing scan rates, thus allowing the calculation[16] of heterogeneous rate constants of about 1×10^{-2} to 2×10^{-2} cm s^{-1}.

The species generated in this first oxidation of the clusters were clearly identified as radical cations $[\text{cluster}]^{\cdot +}$. E.s.r. spectra of the oxidized clusters Pt_2W_2 and Pd_2W_2 were obtained after electrolysing at −30 °C solutions of the clusters (5×10^{-2} mol dm^{-3}) in 1,2-dichloroethane and 0.05 mol dm^{-3} NBu_4ClO_4 at a potential corresponding to the first anodic wave and subsequent freezing of the solution at 106 K (Figure 4). The g values obtained are: $g_{xx} = 1.943$, $g_{yy} = 2.015$, and $g_{zz} = 2.108$ ($\bar{g} = 2.022$) for Pd_2W_2; and $g_{xx} = 1.802$, $g_{yy} = 2.000$, and $g_{zz} = 2.237$ ($\bar{g} = 2.013$) for the Pt_2W_2 cluster. The e.s.r. spectra do not exhibit definite hyperfine structure. The g values obtained are consistent with a hole delocalized on the four metals and weakly interacting with the metallic centres. These results are in agreement with a highest occupied molecular orbital (h.o.m.o.) mainly based on metals in the clusters.

The second oxidation wave (at the r.d.e.) (Table 2) exhibits a limiting current of the same magnitude as that of the first wave (except for chromium clusters in which the second wave is higher than the first). For W- or Mo-containing clusters, potentiostatic coulometry confirms the exchange of one electron per molecule. The limiting current of this second wave is diffusion controlled, like that of the first wave. This second oxidation step of the clusters is followed by chemical decomposition of the electrogenerated species as indicated by cyclic voltammetry. On the time-scale of cyclic voltammetry, this decomposition is fast for Pt_2Cr_2 and for all $Pd_2M^2{}_2$ clusters (no return peak) [Figure 3(*a*)], whereas it is slow enough to compete with the electron transfer for Pt_2W_2 (I_{pc2}/I_{pa2} increases from 0.7 at 0.02 V s^{-1} to 1 at 1 V s^{-1}) [Figure 3(*b*)] and for Pt_2Mo_2 (I_{pc2}/I_{pa2} increases from 0.4 at 0.02 V s^{-1} to 0.6 at 1 V s^{-1}). On the other hand, the voltammetric characteristics of this second oxidation step are dependent on the supporting electrolyte in 1,2-dichloroethane as solvent, probably as a result of ion-pairing effects. In the presence (0.05 mol dm^{-3}) of the following electrolytes, $E_{\frac{1}{2}}$ of the second oxidation step of the Pt_2W_2 clusters shifted from +0.55 V *vs.* s.c.e. in the presence of NBu_4^+ to +0.53 V *vs.* s.c.e. for $N(C_6H_{13})_4^+$ and +0.51 V *vs.* s.c.e. for $N(C_8H_{17})_4^+$, the anion being ClO_4^-. On the other hand, this potential shifted from +0.55 V with ClO_4^- to +0.34 V with HSO_4^-, +0.32 V with F^- ($3H_2O$), and +0.24 V for Br^-, the cation being NBu_4^+.

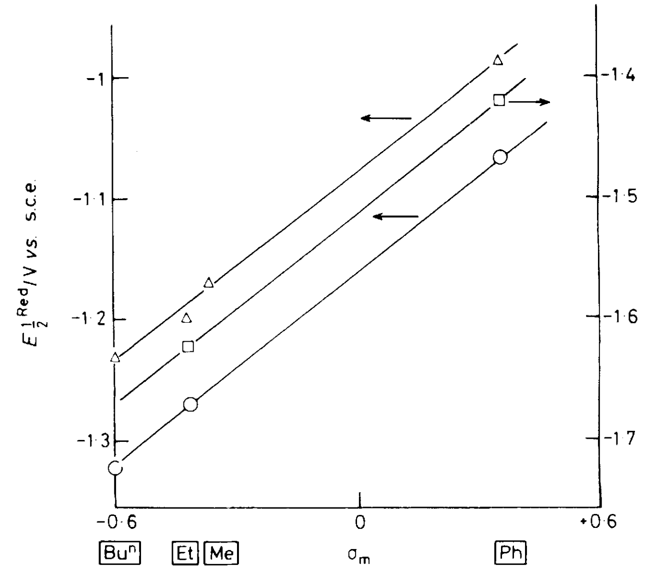


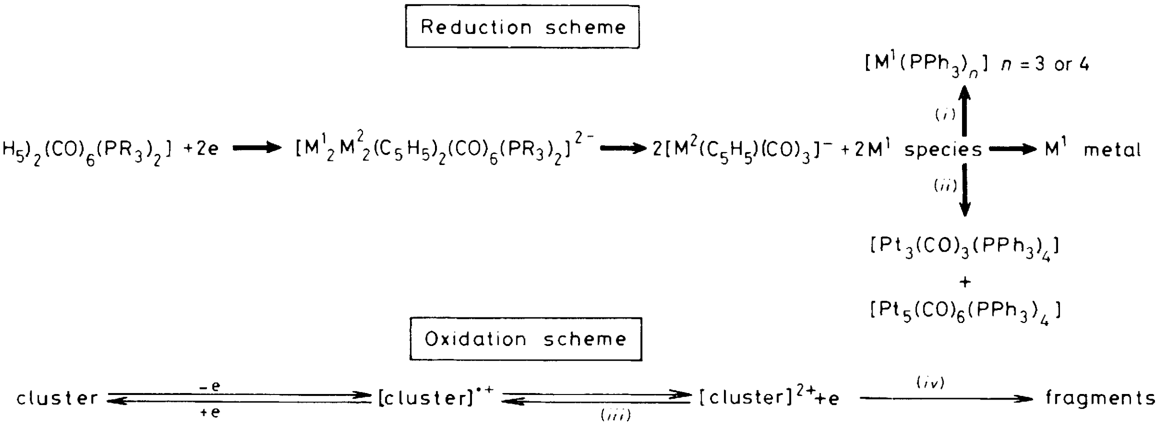
Figure 5. Linear free-energy relationship for the first reduction of the studied clusters (dmf + 0.1 mol dm^{-3} NEt_4ClO_4 platinum electrode): (△) M^1 = Pd, M^2 = Mo; (□), M^1 = Pt, M^2 = W; (○) M^1 = Pd, M^2 = W. $\rho = 0.251$

Consistent with the above co-ordination effects is the observation that changing the solvent modifies also the voltammetric characteristics in oxidation of the clusters. For instance, if 1,2-dichloroethane as solvent is replaced by dmf, the obtained radical cation undergoes chemical reaction in dmf as illustrated by a decrease of I_{pc}/I_{pa} in cyclic voltammetry [*e.g.* for Pt_2W_2 this ratio is 0.7 at 1 V s^{-1} in dmf, *cf.* 1.0 in 1,2-dichloroethane, Figure 3(*b*)].

Substituent Effects.—The effects of substituents R (Me, Et, Bu^n, or Ph) on the electrochemical reactivity were examined in several clusters (M^1 = Pd, M^2 = Mo or W) and also in part (R = Et or Ph) for the clusters with M^1 = Pt and M^2 = W. The corresponding oxidation/reduction potentials are given in Table 3. The measured reduction potentials are linearly correlated with the ordinary Hammett substituent constants, σ.[17] From the corresponding linear free-energy plots (Figure 5) the positive slope ($\rho = +0.251$) is consistent with the observation that the reduction becomes more difficult as the electron-donating effect of R increases, *i.e.* from Ph to Me, Et, and Bu^n.

Table 3. Substituent effects on the oxidation/reduction potentials (V *vs.* s.c.e.) of tetrametallic clusters in dmf + 0.1 mol dm^{-3} NEt_4ClO_4 at a platinum rotating disk electrode (2 000 revolutions min^{-1})

	M^1 = Pd, M^2 = Mo			M^1 = Pd, M^2 = W			M^1 = Pt, M^2 = W		
Ligand R	$E_{\frac{1}{2}}^{Red}$	$E_{\frac{1}{2}}^{Ox_1}$	$E_{\frac{1}{2}}^{Ox_2}$	$E_{\frac{1}{2}}^{Red}$	$E_{\frac{1}{2}}^{Ox_1}$	$E_{\frac{1}{2}}^{Ox_2}$	$E_{\frac{1}{2}}^{Red}$	$E_{\frac{1}{2}}^{Ox_1}$	$E_{\frac{1}{2}}^{Ox_2}$
Ph	−0.99	+0.32	+0.77	−1.07	+0.25	+0.56	−1.42	+0.14	+0.45
Me	−1.17	+0.24	+0.39						
Et	−1.20	+0.25	+0.53	−1.27	+0.16	+0.44	−1.57	+0.12	+0.39
Bu^n	−1.23	+0.26	+0.56	−1.32	+0.18	+0.47			



Scheme. (*i*) Excess of PPh_3, M^1 = Pt or Pd; (*ii*) CO, M^1 = Pt; (*iii*) only for Pt_2W_2 and Pt_2Mo_2 clusters: (*iv*) chemical decomposition

The observed effects of R on the oxidation potentials are much weaker than on the reduction potentials, the oxidation of the phenyl derivatives always requiring a higher energy.

Discussion

All the studied clusters undergo a single two-electron reduction which results in further decomposition to anions $[M^2(\eta^5\text{-}C_5H_5)(CO)_3]^-$ and formally zerovalent M^1-containing species. As indicated in the Scheme, the M^1 fragments generate a metallic deposit on the electrode, in the absence of co-ordinating species, whereas PPh_3 and CO ligands stabilize M^1 in the solution: $[M^1(PPh_3)_n]$ complexes (n = 3 or 4) are formed in the presence of PPh_3, while bubbling CO into the solution yields $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ and $[Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4]$. It is remarkable that the two-electron reduction of polymetallic clusters leads in all the few established examples[5,18] to rupture of a metal–metal bond.

In previously studied examples, the lowest unoccupied molecular orbital (l.u.m.o.) was antibonding and metal centred. In the present case, it is reasonable to assume that the l.u.m.o. is also antibonding and mostly centred on the metal framework, as the disruption of this core results upon the reduction. On the other hand, the observed Hammett plot (Figure 5) indicates that electron-donating ligands make the reduction of the cluster more difficult.

The oxidation of the studied clusters occurs in two distinct one-electron steps. As mentioned above the monocation radicals generated by the oxidation are reasonably stable and were characterized. On the other hand the dications are only stable for $[Pt_2M^2_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2(\mu\text{-}CO)_4(PPh_3)_2]$ (M^2 = Mo or W) on the time-scale of cyclic voltammetry and for other clusters they decompose more rapidly. In contrast to the reduction potentials, the oxidation potentials are rather insensitive to R substituent effects (Table 3). This could indicate that the phosphine ligand only plays a limited role in the h.o.m.o. consistent with e.s.r. results on the monocation radicals.

Further studies are in progress on the electrochemical characteristics of other polymetallic clusters.

Acknowledgements

We thank Dr. D. de Montauzon (Laboratoire de Chimie de Coordination, Toulouse) and Professor C. Lamy (Université of Poitiers) for helpful comments on the e.s.r. results.

References

1 J. A. Ferguson and T. J. Meyer, *Chem. Commun.*, 1971, 623; *J. Am Chem. Soc.*, 1972, **94**, 3409; Trinh-Toan, J. A. Ferguson, T. J. Meyer, and L. F. Dahl, *ibid.*, 1977, **99**, 408; C. L. Hill, J. Renaud, R. H. Holm, and L. E. Mortenson, *ibid.*, p. 2549.
2 J. Rimmelin, P. Lemoine, M. Gross, and D. de Montauzon, *Nouv. J. Chim.*, 1983, **7**, 453.
3 B. M. Peake, R. M. Robinson, T. Simpson, and D. Watson, *J. Chem. Soc., Chem. Commun.*, 1974, 945.
4 J. Rimmelin, P. Lemoine, M. Gross, A. Bashoun, and J. A. Osborn, *Nouv. J. Chim.*, in the press.
5 P. Lemoine, *Coord. Chem. Rev.*, 1982, **47**, 55 and refs. therein.
6 P. Lemoine, A. Giraudeau, M. Gross, R. Bender, and P. Braunstein, *J. Chem. Soc., Dalton Trans.*, 1981, 2059.
7 D. A. Young, *Inorg. Chem.*, 1981, **20**, 2049; B. M. Peake, P. H. Rieger, B. H. Robinson, and J. Simpson, *ibid.*, p. 2540; P. N. Lindsay, B. M. Peake, B. H. Robinson, J. Simpson, H. Honrath, H. Vahrenkamp, and A. M. Bond, *Organometallics*, 1984, **3**, 413.
8 L. R. Byers, V. A. Uchtman, and L. F. Dahl, *J. Am. Chem. Soc.*, 1981, **103**, 1942.
9 R. Jund, P. Lemoine, M. Gross, R. Bender, and P. Braunstein, *J. Chem. Soc., Chem. Commun.*, 1983, 86.
10 R. Bender, P. Braunstein, Y. Dusausoy, and J. Protas, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 596, *J. Organomet. Chem.*, 1979, **172**, C51.

11 R. Bender, P. Braunstein, J. M. Jud, and Y. Dusausoy, *Inorg. Chem.*, 1983, **22**, 3394; 1984, **23**, in the press.
12 P. Braunstein, R. Bender, and J. Kervennal, *Organometallics*, 1982, **1**, 1236.
13 (*a*) R. E. Dessy, P. M. Weissman, and R. L. Pohl, *J. Am. Chem. Soc.*, 1966, **88**, 5117; (*b*) A. Giraudeau, P. Lemoine, M. Gross, and P. Braunstein, *J. Organomet. Chem.*, 1980, **202**, 455.
14 J. Chatt, and P. Chini, *J. Chem. Soc. A*, 1970, 1538.
15 J. P. Barbier, R. Bender, P. Braunstein, J. Fischer, and L. Ricard, *J. Chem. Res.*, 1978 (*S*) 230; (*M*) 2913.
16 R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706; 1965, **37**, 667, 1351.
17 D. H. Mc Daniel, and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420; G. B. Parlin, and D. D. Perrin, *Chem. Soc. Rev.*, 1966, 75; J. Clark and D. D. Perrin, *ibid.*, 1964, 295; L. P. Hammett, 'Physical Organic Chemistry,' 2nd edn., McGraw-Hill, New York, 1970.
18 A. Bonny, T. J. Crane, and N. A. P. Kane-Maguire, *Inorg. Chim. Acta*, 1982, **65**, L83.

Received 9th July 1984; *Paper* 4/1185