ELECTROCHEMISTRY OF CLUSTERS

V *. STUDY OF BINUCLEAR COMPLEXES AND TRINUCLEAR CLUSTERS WITH Pd–Pd AND Pd–Pt BONDS STABILIZED BY Ph$_2$PCH$_2$PPh$_2$ LIGANDS

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Summary

Electrochemical characteristics of ten complexes containing Pd–Pd and Pd–Pt bonds are reported. The syntheses of the new cationic clusters [{PdMCo(CO)$_3$(μ-dppm)$_2$X}(PF$_6$)], M = Pt, X = PPh$_3$; or M = Pd, X = PPhMe$_2$) are described. The electrochemical results are solvent dependent. In 1,2-C$_2$H$_4$Cl$_2$ the bimetallic complexes bridged by two bis(diphenylphosphino)methane (dppm) ligands undergo an irreversible two-electron reduction and an irreversible one-electron oxidation. The reduction potentials mainly depend on the nature of the metal–metal bond, whereas the oxidation potentials are mostly influenced by the nature of the ligand. In DMSO, the tetranuclear [Pd$_2$Co$_2$(CO)$_7$(μ-dppm)$_2$], the trinuclear [Pd$_2$CoI-(CO)$_3$(μ-dppm)$_2$] and [{Pd$_2$Co(CO)$_3$(μ-dppm)$_2$PR$_3$}(PF$_6$)] clusters undergo two quasi-reversible one-electron reduction steps, whereas the corresponding tetranuclear cluster [PtPdCo$_2$(CO)$_7$(μ-dppm)$_2$], and the trinuclear clusters [PtPdCoI(CO)$_3$(μ-dppm)$_2$], and [{PtPdCo(CO)$_3$(μ-dppm)$_2$PR$_3$}(PF$_6$)] undergo a single quasi-reversible two-electron reduction. All the oxidation steps of the clusters are irreversible, the first oxidation step is assigned to the fragment attached to the triangular core: [Co(CO)$_4$]$^-$ and I$^-$, while further oxidation involves the cationic triangular cluster.

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* For parts I–IV see ref. 9–12.

Introduction

Little is known about the electrochemistry of metal–metal bonded palladium(I) and platinum(I) complexes, in spite of the increasing interest in these complexes, initially studied by Balch [1] and by Puddephatt et al. [2]. In contrast the electrochemical reduction of square planar platinum(II) complexes has been intensively studied, and shown to lead to platinum(I) or platinum(0) [3,4]. A chemical reduction of $[Pd_2(\mu\text{-dppm})_2Cl_2]$ (dppm = bis (diphenylphosphino)methane) has been reported [5a], viz.:

$$[Pd_2(\mu\text{-dppm})_2Cl_2] \xrightarrow[\text{dppm}]{\text{NaBH}_4} [Pd(dppm)_2] \qquad (1)$$
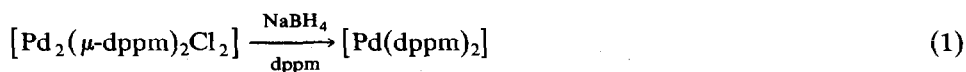
On reduction, the Pd–Pd and Pd–Cl bonds are cleaved, palladium(I) is reduced to palladium(0). The chemical oxidation of $[Pd_2(\mu\text{-dppm})_2X_2]$ by halogens produces isolable mononuclear palladium(II) complexes [6]. In a recent electrochemical study [7] of dinuclear rhodium(I) isocyanide complexes bridged by dppm ligands the role of the solvent appears to be dominant for this type of complexes.

Starting from the binuclear complexes $[PdM(\mu\text{-dppm})_2Cl_2]$ (M = Pd, Pt), new mixed-metal clusters were synthesized [8] by the reaction:

$$[PdMCl_2(\mu\text{-dppm})_2] + 2\,NaCo(CO)_4 \xrightarrow{\text{THF}} [PdMCo_2(CO)_7(\mu\text{-dppm})_2] + 2\,NaCl$$

$$(2)$$
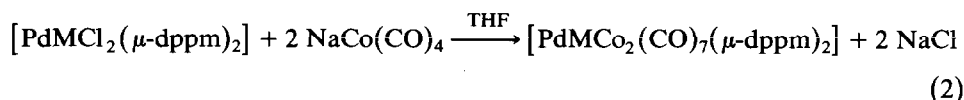
These clusters have a novel structure: the metallic core consists of a PdMCo triangle to which a $[Co(CO)_4]$ group is bonded through a Pd–Co bond (Fig. 1). The exocyclic Pd–Co bond is easily cleaved [8b], as indicated in eq. 3:
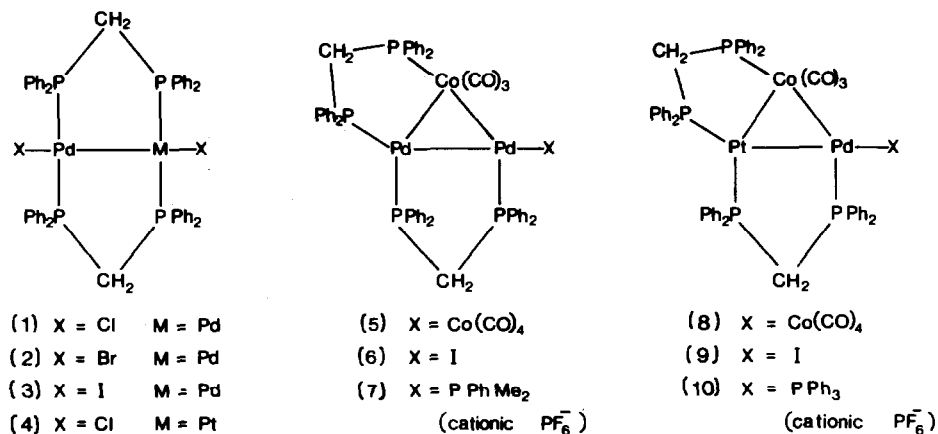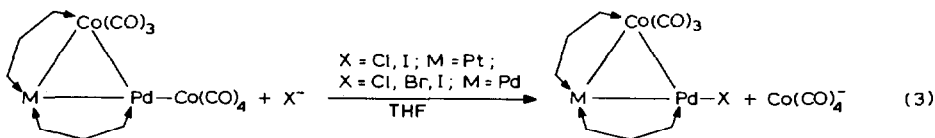

Fig. 1. The studied complexes.

The lability of the exocyclic [Co(CO)$_4$] group offers an enhanced reactivity for anion exchange. Other tetranuclear clusters having tetrahedral [9], butterfly [10] or lozenge [11] metallic cores, it was therefore of interest to compare our previous electrochemical results [9–12] with those obtained for this new family of clusters. The complexes shown in Fig. 1 were studied on a solid electrode (Pt or Au) by rotating disc electrode voltammetry, cyclic voltammetry, and controlled potential coulometry in non aqueous solvents.

Experimental

(a) Electrochemical data

The electrochemical experiments were carried out on Pt or Au electrode, of the same area: 3.14 mm^2, by voltammetry on rotating disc electrode (RDE) (ω 2000 rpm) and by cyclic voltammetry (CV). Voltammetric measurements involved a Bruker E130 M potentiostat and a high impedance mV-meter (Tacussel Minisis 6000 and X-Y Ifelec 3802 Recorder). In the three electrode cell, the auxiliary electrode was a Pt wire and the reference electrode was a saturated calomel electrode (SCE) electrically connected to the non-aqueous solution by a salt bridge containing the same non-aqueous solvent and supporting electrolyte as the studied solution.

Under the conditions we used the ferrocene/ferrocinium couple used as internal reference exhibited the following values: $E_{1/2} = +0.52$ V/vs. SCE in 1.2 C$_2$H$_4$Cl$_2$ + 0.1 M TBAP and $E_{1/2} = +0.41$ V/vs. SCE in DMSO + 0.1 M TEAP (TBAP = tetrabutylammonium perchlorate, TEAP = tetraethylammonium perchlorate, both recrystallized). Controlled potential coulometric measurements were carried out on a Pt or Au (area about 15 cm^2) in a two-compartment cell separated by a glass frit.

(b) Synthesis and spectroscopy

Experiments were carried out using Schlenk-tube techniques, under dry oxygen-free nitrogen. Solvents used for the synthesis of the clusters were distilled under nitrogen from sodium benzophenone ketyl prior to use, except for hexane which was dried and distilled over sodium [8]. Elemental analysis (C, H) were performed by the Service Central de Microanalyses du C.N.R.S. Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Perkin–Elmer 398 spectrophotometer as KBr pellets. The ^{31}P{^{1}H} NMR spectra were recorded at 81.015 MHz on a FT-Bruker SY-200 instrument. Positive phosphorus chemical shifts are downfield from H$_3$PO$_4$.

The compounds 1–3 [13], 4 [14], 5 [8a], 6, 8, 9 [8b] were prepared by published methods.

Synthesis of the complex [{Pd$_2$Co(CO)$_3$(μ-dppm)$_2$(PPhMe$_2$)}(PF$_6$)] (7). PPhMe$_2$ (0.051 ml, 0.39 mmol) was added to a solution of [Pd$_2$Co$_2$(CO)$_7$(μ-dppm)$_2$] (0.508 g, 0.39 mmol) in THF. The solution turned immediately from dark green to red and was stirred in the presence of NH$_4$PF$_6$ (excess). The solution was precipitated with hexane, filtered and the red solid washed with water. Recrystallization in THF/Et$_2$O at −20°C gave 7 as a microcrystalline powder (0.410 g, yield 75% based on Pd). (Anal. Found: C, 52.34; H, 4.02. C$_{61}$H$_{55}$CoF$_6$O$_3$P$_6$Pd$_2$ calcd.: C, 52.05; H, 3.94%); IR (KBr): ν(CO) at 1986(s), 1868(m, br) cm^{-1}.

Preparation of the complex [{PdPtCo(CO)$_3$(μ-dppm)$_2$(PPh$_3$)}(PF$_6$)] (10). A THF (50 ml) solution of [PdPtCoI(CO)$_3$(μ-dppm)$_2$] (0.181 g, 0.135 mmol), PPh$_3$ (0.049 g,

TABLE 1

ELECTROCHEMICAL CHARACTERISTICS OF COMPLEXES **1** TO **4** IN $1,2\text{-}C_2H_4Cl_2 + 0.1$ M TBAP ON PLATINUM ELECTRODE

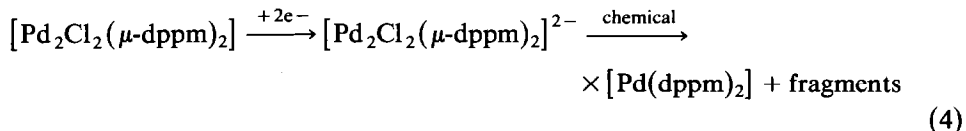| Compounds	Reduction				Oxidation			
	$E_{1/2}{}^a$ (V vs. SCE)	$E_{1/2}{}^a$ (V vs. NHE)	$\log \frac{I}{I_1-I}$ (mV)	n^b coulometry	$E_{1/2}{}^a$ (V vs. SCE)	$E_{1/2}{}^a$ (V vs. NHE)	$\log \frac{I}{I_1-I}$ (mV)	n^b coulometry
1 PPNCl	−1.26	−1.02	110	2	+0.98	+1.22	106	1
					+1.18^d	+1.42		
2 Bu₄NBr	−1.23	−0.99	164	2	+0.84	+1.08	91	1
					+0.86^d	+1.10		
3 Bu₄NI	−1.15	−0.91	152	2	+0.70	+0.94	78	1
					+0.42^d	+0.66		
4	−1.70	−1.46	126	2^c	+0.96	+1.20	90	1

^{a} All signals are irreversible (no return peak on the reverse scan of cyclic voltammetry). ^{b} Experimental value (± 0.1). ^{c} Value obtained by comparison of the wave heights of clusters **1** and **4**. ^{d} The $E_{1/2}$ values of the first oxidation wave of free halides in the same experimental conditions are given for comparison.

0.19 mmol) and TlPF$_6$ (0.08 g, 0.23 mmol) was stirred at room temperature for 0.5 h, after which the volume of the solution was reduced to ca. 10 ml and diethyl ether (10 ml) was added. The solution was filtered through Celite. Complex 10 was obtained as a light red microcrystalline powder by slow diffusion of ether (50 ml) into the solution (0.125 g, 57% based on Pt). (Anal. Found: C, 52.60; H, 3.68. C$_{71}$H$_{59}$CoF$_6$O$_3$P$_6$PdPt calcd.: C, 52.62; H, 3.67%); IR (THF): ν(CO), 2004(s) and 1861(m, br) cm^{-1}. Full experimental and spectroscopic data for 7 and 10 will be reported elsewhere.
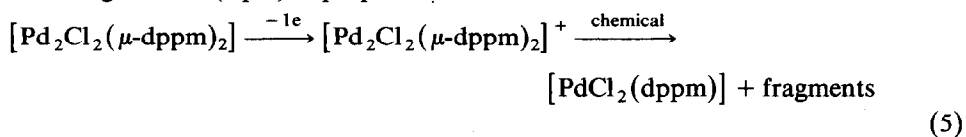
Results and discussion

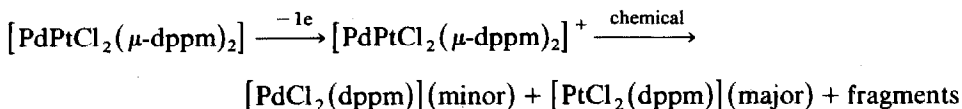### 1. Electrochemical reduction and oxidation of binuclear complexes 1–4

In 1,2-C$_2$H$_4$Cl$_2$ containing 0.1 M Bu$_4$NClO$_4$, the complexes 1 to 4 undergo an irreversible two-electron reduction at $E_{1/2}$ values shown in Table 1. These values are more dependent on the nature of the metal–metal bond (Pd–Pd or Pd–Pt) than on the halogen bonded to the Pd atom. The reduction potentials (Table 1) are cathodically shifted when the Pd–Pd bond is replaced by a Pd–Pt bond, in accord with an increase of the metal–metal interaction, on going from 1 to 4. These results are in agreement with the assumption that they arise from a LUMO, mostly metallic in character. Furthermore, the easier reduction of 3 compared to 1 is in agreement with a decrease of the metal–metal bond strength, resulting from the stronger *trans*-influence of I vs. Cl [13]. After exhaustive reduction of complexes 1 and 4, and solvent removal, the compound [Pd(dppm)$_2$] was identified by ^{31}P{^{1}H} NMR spectroscopy (CDCl$_3$/TBAP δ 24.0 ppm [5b]) among the reduction products. Thus, long time-scale electrolysis results in metal–metal and metal–halogen bond cleavage. The following reduction reaction (eq. 4) is proposed:

$$\left[Pd_2Cl_2(\mu\text{-dppm})_2\right] \xrightarrow{+2e-} \left[Pd_2Cl_2(\mu\text{-dppm})_2\right]^{2-} \xrightarrow{\text{chemical}}$$

$$\times\left[Pd(dppm)_2\right] + \text{fragments} \tag{4}$$

No platinum(0) containing species was identified by ^{31}P NMR in the reduced solution of 4.

Complexes 1–4 undergo an irreversible one-electron oxidation at $E_{1/2}$ values showing the same pattern as those of the free halide anions (Table 1). These values are only a little dependent on the metal, in agreement with the assumption that they arise from a HOMO mainly metal–halogen in character. After exhaustive oxidation of 1 and solvent removal, the complex [PdCl$_2$(dppm)] was identified among the oxidation products by comparison with an authentic sample [15]: ^{31}P{^{1}H} NMR (1,2-C$_2$H$_4$Cl$_2$; TBAP/CDCl$_3$) δ −52.8 ppm . Similarly, long time scale oxidation of 4 led us to identify by ^{31}P{^{1}H} NMR spectroscopy (δ −54.1(s) and δ −64.7(s) ppm, with ^{195}Pt satellites ^1J(Pt–P) 3088 Hz [16]) the complexes [PdCl$_2$(dppm)] (minor) and [PtCl$_2$(dppm)] (major) among the oxidation products. Thus the oxidation of complexes 1 and 4 results in the rupture of the metal–metal bond. The following scheme (eq. 5) is proposed:

$$\left[Pd_2Cl_2(\mu\text{-dppm})_2\right] \xrightarrow{-1e} \left[Pd_2Cl_2(\mu\text{-dppm})_2\right]^+ \xrightarrow{\text{chemical}}$$

$$\left[PdCl_2(dppm)\right] + \text{fragments} \tag{5}$$

$$[PdPtCl_2(\mu\text{-dppm})_2] \xrightarrow{-1e} [PdPtCl_2(\mu\text{-dppm})_2]^+ \xrightarrow{\text{chemical}}$$

$$[PdCl_2(dppm)](\text{minor}) + [PtCl_2(dppm)](\text{major}) + \text{fragments}$$

2. Electrochemical characteristics of clusters 5–10

The electrochemical behaviour of clusters **5–10** is solvent dependent with respect to the nature of the electroactive species present [17]. In $1,2\text{-}C_2H_4Cl_2$ complexes **5** and **8** progressively change colour (from green to red) indicating that a dissociation occurs, and no reproducible electrochemical results could be obtained because this dissociation was followed by decomposition.

In DMSO, the colour change is very rapid but no decomposition occurs, and so reproducible electrochemical results can be obtained. It was shown independently that clusters **5** and **8** dissociate in CH_3CN [8b,c] (donicity = 14.9 [18]) according to eq. 6:

green   red

(**5**, M = Pd ;   (**11**, M = Pd ;

 8, M = Pt)   **12**, M = Pt)

(6)
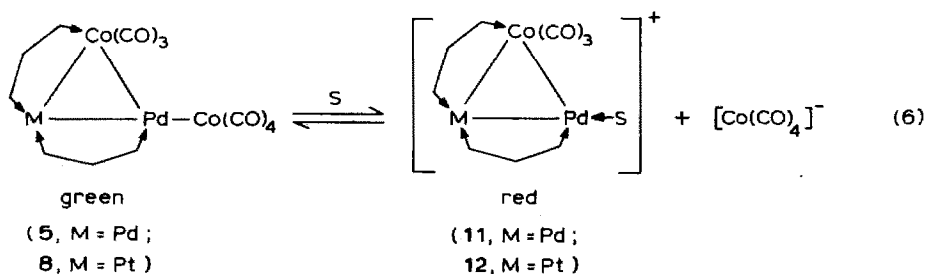
A similar dissociation also occurs in DMSO (DN = 29.8 [18]); the IR absorption at $\nu(CO)$ 1886 cm^{-1} and the electrochemical oxidation step at $+0.20$ V [10,19] indicates the presence of $[Co(CO)_4]^-$. $^{31}P\{^1H\}$ NMR and UV spectroscopy results show that equilibrium 6 is shifted to the right in DMSO. The results described below were obtained in DMSO containing 0.1 M TEAP.

Although we could not find any evidence for dissociation of **6** and **9** in DMSO (eq. 2) using ^{31}P NMR spectroscopy, our electrochemical results indicate however

(**6**, M = Pd ;   (**11**, M = Pd ;

 9 M = Pt)   **12**, M = Pt)

(7)
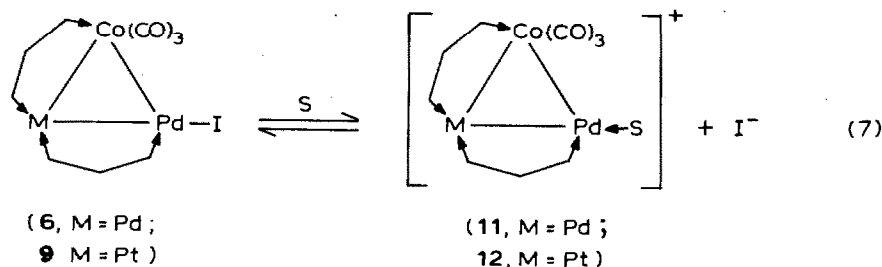
that **6** and **9** are totally dissociated. These apparently contradictory observations could be explained by the very different concentrations used in the NMR experiments ($\sim 10^{-2}$ M) and in the electrochemical measurements ($\sim 10^{-4}$ M).

The cationic clusters **7** and **10** are not dissociated in DMSO. This is consistent with a relatively strong coordination of the monodentate tertiary phosphine to the
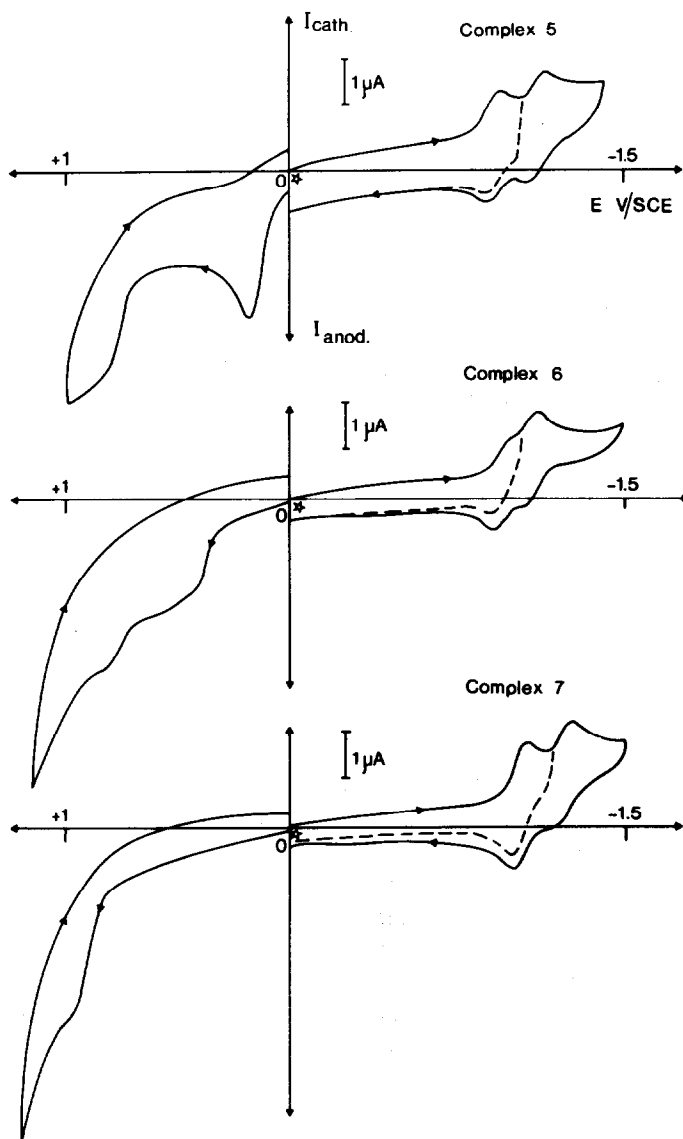
Fig. 2. Cyclic voltammetry of clusters **5–7**. 4×10^{-4} M 1^{-1} in DMSO+0.1 M TEAP on Pt electrode at 0.1 V s^{-1}; 20°C. *start of the scan.

palladium centre [8c]. In DMSO containing 0.1 M TEAP, the clusters **5, 6** and **7**, with Pd–Pd bonds, undergo two reversible one-electron reduction steps (Fig. 2) whereas the clusters **8, 9** and **10**, with Pd–Pt bonds show a single reversible two-electron reduction step (Fig. 3). All these reduction steps are only reversible on the time scale of cyclic voltammetry (the current peak ratio in cyclic voltammetry i_{pa}/i_{pc} are collected in Table 2). As I$^-$ and [Co(CO)$_4$]$^-$ are not reducible in the potential range explored, it can be concluded that the cationic species **11** and **12** (eq.

TABLE 2

ELECTROCHEMICAL RESULTS OF CLUSTERS 5 TO 10 IN DMSO CONTAINING 0.1 M TEAP, ON Pt AND Au ELECTRODES

Compounds	Reduction[a]						First oxidation step[b]			
		$E_{1/2}$ (V vs. SCE)	$E_{1/2}$ (V vs. NHE)	$\log \frac{I}{I_1 - I}$ (mV)	$\frac{I_{pa}}{I_{pc}}$[a]	n coulometry	$E_{1/2}$ (V vs. SCE)	$E_{1/2}$ (V vs. NHE)	$\log \frac{I}{I_1 - I}$ (mV)	n coulometry
5	First step	−0.90	−0.66	67	0.85	1	+0.20	+0.44	79	2
	Second step	−1.15	−0.91	66	0.84	1				
6	First step	−0.96	−0.72	80	0.80	1	+0.37	+0.61	60	2
	Second step	−1.14	−0.90	62	0.96	1				
7	First step	−1.04	−0.80	58	0.97	1	+0.85	+1.09	90	2
	Second step	−1.27	−1.03	84	1.0	1				
8		−1.13	−0.89	50	0.77	2	+0.20	+0.44	78	2
9		−1.13	−0.89	46	0.77	2	+0.40	+0.64	74	2
10		−1.24	−1.00	47	0.75	2	+0.78	+1.02	84	2

[a] All reduction steps are reversible. [b] All oxidation steps are irreversible.
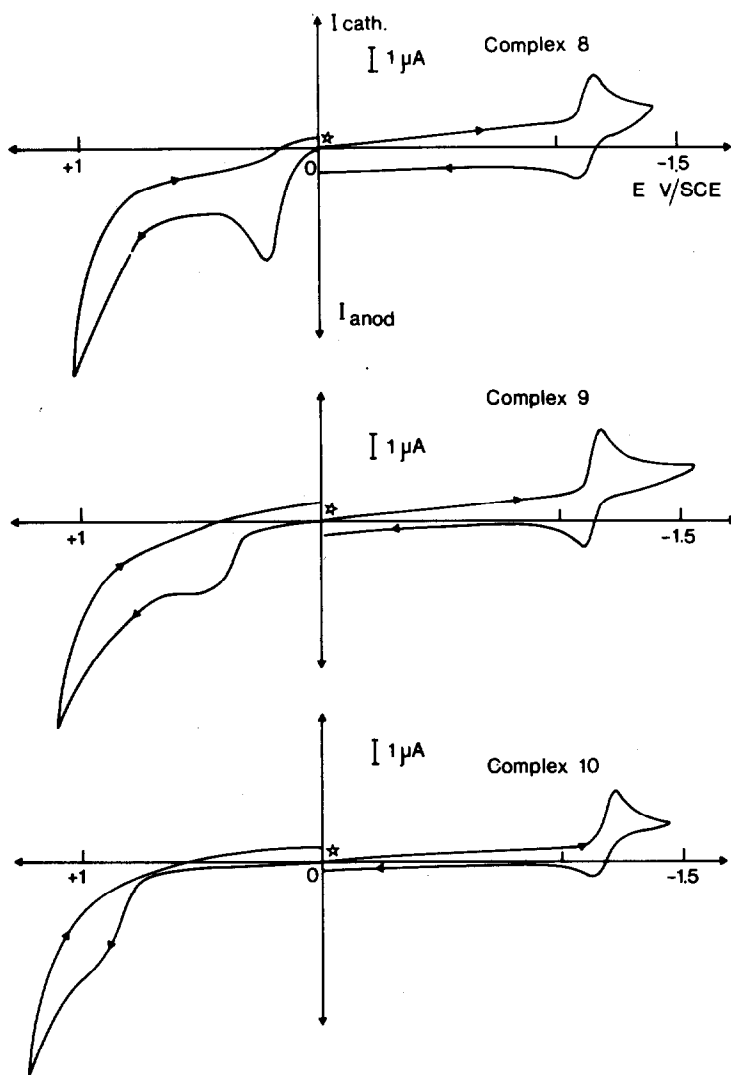
Fig. 3. Cyclic voltammetry of clusters **8–10**. 3×10^{-4} M l^{-1} in DMSO + 0.1 M TEAP on Pt electrode at 0.1 V s^{-1}; 20°C. *start of the scan.

6 and 7), generated by dissociation of clusters **5**, **6**, **8** and **9** in DMSO, are the electroactive species.

Complex **6** undergoes two quasi-reversible one-electron reduction steps at $E_{1/2}$ −0.96 V (wave slope 80 mV/log unit) and $E_{1/2}$ −1.15 V (wave slope 60 mV/log unit). The first broad signal is assigned to the reduction of complex **11**. Indeed, when an excess of Et$_4$NI is added to a solution of **6**, the equilibrium (eq. 7) is shifted to the left and the first wave is cathodically shifted to −1.0 V, whereas the second wave at $E_{1/2}$ −1.15 V remains unaffected. Under these conditions, the wave at −1.0 V is assigned to the reduction of **6**.

Clusters **7** and **10** are reduced at more cathodic potentials (about 100 mV) than

the corresponding clusters **11** and **12**. This is easily accounted for in terms of the increased electron density on the former clusters arising from the phosphine basicity. Clusters **7** and **10** show the same reduction pattern as the cationic clusters **11** and **12** (Fig. 2 and 3), respectively.

All the oxidation steps of complexes **5** to **10** are irreversible. Complexes **5**, **6**, **8** and **9** exhibit several ill-defined oxidation steps; the potential of the first oxidation step (Table 2) varying with the nature of X: $E_{1/2}$ +0.20 V vs. SCE for complexes **5** and **8** and $E_{1/2}$ +0.37 V vs./SCE for complexes **6** and **9**. Coulometric measurements show that complexes **5** and **8** undergo a two-electron oxidation. It was confirmed independently that, under the same experimental conditions, {PPN[Co(CO)$_4$]} (PPN = Ph$_3$P=N=PPh$_3$) is also oxidized at +0.20 V, in a two-electron step, in agreement with the reported oxidation of {PPN[Co(CO)$_4$]} in presence of dimethylphenylphosphine [19]. It can be assumed that DMSO plays a role equivalent to that of PMe$_2$Ph in our experiment.

Exhaustive oxidation of complexes **5** and **8** at +0.3 V vs./SCE does not modify the reduction signals, showing that the triangular cationic species **11** and **12** are still present and are not oxidized at that potential. Complexes **6** and **9** exhibit two close oxidation peaks (Fig. 2 and 3), which are not separated in RDE voltammetry. By controlled coulometry at +0.6 V, we found $n = 2$ (Table 2) for both (**6**) and (**9**). The first oxidation peak corresponds to the oxidation of free I$^-$ in solution [20], and we have confirmed independently that, under our experimental conditions, the oxidation of Et$_4$NI occurs at $E_{1/2}$ +0.38 V (first anodic wave) and $E_{1/2}$ +0.63 V (second anodic wave) in DMSO.

The complexes **5**, **6**, **8** and **9** exhibit further ill-defined oxidation signals. The major signal near +0.80 V vs. SCE may correspond to the oxidation of the triangular cationic species **11** and **12** (eq. 6 and 7). Clusters **7** and **10** undergo a single irreversible two-electron oxidation near $E_{1/2}$ +0.80 V (Table 2), which is assigned to the clusters since PF$_6^-$ is not oxidized at this potential. This is followed by the fragmentation of the metal core as shown by ^{31}P NMR spectroscopy of the oxidized solution of cluster **10**. One of the oxidation fragments was identified as [Pt(dppm)$_2$]$^{2+}$ (δ −36 ppm, ^1J(Pt–P) 2050 Hz).

In conclusion, the binuclear complexes **1–4** undergo irreversible oxidation and reduction steps leading to the rupture of their metal–metal bond. For the trinuclear species, conditions were found for the stabilization of the cationic clusters (donor solvent or phosphine coordination). The clusters containing Pd–Pd bonds behave quite differently (two one-electron reductions) from the corresponding ones containing Pd–Pt bonds (a single two-electron reduction). This is the case for more than one type of ligand attached to the Pd atom (X = DMSO or PR$_3$).

Further studies on the electrode mechanisms and the reversible CO fixation on these clusters are in progress [21].

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