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Electroanalytical Investigation on Dichlorobis(tertiary phosphine)platinum(II) Complexes

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Cis- and trans-dichlorobis(tertiary phosphine)platinum(II) complexes $[PtCl_2(PMe_xPh_{3-x})_2]$ *(x = 0,1,2,3) and* $[PtCl_2(PEt_3)_2]$ *have been investigated by cyclic voltammetry and controlled potential electrolysis in acetonitrile solution by using both platinum and mercury electrodes. The results show that the investigated platinum(II) compounds can be either oxidized or reduced to phosphine complexes of platinum(IV) and platinum(0), respectively. The dependence of the oxidation and reduction potential values on the nature of the phosphine ligands is discussed. Furthermore, it has been found that the trans-complexes are more easily oxidized than the cis-analogues and that a slow cis-trans isomerisation occurs in acetonitrile solution.*

Introduction

The chemistry of platinum coordination compounds has been extensively studied in recent years[1,2] and it is still an active field of research. However, little attention has been given to electrochemical studies of these complexes[3,4], in spite of the useful information which can be obtained on their electronic configuration and on the mechanism of reactions in which they may be involved as catalysts[5]. Furthermore, electrochemical methods might be used to prepare in a simpler way platinum complexes in higher or lower oxidation state.

The present paper reports a study of the electrochemical oxidation and reduction of a series of dichlorobis(phosphine)platinum(II) complexes in which the nature of the tertiary phosphine ligands has been varied.*

Experimental

Chemicals and Reagents

The *cis* and *trans*-platinum complexes, $[PtCl_2(PMe_xPh_{3-x})_2]$ (x = 0–3) and $[PtCl_2(PEt_3)_2]$, were prepared according to the literature methods. All other chemicals were of reagent grade purity. Reagent grade acetonitrile was purified by repeated distillation on phosphorus pentoxide and stored on molecular sieves (3 Å).

The supporting electrolyte, tetrabutylammonium perchlorate (TBAP), was prepared from perchloric acid and tetrabutylammonium hydroxide, recrystallized from ethanol and finally dried in a vacuum oven. 99.99% nitrogen, previously equilibrated to the vapour pressure of acetonitrile, was employed to remove oxygen from the test solutions.

Apparatus and Procedure

The experiments were carried out in a H shaped cell with cathodic and anodic compartments separated by a sintered glass disk at the temperature of 20° C.

All the potential values are referred to an aqueous saturated calomel electrode (SCE). This reference electrode was connected to the cell by an appropriate salt bridge.

The electrical apparatus employed in the cyclic voltammetric experiments and in controlled potential electrolyses has been already described[6].

In the anodic investigation platinum electrodes were used (platinum sphere stationary microelectrode in the voltammetric tests, platinum foil in the controlled potential electrolyses); in the cathodic experiments mercury was used as electrode material (a gold sphere, freshly covered with a mercury layer in the voltammetric tests; a mercury pool in controlled potential electrolyses). In every case the counter electrode was a mercury pool.

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* A preliminary account of this work has been presented at the VII Meeting of Inorganic Chemistry, A.I.C.I., Pesaro, Italy, September 1974.

In all tests 50 ml of 0.1*M* TBAP acetonitrile solution were used and the platinum(II) complexes were added as weighed quantities.

In the controlled potential electrolyses carried out on *cis*-[$PtCl_2(PPh_3)_2$], 30% v/v benzene–acetonitrile was employed as solvent, in order to enhance the solubility of this complex.

Conductometric measurements were carried out by using a KLB 3216 B bridge.

^1H nmr spectra were recorded with a Bruker HF×10.

Recovery of the Oxidation Products

In the controlled potential electrolyses carried out in order to recover the electrolysis products, $NaClO_4$ was preferred to TBAP as supporting electrolyte since its solubility in chloroform is negligible. After completion of the electrolyses, the solvent was evaporated under vacuum and the residual solid was shaken with chloroform in order to separate the insoluble $NaClO_4$ from the soluble oxidation products. Evaporation under vacuum of the chloroform solution gave orange–yellow compounds.

Results

Platinum(II) Complexes Oxidation

Figure 1 shows the cyclic voltammogram recorded on a 10^{-3}*M* *cis*-[$PtCl_2(P(CH_3)_3)_2$] solution with a platinum working microelectrode, in the first cycle. Two rounded anodic peaks (*a* and *b*), the potentials of which slightly shifted towards more positive values in successive cycles, were obtained; the height of the first peak was about a quarter of that of peak *b*. On the reverse scan a cathodic peak (*c*) was observed only when peak *a* was traversed. A similar voltammetric behaviour was observed for the other *cis*-platinum (II) complexes. The rather low reproducibility of both peaks *a* and *b* prevented any accurate electrochemical investigation on the factors controlling their peak heights.

Table I reports the relative potential values of the peaks *a*, *b* and *c* for all the *cis* complexes investigated.

Controlled potential coulometric experiments carried out at potential values corresponding to the anodic peak *a*, showed that two mol of electrons per mol of platinum(II) complex were involved. The colour of the solution turned yellow.

From the beginning the electrolysis current was rather small and decreased very slowly up to the end of the electrolysis. This behaviour is consistent with an electrode process controlled by a preceding chemical reaction[7].

Voltammetric curves recorded at the end of the electrolyses indicated that also peak *b* disappeared together with peak *a*, while only the cathodic peak *c* could be detected, now exhibiting a diffusive character.

By carring out controlled potential coulometric experiments directly at potential values corresponding

TABLE I. Peak Potential Values Obtained on Pt Electrodes.

Compound	Peak *a* E_p/V	Peak *b* E_p/V	Peak *c* E_p/V
cis-[$PtCl_2(PMe_3)_2$]	+ 1.15	+ 1.80	– 0.20
cis-[$PtCl_2(PMe_2Ph)_2$]	+ 1.25	+ 1.85	– 0.20
cis-[$PtCl_2(PMePh_2)_2$]	+ 1.35	+ 1.95	– 0.20
cis-[$PtCl_2(PPh_3)_2$]	+ 1.55	+ 2.00	– 0.20
cis-[$PtCl_2(PEt_3)_2$]	+ 1.15	+ 1.80	– 0.20

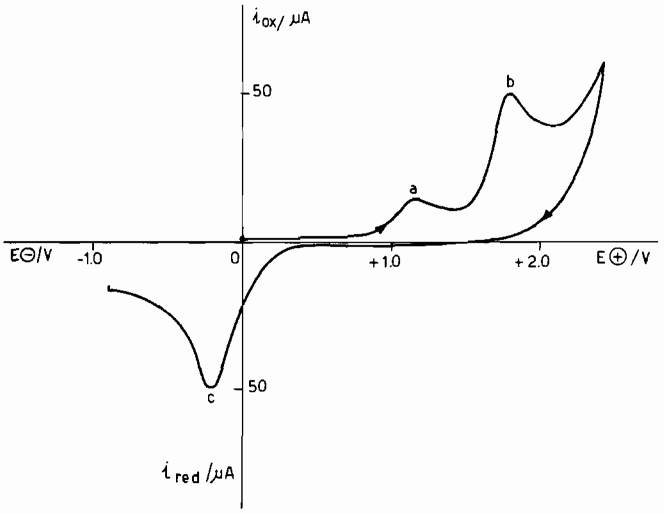

Figure 1. Cyclic voltammetric curve with platinum microelectrode: 10^{-3}*M* *cis*-[$PtCl_2(PMe_3)_2$], 0.1*M* TBAP, CH_3CN soln. Scan rate: 0.2 Vs^{-1}.

to the second anodic peak *b*, two mol of electrons per mol of compound were again obtained. Also in this case the oxidized solution was yellow and peak *c* was again detectable in the cyclic voltammetric tests. In all cases the peak *a* was identified as being due to the oxidation of the corresponding *trans* complexes by comparison with the voltammetric behaviour of authentic samples of these complexes.

The existence of a *cis–trans* equilibrium in acetonitrile solution agrees with the facts that the same n_{e^-} value (two) was found in coulometric experiments carried out both at peak *a* and *b*, and that the same product (peak *c*) was obtained in both cases. Furthermore, the voltammetric picture shown by the *trans* complexes changed with time: at first only the peak *a* was observed, subsequently the height of this peak slowly decreased while peak *b* appeared.

When coulometric tests were performed at potential values corresponding to peak *c* on the previously oxidized platinum(II) solutions (either at peak *a* or peak *b*) a n_{e^-} value of two was again obtained. The solution became colourless and the voltammetric tests showed both peak *a* and *b*, as in the original *cis*-platinum(II) complex solution. In order to check the formation of a platinum(IV) complex in the oxidation processes, the oxidation product was recovered by the procedure described in the experimental section; its elemental analysis agreed with the formula

$$[PtCl_2(CH_3CN)_2(PR_3)_2](ClO_4)_2.$$

In addition the ^1H n.m.r. spectrum in $CDCl_3$ confirms the presence of ligating acetonitrile, its resonance occurring at 2.16 ppm (free CH_3CN occurs at 2.00 ppm). In this connection we have checked that known platinum(IV) complexcs of the type $[PtCl_4(PR_3)_2]$[8] show a reduction peak of the same shape of peak *c* and in the same potential region.

Conductometric measurements carried out in acetonitrile solutions of *cis*-platinum(II) complexes indicated that a dissociation was operative to a slight extent for all the compounds studied.

Platinum(II) Complexes Reduction

The *cis*-platinum(II) complexes did not exhibit cathodic peaks on platinum electrodes with the exception of *cis*-$[PtCl_2(PPh_3)_2]$ which showed a hump in the solvent cathodic discharge.

By using mercury microelectrodes which allow more negative potential values to be reached, all the complexes studied exhibited sharp reduction peaks whose potential values are reported in Table II.

The linear dependence of the peak current both on the concentration of platinum(II) complexes and on the square root of the scan rate (30mV s^{-1}–3V s^{-1}) indicated the diffusive character of these cathodic peaks. It could also be observed that the E_p values shifted towards more cathodic potentials by increasing the scan rate, thus indicating that the processes involved are irreversible.

The *trans*-platinum(II) complexes underwent reduction at the same potential values as the corresponding *cis* complexes.

TABLE II. Peak Potential Values Obtained on Hg Electrodes.

Cis and *Trans* Compound	Peak Potential Value, E_p/V
$[PtCl_2(PMe_3)_2]$	−2.20
$[PtCl_2(PMe_2Ph)_2]$	−1.80
$[PtCl_2(PMePh_2)_2]$	−1.70
$[PtCl_2(PPh_3)_2]$	−1.60
$[PtCl_2(PEt_3)_2]$	−2.20

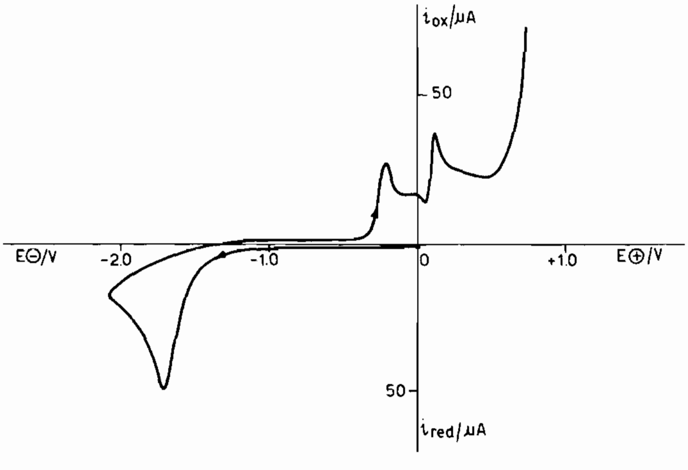

Figure 2. Cyclic voltammetric curve with mercury microelectrode: 10^{-3} *M* *cis*-$[PtCl_2(PMePh_2)_2]$, 0.1 *M* TBAP, CH_3CN soln. Scan rate : 0.2 Vs^{-1}.

The only anodic peaks associated with the cathodic process were those attributable to the oxidation of the mercury electrode in the presence of chloride ion (Figure 2). This assignment was made by comparison with the voltammetric picture exhibited by an acetonitrile solution of tetrabutylammonium chloride.

Controlled potential coulometric experiments showed that for all platinum(II) complexes two mol of electrons per mol of metal were involved. During the electrolyses the solution became progressively orange–brown. Voltammetric tests, performed with mercury electrodes at the end of these electrolyses, revealed the presence of free chloride ions in the solution.

When a platinum microelectrode was used to test the electrolyzed solution, two anodic peaks could be detected: the first, small in height, occurs at about –0.1V and was not diffusive in character. The current relative to this peak quickly decreased with time indicating a poisoning effect of the oxidation product. The process involved is probably the re-oxidation of a Pt(0) species. The second anodic peak, located at + 1.05 V, was attributed to the oxidation of free chloride ions on platinum electrodes by comparison with the voltammetric behaviour of a pure sample of tetrabutylammonium chloride.

In an attempt to isolate the reduction product by the separation procedure described in the experimental section for the oxidation, the electrolysis was carried out in acetonitrile solution with $NaClO_4$ as supporting electrolyte. However, no pure compound could be isolated. Nevertheless, treatment of the benzene extract with gaseous HCl gave hydrido derivatives, a reaction typical of platinum(0) species[9].

Discussion

The results obtained point out that all the investigated platinum(II) complexes can be electrochemically oxidized or reduced in acetonitrile solution.

In the oxidation process platinum(IV) complexes are formed and the coulometric data indicate that this process is a two electron one and no platinum(III) intermediate was observed:

$$\textit{trans}\text{ or }\textit{cis}\text{-}[PtCl_2(PMe_xPh_{3-x})_2] \rightarrow [PtCl_2(PMe_xPh_{3-x})_2]^{2+} + 2\ e^- \text{ (where } x = 0, 1, 2, 3).$$

The platinum(IV) complexes achieve their required hexacoordination by ligation of two solvent molecules as shown by their ^1H n.m.r. spectra.

By comparing the heights of peaks *a* and *b* (Figure 1) it can be seen that the following equilibrium in acetonitrile favours the polar *cis* species:

$$\textit{trans}\text{-}[PtCl_2(PMe_xPh_{3-x})_2] \rightleftarrows \textit{cis}\text{-}[PtCl_2(PMe_xPh_{3-x})_2]$$

In fact, even if peak *a* is kinetic in character (which could be consistent with its rounded shape), the amount of the *trans* species in equilibrium with the *cis* one should be even lower than the amount indicated by its peak height. Moreover, the voltammetric data show that the *cis* compound is more difficult to oxidise that the *trans* one, in agreement with early potentiometric measurements[10]. One of the main factors which dictates this difference is presumably the lower relative energy of the highest filled orbitals of the *cis* isomer.

The conductometric measurements show that a small ionic dissociation of the *cis* complexes occurs in acetonitrile solution, suggesting that the *cis–trans* isomerisation mechanism involves a consecutive displacement *via* an ionic intermediate[11, 12].

The large difference between the oxidation potentials of Pt(II) complexes and the reduction potentials of Pt(IV) (Table I) indicate the complete irreversibility of the investigated electrode systems on platinum electrodes. This irreversibility is mainly due to the change in the structure and the transfer of two electrons occurring during the electrochemical processes.

The coulometric and voltammetric data on mercury electrodes indicate that the following electrochemical reaction operates in all cases:

$$\textit{cis}\text{ or }\textit{trans}\text{-}[PtCl_2(PMe_xPh_{3-x})_2] + 2\ e^- \rightarrow [Pt(PMe_xPh_{3-x})_2] + 2\ Cl^-$$

In all the experiments, both *cis* and *trans*-platinum(II) isomers are reduced at the same potential values. The different energy of the lowest empty *d* orbitals for the two isomers is probably a minor factor compared to other energy variations involved in the complicated reduction process.

The formally two-coordinate Pt(0) species could not be directly characterised because of its high reactivity, but the presence of such a species in the reduced solution of $[PtCl_2(PPh_3)_2]$ is confirmed by its characteristic reaction with HCl.

By considering the peak potential values relative both to the oxidation processes (Table I) and to the reduction ones (Table II), it can be observed that the effects due to the nature of the phosphine groups are consistent with theoretical predictions. Thus by progressively substituting methyl with phenyl groups – that is by enhancing the electron withdrawing effect of the phosphine ligands and hence their ability to stabilise the lower oxidation states – the reduction process becomes easier while the anodic oxidation is made more difficult. On the other hand, no significant difference was observed for the electrochemical behaviour of PMe_3 and PEt_3 derivatives.

That the same reduction potential is exhibited by all the platinum(IV) complexes (peak *c* Table I) can be explained since a small effect of the phosphine groups on the charge density of the platinum atom in a doubly-charged molecule is to be expected.

Finally it can be remarked that we have shown that electrochemical preparation of both platinum(IV) and platinum(0) complexes is feasible.

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