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A Re-investigation of the Electrochemistry of Isomeric $[PtCl_2(PR_3)_2]$ Complexes by Cyclic Voltammetry

J. A. DAVIES* and V. UMA

Department of Chemistry, College of Arts and Sciences, University of Toledo, Toledo, Ohio 43606, U.S.A.

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Introduction

The factors affecting the redox behavior of tertiary phosphine complexes of the platinum metals have been of interest for many years [1], particularly since the catalytic activity of such complexes is often governed by their ability to participate in oxidative addition–reductive elimination sequences [2, 3]. Among the simplest members of this class of compound are the isomeric tertiary phosphine complexes *cis* and *trans*-$[PtCl_2(PR_3)_2]$ and yet the available literature on the electrochemistry of such compounds is in many ways contradictory. In an early study [1] of *cis* and *trans*-$[PtCl_2(P\text{-}n\text{-}Pr_3)_2]$ in a mixed water/phenol solvent system, it was found that the *trans* isomer was more easily oxidized than the *cis*-isomer at a gold electrode. The same conclusion was reached after a cyclic voltammetric study [4] of a series of $[PtCl_2(PR_3)_2]$ complexes in acetonitrile solution at a platinum electrode. These authors report, however, that the Pt(II) → Pt(0) reductions of the series of $[PtCl_2(PR_3)_2]$ complexes occur at the same potential for *cis* and *trans* isomers of a given tertiary phosphine complex, in acetonitrile solution at a gold amalgam electrode [4]. Surprisingly, investigations of these latter systems at a platinum electrode are reported to give rise to no meaningful reductive processes [4].

In order to gain further understanding of the redox behavior of these platinum(II) complexes we have re-investigated the *cis* and *trans*-$[PtCl_2(PR_3)_2]$ systems in acetonitrile and acetonitrile/benzene solvents at both platinum and gold amalgam electrodes by cyclic voltammetry. We have found that our results, and those existing previously, are explicable when the *trans–cis* isomerization of these complexes, and the chemistry of the generated PR_3 ligands themselves, are taken into account. This report concentrates on the Pt(II) → Pt(0) reduction of *cis* and *trans*-$[PtCl_2(PPh_3)_2]$ and the nature of the *trans–cis* isomerization reaction.

Experimental

Cis-$[PtCl_2(PPh_3)_2]$ [5] and *trans*-$[PtCl_2(PPh_3)_2]$ [6] were prepared as previously reported. Acetonitrile (Fischer, HPLC grade) was purified and dried by the literature method [7] and stored over activated 4A molecular sieve. Tributylammonium perchlorate (Aldrich, 98%) was recrystallized twice from ethanol and dried *in vacuo* at 50 °C prior to use as a supporting electrolyte (0.1 *M* concentration). Cyclic voltammograms were obtained by use of a Model CV-1A Bioanalytical Systems control unit equipped with a Houston 100 XY recorder. A single compartment cell, thermostatted to 25.0 ± 0.1 °C, was employed with an Ag/AgCl reference electrode (−35 mV vs SCE), a platinum wire counter-electrode, and platinum or gold amalgam working electrodes. Voltammograms were typically obtained for 3×10^{-3} *M* solutions of complex containing the supporting electrolyte. Benzene was employed as a cosolvent since both isomeric complexes are of very limited solubility in acetonitrile alone.

Results and Discussion

A cyclic voltammogram of *trans*-$[PtCl_2(PPh_3)_2]$ as a freshly prepared solution in acetonitrile/50% benzene at a gold amalgam electrode is shown in Fig. 1. The value of the peak potential, Ep(A), became more negative at higher scan-rates and the peak current was found to increase as the square root of the scan-rate, indicating a diffusive, irreversible process. The reverse scan showed the presence of an oxidative process, peak B, only when the potential of peak A had been traversed. The peak potential, Ep(A), for the reduction of *trans*-$[PtCl_2(PPh_3)_2]$ was determined to be −1.80 V. At a platinum working electrode the peak potential was difficult to determine without ambiguity since it occurred at *ca.* −2 V as a shoulder on the cathodic solvent discharge.

The cyclic voltammetric behavior of *cis*-$[PtCl_2(PPh_3)_2]$ at both platinum and gold amalgam electrodes was monitored as a function of time, in an

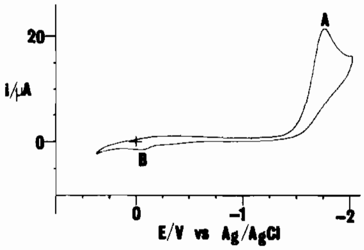

Fig. 1. Cyclic voltammogram of *trans*-$[PtCl_2(PPh_3)_2]$ in CH_3CN/50% C_6H_6 at a gold amalgam electrode (scan rate = 200 mV/sec).

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*Author to whom correspondence should be addressed.

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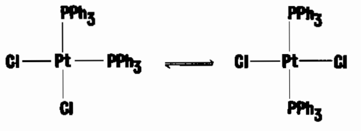
acetonitrile/30% benzene solvent system. Upon dissolution of the complex and rapid degassing, the voltammogram displayed an irreversible, reductive wave at potentials, Ep(C), of −1.60 V (Hg or −1.55 V (Pt) due the *cis*-isomer. After three hours, the voltammogram showed an additional peak as a shoulder at −1.80 V on a mercury electrode. On the platinum working electrode, the peak at −1.55 V was now of diminished intensity and a shoulder on the cathodic solvent discharge (*ca.* −2.0 V) was clearly discernable. Comparison of the data for the *trans*-$[PtCl_2(PPh_3)_2]$ complex with the additional peaks appearing with time in the voltammograms of the *cis*-isomer, indicate that the effects of a *cis-trans* equilibrium are being observed, eqn. 1:



$$\begin{array}{c} PPh_3 \\ | \\ Cl-Pt-PPh_3 \\ | \\ Cl \end{array} \rightleftharpoons \begin{array}{c} PPh_3 \\ | \\ Cl-Pt-Cl \\ | \\ PPh_3 \end{array} \qquad (1)$$

The voltammograms of *cis*-$[PtCl_2(PPh_3)_2]$ after three hours in solution (Fig. 2) show not only the additional peak due to the *trans*-isomer, but also a peak with an extremely low diffusion current which is barely discernable at potentials, Ep(D), of −0.90 V (Hg) or −0.82 V (Pt). It seemed likely that such a peak might be due to a readily reducible cationic intermediate in the isomerization process, such as are commonly postulated to be involved in the catalytic isomerization and nucleophilic displacement reactions of square planar d^8 complexes in general [8]. Independent synthesis and conductiometric studies, to be described in detail later, indicate that this peak is due to the irreversible reduction of $[PtCl(PPh_3)_3]^+$, presumably formed as an intermediate in the isomerization reaction, eqn. 2:

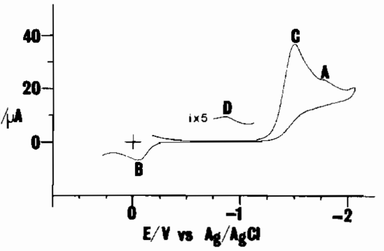
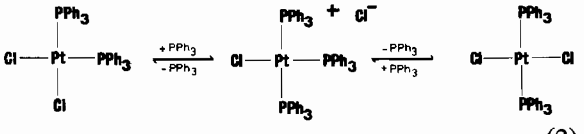


Fig. 2. Cyclic voltammogram of '*cis*-$[PtCl_2(PPh_3)_2]$' in CH_3CN/60% C_6H_6 after 3 hr in solution at a gold amalgam electrode (scan rate = 200 mV/sec).



$$\begin{array}{c} PPh_3 \\ | \\ Cl-Pt-PPh_3 \\ | \\ Cl \end{array} \underset{-PPh_3}{\overset{+PPh_3}{\rightleftharpoons}} \begin{array}{c} PPh_3 \; + \; Cl^- \\ | \\ Cl-Pt-PPh_3 \\ | \\ PPh_3 \end{array} \underset{+PPh_3}{\overset{-PPh_3}{\rightleftharpoons}} \begin{array}{c} PPh_3 \\ | \\ Cl-Pt-Cl \\ | \\ PPh_3 \end{array} \qquad (2)$$

It seems likely, therefore, that previous workers [4] have reported identical peak potentials for the reduction of the *cis* and *trans* isomers because isomerization allowed only the dominant isomer present in solution to be observed under the conditions employed during the study. The fact that reductions at a platinum electrode are reported [4] to give only a hump in the solvent discharge for *cis*-$[PtCl_2(PPh_3)_2]$ suggests that the *trans*-isomer was predominant at the time of measurement (*vide supra*) since *cis*-$[PtCl_2(PPh_3)_2]$ in fact gives a well-defined peak at −1.55 V (Pt). It should be noted, however, that it is the *cis*-geometry that is thermodynamically favored.

The peak potentials we have observed are as expected from a simple consideration of the electron density at the metal center in the isomeric pair [1]. Thus, in the *cis*-isomer, where the π-acceptor PPh_3 ligands may withdraw electron density from different d-orbitals, the electron density at the metal center will be lower than in the *trans*-isomer where these ligands must compete for withdrawal of electron density from the same d-orbital. Clearly, the electron poor *cis*-isomer will be more easily reduced than the electron rich *trans*-isomer, as observed. The cationic complex, $[PtCl(PPh_3)_3]^+$, would be anticipated to be very easily reduced, by these arguments, as is indeed the case.

One further point is worthy of mention in terms of the *cis–trans* isomerization process. The reaction described by eqn. 2 requires the presence of free triphenylphosphine for the catalytic isomerization to occur. Free triphenylphosphine may possibly be generated by solvolysis of the Pt–PPh_3 bond [8] of $[PtCl_2(PPh_3)_2]$ by the coordinating solvent acetonitrile [9], and/or by dissociation of PPh_3 from the platinum(0) complex produced at the cathode. Since the process is catalytic in PPh_3, only a very small amount is necessary for the isomerization process to be initiated. The electrochemistry of PPh_3 in acetonitrile solution has been reported in depth previously [10, 11] and so here we merely note that a cyclic voltammogram of PPh_3 on a platinum electrode has broad peaks at *ca.* 0.00 V (oxidative) and −0.20 V (reductive). Free chloride ion, in the form of NEt_4Cl, also displays a broad oxidative peak at *ca.* 0.0 V on a gold amalgam electrode. Since the voltammograms of $[PtCl_2(PPh_3)_2]$ display an oxidative peak (peak B) only when peaks A and/or C are traversed, the extent of Cl^- or PPh_3 formation by solvolysis of the platinum(II) complex is in fact undetectably small. A comparison of voltammograms of 3×10^{-3} *M* solutions of PPh_3, NEt_4Cl and *cis*-$[PtCl_2(PPh_3)_2]$ demonstrates that the magnitude of the diffusion current of peak B is too large to be attributed solely to Cl^- or PPh_3 and hence is attributed largely to the Pt(0) → Pt(II) oxidation of the platinum(0) complex formed on the cathodic scan. Detection of Cl^- formed during the reduction, or PPh_3 formed by dissociation from the platinum(0) complex is thus masked by this oxidative process.

Finally, it is of interest to note that the reductive peak at –0.20 V in the voltammogram of triphenylphosphine corresponds to the potential reported [4] for the Pt(IV) → Pt(II) reduction of $[PtCl_2(solvent)_2(PPh_3)_2]^{2+}$.

The isomerization reactions reported here are not restricted to $[PtCl_2(PPh_3)_2]$. Similar processes have been observed for complexes of other halide ligands and for complexes of tertiary phosphines other than triphenylphosphine. Clearly, an understanding of these fundamental processes is essential if electrochemical data of such compounds are to be meaningfully interpreted.

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