

Electrochemical Interconversion of Pt(II) and Pt(IV) Tertiary Phosphine Complexes

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Abstract

The electrochemical oxidation of *cis* and *trans*-[PtCl₂(PEt₃)₂] and the electrochemical reduction of *cis*-[PtCl₄(PEt₃)₂] have been investigated using cyclic voltammetry and controlled potential electrolysis. In CH₃CN solutions containing NBu₄ClO₄, oxidation of [PtCl₂(PEt₃)₂] proceeds very slowly at a platinum electrode, producing small amounts of *cis*-[PtCl₄(PEt₃)₂], presumably via chloride abstraction from Pt(II) by Pt(IV). In the presence of chloride ion, oxidation leads to *in situ* generation of chlorine, producing [PtCl₄(PEt₃)₂] efficiently. Excessive oxidation leads to formation of by-products, some of which have their origins in the oxidation of the PEt₃ ligand itself. Electrochemical reduction of *cis*-[PtCl₄(PEt₃)₂] at a Hg pool produces *cis*-[PtCl₂(PEt₃)₂].

Introduction

In recent years there has been renewed interest in the high oxidation state chemistry of the platinum group metals [1] including that of platinum in the oxidation state +IV. As part of a study of the electrochemistry of platinum(II) complexes containing tertiary phosphine ligands [2–8], we have investigated the electrochemical interconversion of Pt(II) and Pt(IV) complexes containing triethylphosphine, with the development of electrosynthetic routes to Pt(IV) complexes as a goal. Historically, the electrochemical interconversion of Pt(II) and Pt(IV) complexes containing neutral donor ligands has received little attention, despite the importance of Pt(II)/Pt(IV) oxidative addition/reductive elimination processes. Although redox potentials of some [PtCl₄L₂]-[PtCl₂L₂] systems (L = phosphine, thioether, amine) were reported some 30 years ago [9] and, indeed, there is more recent interest in electroanalytical investigations of simple Pt(II) and Pt(IV) salts and coordination compounds [10–16], the work of Mazzocchin *et al.* [17] on the electrochemical generation of Pt(IV) phosphine complexes from

Pt(II) precursors appears to be unique in possessing the potential for the development of synthetic methods. With this work [17] as reference, we here report our studies of the electrochemical oxidation of [PtCl₂(PEt₃)₂] and the electrochemical reduction of [PtCl₄(PEt₃)₂].

Results and Discussion

In previous reports we have described the cyclic voltammograms of a number of *cis* and *trans*-[PtCl₂(PR₃)₂] systems [6] over the potential range +0.5 to -2.5 V versus Ag/AgCl (-35 mV versus SCE), including a detailed study [2–4] of the cases where R = Ph. Mazzocchin [17, 18] has described cyclic voltammograms of [PtCl₂(PR₃)₂] complexes over a more extensive potential range, *c.* +2.0 to *c.* -2.2 V versus Ag/AgCl, including the case where R = Et. As background for discussion of controlled potential bulk electrolyses, we here summarize the relevant details of the cyclic voltammograms of *cis*- and *trans*-[PtCl₂(PEt₃)₂] and of *cis*-[PtCl₄(PEt₃)₂].

Cyclic Voltammetry

cis-[PtCl₂(PEt₃)₂]

Cyclic voltammograms of *cis*-[PtCl₂(PEt₃)₂] as a 10⁻³ M solution in acetonitrile (0.08 M tetra(n-butyl)ammonium perchlorate, TBAP) at a platinum working electrode (1.77 mm²) are shown in Fig. 1 over the potential range 0.0 to +2.2 V. Evident

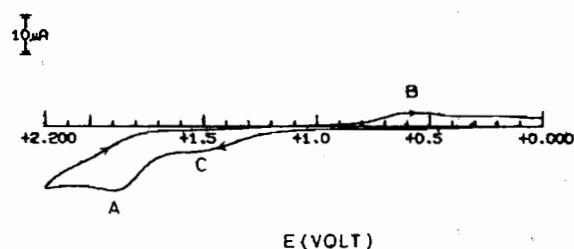


Fig. 1. Cyclic voltammogram of *cis*-[PtCl₂(PEt₃)₂] (10⁻³ M solution) in CH₃CN (0.08 M TBAP) at a Pt working electrode over the potential range 0.0 to +2.2 V. Scan rate = 200 mV s⁻¹.

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from Fig. 1 is an anodic peak at +1.85 V (at 200 mV s^{-1}) which progressively shifts to more positive potentials with increasing current flow as the scan rate is increased (peak A). This feature is in good agreement with an anodic peak described by Mazzocchin [17] at +1.80 V (200 mV s^{-1}), measured on a platinum microelectrode and assigned to the $\text{Pt(II)} \rightarrow \text{Pt(IV)}$ oxidation of *cis*- $[\text{PtCl}_2(\text{PEt}_3)_2]$, in complete agreement with our own assignment (*vide infra*). Also evident in Fig. 1 is a cathodic peak (peak B) at *c.* +0.55 V (at 200 mV s^{-1}) which shifts to more negative potentials with increased current flow as the scan rate is increased. Peak B only appears when peak A is traversed, initially suggesting that this feature may be due to $\text{Pt(IV)} \rightarrow \text{Pt(II)}$ reduction of an electrochemically generated platinum(IV) phosphine species. However, cyclic voltammetry studies of Pt(IV) triethylphosphine complexes and controlled potential bulk reductive electrolyses (*vide infra*) do not confirm this assignment. Additionally Mazzocchin does not report [17] a cathodic peak in the potential range under discussion, but rather a cathodic peak at -0.2 V (at 200 mV s^{-1}) [17], which is outside the range of our present study, but which was assigned to a $\text{Pt(IV)} \rightarrow \text{Pt(II)}$ reduction. Later experiments confirm this assignment. Finally, Fig. 1 also shows that a shoulder on the low potential side of peak A is discernable (marked as peak C in Fig. 1). The peak potential for C is difficult to report unambiguously, but appears to be *c.* +1.5 V at 200 mV s^{-1} . Mazzocchin [17] does not describe this feature, but instead reports [17] a peak at +1.15 V (at 200 mV s^{-1}), assigned to the $\text{Pt(II)} \rightarrow \text{Pt(IV)}$ oxidation of *trans*- $[\text{PtCl}_2(\text{PEt}_3)_2]$, formed by *cis/trans* equilibration of the initial *cis* isomer. Both our studies of $[\text{PtCl}_2(\text{PPh}_3)_2]$ [2–4] and Mazzocchin's work [17, 18] have demonstrated the importance of *cis/trans* equilibration processes in cyclic voltammetry measurements, where we have found [2–4] that initial cycling of the reductive portions of the voltammogram may lead to generation of free phosphine (formed from labile Pt(0) intermediates) which catalyzes the isomerization. In our present study we have typically avoided any potentials more negative than 0.0 V in order to preclude this problem. Thus, the nature of the electrode process leading to observation of peak C is undefined at this stage (*vide infra*).

trans- $[\text{PtCl}_2(\text{PEt}_3)_2]$

For comparison with the *cis* isomer, a cyclic voltammogram of *trans*- $[\text{PtCl}_2(\text{PEt}_3)_2]$, initially free of any *cis*-isomer at the sensitivity level of $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, is shown in Fig. 2. Experimental conditions were as described for measurements of the *cis* isomer (*vide supra*).

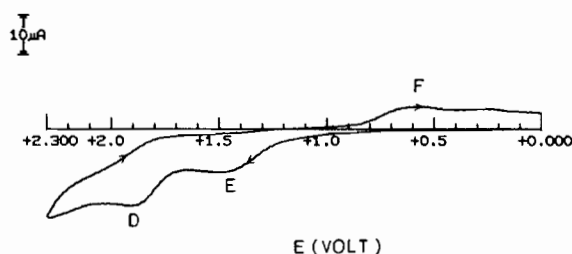


Fig. 2. Cyclic voltammogram of *trans*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ (10^{-3} M solution) in CH_3CN (0.08 M TBAP) at a Pt working electrode over the potential range 0.0 to +2.3 V. Scan rate = 200 mV s^{-1} .

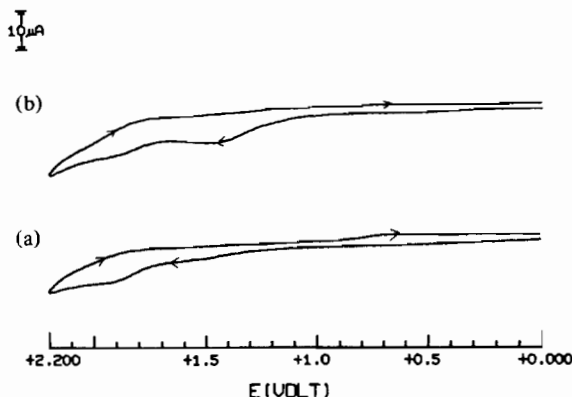


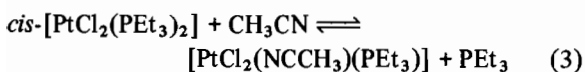
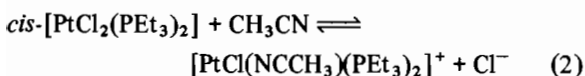
Fig. 3. Cyclic voltammograms of (a) *cis*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ (10^{-3} M solution) and (b) *cis*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ with an equimolar amount of *trans*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ added. Measurements in CH_3CN (0.08 M TBAP) at a Pt working electrode over the potential range 0.0 to +2.2 V. Scan rate = 200 mV s^{-1} .

Figure 2 shows that *trans*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ exhibits a fairly well defined anodic peak at *c.* +1.85 V (peak D) and a less well defined peak (peak E) at *c.* +1.5 V, when measured at a scan rate of 200 mV s^{-1} . A cathodic peak (peak F) appears at *c.* +0.60 V. A comparison of Figs. 1 and 2 shows that the *cis* and *trans* isomers of $[\text{PtCl}_2(\text{PEt}_3)_2]$ exhibit very similar cyclic voltammetry behavior over the positive potential range employed here. For reference, Ahrland and Chatt [9] have estimated the difference in standard redox potentials of the *cis* and *trans* isomers of $[\text{PtCl}_4(\text{P}^n\text{Pr}_3)_2] - [\text{PtCl}_2(\text{P}^n\text{Pr}_3)_2]$ couples to be only about 18 mV.

For comparison, Fig. 3(a) shows a cyclic voltammogram of *cis*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ measured at 200 mV s^{-1} and Fig. 3(b) shows the result of adding an equimolar amount of *trans*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ to this solution, such that the molar amounts of isomers initially in solution are 1:1. Although enhanced current flow is evident upon addition of *trans*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ to the solution of the *cis* isomer, no new peaks are observed in the cyclic voltammogram.

Solution Chemistry

In order to understand the features present in the oxidative portions of the cyclic voltammograms of the *cis* and *trans* isomers of $[\text{PtCl}_2(\text{PEt}_3)_2]$ more completely, it seemed to us to be necessary to consider both the possibility of electroactive impurities in our samples and (i) possible *cis/trans* isomerization (eqn. (1)), (ii) possible Pt–Cl bond solvolysis (eqn. (2)), and (iii) possible Pt–P bond solvolysis (eqn. (3)).



In order to examine the possibility of electroactive impurities in our samples we have synthesized both the *cis* and *trans* isomers of $[\text{PtCl}_2(\text{PEt}_3)_2]$ by two different routes, one starting with K_2PtCl_4 and one starting with PtCl_2 . Samples originating from both starting materials were found to be pure at the sensitivity levels of ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopies and exhibited identical cyclic voltammograms, including the ill-defined anodic peak at *c.* +1.5 and cathodic peak at +0.60 V which are present for both isomers.

Since we anticipated that each of the possible processes represented by eqns. (1)–(3) will be in equilibrium, we sought to measure cyclic voltammograms of the *cis* and *trans* isomers at sub-ambient temperatures. Direct comparisons between cyclic voltammograms measured at different temperatures are complicated by changes in solvent viscosity, ion mobility, etc. [19] but, nonetheless, qualitative comparisons may be of value. Figures 4 and 5 show selected cyclic voltammograms of the *cis* and *trans* isomers respectively measured over the temperature ranges +20 to -15°C . Other experimental conditions were held constant. For both isomers we observe that the anodic peak at -1.85 V (at room temperature) is present over the entire temperature range. However, the ill-defined anodic peak at *c.* +1.5 is not present at low temperatures in either sample and, furthermore, the disappearance of this peak is accompanied by the disappearance of the cathodic peak at *c.* +0.60 V.

Our attempts to elucidate the nature of the electrochemical process leading to the anodic peak observed at *c.* +1.5 V at room temperature, which vanishes along with the cathodic peak at +0.60 V at low temperature, have so far failed to yield a definitive answer. Thus, *cis/trans* isomerization (eqn. (1)) does not appear to be responsible for this feature (see Fig. 3(a) and (b)) while a Pt–Cl solvolysis (eqn. (2)) might be expected to produce detectable

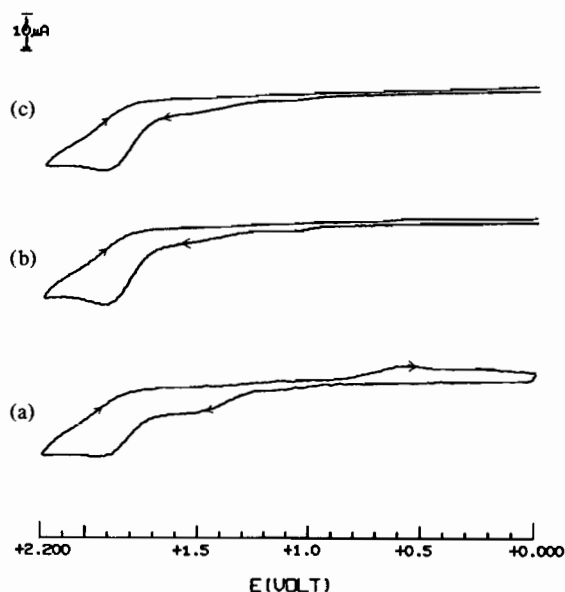


Fig. 4. Cyclic voltammograms of *cis*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ (10^{-3} M solution) in CH_3CN (0.08 M TBAP) at a Pt working electrode over the potential range 0.0 to +2.2 V. Scan rate = 200 mV s^{-1} . Cell temperature: (a) = $+20^\circ\text{C}$; (b) = $+7^\circ\text{C}$; (c) = -10°C .

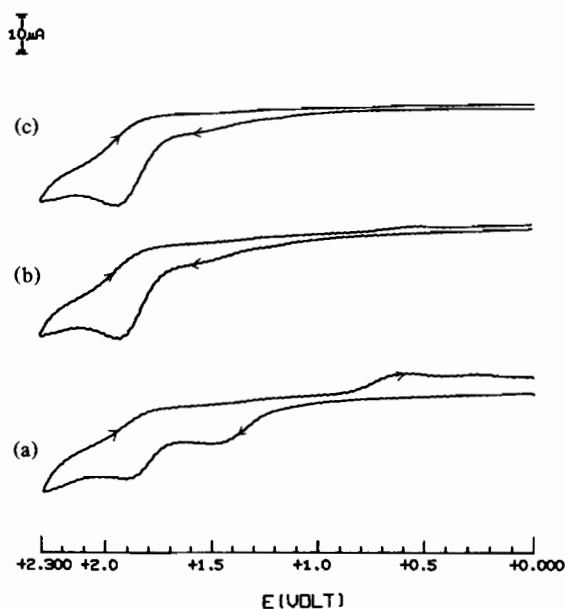


Fig. 5. Cyclic voltammograms of *trans*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ (10^{-3} M solution) in CH_3CN (0.08 M TBAP) at a Pt working electrode over the potential range 0.0 to +2.2 V. Scan rate = 200 mV s^{-1} . Cell temperature: (a) = $+20^\circ\text{C}$; (b) = $+10^\circ\text{C}$; (c) = -10°C .

amounts of chloride ion in solution, provided the equilibrium position is favorable, which would be detected as an anodic peak at +1.1 V under these conditions (i.e. a cyclic voltammogram of NEt_4Cl shows an anodic peak at +1.1 V and a coupled

cathodic peak at +0.95 V at 200 mV s⁻¹ using identical experimental conditions). Similarly, a favorable equilibrium position for eqn. (3) should lead to detectable PEt₃ in solution and this is not observed (i.e. a cyclic voltammogram of PEt₃ shows an anodic peak at +1.2 V at 200 mV s⁻¹ using typical experimental conditions). However, dismissing eqns. (2) and (3) on the basis of not observing dissociation products by cyclic voltammetry is only justified if the equilibria involved lie far to the right. Thus, if eqn. (2), for example, is characterized by a small equilibrium constant, then the peak potential for chloride oxidation will be kinetically controlled (an EC process) and may be very different from that found for bulk added chloride ion. The same rationale is true for the PEt₃ oxidation resulting from eqn. (3). Thus, the electrochemical process leading to the appearance of the anodic peak at +1.5 V and the related cathodic feature at +0.60 V in cyclic voltammograms of both isomers of [PtCl₂(PEt₃)₂] at room temperature remains undefined at this time but is presumably an equilibrium reaction (eqns. 2 or 3) leading to kinetic control of the oxidation process. Further investigations are underway.

Cyclic Voltammetry: *cis*-[PtCl₄(PEt₃)₂]

Chlorine oxidation of *cis*-[PtCl₂(PEt₃)₂] produces *cis*-[PtCl₄(PEt₃)₂]. A cyclic voltammogram of this platinum(IV) complex (initial positive sweep) is shown in Fig. 6. The anodic peaks associated with the oxidation of platinum(II) are of course absent. The presence of a cathodic peak at *c.* -0.30 V on the reverse sweep suggests that prior assignments [17] of cathodic peaks in this general range in cyclic voltammograms of [PtCl₂(PEt₃)₂] complexes (following initial oxidation) as Pt(IV) → Pt(II) reductions are correct. Controlled potential bulk reductive electrolysis of *cis*-[PtCl₄(PEt₃)₂] at -0.3 V leads to formation of *cis*-[PtCl₂(PEt₃)₂] (*vide infra*) confirming this assignment.

Controlled Potential Bulk Electrolysis

cis-[PtCl₂(PEt₃)₂]

Despite uncertainties in some features of the cyclic voltammograms of *cis*-[PtCl₂(PEt₃)₂], we have performed bulk electrolyses using a CH₃CN solution

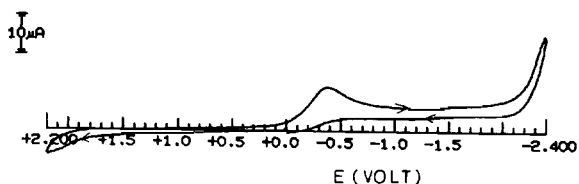


Fig. 6. Cyclic voltammogram of *cis*-[PtCl₄(PEt₃)₂] (10⁻³ M solution) in CH₃CN (0.08 M TBAP) at a Pt working electrode over the potential range -2.4 to +2.2 V. Scan rate = 200 mV s⁻¹.

(0.08 M in TBAP) of the complex at a platinum gauze electrode. Pre-electrolysis of the solvent/electrolyte at +1.90 V was followed by electrolysis of the *cis* isomer at +1.85 V. We found only very low current flow in these experiments, in agreement with Lau and Hubbards' observation [13] that "electro-oxidations of Pt(II) complexes in halide-free solutions are extremely slow, achieving appreciable rates only at potentials sufficiently positive to cause concomitant oxidation of the electrode and solvent". The low current flow observed here is further evidence for a kinetically controlled chemical step preceding the oxidation. Due to almost baseline current flow, conventional coulometry was of little use in establishing the number of electrons involved in the oxidation process. Accordingly, we performed five separate electrolyses for different lengths of time, worked up each individual solution (see 'Experimental'), and examined the ³¹P{¹H} NMR spectra in an attempt to identify platinum(IV) products (see Table 1). One experiment, involving oxidation for 1 h 20 min, showed only the original

TABLE 1. ³¹P{¹H} NMR data: electrochemical oxidation of *cis*-[PtCl₂(PEt₃)₂]

Voltage	Time	NMR data
+1.85	1 h 20 min	δ = 8.7 ppm ¹ J(Pt,P) = 3496 Hz: <i>cis</i> -[PtCl ₂ (PEt ₃) ₂] (100%)
+1.85	2 h 20 min	δ = 8.7 ppm ¹ J(Pt,P) = 3496 Hz: <i>cis</i> -[PtCl ₂ (PEt ₃) ₂] (78%) δ = 54.1 ppm (br) (10%) δ = 13.3 ppm (5%) δ = 8.8 ppm (7%)
+1.85	8 h 0 min	δ = 8.7 ppm ¹ J(Pt,P) = 3496 Hz: <i>cis</i> -[PtCl ₂ (PEt ₃) ₂] (78%) δ = 19.4 ppm ¹ J(Pt,P) = 2045 Hz: <i>cis</i> -[PtCl ₄ (PEt ₃) ₂] (14%) δ = 74.5 ppm (4%) δ = 5.4 ppm (4%)
+1.85	2 h 10 min	δ = 8.7 ppm ¹ J(Pt,P) = 3496 Hz: <i>cis</i> -[PtCl ₂ (PEt ₃) ₂] (41%) δ = 83.1 ppm (br) (16%) δ = 9.5 ppm (br) (10%) δ = 9.9 ppm (5%) δ = 0.3 ppm (4%) δ = 4.7 ppm (7%) δ = 5.3 ppm (8%)
+1.85	2 h 5 min	δ = 8.7 ppm ¹ J(Pt,P) = 3496 Hz: <i>cis</i> -[PtCl ₂ (PEt ₃) ₂] (55%) δ = 19.4 ppm ¹ J(Pt,P) = 2045 Hz: <i>cis</i> -[PtCl ₄ (PEt ₃) ₂] (14%) δ = 63.1 ppm (6%) ^a δ = 6.6 ppm ¹ J(Pt,P) = 3291 Hz (20%) δ = 6.1 ppm (2%) δ = 18.0 ppm (3%)

^aAlso observed in oxidation of PEt₃ alone.

cis-[PtCl₂(PEt₃)₂] in solution. No other resonances were observed. Three experiments involved oxidation for time periods of 2 h to 2 h 30 min. Each spectrum showed the presence of large amounts of *cis*-[PtCl₂(PEt₃)₂] (41%–78% estimated by peak heights) but in only one spectrum we are able to unambiguously identify *cis*-[PtCl₄(PEt₃)₂] (14% by peak heights). Each spectrum contained several unidentified resonances (see ‘Experimental’ and Table 1), including some resonances at low field which we later identified as oxidation products of PEt₃ itself. One oxidation, carried out over 8 h, led to a solution containing *cis*-[PtCl₂(PEt₃)₂] (78% by peak heights) and *cis*-[PtCl₄(PEt₃)₂] (15% by peak height). Other minor resonances were also apparent in the ³¹P{¹H} NMR spectrum (*c.* 7% total peak height). In these experiments we saw no evidence for the formation of [PtCl₂(solvent)₂(PEt₃)₂]²⁺, the anticipated product of oxidation based on previous results [17]. Instead, we observe only low yield formation of [PtCl₄(PEt₃)₂], presumably formed via chloride scavenging by Pt(IV) from Pt(II), accompanied by production of some unidentified by-products. The product mixtures also contained compounds later identified (*vide infra*) as oxidation products of PEt₃ itself. The electrochemical oxidation of *cis*-[PtCl₂(PEt₃)₂] under the conditions described here is thus not a useful synthetic route to Pt(IV) phosphine complexes. The observation of [PtCl₄(PEt₃)₂] in long oxidations suggested to us that chloride dissociation from Pt(II) could be the slow chemical step which precedes the oxidation. However, since we also observe products from PEt₃ oxidation, initial phosphine dissociation cannot be eliminated as the slow step.

cis-[PtCl₂(PEt₃)₂] in the presence of Cl⁻

Hubbard and co-workers have established that halide ions mediate electron transfer processes between electrode surfaces and Pt(II) salts and simple coordination compounds [10–16]. In the case of *cis*-[PtCl₂(PEt₃)₂], however, the potential required for Pt(II) → Pt(IV) oxidation far exceeds that for chloride oxidation. Thus, it seemed likely to us that the use of chloride-containing solutions or chloride-modified electrodes would lead to chlorine generation and/or perhaps facilitate electron transfer from Pt(II). Either outcome would be desirable in the electrogeneration of Pt(IV) phosphine complexes from Pt(II) precursors.

Accordingly, bulk electrolyses of *cis*-[PtCl₂(PEt₃)₂] were performed in 0.08 M TBAP solutions of CH₃CN containing NEt₄Cl (2 equiv. based on Pt). Electrolysis at +1.20 V resulted in significant current flow. The electrolysis was terminated after coulometry indicated an approximate two-electron oxidation based on the concentration of *cis*-[PtCl₂(PEt₃)₂]. Work-up of the oxidized solution, followed by examination by ³¹P{¹H} NMR spectroscopy,

TABLE 2. ³¹P{¹H} NMR data: electrochemical oxidation of *cis*-[PtCl₂(PEt₃)₂] in the presence of chloride ion

Voltage	Time	NMR data
+1.20 ^b	1 h 30 min	δ = 19.4 ppm ¹ J(Pt,P) = 2045 Hz: <i>cis</i> -[PtCl ₄ (PEt ₃) ₂] (100%)
+1.25 ^b	2 h 35 min	δ = 19.4 ppm ¹ J(Pt,P) = 2045 Hz: <i>cis</i> -[PtCl ₄ (PEt ₃) ₂] (45%) δ = 76.8 ppm (br) (22%) ^a δ = 5.3 ppm (16%) δ = 34.0 ppm (8%) δ = 33.7 ppm (9%)
+1.65	1 h 6 min	δ = 19.4 ppm ¹ J(Pt,P) = 2045 Hz: <i>cis</i> -[PtCl ₄ (PEt ₃) ₂] (68%) δ = 76.8 ppm (br) (10%) ^a δ = 63.5 ppm (7%) ^a δ = 30.5 ppm (br) (10%) δ = 29.4 ppm (5%)
+1.40	1 h 30 min	δ = 19.4 ppm ¹ J(Pt,P) = 2045 Hz: <i>cis</i> -[PtCl ₄ (PEt ₃) ₂] (69%) δ = 63.5 (br) (18%) ^a δ = 5.5 ppm (8%) δ = 9.2 ppm (5%)
+1.40	1 h 25 min	δ = 19.4 ppm ¹ J(Pt,P) = 2045 Hz: <i>cis</i> -[PtCl ₄ (PEt ₃) ₂] (70%) δ = 76.8 ppm (br) (10%) ^a δ = 63.5 ppm (br) (10%) δ = 6.4 ppm (10%)

^aAlso observed in oxidation of PEt₃ alone. ^bChloride was added to cell, others used modified electrode.

showed exclusive formation of *cis*-[PtCl₄(PEt₃)₂] (see Table 2). No other resonances were present in the spectrum. In experiments where the electrolysis was more prolonged, other by-products are formed in addition to *cis*-[PtCl₄(PEt₃)₂] (see ‘Experimental’ and Table 2), including compounds formed by oxidation of PEt₃ itself. Experiments employing a platinum gauze electrode, previously soaked in chloride solution, proceed similarly generating significant amounts of *cis*-[PtCl₄(PEt₃)₂] in addition to by-products of the oxidation process.

In these oxidations, evolution of chlorine was confirmed by testing the atmosphere above the solutions with a chlorine-sensitive indicator (see ‘Experimental’). Accordingly it seems that *cis*-PtCl₄(PEt₃)₂ is formed by attack of electrolytically generated chlorine on *cis*-[PtCl₂(PEt₃)₂], rather than by electrochemical oxidation of *cis*-[PtCl₂(PEt₃)₂] followed by attack of chloride ion.

trans-[PtCl₂(PEt₃)₂] in the presence of Cl⁻

The *trans* isomer of [PtCl₂(PEt₃)₂] is electrochemically oxidized, using a platinum gauze electrode previously treated with chloride solution, in a manner similar to that described for the *cis* isomer (see ‘Experimental’). ³¹P{¹H} NMR spectroscopy of the

oxidized solution after work-up showed formation of *cis*-[PtCl₄(PEt₃)₂] (64% by peak heights) and other by-products (see 'Experimental'). No *trans*-[PtCl₄(PEt₃)₂] was detected in solution.

PEt₃

In electrochemical oxidations of *cis*-[PtCl₂(PEt₃)₂] performed in the absence of chloride ion, ³¹P{¹H} NMR spectroscopy of the resulting solutions showed low field resonances indicative of oxidized phosphorus compounds. Similarly, prolonged electrolyses of *cis*-[PtCl₂(PEt₃)₂] or *trans*-[PtCl₂(PEt₃)₂] in the presence of chloride ion (where chlorine evolution has been confirmed) lead to formation of these oxidized phosphorus compounds. Accordingly, we sought to investigate whether these by-products resulted from electrochemical oxidation and/or chlorine oxidation of PEt₃ in our reaction system. There have been a number of studies [20–22] of the electrochemistry of tertiary phosphines and it is not our intention to repeat or review these studies here. Rather we intended to simply establish whether or not by-product formation in our experiments resulted from oxidation of PEt₃. Thus, we performed a bulk electrolysis of a dilute solution of PEt₃ at +1.45 V (i.e. a more positive potential than the anodic peak potential measured by cyclic voltammetry) and examined the ³¹P{¹H} NMR spectrum of the resulting solution after work-up. The spectrum showed a sharp peak at 64 ppm and a very broad peak centered at *c.* 78 ppm which may contain more than one component. We have not attempted to isolate and identify these oxidation products, but note that they are produced as by-products in our oxidation studies of *cis*-[PtCl₂(PEt₃)₂]. Details of comparative spectroscopic data are given in 'Experimental'. Oxidation of PEt₃ with excess chlorine (introduced as the iodobenzene adduct) produced solutions exhibiting the broad resonance at *c.* 78 ppm, but without the sharp signal at 64 ppm. The former component was also present in samples prepared by prolonged oxidation of *cis*-[PtCl₂(PEt₃)₂] in the presence of chloride ion.

These results demonstrate that oxidative electrolysis of *cis*-[PtCl₂(PEt₃)₂] alone, or prolonged electrolysis of *cis* or *trans*-[PtCl₂(PEt₃)₂] in the presence of chloride ion, leads to products formed by oxidation of PEt₃ itself. The involvement of electrochemically generated chlorine in these reactions is distinctly possible.

cis-[PtCl₄(PEt₃)₂]

In order to confirm assignments of cyclic voltammetry data, we have performed bulk reductive electrolyses of *cis*-[PtCl₄(PEt₃)₂] at a mercury pool electrode. Electrolysis at –0.3 V followed by work-up of the reduced solution led to the iden-

tification of *cis*-[PtCl₂(PEt₃)₂] as the only phosphorus-containing compound in solution by ³¹P{¹H} NMR spectroscopy.

Experimental

General Procedure

Acetonitrile (Fischer, ACS grade) was stirred with CaH₂ for 48 h, decanted and distilled from P₄O₁₀. The fraction boiling in the range 82–84 °C was refluxed with CaH₂ for 8 h and then fractionally distilled under argon. The fraction boiling in the range 83–84 °C was stored under argon over Al₂O₃ (MCO, activated) which was activated at 110 °C for 24 h. Tetra(*n*-butyl)ammonium perchlorate (TBAP, G.F.S.) was recrystallized five times from absolute ethanol and dried in vacuum at room temperature prior to use. Tetraethylammonium chloride (Kodak) was heated at 110 °C for 24 h prior to use. *Cis* and *trans*-[PtCl₂(PEt₃)₂] were prepared by the reaction of K₂PtCl₄ with two equivalents of triethylphosphine (Strem) [20] or by the reaction of [PtCl₂(NCCH₃)₂] with two equivalents of triethylphosphine in CH₃CN [21]. ³¹P{¹H} NMR data: *trans* isomer: δ = 12.4 ppm ¹J(Pt–P) = 2420 Hz; *cis* isomer: δ = 8.7 ppm, ¹J(Pt–P) = 3496 Hz. MS data: *M*⁺ = 502. Fragmentation pattern resembles that for other platinum(II) phosphine complexes [22].

³¹P{¹H} NMR spectra were measured on a Jeol FX-90Q spectrometer. Chemical shifts were measured relative to 85% H₃PO₄ as an external standard, with positive values representing deshielding. Mass spectra were measured using a HP5988A spectrometer equipped with a direct insertion probe (DIP).

Cyclic voltammograms were obtained using a Bioanalytical Systems 100 Control Unit. Typically, 10^{–3} M solutions of the platinum complexes in acetonitrile which were 0.08 M in TBAP were employed. A single compartment cell equipped with a Ag/AgCl reference electrode (–35 mV versus SCE), a platinum wire auxiliary electrode, and a platinum working electrode was used. Full details of cyclic voltammetry measurements are given elsewhere [23]. Controlled potential bulk oxidative and reductive electrolyses were performed using a Bioanalytical Systems SP-2 synthetic potentiostat. A three compartment cell was employed which was constructed in-house. The working electrode compartment contained the Ag/AgCl reference electrode and a platinum gauze working electrode for oxidation or a mercury pool electrode for reductions. The auxiliary electrode compartment contains 7 ml of mercury connected to the potentiostat via a platinum spiral wire for oxidations or a platinum wire for reductions. The two compartments were separated by two medium porosity frits. The

cell is equipped with a number of fitted openings to allow inert atmosphere operations and manipulations of solutions.

Controlled Potential Bulk Oxidative Electrolysis of *cis*-[PtCl₂(PEt₃)₂]

Twenty-four hours prior to an experiment, the controlled potential electrolysis cell was charged with alumina (1.0 g) and dried at 110 °C. From this point on, all manipulations of the cell were done under an argon atmosphere at room temperature unless otherwise noted. At the time of the experiment, a small magnetic stir bar was added to the cell which was cooled under an argon stream. One hundred ml of a 0.08 M solution of TBAP in acetonitrile was introduced to the cell via an argon stream. Mercury (7 ml) was extracted with acetonitrile and then added to the auxiliary compartment. The cell was stirred and outgassed for one hour. The solution was then pre-electrolyzed to essentially zero current at the appropriate potential.

The pre-electrolyzed solution was transferred under argon to a Schlenk tube containing *cis*-[PtCl₂(PEt₃)₂] (c. 20 mg) and, for experiments involving the chloride ion, 2 equivalents of tetraethylammonium chloride. After all the chemicals had dissolved, the solution was transferred back to the cell, then purged for 1 h and electrolyzed to essentially zero current at the appropriate potential. The electrolyzed solution was then transferred back to a Schlenk tube under argon and evaporated down to a solid which was then extracted with C₆D₆ (2 ml). ³¹P{¹H} NMR spectroscopy was then used for product identification. Details are given in Table 1. Since products are extracted into C₆D₆ for analysis, there is always the possibility that isomer ratios so measured might differ from isomer ratios in the more polar CH₃CN reaction medium. We have seen no evidence in these experiments that isomer ratios are biased to favor the less polar isomer by extraction into C₆D₆.

For experiments using a modified electrode the general procedure is the same as that described above except for the following details. Twelve hours prior to the experiment the platinum gauze electrode was soaked in a 1 M solution of tetraethylammonium chloride in acetonitrile with stirring. At the time of the experiment, the electrode was taken out, dried with a stream of cool air until no liquid remained on the electrode surface, and then fitted into the cell. *cis*-[PtCl₂(PEt₃)₂] (c. 20 mg) was electrolyzed using the modified electrode (work-up is as previously described). ³¹P{¹H} NMR spectroscopy was used for product identification and details are given in Table 2.

Controlled Potential Bulk Reductive Electrolysis of *cis*-[PtCl₄(PEt₃)₂]

Twenty-four hours prior to an experiment the controlled potential electrolysis cell was charged with alumina (1.0 g) and dried at 110 °C. From this point on, all manipulations were done under an argon atmosphere at room temperature unless otherwise noted. At the time of the experiment, mercury (28 ml), and a small magnetic stir bar were added to the cell which had been cooled under an argon stream. A 0.08 M solution of TBAP in acetonitrile (70 ml) was introduced to the cell via an argon stream. This was allowed to stir and out gas for 1 h. The solution was then pre-electrolyzed to approximately zero current at a potential of -0.5 V.

The pre-electrolyzed solution was then transferred under argon into a Schlenk tube containing *cis*-[PtCl₄(PEt₃)₂] (c. 20 mg). After the complex was dissolved the yellow solution was transferred back into the cell, purged for 1 h and electrolyzed to essentially zero current at a voltage of -0.3 V, resulting in a colorless solution. Coulometry indicated approximately a two-electron reduction with an integration of c. 1.7 electrons/equivalent.

Synthesis of *cis*-[PtCl₄(PEt₃)₂]

Using standard vacuum line techniques *cis*-[PtCl₂(PEt₃)₂] (25 mg) was dissolved in CH₃CN (5 ml) containing Cl₂-IPh (40 mg*) at 25 °C. After 4 h stirring, the solution was evaporated on the vacuum line to yield a yellow solid, which was recrystallized from absolute ethanol and analyzed by ³¹P{¹H} NMR spectroscopy. The data of a C₆D₆ solution of this complex are: δ = 19.4 ppm; ¹J(Pt-P) = 2045 Hz.

Preparation of the Chlorine Indicator

p-Dimethylaminobenzaldehyde (Fisher, 0.78 g) and diphenylamine (Aldrich, 0.69 g) were dissolved (in a one to one molar ratio) in carbon tetrachloride (Fisher, 10 ml) to give a 10% solution. A standard piece of white filter paper was dipped into this solution and air dried. This was then cut into convenient strips and placed over the argon outlet of the electrolysis cell. When chlorine was present the paper turns from white to yellow/green.

Conclusions

Electrochemical oxidation of *cis*-[PtCl₂(PEt₃)₂] in CH₃CN (0.08 M TBAP) solution at a platinum gauze electrode is extremely slow and results in only low conversions to *cis*-[PtCl₄(PEt₃)₂], presumably by chloride scavenging from Pt(II) by electrochemically generated Pt(IV), along with by-product forma-

*Cl₂·IPh was precipitated when chlorine was passed through a solution of iodobenzene.

tion. Some of these by-products have their origins in the oxidation of PEt_3 itself. However, electrolysis in the presence of chloride ion generates chlorine *in situ* which leads to efficient production of *cis*- $[\text{PtCl}_4(\text{PEt}_3)_2]$ from either isomer of $[\text{PtCl}_2(\text{PEt}_3)_2]$, provided overoxidation is avoided. Electrochemical reduction of *cis*- $[\text{PtCl}_4(\text{PEt}_3)_2]$ in CH_3CN (0.08 M TBAP) at a mercury pool electrode leads to clean conversion to *cis*- $[\text{PtCl}_2(\text{PEt}_3)_2]$.

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