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Electrochemical oxidative cleavage of the platinum–hydrogen bond in *trans*-[$PtHCl(PEt_3)_2$]

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Abstract

The electrochemical oxidation of the platinum(II) hydride, *trans*-[$PtHCl(PEt_3)_2$], in CH_3CN containing NBu_4ClO_4 at a platinum gauze electrode produces almost exclusively platinum(II) complexes as products, none of which contain platinum–hydrogen bonds. $^{31}P\{^1H\}$ NMR spectroscopy and independent synthesis identify *trans*-[$PtCl(solvent)(PEt_3)_2$]$^+$ as the major oxidation product. Non-aqueous acid–base titrations on the electrochemically oxidized solutions show that Pt–H cleavage occurs with H^+ formation. The formal overall oxidation process is thus identified as $H^- \rightarrow H^+$ and not Pt(II) → Pt(IV).

Introduction

Platinum(II) hydride complexes of triethylphosphine catalyze the photochemical decomposition of water [1–4], a process of potential significance as a source of fuel. Studies of the mechanism of water decomposition suggest [4] that platinum(IV) hydrides such as [$PtH_2(PEt_3)_3X$]$^{n+}$ are involved as intermediates. High valent hydrides of this general type have typically proved elusive towards complete characterization under catalytic conditions [4] although several examples are known through independent synthesis [5].

Both we [6] and others [7–15] have used electrochemical techniques to probe Pt(II) → Pt(IV) interconversions, including those of complexes of triethylphosphine [6, 15]. Accordingly we sought to examine the electrochemical oxidation of *trans*-[$PtHCl(PEt_3)_2$] as a model platinum(II) hydride and here report the results of this study.

Results and discussion

A cyclic voltammogram of *trans*-[$PtHCl(PEt_3)_2$] as a 10^{-3} M solution in CH_3CN containing NBu_4ClO_4 (TBAP, 0.08 M) at a platinum bead working electrode (1.77 mm^2) over the potential range 0.0 to +2.2 V (versus Ag/AgCl, −35 mV versus SCE) is shown in Fig. 1. At a scan rate of 200 mV s^{-1} an anodic peak is observed at +1.45 V with no associated cathodic peak. The anodic peak shifts to more positive potentials with increasing current flow as the scan rate is increased.

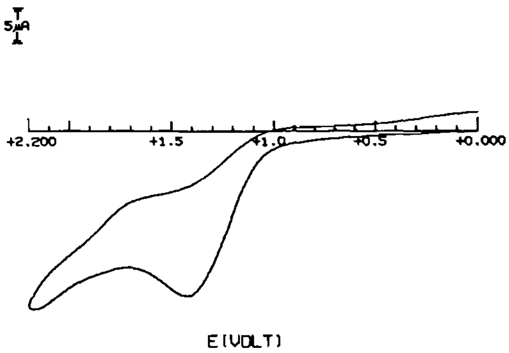

Fig. 1. Cyclic voltammogram of *trans*-[$PtHCl(PEt_3)_2$] as a 10^{-3} M solution in CH_3CN (0.08 M in TBAP) measured at a platinum bead working electrode (1.77 mm^2). Scan rate = 200 mV s^{-1}. Reference electrode: Ag/AgCl (−35 mV vs. SCE).

Controlled potential bulk oxidative electrolyses were performed using a three compartment cell. The cell was equipped with a platinum gauze working electrode and a Ag/AgCl reference electrode in the oxidation compartment which was separated from the reduction compartment by two medium porosity frits. The reduction compartment contained a mercury pool electrode. The hydride, *trans*-[$PtHCl(PEt_3)_2$] was added to a preelectrolyzed solution of TBAP (0.08 M) in CH_3CN. Electrolyses at potentials more positive than +1.45 V (i.e. +1.45 to +1.85 V) were performed under an argon at-

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mosphere until current flow was minimal with coulometry indicating $\sim$2–3 electrons/equivalent transferred. Work-up of the oxidized solution (see 'Experimental') was followed by $^{31}P\{^1H\}$ NMR spectroscopic examination which showed the presence of *trans*-$[PtCl(solvent)(PEt_3)_2]^+$ (from three experiments: $\sim$75–90% by peak heights in the $^{31}P\{^1H\}$ NMR spectrum), along with small amounts of the *cis*- and *trans*-isomers of $[PtCl_2(PEt_3)_2]$ ($\sim$8 and 2–11%, respectively) and a trace of $[PtCl_4(PEt_3)_2]$ ($\sim$0–6%). The identity of *trans*-$[PtCl(solvent)(PEt_3)_2]^+$ was confirmed by independent preparation (see 'Experimental') and by addition of NEt_4Cl to the electrochemically oxidized solutions which caused quantitative conversion of the cation to *trans*-$[PtCl_2(PEt_3)_2]$. Examination of the electrochemically oxidized solutions of *trans*-$[PtHCl(PEt_3)_2]$ by ^1H NMR spectroscopy also failed to show the presence of any complex containing a Pt–H bond.

The cleavage of M–H bonds by electrochemical oxidation has been observed for complexes of both the early and late transition metals [16]. The M–H cleavage process can involve H^+ extrusion from an oxidized metal center, or the formal transfer of $H^{\bullet}$ to an acceptor. Thus, $[IrH(CO)(PPh_3)_3]$ undergoes two sequential one-electron oxidations followed by proton extrusion (eqn. (1)) [17].

$$\begin{tikzcd} {[IrH(CO)(PPh_3)_3]} \arrow[r, "-1e^-"] & {} \\ {[IrH(CO)(PPh_3)_3]^+} \arrow[r, "-1e^-"] & {[IrH(CO)(PPh_3)_3]^{2+}} \arrow[d] \\ & {[Ir(CO)(PPh_3)_3]^+ + H^+} \end{tikzcd} \qquad (1)$$

Related proton extrusion processes are known for complexes of rhodium [17], iron [18], rhenium [19], molybdenum [20] and tungsten [20]. The electrochemical oxidation of $[ReCpH_2(PR_3)_3]$ occurs by a fundamentally different process [21]. Thus, two sequential one-electron oxidations generate the dication $[ReCpH_2(PR_3)_3]^{2+}$ which catalyzes disproportionation of the initially formed monocation. This disproportionation occurs by formal transfer of $H^{\bullet}$ between metal centers, generating Re(III) and Re(V) products (eqn. (2)).

$$2[ReCpH_2(PR_3)_2]^+ \xrightarrow{Re(V)} [ReCpH_3(PR_3)_2]^+ + [ReCpH(PR_3)_2]^+ \qquad (2)$$

A similar M–H cleavage by formal $H^{\bullet}$ transfer to an acceptor has been described for rhodium [17].

For the platinum hydride system of interest here, Pt–H cleavage by $H^{\bullet}$ transfer to an acceptor or H^+ extrusion must both be considered since either route could explain the observed products. Thus, proton extrusion following a two-electron oxidation would produce the observed cation (eqn. (3)).

$$trans\text{-}[PtHCl(PEt_3)_2] \xrightarrow{-2e^-} [PtHCl(PEt_3)_2]^{2+} \xrightarrow{solvent} [PtCl(solvent)(PEt_3)_2]^+ + H^+ \qquad (3)$$

Similarly, hydrogen atom extrusion following a one-electron oxidation would also account for the observed cation (eqn. (4)).

$$trans\text{-}[PtHCl(PEt_3)_2] \xrightarrow{-1e^-} [PtHCl(PEt_3)_2]^{+} \xrightarrow{solvent} [PtCl(solvent)(PEt_3)_2]^+ + H^{\bullet} \qquad (4)$$

In theory, coulometry should differentiate eqns. (3) and (4). In practice, however, *trans*-$[PtCl(solvent)(PEt_3)_2]^+$ is not the sole product of the reaction and formation of small amounts of $[PtCl_2(PEt_3)_2]$ and $[PtCl_4(PEt_3)_2]$ implies chloride scavenging (e.g. from *trans*-$[PtHCl(PEt_3)_2]$ by *trans*-$[PtCl(solvent)(PEt_3)_2]^+$) and a second oxidation process. A product containing no chloride ligands must also be formed to maintain mass balance, but this remains undetected. These factors make unambiguous differentiation between the possible pathways difficult using coulometric data alone. In order to further probe the Pt–H cleavage process, a cooxidation of *trans*-$[PtHCl(PEt_3)_2]$ and chloride ion (in the form of NEt_4Cl) was performed. Such cooxidations typically lead to *in situ* generation of chlorine which oxidatively attacks platinum(II) to produce platinum(IV) [6]. In the present case, electrolysis of a 1:2 mixture of *trans*-$[PtHCl(PEt_3)_2]$ and NEt_4Cl at +1.45 V followed by work-up of the oxidized solution (see 'Experimental') and $^{31}P\{^1H\}$ NMR examination led to identification of $[PtCl_2(PEt_3)_2]$ (from three experiments: *cis*-, $\sim$2–10%; *trans*-, $\sim$98–85%) and *trans*-$[PtCl_4(PEt_3)_2]$ ($\sim$0–5%) as the only phosphorus-containing products.

Analogous chemical oxidations of *trans*-$[PtHCl(PEt_3)_2]$ using molecular chlorine (as its iodobenzene adduct [6]) lead to very similar product distributions: *trans*-$[PtCl_2(PEt_3)_2]$ (from three experiments: $\sim$100–50%), *cis*-$[PtCl_2(PEt_3)_2]$ ($\sim$0–35%) and *trans*-$[PtCl_4(PEt_3)_2]$ ($\sim$0–15%).

These results suggest that *in situ* generation of chlorine in the electrochemical experiments might be followed by oxidative addition to Pt(II) and rapid reductive elimination of HCl to produce $[PtCl_2(PEt_3)_2]$, which may itself be attacked by chlorine. Thus, these experiments suggest that Pt–H cleavage is accompanied by protic acid formation and, if protic acid formation could indeed be detected in systems with and without chloride ion as a co-oxidant, then both types of electrochemical oxidation must be accompanied by formal proton extrusion.

In order to examine this possibility, non-aqueous acid–base titrations were performed [20, 22] on the acetonitrile ($pK_s = 28.6$) solutions generated by electrochemical oxidation using methanolic sodium hydroxide ($1.55–1.75 \times 10^{-2}$ M) as the base and thymol blue ($pK = 13.4$) as the indicator. Table 1 shows the results obtained. Entries 1–3 show that as the amount of *trans*-[$PtHCl(PEt_3)_2$] used in the electrolysis is increased, the amount of base required to neutralize the oxidized solution increases also. Entries 4–6 show that the same is true when *trans*-[$PtHCl(PEt_3)_2$] is co-oxidized with chloride ion. In order to correct for background effects and ensure that artifacts are minimized, acid–base titrations on electrochemically oxidized solutions of *cis*-[$PtCl_2(PEt_3)_2$], where clearly no H^+ extrusion is possible, were performed. Entries 7–9 show that a reproducible and constant amount of base is indeed consumed in these titrations but that the amount of base does not increase as the amount of [$PtCl_2(PEt_3)_2$] used in the oxidation is increased. Similarly, oxidation of NEt_4Cl alone (entries 10–12), followed by titration, results in consumption of base but the amount required does not increase with the amount of NEt_4Cl oxidized. These results are displayed graphically in Fig. 2.

Thus, from these experiments we conclude that eqn. (3) is a reasonable representation of the chemistry that occurs when *trans*-[$PtHCl(PEt_3)_2$] is electrochemically oxidized. The formal oxidation that occurs is thus not $Pt(II) \rightarrow Pt(IV)$ but rather $H^- \rightarrow H^+$. Attempts to observe platinum(IV) hydrides in this system fail as proton extrusion either accompanies oxidation or follows it rapidly.

Experimental

General procedure

Acetonitrile (Fischer, ACS grade) was stirred with CaH_2 for 48 h, decanted and distilled from P_4O_{10}. The fraction boiling in the range 82–84 °C was refluxed with CaH_2 for 8 h and then fractionally distilled under argon. The fraction boiling in the range 82–84 °C was stored under argon over Al_2O_3 (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. *trans*-[$PtHCl(PEt_3)_2$] and *cis*-[$PtCl_2(PEt_3)_2$] were prepared by literature methods [23].

$^{31}P\{^1H\}$ NMR spectra were measured on a Jeol FX-90Q spectrometer. Chemical shifts were measured relative to 85% H_3PO_4 as an external standard, with positive values representing deshielding.

Cyclic voltammograms were obtained using a Bioanalytical Systems 100 Control Unit. Typically, 10^{-3} M solutions of the platinum complexes in acetonitrile which was 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 [24–26]. Controlled potential bulk oxidative electrolyses were performed using a Bioanalytical Systems SP-2 Synthetic Poten-

TABLE 1. Results of acid–base titrations performed on electrochemically oxidized solutions

Entry no.		Substrate (mol × 10^{-5})	Base[a] (mol × 10^{-5})	Mole substrate / Mole base
1	*trans*-[$PtHCl(PEt_3)_2$]	4.06	3.56	1.14
2		5.35	4.83	1.10
3		6.41	6.54	0.98
4	*trans*-[$PtHCl(PEt_3)_2$] + 2 equiv. NEt_4Cl	4.55	3.92	1.16
5		5.41	4.83	1.12
6		6.70	8.90	0.76
7	*cis*-[$PtCl_2(PEt_3)_2$] + 2 equiv. NEt_4Cl	4.40	3.72	1.18
8		4.58	3.69	1.24
9		6.33	3.63	1.74
10	NEt_4Cl	9.04	3.06	3.00
11		10.00	3.47	2.87
12		15.50	2.67	5.80

[a] Value after correction for background (see 'Experimental').

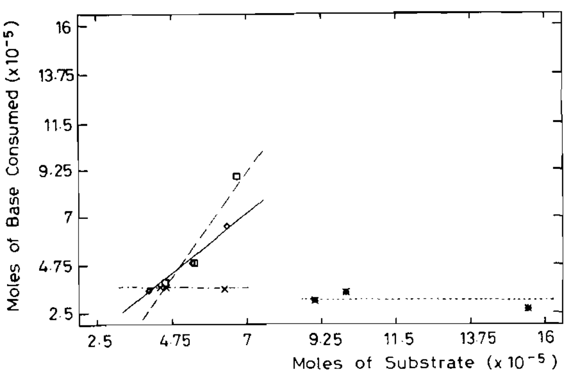

Fig. 2. Plot of mol of base consumed vs. mol of substrate employed in the electrochemical oxidation of the substrates: *trans*-$[PtHCl(PEt_3)_2]$, –◇–; *trans*-$[PtHCl(PEt_3)_2]+2NEt_4Cl$, –□–; *cis*-$[PtCl_2(PEt_3)_2]+2NEt_4Cl$, –×–; NEt_4Cl, –*–.

tiostat. 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. The auxiliary electrode compartment contains 7 ml of mercury connected to the potentiostat via a platinum spiral wire.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 trans-[PtHCl(PEt$_3$)$_2$]

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. A total of 100 ml of a 0.08 M solution of TBAP in acetonitrile was introduced into 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 1 h. 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 *trans*-$[PtHCl(PEt_3)_2]$ (~20 mg) and, for experiments involving 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 C_6H_6 (5 ml), filtered and evaporated down to a solid. The solid was then dissolved in C_6D_6 (1 ml). $^{31}P\{^1H\}$ NMR spectroscopy was used for product identification and data are given in Table 2. Details are given in the text. Since products are extracted into C_6D_6 for analysis, there is always the possibility that product ratios so measured might differ from product ratios in the more polar CH_3CN reaction medium. We have seen no evidence in these experiments that product ratios are biased to favor less polar products by extraction in C_6D_6.

Controlled potential bulk oxidative electrolysis of cis-[PtCl$_2$(PEt$_3$)$_2$]

For standardization of acid–base titrations, the electrochemical oxidation of *cis*-$[PtCl_2(PEt_3)_2]$ was performed using the method we have described previously [6].

Non-aqueous acid–base titrations

NaOH (ACS grade) was weighed and dissolved in CH_3OH in a volumetric flask to make roughly a $1.5–1.8\times10^{-2}$ M solution. The concentration of $NaOH/CH_3OH$ was standardized by titration against benzoic acid (heated at 110 °C in an oven for 24 h prior to titration) which was dissolved in CH_3CN. Thymol blue was used as the indicator (50 mg in 5 ml CH_3CN) with a color change from green to blue at the end point.

After an electrochemical oxidation, the solution was transferred to a flask (previously heated in an oven for 24 h and cooled under argon) and divided into two portions of roughly 45–46 ml. Titrations were performed with the standardized $NaOH/CH_3OH$ using thymol blue/CH_3CN as the indicator.

To correct for background effects, a blank solution consisting of 0.08 M TBAP in CH_3CN was titrated and the amount of base consumed was used as a background value and was subtracted from the values shown as entries 1–12 in Table 1. Similarly, in titrations 4–6, effects due to the presence of NEt_4Cl were corrected for by subtraction of values obtained in titrations 7–9. The resulting values for titrations 4–6 thus correspond to the base required to neutralize the acid produced by hydride oxidation.

Identification of trans-[PtCl(solvent)(PEt$_3$)$_2$]$^+$

Silver hexafluorophosphate (0.01 g) was weighed in a glove-box and transferred to a dried flask. Under an argon steam, CH_3CN (10 ml) was transferred into the flask and stirred until the silver salt had completely dissolved. Under argon, this solution was quickly added to more than 1 equivalent of *trans*-

TABLE 2. $^{31}P\{^{1}H\}$ NMR data for triethylphosphine complexes[a]

Complexes	δ P (ppm)	^{1}J (^{195}Pt, ^{31}P) (Hz)
trans-[PtHCl(PEt$_3$)$_2$]	22.4	2712
cis-[PtCl$_2$(PEt$_3$)$_2$]	8.7 (8.3)	3496 (3501)
trans-[PtCl$_2$(PEt$_3$)$_2$]	11.7 (11.3)	2419 (2390)
trans-[PtCl(solvent)(PEt$_3$)$_2$]$^+$	15.1	2179
trans-[PtCl$_4$(PEt$_3$)$_2$]	4.4 (4.7)	1446 (1443)

[a] For room temperature measurements in C_6D_6 with values for CD_3CN solutions shown in parentheses.

[PtCl$_2$(PEt$_3$)$_2$] dissolved in CH_3CN. Immediately a white cloudy suspension formed. The suspension was stirred for 10 min and then filtered. The resulting solution was evaporated under vacuum and the residue was dissolved in C_6D_6 and quickly transferred to a 5 mm NMR tube for spectroscopic examination. Data are given in Table 2.

Oxidation of trans-[PtHCl(PEt$_3$)] using $C_6H_5I \cdot Cl_2$

In a typical experiment, *trans*-[PtHCl(PEt$_3$)$_2$] (~20 mg) was weighed and transferred to a dried flask. CH_3CN (10 ml) was added to the flask and stirred until the complex had completely dissolved. One equivalent of $C_6H_5I \cdot Cl_2$ was added to the flask and stirred for 4 h. After evaporation to dryness, the residue was dissolved in CD_3CN and transferred to a 5 mm NMR tube for spectroscopic examination. Data are given in Table 2.

Conclusions

Electrochemical oxidation of *trans*-[PtHCl(PEt$_3$)$_2$] produces *trans*-[PtCl(solvent)(PEt$_3$)$_2$]$^+$ via H^+ extrusion and not by H$^\cdot$ transfer. The formal oxidation observed is $H^- \rightarrow H^+$ and not Pt(II) → Pt(IV). Based upon these results, the oxidation of *trans*-[PtRCl(PEt$_3$)$_2$] is of interest since carbocation extrusion may be possible from such systems. Investigations in this area are underway.

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