Reactions of *cis*-[PtCl$_2$(PEt$_3$)$_2$] with Silver Salts in Aqueous Solution, in the Presence or Absence of PEt$_3$

Duncan W. Bruce, Rodney F. Jones, and David J. Cole-Hamilton *

Department of Inorganic, Physical and Industrial Chemistry, University of Liverpool, P.O. Box 147, Liverpool L69 3BX

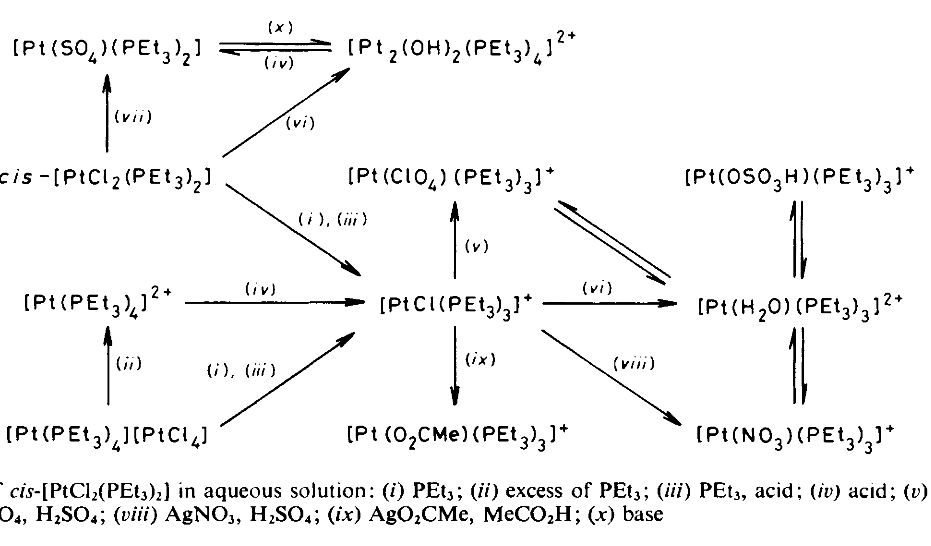
Reaction of AgX (X = NO$_3$ or $\frac{1}{2}$SO$_4$) with *cis*-[PtCl$_2$(PEt$_3$)$_2$] in neutral water affords [Pt$_2$(OH)$_2$(PEt$_3$)$_4$]$^{2+}$ or [Pt(SO$_4$)(PEt$_3$)$_2$] the latter of which can be isolated from dilute sulphuric acid solutions. In water in the presence of PEt$_3$ (2 mol equivalents), [Pt(PEt$_3$)$_4$][PtCl$_4$] gives a mixture of [PtCl(PEt$_3$)$_3$]$^+$ and [Pt(PEt$_3$)$_4$]$^{2+}$ although the latter gives [PtCl(PEt$_3$)$_3$]$^+$ and [PHEt$_3$]$^+$ on acidification. Addition of 2AgX (X = NO$_3$, O$_2$CMe, ClO$_4$, or $\frac{1}{2}$SO$_4$) to these acidified solutions gives [PtX(PEt$_3$)$_3$]$^+$, although, in aqueous solution, complex equilibria apparently exist between the co-ordinated anion and water. The ions [PtX(PEt$_3$)$_3$]$^+$ (X = NO$_3$, ClO$_4$, or O$_2$CMe) can be isolated as their [PF$_6$]$^-$ or [ClO$_4$]$^-$ (X = ClO$_4$) salts. For X = $\frac{1}{2}$SO$_4$, attempts to isolate a product by addition of KPF$_6$ generally led to [PtCl(PEt$_3$)$_3$]$^+$ although on one occasion [Pt(H$_2$O)(PEt$_3$)$_3$]$^{2+}$ was recovered. Reaction of H$_2$ with [PtY(PEt$_3$)$_3$]$^{n+}$ (Y = HSO$_4$, n = 1 ; Y = H$_2$O, n = 2) gives [PtH(PEt$_3$)$_3$]$^+$, which with K$_2$S$_2$O$_8$ gives [PtY(PEt$_3$)$_3$]$^{n+}$. The isolated complexes have been fully characterised by spectroscopic means and their relevance to systems employed in the photochemical decomposition of water is discussed.

During the course of our investigations[1-3] into the photochemical decomposition of water catalysed by [PtH(PEt$_3$)$_3$]$^+$ we have proposed that the platinum-containing product obtained from the near-u.v. photolysis of [PtH(PEt$_3$)$_3$]$^+$ in dilute H$_2$SO$_4$ is [PtY(PEt$_3$)$_3$]$^{n+}$ [Y = HSO$_4$, n = 1; Y = H$_2$O or (SO$_4$)Pt(PEt$_3$)$_3$, n = 2]. We now report details of studies carried out to identify this complex, as well as an apparent heterolytic activation of hydrogen and the reaction of K$_2$S$_2$O$_8$ with [PtH(PEt$_3$)$_3$]$^+$.

Results and Discussion

Reaction of cis-[PtCl$_2$(PEt$_3$)$_2$] *or* [Pt(PEt$_3$)$_4$][PtCl$_4$] *with Silver Salts* (*see Scheme* 1).—(*a*) *In the absence of* PEt$_3$. Reaction of *cis*-[PtCl$_2$(PEt$_3$)$_2$] with 2AgX (X = NO$_3$ or $\frac{1}{2}$SO$_4$) in water at neutral pH leads to a solution containing the known[4] hydroxo-bridged dimer [Pt$_2$(OH)$_2$(PEt$_3$)$_4$]$^{2+}$, which can be precipitated as its [PF$_6$]$^-$ salt, and a new compound whose ^{31}P and ^{195}Pt n.m.r. parameters suggest that it is a bis(phosphine)platinum(II) species (for n.m.r. and analytical data see Tables 1—3). Acidification of such solutions with H$_2$SO$_4$ allows complete conversion to this new compound. It cannot be precipitated with [PF$_6$]$^-$ or [SbF$_6$]$^-$, although addition of NaBPh$_4$ gives a colourless solid which rapidly turns to a yellow oil on standing *in vacuo*, suggesting that decomposition readily occurs. Fast atom bombardment (f.a.b.) mass spectroscopic studies of these acidified solutions clearly show a signal at m/z 528, suggesting the presence of [Pt(SO$_4$)(PEt$_3$)$_2$ + H]$^+$. Indeed, a neutral complex, [Pt(SO$_4$)(PEt$_3$)$_2$], can be extracted into CHCl$_3$ from these solutions. This complex was briefly reported by Jensen[5] in 1936, although unlike its triphenylphosphine analogue[6] it has not been fully characterised until now. Being neutral, it is perhaps surprising that this complex is soluble in water, but we suggest that the complex is sufficiently solvated to confer solubility and this would then account for its inability to be precipitated as a [PF$_6$]$^-$ salt. Interestingly it does not redissolve in water after isolation.

(*b*) *In the presence of added* PEt$_3$. Stirring [Pt(PEt$_3$)$_4$][PtCl$_4$] in neutral water with 2 mol equivalents of PEt$_3$ leads to the formation of a pale green solution containing [PtCl(PEt$_3$)$_3$]$^+$[7] and [Pt(PEt$_3$)$_4$]$^{2+}$.[5,8] In the presence of an excess of



Scheme 1. Reactions of *cis*-[PtCl$_2$(PEt$_3$)$_2$] in aqueous solution: (*i*) PEt$_3$; (*ii*) excess of PEt$_3$; (*iii*) PEt$_3$, acid; (*iv*) acid; (*v*) AgClO$_4$, HClO$_4$; (*vi*) Ag$_2$SO$_4$; (*vii*) Ag$_2$SO$_4$, H$_2$SO$_4$; (*viii*) AgNO$_3$, H$_2$SO$_4$; (*ix*) AgO$_2$CMe, MeCO$_2$H; (*x*) base

Table 1. $^{31}P-\{^1H\}$ N.m.r.[a] spectral data [b] of $[PtX(PEt_3)_3]^{n+}$ in aqueous solution [c] [(i)—(vi)] and as isolated complexes [(vii)—(xi)] [d]

			P *cis* to X		P *trans* to X		
Complex	X	pH	δ/p.p.m.	^1J(Pt–P)/Hz	δ/p.p.m.	^1J(Pt–P)/Hz	^2J(P–P)/Hz
(i)	NO_3	<7	24.21(d)	2 275	3.43(t)	3 642	19.5
(ii)	ClO_4	<7	24.51(d)	2 264	3.63(t)	3 670	19.6
(iii)	$\frac{1}{2}SO_4$	<7	24.7(d)	2 265	3.77(t)	3 652	19.5
(iv)	$\frac{1}{2}SO_4$	7	24.6(d)	2 261	3.60(t)	3 648	19.5
(v)	O_2CMe	<7	19.1(d)	2 389	−1.5(t)	3 447	20.3
(vi)	Cl	<7	18.5(d)	2 250	10.9(t)	3 544	19.4
(vii)	H_2O	*e*	25.3(d)	2 310	5.7(t)	3 760	20.4
(viii)	NO_3	*e*	20.57(d)	2 395	0.26(t)	3 508	19.4
(ix)	ClO_4	*f*	23.46(d)	2 329	7.06(t)	3 861	19.5
(x)	O_2CMe	*e*	20.5(d)	2 437	−0.35(t)	3 323	21.0
(xi)	Cl	*e*	19.6(d)	2 265	10.9(t)	3 467	19.4
(xii)	F[g]	*e*	27.3(dd)	2 330	1.4(dt)	*h*	19.6

[a] Chemical shifts to high frequency of external 85% H_3PO_4. [b] $[PF_6]^-$ resonances omitted. [c] Solutions prepared from *cis*-$[PtCl_2(PEt_3)_2]$ {or $[Pt(PEt_3)_4][PtCl_4]$}, PEt_3, and AgX in water at pH adjusted with HX. [d] As $[PF_6]^-$ salts. [e] In acetone. [f] As $[ClO_4]^-$ salt in CH_2Cl_2. [g] Ref. 11. $^2J(P-F_{cis})$ 32.1, $^2J(P-F_{trans})$ 139.9 Hz. [h] Satellites not seen.

Table 2. $^{31}P-\{^1H\}$ and $^{195}Pt-\{^1H\}$ parameters for $[Pt(PEt_3)_4]^{2+}$, $[Pt(SO_4)(PEt_3)_2]$, and $[Pt_2(OH)_2(PEt_3)_4]^{2+}$

Compound	Solvent	Nucleus	δ/p.p.m.	^1J(Pt–P)/Hz
$[Pt(PEt_3)_4]^{2+}$	Water	^{31}P	4.76(s) [a]	2 238
$[Pt(PEt_3)_4][PF_6]_2$	Me_2CO	^{31}P	5.4(s)[a,b]	2 236
$[Pt(PEt_3)_4]^{2+}$	Water	^{195}Pt	−58.8(qnt) [c]	2 236
$[Pt(SO_4)(PEt_3)_2]$	Dilute H_2SO_4	^{31}P	9.6(s) [a]	3 749
	$CHCl_3$	^{31}P	4.93(s) [a]	3 723
	Water	^{195}Pt	495.8(t) [c]	3 723
$[Pt_2(OH)_2(PEt_3)_4]^{2+}$	Water	^{31}P	7.13(s) [a]	3 442
$[Pt_2(OH)_2(PEt_3)_4][PF_6]_2$	Me_2CO	^{31}P	6.66(s) [a,b]	3 442

[a] Chemical shifts to high frequency of external 85% H_3PO_4. [b] $[PF_6]^-$ resonances omitted. [c] Chemical shifts are to high frequency of $\Xi(^{195}Pt)$ of 21.4 MHz.

Table 3. Microanalytical data for the platinum complexes

	Analysis [a]/%		
Complex	C	H	P
$[Pt(H_2O)(PEt_3)_3][PF_6]_2$	25.25 (25.2)	5.55 (5.5)	17.8 (18.1)
$[Pt(PEt_3)_4][PF_6]_2$	30.05 (30.1)	6.55 (6.25)	19.65 (19.45)
$[PtCl(PEt_3)_3][PF_6]$ [b]	29.6 (29.6)	6.2 (6.15)	17.05 (17.0)
$[Pt(NO_3)(PEt_3)_3][PF_6]$ [c]	28.5 (28.6)	6.0 (6.4)	16.4 (16.4)
$[Pt(ClO_4)(PEt_3)_3][ClO_4]$ [d]	28.6 (28.85)	6.4 (6.0)	12.55 (12.4)
$[Pt(SO_4)(PEt_3)_2]$ [e]	26.75 (27.3)	5.7 (5.7)	11.25 (11.75)
$[Pt(O_2CMe)(PEt_3)_3][PF_6]$	31.95 (31.9)	6.6 (6.4)	15.7 (16.45)
$[Pt_2(OH)_2(PEt_3)_4][PF_6]_2$	24.3 (24.3)	5.8 (5.7)	15.8 (15.7)

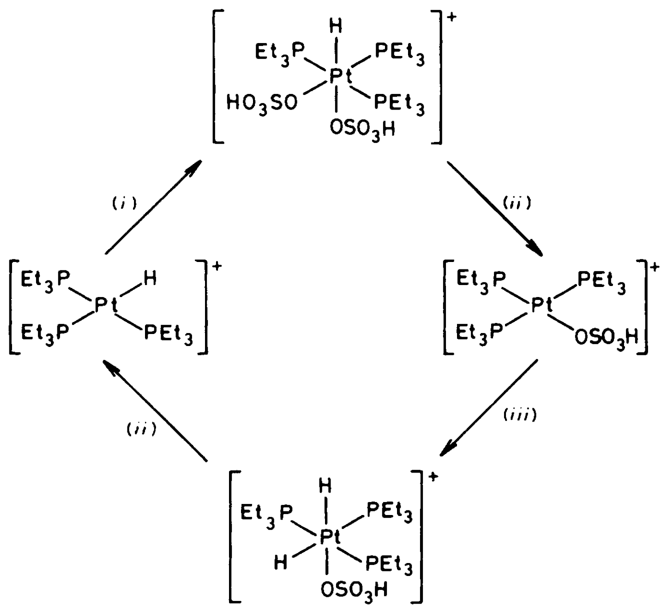
[a] Calculated values in parentheses. [b] Cl 4.85 (4.85)%. [c] N 1.9 (1.9)%. [d] Exploded during Cl analysis. [e] S 5.95 (6.05)%.

PEt_3, $[Pt(PEt_3)_4]^{2+}$ is formed exclusively and can be isolated as its $[PF_6]^-$ salt. Acidification of solutions containing $[Pt(PEt_3)_4]^{2+}$ results in loss of phosphine from the complex {as $[PHEt_3]^+$; $^{31}P-\{^1H\}$ n.m.r. δ 23.1 (s)} and leaves $[PtCl(PEt_3)_3]^+$ as the only platinum-containing species detected in solution. If *cis*-$[PtCl_2(PEt_3)_2]$ is used in place of $[Pt(PEt_3)_4][PtCl_4]$ in the initial reaction at acidic pH, smooth conversion into $[PtCl(PEt_3)_3]^+$ (isolable as its $[PF_6]^-$ salt) is observed.

Stirring *cis*-$[PtCl_2(PEt_3)_2]$ in aqueous HX with 1 mol equivalent of PEt_3 and 2 mol equivalents of AgX (X = NO_3, $\frac{1}{2}SO_4$, ClO_4, or O_2CMe) leads to precipitation of AgCl and the formation of a tris(phosphine)platinum(II) species. For X = O_2CMe, this is $[Pt(O_2CMe)(PEt_3)_3]^+$ but ^{31}P n.m.r. spectra of all solutions obtained for X = NO_3, ClO_4, or $\frac{1}{2}SO_4$ are identical, suggesting either that the cationic platinum species all have identical ^{31}P n.m.r. spectra or that complex equilibria exist involving exchange of X^- with H_2O. We favour the latter suggestion since the ^{31}P n.m.r. spectra (in organic solvents) of the cations, isolated as their $[PF_6]^-$ (or $[ClO_4]^-$) salts, show marked differences in chemical shifts and particularly in their ^1J(Pt–P) coupling constants (see Table 1). We also have direct evidence that at neutral pH, Cl^- exchanges on the n.m.r. time-scale between $[PtCl(PEt_3)_3]^+$ and another chloro-species, perhaps containing silver (see below).

For X = NO_3[7] or O_2CMe, these cationic species can be isolated as their $[PF_6]^-$ salts on addition of aqueous KPF_6 or $[NH_4][PF_6]$, whilst $[Pt(ClO_4)(PEt_3)_3][ClO_4]$ can be extracted from precipitated AgCl with CH_2Cl_2.

All attempts reproducibly to isolate a product containing co-ordinated H_2O, $[SO_4]^{2-}$, or $[HSO_4]^-$ from solutions prepared by reaction of *cis*-$[PtCl_2(PEt_3)_2]$, PEt_3, and Ag_2SO_4 in dilute H_2SO_4 have proved unsuccessful. In all cases, the major product precipitated on addition of KPF_6 or $[NH_4][PF_6]$ is $[PtCl(PEt_3)_3][PF_6]$. This is somewhat surprising in view of the fact that AgCl is insoluble in water, but we believe that chloride ions remain in solution as they will readily form more soluble chlorosilver complexes with any excess of phosphine present.[9] ^{31}P N.m.r. resonances would not be expected from these complexes at 25 °C on account of their substitutional lability.[9] Due to this lability, it is probable that the chloride ion also exchanges between platinum and silver, particularly in neutral solution. Partial support for this contention comes from the observation that the ^{31}P n.m.r. spectra of solutions obtained from *cis*-$[PtCl_2(PEt_3)_2]$, PEt_3, and Ag_2SO_4 at low pH show signals arising from $[PtCl(PEt_3)_3]^+$ (*ca.* 20% of the platinum species present), but on neutralisation, although no precipitation occurs, signals from this compound cannot be observed. Addition of $[NH_4][PF_6]$ to this neutral solution



Scheme 2. Proposed mechanism for thermal interconversion of $[PtH(PEt_3)_3]^+$ and $[Pt(HSO_4)(PEt_3)_3]^+$: (*i*) $[S_2O_8]^{2-}$; (*ii*) $-H_2SO_4$; (*iii*) H_2

still precipitates $[PtCl(PEt_3)_3][PF_6]$, confirming that complex equilibria are set up. Presumably the least soluble species precipitates.

On one occasion, fine needle-shaped crystals grew in the filtrate {after precipitation and removal of $[PtCl(PEt_3)_3][PF_6]$} in sufficient quantity to allow full spectroscopic and microanalytical characterisation as $[Pt(H_2O)(PEt_3)_3][PF_6]_2$. The presence of co-ordinated water, unusual in phosphine complexes of Pt^{II},[10] was confirmed by i.r. spectroscopy [ν(O–H) at 3 640 and 3 575 cm^{-1} and δ(HOH) at 1 625 cm^{-1}]. That the water in this complex is extremely labile is confirmed by the observation that the compound is slowly converted into the known [11] $[PtF(PEt_3)_3][PF_6]$ on standing in acetone (^{31}P n.m.r. evidence), the fluoride arising from $[PF_6]^-$, possibly *via* a complex decomposition pathway.[12,13]

Reaction of $[PtY(PEt_3)_3]^{n+}$ *with* H_2.—Treatment of solutions of $[PtY(PEt_3)_3]^{n+}$ with hydrogen (1 atm, 101 325 Pa) allows [14] smooth conversion into $[PtH(PEt_3)_3]^+$. At first sight it would appear that this represents an example of heterolytic cleavage [15] of the H–H bond. Although this is essentially the case, the mechanism of the reaction probably involves oxidative addition of hydrogen to give the platinum(IV) intermediate $[PtH_2Y(PEt_3)_3]^{n+}$, which loses HY to give $[PtH(PEt_3)_3]^+$. Similar explanations have been proposed for other systems,[15] *e.g.* the reaction of *cis*-$[PtCl_2(PEt_3)_2]$ with hydrogen to give [16] *trans*-$[PtH(Cl)(PEt_3)_2]$ and HCl, although much more forcing conditions are required.

This series of reactions, summarised in Scheme 2, is the exact reverse of those that we have postulated [2,3] for the photochemical production of hydrogen from aqueous acidic solutions of $[PtH(PEt_3)_3]^+$ and shows not only that the production of hydrogen is thermodynamically uphill, but also that $[PtH_2Y(PEt_3)_3]^{n+}$ is a plausible intermediate.

Further support for the platinum(IV) dihydride intermediate comes from work by Ebsworth and co-workers [17] who showed that, in non-aqueous solvents, HCl oxidatively adds to $[PtH(PEt_3)_3]^+$ to give $[PtH_2Cl(PEt_3)_3]^+$. We have not however been able to detect the platinum(IV) intermediate by ^{31}P n.m.r. or f.a.b. mass spectroscopy, and so we cannot rule out the possibility that the production of hydrogen involves photochemical loss of H^- from $[PtH(PEt_3)_3]^+$.

Reaction of $[PtH(PEt_3)_3]^+$ *with* $[S_2O_8]^{2-}$.—Reaction of 1 mol equivalent of $K_2S_2O_8$ with $[PtH(PEt_3)_3]^+$ in dilute sulphuric acid gives $[PtY(PEt_3)_3]^{n+}$ ($Y = H_2O$, $n = 2$; $Y = HSO_4$, $n = 1$). It is probable that this reaction occurs *via* oxidative addition of $H_2S_2O_8$ to the platinum centre to give the platinum(IV) intermediate $[PtH(SO_4H)_2(PEt_3)_3]^+$ which loses H_2SO_4 to give the observed product; this reaction is summarised in Scheme 2. Once again, this supports the mechanism which we have proposed [2,3] for $[S_2O_8]^{2-}$ production.

In addition, $[Pt(SO_4)(PEt_3)_2]$ and PEt_3O are also produced in this reaction, presumably because $[S_2O_8]^{2-}$ oxidises a triethylphosphine ligand from $[PtH(PEt_3)_3]^+$ or $[PtY(PEt_3)_3]^{n+}$.* This would then account for the observed production of small amounts of both $[Pt(SO_4)(PEt_3)_2]$ and PEt_3O on far-u.v. photolysis of sulphuric acid solutions of $[PtH(PEt_3)_3]^+$, as photochemically produced peroxodisulphate [2,3] could carry out this oxidation.

Experimental

Microanalyses were by the Liverpool University Microanalytical Service, Elemental Microanalyses Ltd., and the University of Kent Microanalytical Service. Infrared spectra were recorded on a Perkin-Elmer 577 grating spectrometer either as KBr discs or Nujol mulls between CsI plates. Proton n.m.r. spectra were recorded on Perkin-Elmer R12B or Bruker WM250 spectrometers, ^{31}P and ^{195}Pt n.m.r. spectra on JEOL FX90Q (City of London Polytechnic) or Bruker WM250 (Liverpool) spectrometers operating in the pulse Fourier-transform mode with proton-noise decoupling. Melting points were recorded in air in an Electrothermal melting-point apparatus and are uncorrected.

Analysis by f.a.b. mass spectrometry was performed on a VG Analytical 7070E medium-resolution mass spectrometer. The spectra were obtained in both positive- and negative-ion modes for all samples examined. The samples were loaded onto the target as aqueous or chloroform solutions at *ca.* 1 μg μl^{-1} as 1-μl films. Glycerol was used as the matrix. The atom gun was operated at 8 kV and xenon was employed as the bombarding gas.

Non-aqueous solvents [tetrahydrofuran, diethyl ether, and light petroleum (b.p. 40—60 °C)] were dried before use by distillation from sodium diphenylketyl under nitrogen and water was purified by distillation. All solvents were thoroughly degassed before use and manipulations were carried out under nitrogen using standard Schlenk-line and catheter-tubing techniques.

The complexes $[Pt(PEt_3)_4][PtCl_4]$,[8b] *cis*-$[PtCl_2(PEt_3)_2]$,[8b] $[Pt(PEt_3)_3]$,[18] and $[PtH(PEt_3)_3]^+$ (ref. 19) were prepared by standard literature methods.

Sulphatobis(triethylphosphine)platinum(II).—The salt Ag_2SO_4 (0.31 g, 9.9 × 10^{-4} mol) was stirred overnight, in the dark, with a suspension of *cis*-$[PtCl_2(PEt_3)_2]$ (0.5 g, 9.9 × 10^{-4} mol) in water (20 cm^3). Precipitated AgCl was removed by filtration and the remaining solution was acidified with H_2SO_4 (10 mol dm^{-3}, five drops). Potassium sulphate (0.86 g, 4.95 × 10^{-3} mol) was added and dissolved. This solution was stirred vigorously with chloroform (3 × 20 cm^3) and each time the chloroform layer was separated and dried over Na_2SO_4. The resulting chloroform solution was reduced in volume on a rotary evaporator and light petroleum was added to crystallise the

---

* PEt_3 does not react with oxygen in acidic solution.

complex as fine, colourless needles. Yield 0.107 g (*ca.* 20%), m.p. 230 °C (decomp.); f.a.b. mass spectrum, *m/z* 528 $[Pt(SO_4)(PEt_3)_2 + H]^+$. I.r.: 1 420w (sh), 1 418m, 1 250s, 1 150s, br, 1 042s, 1 015w (sh), 895s, 775s, 745m (sh), 720m (sh), 680w (sh), 650s, 615m, 562m, 525w, 445m, and 400w, br cm^{-1}.

Di-μ-hydroxo-tetrakis(triethylphosphine)diplatinum(II) *Hexafluorophosphate.*—The complex *cis*-$[PtCl_2(PEt_3)_2]$ (0.31 g, 6.2×10^{-4} mol) was stirred with $AgNO_3$ (0.32 g, 1.86×10^{-3} mol) in distilled water (20 cm^3) for *ca.* 7 d. The reaction mixture was filtered (to remove precipitated AgCl) and then added to KPF_6 (1 g) in water (20 cm^3). The resulting colourless precipitate was recovered by filtration, and recrystallisation from acetone–diethyl ether afforded the complex as colourless crystals. Yield 0.29 g (*ca.* 40%). I.r.: ν(O–H) at 3 520 cm^{-1} (lit.,[4] 3 450 cm^{-1}).

Chlorotris(triethylphosphine)platinum(II) *Hexafluorophosphate.*—The salt $[Pt(PEt_3)_4][PtCl_4]$ (0.476 g, 4.7×10^{-4} mol) was stirred with PEt_3 (0.14 cm^3, 2 mol equiv.) in water (30 cm^3) for 3 h. The pale green reaction mixture was treated with a few drops of HCl (10 mol dm^{-3}) until the solution became colourless. It was then added to a solution of $[NH_4][PF_6]$ (1 g) in water (30 cm^3), producing a colourless precipitate which was recovered by filtration. Recrystallisation from acetone–diethyl ether afforded the complex as colourless crystals, m.p. 201—203 °C. Yield 0.29 g (*ca.* 85%). I.r.: ν(Pt–Cl) at 295 cm^{-1}.

Tetrakis(triethylphosphine)platinum(II) *Hexafluorophosphate.*—The salt $[Pt(PEt_3)_4][PtCl_4]$ (0.512 g, 5×10^{-4} mol) was stirred in water (30 cm^3) with excess of PEt_3 (0.9 cm^3, 3×10^{-3} mol) for 3 h, to give a clear green-yellow solution. Addition of this solution to a solution of $[NH_4][PF_6]$ (1 g) in water (30 cm^3) precipitated a yellow solid which was recovered by filtration. Recrystallisation from acetone–diethyl ether afforded the complex as bright yellow needles, m.p. 182—184 °C. Yield 0.58 g (*ca.* 60%).

Acetatotris(triethylphosphine)platinum(II) *Hexafluorophosphate.*—Glacial acetic acid (eight drops) was added to a pale green solution obtained as described for $[PtCl(PEt_3)_3][PF_6]$ along with $Ag(O_2CMe)$ (0.157 g, 9.4×10^{-4} mol). This mixture was stirred overnight to give a precipitate of AgCl which was removed by filtration. The remaining clear, colourless solution was added to a solution of $[NH_4][PF_6]$ (1 g) in water (30 cm^3) producing a colourless precipitate which was recovered by filtration. Recrystallisation from acetone–diethyl ether afforded the complex as colourless crystals, m.p. 179—181 °C. Yield 0.30 g (*ca.* 85%). I.r.: 1 630m, 1 308m, 1 034m, 1 005w (sh), 838s, 763m, 728m, 673m, 635w, 552m, and 410w cm^{-1}.

Perchloratotris(triethylphosphine)platinum(II) *Perchlorate.*—(*a*) The salt $[Pt(PEt_3)_4][PtCl_4]$ (0.66 g, 6.6×10^{-4} mol) was stirred in water (30 cm^3) with PEt_3 (0.2 cm^3, 1.32×10^{-3} mol) for 3 h. Perchloric acid (7 mol dm^{-3}, 0.5 cm^3) was added {producing a white precipitate of $[PtCl(PEt_3)_3][ClO_4]$ (i.r. and n.m.r. evidence)} along with $AgClO_4$ (0.55 g, 2.64×10^{-3} mol) and the mixture was stirred overnight. Precipitated AgCl and product were removed by filtration and dried *in vacuo*, and then stirred in CH_2Cl_2 (20 cm^3) for 2 h. The AgCl was again removed by filtration, the CH_2Cl_2 was reduced in volume on a rotary evaporator, and diethyl ether was added to crystallise the compound as colourless crystals. The complex was identified as $[Pt(ClO_4)(PEt_3)_3][ClO_4]$ by its ^{31}P n.m.r. spectrum.

(*b*) (*i*) The salt $[Pt(PEt_3)_4][PtCl_4]$ (0.492 g) was stirred in water (20 cm^3) with PEt_3 (0.14 cm^3) for 3 h. Hydrochloric acid (10 mol dm^{-3}, eight drops) was added and the solution was stirred for a further 10 min. Excess of $HClO_4$ was then added giving a colourless precipitate of $[PtCl(PEt_3)_3][ClO_4]$ which was recovered by filtration, dried, and recrystallised from CH_2Cl_2–Et_2O. Yield 0.55 g (83%).

(*b*) (*ii*) The salt $[PtCl(PEt_3)_3][ClO_4]$ (0.55 g) was dissolved in CH_2Cl_2 (20 cm^3) and $AgClO_4$ (0.168 g) was added: the mixture was stirred overnight. The next day, precipitated AgCl was removed by filtration through Celite and the product crystallised by addition of Et_2O. Yield {based on $[Pt(PEt_3)_4][PtCl_4]$} = 0.457 g (62.5%). I.r.: ν[ClO_4(ionic)] at 1 050—1 150s, vbr, cm^{-1}; ν[ClO_4(bound)] at 1 030s (sh), 928w cm^{-1}. **CAUTION**: This compound explodes on heating!

Aquatris(triethylphosphine)platinum(II) *Hexafluorophosphate.*—A suspension of $[Pt(PEt_3)_4][PtCl_4]$ (0.806 g) in water (30 cm^3) was stirred with PEt_3 (0.24 cm^3) for 3 h. This produced a clear pale green solution to which Ag_2SO_4 (0.50 g) was added and the mixture was stirred overnight. Precipitated AgCl was removed by successive filtrations through Celite and a solution of $[NH_4][PF_6]$ [1 g in water (30 cm^3)] was added to the clear, colourless filtrate. This produced a heavy white precipitate which was removed by filtration and identified as $[PtCl(PEt_3)_3][PF_6]$. On one occasion, colourless needles grew from the filtrate. These were recovered by filtration and dried *in vacuo*. I.r.: 3 640m, 3 575m, 1 625w, 1 255w, 1 233w (sh), 1 032m, 1 010w (sh), 840s, br, 763m, 740w (sh), 725m, 558s, and 425w, br cm^{-1}. Yield 0.24 g (*ca.* 18%). On standing in acetone, ^{31}P n.m.r. spectra showed that the complex changed to give the known [11] $[PtF(PEt_3)_3]^+$ (see Table 1).

Reaction of $[PtY(PEt_3)_3]^{n+}$ *with* H_2.—The complex *cis*-$[PtCl_2(PEt_3)_2]$ (0.822 g, 1.63×10^{-3} mol) was stirred overnight in dilute sulphuric acid (20 cm^3) with Ag_2SO_4 (0.51 g, 1.63×10^{-3}) and PEt_3 (0.24 cm^3, 1.63×10^{-3} mol). The reaction mixture was filtered twice (to remove precipitated AgCl). Hydrogen was passed through the solution for 18 h. The ^{31}P-{^1H} n.m.r. spectrum showed complete conversion into $[PtH(PEt_3)_3]^+$.

Reaction of $[PtH(PEt_3)_3]^+$ *with* $[S_2O_8]^{2-}$.—The salt $K_2S_2O_8$ (0.067 g, 2.5×10^{-4} mol) was stirred in a sulphuric acid solution of $[PtH(PEt_3)_3]^+$ (10 cm^3, 2.5×10^{-2} mol dm^{-3}) for 4 h. The ^{31}P-{^1H} n.m.r. spectrum showed *ca.* 60% conversion into $[PtY(PEt_3)_3]^{n+}$ ($Y = H_2O$, $n = 2$; $Y = HSO_4^-$, $n = 1$), $[Pt(SO_4)(PEt_3)_2]$, and PEt_3O in the ratio 2 : 1 : 1. Using $K_2S_2O_8$ (0.134 g, 5×10^{-4} mol), complete conversion of hydride occurred into the same products in a 1 : 1 : 1 ratio.

Acknowledgements

We thank Dr. B. Odell (Shell Research Ltd.) for helpful discussions, Johnson Matthey Ltd. for loans of K_2PtCl_4, the S.E.R.C. for studentships (to R. F. J. and D. W. B.), Shell Research Ltd. for a C.A.S.E. award (to D. W. B.), Drs. J. Page and F. Cottee (Shell Research Ltd.) for f.a.b. mass spectra, and Drs. W. McFarlane and B. Wood for ^{195}Pt and ^{31}P n.m.r. spectra under the auspices of the S.E.R.C. low-field service. The high-field n.m.r. instrument was purchased largely with a grant from the S.E.R.C.

References

1 R. F. Jones and D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, 1981, 58.

2 R. F. Jones and D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, 1981, 1245.

3 D. J. Cole-Hamilton, R. F. Jones, J. R. Fisher, and D. W. Bruce, in 'Photogeneration of Hydrogen,' eds. A. Harriman and M. A. West, Academic Press, London, 1982, p. 105.

4 G. W. Bushnell, K. R. Dixon, R. G. Hunter, and J. J. McFarland, *Can. J. Chem.*, 1972, **50**, 3694.

5 K. A. Jensen, *Z. Anorg. Allg. Chem.*, 1936, **229**, 252.

6 J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 1971, 762.

7 G. G. Mather, G. J. N. Rapsey, and A. Pidcock, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 567.

8 (*a*) K. A. Jensen, *Z. Anorg. Allg. Chem.*, 1936, **229**, 225; (*b*) G. W. Parshall, *Inorg. Synth.*, 1970, **12**, 27.

9 E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc.*, 1972, **94**, 6386.

10 J. F. Britten, B. Lippert, C. J. L. Lock, and P. Pilon, *Inorg. Chem.*, 1982, **21**, 1936.

11 M. A. Cairns, K. R. Dixon, and J. J. McFarland, *J. Chem. Soc., Dalton Trans.*, 1975, 1159.

12 G. Smith, D. J. Cole-Hamilton, A. C. Gregory, and N. G. Gooden, *Polyhedron*, 1982, **1**, 97.

13 C. White, S. J. Thompson, and P. M. Maitlis, *J. Organomet. Chem.*, 1977, **134**, 319.

14 R. F. Jones, Ph.D. Thesis, University of Liverpool, 1981.

15 P. J. Brothers, *Prog. Inorg. Chem.*, 1981, **26**, 1.

16 P. N. Rylander, N. Himelstein, D. Steele, and J. Kreidl, *Englehard Ind. Tech. Bull.*, 1962, **3**, 1.

17 I. M. Blacklaws, L. C. Brown, E. A. V. Ebsworth, and F. J. S. Reed, *J. Chem. Soc., Dalton Trans.*, 1978, 877.

18 R. A. Schunn, *Inorg. Chem.*, 1976, **15**, 208.

19 D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1971, **93**, 3543.

Received 28*th November* 1983; *Paper* 3/2107