Chelate-stabilised Primary, Secondary, and Tertiary Alcohol and Alkoxo Platinum(II) Complexes. *X*-Ray Crystal Structure of $[\overline{Pt(Ph_2P}CH_2CH_2\overline{O})_2]\cdot H_2O$†

Nathaniel W. Alcock, Andrew W. G. Platt, and Paul G. Pringle *
Department of Chemistry, University of Warwick, Coventry CV4 7AL

The co-ordination chemistry of the phosphino alcohols Ph_2PCH_2CHROH, R = Me (**1b**) or H (**1c**), with platinum(II) is reported. Ligands (**1b**),(**1c**) form the neutral complexes *cis*-$[PtCl_2(Ph_2PCH_2CHROH)_2]$, R = Me (**4b**) or H (**4c**), which remain unchanged in $CDCl_3$. However, in CD_3OD the fluxional chelate $[PtCl(Ph_2PCH_2CHMeOH)(Ph_2PCH_2CHMeOH)]Cl$ (**2b**) is formed. The bis(alcohol) complex $[Pt(Ph_2PCH_2CHMeOH)_2][ClO_4]_2$ (**5b**) is made by treatment of (**4b**) with $AgClO_4$. Deprotonation of (**4b**) with NEt_3 or (**4c**) with NaOH gives the bis(alkoxo) species $[Pt(Ph_2PCH_2CHRO)_2]$, R = Me (**3b**) or H (**3c**), quantitatively. Treatment of (**4c**) with NEt_3 gives a complex which in solution has the fluxional, binuclear, unsymmetrically alkoxo-bridged structure $[Pt_2(\mu\text{-}Ph_2PCH_2CH_2O)_2(Ph_2PCH_2CH_2OH)_2]Cl_2$ (**6**) and in the solid state probably has the mononuclear structure $[PtCl(Ph_2PCH_2CH_2O)(Ph_2PCH_2CH_2OH)]$ (**8**). The effect of the methyl substituents in the ligand backbone is discussed. Phosphorus-31 n.m.r. evidence shows that the order of *trans* influence of alkoxo ligands is 3° > 2° > 1° but the differences are small. The *X*-ray structure determination of (**3c**) (*R* = 0.038 for 1 885 observed diffractometer-measured reflections) shows square planar co-ordination about Pt, with normal Pt–P [2.228(2) Å] and Pt–O [2.039(5) Å] distances. It is concluded that the stability of the chelate alkoxo complexes is due to the conformation of the chelate ring making β-hydrogen elimination unfavourable.

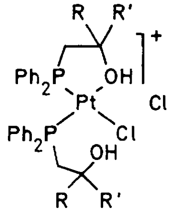
Alcohol- and alkoxo-platinum(II) complexes are generally kinetically unstable with respect to β-hydrogen elimination.[1-6] We have recently shown [1,2] that the phosphino alcohol (**1a**) co-ordinates to platinum(II) *via* P and O to give complex (**2a**) which is readily deprotonated to give the very stable alkoxo species (**3a**). The stability of (**2a**) and (**3a**) may be due to the absence of β-hydrogens, the bulkiness of the ligand, or the presence of the chelate ring. In order to probe these ideas we have investigated the platinum(II) chemistry of the less bulky ligands (**1b**) and (**1c**) which both contain β-hydrogens.

Results and Discussion

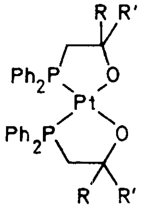
The ligands (**1b**) and (**1c**) were prepared and their platinum(II) complexes made as shown in the Scheme. Ligand (**1b**) is a racemic mixture and hence the bis(ligand)platinum complexes described below are mixtures of D,L and *meso* diastereoisomers.

Treatment of $[PtCl_2(NCBu^t)_2]$ with the ligands (**1b**),(**1c**) in refluxing toluene gave the neutral complexes (**4b**),(**4c**) as the *cis* isomers exclusively, characterised by elemental analysis and i.r. spectroscopy (see Table 1). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**4c**) in $CDCl_3$ at −50 °C was a sharp singlet with ^{195}Pt satellites (Table 2) indicating that the neutral structure (**4c**) persists in solution. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**4b**) shows two sharp singlets in the ratio 3:2 due to the presence of diastereoisomers. There is thus a contrast with the behaviour of (**4a**), since this has the salt structure (**2a**) in $CDCl_3$ solution.[1]

$Ph_2PCH_2CMe_2OH$ (**1a**)
$Ph_2PCH_2CMeHOH$ (**1b**)
$Ph_2PCH_2CH_2OH$ (**1c**)



(**2a**) R = R' = Me
(**2b**) R = Me, R' = H



(**3a**) R = R' = Me
(**3b**) R = Me, R' = H
(**3c**) R = R' = H

Complex (**4c**) is insoluble in methanol but (**4b**) dissolves to give a conducting solution which, from its $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum (at −55 °C), is assigned the salt structure (**2b**). At ambient temperatures the spectrum is a broad singlet with satellites, presumably because of intramolecular OH exchange [equation (1)] similar to the behaviour of (**2a**).

The bis(alcohol) species (**5b**) was made as a diastereoisomeric mixture by treatment of (**4b**) with $AgClO_4$ in acetone (see Tables 1 and 2 for characterising data). Complex (**4c**) did not react with $AgClO_4$ under similar conditions probably because of lack of solubility of (**4c**) in suitable solvents.

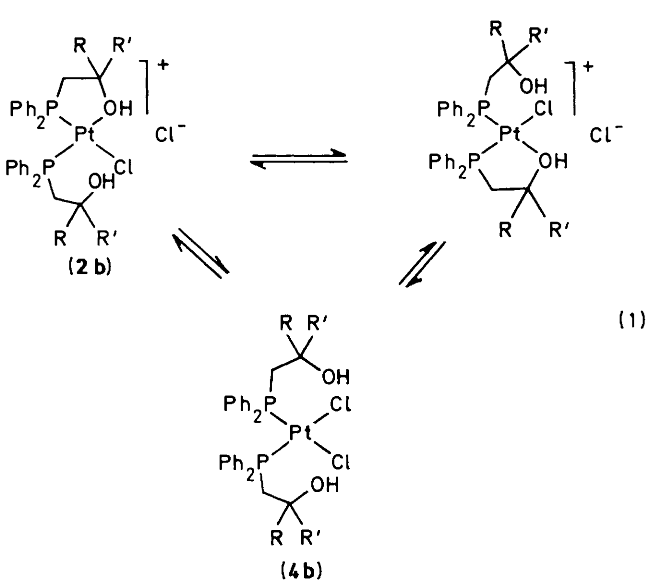
The reactions of (**4b**) and (**4c**) with NEt_3 highlights their different chemistry. The reaction of (**4b**) with NEt_3 resembles

---

* *Present address:* Department of Chemistry, University of Bristol, Bristol BS8 1TS.

† Bis(2-diphenylphosphinoethoxo-*OP*)platinum(II) hydrate.

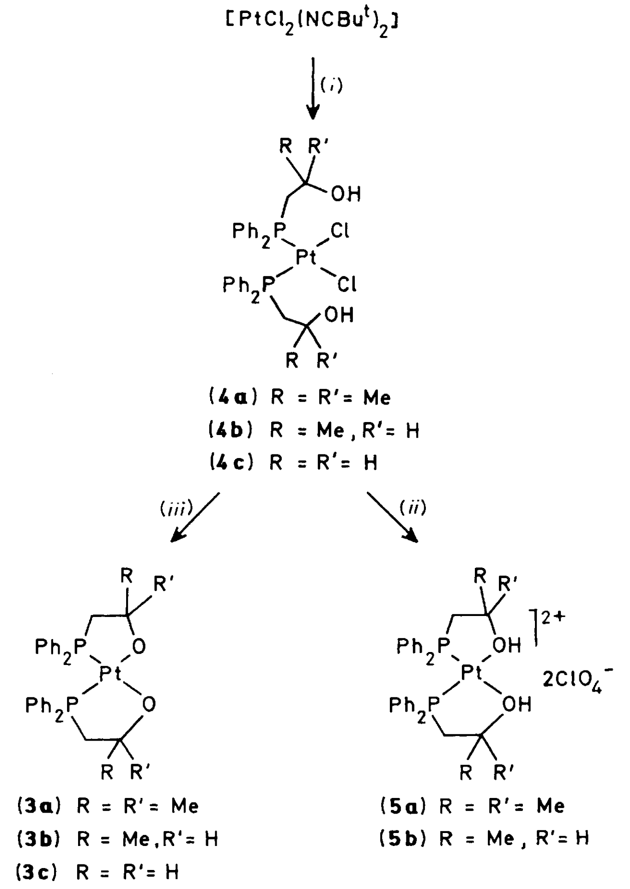
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue I, pp. xvii—xx.



(1)

that of (**4a**) in that smooth deprotonation occurs to give the bis(alkoxo) complex (**3b**) as a mixture of diastereoisomers (see Tables 1 and 2 for characterising data). There was no evidence (^{31}P-{^{1}H} n.m.r.) for monoprotonated species as intermediates.

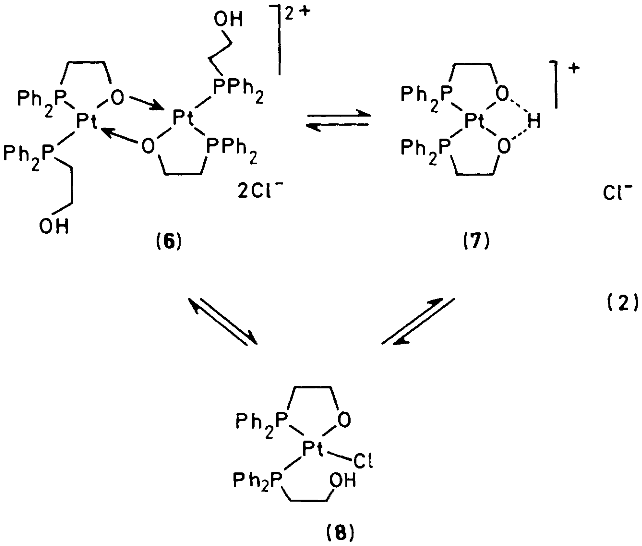
Addition of NEt_3 to a $CDCl_3$ suspension of (**4c**) gives a clear solution of a species (**6**), a product of monodeprotonation.



Scheme. (*i*) 2 equivalents of phosphino alcohol (**1a**)—(**1c**) in toluene; (*ii*) An excess of $AgClO_4$ in toluene–CH_2Cl_2; (*iii*) NEt_3 in $CDCl_3$ for (**3a**) or (**3b**); NaOH in MeOH for (**3c**)

Complex (**6**) has been characterised by elemental analysis, ebullioscopic molecular weight determination which shows that it is binuclear in solution, and a solution conductivity measurement which shows that it is a salt (Table 1). The structure of (**6**) has been assigned principally on the basis of its low-temperature ^{31}P-{^{1}H} n.m.r. spectrum (see Table 2). At −50 °C an AX pattern is observed with ^{195}Pt satellites. A small ^{2}J(PP) indicates that the phosphines are *cis*. One signal (P_A) is at high frequency (indicating that P_A is part of a five-membered chelate ring[1,7]) with a large $^{1}J(\mathrm{PtP_A})$ consistent with P_A being *trans* to the weakly bound bridging alkoxo ligand. The other signal (P_B) is at a more normal shift with ^{1}J(PtP) similar to other values for P *trans* to terminal alkoxo ligands.[1] Complex (**6**) is the first example of a platinum(II) complex containing an unsymmetrically bridging alkoxo ligand.[8]

At ambient temperatures the ^{31}P-{^{1}H} n.m.r. spectrum of (**6**) is a broad singlet and hence the structure is fluxional. Reversible displacement of the alkoxo bridge by chelation of the free alcohol donor to give the symmetrical mononuclear isomer (**7**) [equation (2)] would explain the equilibration of the phosphorus environments on the n.m.r. time-scale. The solid formed upon evaporation of solutions of (**6**) had an i.r. absorption at 310 cm^{-1} typical of ν(Pt–Cl) for Cl *trans* to PR_3 and hence the neutral structure (**8**) is assigned to this solid. In view of the lability of the alkoxo bridge in (**6**) it is likely that (**6**)—(**8**) are exchanging in solution [equation (2)]. The unhindered nature of the ligands in (**6**) probably contributes to its stability, since corresponding alkoxo-bridged complexes are not observed with the more bulky methylated ligand complexes.



(2)

With the stronger base NaOH, complex (**4c**) is smoothly deprotonated to the bis(alkoxo)platinum species (**3c**) (Tables 1 and 2 for characterising data). Like its bulkier analogues (**3a**),(**3b**), complex (**3c**) is stable in air, even in aqueous media. Hence neither the absence of β-hydrogens nor the presence of bulky ligands is a requirement for the kinetic stability of alkoxoplatinum complexes. The major stabilising feature of (**3a**)—(**3c**) is therefore the chelate ring. The conformation of the ring in (**3c**) (see below) orients the β-hydrogens away from the metal, making them unavailable for hydride elimination. A similar rationale has been given by Whitesides and co-workers[9] to explain the stability of metallacycles relative to metal dialkyls.

It is of interest to examine the effect that the methyl substituents in the ligand backbone have on the structures of the complexes. It may be anticipated that two influences will

Table 1. Elemental analyses, i.r., and conductivity data

Complex	Analysis (%)[a] C	H	$M^{a,b}$	ν(PtCl)[c]/cm^{-1}	Λ^d/Ω^{-1} cm^2 mol^{-1}
(3b)	52.65 (52.85)	4.60 (4.75)	677 (681)		
(3c)	48.85 (48.75)	4.35 (4.70)			
(4b)	48.10 (47.75)	4.60 (4.55)		314, 290	
(4c)	46.35 (46.30)	4.10 (4.15)		314, 295	
(5b)	40.85 (40.80)	3.90 (3.90)			184
(6)	48.55 (48.75)	4.15 (4.25)	1 361 (1 378)	310	215

[a] Calculated values in parentheses. [b] Ebullioscopically in $CHCl_3$. [c] As CsCl discs. [d] As 10^{-3} mol dm^{-3} acetone solutions (typical values for 1:1 or 2:1 salts are given in K. K. Chow and C. A. McAuliffe, *Inorg. Chim. Acta*, 1974, **10**, 197; W. W. Fogelmen and H. B. Jonassen, *J. Inorg. Nucl. Chem.*, 1969, **31**, 1536).

Table 2. $^{31}P-\{^1H\}$ N.m.r. data*

Complex	$\delta(P_A)$ p.p.m.	^1J(PtP) Hz	$\delta(P_B)$ p.p.m.	$^1J(PtP_B)$ Hz	$J(P_AP_B)$ Hz	Solvent
(3a)	23.9	3 308				
(3b)	23.5	3 367				
	23.0	3 377				
(3c)	34.2	3 465				
(2a)	30.7	3 749	−1.2	3 937	18	$CDCl_3$
(2b)	30.8	3 654	3.7	3 951	16	CD_3OD
	32.5	3 666	2.4	3 965	16	CD_3OD
(4b)	4.1	3 664				
	1.6	3 788				
(4c)	3.6	3 664				
(5a)	16.0	3 952				$(CD_3)_2CO$
(5b)	25.2	3 985				
	24.3	3 990				
(6)	45.7	4 005	−3.8	3 170	16	

* At 36.4 MHz and 25 °C unless stated otherwise. Chemical shifts are to high frequency of 85% H_3PO_4 (±0.2 p.p.m.). Coupling constants are ±5 Hz. Where there are two P resonances, P_A is in the chelate ring.

operate: (*i*) the inductive effect of the methyl groups will enhance the donor strength of the alcohol or alkoxo ligands; (*ii*) the bulk of the methyl group will assist chelation.[10] These effects have been monitored by $^{31}P-\{^1H\}$ n.m.r. spectroscopy and *X*-ray crystallography.

The value of ^1J(PtP) is a sensitive function of the *trans* influence of the ligand *trans* to the phosphorus. The values of ^1J(PtP) for the alkoxo complexes (**3a**)—(**3c**) are in the order (**3a**) (3 308) > (**3b**) (3 367, 3 377) > (**3c**) (3 465). This is in agreement with the predicted trend (*i*) above but the detected changes in ^1J(PtP) are small (< 5%). Similar small differences in ^1J(PtP) are seen for the alcohol complexes (**2a**)/(**2b**) and (**5a**)/(**5b**) (see Table 2). It can therefore be deduced that the donor enhancement of the methyl substituents is detectable but small; this conclusion was confirmed by the crystallographic results (below).

The chelate-stabilising effect of the methyl substituents may be gauged from the observation of salt formation by chelation to form (**2a**) in $CDCl_3$ whereas the analogous less bulky complexes (**4b**),(**4c**) do not form chelates in this solvent.

X-Ray Crystal Structure.—The crystal structure of complex (**3c**) was determined in order to study the effect of methyl substitution on bond lengths and on the conformation of the ring.

The structure of (**3c**) (Figure, Tables 3 and 4) is very similar to that of its methyl analogue (**3a**).[1] The Pt–P and Pt–O are both slightly longer (by 0.006 and 0.016 Å) in (**3c**); however, neither difference is statistically significant, and they do not indicate weaker bonding in (**3c**). The O–C bond is also of normal length, indicating the absence of any Pt ••• H interaction (as discussed in ref. 1). As with (**3a**), the oxygen atoms attached to Pt form hydrogen bonds to a solvent H_2O, but the present compound lacks the intricate network of solvent hydrogen bonds of (**3a**) and its packing does not show unusual features.

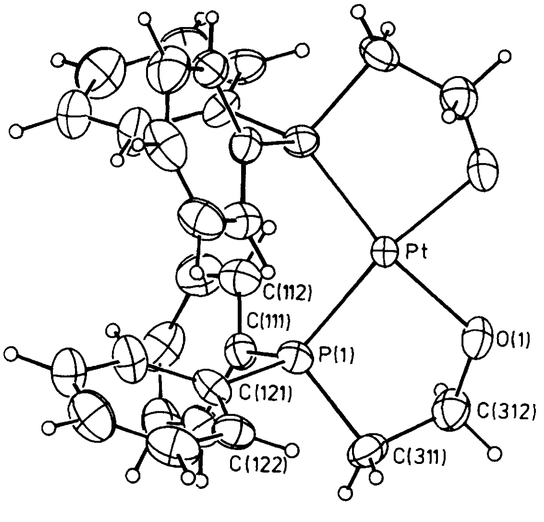


Figure. View of molecule (**3c**), showing the atomic numbering (phenyl groups numbered sequentially)

Table 3. Principal bond lengths (Å) and angles (°) in complex (**3c**)

Pt–P(1)	2.228(2)	O(1)–Pt–P(1)	85.4(2)
Pt–O(1)	2.039(5)	O(1)–Pt–O(1′)	84.7(2)
P(1)–C(111)	1.816(8)	P(1)–Pt–P(1′)	104.5(1)
P(1)–C(121)	1.805(8)	Pt–O(1)–C(312)	114.8(4)
P(1)–C(311)	1.835(8)		
O(1)–C(312)	1.413(10)	O(1)–C(312)–C(311)	112.8(7)
C(311)–C(312)	1.528(11)	C(312)–C(311)–P(1)	104.5(5)
O(1)···O(2)	2.735(10)		

Table 4. Atomic co-ordinates (× 10^4) for complex (**3c**)

Atom	*x*	*y*	*z*
Pt	0	5 542.3(3)	7 500
P(1)	−664(1)	6 758(2)	6 419(1)
O(1)	−497(4)	4 199(5)	6 652(4)
C(111)	142(5)	7 522(6)	5 911(4)
C(112)	1 154(5)	7 552(7)	6 258(5)
C(113)	1 748(6)	8 116(8)	5 849(6)
C(114)	1 341(7)	8 636(8)	5 072(6)
C(115)	321(7)	8 603(8)	4 713(6)
C(116)	−284(7)	8 052(7)	5 117(5)
C(121)	−1 517(5)	7 881(7)	6 564(4)
C(122)	−2 450(5)	7 578(8)	6 620(5)
C(123)	−3 064(6)	8 410(9)	6 813(6)
C(124)	−2 743(7)	9 568(9)	6 968(7)
C(125)	−1 825(7)	9 908(8)	6 928(6)
C(126)	−1 203(6)	9 064(8)	6 713(6)
C(311)	−1 383(6)	5 697(7)	5 632(5)
C(312)	−766(7)	4 553(7)	5 797(5)
O(2)	0	2 090(8)	7 500

Conclusions

We have shown that chelate-alkoxo complexes of platinum are kinetically stabilised by the conformation of the ring orienting the β-hydrogens away from the metal. Our results complement those of Bryndza *et al.*[3] who have recently found that Pt–O bond energies are similar to Pt–C bond energies and the observed instability of alkoxoplatinum complexes is kinetic in origin.

Experimental

The ligand (**1c**) was made by the published procedure[8] and ligand (**1b**) was made similarly. All reactions involving these phosphines were carried out under dry N_2 but the products could be handled in air.

Preparations.—*cis*-$[PtCl_2(Ph_2PCH_2CH_2OH)_2]$ (**4c**). A solution of $Ph_2PCH_2CH_2OH$ (0.35 g, 1.50 mmol) in toluene (5 cm^3) was added to $[PtCl_2(NCBu^t)_2]$ (0.31 g, 0.72 mmol) in toluene (10 cm^3) and the mixture stirred to give a white precipitate. Then the mixture was heated under reflux for 4 h. The pale yellow product was filtered off, washed with light petroleum (b.p. 60—80 °C), and dried *in vacuo*. Yield: 0.48 g (92%). ^1H N.m.r. ($CDCl_3$, 220 MHz): 7.5—7.2 (20 H, m, C_6H_5), 4.12 (4 H, m CH_2OH), 2.70 (4 H, m, CH_2P), and 1.54 (2 H, br, OH).

Complex (**4b**) was made similarly in 85% yield.

cis-$[Pt(Ph_2PCH_2CHMeOH)_2][ClO_4]_2$ (**5b**). A solution of complex (**4b**) 0.22 g, 0.29 mmol) in toluene (20 cm^3) and dichloromethane (10 cm^3) was treated with $AgClO_4$ (0.16 g, 0.77 mmol) in toluene–dichloromethane (5 cm^3) to give a thick white precipitate. The mixture was stirred for 15 min and then the solvent was removed at reduced pressure. The residue was then extracted with dichloromethane (3 × 25 cm^3) and filtered. The filtrate was evaporated to *ca.* 3 cm^3 and then diethyl ether (20 cm^3) added to precipitate the white product (0.203 g, 79%).

$[PtCl(Ph_2PCH_2CH_2O)(Ph_2PCH_2CH_2OH)]$ (**8**). A suspension of complex (**4c**) (0.11 g, 0.15 mmol) in $CHCl_3$ (10 cm^3) was treated with an excess of NEt_3 (0.7 cm^3) to give a clear yellow solution. After 30 min the solution was extracted with water (10 cm^3), the organic layer separated and dried over Na_2CO_3. The product was crystallised by the slow addition of Et_2O (10 cm^3). Yield: 0.08 g, 80%.

$[Pt(Ph_2PCH_2CH_2O)_2]$ (**3c**). A suspension of complex (**4c**) (0.13 g, 0.18 mmol) and NaOH (0.1 g) in methanol (10 cm^3) was stirred for 16 h at 20 °C to give a clear solution. Water (10 cm^3) was then added and the mixture slowly evaporated at reduced pressure to give the white product (0.89 g, 72%). ^1H N.m.r. ($CDCl_3$, 220 MHz): 7.5—7.2 (20 H, m, C_6H_5), 4.08 (4 H, m, CH_2O), and 2.39 (4 H, m, CH_2P). Colourless block-shaped crystals for *X*-ray analysis were obtained by recrystallisation from methanol–water.

Crystal Structure Analysis for Complex (**3c**).—*Crystal data.* $C_{28}H_{28}O_2P_2Pt{\cdot}H_2O$, $M = 671.6$, monoclinic, space group $C2/c$, $a = 14.086(7)$, $b = 11.217(5)$, $c = 16.581(4)$ Å, $\beta = 107.10(3)°$, $U = 2\,504(2)$ Å^3, $Z = 4$, $D_c = 1.78$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 59.2 cm^{-1}, $T = 290$ K, $F(000) = 1\,352$.

Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 50°, with scan range ±1.0 (2θ) around the K_{α_1}–K_{α_2} angles, scan speed 5—29° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections, and showed slight changes during data collection. The data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least squares fit to 15 reflections.

Reflections were processed using profile analysis to give 2 226 unique reflections ($R_{int} = 0.052$); 1 885 were considered observed [$I/\sigma(I) \geqslant 3.0$] and used in refinement; they were corrected for Lorentz, polarisation, and absorption effects, the last by the Gaussian method; maximum and minimum transmission factors were 0.40 and 0.31. Crystal dimensions were 0.20 × 0.20 × 0.26 mm, with bounding faces: $\bar{2}10$, $2\bar{1}0$, $\{001\}$, 110, $\bar{1}\bar{1}0$. Systematic absences: *hkl*, $h + k \neq 2n$; *h*0*l*, $l \neq 2n$, indicating space group $C2/c$ or Cc; the former was chosen initially and shown to be correct by the successful refinement. The Pt atom was located by the Patterson interpretation section of SHELXTL and the light atoms then found on successive Fourier syntheses. The Pt atom and the solvent water lie on two-fold axes. Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.07$ Å^2, and were inserted at calculated positions and not refined; water hydrogen atoms were omitted. Final refinement was on *F* by cascaded least-squares methods refining 155 parameters. Largest positive and negative peaks on a final difference Fourier synthesis were of height ±1.5 e Å^{-3} with the largest peaks near Pt.

A weighting scheme of the form $w = 1[\sigma^2(F) + gF^2]$ with $g = 0.0015$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.038$, $R' = 0.039$. Maximum shift/error in final cycle 0.01. Computing with SHELXTL[11] on a Data General DG30. Scattering factors in the analytical form and anomalous dispersion factors taken from ref. 12. Final atomic co-ordinates are given in Table 4, and selected bond lengths and angles in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, H-atom co-ordinates, and remaining bond lengths and angles.

Acknowledgements

We thank the S.E.R.C. for financial support and Johnson-Matthey for a generous loan of platinum salts.

References

1 N. W. Alcock, A. W. G. Platt, and P. G. Pringle, *J. Chem. Soc., Dalton Trans.*, 1987, 2273 and refs. therein.
2 N. W. Alcock, A. W. G. Platt, and P. G. Pringle, *Inorg. Chim. Acta*, 1987, **128**, 215.
3 H. E. Bryndza, L. K. Fong, R. A. Paciello, W. Tam, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1987, **109**, 1444.
4 H. E. Bryndza, S. A. Kretchmor, and T. H. Tulip, *J. Am. Chem. Soc.*, 1986, **108**, 4805 and refs. therein.
5 J. A. Davis and F. R. Hartley, *Chem. Rev.*, 1981, **81**, 79 and refs. therein.
6 C. D. Montgomery, N. C. Payne, and C. J. Willis, *Inorg. Chem.*, 1987, **26**, 519.
7 P. E. Garrou, *Inorg. Chem.*, 1975, **14**, 1435.
8 A. B. Goel, S. Goel, and D. G. Vanderveer, *Inorg. Chim. Acta*, 1981, **54**, 2169.
9 J. X. McDermott, J. F. White, and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.
10 B. L. Shaw, *J. Organomet. Chem.*, 1980, **200**, 307.
11 G. M. Sheldrick, SHELXTL User Manual, Nicolet Instrument Co., Madison, Wisconsin, 1981.
12 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

Received 1st *February* 1988; *Paper* 8/00493E