Synthesis of Chelate Stabilised Alcohol– and Alkoxo–Platinum(II) Complexes. *X*-Ray Crystal Structure of $[Pt(PPh_2CH_2CMe_2O)_2]\cdot 3.5H_2O$†

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Reaction of the new phosphine $PPh_2CH_2CMe_2OH$ with platinum(II) chloro complexes gives complexes of formula $[PtCl_2(PPh_2CH_2CMe_2OH)_2]$. The *cis* isomer in $CDCl_3$ or CD_3OD solution is in the ionic, chelate form *cis*-$[PtCl(PPh_2CH_2CMe_2OH)(PPh_2CH_2CMe_2OH)]Cl$. At +25 °C, rapid intramolecular –OH exchange takes place. Addition of $AgClO_4$ gives the bis-chelate *cis*-$[Pt(PPh_2CH_2CMe_2OH)_2][ClO_4]_2$. Both of these *cis* species can be readily deprotonated to give the very stable bis(alkoxo) complex $[Pt(PPh_2CH_2CMe_2O)_2]$. The *X*-ray structure of this bis(alkoxo) complex as its $3.5H_2O$ solvate has been determined {$R = 0.029$ for 3 914 observed $[I/\sigma(I) \geqslant 3.0]$ diffractometer-collected reflections}. The Pt atom has square-planar co-ordination, with Pt–O bonds of normal length [average 2.024(3) Å]. Thus the general instability of alkoxoplatinum complexes is attributed to facile β-hydride elimination and not to abnormally long and weak Pt–O bonds. The *trans* isomer forms the fluxional chelate complex *trans*-$[PtCl(PPh_2CH_2CMe_2OH)(PPh_2CH_2CMe_2OH)]Cl$ in CD_3OD, but in $CDCl_3$ it gives a neutral non-chelated species. It is also deprotonated by NEt_3 but only to the non-fluxional mono-alkoxo complex $[PtCl(PPh_2CH_2CMe_2O)(PPh_2CH_2CMe_2OH)]$. The $^{31}P-\{^1H\}$ and ^1H n.m.r. data for the complexes are discussed.

Well characterised alkoxo–platinum complexes are rare[1–7] and those complexes that have been isolated are often extremely moisture-, oxygen-, and temperature-sensitive, decomposing to hydrides *via* β-hydrogen elimination or depositing metal(0).[2–7] It is of interest to know whether the observed chemical instability has a kinetic origin, *i.e.* a facile decomposition pathway, or is due to inherently weak bonding[2,8] between the soft acid, Pt^{II}, and the hard base, OR^-. We decided to investigate this by studying the complexes of the ligand $PPh_2CH_2CMe_2OH$ with platinum(II) in the belief that this would form chelate-stabilised Pt–O bonds.

Results and Discussion

The new phosphine $PPh_2CH_2CMe_2OH$ (**1**) is readily made according to equation (1) (see Experimental section).

$$PPh_3 + 2Li \longrightarrow LiPPh_2 + LiPh \xrightarrow[(ii)\ H_2O]{(i)\ ClCH_2CMe_2OH} \underset{(\mathbf{1})}{PPh_2CH_2CMe_2OH} \quad (1)$$

Alcohol Complexes.—Dichloroplatinum complexes of ligand (**1**) are made as shown in Scheme 1. The *cis* and *trans* assignments are made on the basis of Pt–Cl stretching frequencies (Table 1) and the ^1H n.m.r. pattern for the CH_2 protons:[9] for the *trans* isomer, a virtual triplet and for the *cis* isomer, a 'filled-in' doublet. The two isomers may be interconverted as shown in Scheme 1.

Both *cis*- (**2**) and *trans*-$[PtCl_2(PPh_2CH_2CMe_2OH)_2]$ (**3**) show interesting fluxionality in solution. Thus, at 25 °C, the $^{31}P-\{^1H\}$ n.m.r. spectrum of (**2**) in $CDCl_3$ is a broad singlet with ^{195}Pt satellites which, when cooled to −40 °C sharpens to an AX pattern (data in Table 2). The chelate structure (**2a**) in which the alcohol donor is bonded to the metal is assigned to this solution species for the following reasons: (*i*) the low $^2J(P_AP_B)$ value shows that the phosphines are *cis* to each other; (*ii*) the high-frequency shift of P_A indicates five-membered ring formation;[10] this very useful criterion will be used throughout. Similar spectra are obtained in methanol (at −20 °C) in which (**2**) gives a conducting solution.

Table 1. Elemental analyses,[a] i.r. and conductivity data

Complex	C	H	Λ^b/Ω^{-1} cm^2 mol^{-1}	ν(Pt–Cl)^c/ cm^{-1}
(**2**)	49.20 (49.10)	4.95 (4.90)	78	310, 315
(**3**)	48.85 (49.10)	4.85 (4.90)	81	340
(**4**)	42.56 (43.10)	4.00 (4.15)		310
(**5**)	50.50 (50.30)	4.75 (4.60)		317,291
(**6**)	42.75 (42.20)	4.20 (4.40)		
(**7**)	44.85 (45.40)	4.50 (4.50)	147	365
(**8**)	49.65 (49.75)	5.65 (5.75)	4	
(**12**)	52.65 (52.85)	4.60 (4.75)		335

[a] Calculated values are given in parentheses. [b] In methanol. [c] CsCl disc.

Two possible explanations for the fluxionality of (**2**) are shown in Schemes 2 and 3: interconversion of tautomers (**2a**), (**2b**), and (**2c**) by either reversible Cl^- co-ordination or intramolecular –OH exchange respectively. The solution conductivity of (**2**) in methanol is low for a 1:1 salt which may indicate that neutral tautomers (**2b**) or (**2c**) are present at ambient temperatures.

To elucidate the mechanism of the fluxionality, $[PtCl(PPh_2CH_2CMe_2OH)_2]PF_6$ (**4**) containing no ionic chloride and $[PtCl_2(PMePh_2)(PPh_2CH_2CMe_2OH)]$ (**5**) containing only one alcoholic ligand, (**1**), were prepared (see Experimental section). From its $^{31}P-\{^1H\}$ n.m.r. spectrum, complex (**4**) in methanol shows similar fluxionality to the parent complex (**2**). In contrast, complex (**5**) in methanol is not fluxional; even at +25 °C a sharp AX pattern is seen, consistent with the chelate structure

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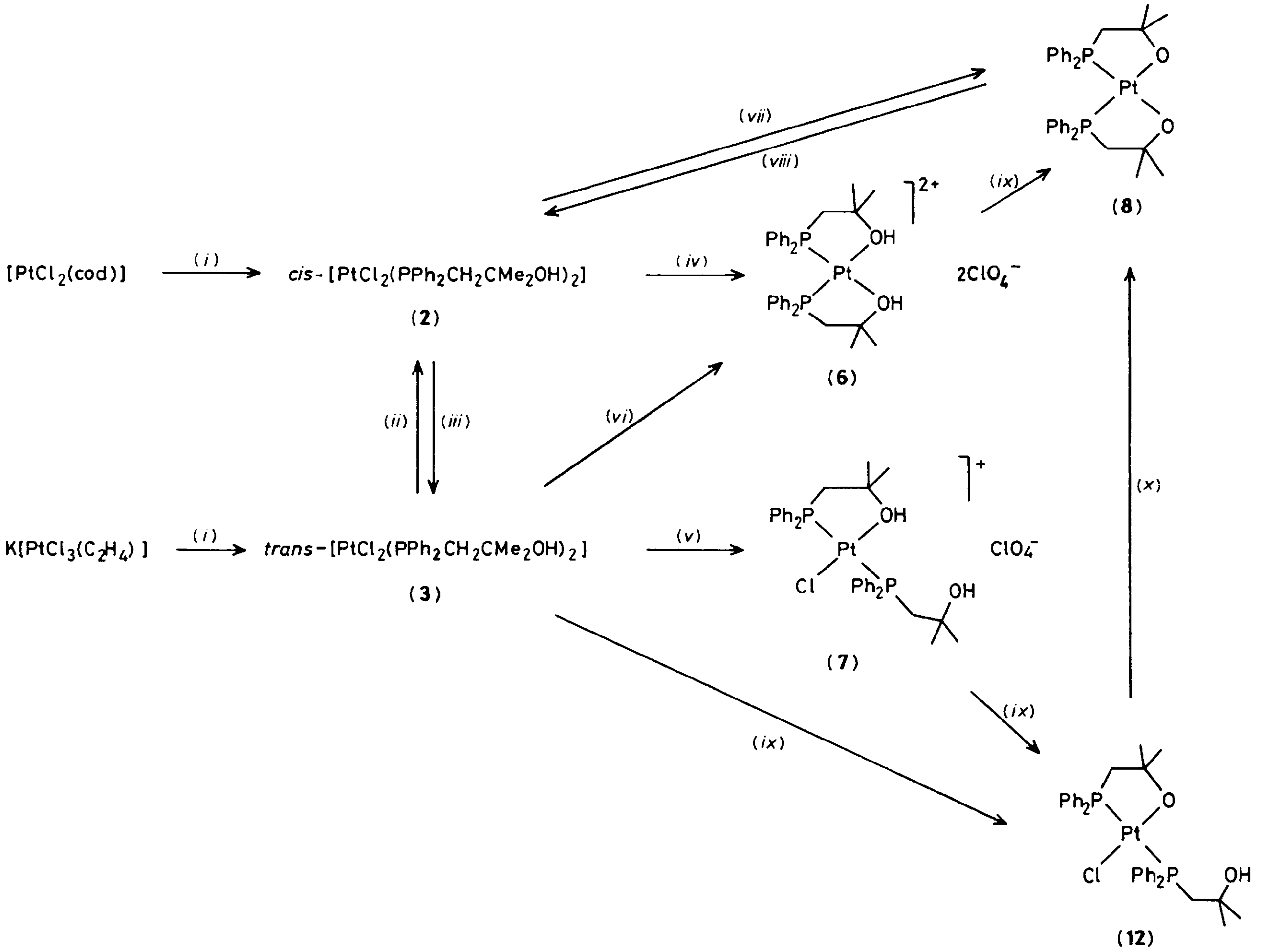
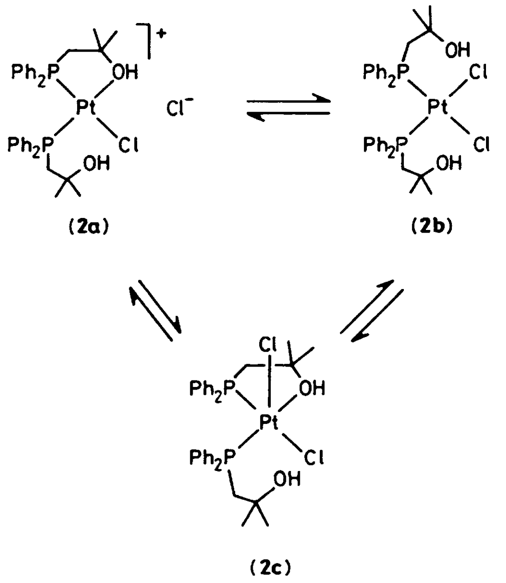
† Bis(3-diphenylphosphino-2-methylpropan-2-olato-*OP*)-platinum(II)–water (1/3.5).

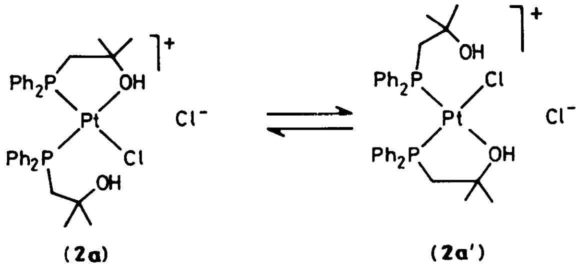
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.



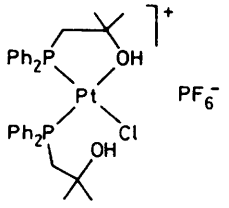
Scheme 1. Reagents and conditions: (*i*) 2 mol equiv. of $PPh_2CH_2CMe_2OH$; (*ii*) trace of $PPh_2CH_2CMe_2OH$, toluene, reflux; (*iii*) trace of complex (**3**), toluene, reflux; (*iv*) 2 mol equiv. $AgClO_4$ in CH_2Cl_2–toluene; (*v*) excess of $AgClO_4$ in CH_2Cl_2–Me_2CO; (*vi*) 2.5 mol equiv. $AgClO_4$, Me_2CO, reflux; (*vii*) NEt_3 in $CHCl_3$, $Li[N(SiMe_3)_2]$ in thf, or NaOH in ethanol; (*viii*) aqueous HCl; (*ix*) NEt_3 in $CDCl_3$; (*x*) NaOH, ethanol, reflux



Scheme 2.



Scheme 3.

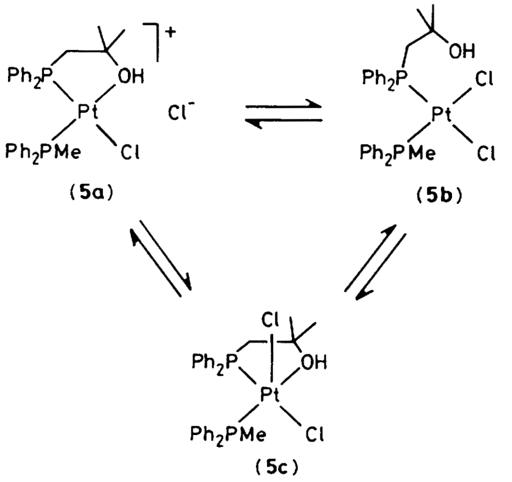


(4)

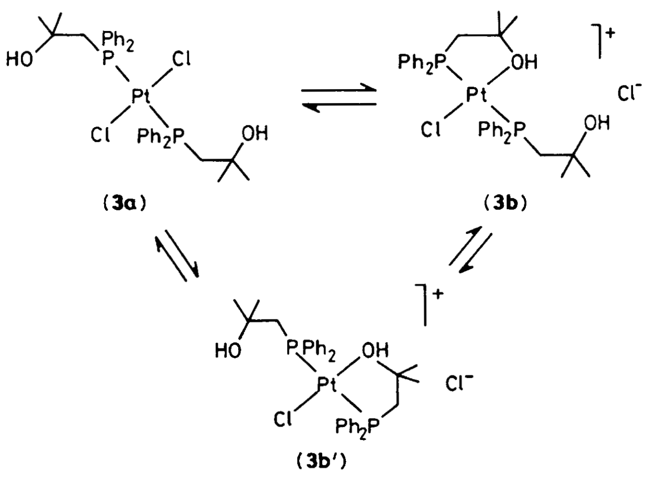
Table 2. ^{31}P-{^1H} N.m.r. data[a]

Complex	Solvent	Temp. (°C)	$\delta(P_A)$/p.p.m.	$^1J(PtP_A)$/Hz	$\delta(P_B)$/p.p.m.	$^1J(PtP_B)$/Hz	$^2J(P_AP_B)$/Hz
(2)	$CDCl_3$	−60	30.7	3 749	−1.2	3 937	18
(3a)	$CDCl_3$	+25	5.0	2 532			
(3b)	CD_3OD	−30	28.5	2 841	9.6	2 778	446
(4)	$(CD_3)_2CO$	−60	30.0	3 660	−4.1	3 936	14
(5b)	$CDCl_3$	+25	6.2[b]	3 736	−4.8	3 677	16
(5a)	CD_3OD	+25	32.2	3 645	−8.4	3 969	20
(6)	$(CD_3)_2CO$	+25	16.0	3 952			
(7)	$CDCl_3$	+25	34.0	2 514	14.8	2 629	423
(8)	$CDCl_3$	+25	23.9	3 308			
(12)	$CDCl_3$	+25	31.0	2 937	12.2	2 864	454
(13)	$CDCl_3$	+25	33.8	3 146			

[a] At 36.4 MHz unless stated otherwise. Chemical shifts are in p.p.m. (±0.5 p.p.m.) to high frequency of 85% H_3PO_4. Coupling constants are in Hz (±5 Hz). Where there are two P atoms, P_A is in the chelate ring unless stated otherwise. [b] P_A is the phosphinoalcohol phosphorus.



Scheme 4.



Scheme 5.

(5a) (see Table 2 for data). Combination of these results unambiguously supports the rapid intramolecular –OH exchange mechanism (Scheme 3) for the fluxionality in methanol.

Complex (5) behaves differently in $CDCl_3$: at 25 °C the ^{31}P-{^1H} n.m.r. spectrum is a slightly broadened AX pattern, different from the AX pattern of (5) in CD_3OD, and consistent with the neutral structure **(5b)** (see Table 2 for data). At −60 °C the spectrum is sharp and shows the presence of two species in approximately 1:1 ratio, assigned structures **(5a)** and **(5b)** by comparison of their ^{31}P n.m.r. parameters. Therefore in $CDCl_3$ the neutral [**(5b)**] and ionic [**(5a)**] structures are present in equilibrium and Cl^- exchange [possibly *via* **(5c)**] leads to the observed broadened spectra at ambient temperatures (Scheme 4). Consequently the equilibria shown in Scheme 2 are likely to be present in solutions of (2) in chlorinated solvents.

The ^{31}P-{^1H} n.m.r. spectrum of the *trans* isomer (3) in $CDCl_3$ is typical of a simple *trans*-$[PtCl_2(PR_3)_2]$ type complex: a sharp singlet with ^{195}Pt satellites (see Table 2 for data); hence structure **(3a)** is assigned. In methanol, however, complex (3) dissolves to give a conducting solution and the ^{31}P-{^1H} n.m.r. spectrum at −30 °C is an AB pattern to which we assign the chelate structure **(3b)** on the basis of (*i*) a high-frequency shift typical of chelation and (*ii*) large $^2J(P_AP_B)$ showing the phosphines are mutually *trans*. A small amount of **(3a)** was also detected in methanol solutions of (3) and at +25 °C, whilst the AB pattern assigned to **(3b)** was broadened, the singlet assigned to **(3a)** remained sharp: this is consistent with the fluxionality being due to rapid –OH exchange [**(3b)** $\rightleftharpoons$ **(3b′)** in Scheme 5] and not rapid equilibration between **(3a)** and **(3b)**, although **(3a)** and **(3b)** are doubtless in equilibrium.

The i.r. spectra (CsCl disc) of **(2)** and **(3)** each show ν(Pt–Cl) bands in the expected positions for complexes of the type *cis*- or *trans*-$[PtCl_2(PR_3)_2]$ and hence indicate that in the solid state these complexes have neutral structures **(2b)** and **(3a)** respectively.

Addition of $AgClO_4$ to the *cis* complex **(2)** in acetone gives the dicationic species **(6)** in 94% yield (see Tables 1—3 for characterising data). This complex, like its precursor **(2)** is a white, air- and moisture-stable solid. Addition of $AgClO_4$ to the *trans* isomer **(3)** gives only the monocation **(7)** which is simply the ClO_4^- salt of the species present in methanolic solutions of **(3)** (see above). Excess of $AgClO_4$ does not give the *trans* isomer of the dicationic species **(6)**; the Pt–Cl bond in **(7)**, which is *trans* to the weak alcohol donor, is very strong as indicated by the high ν(Pt–Cl) (365 cm^{-1}). Under more forcing conditions (16 h reflux in acetone, with $AgClO_4$) the *trans* isomer **(3)** yields the *cis* dicationic species **(6)**. From the principle of antisymbiosis,[8] we should expect the *cis* species **(6)** to be more stable than the *trans* isomer.

The alcohol group is a poor donor for platinum(II) as shown by the large $^1J(PtP)$ value for the *trans* phosphorus in **(2a)**, **(5a)**, and **(6)** and the high frequency of ν(Pt–Cl) for the *trans* chlorine ligand in **(7)**. Nevertheless, the alcohol does co-ordinate to platinum(II) without the assistance of chloride abstraction with Ag^+, unlike the ether donor in $PPh_2CH_2CH_2OMe$[11] and the thioether donor in $PPh_2CH_2CH_2SPh$,[12] neither of which shows evidence of co-ordination to platinum(II) in the absence of Ag^+.

Alkoxo Complexes.—Complex (**2**) is cleanly deprotonated by a variety of bases including NaOH or NEt_3 to give the bis(alkoxo) chelate complex (**8**) in 84% isolated yields. The structure of (**8**) was assigned on the basis of elemental analysis (Table 1), i.r. (absence of Pt–Cl bands), ^{31}P n.m.r. (high-frequency chemical shift due to chelation), and ^1H n.m.r. ('filled-in' doublet for the CH_2 resonance typical of *cis* phosphines, Table 3). The new complex (**8**) is not only air stable but can be recrystallised from aqueous methanol solutions or refluxed in alcoholic KOH for 16 h without any sign of decomposition. This robustness is in sharp contrast to the only other reported[2] mononuclear bis(alkoxo)platinum complex $[Pt(OMe)_2(PPh_2CH_2CH_2PPh_2)]$ (**9**) which shows great thermal lability (decomposition at +25 °C in solution) and sensitivity to water.

The value of $^1J(PtP)$ is a sensitive function of the σ-bonding ability of the ligand *trans* to the phosphine.[3,13] This value for (**8**) is some 300 Hz lower than $^1J(PtP)$ for analogous *cis*-$[PtCl_2P_2]$ complexes suggesting that the alkoxo group is more strongly σ-bonded to platinum than is chlorine.

The structure of (**8**) was confirmed by *X*-ray methods (Figure 1). The square-planar geometry about Pt is slightly distorted by the greater bulk of the phosphine ligands, to give a P–Pt–P angle 105.7(1)° compared to O–Pt–O of 85.7(1)° and similarly the Pt–P–C angles are up to 15° larger than the C–P–C angles (Table 4). The Pt–P distances have normal values [mean 2.222(1) Å]. The Pt–O distances average 2.024(3) Å, and the key question to be answered from the structural results is the significance of this value. Rather than using a covalent radius for Pt^{II}, of uncertain validity, a more realistic comparison can be made with the length of a Pt–C bond. A suitable parallel can be found in $[PtMe_2(PMePh_2)_2]$, which contains a very similar phosphine, and has a Pt–P distance of 2.284(1) Å, close to that in (**8**).[14] Its Pt–C distance is 2.120(4) Å, and the difference of 0.10 Å from the Pt–O distance in (**8**) is very close to the normal difference of 0.11 Å between single bonds from C and from O (*e.g.* in C–C and O–C bonds). Thus the Pt–O bond in (**8**) has exactly the expected length of a standard single bond, and shows no anomalous weakening.

The packing (Figure 2) shows a strong distinction between the hydrophobic and hydrophilic sides of the molecules. The oxygen atoms of the six symmetry-related molecules in one unit cell make up the hydrophilic side, and are held together by a complex network of hydrogen bonds involving the lattice water (Table 4). By contrast, the contacts between unit cells are formed between the phenyl rings of these hexamers, and are entirely hydrophobic.

Table 3. ^1H N.m.r. data[a] for co-ordinated ligand (**1**)

Complex	δ(CH_2)/ p.p.m.	Multiplicity[b]	J(PH)[c]/ Hz	δ(CH_3)/ p.p.m.	δ(OH)/ p.p.m.
(**2**)[d]	2.92	d	12.2	1.46	5.62
(**3**)[e]	2.94	t	8.1	1.07	3.57
(**5**)[d]	3.02	d	12.0	1.16	*f*
(**6**)[d,g]	3.32	d	9.8	1.58	*f*
(**7**)[e,g]	3.12	dd	10.0, 4.5	1.53	3.79
	2.75	d	9.0	1.28	
(**8**)[e]	2.68	d	10.9	1.38	
(**12**)[e]	2.82	dd	13.2, 2.9	1.28	4.69
	2.26	d	9.4	1.12	
(**13**)[d]	2.29	t	9.8	1.40	

[a] In $CDCl_3$ unless otherwise stated. Chemical shifts in p.p.m. (±0.02 p.p.m.) to high frequency of $SiMe_4$ and coupling constants in Hz (±0.2 Hz). [b] Multiplicities: d = 'filled-in' doublet, t = virtual triplet, dd = doublet of doublets. [c] $J(PH) = |^2J(PH) + {}^4J(PH)|$. [d] At 220 MHz. [e] At 90 MHz. [f] Not detected. [g] In $(CD_3)_2CO$.

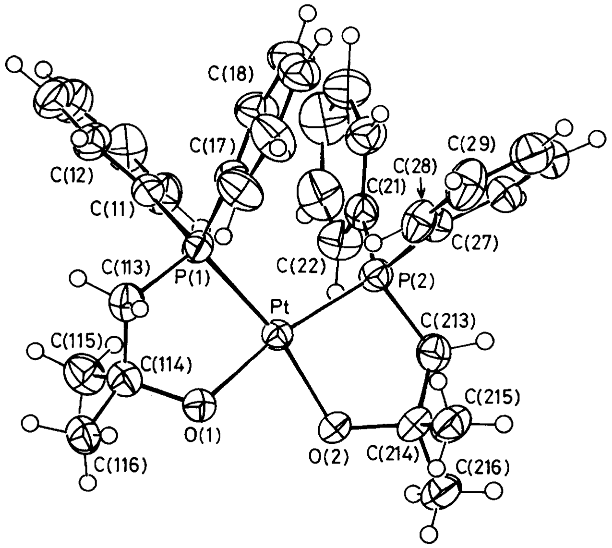


Figure 1. View of the molecule showing the atomic numbering (unnumbered phenyl carbon atoms follow in sequence round each ring)

Table 4. Principal bond lengths (Å) and angles (°); symmetry transformations are given in parentheses

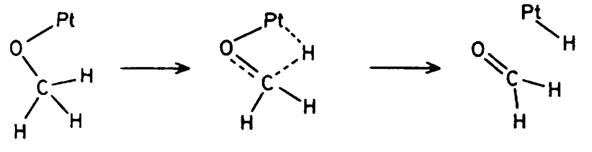
Pt–P(1)	2.219(1)	Pt–O(2)	2.034(3)	P(1)–C(113)	1.833(5)	P(2)–C(213)	1.826(6)
Pt–P(2)	2.226(1)	P(1)–C(11)	1.817(5)	P(2)–C(21)	1.824(6)	O(1)–C(114)	1.412(6)
Pt–O(1)	2.013(4)	P(1)–C(17)	1.811(3)	P(2)–C(27)	1.824(5)	O(2)–C(214)	1.419(6)
P(1)–Pt–P(2)	105.7(1)	O(1)–Pt–O(2)	85.7(1)	C(11)–P(1)–C(113)	106.2(2)	Pt–P(2)–C(213)	101.4(2)
P(1)–Pt–O(1)	84.4(1)	Pt–P(1)–C(11)	119.6(2)	C(17)–P(1)–C(113)	108.1(2)	C(21)–P(2)–C(213)	106.2(3)
P(2)–Pt–O(1)	169.8(1)	Pt–P(1)–C(17)	118.8(2)	Pt–P(2)–C(21)	118.4(2)	C(27)–P(2)–C(213)	105.9(2)
P(1)–Pt–O(2)	170.0(1)	C(11)–P(1)–C(17)	101.9(2)	Pt–P(2)–C(27)	119.0(2)	Pt–O(1)–C(114)	118.5(3)
P(2)–Pt–O(2)	84.2(1)	Pt–P(1)–C(113)	101.4(2)	C(21)–P(2)–C(27)	104.6(3)	Pt–O(2)–C(214)	118.0(3)
O(1)–O(001) (*z,x,y*)	2.827(5)	O(001)–O(004)	2.857(5)	O(002)–O(003) (*y,z,x*)	2.774(5)	O(003)–O(003) (*z,x,y*)	3.041(5)
O(2)–O(001) (*z,x,y*)	2.805(5)	O(001)–O(002) (*y,z,x*)	2.871(5)	O(003)–O(005)	3.001(5)	O(003)–O(003) (*y,z,x*)	3.041(5)
O(2)–O(002) (*z,x,y*)	2.818(5)						

The one report[2] of a similar bis(alkoxo)platinum structure $[Pt(OMe)_2(PPh_2CH_2CH_2PPh_2)]$ (**9**) gave values of 2.039(6) Å (average) for the Pt–O bonds in excellent agreement with our results, despite the instability of the methoxo groups. However, this compound does show an anomalously short O–C bond [1.370(14) Å], whereas the O–C bonds in (**8**) are normal at 1.416(5) Å (average). This adds strength to the suggestion[2] that the ready β-hydride elimination has already begun in the methoxide, with the effect shown in Scheme 6.

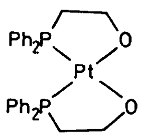
In contrast, in (**8**) the normal O–C bond length, and the great difference in reactivity from (**9**), shows the absence of any incipient intramolecular reaction. Obviously, the absence of β-hydrogen atoms in (**8**) prevents hydride elimination. However, we have recently prepared complex (**10**) (to be reported in a future paper) which has similar stability to (**8**) but contains β-hydrogens and has no bulky CH_3 groups. Thus it is the presence of chelate rings that is the essential stabilising feature in (**8**). Specifically, their orienting effect on the β-substituents, which points them away from the metal, is probably responsible for the stability of these systems; a similar explanation is given for the stability of metallacycles.[15]

Treatment of the bis(alkoxo) complex (**8**) with dilute aqueous HCl gives the dichloro complex (**2**) quantitatively (^{31}P evidence). Hence the conversion of (**2**) $\longrightarrow$ (**8**) is reversible (Scheme 1). It was noticed that the ^{31}P chemical shifts and $^{1}J(PtP)$ values for (**6**) and (**8**) were very sensitive to solvent and temperature. Furthermore, a 1 : 1 mixture of (**6**) and (**8**) gave a single ^{31}P resonance even at −90 °C. We interpret this behaviour in terms of rapid proton-exchange equilibria involving a monoprotonated species (**11**) as shown in Scheme 7.

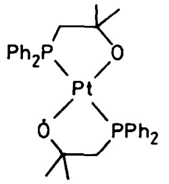
The *trans*-dichloro complex (**3**) or the cationic species (**7**) can also be deprotonated with NEt_3 to give the monodeprotonated species (**12**). The ^{31}P-{^{1}H} n.m.r. spectrum of (**12**) consists of an AB pattern with a high-frequency δ(P) value for the phosphorus



Scheme 6. Postulated cause of short C–O bond length in the dimethoxoplatinum species (**9**) (from ref. 2)



(**10**)



(**13**)

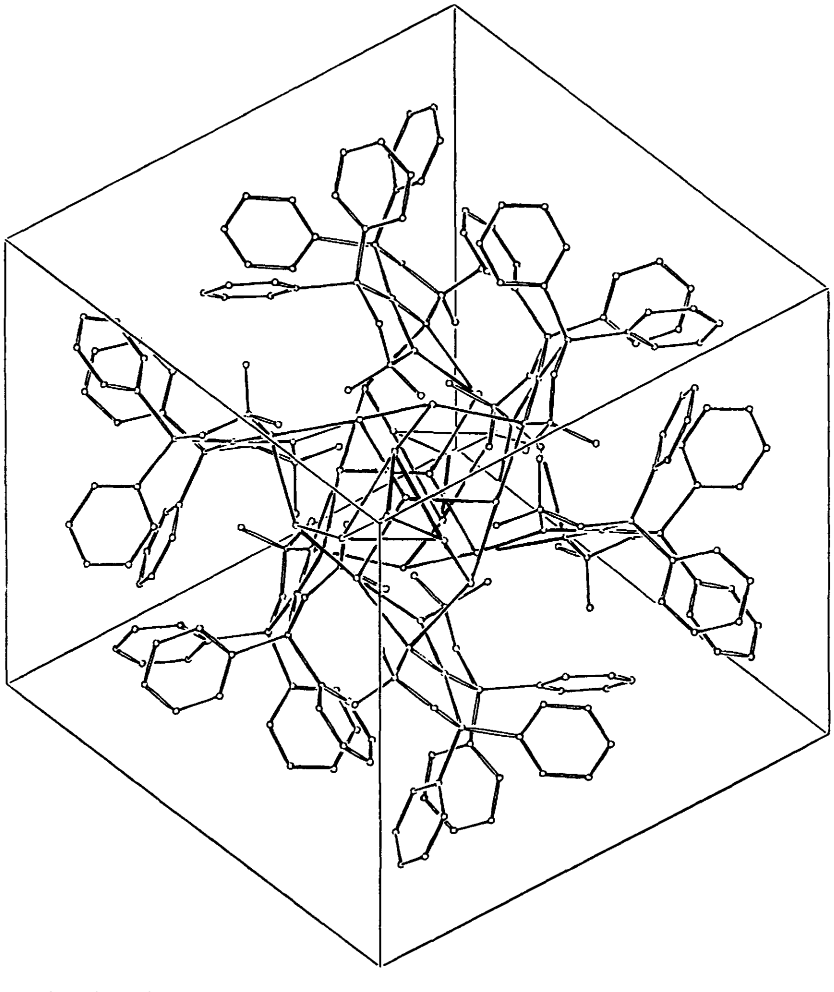
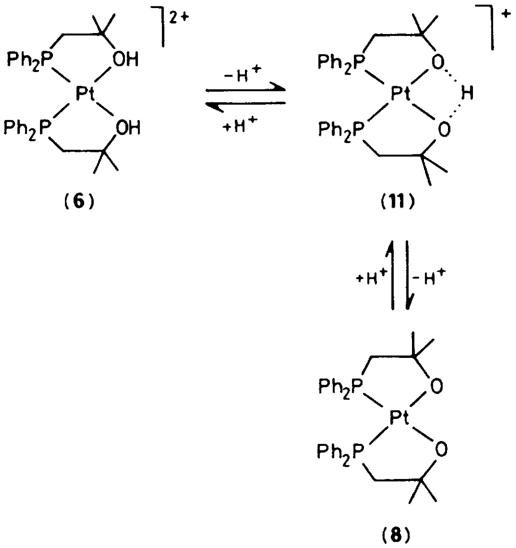


Figure 2. Unit-cell contents, viewed nearly parallel to the three-fold axis, showing the network of hydrogen bonds



Scheme 7.

in the chelate ring and a large ${}^{2}J(P_AP_B)$ value (see Table 2). Complex (**12**) is not fluxional on the n.m.r. time scale at +25 °C, showing that inter- or intra-molecular proton exchange is slow. Under more vigorous deprotonation conditions (NaOH, refluxing ethanol, 1 h) the *trans* species (**3**) gives a mixture of the *cis*-alkoxo complex (**8**) and another species which, from ${}^{31}P$ (Table 2) and ${}^{1}H$ (virtual triplet at 2.29 p.p.m., Table 3) evidence, may be the desired *trans* complex (**13**); this species has not been isolated in pure form.

In conclusion, we have shown that Pt–O bonds are not inherently weak and the previously observed instability is most probably due to kinetic effects (facile β-hydrogen elimination) rather than weak bonding. Incorporation of the O-donor into a chelating ligand has allowed the synthesis of a variety of complexes which contain Pt–OR bonds that are easily handled in air and even in aqueous solutions. By suppressing the β-hydrogen elimination, we are now in a position to study the reactions of the Pt–OR bond. These will be reported in subsequent papers.

Experimental

Phosphine (**1**) was handled under N_2 but all other products could be handled in air. Tetrahydrofuran (thf) was dried by distillation from sodium–benzophenone. Commercial reagents were used without further purification. Hydrogen-1 and ${}^{31}P$ n.m.r. spectra were obtained using Bruker WH90 or WH400, or Perkin-Elmer R34 spectrometers. Infrared spectra were measured using a Perkin-Elmer 580 spectrometer.

Preparation of $PPh_2CH_2CMe_2OH$ (**1**).—Triphenylphosphine (20.0 g, 0.076 mol) and lithium flakes (2.80 g, 0.40 mol) were placed in a three-necked flask (250 cm³) filled with nitrogen. Dry thf (150 cm³) was slowly added to the stirred mixture which was cooled to −15 °C. The resulting mixture was stirred at −10 °C for 1 h and then at +20 °C for a further 2 h. The red solution was then filtered free of the excess of lithium metal, cooled to −70 °C and $ClCH_2CMe_2OH$ (8.0 cm³, 0.078 mol) was added dropwise by syringe over 10 min. After the addition was complete, the mixture was allowed to warm to ambient temperature during which time the red colour disappeared. After 1 h, water (100 cm³) was added and the layers separated. The aqueous layer was extracted with thf (3 × 50 cm³) and the combined organic layer dried over K_2CO_3, filtered and evaporated to give an oil. Distillation at 0.007 mmHg gave two distillates: b.p. 60—120 °C (2.57 g, mainly $PHPh_2$) and b.p. 130—150 °C [14.57 g, 74% of the desired phosphine (**1**)]. ${}^{31}P$ N.m.r. (36 MHz, $CDCl_3$): δ(P) −24.7 p.p.m. ${}^{1}H$ N.m.r. (220 MHz, $CDCl_3$): δ(H) 7.50, m, 4 H; 7.34, m, 6 H; 2.51, d, ${}^{2}J(PH)$ 3.7 Hz, 2 H; 1.96, br s, 1 H; and 1.34, s, 6 H.

Preparation of cis-$[PtCl_2(PPh_2CH_2CMe_2OH)_2]$ (**2**).—A suspension of $[PtCl_2(cod)]$ (0.43 g, 1.15 mmol; cod = cycloocta-1,5-diene) in dichloromethane (10 cm³) was treated with ligand (**1**) (0.66 g, 2.56 mmol) in dichloromethane (5 cm³) and the mixture swirled until all the solid had dissolved. Evaporation of the solvent, followed by addition of diethyl ether (10 cm³) gave the white complex (**2**) in quantitative yield.

Preparation of trans-$[PtCl_2(PPh_2CH_2CMe_2OH)_2]$ (**3**).—The ligand (**1**) (0.19 g, 0.74 mmol) in acetone (5 cm³) was added dropwise over 5 min to a solution of $K[PtCl_3(C_2H_4)]$ (0.15 g, 0.41 mmol) in acetone (5 cm³) giving a turbid solution. Water (5 cm³) was then added and the acetone removed *in vacuo* to give the crude product which was then collected, redissolved in $CHCl_3$, dried over Na_2CO_3, filtered and then evaporated to dryness. Recrystallisation from $CHCl_3$–light petroleum (b.p. 80—100 °C) gave the pale yellow complex (**3**) (0.21 g, 72%).

Preparation of cis-$[PtCl(PPh_2CH_2CMe_2OH)(PPh_2CH_2CMe_2OH)]PF_6$ (**4**).—A suspension of (**2**) (0.10 g, 0.128 mmol) in MeCN (10 cm³) was treated with an excess of KPF_6 (0.10 g, 0.54 mmol) in MeCN (10 cm³). The mixture was stirred for 20 min and then the solvent was evaporated. The solid residue was then extracted with CH_2Cl_2, and the resulting solution filtered, evaporated to dryness and the residue triturated with diethyl ether. Yield: 0.10 g, 88%.

Preparation of cis-$[PtCl_2(PMePh_2)(PPh_2CH_2CMe_2OH)]$ (**5**).—A suspension of $[Pt_2Cl_4(PMePh_2)_2]$ (0.321 g, 0.344 mmol) in dichloromethane (10 cm³) was treated with ligand (**1**) (0.178 g, 0.69 mmol). After 2 min a yellow solution formed which was evaporated to dryness and then the residue triturated with light petroleum (b.p. 30—40 °C) to give the white product (0.46 g, 92%).

Preparation of cis-$[Pt(PPh_2CH_2CMe_2OH)_2][ClO_4]_2$ (**6**).—A solution of (**2**) (0.22 g, 0.28 mmol) in CH_2Cl_2 (10 cm³) and toluene (40 cm³) was treated with a solution of $AgClO_4$ (0.26 g, 1.26 mmol) in CH_2Cl_2–toluene (10 cm³) to give a white precipitate. The mixture was stirred for 1 h and then evaporated to dryness. The residue was then extracted with dichloromethane (3 × 20 cm³) and the solution filtered, reduced to 10 cm³ and then the white product precipitated by the addition of diethyl ether. Yield: 0.24 g, 94%.

Preparation of trans-$[PtCl(PPh_2CH_2CMe_2OH)(PPh_2CH_2CMe_2OH)]ClO_4$ (**7**).—A solution of (**2**) (0.23 g, 0.29 mmol) in CH_2Cl_2–Me_2CO (20 cm³, 1:1) was treated with $AgClO_4$ (0.16 g, 0.77 mmol) in acetone (5 cm³). The resulting white suspension was stirred for 5 min and then evaporated to dryness. The residue was extracted with CH_2Cl_2 (2 × 20 cm³) and the solution filtered, reduced to 5 cm³ and the pale yellow product precipitated by addition of diethyl ether. Yield: 0.22 g, 90%.

Preparation of cis-$[Pt(PPh_2CH_2CMe_2O)_2]$ (**8**).—A solution of $Li[N(SiMe_3)_2]$ (1.30 cm³, 1.0 mol dm⁻³ in thf, 1.30 mmol)

Table 5. Atomic co-ordinates ($\times 10^4$)

Atom	*x*	*y*	*z*
Pt	2 729.1(1)	1 572.7(1)	5 814.3(1)
P(1)	3 648.5(8)	1 738.1(8)	6 784.7(8)
P(2)	2 134.0(8)	401.0(8)	5 968.1(8)
O(001)	3 126(3)	4 311(3)	2 079(4)
O(002)	1 179(4)	3 668(4)	2 993(3)
O(003)	2 239(4)	980(4)	2 187(4)
O(004)	3 444(5)	3 444(5)	3 444(5)
O(005)*	934(8)	934(8)	934(8)
O(1)	3 113(2)	2 654(2)	5 529(2)
O(2)	1 971(2)	1 597(2)	4 856(2)
C(11)	4 519(3)	1 163(3)	6 759(3)
C(12)	5 129(3)	1 336(4)	7 319(3)
C(13)	5 787(4)	899(4)	7 318(4)
C(14)	5 841(4)	289(4)	6 777(4)
C(15)	5 236(4)	107(4)	6 232(4)
C(16)	4 582(3)	552(3)	6 212(4)
C(17)	3 365(3)	1 639(3)	7 788(3)
C(18)	3 430(3)	921(3)	8 120(3)
C(19)	3 143(4)	793(4)	8 852(4)
C(110)	2 786(4)	1 376(4)	9 263(3)
C(111)	2 730(4)	2 100(4)	8 945(4)
C(112)	3 009(4)	2 225(4)	8 206(4)
C(113)	3 990(3)	2 764(3)	6 681(3)
C(114)	3 879(3)	2 931(3)	5 797(3)
C(115)	4 504(4)	2 548(4)	5 310(4)
C(116)	3 933(4)	3 824(3)	5 699(4)
C(21)	2 723(3)	−466(3)	5 931(3)
C(22)	3 048(4)	−696(3)	5 224(4)
C(23)	3 549(4)	−1 291(4)	5 184(4)
C(24)	3 743(4)	−1 685(4)	5 842(5)
C(25)	3 421(4)	−1 486(4)	6 539(4)
C(26)	2 911(3)	−870(3)	6 588(4)
C(27)	1 529(3)	274(3)	6 812(3)
C(28)	1 486(3)	895(4)	7 370(3)
C(29)	1 007(4)	807(4)	7 994(4)
C(210)	566(4)	114(4)	8 061(4)
C(211)	591(4)	−492(4)	7 504(4)
C(212)	1 073(3)	−412(3)	6 882(4)
C(213)	1 456(3)	301(3)	5 101(3)
C(214)	1 259(3)	1 127(3)	4 844(3)
C(215)	682(3)	1 505(4)	5 379(4)
C(216)	913(4)	1 075(4)	4 003(3)

* 0.5 occupancy.

was added dropwise over 5 min to (**2**) (0.40 g, 0.51 mmol) in dry thf (30 cm^3). During the addition the mixture became cloudy but upon complete addition a clear yellow solution was obtained. The solvent was evaporated and the residue extracted with CH_2Cl_2 (3 × 20 cm^3), filtered and then reduced to 5 cm^3. The white product was then precipitated by the addition of light petroleum (b.p. 40—60 °C). Yield: 0.265 g, 84%.

The same product could be made from (**2**) and ethanolic NaOH in 72% yield or from NEt_3 and (**2**) in $CDCl_3$ (quantitative yield by ^{31}P n.m.r.). The isolated product could be recrystallised from aqueous methanol to give the hydrate (**8**)·$3.5H_2O$, whose *X*-ray structure was determined.

Preparation of trans-[$PtCl(PPh_2CH_2CMe_2O)(PPh_2CH_2CMe_2OH)$] (**12**).—A solution of (**3**) (0.31 g, 0.40 mmol) in $CHCl_3$ (10 cm^3) was treated with an excess of NEt_3 (0.5 cm^3) and the resulting solution was stirred for 30 min. The $CHCl_3$ solution was then extracted with water (2 × 25 cm^3) and then dried over K_2CO_3, filtered, reduced to 5 cm^3, and the product precipitated with light petroleum, b.p. 60—80 °C. Yield: 0.21 g, 70%.

Crystal Structure Analysis.—Crystal data. $C_{32}H_{36}O_2P_2Pt$·$3.5H_2O$, $M = 709.7 + 63.1$, rhombohedral, space group $R\bar{3}$, $a = 17.026(2)$ Å, $\alpha = 92.76(1)°$, $U = 4\,917(2)$ Å^3, $Z = 6$, $D_c = 1.56$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 44.4 cm^{-1}, $F(000) = 2\,322$, $T = 290$ K; colourless prisms, crystal dimensions 0.46 × 0.49 × 0.50 mm.

Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 50°, with scan range ±0.9 ° (2θ) around the K_{α_1}–K_{α_2} angles, scan speed 3—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. Laue group $\bar{3}$ with no systematic absences; of the possible space groups, *R*3 and $R\bar{3}$, the latter was selected, and shown to be correct by the successful refinement. A half-sphere of data was examined (10 517 reflections), and then merged to give the unique data. 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 high-angle reflections, 3 914 observed reflections [$I/\sigma(I) \geqslant 3.0$] were used in refinement (5 599 total unique) and corrected for Lorentz, polarisation, and absorption effects, the last with ABSCOR;[16] maximum and minimum transmission factors were 0.44 and 0.28, $R_{merge} = 0.036$.

The heavy atom (Pt) was located by Patterson techniques and the light atoms were then found on successive Fourier syntheses; five molecules of water of crystallisation were found from difference syntheses of which two lay on the three-fold axis (and one was assigned an occupancy of 0.5). Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.07$ Å^2. Those defined by the molecular geometry were inserted at calculated positions and not refined; methyl groups were treated as rigid CH_3 units, with their initial orientation taken from the strongest peak on a difference-Fourier synthesis. Final refinement was by cascaded least-squares methods, with anisotropic thermal parameters for all atoms other than hydrogen (and the half-occupancy water). The largest peak on a final difference-Fourier synthesis was of height 0.8 e Å^{-3}. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.000\,48$ was used. This was shown to be satisfactory by a weight analysis. The final *R* value was 0.029, $R' = 0.029$. Computing was with the SHELXTL system[17] on a Data General DG30 computer.

Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 18. Selected bond lengths and angles are given in Table 4, and final atomic co-ordinates in Table 5.

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References

1 N. W. Alcock, A. W. G. Platt, and P. G. Pringle, *Inorg. Chim. Acta*, 1987, **128**, 215.

2 H. E. Bryndza, J. C. Calabrese, M. Marsi, D. C. Roe, W. Tam, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1986, **108**, 4805 and refs. therein.

3 R. T. Boere and C. J. Willis, *Inorg. Chem.*, 1985, **24**, 1059.

4 H. E. Bryndza, S. A. Kretchmor, and T. H. Tulip, *J. Chem. Soc., Chem. Commun.*, 1985, 977.

5 M. A. Bennett, G. B. Robertson, P. O. Whimp, and T. Yoshida, *J. Am. Chem. Soc.*, 1973, **95**, 3028.

6 A. B. Goel, S. Goel, and D. G. Vanderveer, *Inorg. Chim. Acta*, 1981, **54**, 2169.

7 H. E. Bryndza, *Organometallics*, 1985, **4**, 406.

8 J. A. Davies and F. R. Hartley, *Chem. Rev.*, 1981, **81**, 79 and refs. therein.

9 R. K. Harris, *Can. J. Chem.*, 1964, **42**, 2275.

10 P. E. Garrou, *Inorg. Chem.*, 1975, **14**, 1435.

11 G. K. Anderson and R. Kumar, *Inorg. Chem.*, 1984, **23**, 4064.

12 A. R. Sanger, *Can. J. Chem.*, 1983, **61**, 2214.

13 T. G. Appleton and M. A. Bennett, *Inorg. Chem.*, 1978, **17**, 738.

14 J. M. Wisner, T. J. Bartezak, J. A. Ibers, J. J. Low, and W. A. Goddard, *J. Am. Chem. Soc.*, 1986, **108**, 347.

15 J. X. McDermott, J. F. White, and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.

16 N. W. Alcock, in 'Crystallographic Computing,' ed. F. Ahmed, Munksgaard, Copenhagen, 1970.

17 G. M. Sheldrick, SHELXTL User Manual, Nicolet Instrument Co., Madison, Wisconsin, 1981.

18 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

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