DALTON

Hydroxymethyl bis(phosphines) and their palladium(II) and platinum(II) complexes formed *via* biphasic reactions. Crystal structure of $[Pd\{(HOH_2C)_2PC_6H_4P(CH_2OH)_2\}_2]Cl_2$†

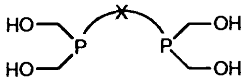
V. Sreenivasa Reddy, Kattesh V. Katti* and Charles L. Barnes

Center for Radiological Research and Missouri University Research Reactor,
Department of Chemistry, University of Missouri, Columbia, MO 65203, USA

The water-soluble bis(phosphines) 1,2-bis[bis(hydroxymethyl)phosphino]benzene and 1,2-bis[bis(hydroxymethyl)phosphino]ethane were synthesized in near-quantitative yields by the catalytic formylation of $H_2PC_6H_4PH_2$ and $H_2PCH_2CH_2PH_2$ in the presence of formaldehyde in aqueous media. Their reactions with *cis*-[Pt(cod)Cl_2] (cod = cycloocta-1,5-diene) and *cis*-[Pd(PhCN)$_2$Cl$_2$] produced water-soluble complexes $[M\{(HOH_2C)_2PC_6H_4P(CH_2OH)_2\}_2]Cl_2$ (M = Pt **1** or Pd **2**) and $[Pd\{(HOH_2C)_2PCH_2CH_2P(CH_2OH)_2\}_2]Cl_2$ **3**, respectively. All the compounds were characterized by ^1H and ^{31}P NMR spectroscopy. The structure of **2** was confirmed by X-ray crystallography.

Water-soluble phosphines have become essential building blocks for the development of transition metal/organometallic compounds that are soluble in aqueous media.[2,3] The utility of transition-metal complexes as catalysts in aqueous media provides unique advantages in terms of performance as compared to the traditional catalytic reactions which are normally carried out in organic media.[4–8] For example, recent studies demonstrate the usefulness of biphasic catalytic reactions in which products soluble in organic media can readily be separated from the aqueous media. In fact, biphasic aqueous-based hydroformylation technology is currently used for the production of butanal on an industrial scale.[9] Catalytic processes by Rhône-Poulenc,[10,12] Montedison[13] and Kuraray[14] for the production of higher olefins, telomers, fine chemicals and pharmaceutical intermediates exemplify the rich applied chemistry of water-soluble transition-metal catalysts. In certain systems it has been demonstrated that the catalysts remain in the aqueous phase, and can easily be separated from the organic phase. The reactants and products stay in the organic phase in the aqueous biphasic oxo catalysts currently used in hydroformylation reactions. In addition to the efficient separation of products, catalysts derived from water-soluble phosphines have found applications in achieving selectivity in specific chemical transformations.

Mono-, di- or tri-sulfonated arylphosphines are commonly used in the development of water-soluble transition-metal complexes and catalysts.[15–17] While sulfonated phosphines offer convenient access to water-soluble ligands in bulk quantities for industrial-scale applications, their lack of purity and the, often encountered, sulfonate-assisted oxidation of phosphines have become major barriers to the utility of this class of phosphines in specific catalytic transformations. New developments in the design of water-soluble phosphines will result in greater strides in the production of catalytically useful water-soluble transition-metal complexes. In particular, the transition-metal chemistry of water-soluble bis(phosphines) has remained relatively unexplored because of the lack of functionalized bis(phosphines) and their precursors. As part of our ongoing research in the development of functionalized bis(phosphines),[18–25] we report herein (*i*) the synthesis and characterization of a new generation of water-soluble bis(phosphines) of the general structure A and (*ii*) their reactions with *cis*-[Pt(cod)Cl_2](cod = cycloocta-1,5-diene) and *cis*-[Pd(PhCN)$_2$Cl$_2$] to produce water-soluble complexes of Pt^{II} and Pd^{II} $[M\{(HOH_2C)_2PC_6H_4P(CH_2OH)_2\}_2]Cl_2$ (M = Pt **1** or Pd **2**) and $[Pd\{(HOH_2C)_2PCH_2CH_2P(CH_2OH)_2\}_2]Cl_2$, **3** respectively and (*iii*) the crystal structure of **2**.



A

X = C_6H_4 or CH_2CH_2

Experimental

All reactions were carried out under purified nitrogen by standard Schlenk techniques. Solvents were purified and dried by standard methods and distilled under nitrogen prior to use. Reagents such as $H_2PC_6H_4PH_2$, $H_2PCH_2CH_2PH_2$, $K_2[PtCl_4]$, [Pd(PhCN)$_2$Cl$_2$] and [Pt(cod)Cl_2] were obtained from Strem Chemical Co. and used without further purification. Nuclear magnetic resonance spectra were recorded on a Bruker ARX-300 spectrometer using D_2O as a solvent. The ^1H chemical shifts are reported in ppm downfield from external standard $SiMe_4$, ^{31}P (121.5 MHz) with 85% H_3PO_4 as an external standard and positive chemical shifts downfield of the standard and ^{195}Pt (64.5 MHz) using D_2O as solvent. Elemental analyses were performed by Onida Research Services, Inc., New York.

Synthesis of 1,2-bis[bis(hydroxymethyl)phosphino]benzene, $(HOH_2C)_2PC_6H_4P(CH_2OH)_2$

Aqueous formaldehyde (0.160 mol) was placed in deionized oxygen-free water (25 cm^3) and purged with nitrogen gas for 20 min at 25 °C. The salt $K_2[PtCl_4]$ (100 mg) was added and purging continued for 10 min. 1,2-Bis(phosphino)benzene (5.0 g, 0.035 mol) was added dropwise to the resulting solution, and stirring continued for 20 min. Removal of the solvent *in vacuo* after filtration afforded the required compound in near-quantitative yield as a colourless viscous oil which solidified upon standing at room temperature for a few days (Found: C, 45.65; H, 6.25. $C_{10}H_{16}O_4P_2$ requires C, 45.80; H, 6.15%). NMR: ^1H, δ 4.20 [m, br, 8 H, P(CH_2OH)] and 7.40 (m, 4 H, C_6H_4); ^{31}P δ −31.2 (s).

---

† Chemistry in Environmentally Benign Media. Part 2.[1]

The compound $(HOH_2C)_2PC_2H_4P(CH_2OH)_2$ was synthesized by a similar procedure using 1,2-bis(phosphino)ethane and aqueous formaldehyde in the presence of $K_2[PtCl_4]$ as catalyst in water[1] (Found: C, 33.70; H, 7.45. $C_6H_{16}O_4P_2$ requires C, 33.65; H, 7.55%). NMR: ^1H, δ 1.52 (m, br, 4 H, CH_2CH_2) and 3.90 [m, br, 8 H, $P(CH_2OH)$]; ^{31}P, δ −25.1 (s).

Synthesis of $[M\{(HOH_2C)_2PXP(CH_2OH)_2\}_2]Cl_2$ ($X = C_6H_4$, M = Pt 1 or Pd 2; $X = C_2H_4$, M = Pd 3)

An aqueous solution (20 cm^3) of the bis(phosphine) (2.0 mmol) was added dropwise to $[Pt(cod)Cl_2]$ or to $[Pd(PhCN)_2Cl_2]$ (1.0 mmol) in dichloromethane (20 cm^3) at 25 °C with constant stirring. The stirring was continued for 30 min and the aqueous layer separated from the organic layer. The aqueous solution was concentrated to ≈5 cm^3 *in vacuo* and evaporated slowly at room temperature to yield crystalline complex(es) in 85–90% yield: $[Pt\{(HOH_2C)_2PC_6H_4P(CH_2OH)_2\}_2]Cl_2$ **1** (Found: C, 30.50; H, 4.15. $C_{20}H_{32}Cl_2O_8P_4Pt$ requires C, 30.40; H, 4.10%). NMR: ^1H, δ 4.80 [m, 16 H, $P(CH_2OH)$] and 8.0 (m, 8 H, C_6H_4); ^{31}P, δ 49.7 (s, $^1J_{PtP}$ = 2203 Hz); $[Pd\{(HOH_2C)_2PC_6H_4P(CH_2OH)_2\}_2]Cl_2$ **2** (Found: C, 34.40; H, 4.55. $C_{20}H_{32}Cl_2O_8P_4Pd$ requires C, 34.25; H, 4.60%). NMR: ^1H, δ 4.80 [m, 16 H, $P(CH_2OH)$] and 8.0 (m, 8 H, C_6H_4); ^{31}P, δ 57.4 (s). $[Pd\{(HOH_2C)_2PC_2H_4P(CH_2OH)_2\}_2]Cl_2$ **3** (Found: C, 23.90; H, 5.20. $C_{12}H_{32}Cl_2O_8P_4Pd$ requires C, 23.80; H, 5.35%). NMR: ^1H, δ 2.28 (m, 8 H, CH_2CH_2) and 4.38 [m, 16 H, $P(CH_2OH)$]; ^{31}P, δ 66.8 (s).

X-Ray data collection and processing

The crystal data and the details of data collection for complex **2** are listed in Table 2. Colourless crystals suitable for X-ray diffraction were obtained by slow evaporation of an aqueous solution at 25 °C. X-Ray data were collected on an Enraf-Nonius CAD-4 diffractometer with Mo-Kα radiation (λ 0.7093 Å) and a graphite monochromator at 22(1) °C. The cell dimensions were obtained from a least-squares fit to the setting angles of 25 reflections with 2θ in the range 20.0–30.0°. The crystal exhibited no significant decay under X-ray irradiation.

The structure was solved by direct methods and subsequently refined by full-matrix least squares minimizing $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = [\sigma^2(F_o) + 0.0005(F_o)^2]$. Atomic scattering factors including anomalous scattering contributions were from ref. 26. Empirical absorption corrections were made using the ψ-scan method, the minimum and maximum transmission factors being 0.887 786 and 0.997 072. All hydrogen atoms were located in Fourier-difference maps and refined with fixed isotropic thermal parameters. The final cycle of the least squares refinement gave an agreement factor R of 0.025 (R' = 0.033). The programs used for the crystallographic computations were as in ref. 27.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

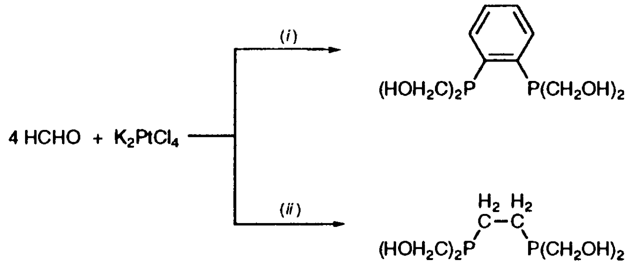
Results and Discussion

The water-soluble hydroxymethyl bis(phosphines) were prepared by catalytic hydroformylation of $H_2PC_6H_4PH_2$ and $H_2PCH_2CH_2PH_2$ in the presence of formaldehyde in 95% yields in aqueous media (Scheme 1). Their chemical constitution was confirmed by ^1H and ^{31}P NMR spectroscopy. The ^{31}P NMR spectra consisted of singlets centred at δ −31.2 and −25.1, suggesting that these novel bis(phosphines) may have similar nucleophilicity to that of the methyl analogue (*i.e.* $Me_2PCH_2CH_2PMe_2$). They are highly soluble in water (> 1 g cm^{-3}), ethanol and sparingly soluble in common organic solvents such as hexane, toluene and chloroform. It is important to note that the introduction of alkyl hydroxy groups on the phosphines has imparted significant oxidative and thermal stability as compared to the methyl or ethyl analogues (*e.g.* $R_2PCH_2CH_2PR_2$; R = Me or Et). For example, the ^{31}P NMR spectrum of undegassed solutions in water indicated the formation of only ≈10% phosphine oxide even after 48 h. They showed remarkable oxidative stability in degassed water as evidenced by the formation of < 5% of the phosphine oxide in 7 d.

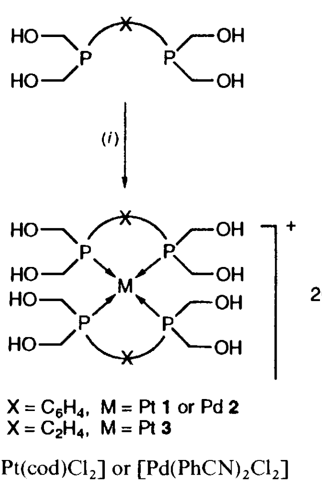
The aqueous solubility of these hydroxymethyl bis(phosphines) presented the prospect of investigating their co-ordination chemistry in water. 1,2-Bis[hydroxymethyl)phosphino]benzene in water, upon interaction with $[Pt(cod)Cl_2]$ or $[Pd(PhCN)_2Cl_2]$ in dichloromethane, produced the corresponding cationic complexes $[M(L-L)_2]Cl_2$ (M = Pt **1** or Pd, **2**) in 85–90% yields (Scheme 2). Their chemical constitution was confirmed by elemental analysis and ^1H and ^{31}P NMR spectroscopy. The ^{31}P NMR spectra consisted of single resonances at δ 49.7 ($^1J_{PtP}$ = 2203 Hz) and 57.4, respectively, indicating a pronounced downfield shift upon co-ordination of the phosphine units to Pt^{II} and Pd^{II}. The analytical data suggested that there are two ligands per metal. The ^1H NMR spectra show multiplets centred at δ 4.80 for the methylene protons suggesting a significant downfield shift compared to the chemical shift of the free bis(phosphines) (δ 4.20).

The interaction of an aqueous solution of 1,2-bis[(hydroxymethyl)phosphino]ethane with *cis*-$[Pd(PhCN)_2Cl_2]$, in dichloromethane, produced the new palladium(II) cationic complex $[Pd\{(HOH_2C)_2PC_2H_4P(CH_2OH)_2\}_2]Cl_2$, **3**, in 90% yield (Scheme 2). The analytical data suggested that there are two ligands per metal. The ^{31}P NMR spectrum consisted of a single resonance at δ 66.8 suggesting that all the phosphorus nuclei had a similar chemical environment.

The structure of complex **2** was further confirmed by X-ray crystallography. An ORTEP diagram of the cation is shown in Fig. 1 and selected bond distances and angles are listed in Table 1. The unit cell consists of two molecules with no unusual inter- or intra-molecular contacts. The geometry around the palladium is square planar and the molecule has a centre of symmetry. Two diphosphine units are co-ordinated to the metal



Scheme 1 (*i*) $C_6H_4(PH_2)_2$-1,2; (*ii*) $H_2PCH_2CH_2PH_2$



Scheme 2 (*i*) $[Pt(cod)Cl_2]$ or $[Pd(PhCN)_2Cl_2]$

Table 1 Selected bond distances (Å) and angles (°) involving non-hydrogen atoms for complex **2**

Pd–P(1)	2.312(1)	P(2)–C(9)	1.849(4)
Pd–P(2)	2.322(1)	P(2)–C(10)	1.839(3)
P(1)–C(1)	1.813(3)	O(1)–C(7)	1.409(4)
P(2)–C(2)	1.818(3)	O(2)–C(8)	1.411(5)
P(1)–C(7)	1.850(1)	O(3)–C(9)	1.422(4)
P(1)–C(8)	1.822(4)	O(4)–C(10)	1.399(4)
P(1)–Pd–P(1^{I})	180.0	P(1)–Pd–P(2)	83.4(3)
P(1)–Pd–P(2^{I})	96.6(3)	P(1^{I})–Pd–P(2^{I})	180.0
P(2)–C(2)–C(1)	117.7(2)	P(1)–C(1)–C(2)	117.3(2)

Symmetry relation: I $-x, 1-y, -z$.

Table 2 Crystal data and details of the structure determination for complex **2**

Formula	$C_{20}H_{32}Cl_2O_8P_4Pd$
M	701.66
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	9.453(2)
b/Å	16.735(3)
c/Å	8.696(1)
β/°	99.02(1)
U/Å^3	1358.7(4)
D_c/g cm^{-3}	1.715
Crystal dimensions/mm	0.10 × 0.20 × 0.40
Z	2
F(000)	712
μ/cm^{-1}	1.15
h,k,l Ranges	−10 to 10, 0–18, 0–9
Unique data	1878
Data with $I > 2\sigma(I)$	1644
No. parameters	160
Largest shift/σ in final cycle	0.0001
Goodness of fit	1.10
R	0.025
R'	0.033

$R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{\frac{1}{2}}$.

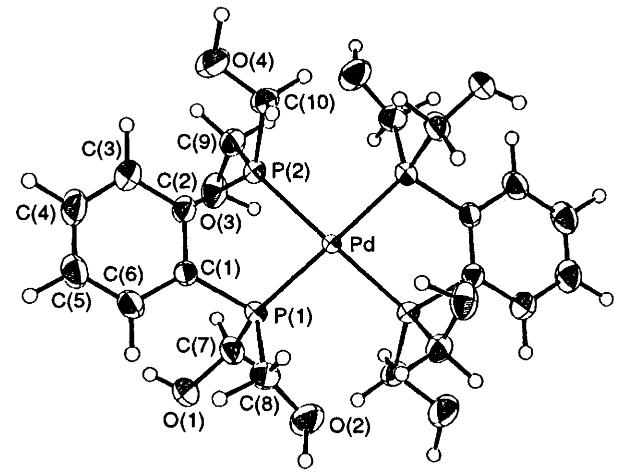


Fig. 1 An ORTEP representation of complex **2**. The thermal ellipsoids are drawn at the 50% probability level

in a chelating fashion. The Pd–P(1) and Pd–P(2) distances are 2.312(1) and 2.322(1) Å, respectively. The P(1)–C(1) and P(2)–C(2) distances are 1.813(5) and 1.818(3) Å. The chelate angle of P(1)–Pd–P(2) [83.4(3)°] is less compared to non-chelate angle of P(1)–Pd–P(2^{I}) [96.6(3)].

In all the reactions discussed above, typically 95–98% of the metal precursor [Pt(cod)Cl_2] or [Pd(PhCN)$_2$$Cl_2$] from the organic phase was transferred into the phosphine-containing aqueous phase in ≈5 min upon simple shaking of the respective solutions. Separation and evaporation of the aqueous phase produced complexes **1**–**3** in analytically pure forms. Their preferential solubility in aqueous media under biphasic conditions is remarkable in terms of the separation of pure samples from these, deceptively complex, reactions. In a study involving the water-soluble monophosphine $P(CH_2OH)_3$, Pringle and co-workers[28] have recently demonstrated that reactions with *cis*-[Pt(cod)Cl_2] or *cis*-[Pd(PhCN)$_2$$Cl_2$] produced PtL_2Cl_2 and PdL_2Cl_2 [L = $P(CH_2OH)_3$], respectively, *via* the simple loss of cod or PhCN.

Table 3 Fractional atomic coordinates for non-hydrogen atoms of complex **2**

Atom	x	y	z
Pd	0	0.5	0
P(1)	0.197 05(9)	0.514 75(5)	0.192 00(10)
P(2)	0.124 38(9)	0.388 96(5)	−0.067 11(10)
O(1)	0.440 2(3)	0.597 8(2)	0.278 5(3)
O(2)	0.123 8(3)	0.613 4(2)	0.403 2(3)
O(3)	0.308 8(3)	0.464 3(2)	−0.222 6(3)
O(4)	0.115 4(3)	0.233 8(2)	−0.133 6(4)
C(1)	0.303 4(3)	0.424 1(2)	0.206 8(4)
C(2)	0.277 1(3)	0.369 9(2)	0.083 3(4)
C(3)	0.367 8(4)	0.304 4(2)	0.078 8(4)
C(4)	0.480 6(4)	0.293 1(2)	0.196 9(5)
C(5)	0.504 8(4)	0.344 5(2)	0.321 8(5)
C(6)	0.416 9(4)	0.410 4(2)	0.328 0(4)
C(7)	0.325 5(4)	0.592 9(2)	0.154 1(4)
C(8)	0.171 6(4)	0.534 1(2)	0.392 1(4)
C(9)	0.209 1(4)	0.400 1(2)	−0.243 6(4)
C(10)	0.025 8(4)	0.294 0(2)	−0.092 4(4)
Cl	0.124 67(11)	0.615 4(6)	0.756 15(11)

Acknowledgements

This work was supported by funds provided by Du Pont Merck pharmaceuticals and by the Departments of Chemistry, Radiology and Research Reactor, University of Missouri. Partial funding of the X-ray difractometer by the National Science Foundation, grant no. CHE[90-11804], is gratefully acknowledged.

References

1 Part 1, V. S. Reddy, K. V. Katti and C. L. Barnes, *Inorg. Chim. Acta*, 1995, **240**, 367.
2 M. Barton and J. D. Atwood, *J. Coord. Chem.*, 1994, **24**, 43; F. Joó and Z. Tóth, *J. Mol. Catal.*, 1980, **8**, 369; D. Sinou, *Bull. Soc. Chim. Fr.*, 1987, 480; M. J. H. Russel, *Platinum Met. Rev.*, 1988, **32**, 179.
3 W. A. Herrmann, J. A. Kuple, J. Kellner, H. Riepl, H. Bahrmann and W. Konkol, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 391; T. Okano, I. Uchida, T. Nakagaki, H. Konishi and J. Kiji, *J. Mol. Catal.*, 1989, **54**, 65; E. Fache, F. Senocq, C. Santini and J. M. Basset, *J. Chem. Soc., Chem. Commun.*, 1990, 1776.
4 E. Wiebus and B. Cornils, *Chem.-Ing.-Tech.*, 1994, **66**, 916.
5 P. Kalck and F. Monteil, *Adv. Organomet. Chem.*, 1992, **34**, 219.
6 W. A. Hermann and C. W. Kohlpaintner, *Angew. Chem., Int. Ed. Engl.*, 1992, **32**, 1524.
7 A. Lubineau, J. Augé and Y. Queneau, *Synthesis*, 1994, **8**, 741.
8 *Aqueous Organometallic Chemistry and Catalysis, NATO Advanced Research Workshop Debrecen*, 29th August–1st September 1994, Preprints.
9 E. G. Kuntz, *Chemtech*, 1987, **17**, 570.
10 D. Morel, Rhône Poulenc Ind., *French Pat.*, 2 486 525, 1980.
11 Rhône Poulenc Ind., *French Pat.*, 2 505 322, 1981.
12 Rhône Poulenc Ind., *French Pat.*, 2 541 675, 1983.
13 L. Cassar, *Chem. Ind.* (*Milano*), 1985, **57**, 256; *Ger. Pat.*, 2 035 902, 1979.
14 Y. Tokito and N. Yoshimura, Kuraray Corp. *US Pat.*, 4 808 756, 1989.
15 S. Ahrland, J. Chatt, N. R. Davies and A. A. Williams, *J. Chem. Soc.*, 1958, 276.
16 A. F. Borowski, D. J. Cole-Hamilton and G. Wilkinson, *Nouv. J. Chim.*, 1978, **2**, 137.

17 F. Joó and M. T. Beck, *React. Kinet. Catal. Lett.*, 1975, **2**, 257.
18 K. V. Katti, V. S. Reddy and P. R. Singh, *Chem. Soc. Rev.*, 1995, 97.
19 V. S. Reddy and K. V. Katti, *Inorg. Chem.*, 1994, **33**, 2695.
20 V. S. Reddy and K. V. Katti, unpublished work.
21 V. S. Reddy, K. V. Katti and C. L. Barnes, *Chem. Ber.*, 1994, **127**, 1355.
22 V. S. Reddy, K. V. Katti and C. L. Barnes, *Chem. Ber.*, 1994, **127**, 979.
23 V. S. Reddy, K. V. Katti and C. L. Barnes, *Inorg. Chem.*, 1995, **34**, 5483.
24 V. S. Reddy, K. V. Katti and C. L. Barnes, *Organometallics*, 1994, **13**, 2391.
25 V. S. Reddy, K. V. Katti and C. L. Barnes, *J. Chem. Soc., Chem. Commun.*, 1995, 317.
26 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol 4.
27 NRCVAX system 1989: E. J. Gabe, Y. L. Page, J.-P. Charland, F. L. Lee and P. S. White, *J. Appl. Crystallogr.*, 1989, **22**, 384; H. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876; C. K. Johnson, ORTEP, A Fortran Thermal Ellipsoid Plot Program, Technical Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, 1976; A. C. Larson, *Crystallographic Computing*, Munksgaard, Copenhagen, 1970, p. 293; Y. L. Page, *J. Appl. Crystallogr.*, 1988, **21**, 983; Y. L. Page and E. J. Gabe, *J. Appl. Crystallogr.*, 1979, **12**, 464; D. Rogers, *Acta Crystallogr., Sect. A*, 1981, **37**, 734.
28 J. W. Ellis, K. N. Harrison, P. A. T. Hoye, A. G. Orpen, P. G. Pringle and M. B. Smith, *Inorg. Chem.*, 1992, **31**, 3026; P. A. T. Hoye, P. G. Pringle, M. B. Smith and K. Worboys, *J. Chem. Soc., Dalton Trans.*, 1993, 269.

Received 14*th July* 1995; *Paper* 5/04577K