Chelate-stabilised Tetrahydrofuran Complexes of Platinum(II). Crystal Structure of $[PtCl(Ph_2PCH_2C_4H_7O)(Ph_2PCH_2C_4H_7O)][PF_6]$ ‡

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

The platinum(II) complexes *cis*- and *trans*-$[PtCl_2(PPh_2CH_2C_4H_7O)_2]$ (**2**) and (**3**) are described. The *cis* isomer (**2**) reacts with $K[PF_6]$ to give the monochelate *cis*-$[PtCl(Ph_2PCH_2C_4H_7O)(Ph_2PCH_2C_4H_7O)][PF_6]$ (**4a**). Complex (**2**) also reacts with $AgClO_4$ to give the bis chelate *cis*-$[Pt(Ph_2PCH_2C_4H_7O)_2][ClO_4]_2$ (**5a**). The tetrahydrofuran (thf) complexes (**4a**) and (**5a**) are compared with closely related alcohol and linear ether complexes and it is deduced that the *trans* influence of the neutral *O*-donors is in the order ROH > thf > R_2O. The *X*-ray structure (R = 0.039 for 5 730 diffractometer observed reflections) of complex (**4a**) confirms the structural assignment; the Pt–O bond length [2.142(4) Å] is somewhat longer than found for covalent Pt–O bonds.

Ethers, and particularly tetrahydrofuran, are common solvents for much palladium(II) and platinum(II) chemistry. Despite the fact that ether co-ordination complexes are doubtless involved as intermediates in many of the reactions in these solvents very few ether complexes of Pd or Pt have been isolated and studied.[1] The reason for this is that the metal–ether bonds are generally weak and hence the complexes are labile and liable to decompose. This lability is of course crucial to the success of solvent complexes as homogeneous catalysts.[2]

One way to stabilise a weak M–L interaction is to incorporate the donor group L into a chelate. Hence we[3,4] and others[5–7] have been able to make *O*-donor complexes by using functionalised phosphines. This paper describes some chelate-stabilised tetrahydrofuran–platinum(II) complexes formed from the ligand $Ph_2PCH_2C_4H_7O$ (**1**). While this work was in progress Lindner *et al.*[8] showed that cobalt and rhodium complexes of (**1**) are useful methanol carboxylation catalysts.

Results and Discussion

The platinum complexes (**2**), (**3**), (**4a**), and (**5a**) of the phosphino ether (**1**) were made by the routes shown in the Scheme and all have been fully characterised (see Table 1).

It is interesting to compare the properties of the closely related cationic species (**4a**)—(**4c**) and (**5a**)—(**5c**). The monochelate alcohol complex (**4c**) is fluxional on the n.m.r. time-scale because of rapid interchange of the two alcohol groups whereas both of the related ether complexes (**4a**) and (**4b**) show no fluxionality at ambient temperatures. This is probably due to the greater nucleophilicity of the alcohol donor. A comparison of the $^1J(PtP)$ values for the phosphorus *trans* to the *O*-donor reveals the orders (**4c**) > (**4a**) > (**4b**), and (**5c**) > (**5a**) > (**5b**), and hence the order of *trans* influence of the *O*-donor is ROH > $CH_2(CH_2)_3O$ > R_2O.

It is unsound to draw any conclusions about the Pt–O bond strengths in these compounds from the $^1J(PtP)$ data alone. Bryndza *et al.*[9,10] have recently shown that Pt–OR and Pt–CH_3 have similar strengths but $^1J(PtP)$ values for phosphines *trans* to OR or CH_3 are very different. The Pt–O bond length is a more reliable guide to Pt–O bond strength and hence we determined the *X*-ray crystal structure of complex (**4a**) so that a direct comparison could be made with the structure of (**4b**).[6]

X-Ray Crystal Structure of (**4a**).—The structure of the cation of (**4a**) is shown in the Figure, and Table 2 gives the principal dimensions. This confirms the expected geometry, and shows that one tetrahydrofuran is co-ordinated, while the other is distant from the Pt. The dative Pt–O bond [2.142(4) Å] is significantly longer than the Pt–O single bonds we have previously examined[3,4] (2.024—2.039 Å), indicating as expected that the dative bond is weaker. Again as expected, Pt–P(2) *trans* to O is shorter than Pt–P(1) *trans* to Cl. These effects are transmitted through the structure, with P(1)–C shorter than P(2)–C, while the O–C distances from the non-bonded O(2) are markedly shorter than the O–C distances involving O(1). The angles around Pt are distorted by the relatively short bite of the $PtPCH_2CHO$ chelate ring, with P–Pt–O angle of 82.8(1)°. The Pt–O bond is however significantly shorter than the Pt–O(Me) bond in (**4b**), of 2.192(7) Å.[6] Although no structure containing co-ordinated R–OH is known these Pt–O bond lengths suggest that the *trans* influence is directly proportional to the Pt–O bond length in these structurally related compounds.

Experimental

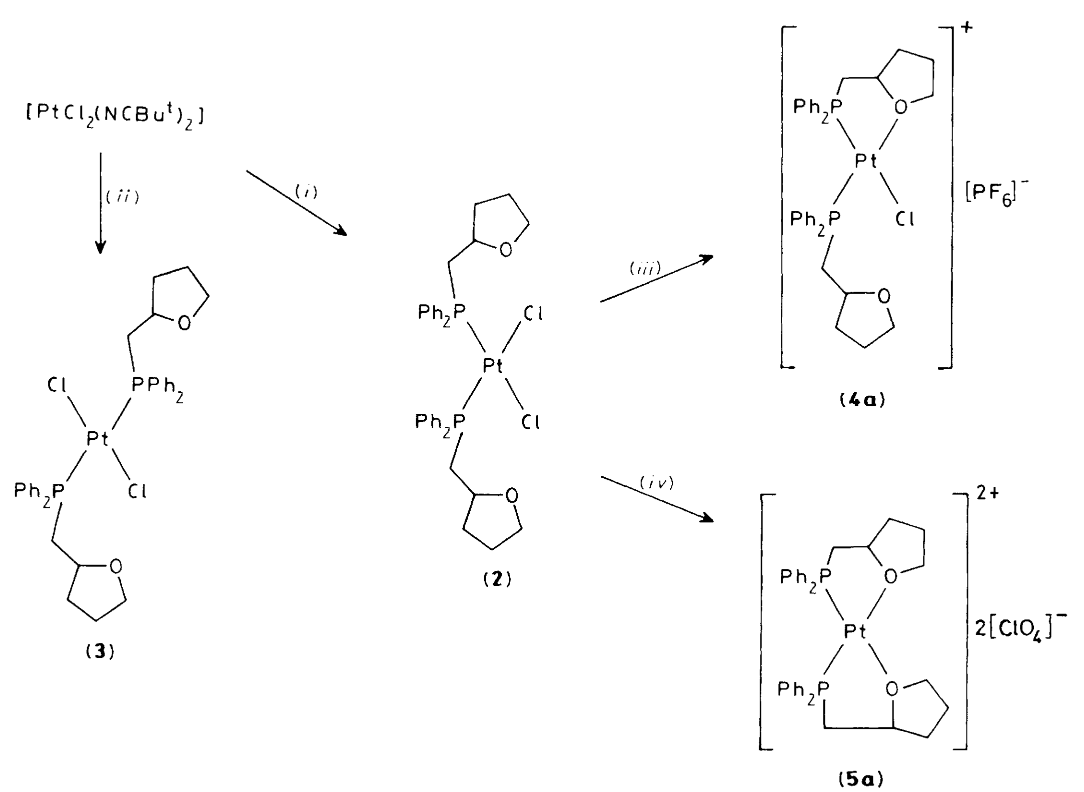
Preparations.—cis- *and* trans-$[PtCl_2(Ph_2PCH_2C_4H_7O)_2]$ (**2**) *and* (**3**). A solution of the ligand $Ph_2PCH_2C_4H_7O$ (630 mg, 2.33 mmol) in acetone (15 cm^3) was added to a solution of $[PtCl_2(NCBu^t)_2]$ (500 mg, 1.16 mmol) in acetone (5 cm^3) and then stirred for 67 h to give a yellow precipitate of the

---

† *Present address:* School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS.

‡ Chloro[2-(diphenylphosphinomethyl)tetrahydrofuran-*OP*][2-(diphenylphosphinomethyl)tetrahydrofuran-*P*]platinum(II) hexafluorophosphate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.



Scheme. (*i*) 2 equiv. of ligand (**1**) in acetone for 30 min; (*ii*) 2 equiv. of ligand (**1**) in acetone for 67 h; (*iii*) KPF_6 in MeCN; (*iv*) $AgClO_4$ in toluene–CH_2Cl_2

Table 1. $^{31}P-\{^1H\}$ N.m.r.[a] and i.r. data[b]

Complex	$\delta(P_A)$[c]	$J(PtP_A)$	$\delta(P_B)$	$J(PtP_B)$	$J(P_AP_B)$	$\nu(Pt-Cl)/cm^{-1}$	Ref.
(**2**)	7.1	3 694				314, 286	This work
(**3**)	9.3	2 566				338	This work
	6.5	3 700					
(**4a**)	32.1	3 662	4.5	4 048	17	320	This work
(**4b**)	36.3	3 630	2.7	4 165	15		5
(**4c**)[d]	30.8	3 654	3.7	3 951	16		4
	32.5	3 666	2.4	3 965	16		
(**5a**)	16.8	4 001					This work
(**5b**)	19.4	4 220					5
(**5c**)[d]	25.2	3 985					4
	24.3	3 990					

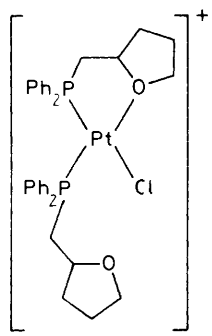
[a] In $CDCl_3$ at 36.4 MHz and 28 °C; chemical shifts (δ) in p.p.m. (±0.1) to high frequency of 85% H_3PO_4 and coupling constants (*J*) in Hz (±0.3). [b] CsCl discs. [c] P_A is part of the chelate ring when present. [d] Diastereoisomers observed.

Table 2. Principal dimensions of complex (**4a**) (lengths in Å, angles in °)

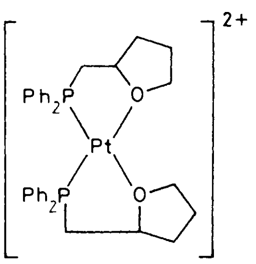
Pt–P(1)	2.240(1)	P(2)–C(13)	1.826(5)
Pt–P(2)	2.217(1)	P(2)–C(19)	1.817(5)
Pt–Cl	2.339(2)	P(2)–C(25)	1.838(5)
Pt–O(1)	2.142(4)	O(1)–C(31)	1.454(7)
P(1)–C(1)	1.802(5)	O(1)–C(34)	1.452(7)
P(1)–C(7)	1.805(6)	O(2)–C(26)	1.397(8)
P(1)–C(30)	1.827(6)	O(2)–C(27)	1.406(11)
P(1)–Pt–P(2)	99.2(1)	Cl–Pt–O(1)	88.5(1)
P(1)–Pt–Cl	169.6(1)	Pt–O(1)–C(31)	118.4(3)
P(1)–Pt–O(1)	82.8(1)	Pt–O(1)–C(34)	127.4(4)
P(2)–Pt–Cl	89.7(1)	C(31)–O(1)–C(34)	110.0(5)
P(2)–Pt–O(1)	177.1(1)	C(26)–O(2)–C(27)	109.5(6)

trans isomer (350 mg, 38%) (Found: C, 50.60; H, 4.80. Calc.: C, 50.65; H, 4.75%). The filtrate was evaporated to give an oil which was then redissolved in acetone (5 cm^3) and then diethyl ether added to precipitate the white *cis* isomer (310 mg, 33%) (Found for acetone solvate (1/1): C, 51.20; H, 5.35. Calc.: C, 51.50; H, 5.35%). Under similar conditions to the above, but by stirring for only 30 min instead of 67 h, the *cis* isomer can be isolated by evaporation in 93% yield.

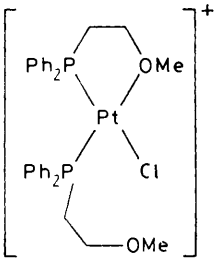
$[PtCl(Ph_2PCH_2C_4H_7O)(Ph_2PCH_2C_4H_7O)][PF_6]$. A solution of $K[PF_6]$ (200 mg) in MeCN (10 cm^3) was added to a solution of complex (**2**) (360 mg, 0.46 mmol) in MeCN (5 cm^3) and the turbid mixture stirred for 16 h. The solvent was then removed *in vacuo* and the residue was extracted with CH_2Cl_2 (3 × 10 cm^3). The turbid solution was then filtered and the filtrate reduced to give an oil from which crystals, suitable for *X*-ray analysis, slowly separated. The crystals were obtained free of the oil by rapid washing with CH_2Cl_2. The yield of crystals was 73 mg. Further product was obtained as a white powder (240 mg, 76% yield in total) by precipitation from the CH_2Cl_2



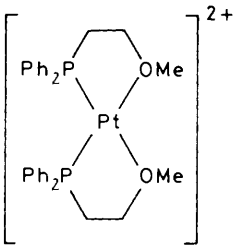
(4a)



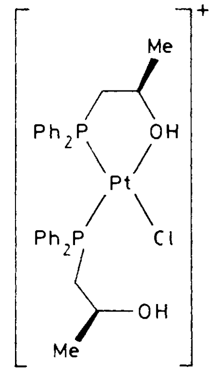
(5a)



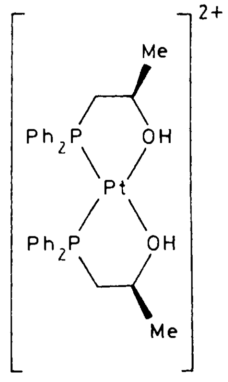
(4b)



(5b)



(4c)



(5c)

solution with diethyl ether (Found: C, 44.2; H, 4.3. Calc.: C, 44.5; H, 4.2%).

$[Pt(Ph_2PCH_2C_4H_7O)_2][ClO_4]_2$. A solution of $Ag[ClO_4]$ (230 mg, 1.1 mmol) in toluene–CH_2Cl_2 (4:1) (10 cm^3) was added to a solution of complex (**2**) (147 mg, 0.18 mmol) in toluene–CH_2Cl_2 (4:1) (70 cm^3). The mixture became cloudy and was stirred for 30 min. The solvent was then evaporated and the resulting residue extracted with CH_2Cl_2 (3 × 25 cm^3). The cloudy CH_2Cl_2 extract was filtered and the filtrate was evaporated to give a white solid which was then recrystallised from acetone–diethyl ether to give the desired product 130 mg (77%) (Found: C, 43.6; H, 4.15. Calc.: C, 43.7; H, 4.1%).

Crystal Structure of Complex (**4a**).—*Crystal data*. $C_{34}H_{38}ClF_6O_2P_3Pt$, $M = 915.5$, triclinic, space group $P\bar{1}$, $a = 9.616(4)$, $b = 11.317(5)$, $c = 16.978(10)$ Å, $\alpha = 92.00(4)$, $\beta = 100.76(3)$, $\gamma = 96.30(3)°$, $U = 1\,801(1)$ Å^3, $Z = 2$, $D_c = 1.61$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 43.59 cm^{-1}, $T = 293$ K.

Table 3. Atom co-ordinates (× 10^4)

Atom	*x*	*y*	*z*
Pt	969.6(2)	1 004.4(1)	2 892.4(1)
P(1)	936.4(13)	2 155.5(11)	1 845.0(7)
P(2)	51.3(14)	2 167.9(12)	3 689.2(8)
P(3)	−2 834.3(19)	8 062.7(15)	1 092.0(11)
F(1)	−1 667(8)	9 097(6)	1 444(7)
F(2)	−2 463(11)	7 512(11)	1 904(4)
F(3)	−4 070(8)	7 061(8)	880(6)
F(4)	−1 707(10)	7 406(8)	734(6)
F(5)	−3 323(10)	8 593(9)	253(5)
F(6)	−3 812(8)	8 877(9)	1 350(6)
F(11)	−3 249(33)	7 314(28)	380(17)
F(12)	−1 693(25)	8 968(22)	775(15)
F(13)	−1 769(35)	7 174(29)	1 489(19)
Cl	966.5(20)	−475.7(12)	3 818.7(9)
O(1)	1 940(4)	−133(3)	2 174(2)
O(2)	3 329(5)	3 064(5)	4 809(3)
C(1)	2 424(6)	3 299(4)	1 923(3)
C(2)	2 584(7)	3 989(6)	1 272(4)
C(3)	3 741(8)	4 857(6)	1 340(4)
C(4)	4 719(8)	5 014(7)	2 027(5)
C(5)	4 617(7)	4 309(7)	2 652(5)
C(6)	3 459(7)	3 464(5)	2 610(4)
C(7)	−687(6)	2 753(5)	1 422(3)
C(8)	−1 910(6)	1 961(6)	1 184(4)
C(9)	−3 188(8)	2 331(7)	845(4)
C(10)	−3 271(9)	3 503(9)	726(5)
C(11)	−2 082(11)	4 320(7)	955(5)
C(12)	−776(8)	3 945(6)	1 308(4)
C(13)	18(6)	3 742(4)	3 497(3)
C(14)	−1 206(7)	4 164(5)	3 142(5)
C(15)	−1 235(8)	5 385(6)	3 023(5)
C(16)	−24(7)	6 174(5)	3 268(4)
C(17)	1 206(8)	5 741(6)	3 607(5)
C(18)	1 233(7)	4 528(6)	3 729(4)
C(19)	−1.811(5)	1 635(5)	3 660(3)
C(20)	−2 578(6)	892(5)	3 032(4)
C(21)	−4 012(7)	544(7)	2 979(5)
C(22)	−4 689(7)	899(7)	3 559(5)
C(23)	−3 926(8)	1 618(10)	4 183(6)
C(24)	−2 478(8)	1 992(8)	4 247(5)
C(25)	904(6)	2 143(5)	4 751(3)
C(26)	2 499(6)	2 051(6)	4 983(4)
C(27)	4 236(12)	3 564(8)	5 518(6)
C(28)	4 402(11)	2 623(9)	6 085(5)
C(29)	2 945(9)	1 914(9)	5 867(5)
C(30)	1 180(6)	1 071(5)	1 073(3)
C(31)	2 292(6)	300(5)	1 431(3)
C(32)	2 371(10)	−809(7)	926(4)
C(33)	2 484(12)	−1 752(7)	1 489(6)
C(34)	1 833(8)	−1 424(5)	2 148(4)

Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 50° with scan range ±1.0° (2θ) around the $K_{\alpha 1} - K_{\alpha 2}$ 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 ($19 < 2\theta < 22°$). Reflections were processed using profile analysis to give 6 360 unique reflections; 5 730 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 0.34 and 0.19. Crystal dimensions were 0.11 × 0.06 × 0.04 mm. No systematic absences.

The Pt atoms were located from a Patterson synthesis and the

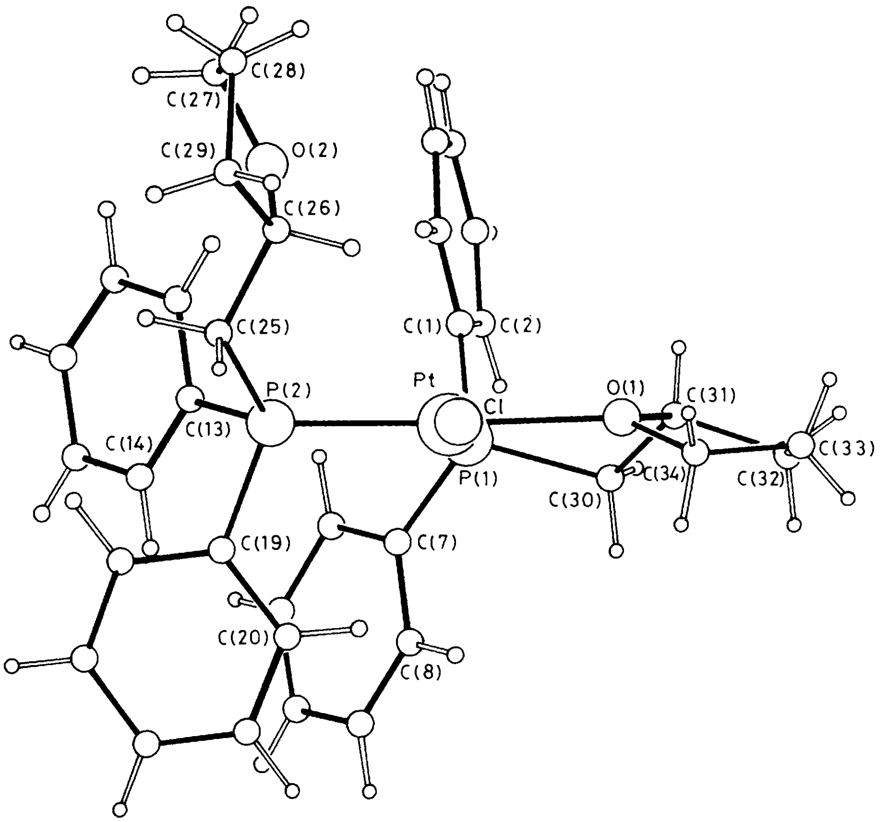


Figure. The cation of complex (**4a**), showing the atomic numbering

light atoms then found on successive Fourier syntheses. The $[PF_6]^-$ group appeared partly disordered, and was described by six full-occupancy F atoms (refined anisotropically, with high thermal parameters), and three additional 0.25 occupancy isotropic F atoms [F(11)—F(13)]. Anisotropic thermal parameters were used for all other non-H atoms. Hydrogen atoms were given fixed isotropic, $U = 0.07$ Å^2, and were inserted at calculated positions and not refined. Final refinement was by cascaded least-squares methods. The largest peaks on a final Fourier difference synthesis of height ± 2.0 e Å^3 were near Pt.

A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.0012$ was used and shown to be satisfactory by a weight analysis. The final R value was 0.039 ($R' = 0.039$). Computing was with the SHELXTL system[11] on a Data General DG30 computer. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 12. Final atomic co-ordinates are given in Table 3.

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

Acknowledgements

We should like to thank Mr. A. Berry for help in determining the crystal structure, Johnson-Matthey plc for a generous loan of platinum salts, and the S.E.R.C. for a grant to support this work.

References

1 J. A. Davies and F. R. Hartley, *Chem. Rev.*, 1981, **81**, 79 and refs. therein.
2 R. H. Crabtree, *Acc. Chem. Res.*, 1979, **12**, 331 and refs. therein.
3 N. W. Alcock, A. W. G. Platt, and P. G. Pringle, *J. Chem. Soc., Dalton Trans.*, 1987, 2273.
4 N. W. Alcock, A. W. G. Platt, and P. G. Pringle, *J. Chem. Soc., Dalton Trans.*, 1989, 139.
5 G. K. Anderson and R. Kumar, *Inorg. Chem.*, 1984, **23**, 4064.
6 G. K. Anderson, E. R. Corey, and R. Kumar, *Inorg. Chem.*, 1987, **26**, 97.
7 R. T. Boere and C. J. Willis, *Inorg. Chem.*, 1985, **24**, 1059.
8 E. Lindner, S. Meyer, P. Wegner, B. Karle, A. Sickinger, and B. Steger, *J. Organomet. Chem.*, 1987, **335**, 59 and refs. therein.
9 H. E. Bryndza, S. A. Kretchmor, and T. H. Tulip, *J. Am. Chem. Soc.*, 1986, **108**, 4805.
10 H. E. Bryndza, L. K. Fong, R. A. Paciello, W. Tam, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1987, **109**, 1444.
11 G. M. Sheldrick, SHELXTL User Manual, Nicolet Instrument Co., Madison, Wisconsin, 1983.
12 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

Received 6*th December* 1988; *Paper* 8/04811H