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Platinum(II) Complexes Containing 1-(Diphenylphosphino)-2-methoxyethane. 31P NMR and Catalytic Studies in the Presence of Tin(II) Chloride and the Crystal and Molecular Structure of [Pt(Ph2PCH2CH2OMe)(Ph2PCH2CH2OMe)Cl]ClO4

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The complexes $[PtCl_{2-n}(Ph_2PCH_2CH_2OMe)_2]^{n+}$ (n = 0, 1, 2) react with $SnCl_2 \cdot 2H_2O$ in acetone or chloroform solution to produce $[PtCl(Ph_2PCH_2CH_2OMe)_3]^+$ and series of tin-containing platinum(II) anions. The tin(II) chloride serves three functions: inserts into Pt–Cl bonds to form the trichlorostannate ligand, acts as a source of chloride ions, and maintains electroneutrality by forming hydroxy–tin cations. Such solutions catalyze the hydrogenation of styrene, the catalytic activity showing little dependence on the solvent employed. The crystal structure of chloro[1-(diphenylphosphino)-2-methoxyethane-*O,P*][1-(diphenylphosphino)-2-methoxyethane-*P*]platinum(II) perchlorate (n = 1) has been determined by X-ray crystallography. It crystallizes in the monoclinic space group $P2_1/c$ with 4 formula units/cell of dimensions a = 10.266 (3), b = 18.767 (7), and c = 16.581 (7) Å and β = 101.23 (3)°. Least-squares refinement of 370 parameters using 3032 reflections yielded R = 0.039. The structure consists of distorted square-planar $[Pt(Ph_2PCH_2CH_2OMe)(Ph_2PCH_2CH_2OMe)Cl]^+$ cations and perchlorate anions. One of the two identical phosphorus–oxygen ligands functions as a bidentate ligand and the second as a unidentate ligand coordinated through the phosphorus atom. The coordinated phosphorus atoms are cis to one another, and a chloro ligand trans to the phosphorus atom of the bidentate ligand completes the square-planar coordination about the Pt(II) center. The Pt–O bond distance of 2.192 (7) Å is the longest reported platinum–ethereal oxygen bond distance.

Introduction

Complexes of the late transition metals containing weak donor ligands, which may be displaced readily by a substrate molecule, are suitable catalyst precursors for olefin hydrogenation and hydroformylation reactions, and examples of the use of such species in homogeneous catalysis are well-known.[1] Metal–ether complexes fall into this category, and, indeed, there is interest in the coordination of phosphino–polyether ligands,[2] particularly those that resemble crown ethers. In the case of [Ni{Ph2P-(CH2CH2O)2CH2CH2PPh2}X2] the ligand can act as a bidentate or as a quadridentate ligand,[3] depending on the solvent employed, but in general, complexes of the platinum-group metals containing coordinated ether functions are rare. We have recently described[4] the preparation and some reactions of a series of platinum(II) complexes containing one diphenylphosphino and one weaker donor moiety, including the ligand 1-(diphenylphosphino)-2-methoxyethane. In the course of this work we prepared the complex [Pt(Ph2PCH2CH2OMe)(Ph2PCH2CH2OMe)Cl]ClO4, which contains one coordinated ether function, and here we report the crystal and molecular structure of this complex.

Solutions of platinum(II) chloride complexes, in the presence of tin(II) chloride, are known to catalyze olefin hydrogenation[5–8] and hydroformylation[7,9] reactions, and the use of mixed-ligand complexes [PtCl2LL′] results in a considerable increase in catalytic activity over the complexes [PtCl2L2].[6,7,10] NMR studies by Pregosin and co-workers[11–14] have indicated that halocarbon so-

lutions of [PtCl2(PR3)2] react with $SnCl_2 \cdot 2H_2O$ by insertion of $SnCl_2$ into one or both of the Pt–Cl bonds, depending on the nature of R and on the Pt:Sn ratio employed. When acetone is used as solvent, it has been shown[15] that the [PtCl2(PEt3)2]/SnCl2 system is complicated by equilibria involving SnCl2 elimination. We have previously shown[7,16] that the species observed in solution for the [PtCl2(L)(PR3)]/SnCl2 system are strongly dependent on the nature of L and on the solvent employed. In halocarbon solvents simple SnCl2 insertion occurs, but in acetone or acetonitrile extensive rearrangement takes place to yield a [PtCl(L)(PR3)2]+ cation and a series of tin-containing platinum(II) anions.

We decided that it would be of interest to study the reactions of platinum(II) complexes containing Ph2PCH2CH2OMe with tin(II) chloride to determine whether the presence of the ether function would affect the nature of the species formed. In this paper we report a 31P{1H} NMR investigation of the $[PtCl_{2-n}(Ph_2PCH_2CH_2OMe)_2]^{n+}/SnCl_2$ (n = 0, 1, 2) system and the results of the catalyzed hydrogenation of styrene as a function of solvent and the Pt:Sn ratio.

Results and Discussion

Description of the Structure. The structure consists of distorted square-planar chloro[1-(diphenylphosphino)-2-methoxyethane-*O,P*][1-(diphenylphosphino)-2-methoxyethane-*P*]platinum(II) cations and perchlorate anions. A perspective drawing of the structure is given in Figure 1. One of the two identical phosphorus–oxygen ligands functions as a bidentate ligand and the second as a unidentate ligand coordinated through the phosphorus atom. The coordinated phosphorus atoms are cis to one another, and a chloro ligand trans to the phosphorus atom of the bidentate ligand completes the square-planar coordination about the Pt(II) center. There is a slight tetrahedral distortion of the square-planar coordination about the platinum center: Cl(1) and P(1) are 0.06 Å above the best plane of the platinum atom and the four atoms

(1) See, for example: Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2134. Davies, J. A.; Hartley, F. R.; Murray, S. G. *Inorg. Chem.* **1980**, *19*, 2299. Sen, A.; Lai, T. W. *Organometallics* **1982**, *1*, 415.

(2) Thewissen, D. H. M. W.; Timmer, K.; Noltes, J. G.; Marsman, J. W.; Laine, R. M. *Inorg. Chim. Acta* **1985**, *97*, 143 and references therein.

(3) Hill, W. E.; Taylor, J. G.; McAuliffe, C. A.; Muir, K. W.; Manojlovic-Muir, L. *J. Chem. Soc., Dalton Trans.* **1982**, 833.

(4) Anderson, G. K.; Kumar, R. *Inorg. Chem.* **1984**, *23*, 4064.

(5) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973; see also references therein.

(6) Billard C.; Clark, H. C.; Wong, C. S. *J. Organomet. Chem.* **1980**, *190*, C105.

(7) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1983**, *22*, 427 and references therein.

(8) Clark, H. C.; Jain, V. K.; Rao, G. S. *J. Organomet. Chem.* **1985**, *279*, 181.

(9) Clark, H. C.; Davies, J. A. *J. Organomet. Chem.* **1981**, *213*, 503.

(10) Anderson, G. K.; Billard, C.; Clark, H. C.; Davies, J. A.; Wong, C. S. *Inorg. Chem.* **1983**, *22*, 439.

(11) Pregosin, P. S.; Sze, S. N. *Helv. Chim. Acta* **1978**, *61*, 1848.

(12) Ostoja Starzewski, K. A.; Pregosin, P. S.; Ruegger, H. *Inorg. Chim. Acta* **1979**, *36*, L445.

(13) Ostoja Starzewski, K. A.; Pregosin, P. S.; Ruegger, H. *Helv. Chim. Acta* **1982**, *65*, 785.

(14) Ostoja Starzewski, K. A.; Pregosin, P. S. *Adv. Chem. Ser.* **1982**, *n196*, 23.

(15) Koch, B. R.; Fazakerley, G. V.; Dijkstra, E. *Inorg. Chim. Acta* **1980**, *45*, L51.

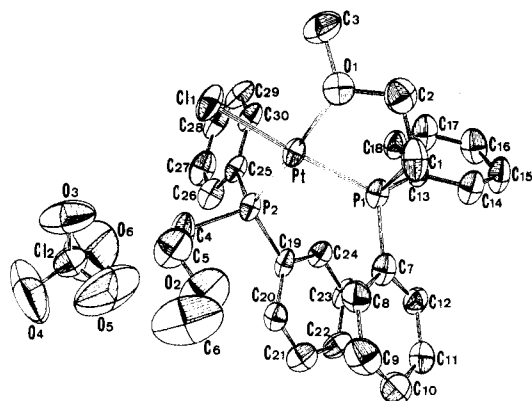(16) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1983**, *22*, 434.

Figure 1. Perspective drawing with atom labels. Atoms have been drawn with 50% probability ellipsoids.

Table I. Selected Bond Distances (Å) and Angles (deg) for Chloro[1-(diphenylphosphino)-2-methoxyethane-*O,P*][1-(diphenyl-phosphino)-2-methoxyethane-*P*]platinum(II) Perchlorate

Bond Distances			
Pt–Cl(1)	2.341 (3)	P(2)–C(25)	1.85 (1)
Pt–P(1)	2.241 (3)	O(1)–C(2)	1.44 (2)
Pt–P(2)	2.227 (3)	O(1)–C(3)	1.46 (2)
Pt–O(1)	2.192 (7)		
		O(2)–C(5)	1.32 (2)
P(1)–C(1)	1.86 (1)	O(2)–C(6)	1.47 (3)
P(1)–C(7)	1.81 (1)		
P(1)–C(13)	1.80 (1)	C(1)–C(2)	1.50 (2)
P(2)–C(4)	1.82 (1)		
P(2)–C(19)	1.80 (1)	C(4)–C(5)	1.52 (2)
Angles			
Cl(1)–Pt–P(1)	171.4 (1)	C(4)–P(2)–C(19)	107.4 (5)
Cl(1)–Pt–P(2)	88.5 (1)	C(4)–P(2)–C(25)	103.5 (6)
Cl(1)–Pt–O(1)	88.9 (2)	C(19)–P(2)–C(25)	102.1 (5)
P(1)–Pt–P(2)	99.6 (1)		
P(1)–Pt–O(1)	83.1 (2)	Pt–O(1)–C(2)	116.6 (6)
P(2)–Pt–O(1)	175.5 (3)	Pt–O(1)–C(3)	120.8 (7)
		C(2)–O(1)–C(3)	111.5 (9)
Pt–P(1)–C(1)	99.2 (4)		
Pt–P(1)–C(7)	119.3 (4)	C(5)–O(2)–C(6)	113.3 (15)
Pt–P(1)–C(13)	116.6 (4)		
C(1)–P(1)–C(7)	105.4 (6)	P(1)–C(1)–C(2)	109.1 (9)
C(1)–P(1)–C(13)	104.7 (6)	O(1)–C(2)–C(1)	109.3 (10)
C(7)–P(1)–C(13)	109.3 (5)		
		P(2)–C(4)–C(5)	117.1 (9)
Pt–P(2)–C(4)	114.6 (4)		
Pt–P(2)–C(19)	118.4 (4)	O(2)–C(5)–C(4)	113.4 (14)
Pt–P(2)–C(25)	109.1 (3)		

coordinated to it, while O(1) and P(2) are the same distance below the best plane. This structure is an unusual example of a mononuclear complex in which two identical ligands are coordinated in different modes.[17]

Selected bond distances and angles are given in Table I. The Pt–O bond length of 2.192 (7) Å is the longest platinum–ether bond length known. Only one other Pt–O distance in a platinum–ether complex has been reported, 2.144 (9) Å in [Pt((F₃-C)CHC(CF₃)=C(CH₃)CH₂OCH₃)(P(C₂H₅)₃)₂]PF₆.[18] The Pt–P distances trans to ethereal oxygen atoms are in close agreement: 2.219 (4) in the latter compound; 2.227 (3) Å in this compound.

The mean C–C bond distance and C–C–C angle for the four phenyl rings are 1.39 (2) Å (range 1.36–1.42 Å) and 120 (1)° (range 118–122°). The perchlorate counterion has a mean Cl–O distance and O–Cl–O angle of 1.36 (2) Å (range 1.30–1.40 Å) and 109 (1)° (range 104–118°).

(17) Other examples of such systems are the following. K[Pt(acac)₂Cl]: Mason, R.; Robertson, G. B.; Pauling, P. J. *J. Chem. Soc. A* **1969**, 485. [Ni(OPDA)₄]Cl₂·2OPDA (OPDA = *o*-phenylenediamine): Elder, R. C.; Koran, D.; Mark H. B. *Inorg. Chem.* **1974**, *13*, 1644.
(18) Clark, H. C.; McBride, S. S.; Payne, N. C.; Wong, C. S. *J. Organomet. Chem.* **1979**, *178*, 393.

Table II. ³¹P{¹H} NMR Data for Platinum(II) Complexes Containing Ph₂PCH₂CH₂OMe (PC₂O)

complex	δ(P)ᵃ	¹J(Pt,P), Hz	²J(P,P), Hz
cis-[PtCl₂(PC₂O)₂]	4.6	3650	
[Pt(PC₂O)(PC₂O)Cl]⁺	2.7 d	4165	15
	36.3 d	3630	
[Pt(PC₂O)₂]²⁺	19.4	4220	
trans-[PtCl(SnCl₃)(PC₂O)₂]	8.2 brᵇ	2270	
[PtCl(PC₂O)₃]⁺	14.4 d	2445	19
	5.0 t	3660	
trans-[PtClH(PC₂O)₂]ᶜ	18.9	2930	
trans-[PtCl(CH₂CH₂Ph)(PC₂O)₂]ᶜ	11.6	2740	

ᵃ Chemical shifts are relative to external H₃PO₄, positive shifts representing deshielding. ᵇ ²J(P,Sn) not observed. ᶜ Recorded in ethanol.

NMR Studies. It has been shown by Pregosin[11–14] that complexes of the type *cis*-[PtCl₂(PR₃)₂] react with tin(II) chloride in halocarbon solvents to produce *cis*- and *trans*-[PtCl(SnCl₃)-(PR₃)₂], when PR₃ is a triarylphosphine. We have previously shown[16] that *cis*-[PtCl₂(CO)(PPh₃)] reacts with SnCl₂·2H₂O in halocarbon solvents by simple insertion of SnCl₂ into one of the platinum–chlorine bonds (eq 1), but in more polar solvents an
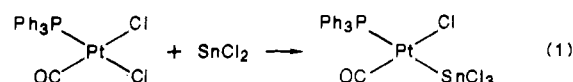
extensive ligand rearrangement takes place to yield a series of ionic species.[7] We have now carried out a ³¹P{¹H} NMR study of the reactions of [PtCl₂₋ₙ(Ph₂PCH₂CH₂OMe)₂]ⁿ⁺ (n = 0, 1, 2) with tin(II) chloride in both chloroform and acetone in order to determine whether the presence of the ether moiety would result in solution behavior different from that observed for *cis*-[PtCl₂-(PR₃)₂].

For the purpose of comparison, we treated a chloroform solution of *cis*-[PtCl₂{P(C₆H₄Me-*p*)₃}₂] (δ(P) 12.6, ¹J(Pt,P) = 3695 Hz) with excess SnCl₂·2H₂O. A yellow solution formed whose ³¹P{¹H} NMR spectrum indicated the presence of *cis*-[PtCl(SnCl₃)}{P-(C₆H₄Me-*p*)₃}₂] (δ(P) 26.3 d, ¹J(Pt,P) = 3060 Hz, ²J(P,P) = 14 Hz; δ(P) 9.1 d, ¹J(Pt,P) = 3655 Hz) and *trans*-[PtCl(SnCl₃){P-(C₆H₄Me-*p*)₃}₂] (δ(P) 17.7, ¹J(Pt,P) = 2300 Hz). The NMR parameters for the cis complex agree well with those reported by Pregosin,[11] and although the trans isomer was not mentioned previously, the observed value of ¹J(Pt,P) in *trans*-[PtCl-(SnCl₃){P(C₆H₄Me-*p*)₃}₂] is similar to those for the analogous complexes containing P(C₆H₄OMe-*p*)₃ or P(C₆H₄Cl-*p*)₃.[11]

When a CDCl₃ solution of *cis*-[PtCl₂(Ph₂PCH₂CH₂OMe)₂] is treated with excess tin(II) chloride and immediately examined spectroscopically, only one phosphorus-containing species is detected. This is identified as *trans*-[PtCl(SnCl₃)-(Ph₂PCH₂CH₂OMe)₂] by comparison of its one-bond platinum–phosphorus coupling constant (Table II) with those of *trans*-[PtCl(SnCl₃){P(C₆H₄Me-*p*)₃}₂] and related complexes. After the solution is allowed to stand, however, the slightly broadened resonances due to this complex diminish in intensity and are replaced by a sharp doublet at δ(P) 14.4 and a triplet at δ(P) 5.0 (each with ¹⁹⁵Pt satellites), due to the [PtCl-(Ph₂PCH₂CH₂OMe)₃]⁺ cation (Table II). After the solution is allowed to stand for 24 h, the conversion is essentially complete. A similar reaction in acetone results in immediate, quantitative conversion to [PtCl(Ph₂PCH₂CH₂OMe)₃]⁺ as the sole phosphorus-containing species in solution.

The observation of [PtCl(Ph₂PCH₂CH₂OMe)₃]⁺ only in the ³¹P{¹H} NMR spectrum allows us to account for only two-thirds of the platinum in the system. In addition, the existence of anionic species in the solution is necessary to maintain electroneutrality. We have not investigated this further in the course of this work, but we have previously shown[7] that treatment with tin(II) chloride of acetone solutions of *cis*-[PtCl₂(CO)(PPh₃)] results in formation of *trans*-[PtCl(CO)(PPh₃)₂]⁺ and a complex array of tin-containing platinum(II) anions. A similar set of anions is likely to

be formed in the present instance also.

The generation of tris(tertiary phosphine)platinum(II) cations on treatment of cis-[PtCl₂(PR₃)₂] with tin(II) chloride is not unknown.[19] In this instance, conversion to [PtCl-(Ph₂PCH₂CH₂OMe)₃]⁺ occurs very readily, especially in acetone solution. It may be that the presence of the ether as a potential coordinating site facilitates this rearrangement, perhaps by displacement of the labile trichlorostannate ligand.[20]

When acetone or chloroform solutions containing [PtCl-(Ph₂PCH₂CH₂OMe)₃]⁺ (obtained by reacting cis-[PtCl₂-(Ph₂PCH₂CH₂OMe)₂] with SnCl₂·2H₂O) are treated with Et₄N⁺Cl⁻, rapid and quantitative conversion to cis-[PtCl₂-(Ph₂PCH₂CH₂OMe)₂] takes place. Since no free ligand is detected, a phosphine migration process must again be involved (eq 2), the entire catalytic system being unstable in the presence of

$$2[\text{PtClL}_3]^+ + \text{"Pt-Sn anion"} \xrightarrow{\text{Cl}^-} 3cis\text{-}[\text{PtCl}_2\text{L}_2] \quad (2)$$
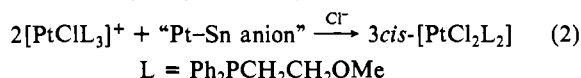
$$\text{L} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{OMe}$$

chloride ions. Indeed, such a system shows no activity toward hydrogenation of styrene.

Addition of excess tin(II) chloride to acetone or chloroform solutions of [Pt(Ph₂PCH₂CH₂OMe)(Ph₂PCH₂CH₂OMe)Cl]-ClO₄ also results in formation of [PtCl(Ph₂PCH₂CH₂OMe)₃]⁺ as the only phosphorus-containing species. In this case the previously observed intermediate, trans-[PtCl(SnCl₃)-(Ph₂PCH₂CH₂OMe)₂], is not detected. Addition of excess tetraethylammonium chloride again causes rapid conversion to cis-[PtCl₂(Ph₂PCH₂CH₂OMe)₂].

The complexes [Pt(Ph₂PCH₂CH₂OMe)₂][X]₂ (X⁻ = ClO₄⁻, BF₄⁻) also react with tin(II) chloride in both chloroform and acetone solutions to produce the [PtCl(Ph₂PCH₂CH₂OMe)₃]⁺ cation. The formation of a chloride-containing product in this case, where the platinum precursor does not contain chloride, indicates that one function of SnCl₂·2H₂O is to act as a source of chloride, as we have suggested previously.[7]

The above reaction chemistry was carried out under ambient conditions and indicates the species present in solution prior to the catalytic reactions. We have also recorded the spectrum of a chloroform solution of cis-[PtCl₂(Ph₂PCH₂CH₂OMe)₂] to which excess SnCl₂·2H₂O had been added, after a typical styrene hydrogenation reaction (vide infra). The spectrum showed the presence of two phosphorus-containing species in solution (δ(P) 16.7, ^1J(Pt,P) = 2915 Hz; δ(P) 9.7, ^1J(Pt,P) = 2760 Hz). The first has been identified as trans-[PtClH(Ph₂PCH₂CH₂OMe)₂], by comparison with an authentic sample prepared by the hydrazine hydrate reduction of cis-[PtCl₂(Ph₂PCH₂CH₂OMe)₂].[21] When an ethanol solution of trans-[PtClH(Ph₂PCH₂CH₂OMe)₂] was treated with styrene, partial reaction occurred over several days to produce the second species,[22] and we suggest this complex is trans-[PtCl(CH₂CH₂Ph)(Ph₂PCH₂CH₂OMe)₂],[23] formed by insertion of styrene into the Pt–H bond.

Catalytic Reactions. We have shown previously[16] that the species formed when cis-[PtCl₂(L)(PR₃)] is reacted with tin(II) chloride are strongly dependent on the solvent employed, and the catalytic activity toward olefin hydrogenation exhibited by these systems is much greater in acetone than in halocarbon solvents.[10] For the complexes containing Ph₂PCH₂CH₂OMe described above, the same phosphorus-containing species, [PtCl-(Ph₂PCH₂CH₂OMe)₃]⁺, is formed in both acetone and chloroform on treatment with SnCl₂·2H₂O, and we decided to investigate whether this is reflected in the catalytic activity of these systems toward the hydrogenation of styrene. The results of these studies are shown in Table III.

(19) Albinati, A.; Pregosin, P. S.; Ruegger, H. *Inorg. Chem.* **1984**, *23*, 3223.
(20) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Organometallics* **1982**, *1*, 64.
(21) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1962**, 5075.
(22) A minor, unidentified species with spectroscopic parameters δ(P) 14.8 and ^1J(Pt,P) = 3620 Hz was also observed.
(23) ^1J(Pt,P) values lie in the range 2700–3200 Hz for complexes of the type trans-[PtClRL₂], depending on the nature of R and L.

Table III. Effects of Complex, Solvent, and Pt:Sn Ratio on the Catalytic Hydrogenation of Styrene to Ethylbenzene[a]

complex[b]	solvent	Pt:Sn ratio	turnover no.[c]
[PtCl₂(PC₂O)₂]	acetone	1:1	56
		1:2	320
		1:5	58
	chloroform	1:1	510
		1:2	200
		1:5	95
		1:20	110
[Pt(PC₂O)(PC₂O)Cl]ClO₄	acetone	1:1	52
		1:2	320
		1:5	110
	chloroform	1:1	220
		1:2	200
		1:5	64
[Pt(PC₂O)₂][ClO₄]₂	acetone	1:1	96
		1:2	160
		1:10	100
	chloroform	1:1	230
		1:2	240
		1:10	310

[a] Catalytic reactions were performed at 60 °C under 600 psi H₂ for 2 h, with a Pt:styrene ratio of 1:3000. [b] PC₂O = Ph₂PCH₂CH₂OMe. [c] Moles of styrene converted to ethylbenzene per mole of platinum per hour.

Table IV. Crystal Data and Summary of Data Collection and Refinement for Chloro[1-(diphenylphosphino)-2-methoxyethane-O,P][1-(diphenyl-phosphino)-2-methoxyethane-P]platinum(II) Perchlorate

formula	PtC₃₀H₃₄Cl₂O₆P₂
fw	818.54
space group	$P2_1/c$
a, Å	10.266 (3)
b, Å	18.767 (7)
c, Å	16.581 (7)
β, deg	101.23 (7)
V, Å³	3133 (3)
Z	4
$F(000)$	1616
d(calcd), g cm⁻³	1.735
d(obsd), g cm⁻³	1.72 (2)
μ(calcd), cm⁻¹	50.2
cryst dimens, mm	0.08 × 0.09 × 0.11
radiation	Mo Kα (λ = 0.710 69 Å)
max 2θ, deg; scan type	46; θ–2θ
scan speed, deg min⁻¹	2
2θ scan range, deg	2θ(Mo Kα₁) – 1.0 to 2θ(Mo Kα₂) + 1.0
no. of reflens scanned	4830
no. of data with $F_o^2 > 3\sigma$	3032
no. of params refined	370
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.039
$R_w = [\sum w\|F_o\| - \|F_c\|^2/\sum w\|F_o\|^2]^{1/2}$	0.046

A consideration of these results reveals a number of features. First of all, the turnover numbers are lower than those found for cis-[PtCl₂(L)(PR₃)]/SnCl₂ (L = CO, thioether, amine) systems[6,10] and are more reminiscent of those found with the symmetrical complexes cis-[PtCl₂L₂] and cis-[PtCl₂(PR₃)₂]. They are higher than those reported recently[8] for [Pt₂(μ-SEt)₂Cl₂(PEt₃)₂]/SnCl₂ systems.

Maximum catalytic activity is reached at Pt:Sn ratios of 1:10 for the cis-[PtCl₂(PR₃)₂]/SnCl₂ systems,[24] whereas the unsymmetrical complexes cis-[PtCl₂(L)(PR₃)] exhibit most effective catalysis of olefin hydrogenation at Pt:Sn ratios of 1:2.[6,10] In the present instance, all three complexes show maximum activity at a Pt:Sn ratio of 1:2 when acetone is used as solvent. No such clear dependence on Pt:Sn ratio is observed when the reactions are carried out in chloroform. Overall, there is no significant difference

(24) Tayim, H. A.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 3420.

Table V. Positional Parameters for Non-Hydrogen Atoms of Chloro[1-(diphenylphosphino)-2-methoxyethane-*O,P*][1-(diphenylphosphino)-2-methoxyethane-*P*]platinum(II) Perchlorate[a]

	x	y	z
Pt	0.02107 (5)	0.03758 (2)	0.18176 (2)
Cl(1)	0.0319 (4)	0.1523 (2)	0.1279 (2)
Cl(2)	0.4593 (4)	0.2912 (2)	0.4636 (2)
P(1)	0.0009 (3)	−0.0774 (2)	0.2137 (2)
P(2)	0.1511 (3)	0.0749 (2)	0.2975 (2)
O(1)	−0.1178 (8)	0.0077 (4)	0.0690 (4)
O(2)	0.4176 (13)	0.0426 (7)	0.2242 (7)
O(3)	0.3747 (13)	0.3096 (9)	0.3927 (8)
O(4)	0.5779 (17)	0.3190 (12)	0.4775 (11)
O(5)	0.4783 (23)	0.2197 (9)	0.4583 (13)
O(6)	0.3924 (21)	0.2981 (12)	0.5294 (11)
C(1)	−0.0653 (13)	−0.1130 (7)	0.1094 (7)
C(2)	−0.1699 (13)	−0.0636 (7)	0.0655 (8)
C(3)	−0.2170 (16)	0.0584 (8)	0.0275 (9)
C(4)	0.2930 (13)	0.1279 (6)	0.2827 (7)
C(5)	0.3614 (16)	0.1059 (9)	0.2134 (10)
C(6)	0.5038 (22)	0.0269 (13)	0.1652 (11)
C(7)	0.1491 (11)	−0.1292 (6)	0.2523 (6)
C(8)	0.2547 (11)	−0.1239 (7)	0.2111 (7)
C(9)	0.3648 (13)	−0.1649 (8)	0.2352 (9)
C(10)	0.3752 (12)	−0.2118 (7)	0.3012 (8)
C(11)	0.2673 (13)	−0.2172 (6)	0.3420 (8)
C(12)	0.1571 (11)	−0.1762 (6)	0.3178 (7)
C(13)	−0.1245 (10)	−0.0986 (5)	0.2723 (6)
C(14)	−0.1610 (12)	−0.1685 (6)	0.2799 (8)
C(15)	−0.2548 (13)	−0.1873 (7)	0.3277 (9)
C(16)	−0.3187 (12)	−0.1319 (7)	0.3633 (8)
C(17)	−0.2827 (13)	−0.0630 (7)	0.3537 (9)
C(18)	−0.1871 (11)	−0.0449 (6)	0.3080 (7)
C(19)	0.2108 (11)	0.0101 (5)	0.3765 (6)
C(20)	0.3409 (11)	−0.0166 (6)	0.3903 (7)
C(21)	0.3841 (12)	−0.0655 (7)	0.4520 (7)
C(22)	0.2979 (12)	−0.0908 (6)	0.5016 (7)
C(23)	0.1690 (12)	−0.0640 (6)	0.4875 (6)
C(24)	0.1262 (11)	−0.0149 (5)	0.4262 (7)
C(25)	0.0562 (11)	0.1364 (5)	0.3510 (6)
C(26)	0.1210 (13)	0.1662 (6)	0.4257 (7)
C(27)	0.0507 (15)	0.2122 (6)	0.4676 (8)
C(28)	−0.0792 (16)	0.2267 (6)	0.4368 (9)
C(29)	−0.1445 (13)	0.1988 (7)	0.3629 (8)
C(30)	−0.0769 (12)	0.1535 (6)	0.3193 (7)

[a] Estimated standard deviations are given in parentheses for the least significant digit(s).

in catalytic activity, however, on changing the solvent from acetone to chloroform, and this is consistent with there being only minor changes in the concentrations of the various species present in solution in each case.

Experimental Section

The $^{31}P\{^1H\}$ NMR spectra were recorded at 40.2 MHz on a JEOL FX-100 spectrometer operating in the Fourier transform mode and were obtained for CDCl$_3$ solutions unless otherwise stated.

Styrene, containing 4-*tert*-butylcatechol as inhibitor, was obtained from Aldrich, and SnCl$_2$·2H$_2$O was purchased from Fisher. The complexes cis-[PtCl$_2$(Ph$_2$PCH$_2$CH$_2$OMe)$_2$], [Pt(Ph$_2$PCH$_2$CH$_2$OMe)-(Ph$_2$PCH$_2$CH$_2$OMe)Cl]ClO$_4$, and [Pt(Ph$_2$PCH$_2$CH$_2$OMe)$_2$][ClO$_4$]$_2$ were prepared as described previously.[4] trans-[PtClH-(Ph$_2$PCH$_2$CH$_2$OMe)$_2$] was prepared by the method of Chatt and Shaw[21]

and was examined spectroscopically and reacted in situ.

High-pressure reactions were carried out in an autoclave constructed in this department by Ted Windsor, using a design similar to that provided by Dr. C. D. Schmulbach, Southern Illinois University—Carbondale.

In a typical hydrogenation experiment, the platinum complex (ca. 10 mg) and SnCl$_2$·2H$_2$O were dissolved in the solvent (5 mL) in a 50-mL glass autoclave liner containing a Teflon-coated magnetic stir bar, and styrene (4.5 mL, 3000 molar equiv) was introduced. The reaction vessel was transferred to the autoclave, and the system was then flushed with hydrogen and pressurized to 600 psi with hydrogen. It was heated thermostatically to 60 °C, and the solution was stirred for 2 h. After this time, the autoclave was cooled to ambient temperature and depressurized, and the solution was removed for analysis.

Gas chromatographic analyses were performed by using a Varian Aerograph Series 1200 chromatograph, equipped with a 6 ft × 0.125 in. 10% SP-2100 on Supelcoport (80/100 mesh) column (available from Supelco, Inc.), and comparison was made with known standards.

Structure Determination

X-ray Structure Analysis of Chloro[1-(diphenylphosphino)-2-methoxyethane-*O,P*][1-(diphenylphosphino)-2-methoxyethane-*P*]platinum(II) Perchlorate. Single crystals obtained by addition of ether to a dichloromethane solution of the compound were mounted on a glass fiber for data collection on a Nicolet P3 diffractometer. Table IV gives the crystal data and a summary of the data collection and refinement.[25] The intensities of three reflections were monitored and revealed a 5% reduction during the data collection; a decay correction was applied to the data. The data were not corrected for absorption. Standard deviations were assigned to the intensities according to the formula $\sigma(I) = [\sigma_{counter}I^2 + (0.03I)^2]^{1/2}$, where $\sigma_{counter} = (I + K^2B)^{1/2}$, I is the net intensity, K is the ratio of scan time to background time, and B is the total background counts. The platinum atom was located from a Patterson map; successive Fourier syntheses revealed the locations of the non-hydrogen atoms. Least-squares refinement was completed with anisotropic thermal parameters assigned to all atoms. Hydrogen atoms bonded to the carbon atoms of the phenyl rings and the methylene carbons were included at calculated positions with C–H distances of 0.95 Å. Scattering factors for the neutral atoms were used; those for platinum were corrected for anomalous dispersion.[26] The largest parameter shift in the final cycle of least-squares refinement was less than 10% of its standard deviation. The error of fit was 1.4, and the maximum electron density of 1.6 e/Å³ in the final difference map was near the Pt atom position. Positional parameters of the non-hydrogen atoms are given in Table V.

Supplementary Material Available: Tables of anisotropic thermal parameters, positional and thermal parameters for hydrogen atoms, and all bond distances and angles (4 pages); observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

(25) Computer programs used for data reduction and in solution and refinement of the structure: SYNCOR, W. Schmonsees' data reduction program; FORDAP; A. Zalkin's Fourier program; ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares and function and error programs; ORTEP, C. K. Johnson's plotting program; HFINDR, A. Zalkin's hydrogen atom finding program.

(26) Ibers, J. A.; Hamilton, W. C., Eds.; *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.