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**The isolation and molecular structure  
of *trans*-[PtCl(COCH<sub>2</sub>CH<sub>2</sub>Ph)(PPh<sub>3</sub>)<sub>2</sub>] · EtOH,  
an intermediate in the hydroformylation of styrene promoted  
by the *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]/SnCl<sub>2</sub> catalytic system**

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**Abstract**

The complex *trans*-[PtCl(COCH<sub>2</sub>CH<sub>2</sub>Ph)(PPh<sub>3</sub>)<sub>2</sub>] · EtOH (**1**) has been synthesized by treating *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] with styrene in EtOH at 100 °C under 50 atm of carbon monoxide and of hydrogen. In combination with SnCl<sub>2</sub> · 2H<sub>2</sub>O, complex **1** is an intermediate in the catalytic hydroformylation of styrene.

The crystal structure of **1** has been determined by X-ray crystallography. The crystals are monoclinic, space group *P*2<sub>1</sub>/*c*, with *a* 10.95(1), *b* 33.16(1), *c* 12.43(1) Å and β 109.59(3)°. The final *R* factor was 0.087 for 4772 observed reflexions. The platinum atom is in a slightly distorted square-planar environment. Selected bond distances are: Pt–P (mean) 2.31 Å, Pt–Cl 2.427(6) Å.

**Introduction**

Platinum/tin systems have attracted much attention as active and regioselective catalysts in the homogeneous olefin hydroformylation [1]. Recently, *trans*-[PtCl(COR)(PPh<sub>3</sub>)<sub>2</sub>] (R = *n*-Pr and *n*-Hex) complexes have been isolated from the reaction mixtures involving hydroformylation of propene or 1-hexene with a catalyst precursor based on the system *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]/SnCl<sub>2</sub> in an alkanol as solvent [2,3].

We report here the synthesis, reactions, and molecular structure of *trans*-[PtCl(COCH<sub>2</sub>CH<sub>2</sub>Ph)(PPh<sub>3</sub>)<sub>2</sub>] · EtOH, which was isolated during the hydroformylation of styrene as described below.

## Experimental

### Materials

Carbon monoxide and hydrogen were purchased from the S.I.O. Company. Alcohol was commercial grade. Styrene was distilled before use. The *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] was prepared from [H<sub>2</sub>PtCl<sub>6</sub>] · 6H<sub>2</sub>O and PPh<sub>3</sub> as described in the literature [4].

### General procedure

Carbonylations were carried out in a stirred stainless steel autoclave of about 75 ml capacity, which was placed in a thermostatted oil bath. The catalyst and reagents were contained in a Pyrex glass bottle placed inside the autoclave in order to avoid contamination from other metallic species and effects arising from the metal surface of the autoclave.

### Synthesis of *trans*-[PtCl(COCH<sub>2</sub>CH<sub>2</sub>Ph)(PPh<sub>3</sub>)<sub>2</sub>] · EtOH

A mixture of 113 mg of *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.14 mmol), 10 mmol of styrene and 10 ml of EtOH were introduced into the bottle which was placed in the autoclave. The autoclave was purged with carbon monoxide, pressurized with 50 atm of CO and 50 atm of H<sub>2</sub> at room temperature, and placed in a thermostatted oil bath, and its temperature was raised to 100 °C in ca. 10 min. After 5 h, the autoclave was cooled in an ice bath, then after ca. 1 day at room temperature it was depressurized. White crystals of **1** were filtered off, washed with EtOH, and dried under vacuum. Yield 60%. Found: C, 60.10; H, 4.91; Cl, 4.02. C<sub>47</sub>H<sub>45</sub>ClO<sub>2</sub>P<sub>2</sub>Pt calcd.: C, 60.42; H, 4.86; Cl, 3.80%.

### Hydroformylation of styrene

In a typical experiment, 0.1 mmol of *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], 0.5 mmol of SnCl<sub>2</sub> · 2H<sub>2</sub>O, 10 mmol of styrene, and 9 ml of methyl ethyl ketone were introduced into the bottle which was then placed in the autoclave. After purging with CO, the autoclave was pressurized at room temperature with hydrogen (50 atm) and carbon monoxide (50 atm). It was then kept at 70 °C for 4 h with stirring. After slow depressurization at room temperature the mixture was analyzed by GLC after the usual work up. The linear/branched isomer ratio was 35/65.

The same ratio was found when complex **1** was used in place of *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>].

### X-ray data

A small crystal with a maximum dimension 0.2 mm was used. Unit-cell parameters were determined by a least squares fit of the angular parameters of 25 medium angle reflexions.

Crystal data are: C<sub>45</sub>H<sub>39</sub>ClO<sub>2</sub>Pt + C<sub>2</sub>H<sub>5</sub>OH, *M* = 933.8, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* 10.95(1); *b* 33.16(1); *c* 12.43(1) Å, β 109.59(3)°, *V* 4254 Å<sup>3</sup>, *D*<sub>c</sub> 1.46 g cm<sup>-3</sup> for *Z* = 4, Mo-*K*<sub>α</sub> radiation, λ 0.7107 Å, μ(Mo-*K*<sub>α</sub>) 39 cm<sup>-1</sup>; neutral

Table 1

Atom coordinates ( $\times 10^4$ )

Atom	x	y	z	Atom	x	y	z
Pt	7877(1)	6027(1)	-1191(1)	C(1)	9183(11)	6323(5)	1678(11)
P(1)	9265(4)	6408(2)	265(4)	C(2)	7995(11)	6203(5)	1758(11)
P(2)	6724(4)	5627(2)	-2715(4)	C(3)	7853(11)	6161(5)	2826(11)
Cl(1)	8322(5)	5427(2)	-3(4)	C(4)	8899(11)	6239(5)	3736(11)
O(1)	7787(13)	6699(4)	-2698(11)	C(5)	10087(11)	6359(5)	3736(11)
O(2)	255(19)	1352(9)	8395(16)	C(6)	10228(11)	6401(4)	2667(11)
C(37)	7346(19)	6497(7)	-1997(19)	C(7)	9041(13)	6953(4)	131(10)
C(38)	6031(20)	6709(7)	-1986(19)	C(8)	8480(13)	7159(4)	826(10)
C(39)	5627(27)	7096(10)	-2647(29)	C(9)	8262(13)	7574(4)	689(10)
C(40)	4376(22)	7241(9)	-2459(25)	C(10)	8604(13)	7782(4)	-143(10)
C(41)	4444(22)	7506(9)	-1569(25)	C(11)	9165(13)	7576(4)	-838(10)
C(42)	3310(22)	7635(9)	-1398(25)	C(12)	9383(13)	7161(4)	-701(10)
C(43)	2109(22)	7498(9)	-2117(25)	C(13)	10958(15)	6307(3)	436(14)
C(44)	2041(22)	7233(9)	-3007(25)	C(14)	11869(15)	6615(3)	578(14)
C(45)	3175(22)	7104(9)	-3178(25)	C(15)	13154(15)	6520(3)	717(14)
C(46)	-640(32)	1101(12)	7605(27)	C(16)	13528(15)	6118(3)	713(14)
C(47)	-1528(44)	939(17)	8048(37)	C(17)	12617(15)	5811(3)	571(14)
				C(18)	11332(15)	5905(3)	432(14)
				C(19)	7760(10)	5302(4)	-3244(8)
				C(20)	7453(10)	5230(4)	-4411(8)
				C(21)	8208(10)	4965(4)	-4796(8)
				C(22)	9269(10)	4773(4)	-4013(8)
				C(23)	9576(10)	4845(4)	-2847(8)
				C(24)	8821(10)	5109(4)	-2462(8)
				C(25)	5693(9)	5871(4)	-4006(11)
				C(26)	6236(9)	6140(4)	-4581(11)
				C(27)	5456(9)	6324(4)	-5586(11)
				C(28)	4133(9)	6239(4)	-6017(11)
				C(29)	3590(9)	5969(4)	-5442(11)
				C(30)	4370(9)	5786(4)	-4437(11)
				C(31)	5630(11)	5281(4)	-2352(10)
				C(32)	5593(11)	4893(4)	-2809(10)
				C(33)	4504(11)	4644(4)	-2548(10)
				C(34)	3852(11)	4783(4)	-1830(10)
				C(35)	4089(11)	5171(4)	-1373(10)
				C(36)	4978(11)	5420(4)	-1634(10)

atomic scattering factors for Pt and H were taken from ref. 5, those for C, O, P, and Cl were from the SHELX program [6]. The effects of anomalous dispersion for Pt were taken into account.

A unique data set up to  $\theta$  25° was obtained on a Philips four-circle diffractometer by the conventional  $\theta/2\theta$  scan, yielding 7345 reflexions of which 4772 with  $I > 3\sigma(I)$  were used in subsequent calculations. The intensities were corrected for Lp and absorption [7]. The structure was solved by Patterson and Fourier techniques, with full-matrix least squares refinement. The phenyl rings were refined as rigid bodies (C-C 1.395 Å; C-H 1.08 Å;  $U_{\text{iso}}$  0.06 Å<sup>2</sup> for H). At convergence the conventional  $R$  value was 0.087. Calculations were performed mainly with the SHELX program. A final Fourier difference map showed no significant feature apart from some residuals peaks (max. 3.8 eÅ<sup>-3</sup>, min -4.6 eÅ<sup>-3</sup>) near the heavy

Table 2

## Bond lengths and angles

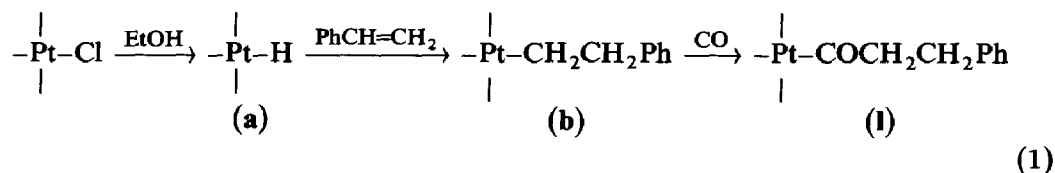
<i>Bond lengths and contact distances (Å)</i>			
Cl–Pt	2.427(6)	P(1)–C(1)	1.81(1)
C(37)–Pt	1.84(2)	P(1)–C(7)	1.82(1)
P(1)–Pt	2.309(5)	P(1)–C(13)	1.82(1)
P(2)–Pt	2.311(5)	P(2)–C(19)	1.84(1)
C(37)–O(1)	1.31(2)	P(2)–C(25)	1.82(1)
C(37)–C(38)	1.61(3)	P(2)–C(31)	1.82(1)
C(38)–C(39)	1.51(3)	O(2)–C(46)	1.40(2)
C(39)–C(40)	1.54(3)	C(46)–C(47)	1.52(3)
O(1)–O(2')	2.81(2)		
<i>Bond angles (deg.)</i>			
Cl–Pt–C(37)	171.3(6)	Pt–P(1)–C(1)	116.5(5)
P(1)–Pt–P(2)	172.5(2)	Pt–P(1)–C(7)	115.9(5)
Cl–Pt–P(1)	91.5(2)	Pt–P(1)–C(13)	111.6(5)
Cl–Pt–P(2)	88.3(2)	Pt–P(2)–C(19)	113.4(4)
C(37)–Pt–P(1)	88.2(6)	Pt–P(2)–C(25)	118.4(5)
C(37)–Pt–P(2)	93.1(6)	Pt–P(2)–C(31)	112.5(4)
Pt–C(37)–O(1)	132.0(2)	C(1)–P(1)–C(7)	101.2(6)
Pt–C(37)–C(38)	119.0(2)	C(1)–P(1)–C(13)	103.7(7)
O(1)–C(37)–C(38)	108.0(2)	C(7)–P(1)–C(13)	107.0(6)
C(37)–C(38)–C(39)	118.0(2)	C(19)–P(2)–C(25)	102.7(5)
C(38)–C(39)–C(40)	107.0(2)	C(19)–P(2)–C(3)	104.8(6)
C(47)–C(46)–O(2)	112.0(2)	C(25)–P(2)–C(31)	103.6(6)

atom, due to series termination effects.

Atomic parameters are listed in Table 1 and bond distances and angles in Table 2. A table of thermal parameters and lists of observed and calculated structure factors are available from the authors.

## Discussion

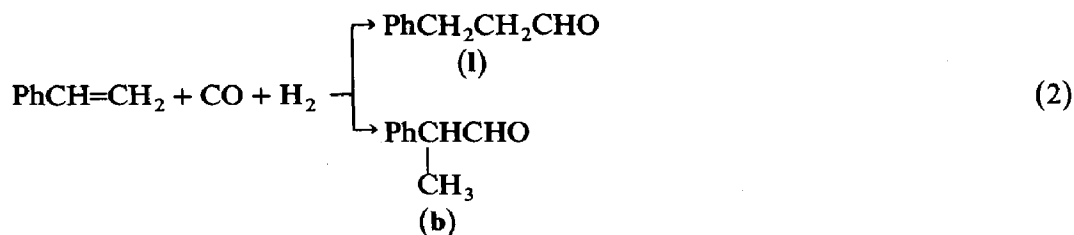
It is likely that complex **1** is formed by insertion of styrene into a Pt–H bond followed by carbon monoxide insertion into a Pt–C bond of the resulting alkylplatinum intermediate (**b**), as shown in eq. 1.



The ability of alcohols to act as hydride source is well known [8] \*.

\* Complex **1** forms even in the absence of molecular hydrogen.

Complex I is probably one of the intermediates in the catalytic hydroformylation of styrene, which occurs only in the presence of  $\text{SnCl}_2$ . The role of  $\text{SnCl}_2$  has been previously established [2,9–11].



Complex I has virtually the same catalytic activity as its precursor, *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ .

As shown in Figs. 1 and 2, the structure consists of discrete molecules with no intermolecular as less than Van der Waals distances. The Pt atom is located in a slightly distorted *trans* square-planar environment. The  $\text{PtP}_2\text{ClC}$  moiety is almost planar, the largest deviation from the relevant least squares plane being 0.15 Å. The

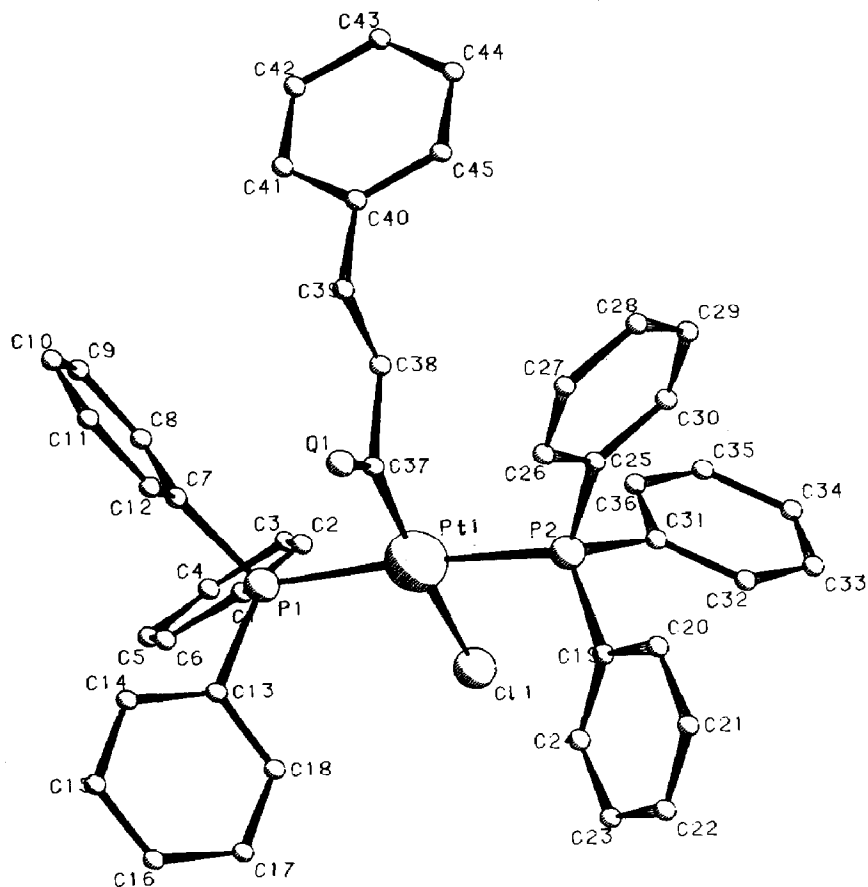


Fig. 1. The crystal structure of *trans*- $[\text{PtCl}(\text{COCH}_2\text{CH}_2\text{Ph})(\text{PPh}_3)_2]$ . The clathrate EtOH molecule is omitted from the figure.

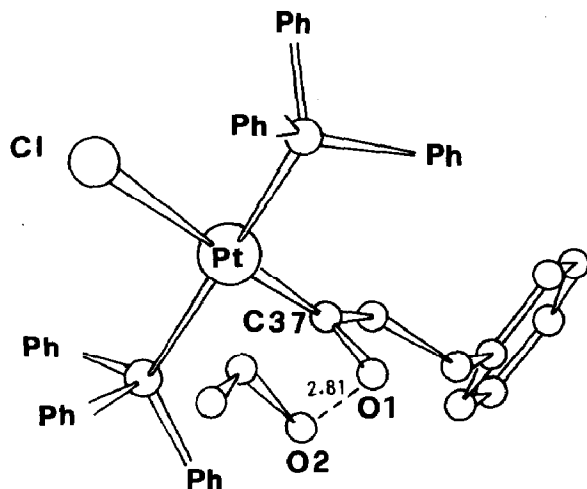


Fig. 2. Hydrogen bonding in *trans*-[PtCl(COCH<sub>2</sub>CH<sub>2</sub>Ph)(PPh<sub>3</sub>)<sub>2</sub>]·EtOH.

mean Pt–P bond distance (2.31 Å) is slightly less than the sum (2.40 Å) of the covalent radii [12] or than that (2.35 Å) of the atomic radii [13], suggesting some double bond character in the Pt–P bond arising from back-donation.

It is noteworthy that some anisotropic components of the temperature factors for the chain atoms and for the attached phenyl atoms are unusually high. This could possibly reflect the unusual thermal motion of a chain not stabilized by secondary interaction, but more probably indicates that the refined model, which is smeared out anisotropically, is the average model for a partially disordered structure.

As far as the Pt–C bond is concerned, the observed value of 1.84(2) Å is very short compared with the sum of the covalent radii (2.07 Å) or that of the atomic radii (2.05 Å), as well as relative to values found in related acylplatinum complexes (mean Pt–C 2.02 Å) [2,3].

Although the position of the C(37) atom is that defined by the least-squares refinement, it is likely to be affected by the observed disorder in the ligand chain. These circumstances, and the relatively high value (1.61 Å) of the associated C(37)–C(38) distance, seem to indicate that the Pt–C bond length is underestimated, and that a value over 1.90 Å would be more realistic.

The O···O distance of 2.81 Å shows the presence of hydrogen bonding between the acyl oxygen and the ethanol hydroxyl. Moreover, the lower value of the  $\nu(\text{C}=\text{O})$  in this complex (1628 cm<sup>-1</sup>) compared with that found in other acyl complexes (1660 cm<sup>-1</sup>) [2,3] confirms that the C=O bond is somewhat longer than a normal double bond.

The NMR parameters of complex I are not significantly different from those reported for other related acyl complexes [11].

The Pt–Cl bond length is longer by more than 0.1 Å than expected for this bond, indicating that the acyl ligand provides a strong *trans* influence, as previously observed [14].

Other structural details are normal and need no comment.

#### Acknowledgements

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