

## The Preparation and Structure of the Bis-vinyl Ether Complex Pt(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)[(MeO<sub>2</sub>C)C=C(OMe)(CO<sub>2</sub>Me)]<sub>2</sub>

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(Received July 2, 1987)

### Abstract

Reaction of the [Pt(dppe)]<sup>2+</sup> cation (where dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) with the activated acetylene dimethyl acetylenedicarboxylate in methanol solution results in the formation of the bis-vinyl ether complex Pt(dppe)[(MeO<sub>2</sub>C)C=C(OMe)(CO<sub>2</sub>Me)]<sub>2</sub>. The compound is characterized by infrared, <sup>1</sup>H and <sup>31</sup>P(<sup>1</sup>H) NMR spectroscopy, elemental analysis and X-ray crystallography.

### Introduction

The preparation and reactivity of cationic acetylene complexes of platinum of the type [Pt(X)L<sub>2</sub>(acetylene)]<sup>+</sup> where L is a phosphine and X a ligand of high *trans* influence is well documented [1]. In general, the reaction chemistry can be described in terms of a carbonium ion model formed as a result of the coordination of the acetylene to an acidic platinum cation which is capable of leading to a dipole-induced reaction [1]. The acetylene is activated to a variety of reactions depending upon the nature of the acetylene, the other ligands on platinum and the solvent chosen. These include the formation of acetylide, carbene and vinyl ether complexes as well as insertion reactions involving the Pt–X bond. Recently there have been reports [2, 3] of the preparation and properties of complexes of the type Pt(dppe)R(OMe) where R = Me or OMe. These complexes have been shown [4, 5] to undergo insertion reactions of both carbon monoxide and tetrafluoroethylene into one or both of the metal–oxygen bonds of the alkoxide ligands via associative mechanisms. These observations have obvious relevance to catalyzed olefin hydrolysis and oxalate ester synthesis. In view of all of the above results we have investigated the chemistry of acetylenic com-

plexes derived from the [Pt(dppe)]<sup>2+</sup> cation that should be even more acidic than those studied by Clark and coworkers. This report concerns the interaction of this cation with the activated acetylene dimethyl acetylenedicarboxylate.

### Results and Discussion

A nitrogen degassed methanol solution of the [Pt(dppe)]<sup>2+</sup> cation, obtained by chloride abstraction from PtCl<sub>2</sub>(dppe), was treated with a large molar excess of dimethyl acetylenedicarboxylate. The clear solution obtained was left stirring for 24 h during which time a white microcrystalline solid was deposited. Colourless crystals suitable for X-ray analysis were obtained by recrystallizing this solid from dichloromethane–methanol, and the structure showed the compound to be the bis-vinyl ether complex Pt(dppe)[(MeO<sub>2</sub>C)C=C(OMe)(CO<sub>2</sub>Me)]<sub>2</sub>.

An ORTEP illustration of the molecule is presented in Fig. 1. Table I lists the final non-H coordinates. Selected bond distances and angles are given in Table II. The structure consists of discrete molecular units, with the closest intermolecular distance being 2.43 Å between O(1) and H(25) (bonded to C(25) in equivalent position (*x* + 0.5, *y* – 0.5, *z*)).

Angles subtended at the Pt atom indicate that the coordination geometry about the Pt centre is essentially square planar. The largest deviation from the least-squares plane defined by the Pt, P, P', C(1), and C(1') atoms is that of P, by 0.033 Å. Two-fold symmetry is crystallographically imposed upon the molecule by the axis of rotation bisecting the P–Pt–P' and C(1)–Pt–C(1') angles.

The Pt–P bond length of 2.286(1) Å is comparable to that observed in other Pt(II) complexes [2] in which dppe is situated *trans* to  $\sigma$ -bound C atoms. The Pt–C(1) bond length of 2.074(4) Å is significantly longer than the value of 1.97(2) Å found in [*cis*-Pt(CO)Cl<sub>2</sub>(EtO<sub>2</sub>CC=C(Cl)CO<sub>2</sub><sup>i</sup>Pr)] [6].

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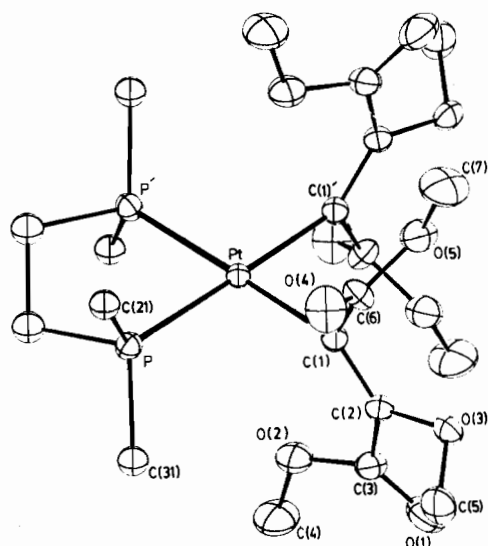


Fig. 1. An ORTEP diagram of  $\text{Pt}(\text{dppe})[(\text{MeO}_2\text{C})\text{C}=\text{C}(\text{OMe})(\text{CO}_2\text{Me})]_2$ . Only phenyl rings  $\alpha$ -C atoms are shown and the hydrogen atoms are omitted for clarity. The thermal ellipsoids are represented by 30% probability contours.

TABLE I. Positional Parameters for the non-H Atoms ( $\times 10^4$ )<sup>a</sup>

Atom	x	y	z
Pt	0	489(1)	2500
P	27(1)	2392(1)	1818(1)
C(1)	13(2)	-1194(5)	1860(2)
C(2)	516(2)	-1958(5)	1701(2)
C(3)	1255(2)	-1770(5)	1940(2)
C(4)	2122(3)	-78(9)	2388(4)
C(5)	549(4)	-3001(7)	732(3)
C(6)	-680(2)	-1645(5)	1529(2)
C(7)	-1624(3)	-3177(9)	1554(4)
O(1)	1666(2)	-2721(5)	1894(2)
O(2)	1412(2)	-424(4)	2207(2)
O(3)	368(2)	-3172(4)	1304(1)
O(4)	-969(2)	-1097(5)	1057(2)
O(5)	-945(2)	-2704(4)	1827(2)
C(11)	225(2)	4144(5)	2249(2)
C(21)	-798(2)	2769(5)	1320(2)
C(22)	-867(3)	3649(7)	810(3)
C(23)	-1517(3)	3980(8)	465(3)
C(24)	-2079(3)	3417(7)	639(3)
C(25)	-2024(3)	2540(7)	1145(3)
C(26)	-1377(3)	2210(7)	1485(3)
C(31)	619(2)	2342(5)	1302(2)
C(32)	1159(3)	3323(6)	1361(3)
C(33)	1603(3)	3213(7)	952(3)
C(34)	1500(3)	2154(7)	514(3)
C(35)	963(3)	1164(7)	447(3)
C(36)	518(3)	1256(6)	845(2)

<sup>a</sup>e.s.d.s in the least significant figure(s) are given in parentheses.

TABLE II. Selected Bond Distances and Angles<sup>a</sup>

Bond	Distance (Å)	Bond	Distance (Å)
Pt-C(1)	2.074(4)	C(3)-O(1)	1.199(6)
C(1)-C(2)	1.326(6)	C(3)-O(2)	1.343(6)
C(1)-C(6)	1.488(6)	O(2)-C(4)	1.431(7)
C(6)-O(4)	1.199(6)	Pt-P	2.286(1)
C(6)-O(5)	1.328(6)	P-C(11)	1.829(5)
O(5)-C(7)	1.436(7)	C(11)-C(11')	1.587(10)
C(2)-O(3)	1.389(5)	P-C(21)	1.825(5)
O(3)-C(5)	1.413(6)	P-C(31)	1.824(4)
C(2)-C(3)	1.478(6)		
Bond	Angle (°)	Bond	Angle (°)
C(1)-Pt-C(1)'	88.1(2)	C(1)-C(2)-O(3)	119.8(4)
C(1)-Pt-P	93.5(1)	C(2)-O(3)-C(5)	116.1(4)
Pt-C(1)-C(6)	113.2(3)	C(1)-C(2)-C(3)	127.5(4)
C(1)-C(6)-O(4)	124.1(5)	C(2)-C(3)-O(1)	123.2(5)
C(1)-C(6)-O(5)	111.7(4)	C(2)-C(3)-O(2)	112.7(4)
C(6)-O(5)-C(7)	115.8(5)	C(3)-O(2)-C(4)	116.4(5)
Pt-C(1)-C(2)	132.4(3)		
P-Pt-P'	85.0(1)	Pt-P-C(21)	113.5(2)
Pt-P-C(11)	107.7(2)	Pt-P-C(31)	121.2(2)
P-C(11)-C(11)'	106.4(5)		

<sup>a</sup>e.s.d.s in the least significant figure(s) are given in parentheses.

This difference may be attributed to the larger *trans* influence of the dppe ligand, compared to that of the chloride ligand. No other atoms of the alkenyl group are situated within bonding distance of the Pt centre. The olefinic nature of the organic ligand is reflected in the 1.326(6) Å length of the C(1)-C(2) vector which is indistinguishable from the value of 1.31(2) Å reported for  $[\text{cis-Pt}(\text{CO})\text{Cl}_2(\text{EtO}_2\text{CC}=\text{C}(\text{Cl})\text{CO}_2^1\text{Pr})]$  [6]. The methylcarboxylate groups are found to be arranged in a *trans* configuration with respect to the double bond. This stereospecificity has been observed previously in related systems using spectroscopic techniques [1]. The planarity of the configuration about the double bond is confirmed by a least-squares plane calculation involving C1, C2 and the olefin substituent atoms (maximum deviation is 0.080 Å by O(3)). A dihedral angle of 92.5°, calculated between the Pt- and olefin-centered planes, is thought to result from the steric interactions between the two *cis* alkenyl ligands. All of the bond lengths and angles associated with the olefin's methoxy and methylcarboxylate substituents, and the dppe ligand are normal.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the complex is that of a singlet with  $^{195}\text{Pt}$  satellites  $\delta = 41.3$  ppm;  $J^1(\text{P}-\text{Pt}) = 2339$  Hz in agreement with equivalent phosphorus atoms. The  $^1\text{H}$  NMR spectrum contains singlets at  $\delta = 3.43$ , 3.38 and 3.37 ppm which

integrate correctly for 2 methoxy and 2 pairs of carboxylate groups against the aryl protons. The methylene protons of the phosphine ligand appear as a characteristic [7] broad multiplet  $\delta = 1.79$  to 1.98 ppm. The infrared spectrum shows a strong carbonyl absorption at  $1696\text{ cm}^{-1}$ , strong carboxylate bands at  $1210$ ,  $1047$  and  $1022\text{ cm}^{-1}$  and a strong ether absorption at  $1111\text{ cm}^{-1}$ .

Thus the product obtained is consistent with nucleophilic attack by the solvent methanol on two moles of coordinated acetylene according to the previously described carbonium ion model [1]. Consequently both of the vinyl ether ligands have the expected stereospecifically formed *trans* configuration [1]. It is interesting to note that while the  $[\text{Pt}(\text{dppe})]^{2+}$  ion is sufficiently acidic to induce solvolysis of two moles of dimethyl acetylenedicarboxylate and tetrafluoroethylene has been reported [2] to insert into the metal–oxygen bond of the complex  $\text{Pt}(\text{dppe})\text{Me}(\text{OMe})$ , there has been no indication of double insertion of tetrafluoroethylene into the complex  $\text{Pt}(\text{dppe})(\text{OMe})_2$  as has been reported [3] for carbon monoxide. In addition we have observed little or only very slow reaction of hexafluoro-2-butyne or tetrafluoroethylene with the  $[\text{Pt}(\text{dppe})]^{2+}$  cation.

## Experimental

$^{31}\text{P}(\text{H})$  NMR spectra were obtained in  $\text{CH}_2\text{Cl}_2$  using a Varian XL200 spectrometer operating at 81 MHz. Spectra were recorded using  $\text{P}(\text{OMe})_3$  as reference but are reported with reference to 85%  $\text{H}_3\text{PO}_4$ .  $^1\text{H}$  NMR spectra were obtained in  $\text{CDCl}_3$  on the same spectrometer operating at 200 MHz and are referenced to TMS. Infrared spectra were determined as KBr discs using a Nicolet 5DX FT-IR spectrophotometer.

$\text{PtCl}_2(\text{dppe})$  (0.1 g) was dissolved in a mixture of  $\text{CH}_2\text{Cl}_2$  (20 ml) and  $\text{CH}_3\text{OH}$  (10 ml). Two equivalents of  $\text{AgPF}_6$  (0.076 g) were then added and after 15 min of stirring the silver chloride was removed by filtration through celite. The filtrate was taken to dryness under reduced pressure and extracted with  $\text{CH}_2\text{Cl}_2$  (20 ml). The solution was filtered through celite to remove excess silver chloride and again taken to dryness under reduced pressure. The resulting cation was then dissolved in nitrogen degassed  $\text{CH}_3\text{OH}$  (25 ml) and dimethyl acetylenedicarboxylate (0.1 ml) added. The clear solution was then stirred under nitrogen for 24 h. The white microcrystalline solid was removed by filtration and dried under vacuum. Yield 0.11 g (78%). Melting point (m.p.)  $305\text{--}309\text{ }^\circ\text{C}$ . Products prepared in this way were used for NMR measurements since samples recrystallized from  $\text{CH}_2\text{Cl}_2$  were impossible to redissolve in  $\text{CH}_2\text{Cl}_2$ . Crystals suitable for X-ray analysis were obtained by

recrystallization from dichloromethane–methanol mixtures as clear colourless crystals. *Anal.* Found: C, 51.2; H, 4.5. Calc. for  $\text{C}_{40}\text{H}_{42}\text{O}_{10}\text{P}_2\text{Pt}$ : C, 51.1; H, 4.5%.

### Crystal Data for $\text{Pt}(\text{dppe})((\text{MeO}_2\text{C})\text{C}=\text{C}(\text{CO}_2\text{Me})-(\text{OMe})_2)$ (I)

$\text{C}_{40}\text{H}_{42}\text{O}_{10}\text{P}_2\text{Pt}$ ,  $M = 939.81$ , monoclinic,  $a = 20.083(3)$ ,  $b = 8.860(2)$ ,  $c = 22.458(2)$  Å,  $\beta = 102.08(1)^\circ$ ,  $U = 3907.8\text{ \AA}^3$  (by least-squares refinement on diffractometer angles for 25 automatically centred reflections,  $\lambda = 0.71069\text{ \AA}$ ), space group  $C2/c$  [8],  $Z = 4$ , site symmetry 2,  $D_c = 1.60\text{ g cm}^{-3}$ . Colourless needles, crystal dimensions  $0.20 \times 0.50 \times 0.09$  mm, crystal bounded by  $\{100\}$ ,  $\{010\}$  and  $\{001\}$ ,  $\mu(\text{Mo K}\alpha) = 37.6\text{ cm}^{-1}$ .

### Data Collection and Processing

Enraf-Nonius CAD4 diffractometer,  $\theta/2\theta$  mode with scan width  $= 0.75 + 0.35 \tan \theta$ , scan speed  $1.5\text{--}11.0^\circ\text{ min}^{-1}$ , graphite monochromated  $\text{Mo K}\alpha$  radiation. 4645 unique reflections ( $1^\circ < 2\theta < 50^\circ$ ,  $hkl$  and  $hk-l$ ); intensity variation 3.6%. Data reduction Enraf-Nonius SDP version 4-0 [9], Gaussian absorption correction with a grid of  $6 \times 14 \times 4$  (relative transmission factors 0.471 to 0.741).

### Structure Solution and Refinement

Solved by Patterson synthesis and difference Fourier syntheses using SHELX76 [10], full-matrix refinement on  $F$ ,  $w^{-1} = \sigma^2(F) + 0.0005F^2$ , 3886 unique reflections with  $F > 6\sigma(F)$ , anisotropic thermal parameters for Pt, P and the olefin non-H atoms, 175 parameters, H atoms were located and included in the final calculation in idealized positions ( $\text{sp}^2$ ,  $\text{C-H} = 0.95\text{ \AA}$  and  $\text{sp}^3$ ,  $\text{C-H} = 1.07\text{ \AA}$ ),  $R = 0.032$ ,  $R_w = 0.034$ ,  $(\Delta/\sigma)_{\text{max}} = 0.12$ , largest peak in final difference map  $0.99\text{ e \AA}^{-3}$  (associated with  $\text{C}(24)$ ), no correction for secondary extinction.

## Acknowledgement

We thank the Natural Sciences and Engineering Council of Canada for operating and equipment grants.

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