

PALLADIUM AND PLATINUM COMPLEXES OF α -KETOESTERS. CRYSTAL STRUCTURE OF *trans*-[Pt{P(C₆H₁₁)₃]₂(H){OC=CHC(Me)(COOEt)OCO}]

A. GRASSI, P. LONGO, A. MUSCO *,

Facoltà di Scienze, Università degli Studi, 84100 Salerno, (Italy)

W. PORZIO

Istituto di Chimica delle Macromolecole del C.N.R., via Bassini 15/A, 20133 Milano (Italy)

and A. SCRIVANTI

Centro di Chimica Metallorganica del C.N.R., c/o Istituto di Chimica Industriale, via Marzolo 9, 35100 Padova (Italy)

(Received January 2nd, 1985)

Summary

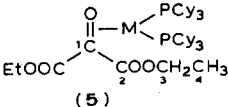
The reactions of M(PCy₃)₂ (**3**) (**a**, M = Pd; **b**, M = Pt; Cy = cyclohexyl) and *trans*-PtH₂(PCy₃)₂ (**4**) with the α -ketoesters diethyloxomalonate (**1**) and ethylpyruvate (**2**) have been investigated. At room temperature **1** coordinates strongly to **3**, whereas **2** yields labile adducts. At higher temperatures **2** reacts with **3b** to yield the enolate *trans*-[Pt(PCy₃)₂(H){OC=CHC(Me)(COOEt)OCO}] (**8**), the structure of which has been determined by X-ray diffraction. The ester **1** behaves like CO₂ in undergoing rapid insertion into the Pt–H bond of **4**. Unexpectedly reaction of **2** with **1** does not yield an insertion product, but again gives complex **8**.

Introduction

There is much interest in the functionalization of unsaturated organic substrates with CO₂ in both catalytic and stoichiometric reactions assisted by transition metal complexes [1]. A molecule which has a carbonyl carbon activated by electron withdrawing groups should also be able to take part in such reactions as more electrophilic analogues of carbon dioxide. It thus appeared to be of interest to study the chemistry of the α -ketoesters diethyl oxomalonate (**1**) and ethyl pyruvate (**2**) with Group VIII transition metals, which are known to be active in the carboxylation

* Present address: Istituto di Scienze Chimiche, Università degli Studi, 61029 Urbino (Italy).

TABLE 1

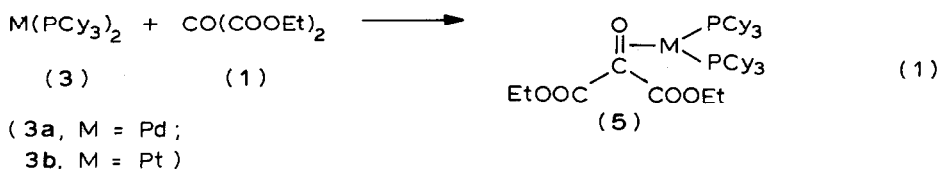
¹³ C NMR DATA ^a OF (δ (ppm), J (Hz))		 (5)				
	P ^A	P ^B	C(1)	C(2)	C(3)	C(4)
5a , M = Pt	27.28 $J(P^A-Pt)$ 3398 $J(P-P)$ 21.7	26.17 $J(P^B-Pt)$ 4840	76.46 $J(C(1)-P)_{trans}$ 30.6 $J(C(1)-P)_{cis}$ 2.4	169.01 $J(C(2)-P)_{trans}$ 6.3 $J(C(2)-Pt)$ 52	59.05	14.67
5b , M = Pd	40.58 $J(P-P)$ 13.0	35.48	84.44 $J(C(1)-P)_{trans}$ 22.4	168.32 $J(C(2)-P)_{cis}$ 6.0	59.25	14.64
1			178.66	160.64	62.96	13.48

^a Toluene-*d*₈.

reactions of unsaturated hydrocarbons [1,2]. The behaviour of these active carbonyl species towards the early transition metals has been extensively studied by Floriani and coworkers [3], and we now report the reactions of **1** and **2** with the 14 electrons complexes $M(PCy_3)_2$ (**3a**, M = Pd; **3b**, M = Pt, Cy = cyclohexyl) and *trans*-PtH₂(PCy₃)₂ (**4**).

Results and discussion

Diethyl oxomalonate (**1**) forms stable 1/1 adducts with Pd(PCy₃)₂ (**3a**) and Pt(PCy₃)₂ (**3b**) (eq. 1).



³¹P and ¹³C NMR data (Table 1) suggest a side-bonded ketone structure (**5**). The ³¹P NMR spectrum displays an AB pattern for the phosphorus nuclei. The carbon chemical shift of the carbonyl group of **1** undergoes an upperfield shift of 94.2 and 102.2 ppm for **5a** and **5b**, respectively, on coordination to the metal. Analogous phosphineplatinum complexes have been previously reported [4,5].

Diethyloxomalonate is displaced on reaction of **5** with carbon monoxide to yield the carbonyl clusters M₃(CO)₃(PCy₃)₃ and M₃(CO)₃(PCy₃)₄ [6]. As expected for a low oxidation state complex **5** undergoes oxidative addition on treatment with methyl iodide to yield *trans*-M(PCy₃)₂(CH₃)I and **1**. Complex **5** reacts smoothly with O₂ to yield **6**, which is structurally similar to the reaction product of M(PCy₃)₂O₂ and CO₂ or ketones [7] (eq. 2).

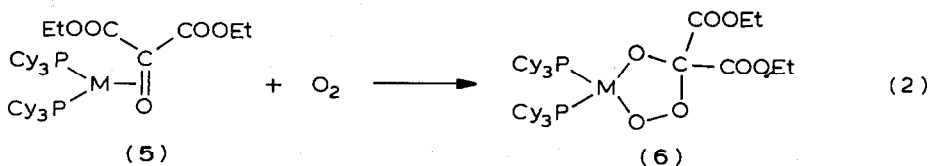


TABLE 2

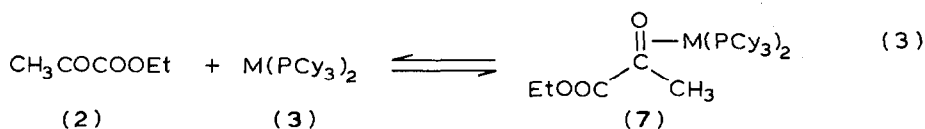
³¹P NMR DATA ^a OF
(δ (ppm), J (Hz))

(7)

	P ^A	P ^B	J (P-P)	J (P ^A -Pt)	J (P ^B -Pt)
7a (M = Pd) ^b	31.82	38.28	5.0		
7b (M = Pt) ^c	26.61	26.09	33.2	5130	2977

^a Toluene-*d*₈. ^b -60°C. ^c -45°C.

Ethyl pyruvate (**2**) also reacts with M(PCy₃)₂ (**3**) according to eq. 3 but, in contrast to the solution with diethyloxomalonate, at room temperature the equilibrium lies well on the left, as is shown by ³¹P NMR spectra run at various temperatures in toluene-*d*₈.

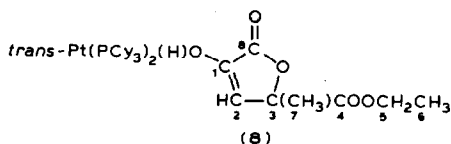


Equimolecular mixtures of **2** and **3** show an AB spectrum at -60°C and -45°C, respectively, for the Pd and Pt complex (Table 2). On increasing the temperature the AB signals collapse and gradually move towards that of uncoordinated ML₂, which is the only species present at temperatures above 18°C for the Pd and 70°C for the Pt complex. At higher temperatures (70°C), 2/1 molar mixtures of ethylpyruvate and Pd(PCy₃)₂ or Pt(PCy₃)₂ display different behaviour. With the Pt-containing mixture a new signal appears at δ 40.08 ppm, with platinum satellites (J (Pt-P) 2861 Hz) as the integrated signal due to Pt(PCy₃)₂ progressively falls until it has disappeared completely at the end of the reaction. The ¹H NMR spectrum of the reaction solution shows a Pt-H resonance at δ -22.40 ppm. No reaction was observed in the Pd case. These findings suggested that Pt(PCy₃)₂ reacted quantitatively with two ethyl pyruvate units to yield a hydrido species. The reaction product was isolated and its NMR parameters (Table 3) suggested structure **8**, which was then fully confirmed by an X-ray structure determination.

The crystal structure of PtO₅C₈H₁₀(PCy₃)₂ (**8**) consists of discrete molecules with no intermolecular distance significantly shorter than the sum of the Van der Waals radii. As shown in Fig. 1, the platinum atom is coordinated to two tricyclohexylphosphine molecules, a lactone moiety, and a hydrogen atom, to form a square planar complex (the mean square displacement from the Pt-P(1)-P(2)-O(1) plane being 0.06 Å). Selected non hydrogen atom distances, angles and, torsion angles are listed in Table 4, and the equations of some best planes through groups of atoms are given in Table 5.

One of the cyclohexyl residues was found to displace a dynamic and/or static

TABLE 3

NMR DATA ^a OF
(δ (ppm), J (Hz))

	Pt-H	H(2)	H(5)	H(6)	H(7)			
¹ H	22.40 <i>J</i> (P-H)14.0 <i>J</i> (Pt-H)1126	5.76 <i>J</i> (H-Pt)4.5	4.11 4.09	1.08	1.88			
¹³ C	C(1) 108.39	C(2) 155.32 <i>J</i> (C-Pt) 6.6	C(3) 80.16	C(4) 172.36	C(5) 61.03	C(6) 14.19	C(7) 25.62	C(8) 171.54
³¹ P	40.08	<i>J</i> (Pt-P) 2861						

^a Toluene-*d*₈.

disorder of two atoms C(41) and C(44), so that the conformation seems to be neither chair nor boat, but an average between the two expected chair conformations, giving rise to a flat distorted ring (Table 5). The refinement of different geometrically derived weighted conformations confirmed the reported atomic average positions for the two carbon atoms. The Pt-P average distance (2.291(6) Å) is comparable with corresponding distances in other complexes containing PCy₃ ligands [8]. These

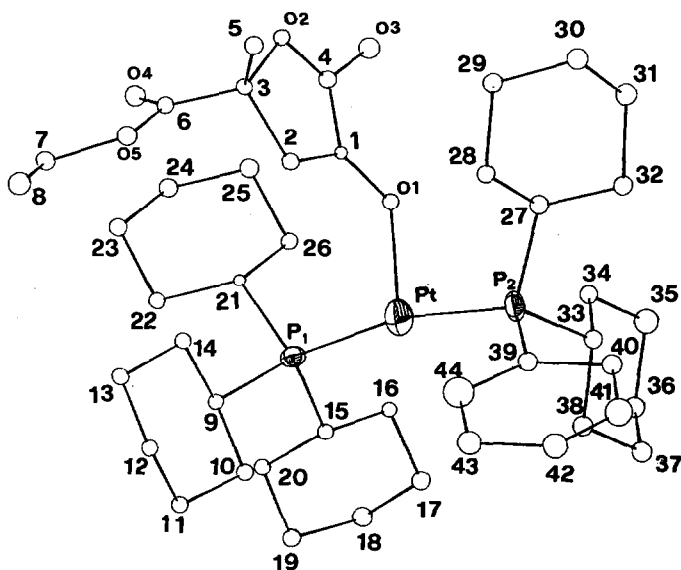


Fig. 1. ORTEP drawing of 8, viewed perpendicularly to the *ab* plane. The C atoms are indicated with their order numbers.

TABLE 4

SELECTED INTERATOMIC DISTANCES (Å), ANGLES AND TORSION ANGLES (deg) OF **8** WITH e.s.d. IN PARENTHESES

Pt–P(1)	2.284(7)	O(1)–C(1)	1.33(4)
Pt–P(2)	2.298(6)	C(1)–C(2)	1.32(4)
Pt–O(1)	2.11(2)	C(1)–C(4)	1.46(4)
		C(2)–C(3)	1.54(5)
P–C _{avg} ^a	1.84(3)	C(3)–C(5)	1.57(5)
		O(2)–C(3)	1.51(3)
C–C _{avg} ^b	1.54(4)	O(2)–C(4)	1.28(5)
		O(3)–C(4)	1.27(4)
		C(3)–C(6)	1.46(4)
		O(4)–C(6)	1.21(3)
		O(5)–C(6)	1.31(3)
		O(5)–C(7)	1.50(4)
		C(7)–C(8)	1.49(5)
P(1)–Pt–P(2)		166.4(1)	
P(1)–Pt–O(1)		96.1(5)	
P(2)–Pt–O(1)		95.3(5)	
Pt–O(1)–C(1)		123.9(9)	
C–C–C _{avg} ^c		110(2)	
P(1)–Pt–O(1)–C(1) ^d	–77	C(2)–C(3)–C(6)–O(5)	–81
P(2)–Pt–O(1)–C(1)	110	O(2)–C(3)–C(6)–O(5)	167
Pt–O(1)–C(1)–C(2)	–5	O(2)–C(3)–C(6)–O(4)	–13
Pt–O(1)–C(1)–C(4)	165		

^a Average value over the six P–C distances of the phosphines. ^b Average value of all C–C bonds in the phosphines. ^c Average value of all C–C–C bond angles in the phosphines. ^d The e.s.d. are ca. 1° for angles containing Pt and ca. 3° for the others. A–B–C–D angle is regarded as positive when, looking along the central bond (B–C), the far bond is rotated clockwise with respect to the near one.

ligands have the expected staggered conformation with respect to each other, with the cyclohexyl moieties in the chair conformation. The bulky ligands are slightly bent towards the H hydrido atom (the P(1)–Pt–P(2) angle is 166.4(1)° owing to the steric requirement of the lactone group. The Pt–O(1) distance (2.11(2) Å) is substantially longer than the sum of covalent radii of Pt (1.35 Å, as derived from Pt₃(PCy₃)₄(CO)₃ [9] and oxygen (0.66 Å [10]) but close to the Pt–O distance in *trans*-PtH(O₂COCH₃)(PCy₃)₂ [8a] (2.13(1) Å). The lactone portion is quite planar (Table 5), and form an angle of 70° with the metal coordination plane and of 73° with the C(3)C(6)O(4)O(5)C(7)C(8) group.

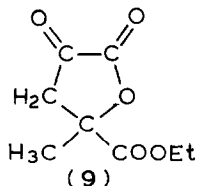
TABLE 5

SELECTED BEST PLANES THROUGH GROUPS OF ATOMS IN **8**

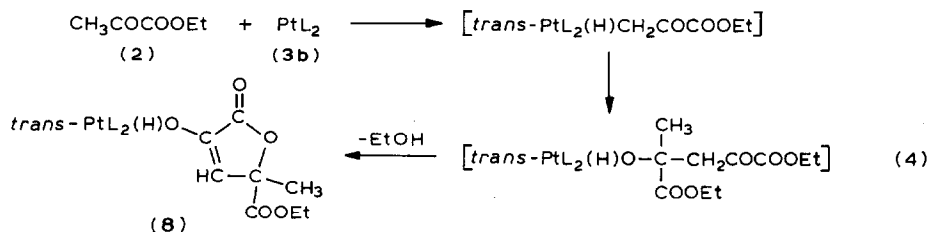
Group	Equation	<i>d</i> ^a
Pt P(1) P(2) O(1)	0.3907x + 0.1730y + 0.0041z – 1.9940 = 0	0.06
O(2) C(1) C(2) C(3) C(4)	–0.8000x – 0.0579y + 0.5966z + 4.3193 = 0	0.05
C(3) C(6) O(4) O(5) C(7)	0.1583x – 0.7674y + 0.6214z – 2.7653 = 0	0.02
C(39)–C(44)	–0.0213x – 0.5620y + 0.8269z + 1.9581 = 0	0.03

^a *d* is the mean square displacement in Å.

Formally **8** is the result of an oxidative addition of lactone **9** to **3b**.

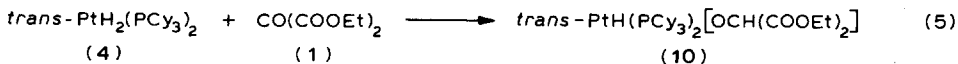


However since lactone **9** is not formed in the reaction mixture when the PtL_2 -ethylpyruvate reaction is run in presence of an excess of pyruvate, compound **8** may be formed according to the sequence indicated in eq. 4. This implies an oxidative addition of a pyruvate molecule followed by rapid insertion of another pyruvate unit, to yield an intermediate which rearranges to **8** with loss of ethanol.

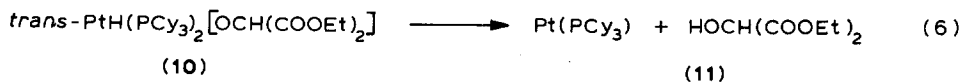


Comparison of the coordination ability of CO_2 , ethyl pyruvate, and diethyloxomalonate to $\text{Pd}(\text{PCy}_3)_2$ (**3a**) and $\text{Pt}(\text{PCy}_3)_2$ (**3b**) indicates the following order of strengths of the bonds to the metals: diethyloxomalonate > ethylpyruvate $\gg$ carbon dioxide. It is noteworthy that a carbon dioxide adduct similar to the well known $\text{Ni}(\text{PCy}_3)_2\text{CO}_2$ [11] was not isolated from **3** even in the presence of liquid carbon dioxide [12].

It is known that carbon dioxide inserts into metal-H bonds to yield formate complexes [1], and it has been shown previously that CO_2 inserts reversibly in the Pt-H bond of $\text{trans-PtH}_2(\text{PCy}_3)_2$ (**4**) to yield the formate complex $\text{trans-Pt}(\text{PCy}_3)_2(\text{H})\text{O}_2\text{CH}$ [8a]. In order to compare further the behaviour of carbon dioxide and α -ketoesters we investigated the insertion of diethyloxomalonate and ethylpyruvate into the Pt-H bond. We found that diethyloxomalonate (**1**) inserts very rapidly into the Pt-H bond of **4** to yield **10** (eq. 5).



Compound **10** was fully characterized by NMR spectroscopy (Table 6). The insertion reaction is not reversible. The ^{31}P NMR spectrum of a toluene solution of **10** does not show other signals when heated to 65°C . On standing at this temperature a slow reaction is observed, the integrated signal of **10** steadily diminishes as that from $\text{Pt}(\text{PCy}_3)_2$ grows. This indicates that a reductive elimination occurs (eq. 6).



Compound **11** was isolated and identified from a preparative scale reaction. The reductive elimination of **11** from **10** is fast in presence of CO .

TABLE 6

NMR DATA^a OF *trans*-Pt(PCy₃)₂(H)[OCH(COOCH₂CH₃)₂]
(δ(ppm), J(Hz))
(10)

¹ H	Pt-H	J(Pt-H)	J(Pt-P)	H(1)	J(H(1)Pt)	H(3)	H(4)
	-22.47	982	15.3	5.24	21	4.11	1.13
³¹ P	40.29	J(Pt-P) 2976					
¹³ C	C(1)	C(2)	J(C(2)-Pt)	C(3)	C(4)		
	86.10	174.33	23.4	59.02	14.48		

^a Toluene-*d*₈.

Ethylpyruvate reacts with **4** in a different way, not involving insertion into the Pt-H bond. In toluene there is a slow reaction at room temperature to yield **8**. The mechanism of this reaction has not been investigated, but suggest that in presence of ethylpyruvate **4** loses dihydrogen to give the PtL₂ species which then reacts with **1**.

Studies of the insertions of α-ketoesters into metal-carbon bonds are now in progress.

Experimental

The ¹H, ¹³C, ³¹P NMR spectra were recorded on a FT80A Varian spectrometer. Elemental analyses were performed at the Istituto di Chimica Generale, Università di Padova. Pd(PCy₃)₂ [13], Pt(PCy₃)₂ [14] and *trans*-PtH₂(PCy₃)₂ [15] were prepared by published procedures. The preparation of the complexes was carried out under dinitrogen purified by passage through BASF Catalyst R3-11. Solvents were dried and degassed before use. Diethyloxomalonate and ethylpyruvate were distilled over P₂O₅. Samples were transferred to NMR tubes using vacuum line techniques.

[Pd(PCy₃)₂diethyloxomalonate] (**5a**)

Diethyloxomalonate (0.34 g, 1.95 mmol) was added to a toluene (15 ml) solution of Pd(PCy₃)₂ (1.30 g, 1.95 mmol). The orange solution was left at room temperature for 15 min and then evaporated. The orange glassy residue was dissolved in heptane (20 ml), and soon afterwards a yellow-orange crystalline material separated, and this was filtered off, washed with cold heptane, and dried under vacuum (1.53 g, 93% yield). Analysis found: C, 61.7; H, 9.1. C₄₁H₇₆O₅P₂Pd calcd.: C, 61.4; H, 9.0%.

[Pt(PCy₃)₂diethyloxomalonate] (**5b**)

Diethyloxomalonate (0.122 g, 0.70 mmol) was added to a solution of Pt(PCy₃)₂ (0.531 g, 0.70 mmol) in toluene (4.5 ml). Heptane (3 ml) was then added. When the solution was kept at 4°C a white microcrystalline solid separated out and this was filtered off, washed with heptane, and dried (0.377 g, 57% yield). Analysis found: C, 55.9; H, 8.4. C₄₁H₇₆O₅P₂Pt calcd.: C, 55.5; H, 8.2%.

[*trans*-Pt(PCy₃)₂(H)OCH(COOEt)₂] (**10**)

Diethyloxomalonate (0.151 g, 0.86 mmol) was added to a toluene solution (5 ml) of *trans*-PtH₂(PCy₃)₂ (0.656 g, 0.86 mmol). Heptane (4 ml) was added. The mixture

was set aside overnight at room temperature, and the white prismatic crystals formed were filtered off, washed with heptane, and dried (0.70 g, 88% yield). Elemental analysis: Found: C, 55.4; H, 8.6. $C_{43}H_{78}O_5P_2Pt$ calcd.: C, 55.4; H, 8.3%. IR (nujol): $\nu(Pt-H)$ 2200 cm^{-1} .

[trans-Pt(PCy₃)₂(H)(OC=CHC(CH₃)(COOEt)OCO)] (8)

Ethyl pyruvate (0.53 mmol, 0.062 g) was added to a toluene solution of *trans*-PtH₂(PCy₃)₂ (0.200 g, 0.26 mmol). The solution was kept at 60°C for 15 h then heptane (4 ml) was added. Storage at 4°C gave white crystals (0.053 g). Further storage at -30°C yielded an additional product (0.120 g, overall yield 66%). Analysis: Found: C, 56.3, H, 8.3. $H_{76}C_{44}O_5P_2Pt$ calcd.: C, 56.1; H, 8.0%. IR (Nujol, cm^{-1}): 2260(sh)-2240 (Pt-H), 1780-1750 (C=O), 1620 (OC=C). Complex **8** may be similarly prepared using Pt(PCy₃)₂ instead of *trans*-PtH₂(PCy₃)₂.

Crystal data for trans-Pt(PCy₃)₂(H)(OC=CHC(CH₃)(COOEt)OCO) (8)

White regularly shaped crystals suitable for X-ray analysis were obtained by slow crystallization from toluene/heptane. Crystal data and procedures used are shown in Table 7. The intensities collected on a four circle Philips PW1100 computer controlled diffractometer were corrected for Lorentz and polarization effects, but no absorption correction was applied in view of the small range variation of the absorbance in the crystal (0.73-0.66). Precise lattice parameters were determined by evaluation of the centers of gravity of the profiles $I = f(\vartheta)$ of the main lattice rows reflections.

The atomic positions were determined by the heavy atom method and refined by least squares procedure involving minimization of $\sum w(F_o - F_c)^2$ with unitary weight factors in the block diagonal approximation. The atomic scattering factors given in

TABLE 7
CRYSTAL DATA AND PROCEDURES

PtP ₂ O ₅ C ₄₄ H ₇₆	<i>a</i> 23.711(8) Å
Mol. wt. 941.5	<i>b</i> 10.298(4) Å
<i>d</i> _c 1.50 g cm ⁻³ (<i>Z</i> = 2)	<i>c</i> 10.320(3) Å
Mo- <i>K</i> _α 36.6 cm ⁻¹	<i>α</i> 112.87(10) Å
Space group <i>P</i> $\bar{1}$	<i>β</i> 82.12(8)°
<i>F</i> (000) 1120 <i>e</i> /cell	<i>γ</i> 99.38(7)°
	<i>V</i> 2081.5(4) Å ³
Scan method	<i>ω</i> -scan
Scan speed	2.4 deg min ⁻¹
Scan width	1.0 deg
Background time	2 × 10 sec
<i>θ</i> range (<i>d</i> _{min})	2-23° (0.91 Å)
Reciprocal space explored	<i>l</i> ≥ 0
Measured reflections	6231
Observed reflections	
(<i>I</i> > 3 σ , σ^2 = peak counts + total background counts)	3466
Approximate crystal size	0.09 × 0.10 × 0.13 mm ³
Wavelength (graphite monochromated)	
Mo- <i>K</i> _α radiation)	0.71069 Å

TABLE 8

ATOMIC FRACTIONAL COORDINATES FOR 8, WITH e.s.d. IN PARENTHESES ^a

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Pt	23501(5)	36189(14)	1319(14)
P(1)	3223(3)	3718(7)	−1126(7)
P(2)	1452(3)	3956(9)	1236(9)
O(1)	2239(8)	1398(19)	−417(19)
O(2)	2746(8)	−1302(19)	186(19)
O(3)	2183(11)	−1663(27)	−1451(27)
O(4)	3914(10)	−593(25)	−241(25)
O(5)	3963(9)	916(24)	1958(24)
C(1)	2505(10)	736(24)	157(25)
C(2)	2850(12)	1243(32)	1194(32)
C(3)	3059(12)	−56(30)	1288(31)
C(4)	2506(13)	−802(33)	−531(34)
C(5)	2876(14)	−225(35)	2737(36)
C(6)	3676(12)	35(31)	899(31)
C(7)	4602(14)	1195(36)	1729(36)
C(8)	4781(18)	2099(44)	3169(45)
C(9)	3819(11)	4842(29)	−33(29)
C(10)	3697(13)	6400(32)	757(32)
C(11)	4189(12)	7238(31)	1649(31)
C(12)	4282(12)	6606(30)	2666(30)
C(13)	4402(12)	5065(31)	1955(32)
C(14)	3924(12)	4154(30)	1009(30)
C(15)	3148(12)	4596(30)	−2321(30)
C(16)	2679(11)	3926(28)	−3240(28)
C(17)	2589(14)	4882(35)	−4039(35)
C(18)	3107(15)	5105(38)	−4988(38)
C(19)	3619(13)	5775(33)	−4004(33)
C(20)	3694(12)	4795(31)	−3261(31)
C(21)	3517(9)	2004(24)	−2041(24)
C(22)	4165(12)	2066(30)	−2621(31)
C(23)	4344(13)	550(33)	−3150(33)
C(24)	3958(14)	−522(35)	−4316(36)
C(25)	3322(14)	−556(36)	−3715(36)
C(26)	3133(12)	920(31)	−3245(31)
C(27)	1097(14)	2337(36)	1566(36)
C(28)	1398(13)	2208(33)	2771(34)
C(29)	1203(15)	672(37)	2781(37)
C(30)	536(17)	424(43)	3030(43)
C(31)	271(17)	644(42)	1847(42)
C(32)	437(14)	2208(36)	1891(37)
C(33)	972(14)	4108(35)	−20(35)
C(34)	974(13)	2837(34)	−1337(34)
C(35)	633(20)	2927(50)	−2468(50)
C(36)	867(16)	4313(40)	−2724(40)
C(37)	843(15)	5579(39)	−1430(39)
C(38)	1199(15)	5514(38)	−280(39)
C(39)	1392(15)	5519(37)	2857(37)
C(40)	758(16)	5852(39)	3400(39)
C(41)	744(23)	7203(57)	4762(57)
C(42)	1245(20)	7975(51)	5418(51)
C(43)	1883(19)	7634(47)	4853(47)
C(44)	1924(26)	6266(66)	3570(66)

^a The atomic coordinates are $\times 10^5$ for platinum and $\times 10^4$ for all the other atoms.

ref. 16 were used; for Pt atom both the real and imaginary dispersion corrections were taken into account.

The refinement was carried out first with isotropic thermal vibration parameter and then with anisotropic ones for Pt and P atoms. The final *R* factor was 0.076. Attempts to locate H atoms by a Fourier only difference map failed; this can be attributable partly to mosaic spreading in the crystal but mainly to some disorder (see the standard deviations of involved C atoms).

Table 8 gives the atomic fractional coordinates. Tables of thermal parameters and structure factors may be obtained from the authors.

Acknowledgment

Thanks are expressed to C.N.R. Programmi Finalizzati for financial support.

References

- 1 (a) R.P.A. Sneed, in G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry* Pergamon Press, Oxford, 1982, Vol. 8, p. 225. (b) D.J. Darensbourg, R. Kudarowski, *Adv. Organometallic Chem.*, 22 (1983) 129.
- 2 H. Hoberg and B.W. Oster, *J. Organomet. Chem.*, 266 (1984) 321 and ref. quoted therein.
- 3 C. Floriani, *Pure Appl. Chem.*, 55 (1983) 1.
- 4 D.A. Clarke, M.M. Hunt and R.D.W. Kemmit, *J. Organomet. Chem.*, 175 (1979) 303; M.M. Hunt, R.D.W. Kemmit, D.R. Russel and P.A. Tucker, *J. Chem. Soc. Dalton*; (1979) 287.
- 5 R.A. Hoad, *J. Chem. Soc. Dalton Trans.*, (1982) 1637.
- 6 G.K. Anderson, H.C. Clark and J. Davies, *Organometallics*, 1 (1982) 550; A. Moor, P.S. Pregosin and M.L. Venanzi, *Inorg. Chim. Acta*, 48 (1981) 153; A. Moor, P.S. Pregosin and M.L. Venanzi, *ibid.*, 61 (1982) 135.
- 7 P.J. Hayward, D.M. Blake, G. Wilkinson and C.J. Nyman, *J. Am. Chem. Soc.*, 92 (1970) 5873.
- 8 A. Immirzi and A. Musco, *Inorg. Chim. Acta*, 22 (1977) L35; (b) A. Immirzi, A. Musco and B.E. Mann, *Inorg. Chim. Acta*, 22 (1977) L37 and ref. quoted therein.
- 9 A. Albinati, G. Carturan and A. Musco, *Inorg. Chim. Acta*, 16 (1976) L3.
- 10 L. Pauling, *The nature of chemical bond*, 3rd edit., Cornell University Press, Ithaca, N.Y., 1960.
- 11 M. Aresta, C.F. Nobile, V.G. Albano, E. Forni, M. Manassero, *J. Chem. Soc. Chem. Comm.*, (1975) 636; M. Aresta, C.F. Nobile, *J. Chem. Soc. Dalton Trans.*, (1977) 708.
- 12 M.G. Mason and J.A. Ibers, *J. Am. Chem. Soc.* 104 (1982) 5153.
- 13 W. Kuran and A. Musco, *Inorg. Chim. Acta*, 12 (1975) 187.
- 14 B.E. Mann and A. Musco, *J. Chem. Soc. Dalton Trans.*, (1980) 776.
- 15 A. Immirzi, A. Musco, G. Carturan and U. Belluco, *Inorg. Chim. Acta*, 12 (1975) L23.
- 16 *International Tables for X-ray Crystallography*, The Kynoch press, Birmingham, 1974, Vol. IV, p. 99 and p. 149.