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The Crystal and Molecular Structure of a *Cis* Dimetalated Complex of Platinum(II)

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A cyclo dimetalated complex of Pt(II), $[Bz_2(C_6H_4CH_2)P]_2Pt$, can be prepared from $(\eta^3$-2-methylallylPtOAc$)_2$ and PBz_3. The X-ray structure determination of this complex is reported here. The crystals are triclinic (space group $P\bar{1}$) with a = *16.536(2),* b = *10.500(1),* c = *10.053(1) Å,* α = *90.27(1),* β = *95.16(3),* γ = *83.84(2) deg, Z = 2,* d_c = *1.54 g cm^{-3}. The structure was solved by Patterson and Fourier methods and refined by l.s. methods to a conventional* R *factor of 0.035, based on 4769 intensities above background.*

The molecule, of approximate C2 symmetry, shows a distorted square planar geometry, the metal atom being coordinated to two phosphorus atoms cis *to each other and to two ortho carbon atoms of two phenyl rings again in mutual* cis *relation. The phosphines thus act as chelating ligands and the resulting five-membered Pt–P–C–C–C rings are puckered. The mean Pt–P and Pt–C distances are 2.277(2) and 2.067(7) Å respectively and the P–Pt–P angle is 106.0(1)°.*

Introduction

In our laboratories it has recently been found that tertiary phosphine Pd complexes are active catalysts in the co-oligomerization reaction of butadiene and CO_2 to yield carboxylic acids, esters and lactons [1, 2]. The reaction is catalyzed by preformed Pd(0) complexes as well as mixtures of (η^3-2-methylallyl PdOAc)$_2$ and the appropriate ligand. In a preliminary screening of the catalytic properties of the corresponding Pt complexes it has been found that they also catalyze the CO_2 butadiene co-oligomerization, although they give a butadiene conversion lower than the Pd based catalysts. Contrary to expectations, in the presence of η^3-2-methylallylPtOAc and PBz_3 no

TABLE I. Crystal Data and Working Conditions of the Title Compound.

Pt $P_2C_{42}H_{40}$		a	16.536(2)	
Mw	801.82	b	10.500(1)	A
d_c	1.54 g cm^{-3} (Z = 2)	c	10.053(1)	
		α	90.27(1)	
$\mu_{MoK\alpha}$	42.2 cm^{-1}	β	95.16(2)	deg
S.G.	$P\bar{1}$	γ	83.84(2)	
F(000)	770 e/cell	V	1728.4(1)	A^3
Scan method		ω-scan		
Scan speed		2.4 deg. min^{-1}		
Scan width		1.2 deg		
Background time		2 × 10 sec		
θ range (d_{min})		3–24° (0.87 A)		
Reciprocal space explored		$l \geq 0$		
Measured reflections		5399		
Observed reflections ($I > 3\sigma$, σ^2 = peak counts + total background counts)		4769		
Approximate crystal size		0.04 × 0.09 × 0.13 mm^3		
Wavelength (graphite monochromated MoKα radiation)		0.71069 A		

TABLE II. Fractional Atomic Coordinates[a] and Isotropic Thermal Vibration Parameters[b] in the Molecule, with e.s.d.'s in Parentheses.

Atom	*x/a*	*y/b*	*z/c*	B_{iso}
Pt	25041(2)	24824(3)	6350(3)	
P(1)	33491(11)	27333(18)	–9891(18)	
P(2)	13446(11)	18291(18)	–4235(17)	
C(1)	4332(5)	2671(8)	–15(8)	308(14)
C(2)	4169(5)	3400(7)	1250(8)	297(14)
C(3)	3405(4)	3351(7)	1730(7)	268(13)
C(4)	3255(5)	4119(7)	2873(8)	304(14)
C(5)	3830(5)	4843(8)	3482(9)	375(16)
C(6)	4577(6)	4859(9)	2977(10)	453(19)
C(7)	4747(5)	4135(9)	1854(9)	398(17)
C(8)	3306(5)	4304(7)	–1808(9)	295(14)
C(9)	2480(5)	4771(7)	–2512(7)	288(13)
C(10)	2269(5)	4497(9)	–3834(9)	405(17)
C(11)	1510(6)	4925(10)	–4449(10)	522(21)
C(12)	957(6)	5668(10)	–3753(10)	523(21)
C(13)	1164(6)	5947(9)	–2431(10)	450(19)
C(14)	1919(5)	5494(8)	–1807(9)	385(16)
C(15)	3444(5)	1543(8)	–2333(8)	336(15)
C(16)	4262(5)	1361(8)	–2910(8)	317(14)
C(17)	4400(6)	2024(9)	–4043(9)	426(18)
C(18)	5162(7)	1847(11)	–4551(11)	573(23)
C(19)	5767(7)	1029(12)	–3925(12)	650(26)
C(20)	5645(7)	347(11)	–2799(12)	606(25)
C(21)	4878(6)	513(10)	–2316(10)	473(19)
C(22)	610(4)	2369(7)	762(7)	264(13)
C(23)	1055(4)	2038(6)	2126(7)	211(11)
C(24)	1888(4)	2107(7)	2271(7)	248(12)
C(25)	2312(5)	1669(8)	3512(8)	317(14)
C(26)	1865(5)	1280(8)	4540(8)	361(16)
C(27)	1040(5)	1300(8)	4372(9)	383(16)
C(28)	621(5)	1690(7)	3166(7)	285(13)
C(29)	1236(4)	90(7)	–518(7)	274(13)
C(30)	1911(5)	–656(7)	–1158(8)	303(14)
C(31)	2627(6)	–1099(9)	–408(9)	424(18)
C(32)	3273(7)	–1779(11)	–1002(11)	560(23)
C(33)	3192(7)	–2025(11)	–2340(11)	592(24)
C(34)	2495(6)	–1615(10)	–3099(10)	521(21)
C(35)	1847(5)	–942(8)	–2515(9)	375(16)

[a] The values are $\times 10^5$ for Pt and P atoms and $\times 10^4$ for C atoms. [b] The values (in A^2) are $\times 10^2$.

butadiene CO_2 telomer was isolated. The failure of the reactiom is due to the separation of the catalyst from the reaction medium as a slightly soluble white crystalline material. An X-ray structure determination of the material was considered worthwhile in order to understand its inertness towards the butadiene CO_2 reaction.

Experimental

Preparation of $[Bz_2C_6H_4CH_2P]_2Pt$

TlOAc (0.18 g, 0.7 mmol) was added to (η^3-2-methylallylPtCl)$_2$ [3] (0.2 g, 0.35 mmol) in dry benzene (15 ml) under nitrogen. The reaction mixture was stirred at room temperature for 1 h and then filtered. After addition of PBz_3 (0.64 g, 2.4 mmol) the solution was siphoned in a stainless steel autoclave (75 ml). The reaction vessel was kept at 110 °C for 20 h. The colourless reaction solution was then diluted with n-heptane (10 ml) and kept at –15 °C. White plate-like crystals suitably for X-ray analysis were obtained.

X-ray Diffraction Experiments

Crystal data and working conditions are reported in Table I. The intensities, collected by means of a Philips PW1100 computer controlled four-circle diffractometer, were corrected for Lorentz and polarization effects and also for absorption, by using an experimental procedure suggested by North *et al.* [4]. The unit cell parameters and the space group symmetry were determined using the standard control program of PW1100 system [5], with a randomly oriented crystal. For precise lattice parameter determination, 47 strong reflections with $10° < \theta < 20°$ were measured by evaluating the centers of gravity of the profiles $I = f(\theta)$ for negative and positive angles. The final lattice parameters were obtained by minimizing $\Sigma(\sin\theta_{obs} - \sin\theta_{calcd})^2$.

Structure Determination

The atomic positions of $[Bz_2(C_6H_4)CH_2P]_2Pt$ were determined by the heavy atom method and refined by the least squares procedure minimizing $\Sigma w(F_o - F_c)^2$ with unitary weight factors, in the block diagonal approximation [6].

The atomic scattering factors given in ref. 7 were used; for Platinum and Phosphorus atoms both the real and imaginary dispersion corrections [7] were taken into account.

TABLE III. Anisotropic Thermal Vibration Parameters for Pt and P Atoms, with e.s.d.'s in Parentheses[a]. Thermal Function is $T = \exp - [U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + U_{12}a^*b^*hk + U_{13}a^*c^*hl + U_{23}b^*c^*kl]/4$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	173(1)	269(1)	205(1)	–121(2)	46(2)	–16(2)
P(1)	195(7)	272(8)	256(8)	–122(12)	67(12)	–29(13)
P(2)	197(7)	258(8)	209(7)	–108(12)	56(11)	–19(12)

[a] The values are $\times 10^2$.

TABLE IV. Selected Interatomic Distances (Å), Bond Angles (deg), and Torsion Angles (deg)[a], with e.s.d.s in Parentheses.

Pt–P(1)	2.276(2)	C(1)–C(2)	1.512(11)
Pt–P(2)	2.278(2)	C(8)–C(9)	1.506(11)
Pt–C(3)	2.062(7)	C(15)–C(16)	1.513(12)
Pt–C(24)	2.071(7)	C(22)–C(23)	1.519(9)
P(1)–C(1)	1.816(8)	C(29)–C(30)	1.487(11)
P(1)–C(8)	1.848(8)	C(36)–C(37)	1.500(10)
P(1)–C(15)	1.841(8)	C–C(phenyl)$_{avg}$	1.385(15)
P(2)–C(22)	1.823(8)		
P(2)–C(29)	1.856(8)		
P(2)–C(36)	1.839(7)		
P(1)–Pt–P(2)	106.0(1)	Pt–P(2)–C(29)	119.0(2)
P(1)–Pt–C(3)	80.3(2)	Pt–P(2)–C(36)	122.3(2)
P(1)–Pt–C(24)	171.4(2)	Pt–C(3)–C(2)	120.7(4)
P(2)–Pt–C(3)	169.1(2)	Pt–C(3)–C(4)	122.9(4)
P(2)–Pt–C(24)	80.0(2)	Pt–C(24)–C(23)	120.4(4)
C(3)–Pt–C(24)	94.8(3)	Pt–C(24)–C(25)	121.8(4)
Pt–P(1)–C(1)	101.2(3)	P(1)–C(1)–C(2)	105.4(5)
Pt–P(1)–C(8)	119.5(2)	P(2)–C(22)–C(23)	104.7(4)
Pt–P(1)–C(15)	120.0(2)	C(1)–C(2)–C(3)	117.2(6)
Pt–P(2)–C(22)	100.3(2)	C(22)–C(23)–C(24)	117.3(6)
C–C–C(phenyl)$_{avg}$	120.0(15)		
Pt–P(1)–C(1)–C(2)	39.4		
Pt–P(1)–C(8)–C(9)	58.5		
Pt–P(1)–C(15)–C(16)	149.7		
Pt–P(2)–C(22)–C(23)	41.7		
Pt–P(2)–C(29)–C(30)	56.8		
Pt–P(2)–C(36)–C(37)	142.8		
P(1)–C(1)–C(2)–C(3)	−32.1		
P(2)–C(22)–C(23)–C(24)	−33.4		
Pt–C(3)–C(2)–C(1)	6.5		
Pt–C(24)–C(23)–C(22)	5.6		
P(1)–Pt–C(3)–C(2)	16.7		
P(2)–Pt–C(24)–C(23)	19.0		
C(1)–P(1)–Pt–C(3)	−28.9		
C(22)–P(2)–Pt–C(24)	−31.1		

[a] The e.s.d.s are 0.5° for Pt–P–C–C angles and 1.0° for Pt–C–C–C angles. The angle A–B–C–D is counted positive when, looking along the central B–C bond, the far bond is rotated clockwise with the respect to the near bond.

The refinement was carried out first with three cycles with isotropic thermal vibration parameters (final *R* factor was 0.070) followed by three more cycles, with anisotropic thermal vibration parameters for Pt and P atoms only (final *R* was 0.041).

A subsequent difference electron density map* revealed peaks ranging from 1.4 to 0.5 e Å^{-3}; some of them attributable to Fourier truncation effect and others corresponding to the expected hydrogen atom positions.

The two final least square cycles, performed by considering also the hydrogen atoms in their calculated positions (thermal vibration parameters were assumed equal to those of the corresponding carbon atoms multiplied by 1.2), gave an *R* factor of 0.035. The mean shift of the last cycle was smaller than 0.3σ.

In Table II the atomic fractional coordinates together with isotropic thermal vibration parameters are reported. Table III gives the anisotropic thermal vibration parameters for Pt and P atoms.

Results and Discussion

The crystal structure consists of the packing of discrete $[Bz_2(C_6H_4CH_2)P]_2$ molecules with no intermolecular distance smaller than the sum of the commonly accepted Van der Waals radii. Figure 1 shows the ORTEP representation of the molecule, which

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*The computer program used was written by A. Immirzi, see ref. 8.

TABLE V. Selected Unweighted best Planes in the Molecule.[a]

Group	*Plane Equation*	δ^b
Pt P(1) P(2) C(3) C(24)	0.35199x – 0.93176y + 0.08906z + 0.82232 = 0	0.135
[Pt 0.020, P(1) 0.132, P(2) –0.140, C(3) –0.169, C(24) 0.158]		
Pt C(3) C(2) C(1)	0.21393x – 0.84527y + 0.48964z + 1.11126 = 0	0.025
[Pt –0.013, P(1) –0.792, C(1) 0.017, C(2) –0.034, C(3) 0.030]		
Pt C(24) C(23) C(22)	–0.03493x + 0.97228y + 0.23119z – 2.52066 = 0	0.022
[Pt –0.011, P(2) –0.85, C(22) 0.014, C(23) –0.029, C(24) 0.026]		
C(2)–C(7)	0.24801x – 0.79138y + 0.55846z + 0.33807 = 0	0.020
C(9)–C(14)	–0.47970x – 0.81845y + 0.31627z + 7.10455 = 0	0.007
C(16)–C(21)	0.33686x + 0.75806y + 0.55846z – 1.85440 = 0	0.008
C(23)–C(28)	–0.04151x + 0.94088y + 0.33619z – 2.66535 = 0	0.019
C(30)–C(35)	–0.48029x – 0.84871y + 0.22138z + 1.14852 = 0	0.006
C(37)–C(42)	–0.09175x – 0.34934y + 0.93249z + 3.09835 = 0	0.003

[a] In square brackets are the deviations (Å) of relevant atoms from the plane. [b] δ is the mean square displacement in Å units.

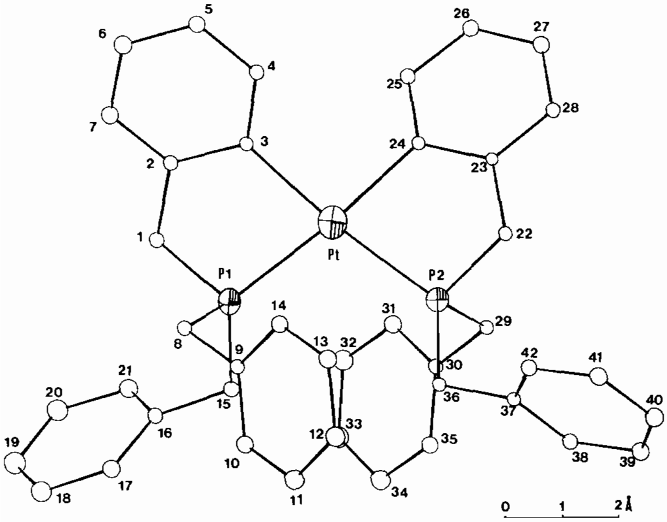

Fig. 1. The molecular structure viewed along a direction normal to the average coordination plane. For the sake of clarity the carbon atoms are labelled with numbers only.

appears very close to be of C2 molecular symmetry. The Platinum atom, which lies on the two fold axis, coordinates the two phosphorus atoms *cis* to each other and two carbon atoms (C(3) and C(24)) also in a *cis* arrangement, giving rise to a distorted square planar complex (see Table V). Each phosphine thus acts as a chelating ligand.

In Table IV principal bond distances, angles and torsion angles are reported. Table V reports relevant best planes through groups of atoms in the molecule. The average small dispersion around the mean value for C–C distances and C–C–C angles of phenyl groups and the small mean square displacements of the C atoms from phenyl group best planes (see Table V), further support the reliability of this structure determination.

The Pt–P average distance 2.277(1) Å is shorter than that observed in *cis*$[(Ph_3P)_2(\sigma\text{-}Ph)Pt(PbPh_3)]$ [9] for the phosphorus atom *trans* to the σ-bonded carbon atom (2.33(1) Å). Therefore the *trans* effect of the carbon atoms C(3) and C(24) is smaller than that observed in the complex of ref. 9.

The Pt–C distances [avg. 2.067(7) Å] are close to those observed in *cis* $[(Ph_3P)_2(\sigma\text{-}Ph)Pt(PbPh_3)]$ [9] [2.06(2) Å] and $[Pt_3(\sigma\text{-}Ph)(PPh_2)_3(PPh_3)_2]$ 2.03(2) Å [10].

It is worth noting that both P–C distances belonging to the five membered rings are significantly

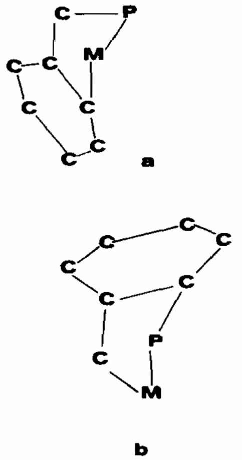

Fig. 2. 'Envelope' type conformation of the five membered ring for the title compound a) and for the complex of ref. 12 b).

shorter [avg. 1.820(8) Å] than the others [avg. 1.846(8) Å]. Also the Pt–P–C angles are smaller for metalated benzyl groups [avg. 100.8(3)°] than for non metalated ones [avg. 120.2(3)°].

Although the planarity of the four Pt co-ordination bonds is roughly fulfilled (see Table V; the dihedral angle of C(3)–Pt–C(24) and P(1)–Pt–P(2) planes is 1.5°), the four valence angles around Platinum atom are considerably displaced from 90°. This fact may be explained on considering that in the formation of the five-membered ring the bond angles must decrease with respect to the usual value, in order to reach a sum less than 3π.

The two five-membered rings show an 'envelope' type conformation: Pt and C atoms lie in the plane, while P atom considerably deviates from it (0.79 Å for P(1) and 0.85 Å for P(2)), (see Table V). It is interesting to compare such a conformation with the different ones presented by the analogous cyclodimetalated complexes: $[IrCl[P(OPh)_2(OC_6H_4)]_2$-$P(OPh)_3$ [11], where the five-membered ring is almost planar, and $RhCl_2(C_6H_5N)_2P(o$-$C_6H_4Me)_2$-(o-$C_6H_4CH_2$) [12], where the 'envelope' conformation occurs, but with a C atom out of the plane instead of the P atom (see Fig. 2). The conformation of the P–C bonds in the phosphines are staggered (see Pt–P–C–C torsion angles in Table IV).

Examples of metalated and dimetalated complexes containing the benzyl moiety have been reported [13–15], showing the possibility of orthometalation of phenyl group. However, to the best of this author's knowledge, this is the first example of a structure of a *cis* dimetalated phosphine complex.

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