

***trans*-Acetato(methoxycarbonyl)bis(triphenylphosphine)palladium(II)**

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**Abstract.** Pd(COOCH<sub>3</sub>)(OCOCH<sub>3</sub>)[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>, C<sub>40</sub>H<sub>36</sub>O<sub>4</sub>P<sub>2</sub>Pd, triclinic, *P*1, *a* = 18.81 (1), *b* = 9.683 (2), *c* = 10.491 (3) Å, α = 99.5 (1), β = 107.2 (1), γ = 94.5 (1)°, *U* = 1776.3 Å<sup>3</sup>, *D<sub>x</sub>* = 1.400 Mg m<sup>-3</sup>, *Z* = 2, μ = 0.70 mm<sup>-1</sup> (Mo Kα). Final *R* = 0.026 for 4967 unique reflections. Pd has square-planar coordination, and the acetate group acts as a unidentate ligand, the Pd–O length being 2.116 (3) Å. The Pd–C bond to the methoxycarbonyl ligand is 1.984 (4) Å, and the mean Pd–P length is 2.339 (2) Å.

**Introduction.** In the course of research into alcohol carbonylation through palladium-based catalysts, two new alkoxycarbonylpalladium complexes, Pd(COOCH<sub>3</sub>)(OCOCH<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub> (I) and Pd(COOCH<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (II), were isolated as intermediate products of the reaction and characterized by spectroscopic methods (Rivetti & Romano, 1978). The complex (I), obtained in the form of single crystals, was submitted to X-ray structural analysis. A colourless crystal in the shape of an irregular prism, with dimensions 0.3 × 0.3 × 0.5 mm, was used for the structural investigation.

Intensities were measured on an automated Siemens AED diffractometer, using the θ–2θ scan mode and the five-points technique (Hoppe, 1969), with Zr-filtered Mo Kα radiation up to (sin θ)/λ = 0.59 Å<sup>-1</sup>.

The unique set collected yielded 4967 reflections with *I* > 3σ(*I*), where σ<sup>2</sup>(*I*) = total counts + (0.005*I*)<sup>2</sup>. No decay in intensity was observed during the run. Cell dimensions were obtained by least squares from about twenty strong reflections accurately centred on the diffractometer.

The structure was solved by usual Patterson and Fourier methods. Isotropic refinement (to *R* = 0.07), followed by a difference synthesis, revealed all the H atoms. These were isotropically refined in the final cycles. The weighting scheme used was that of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) and the function minimized was ∑ [w<sub>i</sub>(F<sub>o</sub> – F<sub>c</sub>)<sup>2</sup>].

No correction for absorption was found necessary. Atomic scattering factors used for neutral atoms were from Stewart, Davidson & Simpson (1965) for H, and from Cromer & Mann (1968) for all others. All computer programs, run on an IBM 370 computer,

were written by Immirzi (1973). Atomic parameters are given in Table 1.\*

**Discussion.** A projected view of the molecular structure is given in Fig. 1. Bond lengths and angles are given in Table 2.

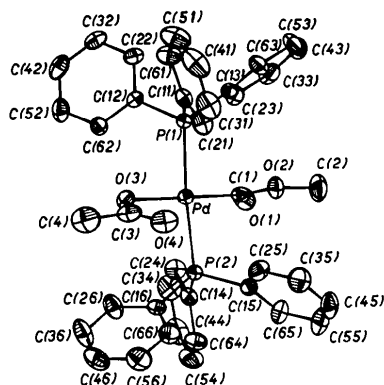
\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34501 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional parameters* (× 10<sup>4</sup>) *with e.s.d.'s in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Pd	2402(1)	2516(1)	2226(1)	C(16)	3311(2)	-333(3)	1024(3)
P(1)	2095(1)	4205(1)	3774(1)	C(26)	3080(2)	-1361(4)	1632(5)
P(2)	2673(1)	969(1)	522(1)	C(36)	3539(3)	-2396(5)	2015(6)
O(1)	1227(1)	3064(3)	-18(3)	C(46)	4218(2)	-2380(5)	1797(5)
O(2)	2284(1)	4572(3)	657(2)	C(56)	4452(2)	-1365(5)	1218(5)
O(3)	2965(1)	1475(3)	3792(2)	C(66)	4002(2)	-339(4)	819(4)
O(4)	4022(1)	2325(3)	3555(3)	H(2 <sup>+</sup> )	1577(25)	5740(47)	-162(47)
C(1)	1851(2)	3428(3)	738(3)	H(2 <sup>''</sup> )	1761(25)	6568(47)	-1341(47)
C(2)	1955(3)	5284(5)	-452(5)	H(2 <sup>'''</sup> )	2315(25)	5785(47)	-540(46)
C(3)	3662(2)	1593(4)	4069(3)	H(4 <sup>+</sup> )	3774(30)	175(55)	5341(56)
C(4)	4048(3)	727(7)	5089(5)	H(4 <sup>''</sup> )	4469(29)	1309(54)	5799(53)
C(11)	2925(2)	5207(3)	5087(3)	H(4 <sup>'''</sup> )	4413(28)	124(54)	4799(54)
C(21)	3593(2)	5346(4)	4777(4)	H(21)	3631(19)	4861(35)	3969(34)
C(31)	4217(2)	6245(5)	5668(5)	H(31)	4693(23)	6273(43)	5436(42)
C(41)	4172(2)	6989(5)	6853(6)	H(41)	4585(25)	7623(46)	7444(46)
C(51)	3521(3)	6834(5)	7208(5)	H(51)	3469(25)	7253(47)	8032(46)
C(61)	2889(2)	5927(4)	6326(4)	H(61)	2408(20)	5737(37)	6605(36)
C(12)	1507(1)	3392(3)	4646(3)	H(22)	1059(20)	5125(38)	5208(38)
C(22)	1067(2)	4173(3)	5262(3)	H(32)	391(23)	4065(43)	6390(43)
C(32)	651(2)	3543(4)	5953(4)	H(42)	392(25)	1738(46)	6463(45)
C(42)	662(2)	2123(5)	6015(4)	H(52)	1105(25)	402(47)	5425(46)
C(52)	1084(2)	1335(4)	5381(4)	H(62)	1762(17)	1449(32)	4283(31)
C(62)	1510(2)	1974(3)	4696(4)	H(23)	655(20)	4376(38)	2032(37)
C(13)	1570(2)	5605(3)	3139(3)	H(33)	-33(26)	5831(48)	1137(48)
C(23)	846(2)	5227(4)	2244(3)	H(43)	501(24)	8274(45)	1755(44)
C(33)	436(2)	6262(5)	1723(4)	H(53)	1721(23)	8949(44)	3289(43)
C(43)	743(3)	7646(5)	2084(5)	H(63)	2339(18)	7240(33)	4106(32)
C(53)	1459(3)	8041(4)	2934(5)	H(24)	1129(21)	382(40)	301(40)
C(63)	1877(2)	7023(4)	3473(4)	H(34)	177(28)	-1139(53)	-1018(51)
C(14)	1858(2)	-179(3)	-694(3)	H(44)	179(23)	-2579(44)	-3147(43)
C(24)	1167(2)	-178(4)	-457(4)	H(54)	1342(23)	-2502(44)	-3402(44)
C(34)	542(2)	-1080(5)	-1356(5)	H(64)	2349(22)	-1071(41)	-1970(40)
C(44)	600(2)	-1957(4)	-2471(5)	H(25)	3918(22)	3077(41)	1329(40)
C(54)	1278(3)	-1957(4)	-2717(4)	H(35)	4583(23)	4447(43)	367(43)
C(64)	1914(2)	-1099(4)	-1807(4)	H(45)	4135(23)	4229(44)	-2034(44)
C(15)	3118(2)	1989(3)	-416(3)	H(55)	3071(22)	2651(42)	-3315(41)
C(25)	3749(2)	2942(4)	372(4)	H(65)	2441(21)	1244(40)	-2305(39)
C(35)	4127(2)	3767(5)	-255(5)	H(26)	2582(24)	-1397(44)	1808(43)
C(45)	3882(2)	3647(5)	-1633(5)	H(36)	3363(24)	-3092(46)	2383(45)
C(55)	3258(3)	2719(3)	-2412(5)	H(46)	4591(26)	-3016(49)	2180(49)
C(65)	2868(2)	1893(4)	-1805(4)	H(56)	4937(25)	-1294(48)	1106(47)
				H(66)	4191(22)	377(41)	483(41)

Table 2. Selected bond lengths (Å) and angles (°)

Pd—P(1)	2.338 (1)	Pd—P(2)	2.339 (1)	Pd—C(1)	1.984 (4)		
Pd—O(3)	2.116 (3)	P(1)—C(11)	1.825 (4)	P(1)—C(12)	1.838 (3)		
P(1)—C(13)	1.837 (4)	P(2)—C(14)	1.824 (3)	P(2)—C(15)	1.823 (4)		
P(2)—C(16)	1.841 (4)	O(1)—C(1)	1.194 (5)	O(2)—C(1)	1.353 (4)		
O(2)—C(2)	1.456 (7)	O(3)—C(3)	1.285 (4)	O(4)—C(3)	1.232 (5)		
C(3)—C(4)	1.519 (9)						
Phenyl rings	1	2	3	4	5	6	Overall mean
C—C (mean)	1.388 (2)	1.386 (2)	1.386 (2)	1.385 (2)	1.384 (3)	1.378 (3)	1.385 (1)
C—H (mean)	0.96 (2)	0.89 (2)	0.88 (2)	0.89 (2)	0.95 (2)	0.96 (2)	0.92 (1)
Mean C—H (methyls)	0.94 (2)						
P(1)—Pd—P(2)	174.4 (2)	P(1)—Pd—C(1)	88.8 (1)	P(1)—Pd—O(3)	91.5 (1)		
P(2)—Pd—C(1)	85.7 (1)	P(2)—Pd—O(3)	94.0 (1)	O(3)—Pd—C(1)	177.4 (1)		
Pd—P(1)—C(11)	112.3 (1)	Pd—P(1)—C(12)	111.7 (1)	Pd—P(1)—C(13)	118.8 (1)		
C(11)—P(1)—C(12)	107.2 (1)	C(11)—P(1)—C(13)	102.6 (1)	C(12)—P(1)—C(13)	103.2 (1)		
Pd—P(2)—C(14)	114.5 (1)	Pd—P(2)—C(15)	109.2 (1)	Pd—P(2)—C(16)	118.6 (1)		
C(14)—P(2)—C(15)	108.2 (1)	C(14)—P(2)—C(16)	100.9 (1)	C(15)—P(2)—C(16)	104.5 (1)		
P(1)—C(11)—C(21)	118.1 (2)	P(1)—C(11)—C(61)	121.9 (2)	P(1)—C(12)—C(22)	121.4 (2)		
P(1)—C(12)—C(62)	119.1 (2)	P(1)—C(13)—C(23)	118.6 (2)	P(1)—C(13)—C(63)	122.9 (2)		
P(2)—C(14)—C(24)	119.0 (2)	P(2)—C(14)—C(64)	121.9 (2)	P(2)—C(15)—C(25)	115.5 (2)		
P(2)—C(15)—C(65)	124.9 (2)	P(2)—C(16)—C(26)	117.8 (2)	P(2)—C(16)—C(66)	123.8 (2)		
Pd—C(1)—O(1)	127.4 (2)	Pd—C(1)—O(2)	110.7 (2)	O(1)—C(1)—O(2)	122.0 (1)		
C(1)—O(2)—C(2)	115.7 (2)	Pd—O(3)—C(3)	114.2 (2)	O(3)—C(3)—O(4)	124.2 (2)		
O(3)—C(3)—C(4)	114.5 (2)	O(4)—C(3)—C(4)	121.3 (3)				
Phenyl rings	1	2	3	4	5	6	Overall mean
C—C—C (mean)	120.00 (8)	119.84 (7)	120.03 (8)	120.00 (8)	119.95 (9)	119.98 (8)	119.96 (3)
Angle at atom		P-bonded	<i>ortho</i>	<i>meta</i>	<i>para</i>		
C—C—C (mean)		119.27 (7)	120.07 (6)	120.26 (6)	120.23 (8)		

Fig. 1. Perspective view of the molecule of Pd(COOCH<sub>3</sub>)(OCOCH<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>.

The central metal atom shows a slightly distorted square-planar coordination, with the two P atoms lying above and C(1) and O(3) lying below this plane (see Table 3). The triphenylphosphine groups, which are *trans*, display a staggered conformation with respect to the P—P axis. The acetate and the methoxycarbonyl groups, which are strictly planar, form dihedral angles of 72 and 84° respectively with the mean coordination plane of the metal.

Table 3. Deviations from the mean planes (Å) of palladium and its four coordinated atoms, of the acetate and of the methoxycarbonyl groups

In each group all atoms were used to calculate the mean plane.					
Pd	0.008 (2)	O(1)	0.007 (3)	O(3)	−0.001 (3)
P(1)	0.034 (2)	O(2)	0.011 (3)	O(4)	−0.002 (3)
P(2)	0.033 (2)	C(1)	−0.013 (3)	C(3)	0.004 (5)
C(1)	−0.042 (3)	C(2)	−0.005 (7)	C(4)	−0.001 (8)
O(3)	−0.035 (3)				

The main feature of the complex is the presence of the acetate group as a unidentate ligand; to our knowledge, all other reported complexes of Pd show this group only as a bidentate ligand, e.g. Pd(OCOCH<sub>3</sub>)<sub>2</sub> (Skapski & Smart, 1970), Pd(OCOCH<sub>3</sub>)( $\eta$ -C<sub>3</sub>H<sub>5</sub>)<sub>2</sub> (Churchill & Mason, 1964) and {Pd(OCOCH<sub>3</sub>)[ONC(CH<sub>3</sub>)<sub>2</sub>]}<sub>3</sub>·0.5C<sub>6</sub>H<sub>6</sub> (Mawby & Pringle, 1971), where the acetate groups form chelate rings through bridging bonds. In this case, however, the classification of this group as a unidentate rather than an unsymmetrical bidentate ligand, is assured by the long O(4)···Pd contact, 2.99 Å, which is almost identical to the sum (3.10 Å) of the van der Waals radii (Bondi, 1964). This contact is even slightly larger than the corresponding contacts involving

the carbonyl O atom (2.87 Å) and the ether O atom (2.78 Å) of the methoxycarbonyl group.

The Pd—O(3) bond length, 2.116 (3) Å, is comparable with the largest values observed in complexes with bridging acetate ligands; in this case it could be related to the short length of the opposite Pd—C bond, 1.984 (4) Å, in agreement with a rather strong *trans* effect of the  $\sigma$ -bonded C atom. Presumably, the same effect is responsible for a partial shift of the electron charge from O(3) to the O(3)—C(3) bond, and from the C(3)=O(4) double bond to O(4), as indicated by the short O—C lengths of 1.285 (4) and 1.232 (4) Å, respectively. The possible interaction of O(4) with the metal orbitals out of the coordination plane cannot be excluded even though it should be very weak, whereas the completely full  $d_z$  axial orbital could exert a strong repulsive effect. No perturbation is observed in the geometry of the methoxycarbonyl ligand [C(1)—O(1), 1.194 (5) and C(1)—O(2), 1.353 (4) Å].

The mean Pd—P and P—C bond lengths, 2.339 (1) and 1.831 (3) Å, and the mean C—C(P-bonded)—C bond angle, 119.27 (7)°, agree with usual values.

The last two values are in good agreement with the molecular geometries of substituted benzene derivatives discussed by Domenicano, Vaciago & Coulson (1975).

The phenyl groups are located, as in other complexes, in such a way that a H atom is directed towards

the central metal atom; in this structure, however, all of the observed Pd...H distances are greater than 3.0 Å, a value corresponding to the sum of the van der Waals radii.

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### (1,6-Dichloro-1,5-cyclooctadiene)(2,4-pentanedionato)rhodium(I)

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**Abstract.** [Rh(C<sub>8</sub>H<sub>10</sub>Cl<sub>2</sub>)(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)], C<sub>13</sub>H<sub>17</sub>Cl<sub>2</sub>O<sub>2</sub>Rh, monoclinic,  $P2_1/c$ ,  $a = 14.96$  (2),  $b = 11.83$  (2),  $c = 18.22$  (2) Å,  $\beta = 116.1$  (2)°,  $V = 2896$  Å<sup>3</sup>,  $Z = 8$ ,  $M_r = 379.1$ , m.p. 406–407 K,  $D_m = 1.70$ ,  $D_x = 1.77$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 1.532$  mm<sup>-1</sup>. The structure has been solved by the heavy-atom method and refined to  $R = 0.087$  for 3808 observed reflexions. The structure contains two independent molecules.

**Introduction.** As part of a systematic study of the correlation between the stereochemistry and catalytic activity of 1,3-substituted Rh chelates (Ječný & Huml, 1974, 1978), the structure of the title compound has been investigated.

A yellow crystal (0.5 × 0.37 × 0.17 mm) was prepared in the laboratory of Dr Hrabák at this Institute. A series of Weissenberg photographs revealed Laue symmetry  $2/m$ , an initial unit cell and the systematic absences  $h0l$ ,  $l = 2n + 1$ ;  $0k0$ ,  $k = 2n + 1$ , the latter giving the space group as  $P2_1/c$ . Least-squares-refined unit-cell parameters were obtained from reflexions measured on a Hilger & Watts Y230/FA126 four-circle automatic off-line diffractometer. Intensities were collected to  $\sin \theta_{\max}/\lambda = 0.61$  Å<sup>-1</sup> [ $\lambda(\text{Mo } K\alpha) = 0.71069$  Å, Zr filter, variable  $\theta$ – $2\theta$  scan, room temperature,  $b$  parallel to  $\varphi$  diffractometer axis]. During the measurement the crystal showed a 10% decrease in intensity of the reference reflexion 040, probably due to