Table 4. *Torsion angles* (°) *in the cyclopentane ring*

φ_0	C(13)–C(9)–C(10)–C(11)	16·62 (2)
φ_1	C(9)–C(10)–C(11)–C(12)	−36·99 (4)
φ_2	C(10)–C(11)–C(12)–C(13)	43·56 (4)
φ_3	C(11)–C(12)–C(13)–C(9)	−33·02 (1)
φ_4	C(12)–C(13)–C(9)–C(10)	10·37 (2)

Conformation parameter (phase angle of pseudorotation): $\Delta = 135°$; $\tan \Delta/2 = (\varphi_2 + \varphi_4) - (\varphi_1 + \varphi_3)/2\varphi_0\,(\sin 36° + \sin 72°)$ (Altona, Geise & Romers, 1968)

The values of the torsion angles (Table 4) in the cyclopentane ring [C(9) to C(13)] indicate a conformation intermediate between a half-chair and an envelope (Gallen, Carrell, Zacharias, Glusker & Stephani, 1975), with a maximum puckering at C(11). The C—C distances of 1·53 Å (mean value) and the C—C—C angles of 105° (mean value) fall within the range of values found for other cyclopentane rings (Altona, Geise & Romers, 1968).

Both phenyl groups are planar and form angles of 59·8 and 31·8° with the C(14), C(15), C(16), C(22) plane. Steric interactions prevent the phenyl rings from being coplanar with this plane. The average C—C distance is 1·38 Å with no systematic variations, and C—C—C angles range from 118 to 122°.

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Acta Cryst. (1980). B**36**, 1395–1397

The Structure of Bis(diphenylphosphinoacetato)palladium(II)

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(*Received* 26 *November* 1979; *accepted* 28 *January* 1980)

Abstract

$C_{28}H_{24}O_4P_2Pd$, $[Pd(C_{14}H_{12}O_2P)_2]$, is monoclinic, space group $P2_1/c$, with $a = 9·494\ (3)$, $b = 23·66\ (1)$, $c = 12·673\ (3)$ Å, $\beta = 116·33\ (2)°$, $Z = 4$. The structure was refined to $R = 0·048$ for 2664 counter reflections $[I > 1·96\sigma(I)]$. The Pd atom is surrounded in a distorted *cis* square-planar arrangement by two P [Pd—P 2·235 (2) Å] and two O atoms [Pd—O 2·076 (5) Å] belonging to two chelating diphenylphosphinoacetato anions.

Introduction

Spectral and other indirect evidence (Růžičková & Podlahová, 1978; Podlahová & Podlaha, 1979) indicate that phosphinoacetic acids and their anions can bond to transition-metal ions as unidentate (P or O) or chelating (P, O) ligands. The unidentate P coordination was confirmed by the structure determination of dibromobis(diphenylphosphinoacetic acid)-palladium(II) (Podlahová, Loub & Ječný, 1979). As the properties of the related complex, bis(diphenylphosphinoacetato)palladium(II), indicated the presence of chelating ligands, the structure determination of this

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0567-7408/80/061395-03$01.00

compound was undertaken to verify the second possible type of phosphinoacetate coordination.

Experimental

The compound studied is precipitated on mixing aqueous solutions containing stoichiometric amounts of $K_2[PdCl_4]$ and sodium diphenylphosphinoacetate. The microcrystalline precipitate could not be crystallized satisfactorily. To obtain single crystals, the slow reaction of the Pd^{II} complex of diethylenetriaminepentaacetic acid (dtpa) with sodium diphenylphosphinoacetate was employed: single crystals were grown at room temperature on prolonged standing of a solution containing 2×10^{-4} *M* $Pd(ClO_4)_2$, 2×10^{-4} *M* dtpa, 4×10^{-4} *M* diphenylphosphinoacetic acid and 0·1 *M* acetate buffer of pH = 5·5, kept in a closed vessel.

The cell dimensions were determined by the least-squares method from 15 reflections measured on an automatic Syntex $P2_1$ diffractometer (Cu $K\alpha$ radiation, graphite monochromator). Intensities were collected from a crystal 0·05 × 0·05 × 0·1 mm for $0 < \theta \leq 40°$. D_m = 1·564 Mg m^{-3} was determined pycnometrically in xylene; D_x = 1·562 Mg m^{-3}. The space group $P2_1/c$ was assumed from systematic absences: *h*0*l*, *l* odd; 0*k*0, *k* odd. Only Lorentz–polarization corrections were employed (μ = 8·51 mm^{-1}).

Structure determination

The position of the Pd atom was obtained from a Patterson synthesis. The remaining non-H atoms were located by a Fourier synthesis and refined by the least-squares method to $R = \sum ||F_o| - |F_c||/\sum |F_o|$ = 0·071 with isotropic temperature factors. Anisotropic temperature factors were refined to *R* = 0·056. The refinement was continued until the changes in the parameters were <0·3σ. The positions of all H atoms were obtained from a difference synthesis. They were assigned the isotropic temperature factors of the atoms to which they are bonded. After refinement of the positions of all the atoms, the final values were *R* = 0·048 and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ = 0·063 with individual weights $w = 1/\sigma^2$. A final difference map showed a maximum peak of 0·3 e Å^{-3}.

Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The Patterson and electron density maps and the full-matrix least-squares refinement were computed with the *TLS* programs (Sklenář, 1973) and interatomic distances and angles with *ORFFE* (Busing, Martin & Levy, 1964) on an ICL 4-72 computer.

Table 1. *Atomic coordinates* (×10⁴, *for* H ×10³) *with e.s.d.'s in parentheses, and isotropic temperature factors for the* H *atoms*

	x	*y*	*z*	*B* (Å²)
Pd	4245·7 (6)	3251·7 (2)	1945·6 (4)	
P(1)	4792 (2)	3094 (1)	3828 (2)	
P(2)	2346 (2)	3903 (1)	1356 (2)	
O(1)	6050 (5)	2676 (2)	2311 (4)	
O(2)	7575 (6)	1998 (2)	3472 (5)	
O(3)	3990 (6)	3359 (2)	242 (4)	
O(4)	2547 (6)	3649 (2)	−1590 (4)	
C(1)	5636 (9)	2388 (3)	3978 (8)	
C(2)	6515 (8)	2347 (3)	3207 (7)	
C(3)	6337 (8)	3555 (3)	4822 (6)	
C(4)	6318 (11)	4126 (4)	4510 (8)	
C(5)	7557 (15)	4470 (5)	5215 (10)	
C(6)	8810 (12)	4269 (5)	6179 (9)	
C(7)	8831 (11)	3714 (6)	6491 (10)	
C(8)	7597 (11)	3356 (5)	5815 (9)	
C(9)	3287 (8)	3050 (3)	4329 (6)	
C(10)	3510 (11)	3248 (4)	5420 (8)	
C(11)	2282 (12)	3172 (4)	5769 (9)	
C(12)	936 (11)	2897 (4)	5043 (9)	
C(13)	722 (10)	2699 (4)	3958 (9)	
C(14)	1883 (9)	2780 (3)	3587 (8)	
C(15)	1442 (9)	3764 (4)	−231 (6)	
C(16)	2756 (8)	3585 (3)	−576 (6)	
C(17)	822 (7)	3924 (3)	1852 (6)	
C(18)	1160 (9)	4146 (3)	2959 (7)	
C(19)	36 (10)	4146 (3)	3378 (8)	
C(20)	−1434 (10)	3930 (4)	2688 (9)	
C(21)	−1802 (10)	3708 (4)	1584 (9)	
C(22)	−685 (9)	3717 (4)	1150 (8)	
C(23)	3151 (8)	4612 (3)	1509 (6)	
C(24)	4572 (9)	4689 (4)	1460 (8)	
C(25)	5237 (11)	5221 (3)	1555 (9)	
C(26)	4428 (11)	5682 (4)	1666 (8)	
C(27)	3006 (11)	5620 (3)	1708 (9)	
C(28)	2371 (10)	5084 (3)	1633 (8)	
H(1)	474 (10)	213 (4)	363 (8)	2·50
H(2)	636 (9)	232 (4)	484 (8)	2·50
H(4)	540 (11)	428 (4)	385 (9)	4·14
H(5)	754 (13)	490 (5)	516 (10)	4·82
H(6)	969 (12)	452 (4)	662 (9)	4·60
H(7)	962 (13)	353 (4)	721 (10)	4·76
H(8)	769 (11)	296 (4)	615 (9)	4·60
H(10)	435 (11)	345 (4)	583 (9)	3·42
H(11)	259 (11)	327 (4)	664 (9)	4·52
H(12)	5 (11)	288 (4)	525 (9)	4·52
H(13)	−37 (11)	261 (4)	337 (9)	3·73
H(14)	150 (9)	274 (3)	272 (8)	2·67
H(15)	65 (10)	347 (4)	−40 (8)	2·55
H(16)	86 (10)	410 (4)	−58 (8)	2·55
H(18)	215 (10)	437 (4)	341 (8)	2·73
H(19)	40 (10)	429 (4)	421 (8)	3·51
H(20)	−216 (11)	389 (4)	311 (9)	3·99
H(21)	−288 (11)	362 (4)	106 (8)	4·32
H(22)	−101 (10)	350 (4)	36 (8)	3·16
H(24)	523 (10)	439 (4)	135 (8)	3·24
H(25)	619 (11)	522 (4)	147 (8)	4·09
H(26)	484 (11)	606 (4)	174 (8)	4·16
H(27)	237 (11)	595 (4)	179 (9)	4·09
H(28)	130 (10)	501 (4)	164 (8)	3·45

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Pd–P(1)	2·236 (2)	P(1)–Pd–P(2)	104·1 (1)
–P(2)	2·234 (2)	P(1)–Pd–O(1)	82·8 (1)
–O(1)	2·074 (5)	P(1)–Pd–O(3)	173·4 (2)
–O(3)	2·078 (5)	P(2)–Pd–O(1)	172·8 (1)
P(1)–C(1)	1·826 (8)	P(2)–Pd–O(3)	82·1 (2)
–C(3)	1·815 (8)	O(1)–Pd–O(3)	91·0 (2)
–C(9)	1·806 (8)	Pd–P(1)–C(1)	98·5 (3)
P(2)–C(15)	1·832 (8)	Pd–P(1)–C(3)	112·0 (3)
–C(17)	1·816 (8)	Pd–P(1)–C(9)	122·6 (2)
–C(23)	1·817 (7)	Pd–P(2)–C(15)	99·1 (3)
C(1)–C(2)	1·545 (13)	Pd–P(2)–C(17)	123·5 (2)
–H(1)	0·98 (9)	Pd–P(2)–C(23)	111·2 (3)
–H(2)	1·01 (9)	C(1)–P(1)–C(3)	107·2 (4)
C(2)–O(1)	1·282 (9)	C(1)–P(1)–C(9)	106·8 (4)
–O(2)	1·227 (10)	C(3)–P(1)–C(9)	108·2 (4)
C(15)–C(16)	1·554 (12)	C(15)–P(2)–C(17)	109·1 (4)
–H(15)	0·98 (9)	C(15)–P(2)–C(23)	104·6 (4)
–H(16)	0·96 (9)	C(17)–P(2)–C(23)	107·4 (4)
C(16)–O(3)	1·286 (9)	O(1)–C(2)–O(2)	124·7 (6)
–O(4)	1·219 (9)	O(3)–C(16)–O(4)	124·4 (6)

Results and discussion

The final atomic parameters are given in Table 1,* bond distances and angles in Table 2.

The structure consists of discrete molecules of the complex (Fig. 1) packed at van der Waals distances. The Pd atom is located in a distorted *cis* square-planar environment formed by two P,O-chelating diphenylphosphinoacetate anions of identical conformation. The PdP_2O_2 moiety is almost planar, the largest deviation from the appropriate least-squares plane being 0·03 Å for Pd. The deviations from the ideal *cis* square arrangement can be primarily attributed to overcrowding on *cis* P atoms due to their bulky phenyl substituents. The two chelate rings cannot contribute significantly to the distortion as these rings are not strained and the distances and angles at donor atoms are close to those for the related complex with unidentate ligands, *cis*-dichlorobis(dimethylphenylphosphine)palladium(II) (Martin & Jacobson, 1971). Compared with the Pd^{II} complex which contains the ligand as the unidentate P donor, the following variations of the distances and angles can be attributed to the chelation: (*a*) the Pd–P distance is shortened by 0·09 Å which is more than can be explained by the influence of a *trans* effect alone (Martin & Jacobson, 1971); (*b*) the C(1)–C(2)–O(1) angle is increased by almost 4°; (*c*) the distortion of the tetrahedral angles at the P atom spans the significantly broader range of 99 to 123·5° [103·5–114·5° for dibromobis(diphenylphosphinoacetic acid)palladium(II) (Podlahová, Loub & Ječný, 1979)].

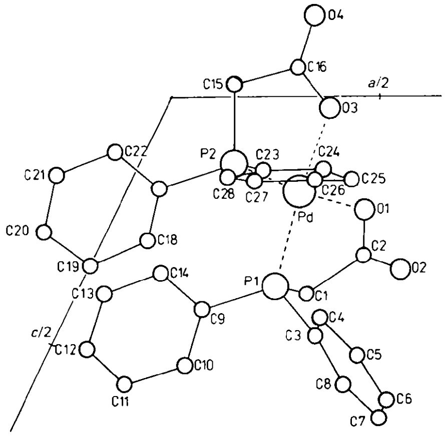

Fig. 1. Projection of the structure along **b** (without H atoms).

The C atoms in the phenyl rings show no significant deviations from the appropriate least-squares planes, the largest deviation being 0·02 Å for C(22). The angles within the rings are all $<3\sigma$ from the normal value. No graphite-like interactions between the phenyl rings exist within the structure.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35127 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.