

of 152 parameters based on  $F^2$  using *XTAL2.4* (Hall & Stewart, 1988). Scale factor, positional parameters for all atoms, anisotropic temperature factors for non-H atoms and isotropic temperature factors for H atoms refined. Also isotropic secondary-extinction correction applied and refined [final value 0.20 (1)]. On  $F^2$ , final  $R = 0.042$ ,  $wR = 0.067$ ,  $w = 1.0/\{\sigma(F^2)\}^2$  where  $\sigma(F^2) = \sigma(I)/(2.0|F|)$ ,  $S = 1.47$ . A structure-factor calculation after the refinement gave  $R = 0.036$ .  $(\Delta/\sigma)_{\max} = 0.01$ ,  $\Delta\rho_{\max} = 0.56$ ,  $\Delta\rho_{\min} = -0.50 \text{ e \AA}^{-3}$ . Scattering factors from *International Tables for X-ray Crystallography* (1974), including those for bonded H atoms. Atomic parameters of non-H atoms are given in Table 1,\* and selected

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and equations of, and deviations from, least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51905 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bond lengths and angles are listed in Table 2. The molecular geometry is shown in Fig. 1.

**Related literature.** A different crystalline modification of this compound (form ii) has been reported by Muthiah, Mazumdar & Chaudhuri (1983). The molecules are identical within experimental error, except for some minor differences in the bonds to Zn.

#### References

- CARRELL, H. L. (1978). *Crystallographic Programs*. The Institute for Cancer Research, Philadelphia, PA 19111, USA.  
 HALL, S. R. & STEWART, J. M. (1988). Editors. *XTAL2.4 User's Manual*. Univs. of Western Australia, Australia, and Maryland, USA.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)  
 MUTHIAH, P. T., MAZUMDAR, S. K. & CHAUDHURI, S. (1983). *J. Inorg. Biochem.* **19**, 237–246.  
 TAYLOR, M. R. (1973). *Acta Cryst.* **B29**, 884–890.

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## Structure of $[P(CH_3)(C_6H_5)_3]_2\{[IPd[CC(=O)(OCH_3)]_4\}_2$

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**Abstract.** Methyltriphenylphosphonium di- $\mu$ -iodo-bis[(tetramethyl 1,2,3,4-buta-1,3-dienetetracarboxylate- $C^1, C^4$ )palladium],  $[P(CH_3)(C_6H_5)_3]_2\{[Pd(C_{12}H_{12}O_8)I]_2\}$ ,  $M_r = 1589.7$ , triclinic,  $P\bar{1}$ ,  $a = 10.811$  (5),  $b = 12.218$  (6),  $c = 14.060$  (5) Å,  $\alpha = 98.61$  (4),  $\beta = 108.98$  (3),  $\gamma = 106.90$  (4)°,  $U = 1618$  (1) Å<sup>3</sup>,  $Z = 1$ , one-half molecule/asymmetric unit,  $D_x = 1.631 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 15.96 \text{ cm}^{-1}$ ,  $F(000) = 788$ ,  $T = 292 \text{ K}$ ,  $R = 0.0331$  for 5828 observed reflections. Each unit cell contains two triphenylmethylphosphonium cations and a dinuclear palladium complex dianion with the Pd atoms bridged by two  $\mu$ -I atoms and each Pd atom chelated by a diacetylido dianion formed from dimethyl acetylenedicarboxylate. The Pd—I distances are 2.690 (1) and 2.677 (1) Å. The Pd structure coordination geometry is close to square planar

with I—Pd—C angles of 96.6 (1) and 175.9 (1)°, a C—Pd—C angle of 79.3 (1)°, and an I—Pd—I angle of 86.4 (1)°. The Pd atom is 0.006 Å out of the plane of the I and C atoms. The cation shows the expected tetrahedral configuration for a four-ligand phosphonium ion with an average C—P—C angle of 109.4 (1)°.

**Experimental.** The synthesis involved reaction of the known neutral metallocycle  $[Pd\{C_4(CO_2CH_3)_4\}-(PPh_3)_2]_n$  (Moseley & Maitlis, 1974) (91 mg, 0.1 mmol) with excess methyl iodide in chloroform at 296 K. Evaporation of the volatiles and recrystallization of the residue from acetone/diethyl ether provided  $[P(CH_3)(C_6H_5)_3]_2\{[IPd[CC(=O)(OCH_3)]_4\}_2$  in 78% isolated yield. <sup>1</sup>H NMR ( $CDCl_3$ ):  $\delta$  7.6–7.7 (*m*, ~30H), 3.57 (*s*, 12H), 3.52 (*s*, 12H), 3.33 (*d*,  $J_{Ph} = 12 \text{ Hz}$ , 6H). Crystals were obtained from slow diffusion of pentane into a  $CCl_4$ -

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Table 1. Atomic coordinates ( $\times 10^4$ ) and thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Pd}(\text{CH}_3)(\text{C}_6\text{H}_5)_3]_2^-$   $[\{\text{IPd}[\text{CC}(\text{=O})(\text{OCH}_3)_4\}_2]$

	x	y	z	$U^*$
Pd	5920.9 (2)	5995.0 (2)	1442.2 (2)	31.8 (1)
I	5487.0 (3)	3781.4 (2)	429.0 (2)	46.3 (1)
P(1)	1004.4 (9)	8106.1 (8)	2046.1 (7)	40.5 (4)
O(1)	6459 (3)	4140 (3)	3439 (2)	65 (1)
O(2)	8157 (3)	4594 (2)	2818 (2)	51 (1)
O(3)	7313 (4)	7017 (4)	5329 (2)	98 (2)
O(4)	9107 (4)	6689 (4)	5114 (3)	89 (2)
O(5)	7016 (4)	9786 (3)	3747 (2)	77 (2)
O(6)	8393 (6)	9281 (4)	4969 (3)	143 (3)
O(7)	6964 (3)	9232 (2)	1596 (2)	54 (1)
O(8)	4761 (3)	8578 (2)	1510 (2)	54 (1)
C(1)	6962 (3)	5906 (3)	2888 (2)	35 (1)
C(2)	7344 (4)	6866 (3)	3664 (3)	39 (1)
C(3)	7016 (4)	7868 (3)	3336 (3)	38 (1)
C(4)	6328 (3)	7636 (3)	2298 (3)	36 (1)
C(5)	7160 (4)	4806 (3)	3097 (2)	42 (1)
C(6)	8058 (4)	6879 (3)	4775 (3)	47 (2)
C(7)	7551 (4)	9037 (3)	4104 (3)	49 (2)
C(8)	5915 (4)	8518 (3)	1787 (3)	41 (1)
C(9)	8342 (5)	3491 (4)	2946 (4)	72 (2)
C(10)	7976 (10)	7140 (8)	6427 (4)	162 (6)
C(11)	7604 (7)	10998 (4)	4383 (4)	89 (3)
C(12)	6675 (6)	10168 (5)	1158 (5)	89 (3)
C(21)	-1238 (2)	6712 (3)	205 (2)	57 (2)
C(22)	-1829	5964	-807	69 (2)
C(23)	-969	5664	-1270	67 (2)
C(24)	483	6111	-722	61 (2)
C(25)	1075	6859	289	51 (2)
C(26)	215	7160	753	41 (1)
C(31)	1162 (2)	6767 (2)	3449 (2)	49 (2)
C(32)	1808	6184	4121	57 (2)
C(33)	3169	6246	4270	65 (2)
C(34)	3885	6890	3747	75 (2)
C(35)	3239	7472	3076	60 (2)
C(36)	1878	7411	2927	39 (1)
C(41)	3291 (3)	10227 (3)	2972 (2)	70 (2)
C(42)	4122	11346	2984	81 (2)
C(43)	3854	11718	2071	82 (3)
C(44)	2753	10971	1147	91 (3)
C(45)	1921	9852	1134	74 (2)
C(46)	2190	9480	2047	46 (2)
C(51)	-287 (4)	8429 (4)	2444 (4)	60 (2)

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

$\text{CH}_2\text{Cl}_2$  (1:1) solution of the complex; yellow,  $0.40 \times 0.38 \times 0.35$  mm. Nicolet *R3m* diffractometer, graphite monochromator, unit cell from least-squares fit of angular settings of 25 reflections ( $20 \leq 2\theta \leq 30^\circ$ ). 6623 reflections,  $4 \leq 2\theta \leq 52^\circ$ ; collected for  $-14 \leq h \leq +14$ ,  $-14 \leq k \leq +14$ ,  $0 \leq l \leq +18$  using  $\omega$  scans, standard reflections  $\bar{6}11$ ,  $10\bar{7}$ ,  $373$  with  $<1\%$  variation. Empirical absorption correction ( $\mu = 15.96 \text{ cm}^{-1}$ ,  $T_{\text{max}}/T_{\text{min}} = 1.04$ ) based on  $\psi$ -scan measurements. 5828 unique observed reflections [ $F_o > 5\sigma(F_o)$ ],  $R_{\text{int}} = 0.0404$ . Multisolution; direct methods (*SOLV*), blocked-cascade least squares on  $F$ , complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). All non-H atoms anisotropic, phenyl rings were rigid bodies, H atoms idealized and updated ( $\text{C-H} = 0.96 \text{ \AA}$ ,  $U = 1.2U$  of attached C). Least-squares refinement on 343 parameters;  $R_F = 3.31\%$ ,  $wR_F = 4.96\%$ ,  $S = 1.25$ ,  $w^{-1} = \sigma^2(F_o) + gF_o^2$ ,  $g = 0.0002$ ;  $(\Delta/\sigma)_{\text{max}} = 0.524$ ;  $(\Delta\rho)_{\text{max}} = 0.849$ ,  $(\Delta\rho)_{\text{min}} = -1.037 \text{ e \AA}^{-3}$ ; *SHELXTL* program library (Sheldrick, 1984).

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $[\text{Pd}(\text{CH}_3)(\text{C}_6\text{H}_5)_3]_2[\{\text{IPd}[\text{CC}(\text{=O})(\text{OCH}_3)_4\}_2]$

Pd-I	2.690 (1)	O(4)-C(6)	1.183 (6)
Pd-C(1)	2.015 (3)	O(5)-C(7)	1.296 (6)
Pd-C(4)	2.021 (3)	O(5)-C(11)	1.443 (5)
Pd-I(a)	2.677 (1)	O(6)-C(7)	1.188 (5)
P(1)-C(26)	1.777 (3)	O(7)-C(8)	1.346 (5)
P(1)-C(36)	1.780 (3)	O(7)-C(12)	1.442 (7)
P(1)-C(46)	1.791 (3)	O(8)-C(8)	1.208 (5)
P(1)-C(51)	1.783 (5)	C(1)-C(2)	1.333 (5)
O(1)-C(5)	1.209 (5)	C(1)-C(5)	1.477 (6)
O(2)-C(5)	1.338 (6)	C(2)-C(3)	1.467 (6)
O(2)-C(9)	1.447 (6)	C(2)-C(6)	1.496 (5)
O(3)-C(6)	1.317 (7)	C(3)-C(4)	1.346 (5)
O(3)-C(10)	1.437 (7)	C(3)-C(7)	1.481 (5)
		C(4)-C(8)	1.476 (5)
I-Pd-C(1)	96.6 (1)	C(2)-C(3)-C(4)	113.7 (3)
I-Pd-C(4)	175.9 (1)	C(2)-C(3)-C(7)	120.4 (3)
C(1)-Pd-C(4)	79.3 (1)	C(4)-C(3)-C(7)	125.6 (4)
I-Pd-I(a)	86.4 (1)	Pd-C(4)-C(3)	116.0 (3)
C(1)-Pd-I(a)	176.8 (1)	Pd-C(4)-C(8)	120.6 (2)
C(4)-Pd-I(a)	97.7 (1)	C(3)-C(4)-C(8)	123.4 (3)
Pd-I-Pd(a)	93.6 (1)	O(1)-C(5)-O(2)	123.4 (4)
C(26)-P(1)-C(36)	110.0 (1)	O(1)-C(5)-C(1)	124.0 (4)
C(26)-P(1)-C(46)	107.8 (1)	O(2)-C(5)-C(1)	112.5 (3)
C(36)-P(1)-C(46)	111.9 (1)	O(3)-C(6)-O(4)	122.5 (4)
C(26)-P(1)-C(51)	110.7 (1)	O(3)-C(6)-C(2)	112.0 (4)
C(36)-P(1)-C(51)	108.8 (2)	O(4)-C(6)-C(2)	125.2 (4)
C(46)-P(1)-C(51)	107.6 (2)	O(5)-C(7)-O(6)	122.3 (4)
C(5)-O(2)-C(9)	115.1 (4)	O(5)-C(7)-C(3)	113.8 (3)
C(6)-O(3)-C(10)	115.6 (6)	O(6)-C(7)-C(3)	123.9 (5)
C(7)-O(5)-C(11)	118.0 (3)	O(7)-C(8)-O(8)	122.2 (4)
C(8)-O(7)-C(12)	115.6 (4)	O(7)-C(8)-C(4)	112.1 (3)
Pd-C(1)-C(2)	115.9 (3)	O(8)-C(8)-C(4)	125.6 (3)
Pd-C(1)-C(5)	122.4 (2)	P(1)-C(26)-C(21)	121.2 (1)
C(2)-C(1)-C(5)	121.4 (3)	P(1)-C(26)-C(25)	118.8 (1)
C(1)-C(2)-C(3)	115.1 (3)	P(1)-C(36)-C(31)	118.9 (1)
C(1)-C(2)-C(6)	120.6 (4)	P(1)-C(36)-C(35)	121.1 (1)
C(3)-C(2)-C(6)	124.3 (3)	P(1)-C(46)-C(41)	120.5 (1)
		P(1)-C(46)-C(45)	119.2 (1)

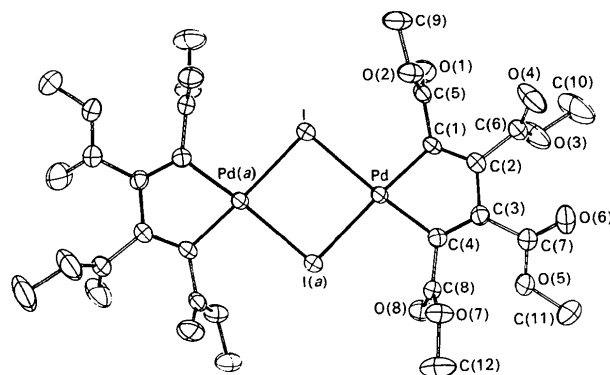


Fig. 1. Structure and labeling scheme for the anionic Pd complex from  $[\text{Pd}(\text{CH}_3)(\text{C}_6\text{H}_5)_3]_2[\{\text{IPd}[\text{CC}(\text{=O})(\text{OCH}_3)_4\}_2]$  with thermal ellipsoids drawn at the 40% probability level.

Atomic and equivalent isotropic thermal parameters are given in Table 1 and bond lengths and angles are given in Table 2. Fig. 1 shows the labeled molecular structure of the crystal. A unit-cell packing diagram is shown in Fig. 2.\*

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51927 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

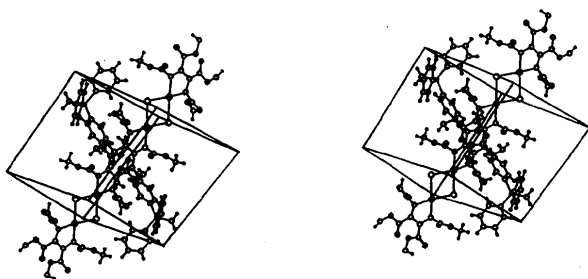


Fig. 2. Unit-cell packing diagram for  $[P(CH_3)(C_6H_5)_3]_2\{[IPd-CC(=O)(OCH_3)_4]_2\}$  as viewed with the  $z$  axis vertical, the  $x$  axis to the right and the  $y$  axis to the left.

**Related literature.** Two related mononuclear structures of palladium metalocycles which contain methyl carboxylate substituents have been reported.

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## Bromo( $\eta^2$ -cyclenphosphoranido)(triphenylphosphino)platinum(II)

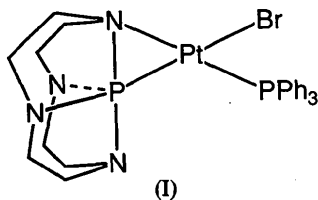
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**Abstract.**  $[PtBr(C_8H_{16}N_4P)(C_{18}H_{15}P)]$ ,  $M_r = 736.5$ , monoclinic,  $P2_1/n$ ,  $a = 11.651(5)$ ,  $b = 14.301(5)$ ,  $c = 15.527(7)$  Å,  $\beta = 93.81(4)^\circ$ ,  $V = 2581(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.90$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $\mu(Mo K\alpha) = 71.70$  cm<sup>-1</sup>,  $F(000) = 1432$ ,  $T = 295$  K, final  $R = 0.043$  for 3399 observed reflections. The cyclenphosphoranido ligand coordinates to the Pt atom through P and one of its N atoms with Pt—P and Pt—N bonds of 2.230(3) and 2.107(8) Å, respectively. A Br atom and a triphenylphosphine group complete the distorted square-planar geometry about Pt, with Pt—Br and Pt—P distances of 2.523(2) and 2.225(3) Å, respectively.

**Experimental.** The title compound (I) was prepared by the reaction of the corresponding Pt—Cl complex with bromobutane, accompanied by elimination of chlorobutane.



(I)

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$[Pd\{CC(=O)(OCH_3)\}_4]$  [norbornadiene] was reported by Brown, Itoh, Suzuki, Hirai & Ibers (1978) and  $[Pd\{CC(=O)(OCH_3)\}_4][C_5H_4PPh_3]$  was reported by Pierpont, Downs, Itoh, Nishiyama & Ishii (1976).

### References

- BROWN, L. D., ITOH, K., SUZUKI, H., HIRAI, K. & IBERS, J. A. (1978). *J. Am. Chem. Soc.* **100**, 8232–8238.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)  
MOSELEY, K. & MAITLIS, P. M. (1974). *J. Chem. Soc. Dalton Trans.* pp. 169–174.  
PIERPONT, C. G., DOWNS, H. H., ITOH, K., NISHIYAMA, H. & ISHII, Y. (1976). *J. Organomet. Chem.* **124**, 93–101.  
SHELDRICK, G. M. (1984). *SHELXTL Users Manual*, version 5.1. Nicolet XRD Corp., Madison, WI, USA.

Crystals of the title compound are colorless polyhedra. Unit-cell parameters by least-squares fit of 25 reflections in the range  $10 < 2\theta < 25^\circ$ . Crystal dimensions  $0.20 \times 0.30 \times 0.10$  mm, space group  $P2_1/n$  from systematic absences ( $0k0$ ,  $k$  odd;  $h0l$ ,  $h+l$  odd); automatic Nicolet  $R3m/V$  diffractometer, graphite-monochromated  $Mo K\alpha$  radiation,  $\theta/2\theta$  scan mode, 4952 reflections measured, 4566 independent reflections in the range  $3 < 2\theta < 50^\circ$ ,  $R_{int} = 0.014$ ,  $hkl$  range  $h - 13 \rightarrow 13$ ,  $k 0 \rightarrow 17$ ,  $l 0 \rightarrow 18$ , 3399 observed reflections with  $I > 3\sigma(I)$ ,  $\sigma(I)$  from counting statistics; three standard reflections remeasured after every 100 reflections did not show any significant change ( $\sim 2\%$ ) in intensity during data collection; Lorentz-polarization correction, absorption correction based on  $\psi$  scans (max., min. transmission = 0.9940, 0.4964), no extinction corrections. Structure solved by direct methods (*SHELXTL-Plus*, Sheldrick, 1988) and subsequent difference Fourier methods. H atoms located in difference Fourier maps, H atoms included in the refinement with geometric constraints in a riding model with isotropic temperature factors fixed at  $0.05$  Å<sup>2</sup>. Final full-matrix least-squares refinement using *SHELXTL-Plus*, all non-H atoms anisotropic, converged to  $R = 0.043$ ,  $wR = 0.050$ ;  $w = 1/[\sigma^2(F_o) + 0.0048(F_o)^2]$ ,  $\sum w(|F_o| - |F_c|)^2$  minimized, 307 parameters,  $S = 0.94$ ,  $(\Delta/\sigma)_{max} = 0.01$ ,