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Structure of Bis(tri-*tert*-butylphosphine)palladium(0)

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Abstract. $[Pd(C_{12}H_{27}P)_2]$, $M_r = 511.038$, monoclinic, $P2_1/a$, $a = 14.389\,(9)$, $b = 13.782\,(10)$, $c = 8.615\,(7)$ Å, $\beta = 123.01\,(6)°$, $V = 1432.51$ Å^3, $Z = 2$, $D_x = 1.190$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ(Mo $K\alpha$) = 7.55 mm^{-1}, $F(000) = 548$, $T = 296$ K, $R = 0.050$, $wR = 0.049$ for 1259 observed reflections. The molecule is centrosymmetric with Pd located at a center of symmetry. The structure is compared with similar bulky tertiary phosphine-coordinated complexes of zero-valent Pd and Pt.

Experimental. A colorless single crystal was obtained by a procedure similar to that described previously (Otsuka, Yoshida, Matsumoto & Nakatsu, 1976). A crystal with approximate dimensions of 0.1 × 0.1 × 0.1 mm was mounted in a glass capillary. All measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo $K\alpha$ radiation and a 12 kW rotating anode generator. Cell constants were obtained from a least-squares refinement using 25 reflections in the range $8 < 2\theta < 26°$. The data were collected at a temperature of 296 ± 1 K using the ω–2θ-scan technique to a maximum 2θ value of 55.0° ($\sin\theta/\lambda = 0.63$ Å^{-1}) corresponding to the range $0 \le h \le 18$, $0 \le k \le 17$, $-12 \le l \le 12$. Scans of $(1.10 + 0.14\tan\theta)°$ were made at a speed of 8.0° min^{-1} (in ω). The weak reflections $[I < 10.0\sigma(I)]$ were rescanned (maximum of two rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. Of the 3181 reflections collected, 2995 were unique ($R_{\rm int} = 0.1153$ based on F^2). Since intensities of three standard reflections measured after very 150 reflections indicated −5.5% decline, a decay correction was made. An empirical absorption correction, based on azimuthal scans of several reflections, was applied with transmission factors ranging from 0.9457 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods, *MITHRIL* (Gilmore, 1984) followed by *DIRDIF* (Beurskens, 1984). The non-H atoms were refined anisotropically. H atoms were included in the calculation of structure factors but were not refined. The full-matrix least-squares refinement minimizing $\sum w(F_o - F_c)^2$, $w = 1/\sigma^2(F_o)$, based on 1259 observed reflections $[I > 3.00\sigma(I)]$ and 124 variable parameters converged with $R = 0.050$, $wR = 0.049$, $S = 1.237$ and $\Delta x_{\max} \le 0.0151\sigma$. $(\Delta\rho)_{\max} = 0.824$ and $(\Delta\rho)_{\min} = -0.630$ e Å^{-3}. Anomalous-dispersion effects were included in F_c. The values for f' and f'' and neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed using the *TEXSAN* crystallographic software package from the Molecular Structure Corporation (1985).

An *ORTEP* drawing of half a molecule is shown in Fig. 1. The atomic coordinates and bonding geometry are given in Tables 1 and 2, respectively.*

Related literature. The Pd atom is located at a center of symmetry with a distance Pd—P of 2.285 (3) Å

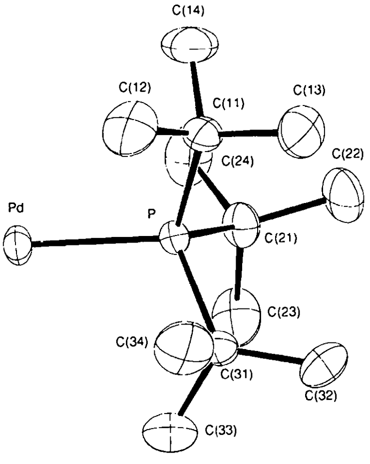

Fig. 1. An *ORTEP* drawing of half a molecule.

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* Lists of structured factors, anisotropic thermal parameters, positional parameters, intramolecular bond angles and distances involving the H atoms and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54577 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0519]

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Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2)

$B_{eq} = (8\pi^2/3)\sum\sum U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ (Fischer & Tillmans, 1988).

	x	y	z	B_{eq}
Pd	0	0	0	3.79 (4)
P	0.1356 (2)	0.1083 (2)	0.1887 (3)	3.19 (8)
C(11)	0.1440 (8)	0.1211 (7)	0.4164 (11)	4.9 (4)
C(12)	0.0265 (10)	0.1255 (9)	0.3742 (16)	8.2 (6)
C(13)	0.2116 (10)	0.2081 (8)	0.5403 (14)	8.2 (6)
C(14)	0.1919 (10)	0.0290 (8)	0.5277 (14)	8.4 (6)
C(21)	0.2769 (7)	0.0657 (7)	0.2424 (13)	4.5 (4)
C(22)	0.3797 (7)	0.1141 (8)	0.4027 (14)	6.9 (5)
C(23)	0.2792 (9)	0.0760 (8)	0.0667 (16)	7.7 (6)
C(24)	0.2851 (9)	−0.0433 (8)	0.2780 (18)	7.8 (6)
C(31)	0.1081 (7)	0.2344 (6)	0.0769 (12)	4.6 (4)
C(32)	0.2042 (9)	0.3048 (7)	0.1616 (15)	7.2 (5)
C(33)	0.0650 (9)	0.2196 (8)	−0.1282 (14)	7.6 (6)
C(34)	0.0099 (10)	0.2807 (8)	0.0753 (16)	8.6 (6)

Table 2. *Bond distances* (Å) *and angles* (°)

Pd—P	2.285 (3)	C(21)—C(22)	1.521 (11)
P—C(11)	1.907 (8)	C(21)—C(23)	1.538 (13)
P—C(21)	1.915 (9)	C(21)—C(24)	1.526 (13)
P—C(31)	1.921 (9)	C(31)—C(32)	1.512 (12)
C(11)—C(12)	1.525 (13)	C(31)—C(33)	1.534 (12)
C(11)—C(13)	1.546 (13)	C(31)—C(34)	1.543 (13)
C(11)—C(14)	1.511 (13)		

P—Pd—P	180.0	P—C(21)—C(22)	117.6 (7)
Pd—P—C(11)	110.1 (3)	P—C(21)—C(23)	108.9 (7)
Pd—P—C(21)	110.8 (3)	P—C(21)—C(24)	107.8 (8)
Pd—P—C(31)	111.8 (3)	C(22)—C(21)—C(23)	108.8 (9)
C(11)—P—C(21)	108.4 (4)	C(22)—C(21)—C(24)	108.6 (9)
C(11)—P—C(31)	108.2 (4)	C(23)—C(21)—C(24)	104.4 (9)
C(21)—P—C(31)	107.4 (4)	P—C(31)—C(32)	117.0 (6)
P—C(11)—C(12)	108.5 (6)	P—C(31)—C(33)	107.4 (7)
P—C(11)—C(13)	116.4 (6)	P—C(31)—C(34)	108.4 (8)
P—C(11)—C(14)	109.0 (7)	C(32)—C(31)—C(33)	109.3 (8)
C(12)—C(11)—C(13)	109.5 (9)	C(32)—C(31)—C(34)	109.4 (8)
C(12)—C(11)—C(14)	104.4 (8)	C(33)—C(31)—C(34)	104.5 (8)
C(13)—C(11)—C(14)	108.4 (8)		

and an angle P—Pd—P of 180.0°. The structures of bulky tertiary phosphine-coordinated Pd or Pt compounds have been determined by several authors to study the steric effects controlling the reactivity of zerovalent noble-metal complexes. The angle P—Pd—P obtained in this study was equal to that found in the same ligands coordinating a Pt compound (Moynihan & Chieh, 1979), and was 3–4° larger than those in the similar Pd or Pt compound with tertiary phosphine ligands consisting of two *tert*-butyl groups and one phenyl group (Otsuka, Yoshida, Matsuda & Nakatsu, 1976; Immirzi & Musco, 1974). The angles in Table 2 show that in each *tert*-butyl group the P—C—C′ angle for the methyl group at the *trans* position to the Pd atom is significantly larger and the angle C—C—C between the other two methyl groups is significantly smaller, reflecting the steric hindrance between the methyl groups.

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Dichloro(3-isopropyl-1,2,4,5,5-pentamethylcyclopenta-1,3-diene)platinum(II)

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Abstract. [$PtCl_2(C_{13}H_{22})$], $M_r = 444.29$, monoclinic, $P2_1/c$, $a = 8.599$ (2), $b = 12.070$ (3), $c = 14.583$ (3) Å, $\beta = 94.64$ (2)°, $V = 1508.5$ (6) Å^3, $Z = 4$, $D_x = 1.956$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 101.09$ cm^{-1}, $F(000) = 848$, $T = 296$ K, $R(F) = 3.08\%$ for 2258 observed reflections and 146 parameters. C(5) is 0.493 Å above the plane formed by C(1), C(2), C(3) and C(4). The structure is a square-planar diolefinic complex of Pt^{II}; none of the five elements of the coordination sphere (two Cl ions, Pt and the midpoints of carbon–carbon double bonds) deviate from planarity by more than 0.02 Å.

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