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Structure of Iodo(methylthiomethylphenyl)bis(triphenylphosphine)palladium(II)

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Abstract. $[PdI\{(C_6H_5)_3P\}_2(C_8H_9S)]$, $M_r = 895{\cdot}12$, monoclinic, $P2_1/c$, $a = 14{\cdot}805\ (2)$, $b = 11{\cdot}070\ (3)$, $c = 24{\cdot}444\ (4)$ Å, $\beta = 104{\cdot}96\ (1)°$, $V = 3870\ (1)$ Å^3, $Z = 4$, $D_m = 1{\cdot}52$, $D_x = 1{\cdot}536$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 14{\cdot}2$ cm^{-1}, $F(000) = 1792$, $T = 295$ K, $R = 0{\cdot}0381$ for 3802 observed reflections with $I > 2{\cdot}5\sigma(I)$. The Pd atom is coordinated in a square-planar fashion by two triphenylphosphine ligands, an iodine atom and a methylthiomethylphenyl group. The triphenylphosphine ligands are in *trans* positions. No short non-bonding interactions between Pd and S are observed.

Introduction. In the course of research into the cross-coupling reaction (Negishi, 1978) catalyzed by $Pd(PPh_3)_4$, we isolated an intermediate $Pd(C_6H_4CH_2SCH_3)(PPh_3)_2I$ by reacting the organic halide [*o*-$C_6H_4(CH_2SCH_3)I$] with excess of $Pd(PPh_3)_4$. We undertook this X-ray analysis to find out whether the coordination geometry about the Pd atom is square-planar or square-based pyramidal with an intramolecularly coordinated S atom in apical position.

Experimental. Crystals obtained by the vapour diffusion method, with dichloromethane as solvent and diethyl ether as precipitant. The crystal selected for study was a block-shaped yellow fragment (0·50 × 0·13 × 0·06 mm) cleaved from a twinned specimen and mounted on a glass fibre. D_m by flotation. Enraf–Nonius CAD-4F diffractometer was used for data collection. Unit-cell parameters and the orientation matrix were determined from the setting angles of 25 reflections ($10 < \theta < 11°$). Unique dataset: 5374 reflections: h0,16; k12,0; l−25,26; $1{\cdot}43 < \theta < 23°$; $\omega/2\theta$ scan; Zr-filtered Mo $K\alpha$ radiation. Three reference reflections (200, 0$\bar{2}$0, 002) measured every hour showed no decay during 86 h exposure time, variation < 2%. The diffraction data were corrected for Lorentz and polarization effects. The standard deviation $\sigma(I)$ was calculated following McCandlish, Stout & Andrews (1975); $\sigma^2(I) = \sigma^2(I)_{cs} + (PI)^2$, $P = 0{\cdot}02$.

The Pd and I atoms were located in a Patterson map and the remaining non-hydrogen atoms were obtained by standard difference Fourier techniques. Correction for absorption was carried out with the program *DIFABS* (Walker & Stuart, 1983). Minimum and maximum absorption corrections 0·888 and 1·071. H atoms were placed on calculated positions. The H atoms of the methyl group were refined in the riding mode on their neighbouring C atom with one overall isotropic parameter. The positional and thermal parameters of the remaining hydrogen atoms were refined individually. The non-hydrogen atoms were refined with anisotropic thermal parameters. Weights were introduced. Final atomic parameters are given in Table 1.†

The structure was refined on F by blocked full-matrix least-squares techniques converging to a final R value of 0·0381; $wR = 0{\cdot}0319$; $w^{-1} = \sigma^2(F)$; $S = 2{\cdot}53$; 3802 observed reflections with $I > 2{\cdot}5\sigma(I)$; 614 parameters; $<\Delta/\sigma> = 0{\cdot}1$; residual density in the final difference Fourier map −0·72 and 0·78 e Å^{-3}.

Scattering factors of Cromer & Mann (1968) were used. Anomalous-dispersion terms were taken from Cromer & Liberman (1970). The calculations were carried out on either the CDC Cyber-855 of the University of Utrecht with *SHELX*76 (Sheldrick, 1976) and *EUCLID* (Spek, 1982) or a local Eclipse S/230 minicomputer with an adapted version of *SHELX*76.

Discussion. Selected interatomic distances, bond angles and torsion angles and their estimated standard deviations are presented in Table 2. The labelling scheme and the molecular geometry are illustrated in Fig. 1.

The monoclinic unit cell contains four molecules of the title compound. The structure consist of a central palladium(II) atom bonded to two triphenylphosphine ligands, an iodide ion and a 2-methylthiomethylphenyl moiety. There are no abnormally short intermolecular contacts. The coordination geometry about the Pd

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters, additional bond lengths and angles and an *ORTEP* plot have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43507 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final positional parameters for the non-hydrogen atoms and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}(\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j)$.

	x	y	z	U_{eq}(Å²)
I	0·42167 (3)	0·36763 (4)	0·24388 (2)	0·0457 (1)
Pd	0·28515 (3)	0·51928 (4)	0·25468 (2)	0·0324 (2)
S	0·2292 (2)	0·9449 (2)	0·2328 (1)	0·0951 (8)
P(1)	0·3355 (1)	0·5050 (1)	0·35286 (6)	0·0354 (5)
P(2)	0·2315 (1)	0·5439 (1)	0·15657 (6)	0·0349 (5)
C(1)	0·4620 (4)	0·5136 (5)	0·3794 (2)	0·036 (2)
C(2)	0·5130 (4)	0·4410 (6)	0·4219 (2)	0·048 (2)
C(3)	0·6094 (5)	0·4552 (7)	0·4406 (3)	0·060 (2)
C(4)	0·6536 (5)	0·5432 (7)	0·4186 (3)	0·064 (2)
C(5)	0·6036 (5)	0·6185 (7)	0·3776 (3)	0·061 (2)
C(6)	0·5083 (4)	0·6020 (6)	0·3571 (2)	0·051 (2)
C(7)	0·2975 (4)	0·3647 (5)	0·3783 (2)	0·041 (2)
C(8)	0·2609 (4)	0·2722 (6)	0·3422 (3)	0·055 (2)
C(9)	0·2308 (5)	0·1656 (7)	0·3615 (4)	0·078 (2)
C(10)	0·2375 (6)	0·1538 (7)	0·4177 (4)	0·085 (2)
C(11)	0·2725 (5)	0·2406 (8)	0·4541 (3)	0·081 (2)
C(12)	0·3023 (5)	0·3459 (6)	0·4354 (3)	0·060 (2)
C(13)	0·2962 (4)	0·6191 (5)	0·3958 (2)	0·040 (2)
C(14)	0·2076 (5)	0·6118 (7)	0·4043 (3)	0·061 (2)
C(15)	0·1759 (5)	0·7004 (8)	0·4351 (3)	0·077 (2)
C(16)	0·2319 (6)	0·7943 (8)	0·4566 (3)	0·082 (2)
C(17)	0·3174 (6)	0·8041 (6)	0·4489 (3)	0·075 (2)
C(18)	0·3499 (5)	0·7170 (6)	0·4183 (3)	0·060 (2)
C(19)	0·1655 (4)	0·4152 (5)	0·1196 (2)	0·039 (2)
C(20)	0·1114 (4)	0·4253 (6)	0·0648 (2)	0·053 (2)
C(21)	0·0705 (5)	0·3243 (7)	0·0362 (3)	0·062 (2)
C(22)	0·0820 (4)	0·2131 (6)	0·0615 (3)	0·060 (2)
C(23)	0·1345 (4)	0·2010 (6)	0·1154 (3)	0·050 (2)
C(24)	0·1773 (4)	0·3027 (5)	0·1447 (2)	0·044 (2)
C(25)	0·3304 (4)	0·5567 (5)	0·1245 (2)	0·036 (2)
C(26)	0·3998 (4)	0·6409 (6)	0·1464 (2)	0·047 (2)
C(27)	0·4793 (4)	0·6469 (6)	0·1278 (3)	0·056 (2)
C(28)	0·4935 (5)	0·5662 (7)	0·0884 (3)	0·066 (2)
C(29)	0·4266 (5)	0·4816 (7)	0·0669 (3)	0·066 (2)
C(30)	0·3444 (4)	0·4760 (6)	0·0847 (2)	0·049 (2)
C(31)	0·1565 (4)	0·6717 (5)	0·1279 (2)	0·038 (2)
C(32)	0·1810 (4)	0·7628 (6)	0·0964 (2)	0·048 (2)
C(33)	0·1214 (5)	0·8596 (6)	0·0773 (3)	0·061 (2)
C(34)	0·0371 (4)	0·8672 (6)	0·0894 (3)	0·058 (2)
C(35)	0·0105 (4)	0·7769 (7)	0·1195 (3)	0·060 (2)
C(36)	0·0685 (4)	0·6802 (6)	0·1383 (2)	0·054 (2)
C(37)	0·1732 (4)	0·6119 (5)	0·2661 (2)	0·038 (2)
C(38)	0·1710 (4)	0·7358 (5)	0·2731 (2)	0·044 (2)
C(39)	0·0923 (5)	0·7883 (6)	0·2829 (3)	0·057 (2)
C(40)	0·0163 (5)	0·7190 (8)	0·2856 (3)	0·076 (2)
C(41)	0·0184 (5)	0·5974 (7)	0·2783 (3)	0·067 (2)
C(42)	0·0959 (4)	0·5420 (6)	0·2687 (3)	0·049 (2)
C(43)	0·2549 (5)	0·8088 (6)	0·2729 (3)	0·062 (2)
C(44)	0·3369 (5)	1·0203 (6)	0·2510 (3)	0·086 (2)

Table 2. *Selected bond distances* (Å) *and angles* (°) *and torsion angles* (°)

I–Pd	2·692 (1)	P(1)–C(1)	1·819 (6)
Pd–P(1)	2·327 (2)	P(1)–C(7)	1·815 (6)
Pd–P(2)	2·339 (2)	P(1)–C(13)	1·831 (6)
Pd–C(37)	2·029 (6)	P(2)–C(19)	1·829 (6)
S–C(43)	1·784 (7)	P(2)–C(25)	1·836 (6)
S–C(44)	1·752 (8)	P(2)–C(31)	1·823 (6)
C(38)–C(43)	1·483 (9)	⟨C(19)–C(24)⟩	1·374 (4)
⟨C(1)–C(6)⟩	1·377 (4)	⟨C(25)–C(30)⟩	1·379 (4)
⟨C(7)–C(12)⟩	1·367 (4)	⟨C(31)–C(36)⟩	1·376 (4)
⟨C(13)–C(18)⟩	1·367 (4)	⟨C(37)–C(42)⟩	1·378 (4)

I–Pd–P(1)	90·58 (4)	C(2)–C(1)–C(6)	118·6 (5)
I–Pd–P(2)	92·12 (4)	P(1)–C(7)–C(8)	121·7 (4)
I–Pd–C(37)	171·6 (2)	P(1)–C(7)–C(12)	122·0 (4)
P(1)–Pd–P(2)	176·95 (5)	C(8)–C(7)–C(12)	116·3 (6)
P(1)–Pd–C(37)	87·0 (1)	P(1)–C(13)–C(14)	120·0 (5)
P(2)–Pd–C(37)	90·5 (1)	P(1)–C(13)–C(18)	122·5 (5)
C(43)–S–C(44)	102·2 (4)	C(14)–C(13)–C(18)	117·4 (6)
Pd–P(1)–C(1)	113·0 (2)	P(2)–C(19)–C(20)	123·3 (4)
Pd–P(1)–C(7)	111·5 (2)	P(2)–C(19)–C(24)	119·6 (4)
Pd–P(1)–C(13)	118·7 (2)	C(20)–C(19)–C(24)	118·8 (5)
C(1)–P(1)–C(7)	107·7 (3)	P(2)–C(25)–C(26)	118·7 (4)
C(1)–P(1)–C(13)	102·1 (3)	P(2)–C(25)–C(30)	118·5 (5)
C(7)–P(1)–C(13)	102·8 (3)	P(2)–C(31)–C(32)	124·2 (5)
Pd–P(2)–C(19)	114·4 (2)	P(2)–C(31)–C(36)	116·6 (5)
Pd–P(2)–C(25)	110·5 (2)	Pd–C(37)–C(38)	124·3 (4)
Pd–P(2)–C(31)	119·8 (2)	Pd–C(37)–C(42)	115·8 (4)
C(19)–P(2)–C(25)	103·4 (3)	C(38)–C(37)–C(42)	119·9 (6)
C(19)–P(2)–C(31)	102·7 (3)	C(37)–C(38)–C(43)	119·6 (6)
C(25)–P(2)–C(31)	104·5 (3)	C(39)–C(38)–C(43)	121·2 (5)
P(1)–C(1)–C(2)	123·6 (5)	C(39)–C(40)–C(41)	119·9 (7)
P(1)–C(1)–C(6)	117·7 (4)	C(37)–C(42)–C(41)	119·4 (6)
C(32)–C(31)–C(36)	116·6 (5)	C(26)–C(25)–C(30)	118·5 (5)

Pd–P(1)–C(1)–C(6)	45·0 (5)	C(37)–Pd–P(1)–C(1)	−144·4 (3)
Pd–P(1)–C(7)–C(8)	12·0 (6)	C(37)–Pd–P(1)–C(7)	94·2 (3)
Pd–P(1)–C(13)–C(14)	79·0 (5)	C(37)–Pd–P(1)–C(13)	−24·9 (3)
Pd–P(2)–C(19)–C(20)	164·8 (4)	C(37)–Pd–P(2)–C(19)	−96·7 (3)
Pd–P(2)–C(19)–C(24)	−21·9 (5)	C(37)–Pd–P(2)–C(25)	147·1 (2)
Pd–P(2)–C(25)–C(26)	−52·0 (5)	C(37)–Pd–P(2)–C(31)	25·7 (3)
Pd–P(2)–C(31)–C(36)	−63·8 (5)	C(37)–C(38)–C(43)–S	136·7 (5)
P(1)–Pd–C(37)–C(38)	88·7 (4)	C(44)–S–C(43)–C(38)	170·1 (5)
P(2)–Pd–C(37)–C(38)	−89·6 (4)		

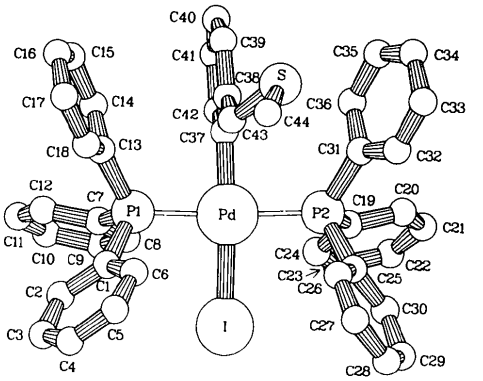

Fig. 1. *PLUTO* (*EUCLID* version: Spek, 1982) drawing of the title compound with adopted numbering scheme. Hydrogen atoms omitted for clarity.

atom may be viewed as square-planar. The triphenylphosphine ligands are positioned *trans*. The S atom lies −1·09 (2) Å away from the plane of the benzyl group to which the S atom is linked and it coordinates neither intramolecularly nor intermolecularly to the Pd atom.

The Pd—P distances that are observed for square-planar Pd compounds lie in the range from 2·319 through 2·342 Å. The Pd—P(1) and Pd—P(2) distances are 2·327 (2) and 2·339 (2) Å respectively.

The Pd—I distance is 2·692 (1) Å. We may compare this with Pd^{II}—I distances of 2·651 Å for μ-allyl-μ-iodobis(triphenylphosphine)palladium (Kobayashi, Iitaka & Yamazaki, 1972), 2·647 to 2·741 Å in (μ-2-iodo)bis[μ-2-bis(diphenylphosphino)methane]-iodomethyldipalladium tetrafluoroborate (Olmstead, Farr & Balch, 1981). The Pd—C distance in the title compound [2·029 (6) Å] lies in the range (1·983–2·089 Å) that is observed for organometallic palladium compounds.

Short non-bonding distances between S and the phenyl ring [C(31)—C(36)] range from 3·80 to 4·12 Å [sum of the van der Waals radii 3·68 Å (Bondi, 1964)]. A short contact between a methylene H and the Pd atom is observed [H(432)···Pd 2·66 (3); C(43)···Pd

3·28 (7) Å; C(43)–H(432)···Pd 119 (3)°]. Short intermolecular contacts include the interaction H(442)···I [1−x, ½+y, ½−z] 2·90 (1); C(44)···I 3·926 (8) Å; C(44)–H(442)···I 158·8 (6)°.

A slight skeletal deformation of the benzene rings of the triphenylphosphine ligands in the title compound is observed. It may be described in terms of an average decrease of 2·3° from 120° of the endocyclic bond angle, opposite to the P atom. Domenicano, Vaciago & Coulson (1975) explain this in terms of hybridization effects and valence-shell electron-pair repulsions.

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Structure of {2,6-Bis[(dimethylamino)methyl]phenyl}iodoplatinum(II)

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Abstract. [PtI($C_{12}H_{19}N_2$)], $M_r = 513{\cdot}28$, monoclinic, $I2/a$, $a = 17{\cdot}044$ (6), $b = 9{\cdot}259$ (3), $c = 18{\cdot}44$ (1) Å, $\beta = 96{\cdot}65$ (4)°, $V = 2890$ (2) Å^3, $Z = 8$, $D_x = 2{\cdot}359$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 119{\cdot}1$ cm^{-1}, $F(000) = 1888$, $T = 294$ K, $R = 0{\cdot}0301$ for 2635 observed reflections with $I > 2\sigma(I)$. Pt is square-planar (within 0·013 Å) coordinated by C(1), I, N(1) and N(2). The molecule has approximate twofold axial symmetry along the Pt–I axis.

Introduction. Recently it appeared that the title compound [=PtI(NCN)] readily forms a very stable complex with I_2 (van Beek, van Koten, Smeets & Spek, 1986). The resulting PtI(NCN)(η^1-I_2) compound is the first example of a complex mimicking the initial stage of the oxidative addition of halogens at d^8 metal centres.

PtI(NCN)(η^1-I_2) has a distorted square-pyramidal coordination with an end-on bonded I_2 molecule occupying the apical position. Two of the NMe groups are located on the opposite side of the η^1 bonded I_2 molecule and seem to shield that side from further attack by I_2.

In order to study this aspect in more detail the structure of the parent compound PtI(NCN) was determined.

Experimental. Transparent yellow prismatic crystal 0·48 × 0·29 × 0·13 mm glued on top of a glass fibre. Enraf–Nonius CAD-4F diffractometer, Zr-filtered Mo $K\alpha$ radiation, cell constants from the angular settings of 12 reflections with $11{\cdot}5 < \theta < 14{\cdot}0°$. Intensity data of 3512 unique reflections were collected within a quarter of the reflection sphere; $-21 \le h \le 22$, $0 \le k \le 12$, $-23 \le l \le 0$; $(\sin\theta/\lambda)_{max} = 0{\cdot}649$ Å^{-1};

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