

in Table 2.* The molecular structure and the atom-numbering scheme are shown in Fig. 1, Fig. 2 shows a stereoscopic view.

Related literature. The structural parameters of this molecule can be compared with those found in the isostructural complex $[\text{Ni}(\text{BBDH})(\text{OH}_2)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (Castiñeiras, Carballo, Hiller & Strähle, 1990), as well as those of the same ligand $[\text{Cu}(\text{BBDH})\text{Cl}]\text{Cl}_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$ (Birker, Helder, Henkel, Krebs & Reedijk, 1982), $[\text{Ni}(\text{BBDH})\text{Br}_2]$ (Smits, Janssen, Beurskens, Van Rijn & Reedijk, 1987), $[\text{Co}(\text{BBDH})(\text{OH}_2)(\text{ONO}_2)](\text{NO}_3) \cdot \text{H}_2\text{O}$ (Castiñeiras, Carballo, Bermejo, Gayoso, Molleda, Hiller & Strähle, 1988), $[\text{Co}(\text{BBDH})(\text{OH}_2)_2]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ (Hiller, Strähle, Castiñeiras, Carballo, Bermejo & Gayoso,

1990), and $[\text{Ni}(\text{BBDH})(\text{OH}_2)_2]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ (Castiñeiras, Hiller, Strähle, Carballo, Bermejo & Gayoso, 1990).

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles, torsion angles, mean-planes data and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53978 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of *trans*-Diiodobis(triphenylphosphine)palladium(II)–Trichloromethane (1/1)

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Abstract. $[\text{Pd}(\text{I})_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]\cdot\text{CHCl}_3$, $M_r = 1004.2$, monoclinic, $C2/c$, $a = 12.630$ (1), $b = 15.237$ (2), $c = 19.893$ (3) Å, $\beta = 91.67$ (1)°, $V = 3827$ (1) Å³, $Z = 4$, $D_m = 1.72$ (2), $D_x = 1.74$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 2.39$ mm⁻¹, $F(000) = 1944$, $T = 300$ K, $R = 0.040$ for 2470 unique reflections. The Pd^{II} atom lies on a crystallographic twofold axis and the monomeric complex is *trans* square planar with no additional ligands in the octahedral positions.

Experimental. The palladium complex obtained in the course of catalytic reaction was provided by Professor Jin Douman, Henan Academy of Sciences, People's Republic of China. Red tabular crystals were grown from trichloromethane solution. D_m measured by flotation in aqueous KI solution. X-ray intensities were measured on a Rigaku AFC-5 four-

circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation, θ - 2θ scan, scan speed 6° min⁻¹ in θ , crystal size 0.10 × 0.13 × 0.30 mm, $-16 \leq h \leq 16$, $0 \leq k \leq 19$, $-25 \leq l \leq 0$ ($4 \leq 2\theta \leq 55^\circ$), 4506 reflections measured, 2548 reflections observed with $|F_o| > 3\sigma(|F_o|)$, 2470 unique ($R_{\text{int}} = 0.017$); lattice constants based on 24 2θ values ($20 < 2\theta < 30^\circ$). Ratio of five standard reflections $0.99 < \sum(|F_o|/|F_o|_{\text{initial}})/5 < 1.01$. Absorption correction (analytical, relative transmission factors 0.72–0.79). Systematic absences (hkl , $h+k$ odd; $h0l$, l odd) indicated the space group to be Cc or $C2/c$. Assuming the centrosymmetric space group $C2/c$, the structure could be solved successfully by direct methods with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); coordinates of all the non-H atoms refined by block-diagonal least squares with anisotropic thermal parameters using the *UNICSIII* system (Sakurai & Kobayashi, 1979); all the H atoms

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Table 1. Positional parameters ($\times 10^4$, $\times 10^5$ for Pd and I) and equivalent isotropic temperature factors ($\times 10$) (Hamilton, 1959)

	x	y	z	B_{eq} (\AA^2)
Pd	0	20883 (4)	75000	24
I	18218 (3)	22539 (3)	69343 (2)	34
P	-922 (1)	2105 (1)	6461 (1)	25
C(1)	-1646 (5)	3145 (4)	6390 (3)	29
C(2)	-1100 (6)	3887 (5)	6573 (4)	43
C(3)	-1583 (7)	4712 (5)	6536 (5)	57
C(4)	-2605 (8)	4756 (5)	6302 (5)	63
C(5)	-3152 (7)	4019 (6)	6121 (5)	59
C(6)	-2682 (6)	3209 (5)	6153 (4)	40
C(7)	-1846 (5)	1206 (4)	6312 (3)	28
C(8)	-2417 (6)	1130 (5)	5707 (4)	41
C(9)	-3067 (7)	395 (6)	5608 (4)	57
C(10)	-3144 (7)	-249 (5)	6069 (5)	56
C(11)	-2583 (8)	-174 (5)	6648 (5)	61
C(12)	-1929 (6)	532 (5)	6789 (4)	43
C(13)	-157 (5)	2049 (4)	5703 (3)	30
C(14)	109 (6)	2765 (5)	5330 (4)	47
C(15)	759 (8)	2690 (6)	4781 (4)	65
C(16)	1176 (7)	1895 (7)	4603 (4)	65
C(17)	911 (6)	1173 (5)	4975 (4)	53
C(18)	269 (6)	1238 (5)	5519 (4)	42
C(19)	5000	2208 (16)	7500	164
Cl(1)	5000	3326 (5)	7500	211
Cl(2)*	5485 (5)	1597 (5)	6923 (3)	103
Cl(3)*	4964 (6)	1941 (7)	8274 (4)	156

* Population parameter for the disordered Cl atoms is 0.5.

of the complex were located on a difference synthesis and refined with isotropic thermal parameters. The Cl(1)—C(19) bond axis of the trichloromethane molecule lies on the twofold axis, and therefore has two possible orientations. The function $\sum w(|F_o| - |F_c|)^2$ was minimized with weights $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$. Final $R = 0.040$, $wR = 0.038$, $S = 1.20$; $\Delta/\sigma < 0.11$; number of reflections/parameters = 9.0; $-0.45 < \Delta\rho < 0.56 \text{ e \AA}^{-3}$. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations were performed with the FACOM M-380R computer of Keio University. Atomic coordinates are given in Table 1,* and selected bond lengths and bond angles in Table 2. The molecular structure is shown in Fig. 1.

Related literature. The Pd^{II} complex has crystallographic twofold symmetry. Interatomic distances between the Pd and β -H atoms of the phenyl groups are too long for one to expect bonding interactions [Pd...H(12) = 3.08 (6) and Pd...H(2) = 3.29 (6) \AA]. Although the color of the title crystal is red, the coordination geometry around the Pd atom is similar to that in the yellow crystals of *trans*-

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Table 2. Selected bond lengths (\AA) and bond angles ($^\circ$)

Pd—I	2.6029 (5)	P—C(7)	1.818 (6)
Pd—P	2.343 (2)	P—C(13)	1.816 (6)
P—C(1)	1.833 (6)		
I—Pd—P	92.32 (5)	C(7)—P—C(13)	100.6 (3)
I—Pd—P ⁱ	87.56 (5)	P—C(1)—C(2)	116.6 (5)
Pd—P—C(1)	108.1 (2)	P—C(1)—C(6)	123.6 (5)
Pd—P—C(7)	115.8 (2)	P—C(7)—C(8)	121.2 (5)
Pd—P—C(13)	118.0 (2)	P—C(7)—C(12)	120.1 (5)
C(1)—P—C(7)	108.8 (3)	P—C(13)—C(14)	123.9 (5)
C(1)—P—C(13)	104.6 (3)	P—C(13)—C(18)	118.4 (5)

Symmetry code: (i) $-x, y, \frac{3}{2} - z$.

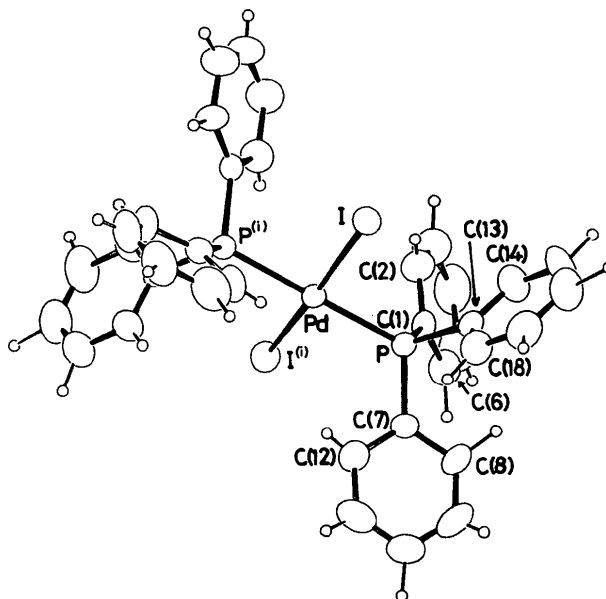


Fig. 1. An ORTEP (Johnson, 1965) drawing of the molecule with 50% probability ellipsoids. H atoms are represented by circles of radius 0.08 \AA. Symmetry code: (i) $-x, y, \frac{3}{2} - z$.

[PdI₂(PPh₃)₂].2CH₂Cl₂, which is monoclinic $P2_1/c$, $Z = 2$ (Debaerdemaeker, Kutoglu, Schmid & Weber, 1973). This is in contrast to the fact that the red crystals of *trans*-[PdI₂(PPhMe₂)₂] have a short Pd...I intermolecular contact of 3.290 (3) \AA and the yellow crystals have no such bond (Bailey & Mason, 1968). The Pd and I atoms of the neighboring molecules are separated by more than 8.448 (1) \AA in the title complex. The structures of the analogous dichloro complex were reported for *trans*-[PdCl₂(PPh₃)₂] (Ferguson, McCrindle, McAlees & Parvez, 1982) and for *trans*-[PdCl₂(PPh₃)₂].1/2(*p*-dichlorobenzene) (Kitano, Kinoshita, Nakamura & Ashida, 1983).

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Chloro[7(*Z*)-chloromethylene-4,4,8,8-tetramethyl-2,10-dithiaundec-5(*Z*)-en-5-yl-S,S]palladium(II)

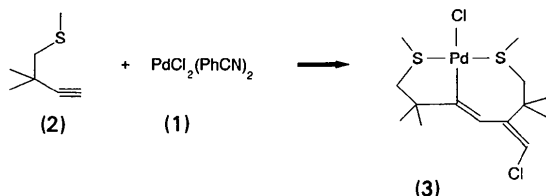
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Abstract. $C_{14}H_{24}Cl_2PdS_2$, $M_r = 433.8$, monoclinic, $P2_1/c$, $a = 9.754$ (4), $b = 10.648$ (2), $c = 17.921$ (2) Å, $\beta = 99.95$ (2)°, $V = 1833$ (1) Å³, $Z = 4$, $D_x = 1.57$ g cm⁻³, Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å), $\mu = 15.0$ cm⁻¹, $F(000) = 880$, $T = 294$ K. $R = 0.039$ for 1044 observed data. Space group unambiguously determined by the systematic absences ($h0l$ absent if $l = 2n + 1$, $0k0$ absent if $k = 2n + 1$). Reaction of dichlorobis(benzonitrile)palladium (1) with 2,2-dimethyl-3-butyn-1-yl methyl sulfide (2) (3 mol equiv.) gave a complex mixture of products; the structure and stereochemistry of the major product (3) was established by this X-ray analysis. The crystal structure contains discrete monomeric molecules separated by normal van der Waals distances. The Pd atom is four-coordinate in a close to square-planar environment; one methylthio moiety is disordered over two sites. Deviations of the atoms from the PdS_2ClC plane are Pd 0.036 (1), S(2) 0.479 (2), S(2') -0.492 (2), S(10) 0.008 (2), Cl 0.073 (2), C(5) -0.104 (3) Å. The exocyclic olefin is oriented so that the Cl atom on C(71) is *cis* to C(6) (Fig. 1). The seven-membered ring has a deformed boat conformation. Principal bond lengths are: Pd—Cl 2.408 (4), Pd—S 2.424 (6), 2.272 (6) and 2.303 (3) and Pd—C 1.980 (11) Å.

Experimental. A yellow prism crystal of (3) measuring $0.23 \times 0.20 \times 0.15$ mm was mounted on a glass fibre in a random orientation. Accurate cell dimensions and crystal orientation matrix determined on a CAD-4 diffractometer from a least-squares refinement of data collected using the setting angles of 25 reflections in the range $10 < \theta < 15^\circ$. Intensities of reflections with indices $h - 9$ to 9, $k 0$ to 10, $l 0$ to 18, with $2 < 2\theta < 42^\circ$ measured; $\omega - 2\theta$ scans; ω -scan width $(0.60 + 0.35 \tan \theta)^\circ$. Intensities of three reflections measured at 3 h intervals showed no evidence of crystal decay. The crystals diffracted poorly and of the 2118 reflections measured only 1044 (49.3%) with $I > 3\sigma(I)$ were labelled observed and used in structure solution and refinement. Data corrected for Lorentz and polarization effects. The structure was solved by the heavy-atom method using the *NRC Crystal Structure Package* (Larson & Gabe, 1978). One sulfur atom and its methyl group are disordered over two sites; these atoms were included with an occupancy factor of 0.5 (from difference map peak heights) for each of two sites. It is probable that carbon atom C(3) (to which the two disordered S atoms are bonded) is itself slightly disordered over two sites but we were unable to resolve this. The structure was refined by block-diagonal least-squares calculations on F , initially with isotropic and later with anisotropic thermal parameters for non-H atoms. H atoms were visible in difference syntheses [except for those of the disordered methyl carbons C(2) and C(2')] and were included at their idealized positions (C—H 0.95 Å, $U_{iso} = 0.05$ Å²) but not refined. The final refinement cycle included 190 variable parameters. Final $R = 0.039$, $wR = 0.034$, $w = 1/\sigma^2(F)$, $S = 1.96$, $\Delta/\sigma = 0.01$. Density in the final



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