THE CRYSTAL STRUCTURE OF DIIODO((o-METHYLTHIOPHENYL)DIPHENYLPHOSPHINE)-PALLADIUM(II), A COMPLEX EXHIBITING A LARGE STRUCTURAL *trans* INFLUENCE

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Summary

The crystal structure of the title compound has been determined by conventional X-ray diffraction techniques. The red diamond-shaped crystals are monoclinic, space group $P2_1/n$, a 8.914(4), b 16.090(12), c 14.991(5) Å, β 95.97(2)°, V 2138.44 Å^3, Z = 4. Refinement by full-matrix least-squares methods employed anisotropic thermal parameters for all non-hydrogen atoms and isotropic temperature factors for hydrogen atoms, and returned final residuals of R = 0.028 and R_w = 0.028.

The complex is monomeric, with a square planar coordination geometry comprising the S and P atoms of the bidentate (o-methylthiophenyl)diphenylphosphine ligand and the two iodine atoms. The Pd—I distance *trans* to P is 2.658(1) Å whereas that *trans* to S is 2.602(1) Å. The difference of 56 standard deviations illustrates the greater structural *trans* influence of phosphine over thioether donors. The Pd—P and Pd—S distances of 2.250(2) and 2.288(2) Å, respectively, are normal. Two phenyl hydrogen atoms approach the Pd atom in the axial regions above and below the square plane at distances of 2.98 and 2.99 Å.

Introduction

The predominant bonding geometry of palladium(II) complexes is four-coordinate square planar, although penta- and hexa-coordinate complexes are known [1]. In solution, solvation can increase the coordination number to five or six [2] and in the solid state, weak axial interactions may convert an otherwise square planar complex into one of quasi higher coordination [3]. Recently, interest has focussed on axial interactions by α-hydrogen atoms of the phenyl groups of coordinated phosphines, since many tertiary phosphine complexes

are good catalysts for olefin isomerisation [4] and homogeneous hydrogenation reactions [5]. A related phenomenon is that of auto-oxidation in square planar d^8 complexes by intramolecular hydrogen transfer from alkyl or aryl groups of phosphine ligands to the metal [6].

The complex diiodo((o-methylthiophenyl)diphenylphosphine)palladium(II) has been prepared by Professor D.W. Meek, of the Ohio State University [7]. In solution, its electronic spectrum is consistent for a planar four-coordinate geometry, but it is possible that in the solid state its coordination number is raised by iodide bridging or other axial interactions. We have therefore undertaken the determination of its crystal structure to establish its precise solid state geometry. The structure will also be of interest in that it will provide useful additional data on the structural *trans* influence in *cis*-dihalo palladium(II) complexes.

Experimental

The vermillion diamond-shaped crystals were generously supplied by Professor D.W. Meek of the Ohio State University. That selected for intensity data collection was developed on the forms {0 1 0}, {1 1 1} and {0 1 1} and measured approximately $0.36 \times 0.26 \times 0.12$ mm. Preliminary X-ray photographs showed monoclinic diffraction symmetry, with systematically absent reflections (h 0 l when $h + l = 2n + 1$, 0 k 0 when $k = 2n + 1$) corresponding to space group $P2_1/n$. This alternative setting for space group $P2_1/c$ (No. 14) was chosen in order to keep the β angle reasonably near to 90°. Unit cell dimensions were derived from the observed counter angles of axial reflections on a Stoe Weissenberg diffractometer.

Crystal data. $C_{19}H_{17}I_2PPdS$, $M = 668.58$, Monoclinic, a 8.914(4), b 16.090(12), c 14.991(5) Å, β 95.97(2)°, V 2138.44 Å³, space group $P2_1/n$, $Z = 4$, $d_m = 2.22(4)$ by flotation in bromoform/n-hexane, $d_c = 2.08$, $F(000) = 1256$, Mo-K_α radiation of $\lambda = 0.7107$ Å, graphite monochromator, $\mu(\text{Mo-}K_\alpha) = 36.50$ cm⁻¹.

Intensity data were collected for the layers h 0 l through h 16 l to $\theta(\max) = 25°$ using an ω scan technique, the optimum scan width being computed for each reflection [8]. The scan rate was 1° min⁻¹ with stationary background measurements of 20 s at each end of the scan range. The data were corrected for Lorentz, polarisation and absorption effects. The maximum and minimum transmission coefficients applied to F were 0.8067 and 0.6523, respectively, the absorption program used being a local version of ABSCOR [9]. The data set consisted of 2755 observed ($I > 3\sigma(I)$) and 630 unobserved unique reflections.

Structure determination and refinement

Positions for the palladium and two iodine atoms were deduced from the Patterson synthesis and the remaining non-hydrogen atoms from a subsequent electron density map. These calculations and the subsequent refinement were carried out using SHELX [10]. Atomic scattering factors and dispersion corrections were from standard listings [11]. The full least-squares matrix was used to

minimise the function $\Sigma w(|F_0| - |F_c|)^2$. Initial refinement cycles employed unit weights and isotropic temperature factors. When the five heaviest atoms were assigned anisotropic thermal parameters the residual R was reduced from 0.13 to 0.059. Absorption corrections were applied at this stage, and a re-run of the previous cycle returned $R = 0.045$. The final two refinement cycles were computed in two blocks, and employed anisotropic thermal parameters for all non-hydrogen atoms, methyl hydrogen atoms constrained as a group with temperature factors tied to a common variable; isotropic hydrogen atoms of benzene rings (initially in calculated positions), a weighting parameter g [$w \propto 1/(\sigma^2(F) + gF^2)$], and an isotropic extinction parameter x [$F_c = F(1 - xF^2/\sin\theta)$]. Final values were $R = 0.0277$, $R_w = 0.0275$ [$R_w = (\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2)^{1/2}$], $g = 1.57 \times 10^{-4}$, $x = 8.5(7) \times 10^{-8}$. No correlation matrix elements were listed as exceeding 0.5. A difference electron density synthesis was calculated with all H atoms excluded. All reappeared as well resolved peaks. As the least-squares refinement had resulted in short C—H distances for H(11) and H(19) the final positions for these two atoms are those from the difference Fourier map.

The final atomic positions are listed in Table 1. The molecular geometry, atomic numbering scheme, and anisotropic thermal ellipsoids are shown in Fig. 1. A list of thermal parameters, and tables of observed and calculated structure factors are available on request from the authors (G.R.C.).

Description of the structure

The crystals are composed of discrete molecules. The molecules possess no symmetry, and both enantiomorphic forms are present in an equimolar mixture

TABLE 1

ATOMIC POSITIONS FOR DIIODO((o-METHYLTHIOPHENYL)DIPHENYLPHOSPHINE)-PALLADIUM(II)

| Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Pd	0.24981(5)	0.16390(3)	0.14487(3)	C(16)	0.2691(9)	0.4710(4)	—0.0094(5)
I(1)	0.13607(6)	0.08008(3)	0.27501(3)	C(17)	0.1453(8)	0.4699(4)	—0.0741(4)
I(2)	0.31855(7)	0.29348(3)	0.24471(3)	C(18)	0.0913(7)	0.3959(4)	—0.1093(4)
S	0.1752(2)	0.0564(1)	0.0506(1)	C(19)	0.1582(7)	0.3217(4)	—0.0795(4)
P	0.3567(2)	0.2236(1)	0.0313(1)	H(1A)	0.269(1)	—0.056(1)	0.150(1)
C(1)	0.2926(12)	—0.0325(7)	0.0852(8)	H(1B)	0.409(1)	—0.012(1)	0.089(1)
C(2)	0.2445(7)	0.0800(3)	—0.0540(4)	H(1C)	0.274(1)	—0.081(1)	0.036(1)
C(3)	0.3265(8)	0.1523(3)	—0.0639(4)	H(4)	0.441(7)	0.219(4)	—0.154(4)
C(4)	0.3791(10)	0.1680(5)	—0.1468(5)	H(5)	0.389(9)	0.131(5)	—0.280(6)
C(5)	0.3505(11)	0.1131(5)	—0.2166(5)	H(6)	0.241(7)	0.002(4)	—0.257(5)
C(6)	0.2620(10)	0.0432(5)	—0.2073(5)	H(7)	0.154(10)	—0.024(6)	—0.110(6)
C(7)	0.2108(9)	0.0254(4)	—0.1242(5)	H(9)	0.587(8)	0.166(5)	0.168(5)
C(8)	0.5591(6)	0.2367(3)	0.0523(3)	H(10)	0.847(7)	0.181(4)	0.186(5)
C(9)	0.6375(7)	0.1965(4)	0.1256(4)	H(11)	0.985	0.270	0.083
C(10)	0.7939(8)	0.2032(4)	0.1396(5)	H(12)	0.844(10)	0.319(6)	—0.028(6)
C(11)	0.8691(7)	0.2491(5)	0.0802(6)	H(13)	0.598(8)	0.314(5)	—0.050(5)
C(12)	0.7936(7)	0.2887(5)	0.0090(5)	H(15)	0.416(8)	0.400(4)	0.061(5)
C(13)	0.6389(7)	0.2825(4)	—0.0055(5)	H(16)	0.315(9)	0.527(6)	0.015(5)
C(14)	0.2795(6)	0.3214(3)	—0.0135(3)	H(17)	0.106(6)	0.525(3)	—0.098(3)
C(15)	0.3343(8)	0.3970(4)	0.0211(4)	H(18)	0.015(8)	0.399(4)	—0.156(5)
				H(19)	0.108	0.275	—0.100
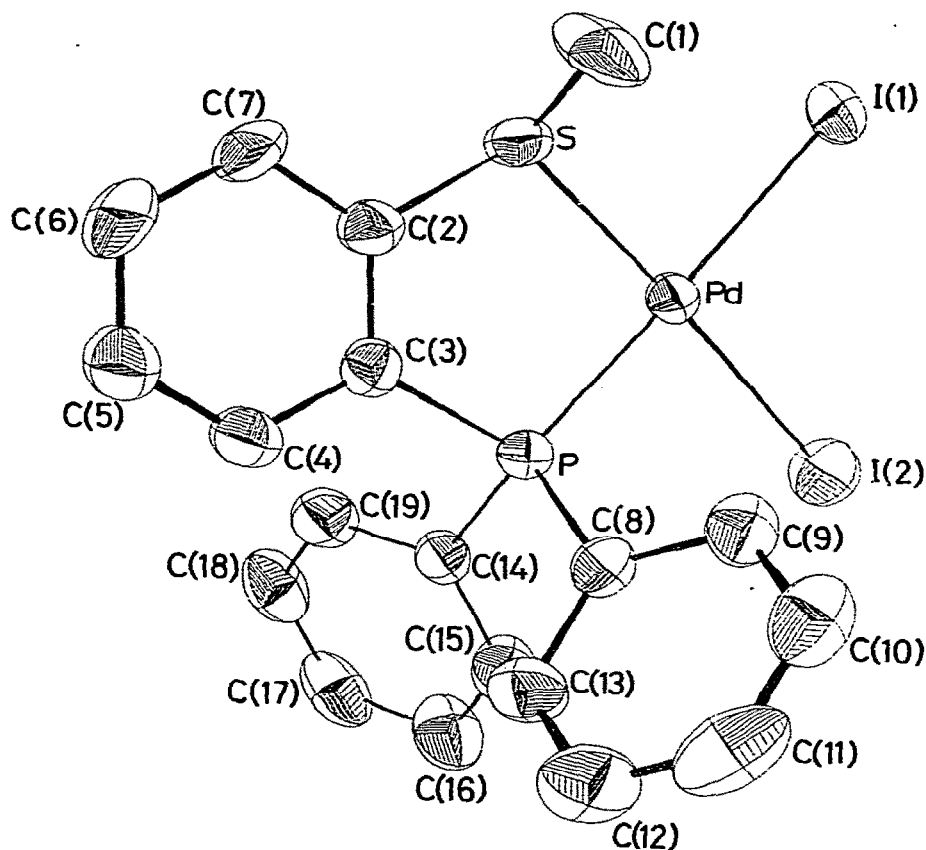
Fig. 1. The molecular geometry of diiodo((o-methylthiophenyl)diphenylphosphine)palladium(II), showing the atomic numbering scheme and 50% probability anisotropic thermal ellipsoids.

as required by the centrosymmetric space group. The coordination geometry is square planar, the donor atoms being the S and P atoms of the bidentate (o-methylthiophenyl)diphenylphosphine ligand, and two iodine atoms. There is no iodide bridging in the solid state. However, two hydrogen atoms (one intra-molecular, the other intermolecular) approach the palladium atom in the axial regions above and below the square plane to bring about weak quasi-higher coordination.

The coordination square plane is in fact distorted by a 5.7° tetrahedral twist about the line passing through the Pd atom and the centre of mass of the two I atoms. The equation of the plane best fitting the atoms Pd, I(1), I(2), S and P is $-0.8599X + 0.4273Y - 0.2793Z - 1.1927 = 0$, with reference to orthogonalised axes. Displacements of the atoms from this plane are Pd -0.004, I(1) -0.076, I(2) 0.078, S 0.095, and P -0.092 Å. The extent of distortion of the coordination square plane is further reflected in the deviations from 90° of the angles at Pd, in particular I(1)—Pd—I(2) 94.0° and I(1)—Pd—S 87.8°. The opening of the I(1)—Pd—I(2) angle is consistent with a repulsion between the large iodine atoms, whereas the closing of the I(1)—Pd—S angle (rather than

I(2)—Pd—P) is consistent with there being less steric hindrance to the movement of the iodine atom on the "sulphur-side" of the molecule.

Bond lengths and angles are listed in Tables 2 and 3, respectively, together with their least-squares estimated standard deviations. The Pd—I(1) distance is 2.658(1) Å while the Pd—I(2) distance is 2.602(1) Å. The Pd—I(2) distance is similar to the Pd—I distances found in other complexes, e.g. 2.576(13) Å in *trans*-diiodobis(dimethyl-*o*-methylthiophenylarsine)palladium(II) [12], 2.638, 2.619(3) Å in the red isomer and 2.592(3) Å in the yellow isomer of *trans*-diiodobis(dimethylphenylphosphine)palladium(II) [13], 2.611, 2.587(6) Å in *trans*-diiodobis(t-butylisonitrile)palladium(II) [14], and 2.587(1) Å in *trans*-diiodobis(triphenylphosphine)palladium(II) [15]. All of the above are *trans*-diiodo complexes, and in some the Pd—I bond lengths are required to be identical by the constraints of space group symmetry. The other two show differences in the Pd—I bond distances of 0.019 and 0.024 Å (corresponding to 6 and 4 σ, respectively). The small differences possibly reflect nothing more than slightly inequal crystal packing forces resulting from asymmetries in the dispositions of neighbouring atoms. In the present *cis* complex, the difference in the Pd—I bond lengths is much greater at 0.056 Å. The structural *trans* influences of sulphur (thioether) and iodine donors are similarly weak, and we note that the Pd—I(2) distance is approximately the same as the Pd—I bonds in the *trans*-diiodo complexes cited earlier. The lengthening of Pd—I(1) relative to Pd—I(2) corresponds to 56 standard deviations, and is the largest manifestation of which we are aware for any Pd complex of a structural *trans* influence. The longer bond is situated *trans* to P, the shorter *trans* to S.

TABLE 2

BOND LENGTHS (Å) FOR DIIODO((*o*-METHYLTHIOPHENYL)DIPHENYLPHOSPHINE)-PALLADIUM(II)

Pd—I(1)	2.658(1)	C(6)—C(7)	1.400(11)
Pd—I(2)	2.602(1)	C(8)—C(9)	1.398(8)
Pd—S	2.288(2)	C(8)—C(13)	1.389(9)
Pd—P	2.250(2)	C(9)—C(10)	1.392(9)
S—C(1)	1.815(11)	C(10)—C(11)	1.382(11)
S—C(2)	1.785(7)	C(11)—C(12)	1.360(11)
P—C(3)	1.828(7)	C(12)—C(13)	1.376(9)
P—C(8)	1.812(5)	C(14)—C(15)	1.390(8)
P—C(14)	1.818(5)	C(14)—C(19)	1.388(8)
C(2)—C(3)	1.391(9)	C(15)—C(16)	1.382(9)
C(2)—C(7)	1.380(9)	C(16)—C(17)	1.391(10)
C(3)—C(4)	1.396(10)	C(17)—C(18)	1.369(9)
C(4)—C(5)	1.374(10)	C(18)—C(19)	1.388(9)
C(5)—C(6)	1.388(12)		
C(1)—H(1A)	1.08	C(11)—H(11)	1.08
C(1)—H(1B)	1.08	C(12)—H(12)	0.90(9)
C(1)—H(1C)	1.08	C(13)—H(13)	0.88(8)
C(4)—H(4)	1.00(7)	C(15)—H(15)	0.90(7)
C(5)—H(5)	1.08(9)	C(16)—H(16)	1.04(9)
C(6)—H(6)	1.00(7)	C(17)—H(17)	1.01(5)
C(7)—H(7)	0.98(9)	C(18)—H(18)	0.93(7)
C(9)—H(9)	0.95(8)	C(19)—H(19)	0.91
C(10)—H(10)	0.88(6)		

TABLE 3

BOND ANGLES (degrees) FOR DIODO((o-METHYLTHIOPHENYL)DIPHENYLPHOSPHINE)-PALLADIUM(II)

I(1)—Pd—I(2)	94.0(0)	C(3)—C(4)—C(5)	120.6(7)
I(1)—Pd—S	87.8(0)	C(4)—C(6)—C(6)	120.4(7)
I(1)—Pd—P	174.6(0)	C(5)—C(6)—C(7)	119.8(7)
I(2)—Pd—S	175.4(0)	C(2)—C(7)—C(6)	118.9(7)
I(2)—Pd—P	90.0(0)	P—C(8)—C(9)	119.3(4)
S—Pd—P	88.5(1)	P—C(8)—C(13)	121.3(4)
Pd—S—C(1)	107.3(4)	C(9)—C(8)—C(13)	119.3(5)
Pd—S—C(2)	106.0(2)	C(8)—C(9)—C(10)	119.6(6)
C(1)—S—C(2)	100.2(4)	C(9)—C(10)—C(11)	119.3(6)
Pd—P—C(3)	106.5(2)	C(10)—C(11)—C(12)	121.4(6)
Pd—P—C(8)	114.3(2)	C(11)—C(12)—C(13)	119.8(7)
Pd—P—C(14)	118.3(2)	C(8)—C(13)—C(12)	120.6(6)
C(3)—P—C(8)	105.8(3)	P—C(14)—C(15)	121.0(4)
C(3)—P—C(14)	103.6(3)	P—C(14)—C(19)	120.2(4)
C(8)—P—C(14)	107.1(2)	C(15)—C(14)—C(19)	118.7(5)
S—C(2)—C(3)	120.4(5)	C(14)—C(15)—C(16)	120.7(6)
S—C(2)—C(7)	117.9(5)	C(15)—C(16)—C(17)	119.7(6)
C(3)—C(2)—C(7)	121.7(6)	C(16)—C(17)—C(18)	120.1(6)
P—C(3)—C(2)	118.5(5)	C(17)—C(18)—C(19)	120.1(6)
P—C(3)—C(4)	123.0(5)	C(14)—C(19)—C(18)	120.6(5)
C(2)—C(3)—C(4)	118.4(6)		
H(4)—C(4)—C(3)	119(4)	H(12)—C(12)—C(11)	120(5)
H(4)—C(4)—C(5)	120(4)	H(12)—C(12)—C(13)	120(5)
H(5)—C(5)—C(4)	117(4)	H(13)—C(13)—C(8)	125(5)
H(5)—C(5)—C(6)	123(4)	H(13)—C(13)—C(12)	114(5)
H(6)—C(6)—C(5)	122(4)	H(15)—C(15)—C(14)	122(5)
H(6)—C(6)—C(7)	118(4)	H(15)—C(15)—C(16)	117(5)
H(7)—C(7)—C(2)	116(5)	H(16)—C(16)—C(15)	120(4)
H(7)—C(7)—C(6)	126(5)	H(16)—C(16)—C(17)	121(4)
H(9)—C(9)—C(8)	122(4)	H(17)—C(17)—C(16)	117(3)
H(9)—C(9)—C(10)	119(4)	H(17)—C(17)—C(18)	122(3)
H(10)—C(10)—C(9)	122(4)	H(18)—C(18)—C(17)	116(4)
H(10)—C(10)—C(11)	118(4)	H(18)—C(18)—C(19)	123(4)
H(11)—C(11)—C(10)	132	H(19)—C(19)—C(14)	127(6)
H(11)—C(11)—C(12)	106	H(19)—C(19)—C(18)	113(6)

Palladium—phosphine bond distances span a range from approximately 2.22 to 2.35 Å. A representative selection of such bonds in square-planar palladium(II) complexes are listed in Table 3 in order of increasing bond length. The shortest bonds are those situated *trans* to halogens, O, S or N donors, which exert only weak structural *trans* influences. The longer Pd—P bonds are found in *trans*-diphosphine complexes. The consistencies of the Pd—P distances would indicate that crystal packing forces are not significantly influencing the inner coordination geometries in these complexes. It is anticipated that the upper end of the range will be extended when structural studies have been performed on palladium complexes containing phosphine ligands *trans* to stronger *trans*-influential ligands such as hydrides.

The Pd—S distance of 2.288(2) Å is compared with those in other Pd-thio-ether complexes in Table 4. A similar variation in bond lengths occurs as the nature of the ligand occupying the *trans* position is varied. It is noted that for

TABLE 4

PALLADIUM—PHOSPHORUS BOND LENGTHS

Complex	Pd—P (Å)	Atom or group trans to P	Ref.
[C$_2$H$_5$N(PPh$_2$)$_2$]PdCl$_2$	2.224(4)	Cl	18
(PPh$_3$)Pd[PhNC(OMe)S]$_2$	2.232(2)	N	19
Pd(Ph$_2$PCH$_2$CO$_2$)$_2$	2.234(2)	O (acetate)	20
	2.236(2)	O (acetate)	
(PMe$_2$Ph)Pd(1-η-C$_4$To$_4$Ph)(acac)	2.239(2)	O	21
[Ph$_2$P(CH$_2$)$_3$N(CH$_3$)$_2$]Pd(SCN)(NCS)	2.243(2)	-NCS	22
[Ph$_2$P(CH$_2$)$_2$PPh$_2$]Pd(SCN)(NCS)	2.245(4)	-NCS	23
	2.260(4)	-SCN	
[C$_6$H$_4$(SMe)PPh$_2$]PdI$_2$	2.250(2)	I	This work
cis-[PhMe$_2$P)$_2$PdCl$_2$]	2.260(2)	Cl	24
[(PPh$_3$)Pd(μ-SC$_6$F$_5$)$_2$]$_2$	2.294(11)	μ-SC$_6$F$_5$	25
[(PPh$_3$)$_2$PdCl(C$_6$H$_4$N=NC$_6$H$_5$)]	2.306(5)	PPh$_3$	26
[(π-C$_4$H$_7$)PdCl(PPh$_3$)]	2.31	π-allyl	27
[(π-C$_3$H$_5$)Pd(PPh$_3$)(SnCl$_3$)]	2.317(3)	π-allyl	28
(PPh$_3$)$_2$Pd(C$_4$H$_4$O$_3$)	2.320(2)	σ-C	29
	2.349(2)	σ-C	
trans-[(PMe$_2$Ph)$_2$PdI$_2$] (red)	2.326(7)	PMe$_2$Ph	13
	2.338(8)	PMe$_2$Ph	
trans-[(PPh$_3$)$_2$PdI$_2$]	2.331(2)	PPh$_3$	15
[PhMeP(CH$_2$)$_2$PPhMe]$_2$PdCl$_2$	2.333	PPhMeCH$_2$-	30
trans-[(PMe$_2$Ph)$_2$PdI$_2$] (yellow)	2.333(7)	PMe$_2$Ph	13

both Pd—P and Pd—S, the distances *trans* to I are often longer than those *trans* to Cl, which may be contrary to expectations.

The packing of the molecules into the unit cell is shown in the stereopair diagrams of Fig. 2. No non-hydrogen intermolecular contacts are shorter than 3.65 Å, and crystal packing forces are expected to make little contribution to the observed molecular geometry. Only five hydrogen atoms approach other atoms to within the sums of their respective Van der Waals' radii, and these are all I(1)···H contacts of between 2.8 and 3.3 Å. It is most significant that all these contacts are encroaching upon I(1), yet Pd—I(1) is longer than Pd—I(2). Clearly, the lengthening of Pd—I(1) over Pd—I(2) is electronic in origin, rather than a consequence of crystal packing forces.

The two most interesting interactions are H(9)···Pd 2.99 Å, and H(11)···Pd 2.98 Å. Atom H(9) is attached to the α-carbon of a phenyl ring and the contact is intramolecular, whereas H(11) is on the γ-carbon of the same phenyl ring, but the interaction involves atom H(11) on the molecule translated one unit cell in the a direction, and is intermolecular. The presence of hydrogen atoms in the "octahedral" coordinated sites of the palladium atom is similar to the situation found in the red and yellow isomers of *trans*-diiodobis(dimethylphenylphosphine)palladium(II) [13]. The red isomer has two phenyl hydrogen atoms making intramolecular approaches to the metal at distances of 2.84 and 2.85 Å. In the yellow isomer the "octahedral" sites are occupied by phenyl hydrogen atoms of two neighbouring molecules, with longer Pd···H distances of 3.28 Å. In both cases the hydrogen atoms are attached to the α-carbon atoms of the phenyl rings. In all these examples the distances are sufficiently large to
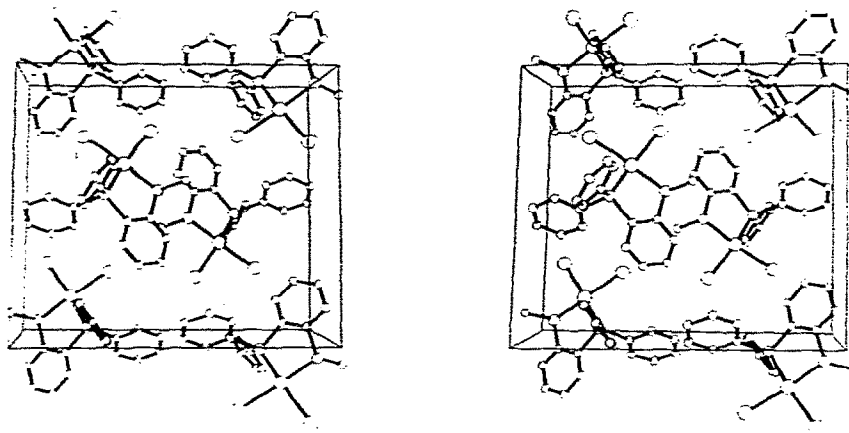
Fig. 2. Stereo-pair diagrams showing the molecular packing.

suggest that the hydrogen atoms merely fill the spaces above the octahedral sites. However, the symmetry and consistency with which the sites are occupied point to some kind of stronger interaction. In recent years, very strong C—H···M interactions have been observed. Perhaps the best example is that of the combined X-ray and neutron diffraction studies of $[Fe(P(OCH_3)_3)_3-(\eta^3-C_8H_{13})]^+[BF_4]^-$, where a C—H···Fe three-centre two-electron interaction was found with H···Fe of 1.874(3) Å and a concomitant stretching of the aliphatic C—H bond to 1.164(3) Å occurred [16]. Other somewhat longer distances have been observed by other workers [17], and it is likely that in time a continuum of bonds will be found to bridge the gap between strong C—H···M interactions and the weak interactions such as those found in the present complex.

TABLE 5

PALLADIUM—SULPHUR (THIOETHER) BOND LENGTHS

Complex	Pd—S (Å)	Atom or group trans to S	Ref.
(S-Methyl-L-cysteine)PdCl$_2$ · H$_2$O	2.230(1)	Cl	31
	2.261(3)	Cl	
Pd(C$_{10}$H$_{22}$N$_2$OS$_2$)(NO$_3$)$_2$	2.261(1)	N	32
	2.267(1)	N	
Pd(C$_{18}$H$_{36}$N$_2$O$_4$S$_2$)Cl$_2$	2.264(1)	Cl	33
	2.265(1)	Cl	
Pd(methionine-H)Cl$_2$	2.265(4)	Cl	34
Pd[(CH$_3$SCH$_2$)$_2$](t-BuCHCH$_2$CH$_2$CH(Cl)-t-Bu)	2.268(7)	Cl	35
	2.400(7)	—CH$_<$	
[C$_6$H$_4$(SMe)PPh$_2$]PdI$_2$	2.288(2)	I	This work
C$_{34}$H$_{28}$PdS$_4$	2.292(3)	S=C$_<$	36
	2.308(2)	S=C$_<$	
Pd$_2$Br$_2$(SMe$_2$)$_2$	2.30(2)	Br bridging	37

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