Intramolecular hydrogen bonds between N—H groups and O atoms of the perchlorate ions are shown in Fig. 2. The hydrogen-bonding network is in a fairly symmetric arrangement and contributes a significant stabilizing effect in the whole molecule.

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cis-Dichlorobis(methyldiphenylphosphine)palladium(II)

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Abstract. $[PdCl_2\{P(CH_3)(C_6H_5)_2\}_2]$, $M_r = 577{\cdot}7$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}010$ (2), $b = 14{\cdot}542$ (3), $c = 17{\cdot}028$ (4) Å, $V = 2478{\cdot}7$ (9) Å^3, $Z = 4$, $D_x = 1{\cdot}55$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 10{\cdot}95$ cm^{-1}, $F(000) = 1168$, $T = 290$ K, $R = 0{\cdot}030$ for 1919 unique observed reflections. The homogeneous crystals contain the *cis*-isomer, although in solution the title compound exists as a mixture of *cis*- and *trans*-isomers. The square-planar palladium coordination has P—Pd—P [98·9 (1)°] slightly larger than the Cl—Pd—Cl angle [89·9 (1)°]. Bond distances are Pd—P 2·265 (2) Å and Pd—Cl 2·341 (2) Å.

Introduction. The title compound was prepared by the method of Grim & Keiter (1970). It was dissolved in $CHCl_3$ to give a yellow solution and a solution of excess $SnCl_2.2H_2O$ in ethanol was added. This produced a deep-red colour, believed to be due to (Ph_2MeP)-$Pd[SnCl_2]_2$. Slow evaporation at ambient temperature gave large yellow crystals, which were shown by the X-ray determination to be unchanged starting material.

Experimental. Crystal character: well shaped blocks. Data collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ 50°, with scan range ±0·9° (2θ) around $K\alpha_1 - K\alpha_2$ angles, scan speed 2–29° min^{-1}, depending on intensity of a 2 s pre-scan; backgrounds measured at each end of scan for 0·25 of scan time. *hkl* ranges: 0–11, 0–17, 0–20. Three standard reflections monitored every 200 reflections, and rescaled following a very slight decrease during data collection; unit-cell dimensions and standard deviations obtained by least-squares fit to 15 reflections ($20 < 2\theta < 22°$). Reflections processed using profile analysis to give 2519 unique reflections; 1919 considered observed [$I/\sigma(I) \geq 3{\cdot}0$] and used in refinement, corrected for Lorentz, polarization and absorption effects, the last with *ABSCOR* (Alcock, 1970), maximum and

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minimum transmission factors 0·88 and 0·86. Crystal dimensions 0·4 × 0·2 × 0·2 mm, with bounding faces {011}, {101}. Systematic absences $h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; $00l$, $l \neq 2n$ indicate space group $P2_12_12_1$.

Some difficulty was experienced in the initial structure solution because of the expectations that the compound contained a $PdSn_2$ unit; in due course, the heavy atom was located by Patterson techniques and the light atoms were then found on successive Fourier syntheses. Anisotropic temperature factors for all non-H atoms. H atoms given fixed isotropic temperature factors, $U = 0{\cdot}07$ Å^2. Those defined by the molecular geometry inserted at calculated positions and not refined; methyl groups treated as rigid CH_3 units, with their initial orientation taken from the strongest peak on a difference Fourier synthesis. Hand of the individual chiral crystal chosen checked by refinement of f'' multiplier. Final refinement on F by cascaded least-squares methods. Largest positive and negative peaks on a final difference Fourier synthesis of height $\pm 0{\cdot}3$ e Å^{-3}. Weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0{\cdot}00025$ used and shown to be satisfactory by a weight analysis. Final $R = 0{\cdot}030$, $wR = 0{\cdot}029$. Maximum Δ/σ in final cycle 1·0. Computing with *SHELXTL* (Sheldrick, 1981) on a Data General NOVA3, apart from absorption correction on a Burroughs B6800. Scattering factors in the analytical form and anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates are given in Table 1, and bond lengths and angles in Table 2.*

Discussion. Fig. 1 shows the molecular structure of the title compound. The phosphines are oriented to provide a close face-to-face contact between two phenyl groups, with a dihedral angle between these groups of 10·9 (2)°. The P—Pd—P angle is rather larger than 90°, presumably because of repulsion between the phosphine ligands, and the correspondingly inward-facing Pd—P—C angles are considerably larger than tetrahedral [116·8 (2); 119·8 (2)°]. These angles are also indicative of steric strain, through to a slightly lesser extent than in the very crowded $[PdCl_2(PPr^n_3)_2]$ (Alcock, Kemp & Wimmer, 1981) [angles 120·7 (2); 121·5 (2)°].

The title compound is isomorphous with modification (I) of the corresponding Pt compound (Kin-Chee, McLaughlin, McPartlin & Robertson, 1982). Comparison of the Pd—X and Pt—X distances in these compounds gives a surprising result. The M—Cl values show the expected trend, with Pt—Cl 0·009 Å larger than Pd—Cl, but the Pt—P distance is less than the

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (Å^2 ×10^3)

	x	y	z	U_{eq}*
Pd(1)	3781·8 (5)	270·7 (4)	8485·3 (3)	28 (1)
P(1)	6021 (2)	170 (1)	8326·3 (8)	29 (1)
P(2)	3212 (2)	688 (1)	7247 (1)	34 (1)
Cl(1)	1487 (2)	125 (1)	8708 (1)	55 (1)
Cl(2)	4192 (2)	−25 (2)	9817 (1)	49 (1)
C(11)	6733 (7)	−790 (5)	8846 (4)	43 (2)
C(12)	6914 (7)	1155 (5)	8716 (3)	29 (2)
C(13)	6201 (8)	1893 (4)	9024 (4)	37 (2)
C(14)	6866 (9)	2628 (5)	9371 (5)	53 (3)
C(15)	8235 (7)	2627 (5)	9427 (4)	54 (3)
C(16)	8924 (8)	1893 (5)	9127 (4)	53 (3)
C(17)	8286 (7)	1168 (5)	8777 (4)	45 (3)
C(18)	6623 (6)	−59 (4)	7338 (3)	29 (2)
C(19)	7617 (7)	440 (5)	6966 (4)	37 (2)
C(110)	8058 (7)	158 (5)	6223 (4)	47 (2)
C(111)	7502 (7)	−586 (5)	5854 (4)	50 (3)
C(112)	6479 (9)	−1081 (5)	6222 (4)	49 (3)
C(113)	6096 (7)	−831 (4)	6966 (4)	40 (2)
C(21)	2567 (8)	−288 (6)	6722 (4)	56 (3)
C(22)	4440 (7)	1239 (5)	6617 (4)	43 (2)
C(23)	4593 (9)	1027 (6)	5836 (4)	83 (4)
C(24)	5430 (10)	1515 (7)	5365 (6)	63 (4)
C(25)	6141 (9)	2249 (6)	5662 (5)	91 (4)
C(26)	5987 (9)	2484 (6)	6439 (6)	69 (4)
C(27)	5152 (9)	1986 (6)	6921 (5)	56 (3)
C(28)	1895 (7)	1549 (4)	7197 (4)	36 (2)
C(29)	1078 (8)	1597 (5)	6551 (5)	53 (3)
C(210)	150 (9)	2295 (6)	6497 (6)	64 (3)
C(211)	49 (7)	2951 (5)	7054 (5)	59 (3)
C(212)	860 (8)	2901 (6)	7712 (5)	55 (3)
C(213)	1781 (8)	2198 (6)	7784 (5)	52 (3)

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

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

Pd(1)–P(1)	2·262 (2)	Pd(1)–P(2)	2·267 (2)
Pd(1)–Cl(1)	2·338 (2)	Pd(1)–Cl(2)	2·344 (2)
P(1)–C(11)	1·802 (7)	P(1)–C(12)	1·815 (7)
P(1)–C(18)	1·819 (6)	P(2)–C(21)	1·798 (8)
P(2)–C(22)	1·817 (7)	P(2)–C(28)	1·819 (7)
C(12)–C(13)	1·391 (9)	C(12)–C(17)	1·376 (10)
C(13)–C(14)	1·391 (10)	C(14)–C(15)	1·374 (12)
C(15)–C(16)	1·370 (11)	C(16)–C(17)	1·369 (11)
C(18)–C(19)	1·385 (9)	C(18)–C(113)	1·392 (9)
C(19)–C(110)	1·402 (9)	C(110)–C(111)	1·368 (10)
C(111)–C(112)	1·399 (11)	C(112)–C(113)	1·373 (10)
C(22)–C(23)	1·374 (10)	C(22)–C(27)	1·399 (11)
C(23)–C(24)	1·360 (13)	C(24)–C(25)	1·379 (13)
C(25)–C(26)	1·375 (13)	C(26)–C(27)	1·377 (12)
C(28)–C(29)	1·373 (11)	C(28)–C(213)	1·379 (11)
C(29)–C(210)	1·379 (12)	C(210)–C(211)	1·349 (12)
C(211)–C(212)	1·386 (12)	C(212)–C(213)	1·382 (11)

P(1)–Pd(1)–P(2)	98·9 (1)	P(1)–Pd(1)–Cl(1)	170·7 (1)
P(2)–Pd(1)–Cl(1)	85·9 (1)	P(1)–Pd(1)–Cl(2)	86·0 (1)
P(2)–Pd(1)–Cl(2)	173·1 (1)	Cl(1)–Pd(1)–Cl(2)	89·9 (1)
Pd(1)–P(1)–C(11)	112·5 (2)	Pd(1)–P(1)–C(12)	113·2 (2)
C(11)–P(1)–C(12)	103·7 (3)	Pd(1)–P(1)–C(18)	116·8 (2)
C(11)–P(1)–C(18)	100·6 (3)	C(12)–P(1)–C(18)	108·7 (3)
Pd(1)–P(2)–C(21)	110·0 (3)	Pd(1)–P(2)–C(22)	119·8 (2)
C(21)–P(2)–C(22)	107·3 (3)	Pd(1)–P(2)–C(28)	114·2 (2)
C(21)–P(2)–C(28)	105·0 (3)	C(22)–P(2)–C(28)	99·2 (3)
P(1)–C(12)–C(13)	119·6 (5)	P(1)–C(12)–C(17)	122·0 (5)
C(13)–C(12)–C(17)	118·3 (6)	C(12)–C(13)–C(14)	120·4 (7)
C(13)–C(14)–C(15)	120·5 (7)	C(14)–C(15)–C(16)	118·4 (7)
C(15)–C(16)–C(17)	121·8 (7)	C(12)–C(17)–C(16)	120·6 (7)
P(1)–C(18)–C(19)	124·4 (5)	P(1)–C(18)–C(113)	116·3 (5)
C(19)–C(18)–C(113)	119·1 (6)	C(18)–C(19)–C(110)	119·0 (7)
C(19)–C(110)–C(111)	121·2 (7)	C(110)–C(111)–C(112)	119·9 (6)
C(111)–C(112)–C(113)	118·7 (7)	C(18)–C(113)–C(112)	121·9 (6)
P(2)–C(22)–C(23)	123·2 (6)	P(2)–C(22)–C(27)	117·9 (5)
C(23)–C(22)–C(27)	118·4 (7)	C(22)–C(23)–C(24)	121·5 (8)
C(23)–C(24)–C(25)	120·4 (9)	C(24)–C(25)–C(26)	119·2 (8)
C(25)–C(26)–C(27)	120·7 (8)	C(22)–C(27)–C(26)	119·8 (8)
P(2)–C(28)–C(29)	120·3 (5)	P(2)–C(28)–C(213)	119·8 (5)
C(29)–C(28)–C(213)	119·7 (7)	C(28)–C(29)–C(210)	119·5 (8)
C(29)–C(210)–C(211)	121·6 (8)	C(210)–C(211)–C(212)	119·2 (8)
C(211)–C(212)–C(213)	120·0 (8)	C(28)–C(213)–C(212)	119·9 (8)

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42420 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

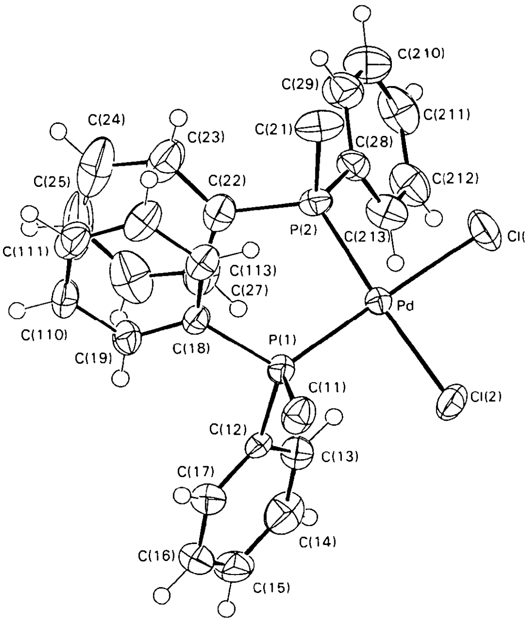

Fig. 1. The molecular structure of the title compound, showing the atomic numbering. Methyl H atoms are omitted for clarity.

Pd—P distance by 0·016 Å. This might be due to the increased steric strain associated with the (presumably) smaller Pd atom, but it can be better explained as resulting from a larger *trans*-effect with Pd than Pt. The Pd—P and Pd—Cl distances fall within the normal range (Palenik, Mathew, Steffan & Beran, 1975).

The title compound exists in solution as a mixture of the *cis*- and *trans*-isomers (Redfield & Nelson, 1973). From solid state ^{13}C NMR measurements, Bodenhausen, Deli, Anklin & Pregosin (1983) have claimed that the solid contains equal amounts of the two isomers. However, the present results show unequivocally that this is a misinterpretation. The NMR inequivalence which leads to the appearance of two sets of phosphine signals must arise because of the crystallographic and therefore environmental inequivalence of the two ligands, which can be seen most markedly in the different Pd—P—C angles noted above. This must also be the correct explanation for the 50:50 ratio of *cis*- and *trans*-isomers of $[PdCl_2(PMe_2Ph)_2]$ claimed by Bodenhausen *et al.* (1983), which is again at variance with X-ray results (Martin & Jacobson, 1971). A similar solid-state inequivalence has been reported for $[PPh_3CuBr]_4$ (Barron, Dyason, Engelhardt, Healy & White, 1984). Clearly any claimed identification of isomers by solid-state NMR in which the ratio of isomers corresponds to the number of chemically equivalent groups in the compound must be treated as suspect until the groups have been shown also to be crystallographically equivalent.

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Structure and Conformation of *cis*-Dichloro[1,1,1-trifluoro-2,3-bis(methylthio)propane]platinum(II), *cis*-$[PtCl_2\{cis\text{-}CH_3SCH_2CH(CF_3)SCH_3\}]$

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Abstract. $C_5H_9Cl_2F_3PtS_2$, $M_r = 456{\cdot}2$, tetragonal, $P4_2/n$ (origin at $\bar{1}$), $a = 17{\cdot}559\,(3)$, $c = 8{\cdot}139\,(3)$ Å, $U = 2509\,(1)$ Å^3, $Z = 8$, $D_x = 2{\cdot}415$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 120{\cdot}5$ cm^{-1}, $F(000) = 1680$, $T = 293$ K, $R = 0{\cdot}029$ for 1298 unique reflections with $I \geq 3\sigma(I)$. The *S*-methyl substituents are mutually *syn*.

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