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Orthorhombic and Monoclinic Allotropes of *cis*-[$PtCl_2(PMePh_2)_2$], *cis*-Dichlorobis(methyldiphenylphosphine)platinum(II): Structure Analyses

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Abstract

The crystal-structure analysis of two stable allotropes of *cis*-[$PtCl_2(PMePh_2)_2$] ($C_{26}H_{26}Cl_2P_2Pt$, $M_r = 666{\cdot}44$) is reported. (I) is orthorhombic, space group $P2_12_12_1$ with $a = 10{\cdot}0271\,(6)$, $b = 14{\cdot}5578\,(6)$, $c = 17{\cdot}0528\,(8)$ Å, $Z = 4$, $V = 2489{\cdot}24$ Å^3, $D_m = 1{\cdot}77\,(2)$, $D_c = 1{\cdot}778$ Mg m^{-3}, $F(000) = 1296$, μ(Cu $K\alpha$) = 14·025 mm^{-1}, $T = 294\,(1)$ K. (II) is monoclinic, space group $P2_1/c$ with $a = 12{\cdot}8639\,(9)$, $b = 13{\cdot}6580\,(3)$, $c = 18{\cdot}9963\,(14)$ Å, $\beta = 131{\cdot}312\,(6)^\circ$, $Z = 4$, $V = 2506{\cdot}93$ Å^3, $D_m = 1{\cdot}76\,(1)$, $D_c = 1{\cdot}766$ Mg m^{-3}, $F(000) = 1296$, μ(Cu $K\alpha$) = 13·926 mm^{-1}, $T = 294\,(1)$ K. Full-matrix least-squares refinements, with fixed H atoms, converged with $R = 0{\cdot}024$ for (I) (2296 reflections) and 0·019 for (II) (3220 reflections). Molecules in both allotropes are essentially *cis* square planar, with similar small tetrahedral deformations of the coordination spheres. In (II) the $PMePh_2$ ligands are disposed less symmetrically than in (I), resulting in inequivalence of the Cl—Pt—P angles [90·77 (4) and 83·43 (4)°] and of the Pt—Cl distances [2·359 (1) and 2·345 (1) Å]. The Pt—P distances are equivalent within experimental error [mean 2·245 (1) Å]. Corresponding mean bond distances for (I) are Pt—P, 2·249 (1) and Pt—Cl, 2·350 (1) Å.

Introduction

In the course of attempting to recrystallize *trans*-[$PtCl(COCH_3)(PMePh_2)_2$] from chlorinated solvents, excellent crystals (I) exhibiting well-defined *mmm* symmetry were obtained from ethanol/chloroform solution. The discrepancy between the observed density [1·77 (2) Mg m^{-3}, measured by flotation in aqueous BaI_2] and that calculated for the above formulation (1·798 Mg m^{-3}) was larger than expected, but consistent with imperfect wetting. Accordingly, the discrepancy was ignored and diffraction data were collected with these crystals. Subsequent solution of the structure showed the product to be *cis*-[$PtCl_2(PMePh_2)_2$]. Since the detailed structure of this molecule permits some quantification of the *trans* influence of the $PMePh_2$ ligand (on Pt—Cl bond distances) refinement of the structure was continued. Attempts to obtain crystals of the acyl complex were also continued. An apparently successful recrystallization from C_6H_6/EtOH/*n*-hexane under rigorously dry conditions yielded well-formed crystals (II) with $2/m$ symmetry. Observed and calculated densities were in excellent agreement (apparently) and, hence, a second set of data was collected on the assumption that this time we had the acyl complex. It was, in fact, a second crystalline modification of *cis*-[$PtCl_2(PMePh_2)_2$] and the density agreement was traced to a numerical error. However, despite being derived from a common precursor, *trans*-[$PtCl(COCH_3)(PMePh_2)_2$], and both having the *cis* conformation at Pt, molecules in (I) and (II) exhibit distinct conformational differences. Therefore, it seemed worthwhile to refine (II) to convergence also, with a view to investigating the effects of the conformational differences on metal–ligand bond lengths and angles.

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Structure analysis

Reflection intensities were recorded on a Picker FACS-1 diffractometer in θ–2θ continuous scan mode (scan velocity 2° min^{-1} 2θ, 2 × 10s background counts at scan extremes, $3 \leq 2\theta \leq 127°$, Cu $K\bar{\alpha}$ radiation, graphite-crystal monochromator, $T = 294 \pm 1$ K). Reflection forms $h,k,\pm l$ (2 unique sets) were recorded for (I) and cell dimensions and crystal orientation matrices were determined by least squares from observed setting angles for 12 high-angle well-dispersed reflections ($2\theta \geq 85°$, $\lambda = 1{\cdot}54051$ Å). Crystal dimensions were 0·12 × 0·16 × 0·20 mm for (I) and 0·18 × 0·08 × 0·17 mm for (II) in **a**, **b** and **c*** directions respectively.

Intensities of three standard reflections were remeasured after every 50 unique data. No significant crystal degradation was perceptible. Reflection data with $I \geq 3\sigma(I)$ and with background imbalance $\Delta < 3\sigma(\Delta)$ were accepted and reduced to $|F_o|$ and $\sigma(F_o)$ values, with instrumental uncertainty constants $\rho = 0{\cdot}03$ for (I), 0·02 for (II) (Busing & Levy, 1957; Corfield, Doedens & Ibers, 1967). Data were also corrected for absorption (de Meulenaer & Tompa, 1965): transmission factors varied from 0·200 to 0·353 for (I) and from 0·361 to 0·641 for (II). In subsequent refinements, data were also corrected for secondary extinction (Zachariasen, 1963). Statistical R values (R_s) for the terminal data sets (Robertson & Whimp, 1975) were 0·008 (I, 2296 unique reflections) and 0·011 (II, 3220 reflections). Both structures were solved by Patterson and Fourier techniques and refined first by block-diagonal then full-matrix least squares [minimizing $\sum w||F_o| - |F_c||^2$ with $w = 1/\sigma^2(F_o)$]. Except for H, scattering factors were taken from Cromer & Mann (1968) and were corrected for both real and imaginary anomalous-scattering components. The Stewart, Davidson & Simpson (1965) values were used for H. Refinement of scattering models not including H atoms converged with $R = 0{\cdot}030$ (I) and 0·031 (II). Difference syntheses calculated at this stage revealed maxima corresponding to all the phenyl and methyl H atoms. Contributions from these atoms were included in the scattering model with the phenyl H atoms in calculated positions (C—H = 0·95 Å) and the methyl H in positions located from the difference syntheses. H-atom coordinates and assumed thermal parameters ($B_H = 1{\cdot}1 \times B_C$) were not altered subsequently. Full-matrix refinement converged [with values for (II) given in parentheses] with $R = 0{\cdot}024$

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	(I)				(II)			
	x	y	z	B_{eq} (Å^2)	x	y	z	B_{eq} (Å^2)
Pt	−0·12110 (3)	0·02825 (2)	0·15319 (1)	2·11 (1)	0·24078 (1)	0·15609 (1)	0·16525 (1)	2·55(1)
Cl(1)	−0·08384 (20)	−0·00487 (15)	0·02009 (9)	3·8 (1)	0·07162 (11)	0·12270 (7)	0·17481 (8)	4·20 (6)
Cl(2)	−0·35041 (18)	0·01531 (15)	0·12723 (13)	4·2 (1)	0·37063 (11)	0·02372 (7)	0·26803 (7)	4·22 (6)
P(1)	−0·17908 (18)	0·06910 (11)	0·27567 (10)	2·6 (1)	0·40511 (10)	0·15757 (6)	0·15511 (7)	2·77 (5)
P(2)	0·10133 (16)	0·01923 (11)	0·16853 (9)	2·2 (1)	0·12869 (9)	0·29290 (6)	0·08297 (7)	2·65 (5)
C(101)	−0·2436 (9)	−0·0284 (6)	0·3282 (5)	4·1 (5)	0·5743 (4)	0·1827 (3)	0·2690 (3)	4·1 (2)
C(201)	−0·1744 (8)	−0·0780 (5)	0·1161 (4)	3·2 (4)	0·2404 (4)	0·3969 (3)	0·1150 (3)	3·5 (2)
C(111)	−0·3095 (7)	0·1555 (5)	0·2803 (4)	2·8 (3)	0·4163 (4)	0·0398 (3)	0·1159 (3)	3·2 (2)
C(112)	−0·3239 (8)	0·2212 (5)	0·2217 (5)	3·9 (4)	0·3034 (5)	−0·0233 (3)	0·0639 (3)	5·0 (3)
C(113)	−0·4148 (9)	0·2922 (5)	0·2306 (6)	4·6 (5)	0·3088 (6)	−0·1084 (4)	0·0266 (4)	6·3 (4)
C(114)	−0·4951 (8)	0·2963 (6)	0·2950 (6)	4·6 (5)	0·4256 (7)	−0·1325 (4)	0·0422 (4)	6·9 (4)
C(115)	−0·4843 (9)	0·2293 (7)	0·3521 (5)	4·6 (5)	0·5362 (5)	−0·0699 (4)	0·0922 (4)	6·0 (4)
C(116)	−0·3910 (8)	0·1606 (6)	0·3452 (4)	4·0 (4)	0·5327 (4)	0·0155 (4)	0·1294 (3)	4·7 (3)
C(121)	−0·0566 (7)	0·1255 (5)	0·3380 (4)	3·2 (4)	0·3919 (3)	0·2367 (2)	0·0725 (3)	2·8 (2)
C(122)	0·0142 (9)	0·1999 (6)	0·3074 (5)	3·9 (5)	0·2861 (4)	0·2200 (3)	−0·0227 (3)	3·2 (2)
C(123)	0·0976 (10)	0·2507 (7)	0·3551 (7)	6·0 (7)	0·2721 (4)	0·2765 (3)	−0·0887 (3)	3·8 (2)
C(124)	0·1141 (12)	0·2255 (9)	0·4329 (7)	6·5 (8)	0·3684 (5)	0·3508 (3)	−0·0586 (3)	4·2 (3)
C(125)	0·0455 (12)	0·1529 (9)	0·4618 (6)	6·3 (7)	0·4725 (5)	0·3677 (3)	0·0347 (3)	4·2 (3)
C(126)	−0·0413 (10)	0·1026 (7)	0·4168 (5)	4·5 (5)	0·4850 (4)	0·3117 (3)	0·1008 (3)	3·4 (2)
C(211)	0·1614 (6)	−0·0046 (4)	0·2671 (4)	2·4 (3)	0·0193 (3)	0·2779 (2)	−0·0419 (2)	2·8 (2)
C(212)	0·2616 (8)	0·0450 (5)	0·3046 (4)	3·1 (4)	−0·0059 (4)	0·3534 (3)	−0·1006 (3)	3·5 (2)
C(213)	0·3047 (9)	0·0159 (6)	0·3784 (4)	3·8 (4)	−0·0850 (5)	0·3366 (3)	−0·1955 (3)	4·1 (3)
C(214)	0·2485 (9)	−0·0590 (6)	0·4144 (4)	3·8 (4)	−0·1391 (4)	0·2451 (3)	−0·2327 (3)	4·3 (3)
C(215)	0·1530 (9)	−0·1075 (5)	0·3785 (5)	3·6 (4)	−0·1178 (4)	0·1703 (3)	−0·1763 (3)	4·3 (2)
C(216)	0·1078 (8)	−0·0810 (5)	0·3037 (4)	3·0 (3)	−0·0385 (4)	0·1858 (3)	−0·0811 (3)	3·4 (2)
C(221)	0·1884 (7)	0·1182 (5)	0·1292 (4)	2·8 (4)	0·0168 (4)	0·3447 (2)	0·1007 (3)	2·9 (2)
C(222)	0·3281 (8)	0·1169 (6)	0·1230 (4)	3·4 (4)	−0·1237 (4)	0·3573 (3)	0·0293 (3)	3·7 (2)
C(223)	0·3939 (8)	0·1910 (7)	0·0887 (5)	4·3 (4)	−0·2023 (4)	0·4022 (3)	0·0452 (3)	4·6 (3)
C(224)	0·3233 (9)	0·2629 (6)	0·0572 (5)	4·1 (5)	−0·1414 (5)	0·4352 (3)	0·1335 (4)	4·8 (3)
C(225)	0·1842 (9)	0·2642 (5)	0·0620 (5)	3·8 (4)	−0·0021 (5)	0·4213 (3)	0·2057 (3)	4·6 (3)
C(226)	0·1177 (8)	0·1905 (5)	0·0978 (4)	2·9 (3)	0·0778 (4)	0·3773 (3)	0·1906 (3)	3·8 (2)

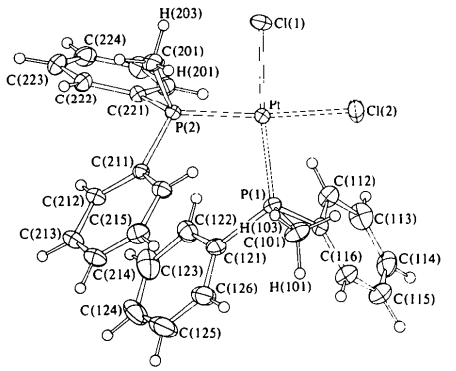

Fig. 1. Molecular conformation and atom nomenclature for (I).

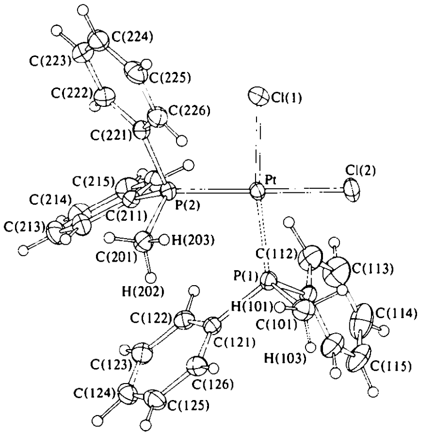

Fig. 2. Molecular conformation and atom nomenclature for (II).

(0·019), R_w = 0·037 (0·025), a shift to e.s.d. ratio <0·05 (0·02) everywhere, and $s = \{\sum w(|F_o| - |F_c|)^2/(m-n)\}^{1/2}$ = 1·792 (1·723). Extinction coefficients at convergence were 0·776 × 10^{-6} (0·416 × 10^{-4}) and absolute magnitudes of residual maxima in the terminal difference maps were <0·7 (0·5)e Å^{-3} everywhere. Reversing the sign of the imaginary anomalous-scattering component for (I), which has the non-centrosymmetric space group $P2_12_12_1$, increased R from 0·02 to 0·041. The increase is significant at better than 1% (Hamilton, 1965) and therefore the model has the correct absolute configuration. Positional and thermal parameters are given in Table 1.* Atom nomenclature is defined in Figs. 1 and 2. The thermal ellipsoids depict 50% probability surfaces and the H atoms are depicted as hard spheres of arbitrary radius. The figures were drawn with *ORTEP* (Johnson, 1976). All computations were performed on the Univac 1100-42 computer at the Australian National University Computing Centre with programs which have been described elsewhere (Robertson & Whimp, 1975).

Description of structures and discussion

In both (I) and (II) the Pt atom has planar coordination geometry with the slight tetrahedral distortion frequently observed for d^8 metal ions with bulky ligands. Atom deviations from the best planes through the PtP_2Cl_2 moieties are similar in both cases, Table 2. The most striking difference between molecules in (I) and (II) is apparent from Figs. 1 and 2. In (I) the closest contact between the two *cis*-(methyldiphenylphosphine) ligands involves two approximately parallel phenyl rings (dihedral angle 11·0°), an arrangement common in *cis*-triphenylphosphine compounds (Russell & Tucker, 1975). However in (II), although the first phosphine is in a very similar orientation to that in (I), the second is rotated so that its methyl group points towards the phenyl group of the first ligand. Consequently the closest contacts between the *cis*-phosphines in (II) are between these two groups.

The conformational differences are reflected in differences between the chemically equivalent bond lengths and angles, Table 3 (bond lengths and angles in the phenyl groups are given in Tables 4 and 5). The most notable differences are those which occur between bond angles at the Pt atoms. In (I) the angles between adjacent chloro and phosphine ligands are nearly identical [Cl(1)—Pt—P(2), 86·71 (6); Cl(2)—Pt—P(1), 86·74 (7)°], whereas in (II) the corresponding angles differ by 7·34 (6)° [Cl(1)—Pt—P(2), 90·77 (4); Cl(2)—Pt—P(1), 83·43 (4)°]. Correspondingly, the Pt—Cl distances in (I) are also nearly identical [2·350 (2) and 2·349 (2) Å] while those in (II) differ by 0·014 (2) Å [Pt—Cl(1), 2·345 (1); Pt—Cl(2), 2·359 (1) Å]. Both these and the other small differences manifest in Table 3 result almost entirely from the differing intramolecular non-bonded interactions in the two conformers. Thus, the marked differences in Cl—Pt—P angles are clearly related to the different ways in which the interligand

Table 2. *Atom deviations* (Å) *from the coordination planes with e.s.d.'s in parentheses*

Atoms defining planes	Atom	Deviations (Å)	
PtCl(1)Cl(2)P(1)P(2)		(I)	(II)
	Pt	0·0020 (2)	0·0009 (1)
	Cl(1)	0·087 (2)	0·150 (1)
	Cl(2)	−0·167 (2)	−0·157 (1)
	P(1)	0·061 (2)	0·109 (1)
	P(2)	−0·099 (2)	−0·115 (1)

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and stereoscopic packing diagrams have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36117 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected bond lengths* (Å) *and angles* (°)

	(I)	(II)
Pt—Cl(1)	2·3504 (16)	2·3447 (10)
Pt—Cl(2)	2·3491 (18)	2·3589 (9)
Pt—P(1)	2·2480 (17)	2·2459 (11)
Pt—P(2)	2·2495 (16)	2·2446 (6)
P(1)—C(101)	1·800 (8)	1·822 (4)
P(1)—C(111)	1·816 (7)	1·817 (4)
P(1)—C(121)	1·820 (7)	1·818 (4)
P(2)—C(201)	1·827 (7)	1·816 (4)
P(2)—C(211)	1·818 (6)	1·801 (4)
P(2)—C(221)	1·813 (8)	1·824 (4)
Mean H—C(Me)	0·98	0·98
Cl(1)—Pt—Cl(2)	87·54 (7)	88·46 (4)
Cl(1)—Pt—P(1)	173·02 (7)	169·30 (3)
Cl(1)—Pt—P(2)	86·71 (6)	90·77 (4)
Cl(2)—Pt—P(1)	86·74 (8)	83·43 (4)
Cl(2)—Pt—P(2)	171·01 (7)	173·09 (4)
P(1)—Pt—P(2)	99·43 (6)	98·11 (3)
Pt—P(1)—C(101)	110·3 (3)	110·7 (2)
Pt—P(1)—C(111)	114·2 (2)	111·2 (1)
Pt—P(1)—C(121)	119·2 (2)	121·5 (1)
Pt—P(2)—C(201)	112·7 (3)	114·5 (1)
Pt—P(2)—C(211)	116·6 (2)	114·0 (1)
Pt—P(2)—C(221)	112·8 (2)	114·6 (1)
C(101)—P(1)—C(111)	105·4 (4)	107·3 (2)
C(101)—P(1)—C(121)	107·9 (4)	105·7 (2)
C(111)—P(1)—C(121)	98·5 (3)	99·2 (2)
C(201)—P(2)—C(211)	99·9 (3)	106·8 (2)
C(201)—P(2)—C(221)	104·0 (3)	100·4 (2)
C(211)—P(2)—C(221)	109·5 (3)	105·2 (2)
Mean P—C(Me)—H	115	111
Mean H—C(Me)—H	106	111

Table 4. *Bond lengths* (Å) *and angles* (°) *in the phenyl groups in* (I)

	m = 1, *n* = 1	*m* = 1, *n* = 2	*m* = 2, *n* = 1	*m* = 2, *n* = 2
C(*mn*1)—C(*mn*2)	1·39 (1)	1·40 (1)	1·39 (1)	1·40 (1)
C(*mn*2)—C(*mn*3)	1·39 (1)	1·38 (1)	1·40 (1)	1·39 (1)
C(*mn*3)—C(*mn*4)	1·36 (1)	1·39 (2)	1·37 (1)	1·37 (1)
C(*mn*4)—C(*mn*5)	1·38 (1)	1·35 (2)	1·34 (1)	1·40 (1)
C(*mn*5)—C(*mn*6)	1·37 (1)	1·37 (1)	1·41 (1)	1·40 (1)
C(*mn*6)—C(*mn*1)	1·38 (1)	1·39 (1)	1·38 (1)	1·38 (1)
P(*m*)—C(*mn*1)—C(*mn*2)	121·3 (6)	118·4 (6)	124·4 (5)	119·8 (6)
P(*m*)—C(*mn*1)—C(*mn*6)	120·0 (6)	122·0 (6)	116·2 (5)	120·2 (6)
C(*mn*2)—C(*mn*1)—C(*mn*6)	118·6 (7)	119·3 (7)	119·3 (6)	119·6 (7)
C(*mn*1)—C(*mn*2)—C(*mn*3)	120·2 (8)	120·2 (9)	118·7 (7)	119·6 (8)
C(*mn*2)—C(*mn*3)—C(*mn*4)	120·6 (8)	119·6 (11)	121·1 (8)	120·7 (8)
C(*mn*3)—C(*mn*4)—C(*mn*5)	119·3 (7)	119·7 (10)	120·6 (7)	120·1 (8)
C(*mn*4)—C(*mn*5)—C(*mn*6)	120·5 (8)	122·3 (10)	120·0 (7)	119·3 (8)
C(*mn*5)—C(*mn*6)—C(*mn*1)	120·8 (8)	118·8 (9)	120·3 (7)	120·6 (7)

Table 5. *Bond lengths* (Å) *and angles* (°) *in the phenyl groups in* (II)

	m = 1, *n* = 1	*m* = 1, *n* = 2	*m* = 2, *n* = 1	*m* = 2, *n* = 2
C(*mn*1)—C(*mn*2)	1·391 (5)	1·388 (5)	1·390 (5)	1·378 (5)
C(*mn*2)—C(*mn*3)	1·386 (6)	1·378 (6)	1·385 (6)	1·376 (6)
C(*mn*3)—C(*mn*4)	1·366 (7)	1·398 (6)	1·376 (6)	1·377 (7)
C(*mn*4)—C(*mn*5)	1·368 (8)	1·362 (6)	1·371 (6)	1·372 (6)
C(*mn*5)—C(*mn*6)	1·380 (7)	1·386 (6)	1·385 (6)	1·375 (6)
C(*mn*6)—C(*mn*1)	1·382 (6)	1·387 (5)	1·398 (5)	1·400 (6)
P(*m*)—C(*mn*1)—C(*mn*2)	120·8 (3)	118·7 (3)	122·5 (3)	123·3 (3)
P(*m*)—C(*mn*1)—C(*mn*6)	120·4 (3)	122·7 (4)	118·8 (3)	118·2 (3)
C(*mn*2)—C(*mn*1)—C(*mn*6)	118·5 (4)	118·6 (4)	118·6 (4)	118·4 (4)
C(*mn*1)—C(*mn*2)—C(*mn*3)	120·2 (4)	121·4 (4)	120·2 (4)	121·1 (4)
C(*mn*2)—C(*mn*3)—C(*mn*4)	120·6 (5)	119·0 (4)	120·4 (4)	120·2 (4)
C(*mn*3)—C(*mn*4)—C(*mn*5)	119·4 (5)	120·0 (4)	120·2 (4)	119·4 (4)
C(*mn*4)—C(*mn*5)—C(*mn*6)	120·9 (5)	120·7 (4)	120·1 (4)	120·9 (4)
C(*mn*5)—C(*mn*6)—C(*mn*1)	120·4 (4)	120·2 (4)	120·5 (4)	120·0 (4)

repulsions are minimized. Because of the steric requirements of the bulky methyldiphenylphosphine ligands, the electronic preference of the Pt^{II} ion for 90° metal–ligand interbond angles cannot be satisfied.

In (I) the large P—Pt—P angle [99·43 (3)°] allows the two parallel (contacting) phenyl groups, on P(1) and P(2) respectively, to achieve separations approaching normal van der Waals distances (*ca* 3·4 Å). Even so, the two C atoms attached directly to the P atoms are very close [C(121)···C(211), 3·14 Å] and any further reduction in the P—Pt—P angle would be highly unfavourable energetically. However, in this conformer the two remaining organo groups on each P atom are staggered relative to the Pt–Cl bonds. Therefore, approximately square-planar coordination can be maintained by almost equal reductions of the Cl—Pt—P angles (from 90°) to 86·71 (6) and 86·74 (7)° respectively, and of the Cl—Pt—Cl angle to 87·54 (7)°. The resultant closest H···Cl and C···Cl (intramolecular) contacts are H(203)···Cl(1) 2·77, C(201)···Cl(1) 3·24 and C(111)···Cl(2) 3·34 Å.

In (II) the dissimilar orientations of the two phosphine ligands require that minimization of the interligand repulsions occurs *via* asymmetric relaxation of the metal–ligand interbond angles. Again, separations approaching normal van der Waals contacts between the phosphine ligand substituents are achieved by substantially opening the P—Pt—P angle [98·11 (3)°]. In this case, however, approximately planar coordination cannot be maintained by equal reductions in the Cl—Pt—P (and Cl—Pt—Cl) angles. Indeed the Cl(1)—Pt—P (2) angle [90·77 (4)°] is actually slightly larger than the ideal value (90°) and any reduction is effectively precluded by the nearly eclipsed configuration of the phosphine relative to the Pt–Cl(1) bond, and the consequent short C(221)···Cl(1) contact (3·22 Å). Accordingly, compensation for the large P—Pt—P angle is brought about mainly by a reduction in the Cl(2)—Pt—P(1) angle to 83·43 (4)° with closest interligand contacts H(102)···Cl(2) 2·71 and C(111)···Cl(2) 3·31 Å. The larger Cl—Pt—Cl angle in (II) [88·46 (4), *cf.* 87·54 (7)° for (I)] is unexpected in view of the large distortion of the Cl(2)—Pt—P(1) angle and the slightly shorter Cl(2)···phosphine contacts. However, there are two quite short H···Cl(2) interactions (2·69 and 2·7 Å) which may be responsible for the increase in the interbond angle.

The substantial differences in metal–ligand interbond angles in (I) and (II) might be expected to result in differences in the metal–ligand bond lengths. Despite

Table 6. *Variation of* Pt–Cl *distances* (Å) *with cis and trans metal–ligand interbond angles*

		trans Cl–Pt–P angle (°)	*cis* Cl–Pt–P angle (°)	Deviation of *cis* angle from 90°
Pt–Cl(1) (II)	2·345	169·30	90·77	+0·77°
Pt–Cl(2) (I)	2·349	171·01	86·74	−3·26
Pt–Cl(1) (I)	2·350	173·02	86·71	−3·29
Pt–Cl(2) (II)	2·359	173·09	83·43	−6·57

the fact that the angular differences are due to different relative orientations of the phosphine ligands, the Pt–P distances are very similar in both conformers: the difference between the mean values in (I) and (II) being only 0·0035 (14) Å. However, there are significant differences in the Pt–Cl lengths. In (I), where both phosphines are similarly oriented (with respect to Cl) and the *cis* Cl–Pt–P angles are equivalent, the Pt–Cl distances are identical to within experimental error [2·350 (2) and 2·349 (2) Å]. In contrast, the asymmetric phosphine orientation in (II) results in inequivalent Pt–Cl distances [2·345 (1) and 2·359 (1) Å; $\Delta/\sigma = 10$]. Not unexpectedly the average value (2·352 Å) is very close to that in (I) [2·350 (1) Å]. Both the Pt–P and Pt–Cl distances in the present complex are marginally smaller than those in *cis*-[$PtCl_2(PEt_3)_2$] [Pt–P 2·259 (2); Pt–Cl, 2·361 (6) Å; Manojlović-Muir, Muir & Solomun (1977)] consistent with the expectation of a slightly higher *trans* influence and slightly greater effective σ-orbital radius for the trialkylphosphine ligand (Appleton, Clark & Manzer, 1973).

The relatively high *trans* influence of phosphine ligands in square-planar Pt^{II} complexes led us to consider the possibility that the Pt–Cl distances in (I) and (II) may be related to the linearity of the *trans* P–Pt–Cl atoms. However, as is apparent from Table 6, despite a general increase in Pt–Cl distance with increased linearity, the correlation is not convincing in detail. It may be more relevant that the shortest Pt–Cl distance occurs when the *cis* Cl–Pt–P angle is closest to the ideal value of 90°. Indeed the deviations of the *cis* Cl–Pt–P angles from 90° (Table 6) show an almost linear relationship to the Pt–Cl length. The likely occurrence of a similar correlation in *cis*-[$PtCl_2(PMe_3)_2$] (Messmer, Amma & Ibers, 1967) is a tempting subject for speculation, the Pt–Cl distances differing by *ca* 0·02 Å and the Cl–Pt–P angles by *ca* 6°. Unfortunately the precision of the bond-length estimates is fairly low and the differences, though relatively large, are not statistically significant.

The present structures exhibit two other features of interest. First, Pt···H contacts of the type described as non-primary valence interactions (Bennett, Donaldson, Hitchcock & Mason, 1975) are observed in both isomers [2·91 to H(226) in (I); 2·85 Å to H(112) in (II)]. Secondly, and altogether less commonly, both isomers exhibit very short Cl···H(Me) contacts [2·77 to H(203) in (I); 2·71 Å to H(102) in (II)]. Similar interactions to *o*-phenylene H atoms have been reported in planar Rh^I complexes (de Boer, Rogers, Skapski & Troughton 1966; Napier, Meek, Kirchnev & Ibers, 1973).

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