planes which is 54·5° (90° for tetrahedral, 0° for square planar). Previously studied $CuCl_4^{2-}$ anions have shown a variable range of values from $\theta = 124°$ and $\beta = 67·9°$ in Cs_2CuCl_4 (Helmholz & Kruh, 1952) to $\theta = 180°$ and $\beta = 0°$ in bis(*N*-methylphenethylammonium)$CuCl_4$ (Harlow, Wells, Watt & Simonsen, 1974). This distortion of geometry has been associated with a monotonic variation in the *d*–*d* transition energies (Willett, Haugen, Lebsack & Morrey, 1974; Battaglia, Bonamartini-Corradi, Marcotrigiano, Menabue & Pellacani, 1979) and the electronic structure of the ion (Solomon, Hare, Dooley, Dawson, Stephens & Gray, 1980). The role of hydrogen bonding in stabilizing the square-planar configuration through removal of charge from the chloride ion has been argued (Geiser & Willett, 1984). Thus, with weak hydrogen bonding electrostatic forces dominate, yielding a geometry close to tetrahedral, while with strong hydrogen bonding the crystal field stabilization energy dominates, giving a geometry closer to square planar.

The tetrabromide structure is analogous to that of the tetrachloride (Fig. 1*c*). The cation bond angles and distances were within two standard deviations of those obtained for the chloride salt. The only significant difference lies in the Cu—Br *vs* Cu—Cl distance (average) of 2·377 (1) *vs* 2·240 (1) Å and the *trans* Br—Cu—Br angle *vs* the Cl—Cu—Cl angle of 137 (1) *vs* 140 (1)°. The compression of the coordination sphere towards tetrahedral geometry is as expected upon replacement of the chloride ions by the larger bromide ion.

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Structure of *cis*-Dichlorobis(dimethylphenylphosphine)platinum(II)

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Abstract. $[PtCl_2(C_8H_{11}P)_2]$, $M_r = 542·3$, triclinic, $P\bar{1}$, $a = 9·127$ (2), $b = 10·286$ (3), $c = 10·890$ (2) Å, $\alpha = 74·40$ (2), $\beta = 70·24$ (2), $\gamma = 88·23$ (2)°, $V = 924·7$ (4) Å^3, $Z = 2$, $D_x = 1·947$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 81·2$ cm^{-1}, $F(000) = 520$, $T = 294$ K, $R = 0·026$ for 4693 unique observed reflections. The average Pt—P and Pt—Cl distances are 2·244 (2) and 2·357 (3) Å, respectively.

Introduction. During investigation of insertion reactions in Pt^{II} σ-allyl complexes, we had the opportunity of obtaining crystals of the title compound. The structure was determined in order to obtain further insight into the electronic and steric effects of phosphine ligands.

Experimental. Crystal approximately 0·11 × 0·32 × 0·50 mm. Weissenberg and precession photographs indicated the crystal to be triclinic. Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation; lattice parameters refined by least-squares fit of 25 reflections in the range $17 < \theta < 21°$. Intensity data measured by the $\omega/2\theta$ scan technique, ω scan angle $= (1·3 + 0·35\tan\theta)°$; variable scan rate, 0·9–5° min^{-1}. Three standard reflections ($\bar{7}\bar{4}\bar{4}$, $\bar{7}40$, $\bar{7}4\bar{5}$), monitored every 3000 s, showed no decay throughout

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Table 1. *Final positional parameters and equivalent isotropic thermal parameters of the non*-H *atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + (ab\cos\gamma)B(1,2) + (ac\cos\beta)B(1,3) + (bc\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq}(Å^2)
Pt	0·03240 (2)	−0·22791 (2)	−0·02443 (2)	2·022 (3)
Cl(1)	−0·0693 (2)	−0·3441 (2)	0·2083 (1)	3·79 (3)
Cl(2)	−0·2279 (2)	−0·1911 (2)	−0·0108 (2)	4·26 (4)
P(1)	0·2699 (1)	−0·2874 (1)	−0·0218 (1)	2·33 (2)
P(2)	0·1194 (1)	−0·0917 (1)	−0·2372 (1)	2·32 (2)
C(1)	0·3615 (6)	−0·1713 (7)	0·0352 (5)	3·7 (1)
C(2)	0·2714 (8)	−0·4533 (7)	0·0915 (6)	4·2 (1)
C(3)	0·4113 (5)	−0·3073 (5)	−0·1784 (5)	2·39 (9)
C(4)	0·5558 (6)	−0·2330 (6)	−0·2427 (5)	3·1 (1)
C(5)	0·6604 (7)	−0·2588 (7)	−0·3580 (6)	4·2 (1)
C(6)	0·6232 (9)	−0·3582 (7)	−0·4095 (6)	4·7 (2)
C(7)	0·4823 (8)	−0·4319 (7)	−0·3452 (6)	4·4 (1)
C(8)	0·3750 (7)	−0·4055 (6)	−0·2308 (5)	3·3 (1)
C(9)	0·2836 (6)	0·0234 (5)	−0·2734 (5)	3·0 (1)
C(10)	−0·0193 (7)	0·0245 (7)	−0·2812 (7)	3·9 (1)
C(11)	0·1694 (6)	−0·1775 (5)	−0·3687 (5)	2·39 (9)
C(12)	0·0689 (7)	−0·2826 (6)	−0·3539 (5)	3·6 (1)
C(13)	0·0969 (9)	−0·3476 (7)	−0·4556 (6)	4·5 (1)
C(14)	0·2243 (9)	−0·3080 (7)	−0·5718 (6)	4·2 (1)
C(15)	0·3253 (8)	−0·2042 (7)	−0·5876 (6)	4·2 (1)
C(16)	0·2977 (7)	−0·1369 (6)	−0·4864 (6)	3·6 (1)

data collection. Orientation matrix checked every 300 reflections. 5363 independent reflections collected ($2.5 \leq \theta \leq 30°$; $-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $0 \leq l \leq 15$), 4693 significant [$I \geq 3.0\sigma(I)$]. The standard deviation of observed structure-factor amplitudes based on counting statistics. Empirical absorption correction applied using ψ scans of four reflections at $\chi > 80°$ (correction factors in the range 0·593–0·999, average transmission factor 0·78). No extinction corrections. Lorentz and polarization corrections applied and data reduced to $|F_o|$ values. Structure solved by the heavy-atom method. H atoms located at calculated positions and held constant during the least-squares refinement. Refinement using full-matrix least-squares method with anisotropic thermal factors for non-H atoms led to $R = 0.026$, $wR = 0.033$, $S = 1.56$, $(\Delta/\sigma)_{max} = 0.04$. Function minimized $\sum w(|F_o| - |F_c|)^2$, $w = 1$. Residual electron density in final ΔF maps around Pt atoms: max. = 0·84 e Å^{-3}. Atomic scattering factors, anomalous-dispersion terms and programs as in Enraf–Nonius (1975). All computations carried out on a PDP 11/44. Final positional and thermal parameters with their standard deviations are listed in Table 1.*

Discussion. Bond distances and angles are given in Table 2. The crystal structure consists of discrete molecules, shown in Fig. 1 with the atom numbering scheme.

The Pt atom displays a slight tetrahedral distortion from planar coordination geometry. Atom deviations from the best least-squares plane defined by Pt, Cl(1), Cl(2), P(1) and P(2) are 0·026 (0), −0·121 (2), 0·106 (2), 0·106 (1) and −0·117 (1) Å, respectively.

It has already been observed that Pt—P bond lengths increase with decrease in the electronegativity of groups on phosphorus (Hitchcock, Jacobson & Pidcock, 1977). In fact, passing from PF_3 to PEt_3, the Pt—P bond length, *trans* to Cl, increases from 2·141 (3) to 2·272 (3) Å. This trend parallels the decrease of the electronic parameter ν (Tolman, 1977), from 2110·8 for PF_3 to 2061·7 cm^{-1} for PEt_3. However, inspection of Table 3, where Pt—P distances in related *cis*-$PtCl_2$ diphosphine complexes are listed in decreasing order of

Table 2. *Bond lengths* (Å) *and angles* (°) *with their e.s.d.'s in parentheses*

Pt—Cl(1)	2·359 (1)	C(3)—C(8)	1·384 (6)
Pt—Cl(2)	2·355 (1)	C(4)—C(5)	1·383 (6)
Pt—P(1)	2·242 (1)	C(5)—C(6)	1·390 (9)
Pt—P(2)	2·245 (1)	C(6)—C(7)	1·373 (9)
P(1)—C(1)	1·822 (5)	C(7)—C(8)	1·387 (7)
P(1)—C(2)	1·820 (5)	C(11)—C(12)	1·379 (6)
P(1)—C(3)	1·816 (4)	C(11)—C(16)	1·384 (6)
P(2)—C(9)	1·806 (4)	C(12)—C(13)	1·391 (7)
P(2)—C(10)	1·808 (5)	C(13)—C(14)	1·369 (8)
P(2)—C(11)	1·804 (4)	C(14)—C(15)	1·369 (8)
C(3)—C(4)	1·401 (6)	C(15)—C(16)	1·403 (7)
Cl(1)—Pt—Cl(2)	86·55 (5)	C(9)—P(2)—C(11)	107·3 (2)
Cl(1)—Pt—P(1)	88·36 (4)	C(10)—P(2)—C(11)	102·4 (2)
Cl(1)—Pt—P(2)	172·23 (4)	P(1)—C(3)—C(4)	122·9 (3)
Cl(2)—Pt—P(1)	173·31 (5)	P(1)—C(3)—C(8)	117·3 (3)
Cl(2)—Pt—P(2)	90·79 (4)	C(3)—C(4)—C(5)	119·5 (5)
P(1)—Pt—P(2)	94·80 (4)	C(4)—C(5)—C(6)	120·4 (5)
Pt—P(1)—C(1)	112·1 (2)	C(5)—C(6)—C(7)	119·9 (5)
Pt—P(1)—C(2)	114·3 (2)	C(6)—C(7)—C(8)	120·3 (5)
Pt—P(1)—C(3)	117·4 (1)	C(7)—C(8)—C(3)	120·1 (5)
C(1)—P(1)—C(2)	104·7 (3)	P(2)—C(11)—C(12)	117·8 (3)
C(1)—P(1)—C(3)	107·1 (2)	P(2)—C(11)—C(16)	122·8 (3)
C(2)—P(1)—C(3)	99·7 (2)	C(11)—C(12)—C(13)	120·4 (5)
Pt—P(2)—C(9)	114·6 (2)	C(12)—C(13)—C(14)	120·5 (5)
Pt—P(2)—C(10)	114·6 (2)	C(13)—C(14)—C(15)	119·8 (5)
Pt—P(2)—C(11)	115·0 (1)	C(14)—C(15)—C(16)	120·4 (5)
C(9)—Pt—C(10)	101·2 (2)	C(11)—C(16)—C(15)	119·8 (5)

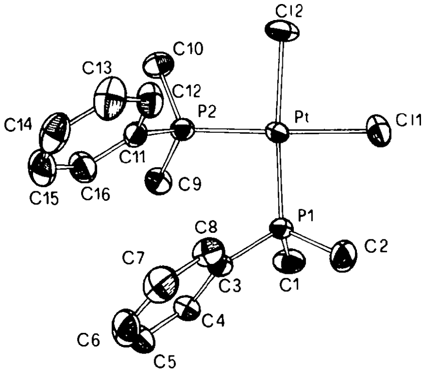

Fig. 1. View of the molecule, showing the atomic numbering (H atoms omitted for clarity).

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43745 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Average* Pt—P *and* Pt—Cl *distances* (Å) *in cis-*L_2PtCl_2 *complexes with electronic,* ν (cm^{-1}), *and steric,* θ (°), *parameters of ligands L*

L	Pt—P*	Pt—Cl*	ν	θ	Ref.
PF_3†	2·142 (3)	2·305 (3)	2110·8	104	(*a*)
$P(OPh)_3$†	2·182 (2)	2·344 (2)	2085·3	128	(*b*)
$PPh_2(OCH_2C_4H_8)$	2·223 (3)	2·364 (8)	2072§	133§	(*c*)
PPh_3	2·258 (10)	2·345 (16)	2068·9	145	(*d*)
PBz_2Ph	2·246 (4)	2·355 (4)	2067·6	158	(*e*)
$PMePh_2$	2·247 (2)	2·351 (6)	2067·0	136	(*f*)
PMe_2Ph	2·244 (2)	2·357 (3)	2065·3	122	(*g*)
PMe_3	2·243 (10)	2·373 (6)	2064·1	118	(*h*)
PEt_3‡	2·272 (3)	2·357 (3)	2061·7	132	(*a*)

(*a*) Hitchcock, Jacobson & Pidcock (1977). (*b*) Caldwell, Manojlović-Muir & Muir (1977). (*c*) Bartczak, Youngs & Ibers (1984). (*d*) Anderson, Clark, Davies, Ferguson & Parvez (1982). (*e*) Alcock & Nelson (1982). (*f*) Kin-Chee, McLaughlin, McPartlin & Robertson (1982). (*g*) Present work. (*h*) Del Pra & Zanotti (1979), Messmer, Amma & Ibers (1967).

* When *L* ligands are the same, the e.s.d. in parentheses is the error of the mean.

† *cis* to PEt_3.

‡ *cis* to PF_3.

§ Estimated value, close to that of $PPh_2(OEt)$.

ν, shows that there are some deviations from this general trend. Compounds from PPh_3 to PMe_3 have comparable Pt—P distances, in spite of the slight but continuous decrease of the ν factor. It seems likely that such deviations arise from steric effects, due to the bulkiness of the phosphine ligands, measured by Tolman's cone angle θ (Tolman, 1977). In fact, PPh_3, PBz_2Ph and $PMePh_2$ have the higher cone angles in Table 3 and hence exert stronger intraligand repulsions lengthening the Pt—P distances with respect to those of the PMe_2Ph and PMe_3 derivatives.

However, the definition of θ just gives a rough measure of steric effects, especially in the solid state. Phosphines of the PR_2R' type can assume a conformation which with small changes in bond angles is able to minimize intra- and intermolecular steric interactions, reducing the lengthening of the metal–phosphorus bond. Therefore, it is not surprising that in the PBz_2Ph complex (Alcock & Nelson, 1982), the Pt—P distance of 2·246 (4) Å is comparable, within experimental errors, to the 2·258 (10) Å of the PPh_3 complex, in spite of the greater θ value, estimated for PBz_2Ph (158°; Tolman, 1977).

As expected, the Pt—P distance, *trans* to Cl, is markedly shorter than those found in *trans* Pt^{II} diphosphine complexes, which range from 2·314 (8) to 2·371 (2) Å (Del Pra & Zanotti, 1980).

Besides the electronic *trans* influence effects of P ligands, Pt—P distances are affected by steric effects, especially in overcrowded molecules such as *trans*-diiodobis(tricyclohexylphosphine)platinum(II) (Alcock & Leviston, 1974).

The mean Pt—Cl distance of 2·357 (3) Å is within the range of values reported for Pt—Cl bonds *trans* to phosphines of comparable basicity, related to the ν factors (Table 3). As for the Pt—P distances, the Pt—Cl bond length *trans* to PF_3 is significantly shorter than that *trans* to PEt_3 (Hitchcock *et al.*, 1977, Fig. 3). The trend, however, is not well defined and too few data are available to discuss details in terms of ν and θ parameters. Furthermore, packing effects, even if often underestimated, can affect bond distances, as shown by the differences in chemically equivalent Pt—Cl and also Pt—P bond lengths, observed in the PMe_3 (Del Pra & Zanotti, 1979) and PPh_3 derivatives (Anderson, Clark, Davies, Ferguson & Parvez, 1982). This is particularly evident in *cis*-$(PMePh_2)_2PtCl_2$ (Kin-Chee, McLaughlin, McPartlin & Robertson, 1982), which exists in two polymorphic forms, both constituted of monomeric molecules. While in the orthorhombic form the two Pt—Cl distances are equal within 1σ [2·350 (2), 2·349 (2) Å], in the monoclinic form they are markedly different [2·345 (1), 2·359 (1) Å], owing to the asymmetric arrangement of the phosphines in the latter polymorph.

It is worth noting that one of the Pt—Cl distances [2·382 (7) Å] in *cis*-$(PMe_2Ph)_2PtCl_2.HgCl_2$ is slightly longer than the average value found in the title complex [2·357 (3) Å], as the result of coordination to Hg of the Pt chlorine atoms (Baker, Braithwaite & Nyholm, 1972). This could explain the observed lowering of the Pt—Cl stretching frequencies on passing from the parent compound to the $HgCl_2$ addition complex.

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