Stalling, W. C., Pattridge, K. A., Strong, R. K. & Ludwig, M. L. (1985). *J. Biol. Chem.* **260**, 16424–16432.
Sugiura, Y., Kawabe, H., Tanaka, H., Fujimoto, S. & Ohara, A. (1981). *J. Biol. Chem.* **256**, 10664–10670.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.
Wieghardt, K. (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 1153–1172.

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(2-Aminophenyl)diphenylphosphinedichloroplatinum(II) Acetone Solvate, $[PtCl_2(Ph_2PC_6H_4NH_2)].C_3H_6O$

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Abstract. $C_{18}H_{16}Cl_2NPPt.C_3H_6O$, $M_r = 601{\cdot}4$, triclinic, $P\bar{1}$, $a = 9{\cdot}381\,(1)$, $b = 14{\cdot}352\,(1)$, $c = 8{\cdot}944\,(2)$ Å, $\alpha = 107{\cdot}37\,(1)$, $\beta = 103{\cdot}83\,(1)$, $\gamma = 78{\cdot}71\,(1)°$, $V = 1106\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}806$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 66{\cdot}90$ cm^{-1}, $F(000) = 580$, $T = 293\,(1)$ K, $R = 0{\cdot}026$ for 3457 observed reflections. The square planar Pt atom is coordinated by two Cl atoms [Pt—Cl 2·369 (1), 2·300 (1) Å] and the P and N atoms derived from a chelating (2-aminophenyl)diphenylphosphine ligand [Pt—P 2·188 (1), Pt—N(1) 2·048 (4) Å and P(1)—Pt—N(1) 86·3 (1)°]. Centrosymmetric molecules associate *via* N—H···Cl contacts and the acetone molecule of solvation hydrogen bonds to the second amine proton.

Introduction. The hybrid ligand (2-aminophenyl)diphenylphosphine, $Ph_2PC_6H_4NH_2$, displays facile and reversible deprotonation at the aromatic amino group upon coordination to transition metals (Ansell, McPartlin, Tasker, Cooper & Duckworth, 1983; Cooper, Downes, Goodwin, McPartlin & Rosalky, 1983). Bis-chelating complexes of this ligand with Ni^{II}, Pt^{II} and Rh^{I} have been used to study geometric isomerism (Cooper & Downes, 1981) and metal-template catalyzed synthesis of the multidentate P,N-ligand, *N,N'*-bis[2-(diphenylphosphino)phenyl]propane-1,3-diamine (Cooper, Duckworth, Hambley, Organ, Henrick, McPartlin & Parekh, 1989). Serendipitous crystallization of the precursor complex $[PtCl_2(Ph_2PC_6H_4NH_2)]$ from acetone gave a novel hydrogen-bonded acetone solvate, the structure of which is reported herein.

Experimental. $[PtCl_2(Ph_2PC_6H_4NH_2)]$ was prepared as in the literature (Downes, 1978) and crystals for the X-ray study were obtained as a mono acetone solvate from an acetone solution of the compound; m.p. 339–343 K (dec.). Enraf–Nonius CAD-4F diffractometer controlled by a PDP8/*A* computer, graphite-monochromated Mo $K\alpha$ radiation; ω–2θ scan technique. Cell parameters by least squares on 25 reflections ($2 \leq \theta \leq 11°$) (de Boer & Duisenberg, 1984) on a 0·12 × 0·12 × 0·50 mm crystal. Analytical absorption correction applied; max. and min. transmission factors 0·517 and 0·410 (*SHELX76*; Sheldrick, 1976). 4364 reflections ($1{\cdot}5 \leq \theta \leq 25{\cdot}0°$) measured in the range $-11 \leq h \leq 11$, $-17 \leq k \leq 17$, $-10 \leq l \leq 1$. No significant variation in the net intensity of three reference reflections ($22\bar{1}$, $22\bar{2}$, $43\bar{3}$) measured every 7200 s. 3894 unique reflections (R_{merge} 0·011) and 3457 satisfied $I \geq 2{\cdot}5\sigma(I)$. Structure solved by Patterson method, full-matrix least-squares refinement on 245 parameters based on F (*SHELX76*; Sheldrick, 1976). Anisotropic thermal parameters for non-H atoms and H atoms included at their calculated positions and assigned a common isotropic thermal parameter. At convergence $R = 0{\cdot}026$, $wR = 0{\cdot}027$, $w = [\sigma^2(F) + 0{\cdot}0018|F|^2]^{-1}$, $S = 0{\cdot}79$, $(\Delta/\sigma)_{\max} \leq 0{\cdot}001$, $\Delta\rho_{\max} = +2{\cdot}01$, $\Delta\rho_{\min} = -1{\cdot}70$ e Å^{-3}; no extinction correction applied. Scattering factors for neutral Pt corrected for f' and f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149) and for the remaining atoms as incorporated in *SHELX76* (Sheldrick, 1976). All calculations on SUN4/280 computer system. Atomic parameters are given in Table 1,

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Table 1. *Fractional atomic coordinates and B_{eq} values* (Å^2)

$$B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	B_{eq}
Pt	0·34780 (2)	0·17969 (1)	0·02321 (2)	2·75
P(1)	0·3934 (1)	0·3057 (1)	0·2294 (1)	2·69
Cl(1)	0·3248 (2)	0·0372 (1)	−0·1943 (2)	4·32
Cl(2)	0·0952 (1)	0·2175 (1)	0·0013 (2)	4·53
N(1)	0·5729 (4)	0·1461 (3)	0·0437 (5)	3·26
C(1)	0·5943 (4)	0·2882 (3)	0·2776 (5)	2·84
C(2)	0·6626 (5)	0·2138 (3)	0·1724 (5)	2·95
C(3)	0·8163 (5)	0·1992 (3)	0·1901 (6)	3·58
C(4)	0·8984 (6)	0·2582 (4)	0·3146 (7)	4·11
C(5)	0·8315 (5)	0·3322 (3)	0·4265 (6)	3·66
C(6)	0·6785 (5)	0·3477 (3)	0·4080 (6)	3·58
C(11)	0·3312 (4)	0·3088 (3)	0·4077 (5)	3·26
C(12)	0·2585 (6)	0·3925 (4)	0·4982 (6)	4·42
C(13)	0·2166 (6)	0·3891 (5)	0·6365 (6)	5·21
C(14)	0·2455 (7)	0·3039 (5)	0·6822 (7)	6·13
C(15)	0·3138 (8)	0·2214 (6)	0·5902 (9)	7·37
C(16)	0·3587 (7)	0·2223 (4)	0·4545 (7)	5·61
C(21)	0·3370 (4)	0·4269 (3)	0·1949 (5)	2·82
C(22)	0·4394 (5)	0·4833 (3)	0·1881 (6)	3·82
C(23)	0·3929 (7)	0·5748 (4)	0·1561 (7)	4·90
C(24)	0·2457 (6)	0·6110 (3)	0·1312 (6)	4·24
C(25)	0·1423 (6)	0·5561 (4)	0·1386 (7)	4·32
C(26)	0·1864 (5)	0·4635 (3)	0·1689 (6)	3·76
O(1)	0·3042 (5)	0·8560 (3)	0·2221 (5)	6·55
C(31)	0·2086 (7)	0·9073 (4)	0·2891 (7)	4·61
C(32)	0·1313 (12)	1·0002 (5)	0·2448 (12)	9·69
C(33)	0·1523 (9)	0·8744 (5)	0·4053 (7)	7·19

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°)

Pt—Cl(1)	2·369 (1)	Pt—Cl(2)	2·300 (1)
Pt—P(1)	2·188 (1)	Pt—N(1)	2·048 (4)
P(1)—C(1)	1·815 (4)	P(1)—C(11)	1·810 (4)
P(1)—C(21)	1·812 (4)	N(1)—C(2)	1·472 (6)
C(1)—C(2)	1·362 (6)		

Cl(1)—Pt—Cl(2)	92·2 (1)	Cl(1)—Pt—P(1)	174·1 (1)
Cl(1)—Pt—N(1)	88·0 (1)	Cl(2)—Pt—P(1)	93·6 (1)
Cl(2)—Pt—N(1)	179·8 (1)	P(1)—Pt—N(1)	86·3 (1)
Pt—P(1)—C(1)	102·0 (1)	Pt—P(1)—C(11)	116·7 (2)
Pt—P(1)—C(21)	116·7 (1)	C(1)—P(1)—C(11)	106·3 (2)
C(1)—P(1)—C(21)	106·9 (2)	C(11)—P(1)—C(21)	107·3 (2)
Pt—N(1)—C(2)	116·3 (3)	P(1)—C(1)—C(2)	115·6 (3)
N(1)—C(2)—C(1)	119·3 (4)		

selected interatomic parameters in Table 2* and numbering scheme used is shown in Fig. 1 which was drawn with *ORTEP* (Johnson, 1976) at 15% probability levels.

Discussion. The Pt atom in [$PtCl_2(Ph_2PC_6H_4NH_2)$] exists in a distorted square planar geometry defined by two Cl atoms and the P and N donor atoms of the bidentate (2-aminophenyl)diphenylphosphine ligand. The deviations from the least-squares plane defined by the Pt, Cl(1), Cl(2), P(1) and N(1) atoms are 0·0008 (2), −0·028 (1), −0·003 (2), −0·019 (1) and −0·019 (4) Å, respectively. The Pt—Cl bond distances are slightly different, with the longer bond [2·369 (1) Å] being *trans* to the P(1) atom [174·1 (1)°] and the shorter Pt—Cl(2) bond of 2·300 (1) Å being *trans* to the N(1) atom [179·8 (1)°]. The different Pt—Cl bond distances are consistent with the relative *trans* influence of the amine and phosphine ligands in Pt complexes (Appleton, Clark & Manzer, 1973).

The (2-aminophenyl)diphenylphosphine ligand coordinates in the bidentate mode *via* the P [2·188 (1) Å] and N [2·048 (4) Å] atoms. The five-membered chelate ring thus formed, *i.e.* PtPCCN, is planar to ± 0·067 (4) Å and forms a dihedral angle of 0·7° with the square plane about the Pt atom. Bidentate coordination for this ligand has been observed previously in the structures of *cis*-[$RhCl_2$-

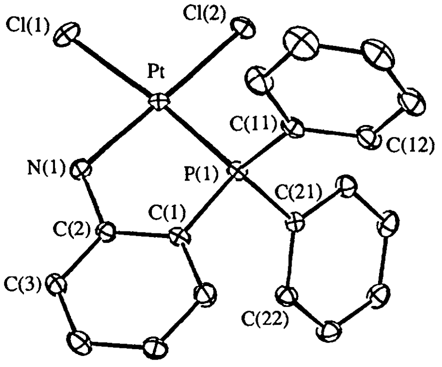

Fig. 1. Molecular structure and crystallographic numbering scheme employed for [$PtCl_2(Ph_2PC_6H_4NH_2)$].

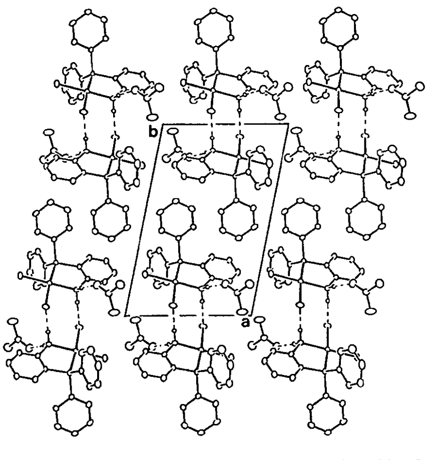

Fig. 2. Unit-cell contents viewed down the [001] direction (*ORTEP*; Johnson, 1976).

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* Lists of structure factors, anisotropic thermal parameters, all interatomic parameters, mean-plane data and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54218 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

($Ph_2PC_6H_4NH_2$)($Ph_2PC_6H_4NH$)] (Organ, Cooper, Henrick & McPartlin, 1984), and in the *cis* and *trans* isomers of the [$Pt(Ph_2PC_6H_4NH_2)]^{2+}$ cation (Cooper *et al.*, 1983). Monodentate coordination, *via* the P atom, has also been observed for this ligand in the Ag salts [$Ag(NO_3)(Ph_2PC_6H_4NH_2)_2(EtOH)_2$] and [$Ag(NO_3)(Ph_2PC_6H_4NH_2)_3$] (Tiekink, 1990).

In the crystal lattice there are significant intermolecular contacts involving the complex and the acetone molecule of crystallization. A [001] projection of the unit-cell contents is shown in Fig. 2 in which the layer-like nature of the lattice is emphasized. Centrosymmetric pairs of the complex associate *via* hydrogen-bonding contacts between the H(2*n*) atom and the Cl(1)′ atom such that the H(2*n*)···Cl(1)′ separation is 2·26 (1) Å and the N(1)—H(2*n*)···Cl(1)′ angle is 160 (1)°. The centrosymmetric pairs aggregate into layers separated from each other by phenyl-rich regions. Associated with each centrosymmetric pair are two acetone molecules which each form a hydrogen bond with an H(1*n*) atom; H(1*n*)···O(1) 1·92 (1) Å and N(1)—H(1*n*)···O(1) 165 (1)°. The known acidity of the amino H atoms of the coordinated (2-aminophenyl)diphenylphosphine ligand (which leads to formation of bis-chelate amido complexes) is clearly illustrated by this hydrogen-bonded, centrosymmetric structure.

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References

ANSELL, C. W. G., MCPARTLIN, M., TASKER, P. A., COOPER, M. K. & DUCKWORTH, P. A. (1983). *Inorg. Chim. Acta*, **76**, L135.

APPLETON, T. G., CLARK, H. C. & MANZER, L. E. (1973). *Coord. Chem. Rev.* **10**, 335–422.

BOER, J. L. DE & DUISENBERG, A. J. M. (1984). Enraf–Nonius CAD-4F diffractometer software update. February 1984. Groningen and Utrecht, The Netherlands.

COOPER, M. K. & DOWNES, J. M. (1981). *J. Chem. Soc. Chem. Commun.* pp. 381–382.

COOPER, M. K., DOWNES, J. M., GOODWIN, H. J., MCPARTLIN, M. & ROSALKY, J. M. (1983). *Inorg. Chim. Acta*, **76**, L155–L156.

COOPER, M. K., DUCKWORTH, P. A., HAMBLEY, T. W., ORGAN, G. J., HENRICK, K., MCPARTLIN, M. & PAREKH, A. (1989). *J. Chem. Soc. Dalton Trans.* pp. 1067–1073.

DOWNES, J. M. (1978). PhD Dissertation, Univ. of Syndey, Australia.

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

ORGAN, G. J., COOPER, M. K., HENRICK, K. & MCPARTLIN, M. (1984). *J. Chem. Soc. Dalton Trans.* pp. 2377–2382.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

TIEKINK, E. R. T. (1990). Unpublished results.

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cis,cis-[Bis(dimethylphosphino)methane]tetrachlorodipalladium(II)

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Abstract. $C_{10}H_{28}Cl_4P_4Pd_2$, $M_r = 626·84$, monoclinic, $P2_1/c$, $a = 8·893$ (1), $b = 9·712$ (2), $c = 12·745$ (3) Å, $\beta = 103·38$ (1)°, $V = 1071·0$ (0·6) Å^3, $Z = 2$, $D_x = 1·94$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 24·5$ cm^{-1}, $F(000) = 616$, $T = 294$ (1) K, $R = 0·029$ for 1574 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ of 2371 total data. The dimeric complex is centrosymmetric and contains two *cis* $PdCl_2$ fragments held together by two bridging $Me_2PCH_2PMe_2$ ligands forming an eight-membered bimetallic ring. Principal bond lengths (Å) and angles (°) are Pd—Cl 2·360 (1), 2·353 (1); Pd—P 2·264 (1), 2·265 (1); P—C 1·799 (6) to 1·829 (5); P—Pd—P 100·67 (5); *cis* P—Pd—Cl 84·35 (5), 86·56 (5); *trans* P—Pd—Cl 172·81 (4), 172·46 (5); Cl—Pd—Cl 88·65 (5); P—C—P 119·3 (3).

Introduction. The *cis,cis* binuclear structure adopted by complexes of platinum(II) and the ligand $Me_2PCH_2PMe_2$, dmpm, is reported to be a consequence of steric effects (Azam, Ferguson, Ling, Parvez, Puddephatt & Srokowski, 1985). Actually, the formation of [$Pt_2Cl_4(Me_2PCH_2PMe_2)_2$], [$Pt_2Me_4(Me_2PCH_2PMe_2)_2$] and [$Pt_2Me_4(Et_2PCH_2PEt_2)_2$] is due to the lack of steric effects that would otherwise stabilize a strained four-membered ring if the diphosphine ligand were to chelate to a single metal center (Manojlović-Muir, Muir, Frew, Ling, Thomson & Puddephatt, 1984). The small steric effect of the methyl substituents on the phosphorus in dmpm favors dimer formation over formation of a monomeric chelate in accord with the Thorpe–Ingold

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