$(Ph_2PC_6H_4NH_2)(Ph_2PC_6H_4NH)]$ (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)

BY JULIAN A. DAVIES, A. ALAN PINKERTON AND MARK VILMER

Department of Chemistry, University of Toledo, Toledo, Ohio 43606, *USA*

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Abstract. $C_{10}H_{28}Cl_4P_4Pd_2$, $M_r = 626\cdot84$, monoclinic, $P2_1/c$, $a = 8\cdot893$ (1), $b = 9\cdot712$ (2), $c = 12\cdot745$ (3) Å, $\beta = 103\cdot38$ (1)°, $V = 1071\cdot0$ (0·6) Å^3, $Z = 2$, $D_x = 1\cdot94$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 24\cdot5$ cm^{-1}, $F(000) = 616$, $T = 294$ (1) K, $R = 0\cdot029$ 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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effect (Ling & Puddephatt, 1983). The eight-membered bimetallic ring that is formed effectively isolates two square-planar metal centers while keeping the dimer intact. We report herein an analogous *cis,cis* binuclear eight-membered ring complex of palladium(II), $[Pd_2Cl_4(Me_2PCH_2PMe_2)_2]$, whose structure was determined by single-crystal X-ray diffraction methods.

Experimental. The title compound was prepared by dissolving $[Pd_2Cl_2(Me_2PCH_2PMe_2)_2]$ in nitromethane at room temperature. After several weeks pale yellow elongated plates suitable for single-crystal X-ray structure determination precipitated out of solution. Crystal 0·25 × 0·23 × 0·09 mm; Enraf–Nonius CAD-4 computer-controlled κ-axis diffractometer, graphite monochromator; cell dimensions from the setting angles of 25 reflections, $12 < \theta < 20°$; ω–2θ scan-type backgrounds from analysis of the scan profile (Blessing, Coppens & Becker, 1974); empirical absorption correction; relative transmission coefficients, 0·955 to 0·999; maximum $2\theta = 52{\cdot}0°$; *hkl* range *h* 0 to 10, *k* 0 to 11, *l* −15 to 15; three standard reflections, average decay 1·0%, intensities adjusted accordingly; 2371 data, 2226 unique, $R_{\rm int} = 2{\cdot}2\%$, structure solved by Patterson and Fourier methods; refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 4F_o^2/\sigma^2(F_o^2)$, 147 parameters; 1574 reflections with $F_o^2 > 3\sigma(F_o^2)$; H atoms refined as riding atoms in ideal positions with fixed isotropic thermal parameters ($1{\cdot}3 \times B_{\rm eq}$ of attached C atoms), anisotropic thermal parameters for non-H atoms: final $R = 0{\cdot}029$, $wR = 0{\cdot}037$; maximum shift to e.s.d. = 0·01; maximum and minimum of ΔF synthesis 0·47 (8) e Å^{-3} and −0·42 (8) e Å^{-3}; e.s.d. of observations of unit weight = 1·08, atomic scattering factors for neutral Pd, Cl, P, C and spherically bonded H atoms and values of f' and f'' for all atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV; Table 2.2, pp. 71–102; Table 2.3.1, pp. 149–150); computer programs *SDP/VAX* (Frenz, 1978). Fig. 1 showing atom-numbering scheme produced with *ORTEP*II (Johnson, 1971).

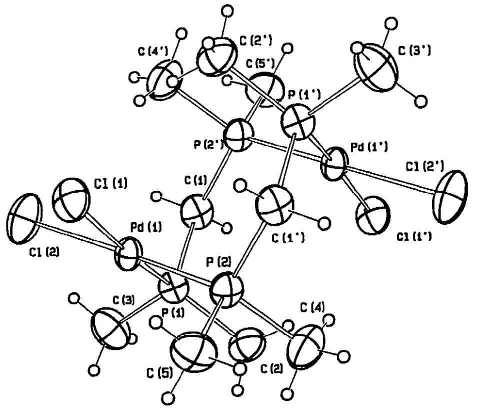

Fig. 1. *cis,cis*-[Bis(dimethylphosphino)methane]tetrachlorodipalladium(II) showing the atom-numbering scheme (50% probability ellipsoids for all non-H atoms.)

Table 1. *Positional parameters and their e.s.d.'s*

	x	*y*	*z*	*B* (Å^2)
Pd(1)	0·57415 (4)	0·43823 (4)	0·36202 (2)	2·286 (6)
Cl(1)	0·4911 (2)	0·5928 (1)	0·21736 (9)	3·55 (3)
Cl(2)	0·8294 (2)	0·4702 (2)	0·3445 (1)	4·77 (3)
P(1)	0·6765 (1)	0·3100 (1)	0·50957 (9)	2·54 (2)
P(2)	0·3187 (1)	0·4171 (1)	0·35613 (9)	2·59 (2)
C(1)	0·7698 (5)	0·4184 (5)	0·6226 (4)	3·0 (1)
C(2)	0·5656 (6)	0·1915 (5)	0·5698 (4)	3·6 (1)
C(3)	0·8323 (6)	0·1977 (6)	0·4920 (5)	4·4 (1)
C(4)	0·2380 (6)	0·2985 (6)	0·4372 (4)	4·1 (1)
C(5)	0·2122 (6)	0·3661 (6)	0·2230 (4)	3·9 (1)

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°)

Numbers in parentheses are e.s.d.'s in the least significant digits. Primed atoms refer to symmetry equivalent atoms.

Pd(1)—Cl(1)	2·360 (1)	P(1)—C(2)	1·799 (6)
Pd(1)—Cl(2)	2·353 (1)	P(1)—C(3)	1·817 (6)
Pd(1)—P(1)	2·264 (1)	P(2)—C(4)	1·803 (6)
Pd(1)—P(2)	2·265 (1)	P(2)—C(5)	1·811 (5)
P(1)—C(1)	1·822 (5)	P(2)—C(1′)	1·829 (5)

Cl(1)—Pd(1)—Cl(2)	88·65 (5)	Pd(1)—P(1)—C(3)	113·6 (2)
Cl(1)—Pd(1)—P(1)	172·81 (4)	C(1)—P(1)—C(2)	103·1 (2)
Cl(1)—Pd(1)—P(2)	84·35 (5)	C(1)—P(1)—C(3)	102·9 (2)
Cl(2)—Pd(1)—P(1)	86·56 (5)	C(2)—P(1)—C(3)	100·2 (3)
Cl(2)—Pd(1)—P(2)	172·46 (5)	Pd(1)—P(2)—C(4)	124·6 (2)
P(1)—Pd(1)—P(2)	100·67 (5)	Pd(1)—P(2)—C(5)	111·1 (2)
Pd(1)—P(1)—C(1)	111·2 (2)	C(4)—P(2)—C(5)	99·8 (3)
Pd(1)—P(1)—C(2)	123·5 (2)	P(1)—C(1)—P(2′)	119·3 (3)
Pd(1)—P(2)—C(1′)	112·3 (2)	C(4)—P(2)—C(1′)	103·4 (2)
C(5)—P(2)—C(1′)	103·2 (2)		

Cl(1)—Pd(1)—P(1)—C(1)	26·0 (4)	Cl(2)—Pd(1)—P(2)—C(1′)	−81·2 (4)
Cl(2)—Pd(1)—P(1)—C(1)	74·3 (2)	P(1)—Pd(1)—P(2)—C(1′)	115·5 (2)
P(2)—Pd(1)—P(1)—C(1)	−107·9 (2)	Pd(1)—P(1)—C(1)—P(2′)	38·3 (3)
Cl(1)—Pd(1)—P(2)—C(1′)	−59·3 (2)	Pd(1)—P(2)—C(1′)—P(1′)	−48·6 (3)

Discussion. Final atomic coordinates for all non-constrained atoms are listed in Table 1.* Bond lengths and bond angles are listed in Table 2.

The asymmetric unit comprises half a molecule (one $PdCl_2$ fragment and the equivalent of one $Me_2PCH_2PMe_2$ ligand) related to the other half by a crystallographic center of inversion. The molecule has approximate C_{2h} symmetry with the noncrystallographic twofold axis passing through the two methylene C atoms [C(1), C(1′)] and the noncrystallographic mirror containing the two Pd atoms and

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* Lists of structure factors, anisotropic thermal parameters, the complete list of coordinates including H atoms and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54189 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bisecting pairs of *cis* C and *cis* P atoms on the approximately square-planar metal centers. The symmetrical C_{2h} twist-chair conformation of the eight-membered ring [internal ring torsion angles are 107·9 (2)–115·5 (2)° at Pd—P bonds and 38·3 (3)–48·6 (3)° at P—CH_2 bonds, angles involving the same P atom being of opposite sign] compares favorably to that found in [$Pt_2Me_4(Me_2PCH_2PMe_2)$] (internal ring torsion angles of 109–114° at Pt—P bonds and 42–54° at P—CH_2 bonds) (Ling & Puddephatt, 1983). The bond angles within the eight-membered $Pd_2P_4C_2$ ring are slightly distorted from the ideal values of 90° at palladium and 109·5° at phosphorus and carbon. The P—Pd—P angle is 100·67 (5)° with the P—C—P angle being 119·3 (3)°. There are three sets of Pd—P—C angles. This is not just due to the presence of both methyl and methylene C atoms but also due to steric effects analogous to those found in [$Pt_2Me_4(Me_2PCH_2PMe_2)$] (Manojlović-Muir, Muir, Frew, Ling, Thomson & Puddephatt, 1984). The average Pd—P—C angle involving the two methylene C atoms is 111·7 (2)°. The average Pd—P—C angle involving the axial methyl groups, C(2) and C(4), is 124·0 (2)° and the average Pd—P—C angle involving the equatorial methyl groups, C(3) and C(5), is 112·3 (2)°. The Pd—Cl bond distances of 2·360 (1) and 2·353 (1) Å are comparable to the average Pd—Cl bond distance in analogous compounds: 2·362 (3) Å in *cis*-[$PdCl_2\{P(CH_3)_2C_6H_5\}_2$] (Martin & Jacobson, 1971), 2·357 Å in *cis*-[$PdCl_2\{(C_6H_5)_2PCH_2P(C_6H_5)_2\}$] (Steffen & Palenik, 1976), 2·359 Å in *cis*-[$PdCl_2\{(C_6H_5)_2PC_2H_4P(C_6H_5)_2\}$] (Steffen & Palenik, 1976), 2·354 Å in *cis*-[$PdCl_2\{(C_6H_5)_2PC_3H_6P(C_6H_5)_2\}$] (Steffen & Palenik, 1976) and 2·341 Å found in *cis*-[$PdCl_2\{P(CH_3)(C_6H_5)_2\}_2$] (Alcock & Nelson, 1985). The Pd—P distances of 2·264 (1) and 2·265 (1) Å are slightly less than the median Pd—P bond distance of 2·281 (8) Å found in palladium trimethylphosphine complexes (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989).

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References

Alcock, N. W. & Nelson, J. H. (1985). *Acta Cryst.* **C41**, 1748–1750.

Azam, K. A., Ferguson, G., Ling, S. S. M., Parvez, M., Puddephatt, R. J. & Srokowski, D. (1985). *Inorg. Chem.* **24**, 2799–2802.

Blessing, R. H., Coppens, P. & Becker, P. (1974). *J. Appl. Cryst.* **7**, 488–492.

Frenz, B. A. (1978) *The Enraf–Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.

Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

Ling, S. S. M. & Puddephatt, R. J. (1983). *Inorg. Chim. Acta*, **77**, L95–L96.

Manojlović-Muir, L., Muir, K. W., Frew, A. A., Ling, S. S. M., Thomson, M. A. & Puddephatt, R. J. (1984). *Organometallics*, **3**, 1637–1645.

Martin, L. L. & Jacobson, R. A. (1971). *Inorg. Chem.* **10**(8), 1795–1798.

Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* p. S1.

Steffen, W. L. & Palenik, G. J. (1976). *Inorg. Chem.* **15**(10), 2432–2438.

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Structures of [$CoCl(C_{18}H_{15}P)_3$] and [$NiCl(C_{18}H_{15}P)_3$].C_7H_8

By Juanita M. Cassidy and Kenton H. Whitmire*

Department of Chemistry, Rice University, PO Box 1892, Houston, TX 77251, USA

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Abstract. Chlorotris(triphenylphosphine)cobalt, $M_r = 881·26$, trigonal, $P3$, $a = 19·151$ (4), $c = 10·543$ (2) Å, $V = 3349$ (1) Å^3, $Z = 3$, $D_x = 1·31$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 5·84$ cm^{-1}, $F(000) = 1374$, $T = 296$ K, $R = 0·040$, $wR = 0·049$ for 3860 unique reflections with $I > 3\sigma(I)$. The molecule $CoCl[P(C_6H_5)_3]_3$ consists of three triphenylphosphine ligands and one chlorine atom bonded to cobalt in a distorted tetrahedral coordination geometry. Three independent molecules are found in the unit cell with each Co—Cl bond situated on a crystallographic threefold rotation axis. Chlorotris(triphenylphosphine)nickel–toluene (1/1), $M_r = 973·11$, triclinic, $P\overline{1}$, $a = 13·161$ (2), $b = 20·026$ (5), $c = 10·110$ (2) Å, $\alpha =$

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* Author to whom correspondence should be addressed.

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