Acta Cryst. (1986). C**42**, 1695–1697

trans-Dichloro(tricyclohexylphosphino)(triphenylphosphino)platinum(II)

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(*Received* 23 *April* 1986; *accepted* 20 *June* 1986)

Abstract. $[\mathrm{PtCl_2(C_6H_{11}P)_3(C_6H_5P)_3}]$, $M_r = 808{\cdot}72$, triclinic, $P1$, $a = 10{\cdot}031$ (2), $b = 10{\cdot}593$ (2), $c = 18{\cdot}220$ (6) Å, $\alpha = 91{\cdot}56$ (2), $\beta = 102{\cdot}85$ (2), $\gamma = 111{\cdot}61$ (2)°, $V = 1742{\cdot}1$ Å^3, $Z = 2$, $D_x = 1{\cdot}542$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71073$ Å, $\mu(\mathrm{Mo}\ K\alpha) = 4{\cdot}34$ mm^{-1}, $F(000) = 812$, $T = 291$ K, final $R = 0{\cdot}018$ for 4747 unique observed reflections with $I > 3\sigma(I)$. The platinum atom is four-coordinated with square-planar geometry. The phosphine ligands are oriented *trans* and have their organic substituents in a staggered orientation. The phenyl rings of the triphenylphosphine are planar, and the cyclohexyl rings are in chair conformations. Selected geometrical details are: ⟨Pt—Cl⟩ = 2·303 (2), ⟨Pt—P⟩ = 2·322 (6), ⟨C—C(phenyl)⟩ = 1·378 (12), ⟨C—C(cyclohexyl)⟩ = 1·525 (8) Å.

Introduction. The crystal structure determination of the title compound is a continuation of our studies of the effect of steric bulk in the coordination geometry of transition metals by phosphine ligands. In the use of metal complexes as catalysts, trisubstituted phosphine ligands may be used to stabilize the complex and also influence the reactions of the complex by the steric interactions between the substituents on the phosphine ligand and the incoming substrate. Methods of describing the steric bulk of phosphine ligands are through its cone angle (Tolman, 1970) or the corresponding ligand profile (Alyea, Dias, Ferguson & Restivo, 1977; Richardson & Payne, 1977; Smith & Oliver, 1978; Ferguson, Roberts, Alyea & Khan, 1978) defined by the atomic coordinates from structure determinations. The structure of the title compound was undertaken to determine the ligand profiles of two bulky phosphine ligands in this complex.

Experimental. Crystals of the title compound obtained from Dr H. C. Clark of the University of Guelph; colorless, rectangular-shaped crystal, 0·19 × 0·28 × 0·47 mm, glass fibre mount, Enraf–Nonius CAD-4F four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; cell constants from setting angles of 25 reflections ($4{\cdot}8 \leq \theta \leq 12{\cdot}6°$); correction for Lorentz, polarization effects, empirical absorption correction (North, Phillips & Mathews, 1968), $t(\mathrm{min})/t(\mathrm{max}) = 0{\cdot}740/1{\cdot}000$; 291 K; intensity data collected by ω–2θ scan technique, variable scan rate of 0·38 to 3·35° min^{-1}, intensities of two check reflections (464 and 373) measured every 2 h revealed only random deviations (<1%) from mean intensities; 5890 reflections collected ($3 < 2\theta < 50°$, h: 0→11, k: −12→12, l: −11→11), 5688 unique reflections ($R_{\mathrm{int}} = 0{\cdot}013$), 4747 reflections with $I > 3\sigma(I)$ used in solution and refinement of the structure using *VAXSDP* (Enraf–Nonius, 1982); heavy atoms located by *MULTAN*11/82 (Main, 1982), remainder of non-hydrogen atoms by difference Fourier technique; H atoms calculated and constrained to ride on attached carbon atom with $B = 5{\cdot}0$ Å^2; full-matrix least-squares refinement of 371 parameters on F yielded $R = 0{\cdot}0181$, $wR = 0{\cdot}0177$, $w = \sigma(F_o)^{-2}$ with $\sigma(F_o) = \{I_p + I_b + [0{\cdot}03(I_p - I_b)]^2\}^{1/2}$, where I_p and I_b were the peak and background counts, respectively; $S = 0{\cdot}721$, maximum shift-to-e.s.d. ratio of a parameter in final least-squares cycle was 0·001; maximum positive and minimum negative density on final difference Fourier map, 0·9 (1) and −0·9 (1) e Å^{-3}; secondary-extinction factor (g), 4·1 (6) × 10^{-8} refined using the equation $|F_o| = |F_c|/(1 + gI_c)$, where I_c is the calculated intensity; scattering factors and anomalous-dispersion terms taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The final atomic parameters are given in Table 1.† Stereodrawings of the asymmetric unit and unit-cell contents are shown in Figs. 1 and 2, respectively. Selected interatomic distances and angles are presented in Table 2.

The Pt atom has square-planar coordination, being coordinated by tricyclohexylphosphine and triphenylphosphine ligands and two chloride ions. Bond distances around the platinum atom are quite normal when compared with those reported in *Bond Index of the*

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† Lists of structure factor amplitudes, H-atom coordinates, anisotropic thermal parameters, bond distances and angles, dihedral angles, and illustrations of the ligand profiles about the phosphine P atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43169 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/86/121695-03$01.50

Determination of Inorganic Crystal Structures (1981), and the corresponding angles are slightly distorted owing to the bulk of the phosphine ligands. The five atoms of the coordination plane [Pt, Cl(1), Cl(21), P(1), and P(2)] have a maximum deviation of 0·012 Å from their mean plane.

The phosphine ligands have their organic substituents in a staggered orientation relative to the coordination plane. The P–C distances are normal as are the related C–P–C angles. The three cyclohexyl rings of the tricyclohexylphosphine ligand are each in a chair conformation. The absolute value of the endocyclic torsion angles varies from 54·3 to 59·6° with an average of 56·6°. These values are in agreement with those found in other compounds, *e.g.* Smith & Oliver (1978). In addition, the results from ring-puckering calculations (Cremer & Pople, 1975) are consistent with this assignment. The phenyl rings of the triphenylphosphine are regular with only minimal angular distortion. The deviation of each phenyl C atom from its mean plane is less than 0·011 Å, showing the absence of any out-of-plane distortions.

Table 1. *Positional parameters* ($\times 10^5$ *for* Pt, Cl *and P*, $\times 10^4$ *for* C) *and equivalent isotropic thermal parameters* ($\times 10^4$ *for* Pt, Cl *and* P, $\times 10^3$ *for* C) *with standard deviations in parentheses*

	x	y	z	U_{eq}(Å^2)*
Pt	−23078 (2)	25974 (1)	−25638 (1)	260 (1)
Cl(1)	−26312 (11)	41867 (9)	−18110 (6)	452 (3)
Cl(2)	−20796 (11)	10148 (10)	−33693 (6)	442 (3)
P(1)	−16160 (9)	15259 (9)	−15327 (6)	264 (3)
P(2)	−30907 (10)	36418 (9)	−35784 (6)	305 (3)
Ring *A*				
C(1)	−2514 (4)	−348 (3)	−1743 (2)	31 (1)
C(2)	−4197 (4)	−889 (4)	−2078 (2)	38 (1)
C(3)	−4767 (5)	−2411 (4)	−2366 (3)	51 (2)
C(4)	−4375 (5)	−3231 (4)	−1748 (3)	47 (1)
C(5)	−2724 (4)	−2665 (4)	−1385 (3)	45 (1)
C(6)	−2152 (4)	−1151 (4)	−1090 (2)	39 (1)
Ring *B*				
C(7)	−1922 (4)	2126 (4)	−642 (2)	30 (1)
C(8)	−3564 (4)	1606 (4)	−638 (2)	38 (1)
C(9)	−3754 (4)	2363 (5)	30 (3)	51 (1)
C(10)	−2823 (5)	2213 (5)	782 (3)	59 (2)
C(11)	−1210 (4)	2662 (5)	773 (3)	50 (1)
C(12)	−1016 (4)	1915 (4)	102 (2)	40 (1)
Ring *C*				
C(13)	388 (4)	1896 (3)	−1285 (2)	31 (1)
C(14)	1276 (4)	3450 (4)	−1143 (3)	43 (1)
C(15)	2933 (4)	3773 (4)	−900 (3)	51 (1)
C(16)	3434 (4)	3111 (4)	−1473 (3)	52 (1)
C(17)	2559 (4)	1573 (4)	−1611 (3)	49 (1)
C(18)	899 (4)	1236 (4)	−1867 (3)	42 (1)
Ring *D*				
C(19)	−5037 (4)	3314 (4)	−3666 (2)	38 (1)
C(20)	−5978 (5)	1956 (5)	−3705 (3)	58 (2)
C(21)	−7479 (5)	1617 (6)	−3775 (3)	78 (2)
C(22)	−8031 (5)	2621 (6)	−3783 (3)	78 (2)
C(23)	−7121 (5)	3953 (5)	−3733 (3)	72 (2)
C(24)	−5612 (4)	4312 (4)	−3670 (3)	53 (1)
Ring *E*				
C(25)	−2130 (4)	5482 (4)	−3543 (2)	34 (1)
C(26)	−892 (4)	6198 (4)	−2962 (2)	42 (1)
C(27)	−177 (5)	7603 (5)	−2942 (3)	55 (2)
C(28)	−703 (5)	8277 (4)	−3498 (3)	59 (1)
C(29)	−1886 (5)	7577 (4)	−4077 (3)	63 (2)
C(30)	−2601 (5)	6176 (4)	−4115 (3)	51 (1)
Ring *F*				
C(31)	−2982 (4)	3047 (4)	−4500 (2)	33 (1)
C(32)	−1596 (4)	3434 (4)	−4642 (3)	48 (1)
C(33)	−1422 (5)	2974 (5)	−5316 (3)	59 (2)
C(34)	−2624 (5)	2118 (5)	−5854 (3)	63 (2)
C(35)	−4009 (5)	1713 (5)	−5728 (3)	66 (2)
C(36)	−4190 (4)	2182 (5)	−5052 (3)	52 (2)

* Equivalent isotropic thermal parameter U_{eq} defined as: $\frac{1}{3}(U_{11} + U_{22} + U_{33} + U_{12}\cos\gamma + U_{13}\cos\beta + U_{23}\cos\alpha)$.

The illustrations from the ligand profile calculations have been deposited.* The cone angles (Tolman, 1977) are 164 and 154° for the tricyclohexylphosphine and triphenylphosphine ligands, respectively. For the title compound the maximum (minimum) half-cone angles are 86 (48) and 85 (38)° for the tricyclohexylphosphine and triphenylphosphine ligands, respectively. These values and the areas enclosed within the ligand profile plots for the ligands show the slightly larger steric bulk of the tricyclohexylphosphine ligand relative to that of the triphenylphosphine ligand, as predicted.

The authors gratefully acknowledge the financial support of this work by the Robert A. Welch Foundation through grant AA-668 and Baylor University.

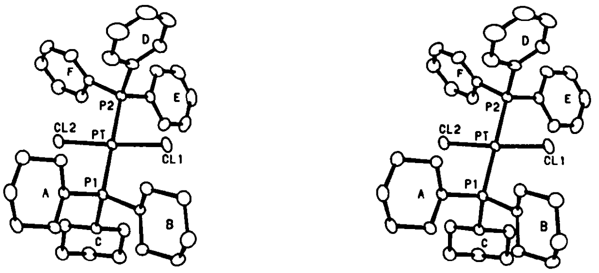

Fig. 1. Stereodrawing of the title compound displaying ellipsoids of 20% thermal probability. Hydrogen atoms are omitted for clarity. The organic substituents are labelled *A* [C(1)–C(6)], *B* [C(7)–C(12)], *C* [C(13)–C(18)], *D* [C(19)–C(24)], *E* [C(25)–C(30)] and *F* [C(31)–C(36)].

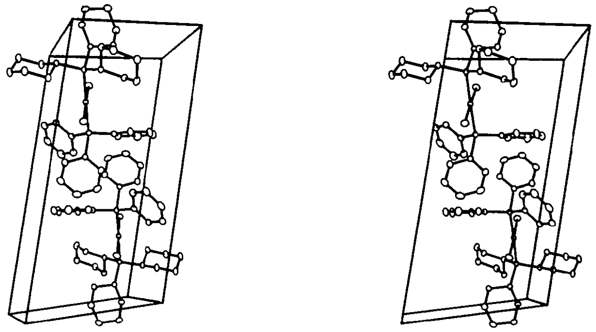

Fig. 2. Stereodrawing of the unit-cell contents viewed down the *b* axis with the *a* axis horizontal.

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* See deposition footnote.

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

Pt–Cl(1)	2·301 (1)	Cl(1)–Pt–Cl(2)	176·97 (4)
Pt–Cl(2)	2·305 (1)	Cl(1)–Pt–P(1)	92·63 (4)
Pt–P(1)	2·327 (1)	Cl(1)–Pt–P(2)	86·23 (4)
Pt–P(2)	2·316 (1)	Cl(2)–Pt–P(1)	90·00 (4)
		Cl(2)–Pt–P(2)	91·09 (4)
P(1)–C(1)	1·841 (3)	P(1)–Pt–P(2)	177·62 (4)
P(1)–C(7)	1·854 (4)		
P(1)–C(13)	1·845 (4)	Pt–P(1)–C(1)	111·4 (1)
		Pt–P(1)–C(7)	113·4 (1)
P(2)–C(19)	1·822 (4)	Pt–P(1)–C(13)	112·2 (1)
P(2)–C(25)	1·821 (3)	C(1)–P(1)–C(7)	111·1 (2)
P(2)–C(31)	1·817 (4)	C(1)–P(1)–C(13)	104·9 (2)
		C(7)–P(1)–C(13)	103·2 (2)
		Pt–P(2)–C(19)	107·9 (1)
		Pt–P(2)–C(25)	117·6 (1)
		Pt–P(2)–C(31)	116·3 (1)
		C(19)–P(2)–C(25)	107·0 (2)
		C(19)–P(2)–C(31)	105·9 (2)
		C(25)–P(2)–C(31)	101·1 (2)

		Distances		Angles	
Ring		Mean	Range	Mean	Range
A	C(1)–C(6)	1·527 (9)	1·513–1·537	110·6 (10)	109·3–111·8
B	C(7)–C(12)	1·525 (6)	1·514–1·535	110·8 (8)	109·8–111·7
C	C(13)–C(18)	1·525 (8)	1·512–1·538	111·0 (5)	110·3–111·8
D	C(19)–C(24)	1·379 (14)	1·356–1·394	120·0 (5)	118·9–120·3
E	C(25)–C(30)	1·378 (13)	1·350–1·389	120·0 (5)	119·2–120·6
F	C(31)–C(36)	1·378 (9)	1·363–1·389	120·0 (9)	118·1–121·1

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Acta Cryst. (1986). C**42**, 1697–1699

Structure of a Cyclization Product of a Cobalt-Mediated Hetero [2 + 2 + 2] Cycloaddition

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(*Received* 9 *October* 1985; *accepted* 30 *May* 1986)

Abstract. (η^5-Cyclopentadienyl)(1,2,3,11b-η^4-3-methoxy-7-oxo-2-trimethylsilyl-3a-*endo*,4,5,6,7,11c-*endo*-hexahydro-1*H*-pyrrolo[3,2,1-*de*]phenanthridine)cobalt, $[Co(C_5H_5)(C_{19}H_{23}NO_2Si)]$, $M_r = 449{\cdot}6$, monoclinic, $P2_1/n$, $a = 15{\cdot}891$ (2), $b = 8{\cdot}825$ (1), $c = 15{\cdot}185$ (2) Å, $\beta = 96{\cdot}45$ (1)°, $V = 2116{\cdot}1$ (4) Å^3, $Z = 4$, $D_m = 1{\cdot}38$, $D_x = 1{\cdot}41$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 8{\cdot}83$ cm^{-1}, $F(000) = 944$, $T = 298$ K. The structure was refined to a final $R = 0{\cdot}025$ for 2319 unique observed reflections. The product heterocycle and the cyclopentadienyl ligand form a distorted sandwich about the cobalt atom. The dihedral angle between the planes of the sandwich fragments is 9·2°. The cobalt-to-cyclopentadienyl-centroid distance is 1·686 Å, and the average distance from the cobalt to the carbons of the heterocyclic diene is 2·021 Å.

Introduction. The title compound (2) was one of two products (both shown in the scheme) of a cobalt-mediated hetero [2 + 2 + 2] cycloaddition reaction. The regiochemistry of this hetero reaction, although similar to the non-hetero systems studied extensively by Vollhardt and his group (Vollhardt, 1984), is not well understood. The relative positions of the trimethylsilyl

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0108-2701/86/121697-03$01.50