

Fig. 1. View of the asymmetric unit showing atom numbering. The second orientation of the disordered quinoxalium cation is marked with primes. Thermal ellipsoids are drawn at the 50% probability level.

lengths and angles in Table 2. The atomic numbering scheme for the asymmetric unit is shown in Fig. 1 (Johnson, 1976) and the packing in Fig. 2 (Motherwell & Clegg, 1978).

**Related literature.** The  $[\text{CoCl}_4]^{2-}$  tetrahedron is described, for example, by Søtøfte & Nielsen (1981)

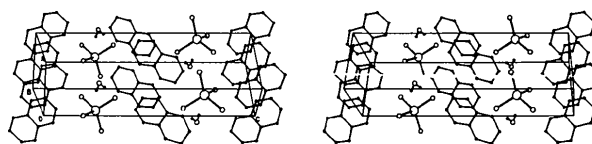


Fig. 2. Stereoview of the structure of  $(\text{C}_8\text{H}_7\text{N}_2)_2[\text{CoCl}_4]\cdot\text{H}_2\text{O}$ . Only one orientation of the disordered quinoxalium cation is shown. **A** is vertical, **B** is into plane of paper and **C** is horizontal.

and Campayo, Navarro, Cana & Foces-Foces (1987) and the quinoxaline molecule by Lipkowski, Andreotti & Sgarabotto (1977).

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*Acta Cryst.* (1991). **C47**, 874–876

## Chloro(tri-*tert*-butylphosphino-*C,P*)(tricyclohexylphosphine)platinum(II)

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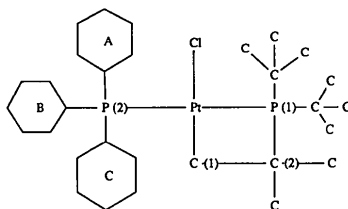
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(Received 25 July 1990; accepted 8 October 1990)

**Abstract.** (*SP-4-4*)-Chloro[2-(di-*tert*-butylphosphino)-2-methylpropyl-*C,P*](tricyclohexylphosphine)platinum(II),  $\text{C}_{30}\text{H}_{59}\text{ClP}_2\text{Pt}$ ,  $M_r = 712.27$ , triclinic,  $P\bar{1}$ ,  $a = 9.986(2)$ ,  $b = 12.998(4)$ ,  $c = 14.170(5)$  Å,  $\alpha = 106.18(3)$ ,  $\beta = 94.18(2)$ ,  $\gamma = 91.59(2)^\circ$ ,  $V = 1760.95$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.343$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 4.21$  mm<sup>-1</sup>,  $F(000) = 728$ ,  $T = 294$  K, final  $R = 0.055$  for 4109 unique observed reflections with  $I > 3\sigma(I)$ . The geometry of the central atom (Pt) is square planar, mean deviation from planarity is 0.011(9) Å. The phosphine ligands are oriented *trans* across the square-planar geometry. The bond angles centered about the Pt atom are distorted owing to the steric bulk of the ligands and

the formation of the four-membered ring, Pt—P(1)—C(2)—C(1), which is severely distorted. The cyclohexyl substituent rings associated with P(2) are in chair conformations and in a staggered orientation. A ligand bulk calculation for the PCy<sub>3</sub> group yields a cone angle,  $\theta$ , of 136°. Selected geometrical details are: Pt—Cl = 2.409(2), Pt—P = 2.283(14), Pt—C(1) = 2.043(9), P(1)—C = 1.881(10), P(2)—Cy = 1.856(10), C—C = 1.55(3), and C—C (cyclohexyl) = 1.52(2) Å.

**Experimental.** Crystals of the title compound obtained from Dr H. C. Clark of Dalhousie University, Halifax, Canada; off-white, 0.35 × 0.20 ×



0.35 mm, glass fiber mount, Enraf-Nonius CAD-4F four-circle diffractometer, graphite-monochromatized Mo  $K\alpha$  radiation, take-off angle  $5.8^\circ$ ; cell parameters obtained from twenty-five reflections ( $4.0 \leq \theta \leq 18.2^\circ$ ); correction for Lorentz, polarization effects; intensity data collected by  $\omega$ - $2\theta$  scan method, variable scan rate of  $0.38$ – $3.35^\circ \text{ min}^{-1}$ ; intensities of two standard reflections ( $03\bar{3}$ ,  $\bar{6}4\bar{6}$ ) measured as a function of time (every 2 h) showed a slow decay of  $-0.0795\% \text{ h}^{-1}$  which constituted a maximum correction of 1.12585; 4903 measured reflections, 4583 unique observed reflections ( $3 < 2\theta < 45^\circ$ ;  $h: 0 \rightarrow 10$ ,  $k: -14 \rightarrow 14$ ,  $l: -15 \rightarrow 15$ ), 4109 reflections with  $I > 3\sigma(I)$  used in the solution and refinement of the structure using SDP (Enraf-Nonius, 1979);  $R_{\text{int}} = 0.030$ ; Pt atom located by DIRDIF (Beurskens, 1985), remainder of non-H atoms located by difference Fourier technique; H atoms idealized at fixed positions with  $B_{\text{iso}} = 5.0 \text{ \AA}^2$ ; full-matrix least-squares refinement on  $F$  yielded  $R = 0.055$ ,  $wR = 0.056$ ,  $w = 1/\sigma^2(F_o)$  with  $\sigma(F_o) = \{I_p + I_b + [0.02(I_b - I_p)^2]\}^{1/2}$ , where  $I_p$  and  $I_b$  are the peak and background counts respectively,  $S = 2.097$ ,  $g = 3.7(4) \times 10^{-7} \text{ e}^{-2}$ , 308 refined parameters, maximum shift-to-e.s.d. of a parameter in final least-squares cycle was 0.002; maximum positive and minimum negative densities on final difference Fourier map  $2.6(4)$  and  $-1.0(4) \text{ e \AA}^{-3}$  in the vicinity of Pt atom; scattering factors and anomalous-dispersion terms taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 72–151).

Final atomic fractional coordinates with equivalent isotropic thermal parameters are tabulated in Table 1.\* Bond distances and bond angles are listed in Table 2. An ORTEP (Johnson, 1971) stereoscopic drawing of the title compound appears in Fig. 1. The geometry of the central atom (Pt) is square-planar, mean deviation from planarity is  $0.011(9) \text{ \AA}$ .

**Related literature.** The shape of the tricyclohexylphosphine ligand is very similar to those found in previous structural analyses (Mullica, Oliver,

\* Lists of structure factors, anisotropic thermal parameters, torsion and dihedral angles, and H-atom parameters, and an illustration of the ligand profile about the phosphine P(2) atom have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53627 (67 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic positions and equivalent isotropic thermal ( $\times 10^3$ ) parameters with standard deviations in parentheses for  $\text{Cl}(\text{PCy}_3)\text{Pt}[\text{P}(\text{tert-Bu})_2\text{C}(\text{CH}_3)_2\text{CH}_2]$

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Pt	0.31916 (3)	0.28916 (3)	0.24993 (2)	36.5 (2)
Cl	0.1256 (3)	0.2506 (3)	0.3286 (2)	90 (2)
P(1)	0.4724 (3)	0.1922 (2)	0.3094 (2)	39 (1)
P(2)	0.2016 (2)	0.3918 (2)	0.1677 (2)	36 (1)
C(1)	0.499 (1)	0.301 (1)	0.1924 (8)	57 (6)
C(2)	0.572 (1)	0.1977 (9)	0.2033 (8)	56 (6)
C(3)	0.528 (2)	0.109 (1)	0.108 (1)	82 (8)
C(4)	0.727 (1)	0.212 (1)	0.219 (1)	90 (10)
C(10)	0.433 (1)	0.0510 (8)	0.310 (1)	65 (7)
C(11)	0.325 (2)	0.004 (1)	0.223 (1)	90 (10)
C(12)	0.362 (2)	0.054 (1)	0.409 (1)	101 (9)
C(13)	0.553 (2)	-0.018 (1)	0.300 (1)	88 (8)
C(20)	0.559 (1)	0.2746 (9)	0.4317 (8)	57 (6)
C(21)	0.446 (2)	0.299 (1)	0.5061 (9)	89 (9)
C(22)	0.676 (2)	0.218 (1)	0.469 (1)	88 (9)
C(23)	0.611 (1)	0.383 (1)	0.421 (1)	78 (9)
C(31)	0.124 (1)	0.3068 (8)	0.0469 (7)	46 (5)
C(32)	0.228 (1)	0.262 (1)	-0.0248 (9)	56 (6)
C(33)	0.163 (1)	0.191 (1)	-0.1232 (9)	73 (8)
C(34)	0.072 (2)	0.103 (1)	-0.108 (1)	83 (9)
C(35)	-0.036 (2)	0.149 (1)	-0.038 (1)	78 (8)
C(36)	0.030 (1)	0.219 (1)	0.0609 (9)	67 (8)
C(41)	0.306 (1)	0.4942 (8)	0.1353 (7)	42 (5)
C(42)	0.239 (1)	0.554 (1)	0.0667 (8)	65 (6)
C(43)	0.338 (1)	0.6251 (9)	0.0360 (9)	70 (7)
C(44)	0.417 (1)	0.7022 (9)	0.1224 (9)	68 (7)
C(45)	0.482 (1)	0.644 (1)	0.1881 (9)	66 (7)
C(46)	0.379 (1)	0.5727 (9)	0.2249 (8)	56 (6)
C(51)	0.056 (1)	0.4559 (9)	0.2322 (7)	47 (5)
C(52)	-0.041 (1)	0.507 (1)	0.1783 (9)	66 (6)
C(53)	-0.166 (1)	0.536 (1)	0.232 (1)	82 (8)
C(54)	-0.131 (1)	0.603 (1)	0.335 (1)	86 (9)
C(55)	-0.027 (1)	0.554 (1)	0.393 (1)	80 (8)
C(56)	0.095 (1)	0.524 (1)	0.3358 (9)	59 (7)

Table 2. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

Pt—Cl	2.409 (2)	C(1)—C(2)	1.58 (1)		
Pt—P(1)	2.269 (3)	C(2)—C(3)	1.54 (1)		
Pt—P(2)	2.297 (2)	C(2)—C(4)	1.55 (1)		
Pt—C(1)	2.043 (9)	C(10)—C(11)	1.54 (1)		
P(1)—C(2)	1.878 (8)	C(10)—C(12)	1.62 (2)		
P(1)—C(10)	1.871 (8)	C(10)—C(13)	1.52 (2)		
P(1)—C(20)	1.894 (9)	C(20)—C(21)	1.57 (2)		
P(2)—C(31)	1.860 (8)	C(20)—C(22)	1.54 (1)		
P(2)—C(41)	1.842 (8)	C(20)—C(23)	1.54 (2)		
P(2)—C(51)	1.867 (7)				
Cl—Pt—P(1)	99.81 (8)	C(1)—C(2)—C(4)	114.7 (8)		
Cl—Pt—P(2)	93.00 (7)	C(3)—C(2)—C(4)	110.6 (8)		
Cl—Pt—C(1)	169.6 (2)	P(1)—C(10)—C(11)	106.6 (7)		
P(1)—Pt—P(2)	167.04 (7)	P(1)—C(10)—C(12)	108.4 (7)		
P(1)—Pt—C(1)	70.0 (2)	P(1)—C(10)—C(13)	114.0 (7)		
P(2)—Pt—C(1)	97.1 (2)	C(11)—C(10)—C(12)	106.5 (10)		
Pt—P(1)—C(2)	86.8 (3)	C(11)—C(10)—C(13)	110.2 (9)		
Pt—P(1)—C(10)	121.7 (3)	C(12)—C(10)—C(13)	110.8 (9)		
Pt—P(1)—C(20)	110.8 (3)	P(1)—C(20)—C(21)	106.3 (7)		
C(2)—P(1)—C(2)	111.7 (4)	P(1)—C(20)—C(22)	112.9 (6)		
C(2)—P(1)—C(10)	111.8 (4)	P(1)—C(20)—C(23)	109.1 (6)		
C(10)—P(1)—C(2)	111.6 (4)	C(21)—C(20)—C(22)	111.9 (9)		
Pt—P(2)—C(31)	110.4 (3)	C(21)—C(20)—C(23)	107.0 (8)		
Pt—P(2)—C(41)	114.4 (2)	C(22)—C(20)—C(23)	109.3 (9)		
Pt—P(2)—C(51)	113.6 (2)	P(2)—C(31)—C(32)	112.4 (6)		
C(31)—P(2)—C(41)	104.2 (3)	P(2)—C(31)—C(36)	110.9 (6)		
C(31)—P(2)—C(51)	103.8 (3)	Pt—C(1)—C(2)	103.6 (5)		
C(41)—P(2)—C(51)	109.5 (4)	P(1)—C(2)—C(3)	113.2 (7)		
P(1)—C(2)—C(1)	91.1 (5)	P(2)—C(51)—C(52)	118.2 (6)		
P(1)—C(2)—C(4)	119.6 (6)	P(2)—C(41)—C(46)	112.5 (6)		
P(2)—C(41)—C(42)	117.5 (5)	P(2)—C(51)—C(56)	113.1 (5)		
C(1)—C(2)—C(3)	105.5 (7)				
Ring	Mean	Range	Mean	Range	
A	C(31)—C(36)	1.526 (7)	1.521–1.537	111.3 (7)	110.3–112.2
B	C(41)—C(46)	1.52 (3)	1.481–1.582	111 (2)	108.2–112.6
C	C(51)—C(56)	1.51 (2)	1.472–1.536	112 (1)	110.1–113.6

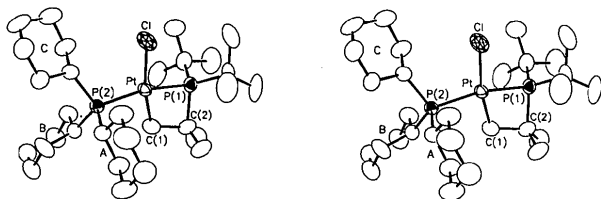


Fig. 1. An ORTEP stereoview of Cl(PCy<sub>3</sub>)Pt[P(*tert*-Bu)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>] with 50% probability ellipsoids.

Sappenfield & Grossie, 1986; Mullica, Oliver & Grossie, 1987). Organometallic compounds containing PR<sub>3</sub> ligands have been shown to be excellent catalysts for hydrogen-transfer and polymerization reactions. The steric contribution of such ligands greatly influences both rates and stereochemistries of products (Chow, Clark, Fraenkel, Grossie, Hampden-Smith, Mullica & Ruegger, 1991). Ligand bulk calculations using the program CONE (Smith & Oliver, 1978) help evaluate the stereochemistry.

The authors wish to acknowledge the financial support of this work by the Robert A. Welch Foundation (grant No. AA-668) and Baylor University.

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*Acta Cryst.* (1991). C47, 876–878

## Structure of a Heptanuclear Tungsten–Copper Complex, (Ph<sub>4</sub>P)<sub>2</sub>[Cu<sub>5</sub>W<sub>2</sub>O<sub>2</sub>S<sub>6</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>3</sub>].DMF

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(Received 13 August 1990; accepted 4 October 1990)

**Abstract.** Bis(tetraphenylphosphonium) bis( $\mu$ -*N,N*-diethyldithiocarbamato-3 $\kappa$ S:4 $\kappa$ S:5 $\kappa$ S:6 $\kappa$ S)-(diethyldithiocarbamato-7 $\kappa$ S)-hexa- $\mu$ <sub>3</sub>-sulfido-1 $\kappa^3$ S:2 $\kappa^3$ S:-3 $\kappa^2$ S:4 $\kappa^3$ S:6 $\kappa^3$ S:7 $\kappa^2$ S-pentacopperdi(oxotungsten)-dimethylformamide (1/1), 2[(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P]<sup>+</sup>. [Cu<sub>5</sub>W<sub>2</sub>(C<sub>5</sub>H<sub>10</sub>NS<sub>2</sub>)<sub>3</sub>O<sub>2</sub>S<sub>6</sub>]<sup>2-</sup>. C<sub>3</sub>H<sub>7</sub>NO, *M<sub>r</sub>* = 2106.5, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 25.210 (3), *b* = 22.507 (10), *c* = 14.038 (9) Å,  $\beta$  = 100.70 (5)°, *V* = 7826.5 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.788 g cm<sup>-3</sup>, Mo *K*α radiation,  $\lambda$  = 0.71073 Å,  $\mu$  = 47.2 cm<sup>-1</sup>, *F*(000) = 4160, *T* = 296 (1) K, *R* = 0.059 and *wR* = 0.064 for 6359 reflections with *I* > 3σ(*I*). The anion consists of two defective cubane-like units OWS<sub>3</sub>Cu<sub>2</sub> and OWS<sub>3</sub>Cu<sub>3</sub> linked by two weak Cu—S bonds and two bridging S<sub>2</sub>CNEt<sub>2</sub><sup>-</sup> ligands.

**Experimental.** The title compound was prepared by reaction of (NH<sub>4</sub>)<sub>2</sub>WO<sub>2</sub>S<sub>2</sub>, CuCl, NaS<sub>2</sub>CNEt<sub>2</sub>·3H<sub>2</sub>O

and Ph<sub>4</sub>PBr in DMF solution and a crystal suitable for X-ray analysis was grown in a solution of DMF/Et<sub>2</sub>O. Details of the sample preparation and the crystal growth are similar to that of (Et<sub>4</sub>N)<sub>2</sub>[Mo<sub>2</sub>Cu<sub>5</sub>O<sub>2</sub>S<sub>6</sub>(S<sub>2</sub>CNMe<sub>2</sub>)<sub>3</sub>] (Liu, Cao, Lei, Wu, Wei, Huang, Hong & Kang, 1990).

Diffraction intensities were collected from a purple-red crystal 0.65 × 0.30 × 0.20 mm in the  $\theta$ -2 $\theta$  scan mode on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo *K*α radiation. Cell constants were obtained from least-squares refinement of 24 reflections, using the setting angles around 14°, measured by the computer-controlled diagonal slit method of centering. 11490 reflections were collected in the range 2 < 2 $\theta$  < 46° (-27 < *h* < 0, -24 < *k* < 0, -15 < *l* < 15). The intensities were monitored by 3 representative reflections. The data were corrected for fluctuation in the monitored reflections (between 1.000 and 0.818), the *L<sub>p</sub>* factor and empirical absorption (between 1.042 and 0.917),

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