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## The *trans* Influence of the Silyl Ligand. Structure of *trans*-[PtCl(SiPh<sub>3</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>]

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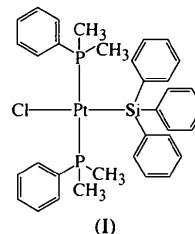
### Abstract

In the crystal structure of *trans*-chlorobis(dimethylphenylphosphine)(triphenylsilyl)platinum(II), [PtCl(C<sub>18</sub>H<sub>15</sub>Si)(C<sub>8</sub>H<sub>11</sub>P)<sub>2</sub>], the Pt atom coordinates to one Si and one Cl atom, and to two P atoms in mutual *trans* positions. The coordination geometry is distorted square planar with distances Pt—Si 2.321 (2), Pt—Cl 2.465 (2) and Pt—P 2.282 (2) and 2.322 (2) Å. The silyl ligand shows a very large *trans* influence on the Pt—Cl distance.

### Comment

From IR spectroscopy studies, Chatt, Eaborn & Ibekwe (1966) have postulated that silicon should have an exceptionally high ground-state *trans* influence. This was further supported by a crystal structure determination of *trans*-[PtCl(SiMePh<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>], which revealed a Pt—Cl distance of 2.45 (1) Å (Kapoor, 1968), almost 0.15 Å longer than in PtCl<sub>4</sub><sup>2-</sup> (Bengtsson & Os-

karsson, 1992). The crystal structure determination of this silicon compound was based on film data, resulting in fairly high e.s.d.'s of distances and angles. For a quantitative discussion of the *trans* influence more accurate data are needed. For this purpose we decided to determine the structure of *trans*-[PtCl(SiPh<sub>3</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>], (I).



The compound is composed of tetrahedrally distorted square-planar mononuclear [PtCl(SiPh<sub>3</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] complexes. The shortest Pt···Pt distance is 8.954 (2) Å. The structure and atomic numbering are shown in Fig. 1. In spite of the fact that the crystal structure is determined far below the melting point, 443 K (Chatt, Eaborn, Ibekwe & Kapoor, 1970), the displacement ellipsoids of the C atoms, especially in the phenyl rings C(10)–C(15) and C(50)–C(55), show large anisotropic movements of these atoms. The angles about the Pt atom vary from 85.73 (6) to 95.05 (7)°. This distortion is most likely caused by the large and bulky ligands. Deviations from the least-squares plane through the coordination plane are Pt 0.0025 (3), Si –0.179 (2), Cl –0.370 (2), P(1) 0.201 (2) and P(2) 0.184 (2) Å. The methyl group C(26) (Fig. 1) is approximately located in the coordination plane (0.214 Å out of the least-squares plane). This causes some repulsion between the phosphine and the silyl ligand, the shortest contact being C(26)···C(40) 3.22 (1) Å. The interaction moves the whole phosphine ligand towards the chloride ion, making the Cl—Pt—P(2) angle as small as 85.73 (6)°. The dihedral angle between the least-squares planes through the phenyl rings C(10)–C(15) and C(50)–C(55) is rather small, at 16° (Fig. 1). The closest non-H contact between these phenyl rings is between C(10) and C(50), the distance being 3.25 Å and indicating van der Waals contacts. The phosphine ligands push the chloride ion out of the coordination plane since the P(1)···Cl [3.286 (3) Å], C(16)···Cl [3.29 (1) Å] and P(2)···Cl [3.258 (3) Å] distances are all shorter than the van der Waals distances. It may be concluded that the distortion of the coordination geometry is most likely caused by intramolecular contacts.

The Pt—P distances [2.282 (2) and 2.322 (2) Å] do not differ significantly from those distances found in other *trans*-phosphines, e.g. *trans*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (2.300 Å; Messmer & Amma, 1966) and those compounds in Table 3. The difference between Pt—P(1) [2.282 (2) Å] and Pt—P(2) [2.323 (2) Å] is highly sig-

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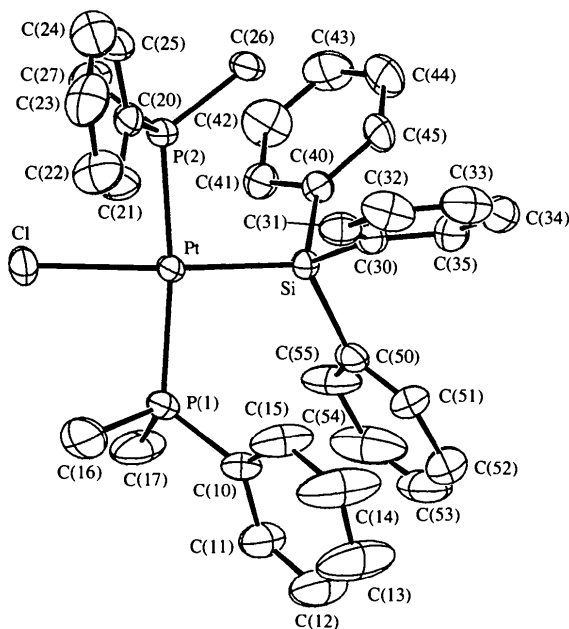


Fig. 1. Molecular structure and atomic numbering in the title compound. The displacement ellipsoids are drawn at 50% probability.

nificant but could be considered to be mainly a steric effect. The Pt—Si distances are not significantly different from those found in similar compounds (Table 3). The Pt—Cl distance [2.465 (2) Å] is not significantly different from that found in *trans*-[PtCl(SiMePh<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] [2.45 (1) Å; McWeeny, Mason & Towel, 1969]. However, a weakening of the Pt—Cl bond in the SiPh<sub>3</sub> complex as compared with the SiMePh<sub>2</sub> complex is indicated by the far IR spectra of these compounds:  $\nu(\text{Pt—Cl})$  239 and  $\nu(\text{Pt—Cl})$  242 cm<sup>-1</sup>, respectively (Chatt, Eaborn, Ibekwe & Kapoor, 1970). The Pt—Cl distance in the title compound is 0.161 Å longer than found in PtCl<sub>4</sub><sup>2-</sup> (80 e.s.d.'s) (Bengtsson & Oskarsson, 1992). This difference shows a very large *trans* influence of the Si atom on the Cl atom compared with Cl on Cl. It is in the same range as those found in similar compounds (Table 3). The Pt—Cl bond distance is *ca* 0.06 Å longer than that found *trans* to the C-bonded phenyl group in *trans*-[PtCl(Me<sub>2</sub>S)<sub>2</sub>(Ph)] (2.40 Å), indicating that the *trans* influence of the silyl group is even larger than for the phenyl group (Kukushkin, Löqvist, Norén, Oskarsson & Elding, 1992; Löqvist, Kukushkin, Oskarsson, Elding & Leipoldt, 1993; Wendt, Elding & Oskarsson 1993).

## Experimental

The title compound was prepared by the interaction of *cis*-[PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] with triphenylsilane in boiling benzene-triethylamine solution (Chatt, Eaborn, Ibekwe & Kapoor, 1967). Single crystals were formed on cooling to room temperature.

## Crystal data

[PtCl(C<sub>18</sub>H<sub>15</sub>Si)(C<sub>8</sub>H<sub>11</sub>P)<sub>2</sub>]  
*M<sub>r</sub>* = 766.26  
 Orthorhombic  
*Pbca*  
*a* = 10.716 (1) Å  
*b* = 17.431 (4) Å  
*c* = 35.029 (7) Å  
*V* = 6543 (1) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.556 Mg m<sup>-3</sup>

Mo *K*α radiation  
 $\lambda$  = 0.7107 Å  
 Cell parameters from 39 reflections  
 $\theta$  = 9.6–25.5°  
 $\mu$  = 4.569 mm<sup>-1</sup>  
*T* = 295 K  
 Prism  
 0.40 × 0.26 × 0.25 mm  
 Yellow

## Data collection

CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  
 by integration from crystal shape  
 $T_{\min}$  = 0.266,  $T_{\max}$  = 0.374  
 7109 measured reflections  
 7082 independent reflections

3526 observed reflections  
 $[I > 3\sigma(I)]$   
 $\theta_{\max}$  = 26.0°  
 $h = 0 \rightarrow 13$   
 $k = 0 \rightarrow 21$   
 $l = 0 \rightarrow 43$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: 2.10%

## Refinement

Refinement on *F*  
*R* = 0.0299  
*wR* = 0.0336  
*S* = 1.302  
 3526 reflections  
 379 parameters  
 $w = 1/\sigma^2(F)$   
 $(\Delta/\sigma)_{\max} = 0.0094$

$\Delta\rho_{\max} = 1.27 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.74 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i>
Pt	0.34567 (2)	0.05467 (1)	0.64573 (7)	2.78 (1)
Cl	0.5290 (2)	0.0063 (1)	0.68073 (5)	5.2 (1)
P(1)	0.4743 (2)	0.0734 (1)	0.59466 (5)	4.2 (1)
P(2)	0.2452 (2)	0.0533 (1)	0.70446 (5)	3.43 (8)
Si	0.1623 (2)	0.0703 (1)	0.61136 (5)	2.76 (8)
C(10)	0.4383 (7)	0.1422 (4)	0.5584 (2)	4.0 (4)
C(11)	0.467 (1)	0.1316 (5)	0.5201 (2)	5.9 (5)
C(12)	0.446 (1)	0.1882 (6)	0.4936 (3)	8.5 (7)
C(13)	0.393 (2)	0.2551 (7)	0.5049 (4)	12 (1)
C(14)	0.360 (2)	0.2666 (6)	0.5419 (4)	12 (1)
C(15)	0.383 (1)	0.2109 (5)	0.5688 (2)	7.2 (6)
C(16)	0.6229 (8)	0.1187 (9)	0.6110 (3)	10.5 (8)
C(17)	0.516 (1)	-0.0138 (8)	0.5701 (3)	8.5 (8)
C(20)	0.3055 (6)	0.1332 (5)	0.7327 (2)	3.7 (3)
C(21)	0.3874 (8)	0.1850 (5)	0.7176 (2)	4.9 (4)
C(22)	0.426 (1)	0.2477 (6)	0.7384 (3)	6.7 (6)
C(23)	0.386 (1)	0.2612 (6)	0.7735 (3)	6.9 (6)
C(24)	0.307 (1)	0.2073 (7)	0.7902 (3)	7.2 (6)
C(25)	0.2673 (8)	0.1433 (6)	0.7699 (2)	5.6 (5)
C(26)	0.0785 (7)	0.0666 (6)	0.7099 (2)	4.9 (5)
C(27)	0.273 (1)	-0.0325 (6)	0.7327 (3)	5.5 (5)
C(30)	0.0803 (7)	0.1657 (4)	0.6186 (2)	3.5 (3)
C(31)	0.1322 (7)	0.2227 (4)	0.6412 (2)	4.4 (4)
C(32)	0.073 (1)	0.2922 (5)	0.6462 (3)	6.1 (5)
C(33)	-0.036 (1)	0.3072 (6)	0.6289 (3)	7.1 (6)
C(34)	-0.092 (1)	0.2525 (7)	0.6063 (3)	6.4 (5)
C(35)	-0.0318 (8)	0.1820 (5)	0.6009 (2)	5.1 (4)
C(40)	0.0555 (6)	-0.0110 (4)	0.6266 (2)	3.2 (3)
C(41)	0.1066 (8)	-0.0837 (5)	0.6335 (2)	4.4 (4)

C(42)	0.032 (1)	-0.1445 (5)	0.6459 (3)	6.8 (5)
C(43)	-0.093 (1)	-0.1341 (6)	0.6515 (3)	6.4 (6)
C(44)	-0.1446 (8)	-0.0644 (6)	0.6446 (3)	6.2 (5)
C(45)	-0.0719 (7)	-0.0044 (5)	0.6325 (2)	4.4 (4)
C(50)	0.1689 (6)	0.0566 (5)	0.5576 (2)	4.1 (3)
C(51)	0.1429 (8)	0.1120 (6)	0.5315 (2)	6.4 (5)
C(52)	0.141 (1)	0.100 (1)	0.4927 (3)	10 (1)
C(53)	0.166 (1)	0.031 (1)	0.4790 (3)	10 (1)
C(54)	0.192 (1)	-0.028 (1)	0.5025 (4)	11 (1)
C(55)	0.194 (1)	-0.0136 (6)	0.5423 (2)	7.1 (6)

Table 2. Selected geometric parameters (Å, °)

Pt—Cl	2.465 (2)	Pt—P(2)	2.322 (2)
Pt—P(1)	2.282 (2)	Pt—Si	2.321 (2)
Cl...H(C25 <sup>i</sup> )	2.96	C(34)...H(C12 <sup>iii</sup> )	2.91
C(32)...H(C23 <sup>ii</sup> )	2.93	C(23)...C(32 <sup>i</sup> )	3.50 (1)
Cl—Pt—P(1)	87.55 (7)	Pt—P(1)—C(17)	113.7 (4)
Cl—Pt—P(2)	85.73 (6)	Pt—P(2)—C(20)	107.9 (3)
Cl—Pt—Si	166.74 (7)	Pt—P(2)—C(26)	123.3 (3)
P(1)—Pt—P(2)	167.44 (7)	Pt—P(2)—C(27)	114.5 (3)
P(1)—Pt—Si	95.05 (7)	Pt—Si—C(30)	115.2 (2)
P(2)—Pt—Si	93.90 (6)	Pt—Si—C(40)	106.1 (2)
Pt—P(1)—C(10)	121.5 (3)	Pt—Si—C(50)	117.9 (2)
Pt—P(1)—C(16)	109.6 (3)		

Symmetry codes: (i)  $\frac{1}{2} + x, y, \frac{3}{2} - z$ ; (ii)  $x - \frac{1}{2}, y, \frac{3}{2} - z$ ;  
(iii)  $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$ .

Table 3. Comparison of some silyl compounds

Compounds: (a) *trans*-[PtCl(SiMePh<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] (McWeeny, Mason & Towel, 1969; Kapoor, 1968); (b) *trans*-[PtCl{SiMePh(1-naphthyl)}-(PMe<sub>2</sub>Ph)<sub>2</sub>] (Hitchcock, 1976); (c) *trans*-[PtCl(SiPh<sub>3</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] (this work); (d) *trans*-[PtCl{Si(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N}(PMe<sub>2</sub>Ph)<sub>2</sub>] (Eaborn, Odell, Pidcock & Scollary, 1976); (e) *trans*-[PtBr(SiMe<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>] (Yamashita, Hayashi, Kobayashi, Tanaka & Goto, 1988).

Compound	Pt—Cl	Pt—Si	Pt—P
(a)	2.45 (1)	2.29	2.28, 2.28
(b)	2.462 (2)	2.317 (2)	2.292 (2), 2.306 (2)
(c)	2.465 (2)	2.321 (2)	2.282 (2), 2.323 (2)
(d)	2.471	2.292	2.300, 2.308
(e)	2.604 (6)*	2.330 (17)	2.296 (15), 2.299 (15)

\* Pt—Br.

The H-atoms of all phenyl rings were placed in calculated positions and were included in the structure-factor calculations. *x, y, z* for the H-atoms on the methyl groups were refined except for those attached to C(16), which were not found.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *Xtal3.2 LATCON* (Schwarzenbach & King, 1992). All subsequent calculations were carried out using *TEXSAN* (Molecular Structure Corporation, 1989). The structure was determined from Patterson and difference Fourier maps and refined by full-matrix least squares.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1204). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Contrasting Structures of Two Adducts of Zinc Crotonate with Substituted Pyridines

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### Abstract

Despite their closely similar empirical formulae and the very small difference in the substituted pyridine bases used in their syntheses, the structures of tetrakis( $\mu$ -crotonato-*O:O'*)bis(4-cyanopyridine-*N*)dizinc(II) (1), [Zn<sub>2</sub>(C<sub>4</sub>H<sub>5</sub>O<sub>2</sub>)<sub>4</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>], and catenapoly[{(crotonato-*O:O'*)(4-vinylpyridine-*N*)zinc}- $\mu$ -crotonato-*O:O'*] (2), [Zn(C<sub>4</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>7</sub>H<sub>7</sub>N)]<sub>n</sub>, are markedly different. Compound (1) is dimeric with four crotonate ligands bridging a pair of Zn atoms, each of which car-