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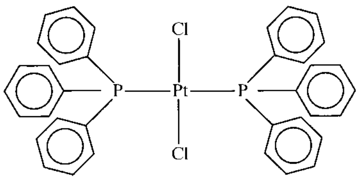
Two different crystals (A and B) were used to structurally characterize *trans*-[$PtCl_2(PPh_3)_2$] and to study random and systematic errors in derived parameters. The compound is isomorphous with *trans*-[$PdCl_2(PPh_3)_2$] and with one of the polymorphs of *trans*-[$PtMeCl(PPh_3)_2$] reported previously. Half-normal probability plot analyses based on A and B show realistic s.u.'s and negligible systematic errors. R.m.s. calculations give very good agreement between A and B, 0.0088 Å. Important geometrical parameters are Pt—P = 2.3163 (11) Å, Pt—Cl = 2.2997 (11) Å, P—Pt—Cl = 87.88 (4) and 92.12 (4)°. Half-normal probability plots and r.m.s. calculations were also used to compare the title compound with the palladium analogue, showing small systematic differences between the compounds. The torsion angles around the Pt—P bond were found to be very similar to those reported for isomorphous complexes, as well as to the torsion angles around the Pt—As bond in *trans*-[$PtCl_2(AsPh_3)_2$]. The NMR coupling constants for the title compound are similar to Pt—P coupling constants reported for analogous *trans* complexes.

Comment

Transition metal complexes containing phosphine, arsine and stibine ligands are widely being investigated in various fields of organometallic chemistry (Spessard & Miessler, 1996). Since the structure of both *cis*-[$PtCl_2(PPh_3)_2$] (Anderson *et al.*, 1982) and *cis*-[$PtCl_2(SbPh_3)_2$] (Wendt *et al.*, 1998) are known we decided to investigate systematically the dichloroplatinum complexes containing ligands with group 15 donor atoms. Crystallographic studies on *cis*- and *trans*-[$PtCl_2(AsPh_3)_2$] (Johansson & Otto, 2000; Johansson *et al.*, 2000) were recently completed and here we report the structure of the *trans*-[$PtCl_2(PPh_3)_2$], (I). All attempts to synthesize *trans*-[$PtCl_2(SbPh_3)_2$] have been unsuccessful so far.



(I)

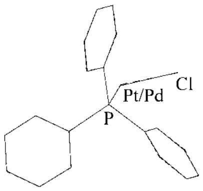
[$PtCl_2(L)_2$] (L = tertiary phosphine, arsine or stibine) complexes can conveniently be prepared by the substitution of SMe_2 from [$PtCl_2(SMe_2)_2$]. When using PPh_3 or $SbPh_3$ the *cis* isomers were exclusively obtained. In the case of $L = AsPh_3$, however, the *trans* isomer was predominantly obtained, with the amount of *cis* isomer formed contributing less than 1% to the total yield.

Two different crystals were used in order to study random and systematic errors in derived quantities. Roughly the same θ_{max}, 31.7°, was reached in both data collections but the number of reflections are about 35% larger for B.

An r.m.s. calculation is one way to compare similar structures (Sheldrick, 1997). R.m.s. calculation on the structures from crystals A and B, gives a value of 0.0088 Å, indicating excellent agreement between the two structure determinations. Half-normal-probability plot analysis (Albertsson & Schultheiss, 1974) may be used to (i) investigate the reliability of the s.u.'s and (ii) identify systematic differences. For 21 non-H atoms (half the complex), 57 independent interatomic distances ($3n$-6) completely describe the complex. Crystals A and B show linearity with all the 57 distances (R = 0.99), with a slope of 0.976 ± 0.032 and an intercept -0.019 ± 0.032 (95% confidence interval), indicating realistic s.u.'s and negligible systematic errors. The larger completeness of the data set for crystal B (95.8 and 94.5% for A) does not influence the structure refinement.

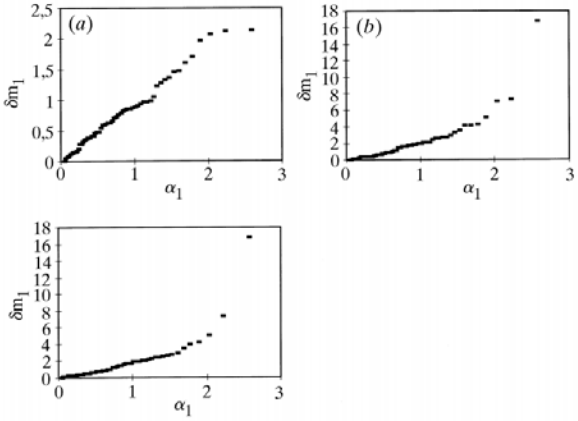
Since there are no observable differences between the structures derived from crystal A and B only structure A will be discussed here. The title compound crystallizes on an inversion centre as square planar moieties with the bulky phosphine ligands in a *trans* orientation. The Pt—P bond length of 2.3163 (11) Å and the Pt—Cl bond length of 2.2997 (11) Å are within the normal range for bonds of this type. The complex exhibits a distorted square-planar geometry with P—Pt—Cl = 87.88 (4) and P—Pt—Cl^i = 92.12 (4)° [symmetry code: (i) $-x,-y,-z$]. All three P—C bonds are equal in length [1.820 (2) Å] even though the C31—P—Pt angle [117.60 (11)°] deviate significantly from the other two angles [average 111.90 (11)°]. Similar observations are made for the Pd analogue (Ferguson *et al.*, 1982) As generally observed, the average C—P—C angle 104.83 (15)° are smaller than for an ideal tetrahedral arrangement.

Comparison with the isomorphous palladium complex (Ferguson *et al.*, 1982) has also been made both by r.m.s. calculations and half-normal probability plots. Low r.m.s. values are found with both crystal structures A and B, 0.0218 and 0.0216 Å respectively. The good correlation between A and the Pd complex is shown in the r.m.s. plot in Scheme 1.



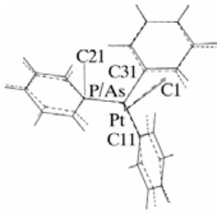
Scheme 1

Parts (a) and (*c*) of Scheme 2 show crystal structure A compared to the Pd complex using half-normal probability plot analysis. Part (*b*) of Scheme 2, based on independent distances, shows linearity up to 54 distances (R = 0.98), with a slope of 2.097 ± 0.088 and intercept −0.223 ± 0.076 (95% confidence interval). The negative intercept indicates that there are small systematic differences between the platinum and the palladium structures. A slope of 2 indicates that the underestimation of the s.u.'s is about 2. We have earlier stated that the s.u.'s are roughly correct estimated for the platinum complex and this indicates an underestimation of the s.u.'s in the palladium complex. The largest systematic differences between the two compounds (Scheme 2), which is based on dependent distances, are shown in Table 1. The largest differences are in the Pt/Pd—P and Pt/Pd—Cl bonds and in the angles around the metal and the P atoms.



Scheme 2

In Table 2, torsion angles for the title compound are compared to those found for related structures in the literature. The title compound is isomorphous to one form of *trans*-[PtMeCl(PPh$_3$)$_2$] (Otto *et al.*, 1994) of which two polymorphs are reported in the literature. The other polymorph of *trans*-[PtMeCl(PPh$_3$)$_2$] (Bardi & Piazzesi, 1981) is isomorphous to the analogous AsPh$_3$ complex (Otto *et al.*, 1995). Although good agreement was found between the Cl—Pt—P—C torsion angles of the title compound and the isomorphous *trans*-[PtMeCl(PPh$_3$)$_2$] complex, small differences were found on all three angles ranging from 0.8 (3)-1.9 (3)°. Surprisingly it also shows very good agreement with two of the torsion angles in the *trans*-[PtCl$_2$(AsPh$_3$)$_2$] complex and only deviates by 2.99 (16)° on the third angle. The *trans*-[PtCl$_2$(AsPh$_3$)$_2$] complex was found to have almost identical torsion angles in four different solvated forms thereof (Johansson *et al.*, 2000). R.m.s. calculation of the title compound and the corresponding AsPh$_3$ complex gives a value of 0.1988 indicating some differences between the structures. A superimposition of the two complexes, however, shows these differences to be mainly due to a slight twist in the phenyl rings (Scheme 3). The torsion angles of the other polymorph of *trans*-[PtMeCl(PPh$_3$)$_2$] is in fair agreement with the isomorphous *trans*-[PtMeCl(AsPh$_3$)$_2$] complex, but both differ significantly from the other compounds discussed.



Scheme 3

In Table 3, the title compound is compared with some related complexes in terms of crystallographic parameters and first order Pt—P coupling constants ($^1J_{PtP}$). Multinuclear NMR spectroscopy can give valuable information to the coordination mode of NMR active elements, such as ^{31}P and ^{195}Pt. It is well known that the first order M—P coupling constants enable quite good estimations of the M—P (M = NMR active transition metal) bond length for a specific system. In this sense, estimations of bond strength and the *trans* influence of the ligand under investigation can be obtained (Steyn *et al.*, 1997). Major differences in the Pt—P [0.058 (2) Å shorter *trans* to Cl] and Pt—Cl [0.045 (2) Å longer *trans* to PPh$_3$] bond distances were observed between the *cis*- and *trans*-[PtCl$_2$(PPh$_3$)$_2$] isomers. This is resulting from the smaller *trans* influence of Cl compared to PPh$_3$. These differences are also reflected in the Pt—P coupling constants of 3671 and 2627 Hz for the *cis* and *trans*isomers, respectively. The other Pt—P coupling constants show the same trend, except for P(C$_6$H$_{11}$)$_3$ which has a larger coupling constant than expected. This observation is probably due to the higher electron donating capability of P(C$_6$H$_{11}$)$_3$, compared to PPh$_3$. Surprisingly, equivalent Pt—Cl bond distances are observed for the two analogous complexes *trans*-[PtCl$_2$L$_2$] with L = PPh$_3$ and AsPh$_3$ [2.2997 (11) and 2.3012 (12) Å, respectively], even though the Pt—As bond [2.4101 (4) Å] is significantly elongated compared to the Pt—P bond [2.3163 (11) Å].

Experimental

PPh$_3$ (2 g, 7.63 mmol) was added to a mixture of *cis*- and *trans*-[PtCl$_2$(SMe$_2$)$_2$] (1 g, 2.55 mmol) in acetone (30 ml) and stirred for 30 min. White *cis*-[PtCl$_2$(PPh$_3$)$_2$] precipitated from the reaction medium in almost quantitative yields and was isolated by filtration. *trans*-[PtCl$_2$(PPh$_3$)$_2$] was prepared by photochemical isomerization of *cis*-[PtCl$_2$(PPh$_3$)$_2$] as described by Mastin & Haake (1970). A mixture of *cis*-[PtCl$_2$(PPh$_3$)$_2$] (1 g, 1.27 mmol) in chloroform (300 ml) was irradiated with a

240 W medium pressure mercury lamp equipped with a filter to cut out radiation with wavelengths above 366 nm. After 5 h, the chloroform was evaporated at reduced pressure and the remaining solids extracted with benzene to yield a yellow solution containing the desired product. Recrystallization from a benzene/methanol solution gave crystals suitable for X-ray analysis and two were selected for structure analysis. Both data sets was collected with a SMART CCD system with ω scan, -0.3° per frame and 5 s per frame. The detector distance was set to 4 cm for both crystal A and B. The number of reflections is about 35% larger for crystal B compared to A resulting in a more complete data set as well as larger redundancy, 95.8% and 94.5% in B and A, respectively. Spectral data: ^{31}P NMR (CDCl$_3$, 121.497 MHz, 85% H_3PO_4 = 0 p.p.m.): 20.51 (triplet due to 34% ^{195}Pt), $^1J_{PtP}$ = 2627 Hz.

Compound (A)

Crystal data

$[PtCl_2(C_{18}H_{15}P)_2]$
$M_r = 790.53$
Triclinic, $P\overline{1}$
$a = 9.1857\ (18)$ Å
$b = 9.6334\ (19)$ Å
$c = 10.379\ (2)$ Å
$\alpha = 72.44\ (3)^\circ$
$\beta = 88.50\ (3)^\circ$
$\gamma = 68.19\ (3)^\circ$
$V = 809.1\ (3)$ Å^3

$Z = 1$
$D_x = 1.622$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6593 reflections
$\theta = 2$–30°
$\mu = 4.623$ mm^{-1}
$T = 293\ (2)$ K
Rectangular plate, yellow
0.28 × 0.13 × 0.05 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.358$, $T_{max} = 0.802$
6837 measured reflections

4744 independent reflections
4740 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0223$
$\theta_{max} = 31.64^\circ$
$h = -11 \rightarrow 13$
$k = -9 \rightarrow 14$
$l = -13 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.060$
$S = 0.911$
4744 reflections
187 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0326P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.836$ e Å^{-3}
$\Delta\rho_{min} = -1.130$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (A).

Pt—Cl	2.2997 (11)	P—C21	1.819 (3)
Pt—P	2.3163 (11)	P—C31	1.820 (3)
P—C11	1.819 (3)		
Cl—Pt—P	87.88 (4)	C21—P—C31	104.23 (15)
Cl^i—Pt—P	92.12 (4)	C11—P—Pt	111.97 (10)
C11—P—C21	106.49 (14)	C21—P—Pt	111.83 (11)
C11—P—C31	103.77 (15)	C31—P—Pt	117.60 (11)

Symmetry codes: (i) $-x, -y, -z$.

Table 2
Interatomic distances with largest δm_i values for the platinum complex when compared to the palladium complex.

δm_i	Distance[a]	Order no[b]
16.80	Pt—P	1
7.34	Pt—Cl	1
7.04	Pt—C31	2
5.07	Cl—P	2
4.31	Pt—C21	2
4.19	C14—C16	2
4.18	C14—C15	1

Notes: (*a*) Numbering corresponds to the platinum complex; (*b*) 1st and 2nd order number represents the closest distances between 2 atoms separated by 1 or 2 formal bonds.

Table 3
Comparative torsion angles for selected *trans*-[Pt*R*Cl(*L*)$_2$] (*R* = Cl or Me, *L* = PPh$_3$ or AsPh$_3$) complexes..

Complex	T1[a] (°)	T2[b] (°)	T3[c] (°)
trans-[PtCl$_2$PPh$_3$)$_2$] (A)[d]	104.58 (10)	−135.99 (11)	−16.45 (13)
trans-[PtCl$_2$PPh$_3$)$_2$] (B)[d]	104.68 (11)	−136.03 (12)	−15.27 (13)
trans-[PtCl$_2$AsPh$_3$)$_2$][e]	104.22 (10)	−138.98 (12)	−16.66 (12)
trans-[PtMeCl(PPh$_3$)$_2$][f]	105.4 (3)	−135.1 (3)	−14.6 (3)
trans-[PtMeCl(PPh$_3$)$_2$][g]	108.613	−130.248	−13.361
	113.870	−126.255	−4.954
trans-[PtMeCl(AsPh$_3$)$_2$][h]	109.6 (3)	−128.8 (3)	−12.6 (3)
	115.7 (3)	−125.6 (3)	−3.8 (3)

Notes: (*a*) T1 = Cl—Pt—*L*—C11; (*b*) T2 = Cl—Pt—*L*—C21; (*c*) T3 = Cl—Pt—*L*—C31; (*d*) this study; (*e*) Johansson *et al.* (2000); (*f*) isomorph of the title compound (Otto *et al.*, 1994); (*g*) polymorph of *f*, PPh$_3$ ligands unequivalent, no s.u.'s available (Bardi & Piazzesi, 1981); (*h*) isomorph of *g*, AsPh$_3$ ligands unequivalent (Otto *et al.*, 1995)

Table 4
Comparative crystallographic and NMR[a] data for selected [PtCl$_2$(L)$_2$] (*L* = P or As ligand) complexes..

L	Pt—*L* (Å)	Pt—Cl (Å)	$^1J_{PtP}$ (Hz)
PPh$_3$(A)[b]	2.3163 (11)	2.2997 (11)	2627
PPh$_3$(B)[b]	2.3187 (12)	2.2997 (11)	2627
PPh$_3$[c]	2.258 (2)	2.345 (2)	3671
PPh$_2$Fc[d]	2.318 (2)	2.301 (2)	2620
P(C$_6$H$_{11}$)$_3$[e]	2.337 (2)	2.317 (2)	2824
PEt$_3$[f]	2.298 (18)	2.294 (9)	2900
AsPh$_3$[g]	2.4101 (4)	2.3012 (12)	

Notes: (*a*) *ca* 5 m*M* in CDCl$_3$; (*b*) this Study; (*c*) *cis* isomer, Anderson *et al.* (1982); (*d*) Otto & Roodt (1997); (*e*) Del Pra & Zanotti (1980); (*f*) Messmer & Amma (1966); (*g*) Johansson *et al.* (2000)

Compound (B)

Crystal data

$[PtCl_2\{P(C_6H_5)_3\}_2]$
$M_r = 790.53$
Triclinic, $P\bar{1}$
$a = 9.1857\ (18)$ Å
$b = 9.6334\ (19)$ Å
$c = 10.379\ (2)$ Å
$\alpha = 72.44\ (3)^\circ$
$\beta = 88.50\ (3)^\circ$
$\gamma = 68.19\ (3)^\circ$
$V = 809.1\ (3)$ Å^3
$Z = 1$
$D_x = 1.622$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4853 reflections
$\theta = 3$–30°
$\mu = 4.623$ mm^{-1}
$T = 293\ (2)$ K
Rectangular plate, yellow
0.31 × 0.14 × 0.08 mm

Data collection

Siemens SMART CCD diffractometer
ω- scans
Absorption correction: empirical absorption corrections using *SADABS* (Sheldrick, 1996)
$T_{\min} = 0.328$, $T_{\max} = 0.709$
9288 measured reflections
4881 independent reflections
4434 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0299$
$\theta_{\max} = 31.71^\circ$
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 13$
$l = -15 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0330$
$wR(F^2) = 0.0574$
$S = 0.955$
4881 reflections
187 parameters
riding model
$w = 1/[\sigma^2(F_o^2) + (0.0273P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max} = 0.675$ e Å^{-3}
$\Delta\rho_{\min} = -1.098$ e Å^{-3}

Table 5
Selected geometric parameters (Å, °) for (B).

Pt—Cl	2.2997 (11)	P—C21	1.819 (3)
Pt—P	2.3187 (12)	P—C31	1.824 (3)
P—C11	1.816 (3)		
Cl$^{\rm i}$—Pt—P	92.12 (4)	C11—P—Pt	111.93 (10)
Cl—Pt—P	87.88 (4)	C21—P—Pt	111.93 (11)
C11—P—C21	106.35 (14)	C31—P—Pt	117.39 (11)
C11—P—C31	103.85 (15)		
C21—P—C31	104.45 (15)		

Symmetry codes: (i) $-x, -y, -z$.

The crystallographic raw data frames were integrated, the reflections reduced and corrections were applied for Lorentz and polarization effects.

For A and B, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1997); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

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