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[Bis(3-diphenylphosphinopropyl)phenylphosphine-κ^3P,P',P'']chloroplatinum(II) perchlorate

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Key indicators

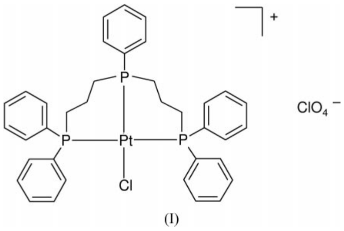
Single-crystal X-ray study
T = 145 K
Mean σ(C–C) = 0.020 Å
R factor = 0.092
wR factor = 0.221
Data-to-parameter ratio = 16.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The crystal structure of the title complex, $[PtCl(C_{36}H_{37}P_3)]ClO_4$, at 145 K contains the trimethylene-bridged triphosphine chelate ligand $Ph_2P(CH_2)_3PPh(CH_2)_3PPh_2$ coordinated in a tridentate manner to the Pt^{II} atom. The coordination geometry about Pt is distorted from square planar as a consequence of the geometrical constraints of the chelating ligand.

Comment

Platinum metal complexes of triphosphine chelate ligands $R_2P(CH_2)_3PR'(CH_2)_3PR_2$ (R,R' = alkyl, aryl) have been investigated for their capabilities to activate catalytically small molecules such as CO_2 or H_2 (Niewahner & Meek, 1982; Wander *et al.*, 1996). The interest in this field has led to the preparation of a range of Pd^{II}, Pt^{II} and Rh^{I} complexes of the triphosphine chelate ligand $Ph_2P(CH_2)_3PPh(CH_2)_3PPh_2$ (ttp) and its closely related trimethylene-bridged phosphine analogues with various *R* substituents, some of which have been characterized crystallographically (Wander *et al.*, 1996; Nappier *et al.*, 1973; Tau & Meek, 1979; Goikhman *et al.*, 2002). We are currently investigating the relationship between structure and reactivity of Pt^{II} complexes coordinated in a tridentate manner by the triphosphine ligands (ttp) and $PhP(CH_2CH_2PPh_2)_2$ (triphos), or by the mixed phosphine–thioether ligand $S(CH_2CH_2PPh_2)_2$ (PSP) (Andreasen *et al.*, 1999). Of special interest ia the manner in which the coordination geometry is affected by the size of the chelate ring, and the influence that this geometry has on the reactivity of the respective Pt^{II} complexes.



(I)

In the title complex, $[Pt(ttp)Cl]ClO_4$, (I), all three phosphine donors of the ttp ligand are coordinated to the Pt^{II} centre, with the chloride ligand occupying the fourth coordination site. The coordination geometry is distorted from square-planar such that the P2—Pt1—P3 angle of 171.59 (11)° is smaller than the other *trans* angle [P1—Pt1—Cl1 = 179.46 (12)°]. Both of the *cis*-P—Pt—P angles are greater than 90° [P1—Pt1—P3 = 91.62 (11)° and P1—Pt1—P2 = 93.38 (11)°], while the corresponding *cis*-P—Pt—Cl angles are somewhat smaller [P3—Pt1—Cl1 = 88.24 (11)° and P2—Pt1—Cl1 = 86.82 (11)°]. This is consistent with other Pt^{II} and Pd^{II}

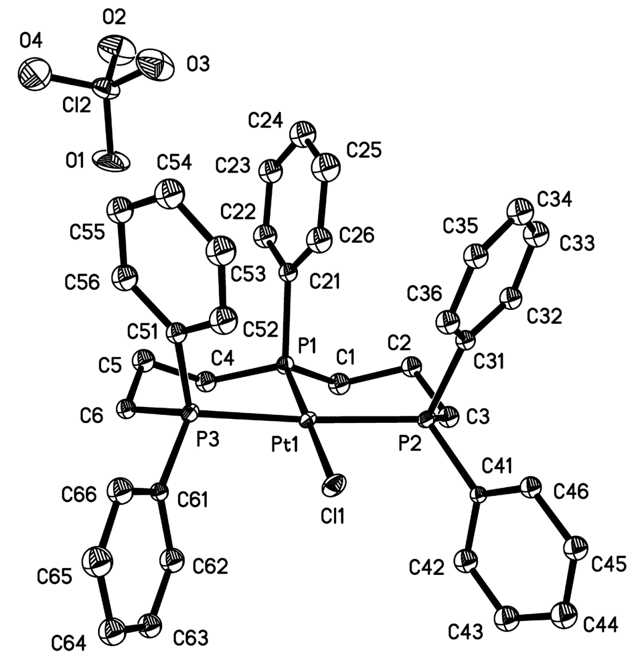


Figure 1
The structure of the title complex, with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

complexes of trimethylene-bridged chelate ligands, in which the *cis*-*X*—Pt—*Y* angles between two connected donors of a chelate ring are generally greater than 90° (Wander *et al.*, 1996; Cheng *et al.*, 1997; Loeb & Mansfield, 1996). Non-chelated tris(tertiary phosphine) complexes may also show *cis*-P—Pt—P angles well above 90°, for example [PtCl(PMe$_3$)$_3$]Cl (Favez *et al.*, 1980), with reported angles in the range 94.49 (9)–100.09 (9)°. In contrast, complexes of chelate ligands incorporating ethylene linkages between the phosphine-donor atoms generally exhibit *cis*-P—Pt—P bite angles significantly less than 90°. This is also observed in the Pt^{II} complexes of triphos and PSP [*cis*-P—Pt—P/S angles in the range 84.0 (1)–86.6 (2)°; Andreasen *et al.*, 1999; Sevillano *et al.*, 1999; Annibale *et al.*, 2000] and can be ascribed to the ring strain associated with five-membered chelate rings.

The Pt—P bond distances to the terminal phosphine groups in the title complex [Pt1—P3 = 2.302 (3) Å and Pt1—P2 = 2.313 (3) Å] are well within the range usually observed for two mutually *trans* PPh$_2$ moieties in Pt^{II} complexes (Andreasen *et al.*, 1999; Sevillano *et al.*, 1999; Annibale *et al.*, 2000). The bond distance to the central phosphine donor of the ttp ligand is significantly shorter [Pt1—P1 = 2.239 (3) Å]. This feature conforms to the difference in *trans* influence of chloride compared to phosphines (Favez *et al.*, 1980). It is also of interest to compare the Pt1—P1 bond distance in the title complex with the distance of 2.207 (2) Å to the central phosphine donor in [Pt(triphos)Cl]Cl (Sevillano *et al.*, 1999). The shorter Pt—P distance in the latter may be attributed to the ring strain of its ethylene-bridged chelate system. The Pt1—Cl1 bond distance of 2.365 (3) Å in the title complex is in good agreement with literature values for chloride *trans* to tertiary phosphine ligands (Favez *et al.*, 1980; Sevillano *et al.*, 1999).

Experimental

The tridentate chelate ligand bis(3-diphenylphosphinopropyl)-phenylphosphine, ttp (C$_{36}$H$_{37}$P$_3$), was synthesized according to a published method (Green & Meek, 1990). The title complex [Pt(ttp)Cl]ClO$_4$ was prepared by a slightly modified version of the literature method (Tau, 1978). A water/ethanol solution of K$_2$PtCl$_4$ was added to a toluene solution of ttp and the mixture was refluxed for five hours. The toluene phase was discarded and the volume of the residual aqueous/ethanolic solution was reduced to a few ml under reduced pressure. A portion of ethanol was added and the salt [Pt(ttp)Cl]Cl was precipitated by addition of excess cyclohexane. The product was isolated by filtration. The elemental analysis and multinuclear NMR spectra of this compound are in agreement with the chemical formula (Klint, 1996). The title complex was precipitated as its perchlorate salt by addition of a saturated aqueous LiClO$_4$ solution to a water/ethanol solution of the purified salt [Pt(ttp)Cl]Cl. Crystals suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into an acetonitrile solution of the complex.

Crystal data

[PtCl(C$_{36}$H$_{37}$P$_3$)]ClO$_4$
M_r = 892.56
Orthorhombic, $P2_12_12_1$
a = 10.256 (3) Å
b = 15.738 (5) Å
c = 20.980 (6) Å
V = 3386.4 (18) Å^3
Z = 4
D_x = 1.751 Mg m^{-3}
D_m = 1.70 Mg m^{-3}
Density measured by flotation in CCl$_4$ and CH$_2$ClBr at 293 K
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 17.7–22.2°
μ = 10.87 mm^{-1}
T = 145 (2) K
Prism, colourless
0.21 × 0.21 × 0.07 mm

Data collection

Enraf–Nonius CAD-4*F* diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: by integration (*ABSORB* in *Xtal*3.2; Hall *et al.*, 1992)
$T_{\min}$ = 0.147, $T_{\max}$ = 0.530
3784 measured reflections
3784 independent reflections
3702 reflections with $I > 2\sigma(I)$
$\theta_{\max}$ = 73.9°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 26$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.092
$wR(F^2)$ = 0.221
S = 1.13
3784 reflections
236 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1922P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 11.86 e Å^{-3}
$\Delta\rho_{\min}$ = −4.98 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0016 (2)
Absolute structure: Flack (1983); no Friedel pairs
Flack parameter = −0.02 (2)

The data set comprises only the unique octant of reflections and the refined structure is of relatively low precision. The large maximum and minimum residual electron density of 10.78 and −6.05 e Å^{-3}, respectively, are close to atom Pt1. The data do not support anisotropic refinement of the C atoms, and these were refined with isotropic displacement parameters. H atoms were positioned geometrically and allowed to ride during subsequent refinement, with C—H = 0.95 (aromatic) or 0.99 Å (aliphatic) and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *CAD*-4*F Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4*F Software*; data reduction: *DATARED* (Norrestam & Nielsen, 1982), and *ADDREF* and *SORTRF* in *Xtal*3.2 (Hall *et al.*, 1992); program(s) used to solve structure: *SHELXTL*

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(Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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