Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Dichloro[2-(2-Diphenylphosphino)-*N*-(1-phenylethyl)-benzylamine-C^{α},*P*]platinum

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Received 25 January 2001
Accepted 5 February 2001
Online 13 February 2001

The [$PtCl_2(C_{27}H_{26}NP)$] complex consists of a five-membered *P*,*C*-chelate ring, from the 2-(2-diphenylphosphino)-*N*-(1-phenylethyl)benzylamine ligand, coordinating a platinum metal centre; the square-planar environment is completed by two *cis*-chloro ligands. The rigidity of the aromatic *o*-phenylene backbone produces a shallow twist conformation for the *P*,*C*-chelate. The diphenyl groups on phosphorus are arranged in a face-on/edge-on orientation. The non-chelating pendant ammonium group forms weak intermolecular N—H···Cl contacts.

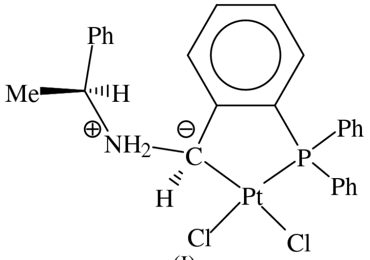
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.010 Å
R factor = 0.031
wR factor = 0.065
Data-to-parameter ratio = 18.9

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

Comment

Chelating ligands with rigid backbones are used to increase the stability of metal complexes; those attached to platinum group metal ions can potentially produce robust stereoselective catalysts. Diphosphine ligands offer backbone flexibility with a large P—*M*—P bite angle, whilst their bidentate nitrogen analogues tend to be more rigid and form smaller N—*M*—N chelate angles. Asymmetric phosphino–amine ligands benefit from the 'hard' amine group which is more labile, and the softer high chelate stability of the phosphine group (Blacker *et al.*, 2000). Cyclometalation reactions involving phosphino–carbon ligands generally form *P*,*C*-chelating or bridging species depending on the nature of the phosphorus substituents and other auxiliary ligands (Portnoy *et al.*, 1995).



(I)

The title compound, (I), was formed unexpectedly in the attempted synthesis of [$PtCl\{C(O)Me\}(C_{27}H_{24}NP)$] (Ankersmit *et al.*, 1996). A variety of reagents participate in addition reations with the polarized C═N double bond; further protonation can create a more stable but reactive intermediate (Harada, 1970). Following a similar procedure, the AgO_3SCF_3 species reduced the imine group to an ammonium ion [C—N bond distances of 1.519 (7) and 1.513 (8) Å], and created a five-membered *P*,*C*-chelate ring, C19—Pt—P1 = 85.15 (16)°. Six-membered *P*,*N*-chelate rings incorporating the imine based precursor have been observed in palladium dichloride [$PdCl_2(C_{27}H_{24}NP)$], (II), and platinum

DOI: 101107/S1600536801002586

diiodide [$PtI_2(C_{27}H_{24}NP)$] complexes, (III) (Ankersmit *et al.*, 1996). These compounds, by comparison, have larger (N—Pt—P) bite angles, and smaller C—N bond distances typical of the starting ligand [87.37 (14)°/1.272(8) Å and 88.3 (2)°/1.273(12) Å for (II) and (III), respectively]. The ammonium ion of (I), rather than forming the *P*,*N*-chelate, participates in weak N—H···Cl hydrogen-bond contacts (Table 2) along the [010] direction in the crystal. The square-planar environment around platinum is fairly distorted; despite the restraint of the *o*-phenylene backbone, *cis* and *trans* angles deviate by up to 6° (Table 1). The P1—Pt1—Cl2 angle of 95.70 (6)° has widened to accommodate the larger phosphine group compared to the smaller substituents on the carbon side of the *P*,*C*-chelating ligand; C19—Pt1—Cl1 = 90.68 (17)°. The Pt—P bond length of 2.1769 (14) Å is unexceptional and comparable to the value of 2.217 (2) Å in (II). Although there are few characterized *P*,*C*-chelate species with platinum ions, the Pt1—C19 of 2.039 (6) Å can be compared to that observed in the dichloride bridged platinum species [$Pt_2Cl_2(P_2C_{54}H_{64})$] (Alyea *et al.*, 1989). The Pt—Cl bonds in (I), 2.3728 (15) and 2.3802 (15) Å, are in good agreement with each other and consistent with values found in the literature. Platinum–halide bonds *trans* to carbon bonded ligands generally exert a greater *trans* influence than phosphorus moieties (Gandelman *et al.*, 1997). The corresponding Pt—Cl bond values [2.345 (3) and 2.347 (3) Å] in dichloro(dimethyliminomethyl)(triphenylphosphine)platinum (Barefield *et al.*, 1982) follow a similar trend to those in (I). The torsion angles around the five atom Pt—P—C—C—C ring (Table 1) are consistent with those of a (shallow) twist conformation. The diphenyl groups on P1 are arranged in a face-on/edge-on orientation as observed in many bidentate diphosphine chelate systems. The pendant amine arm is bent back towards the metal square plane such that the phenyl ring is almost parallel to the *o*-phenylene group.

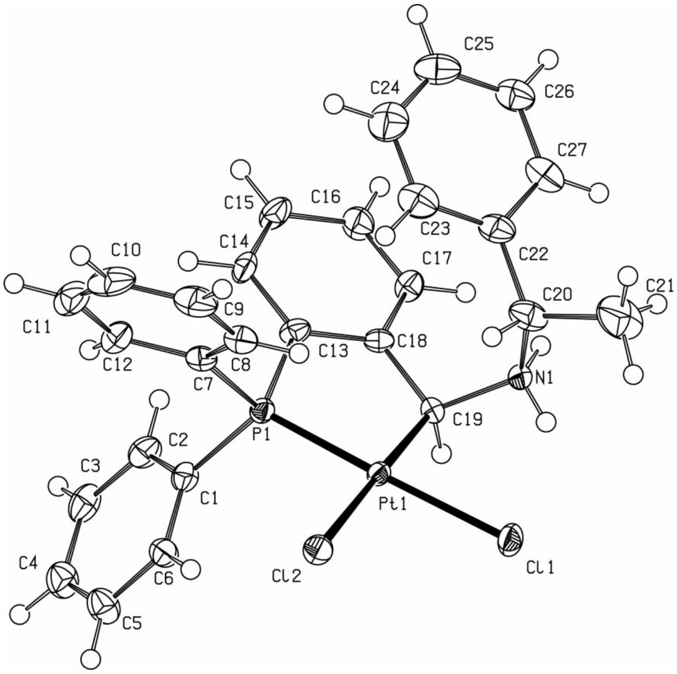


Figure 1
PLATON/*ORTEP* representation (Spek, 2000) of (I) with displacement ellipsoids at 50% probability level.

Experimental

The complex was formed as a by-product in the attempted synthesis of [$PtCl\{C(O)Me\}(C_{27}H_{24}NP)$], for which complete details have been reported (Ankersmit *et al.*, 1996). Yellow crystals of (I) were obtained from recrystallization in a solution of $CDCl_3$.

Crystal data

[$PtCl_2(C_{27}H_{26}NP)$]
M_r = 661.45
Orthorhombic, $P2_12_12_1$
a = 10.0849 (9) Å
b = 10.6081 (7) Å
c = 22.917 (3) Å
V = 2451.7 (4) Å^3
Z = 4
D_x = 1.792 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 20 reflections
θ = 11.6–13.9°
μ = 6.02 mm^{-1}
T = 150 (2) K
Block, yellow
0.50 × 0.38 × 0.25 mm

Data collection

Enraf–Nonius CAD-4T diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DELABS* in *PLATON*; Spek, 2000)
$T_{\min}$ = 0.077, $T_{\max}$ = 0.222
6345 measured reflections
5607 independent reflections

5121 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.023
$\theta_{\max}$ = 27.5°
h = 0 → 13
k = −13 → 13
l = 0 → 29
3 standard reflections
frequency: 60 min
intensity decay: 2.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.065
S = 1.06
5607 reflections
296 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0259P)^2 + 2.9856P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.90 e Å^{-3}
$\Delta\rho_{\min}$ = −1.21 e Å^{-3}
Absolute structure: Flack (1983); 3181 Friedel pairs
Flack parameter = 0.000 (8)

Table 1
Selected geometric parameters (Å, °).

Pt1—P1	2.1769 (14)	Pt1—C19	2.039 (6)
Pt1—Cl1	2.3728 (15)	N1—C19	1.519 (7)
Pt1—Cl2	2.3802 (15)	N1—C20	1.513 (8)
C19—Pt1—P1	85.15 (16)	C19—Pt1—Cl2	178.95 (18)
C19—Pt1—Cl1	90.71 (17)	P1—Pt1—Cl2	95.70 (5)
P1—Pt1—Cl1	175.67 (6)	Cl1—Pt1—Cl2	88.43 (5)
C19—Pt1—P1—C13	−11.6 (3)	C13—C18—C19—Pt1	−7.6 (7)
Pt1—P1—C13—C18	11.2 (5)	P1—Pt1—C19—C18	11.8 (4)
P1—C13—C18—C19	−3.2 (7)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···Cl1$^{\rm i}$	0.95 (7)	2.46 (6)	3.330 (5)	152 (5)
N1—H1A···Cl2$^{\rm i}$	0.85 (7)	2.76 (7)	3.294 (5)	122 (5)

Symmetry code: (i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

An initial absorption correction performed using three ψ-scans measurements revealed large residual density peaks around the platinum metal (maximum and minimum being 4.16 and -3.86e Å^{-3}, respectively). The highest peaks were arranged in a regular pattern around the metal centre indicative of the crystal habit. Presumably if a smaller crystal could have been selected, the problem may have been reduced and not caused such a significant effect. The $R_{\rm int}$ value of 0.053 for the ψ-scan data is relatively high, considering the complex contains a platinum metal ion, thus this absorption correction was deemed to be of insufficient quality. Unfortunately a numerical correction, from the crystal faces, was not feasible at the time of the measurement. Consequently, the final refinement utilized data from an absorption correction using *DELABS* (*PLATON*: Spek, 2000). As expected, significantly better residual density values and a decrease in the $R_{\rm int}$ (to 0.023) are observed. The displacement ellipsoids from both datasets are similar. H atoms attached to C atoms were constrained and allowed to ride on their carrier atoms with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. The coordinates of H1*A* and H1*B* (on N1) were allowed to refine freely with their displacement parameters set at $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm N})$.

Data collection: locally modified *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *SET*4 (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *DIRDIF*99 (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *PLATON*.

The authors wish to thank Dr H. A. Ankersmit and Professor Dr K. Vrieze, University of Amsterdam, The Netherlands, for the provision of crystals. The investigations were supported by the Chemical Sciences of the Netherlands Organization of Scientific Research (CW–NWO).

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