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cis-Dichloridobis{dimethyl[3-(9-phosphabicyclo[3.3.1]non-9-yl)propyl]amine-κP}platinum(II)

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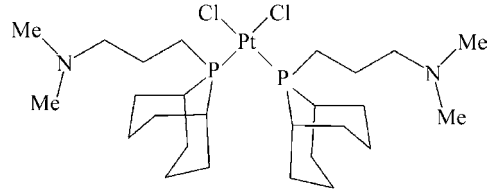
The title compound, $[PtCl_2(C_{13}H_{26}NP)_2]$, is a rare example of a sterically bulky ligand adopting a *cis* geometry in a square-planar complex. It crystallizes on a twofold rotation axis which bisects the Pt centre and the P—Pt—P′ and Cl—Pt—Cl′ angles. The ligand exhibits a random packing disorder in the *N*,*N*-dimethylpropylamine substituent, with the two orientations refining to occupancies of 0.404 (15) and 0.596 (15). Weak intermolecular interactions between a Cl and a H atom of the ligand of a neighbouring molecule result in extended chains along the *a* axis. The effective cone angle for the dimethyl[3-(9-phosphabicyclo[3.3.1]non-9-yl)propyl]amine (Phoban[3.3.1]-C_3NMe_2) ligand was determined as being in the range 160–181°, depending on the choice of atoms used in the calculations.

Comment

Phoban ligands are derived from the radical addition reaction of *cis*,*cis*-1,5-cyclooctadiene (COD) with an RPH_2 moiety (R = H or other suitable monoanionic group such as alkyl or aryl). A mixture of symmetrical and unsymmetrical adducts is obtained, *viz*. 9-*R*-9-phosphabicyclo[3.3.1]nonane and 9-*R*-9-phosphabicyclo[4.2.1]nonane, respectively (Van Winkle *et al.*, 1969). It has been shown that the two isomers may be conveniently separated by selective protonation and aqueous extraction of the [3.3.1] isomer, which is substantially more basic than the [4.2.1] isomer (Eberhard *et al.*, 2005). These ligands are of significant industrial importance in a number of homogeneously catalysed processes, the most notable being modified cobalt hydroformylation, as used by Shell (Van Winkle *et al.*, 1969).

We previously conducted a systematic evaluation of the steric and electronic aspects of these ligands (Bungu & Otto, 2007*a*) through their respective phosphine selenides. In addition, their catalytic performance was evaluated in phosphine-modified cobalt hydroformylation reactions (Bungu & Otto, 2007*b*). The Phoban-C_3NMe_2 ligand (both isomers) represents an interesting derivative, since it contains a tertiary alkyl amine substituent that could potantially coordinate to metal centres in addition to the P atom. It could also act as a hemilabile pendant group or facilitate intermolecular interactions with substrate molecules in solution.

In order to investigate the coordination mode of these ligands, we reacted $PtCl_2$(COD) with a solution containing a mixture of both ligand isomers totalling two molar equivalents. Crystals of the the title compound, (I), were obtained from the reaction mixture after the volume of the original solution had been reduced by about 60% by slow evaporation. Although ^{31}P NMR analysis indicated a mixture of species in solution, crystals of (I) suitable for X-ray diffraction were selectively obtained at this point. This is in accordance with our previous work (Bungu & Otto, 2007*a*,*b*), where the [3.3.1] isomers of different Phoban derivatives were found to display a higher degree of crystallinity than the corresponding [4.2.1] isomers.



(I)

Compound (I) crystallizes with a distorted square-planar geometry on a twofold rotation axis bisecting the Pt metal centre and bisecting the P1—Pt1—P1^{i} and Cl1—Pt1—Cl1^{i} [symmetry code: (i) $x, -y, \frac{1}{2} - z$] angles (see Fig. 1). The bulky ligands adopt the thermodynamically preferred *cis* orientation (from a bond energy perspective), as opposed to a sterically governed *trans* orientation. The ligand exhibits a random packing disorder in the *N*,*N*-dimethylpropylamine substituent, with the two orientations refining to occupancies of 0.404 (15) and 0.596 (15) for fragments *A* and *B*, respectively (see Fig. 2).

The Pt1—P1 and Pt1—Cl1 bond distances are within the expected ranges at 2.2571 (11) and 2.3614 (11) Å respectively (Table 2). All bond angles in the coordination environment of the metal centre deviate significantly from what would be expected for a square-planar geometry. The wide P1—Pt1—P1^{i} angle of 97.46 (6)° and the narrow Cl1—Pt1—Cl1^{i} angle of 86.23 (6)° are a reflection of the steric impact of the two bulky phosphine ligands being in close proximity [symmetry code: (i) $x, -y, -z + \frac{1}{2}$]. In general, the adoption of *cis* or *trans* geometry is governed by both the steric and electronic properties of the ligands. Strongly coordinating ligands, such as phosphines, tend to favour mutually *cis* orientation, but with increasing steric demand of the ligands a *trans* geometry may be adopted. Compound (I) represents a rare example of sterically bulky ligands (effective cone angle in the range 160–181°) displaying mutually *cis* geometry. In comparison, the *trans* isomer was obtained in *trans*-$[PtCl_2(PBz_3)_2]$ (PBz_3 is tribenzylphosphine), where effective cone angles of 160 and 162° were calculated

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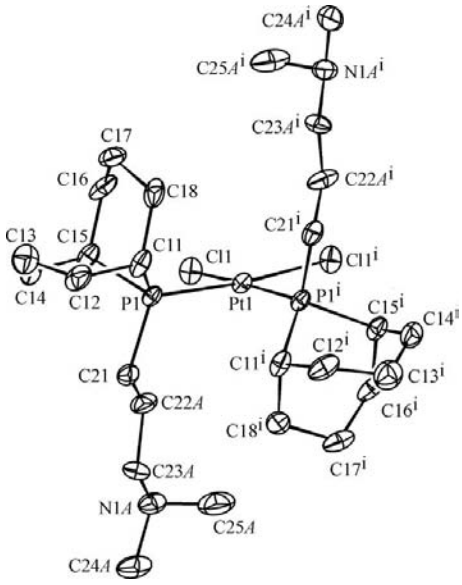

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms and one component of the disorder have been omitted for clarity. [Symmetry code: (i) $x, -y, \frac{1}{2} - z$.]

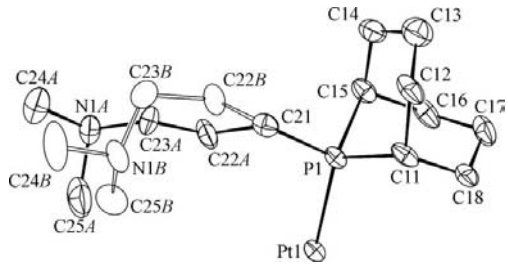

Figure 2
A perspective view illustrating the disorder in the *N*,*N*-dimethylpropylamine substituent of (I). The occupancy for orientation *A* (shaded octants and solid bonds) refined to 0.404 (15) and that for orientation *B* (open spheres and bonds) to 0.596 (15). H atoms and the rest of the molecule have been omitted for clarity.

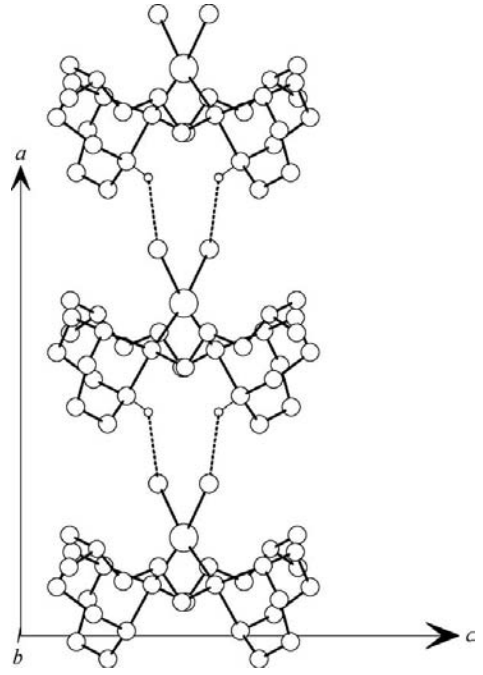

Figure 3
Extended molecular chains in the *a*-axis direction due to weak intermolecular interactions between atom Cl1 and atom H11^{ii} of an adjacent molecule [symmetry code: (ii) $x - \frac{1}{2}, -y, z$]. H atoms not involved in the interactions were removed for clarity.

for the two independent molecules, each of $\overline{1}$ symmetry, in the unit cell (Johansson *et al.*, 2002). All P—C bond distances and C—P—C angles are within normal ranges for molecules such as these (Bungu & Otto, 2007*a*,*b*).

The orientation of the phosphine ligands seems to be directed by an intramolecular interaction between the H atom on atom C15 and atom Cl1 [Cl1···C15 = 3.234 (5) Å, Cl1···H15 = 2.72 Å and Cl1···H15—C15 = 114°]. This results in the smaller sections of the ligands facing each other, with the larger C_3NMe_2 substituents occupying opposite sides of the equatorial plane. In addition, weak intermolecular interactions are observed between atom Cl1 and atom H11^{ii} [symmetry code: (ii) $x - \frac{1}{2}, -y, z$] of a neighbouring molecule, creating extended chains along the *a* axis (Fig. 3) [Cl1···C11 = 3.562 (5) Å, Cl1···H11 = 2.75 Å and Cl1···H11—C11 = 141°]. No close interactions were found between the amine functional group and a Pt or Cl atom.

Describing the steric demand of phosphine ligands has been the topic of many studies and a variety of models have been developed (Bunten *et al.*, 2002). In practice, the Tolman cone angle (Tolman, 1977) is still the most commonly used model, due to its simplicity and ease of calculation. According to this model, a cylindical cone is constructed from a point 2.28 Å from P, just touching the van der Waals radii of the outermost atoms of the ligand. In addition, all substituents on P should be adjusted to occupy the smallest possible space; since ball-and-stick models were originally used, this could be done manually. In the case of tri-*n*-alkylphosphines, this would thus result in all ligands containing alkyl chains longer than ethyl having the same steric demand as PEt_3, since the rest of the chain would fall within the 'slipstream' of the ligand. With the development of user-friendly graphics software for crystallography, it has become more common to determine cone angles using the geometry obtained during a crystal structure determination. This principle has been further developed (Otto, 2001) into the concept of the 'effective cone angle', where the crystallographically determined metal—P bond distance is used and the cone is determined as that touching the van der Waals radii of the outermost atoms of the ligand. Using the Pt—P bond distance obtained in this study, but calculating the cone to the outermost H atoms on C22*A* and C22*B* (as representative of the *N*,*N*-dimethylpropylamine substituent), results in values of 168 and 160° for orientations *A* and *B*, respectively. Even though not in close proximity to Pt1 (±4.2–4.7 Å), the outermost point on this substituent is, however, a H atom on one of the methyl groups on the amine, and using this in the calculations results in values of 179 and 181° for orientations *A* and *B*, respectively. These values should be regarded with some caution when interpreting metal reactivities in terms of

the steric bulk of the ligands, as they may not reflect the true environment surrounding the metal.

Experimental

The Phoban-C_3NMe_2 ligand (mixture of isomers) was prepared as described previously (Bungu & Otto, 2007*a*). All manipulations involving the free ligand were performed using degassed solvents and working under a positive argon atmosphere to prevent oxidation. $PtCl_2$(COD) (COD is *cis*,*cis*-1,5-cyclooctadiene) (125 mg, 0.33 mmol) was dissolved in dichloromethane (5 ml) and a dichloromethane solution of the ligand mixture (1.08 ml, 618 m*M*, 0.67 mmol) was subsequently added. The resulting reaction mixture was stirred overnight and a portion was subjected to ^{31}P NMR analysis. ^{31}P ($CDCl_3$): δ *cis*-[$PtCl_2$(Phoban[3.3.1]-C_3NMe_2)$_2$] −0.40 (*t*, $^1J_{Pt-P}$ = 3536 Hz); *cis*-[$PtCl_2$(Phoban[4.2.1]-C_3NMe_2)$_2$] 29.79 (*t*, $^1J_{Pt-P}$ = 3432 Hz); *cis*-[$PtCl_2$(Phoban[3.3.1]-C_3NMe_2)(Phoban[4.2.1]-C_3NMe_2)] 1.76 ([3.3.1]-isomer, *td*, $^1J_{Pt-P}$ = 3524 Hz, $^2J_{P-P}$ = 15 Hz), 31.31 ([4.2.1]-isomer, *td*, $^1J_{Pt-P}$ = 3443 Hz, $^2J_{P-P}$ = 15 Hz). Slow evaporation of the solvent (dichloromethane) from the residual reaction mixture resulted in crystals of compound (I) being obtained.

Crystal data

$[PtCl_2(C_{13}H_{26}NP)_2]$
M_r = 720.63
Orthorhombic, *Ibca*
a = 14.9247 (7) Å
b = 19.0706 (9) Å
c = 20.8432 (10) Å
V = 5932.5 (5) Å^3
Z = 8
Mo *K*α radiation
μ = 5.04 mm^{-1}
T = 100 K
0.12 × 0.11 × 0.05 mm

Data collection

Bruker X8 APEXII 4K KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.651, T_{max} = 0.873
(expected range = 0.583–0.781)
29798 measured reflections
3700 independent reflections
2384 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.073
S = 1.00
3700 reflections
202 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.62 e Å^{-3}
$\Delta\rho_{min}$ = −0.57 e Å^{-3}

The random packing disorder in the *N*,*N*-dimethylpropylamine part of the ligand was modelled as two orientations with occupancies summing to unity. Occupancies of 0.404 (15) and 0.596 (15) were obtained for components *A* and *B*, respectively. No restraints were required to stabilize the refinement, but it was noted that the C21—C22*A* and C21—C22*B* bond distances differed significantly by 0.190 (16) Å and a similarity restraint was subsequently introduced for these two distances. The restraint did not have a marked effect on the geometrical parameters within the coordination polyhedron, or on the refinement statistics. All H atoms were placed in geometrically idealized positions, with C—H distances of 0.98 Å for CH, 0.97 Å for CH_2 or 0.96 Å for CH_3, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C) for CH and CH_2 or 1.5U_{eq}(C) for CH_3. The maximum residual electron density of 1.62 e Å^{-3} is located 0.83 Å from Pt1.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 2001); software used to prepare material for publication: *SHELXL97*.

Table 1
Selected geometric parameters (Å, °).

Pt1—P1	2.2571 (11)	Cl1···H11^{i}	2.75
Pt1—Cl1	2.3614 (11)	Cl1···H15	2.72
P1—C11	1.840 (5)	Cl1···C11^{i}	3.562 (5)
P1—C15	1.837 (4)	Cl1···C15	3.234 (5)
P1—C21	1.821 (5)		
P1—Pt1—P1^{ii}	97.46 (6)	C11—P1—C21	108.9 (2)
P1^{ii}—Pt1—Cl1	172.79 (4)	C15—P1—C21	104.4 (2)
P1—Pt1—Cl1	88.33 (4)	Pt1—P1—C11	118.32 (17)
Cl1—Pt1—Cl1^{ii}	86.23 (6)	Pt1—P1—C15	115.50 (16)
C11—P1—C15	94.8 (2)	Pt1—P1—C21	112.89 (16)

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

Table 2
Comparison of molecular geometry parameters (Å, °) for *cis*-[$PtCl_2$-$(P)_2$] complexes (Å, °).

P	Pt—Cl	Pt—P	Cl—Pt—Cl	P—Pt—P	Reference
PMe_3	2.364 (8) 2.388 (9)	2.256 (8) 2.239 (6)	87.7 (3)	96.2 (4)	*a*
PEt_3	2.364 (2) 2.374 (2)	2.264 (2) 2.262 (2)	85.66 (9)	98.39 (7)	*b*
PCy_3†		2.299 (4) 2.289 (3)	82.1 (1)	107.6 (1)	*c*
Phoban[3.3.1]-C_3NMe_2	2.3614 (11)	2.2571 (11)	86.23 (6)	97.46 (6)	*d*
PPh_3	2.329 (3) 2.360 (3)	2.267 (3) 2.244 (3)	86.65 (7)	97.44 (7)	*e*

† Pt—Cl bond distance not reported. References: (*a*) Messmer *et al.* (1967); (*b*) Otto & Muller (2001); (*c*) Cameron *et al.* (1989); (*d*) this work; (*e*) Anderson *et al.* (1982).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3190). Services for accessing these data are described at the back of the journal.

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