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trans-Dichloridobis(4,8-dimethyl-2-phenyl-2-phosphabicyclo[3.3.1]-nonane-κP)platinum(II)

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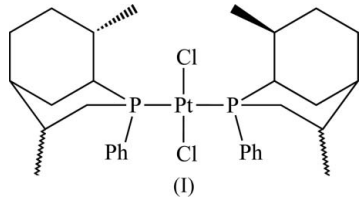
The crystal structure of the title compound, *trans*-[$PtCl_2$-($C_{16}H_{23}P$)$_2$], has been determined at 100 K. The Pt atom is located on a twofold axis and adopts a distorted square-planar coordination geometry. The structure is only the second example of a coordination complex containing a derivative of the 4,8-dimethyl-2-phosphabicyclo[3.3.1]nonane (Lim) phosphine ligand family. The ligand contains four chiral C atoms, with the stereochemistry at three of these fixed during synthesis, therefore resulting in two possible ligand stereoisomers. The compound crystallizes in the chiral space group $P4_32_12$ but is racemic, comprising an equimolar mixture of both stereoisomers disordered on a single ligand site. The effective cone angles for both isomers are the same at 146°.

Comment

Lim ligands (2-*Q*-4,8-dimethyl-2-phosphabicyclo[3.3.1]nonane) are derived from the radical addition reaction of the monoterpene *R*-(+)-limonene with a QPH_2 molecule, where *Q* = H or some other suitable monoanionic group such as alkyl or aryl, resulting in a racemic mixture of ligands being obtained. Although the phosphine Lim backbone contains four chiral C atoms, the stereochemistry at three of these sites is fixed, *viz.* C1 (*R*), C5 (*R*) and C8 (*S*), while C4 can have either an *R* or *S* configuration. This stereochemistry is a consequence of performing the synthesis with the optically pure terpene and the mechanism of addition to the P atom (Robertson *et al.*, 2001).

Chiral phosphine ligands are of general interest in coordination chemistry and catalysis, and ligands of the Lim family have been shown to display exceptional qualities in the modified cobalt hydroformylation of alkenes to give alcohols directly (Steynberg *et al.*, 2002; Crause *et al.*, 2003; Dwyer *et al.*, 2004). The only other crystal structure in the open literature of a coordination compound containing a member of the Lim ligand family, [$Co(CO)_3$(Lim-C18)]$_2$ (Lim-C18 is the 4*R* isomer of 2-octadecyl-4,8-dimethyl-2-phosphabicyclo[3.3.1]-nonane), was obtained during such a study (Polas *et al.*, 2003).

In order to investigate further the coordination mode of these ligands, we prepared [$PtCl_2$(Lim-Ph)$_2$] by reaction of [$PtCl_2$(COD)] (COD is *cis*,*cis*-cycloocta-1,5-diene) with two molar equivalents of a solution containing a mixture of both Lim-Ph isomers. Recrystallization as described in the *Experimental* section resulted in crystals of (I) being obtained.



(I)

Compound (I) crystallizes with a distorted square-planar coordination geometry, with a twofold rotation axis passing through the Pt metal centre and bisecting the P2—Pt1—P2^i and Cl1—Pt1—Cl1^i angles [symmetry code: (i) *y*, *x*, −*z*] (Fig. 1). The Lim-Ph ligands adopt a *trans* orientation, suggesting significant steric bulk, although *cis* isomers have been observed in solution using ^{31}P NMR (*vide infra*). The coordination geometry deviates significantly from ideal square planar, with P2—Pt1—P2^i and Cl1—Pt1—Cl1^i angles of 170.97 (9) and 175.49 (8)°, respectively. Interestingly, the C11 methyl groups, which contribute significantly to the overall steric bulk of the Lim-Ph ligands, occupy the same side of the equatorial plane, with a closest contact of only 3.655 (13) Å between C11 and C11^i. This interaction manifests itself in the deviation of the P atoms below the equatorial plane. In addition, the presence of these two methyl substituents effectively blocks one apical position of the Pt atom, with Pt1···C11 contacts of only 3.563 (6) Å. The Pt1—P2 bond distance of 2.3088 (14) Å is within the expected range, while the Pt1—Cl1 distance of 2.3320 (13) Å is quite long. This elongation is probably a consequence of the steric repulsion of the two bulky phosphine ligands and the resulting distortion from square planarity. The deviations in the bond angles from

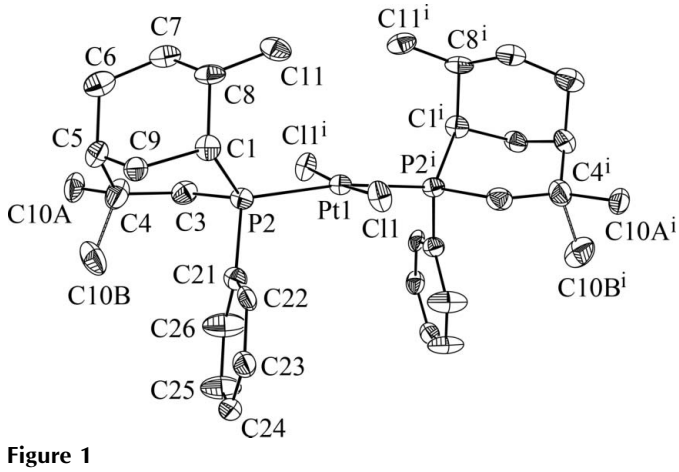


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. [Symmetry code: (i) *y*, *x*, −*z*.]

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the ideal value of 180° would impact negatively on the efficiency of the relevant orbital overlap between the atoms involved. Table 1 presents a comparison with related structures, also containing bulky ligands, taken from the open literature, to illustrate this effect.

The Lim-Ph ligand exhibits disorder in the orientation of the C10 methyl group, with components *A* and *B* corresponding to the 4*R* and 4*S* isomers, respectively (Fig. 1). Refinement of the site occupancies for C10*A* and C10*B* yielded values that did not differ significantly from 0.5 and the occupancies were therefore constrained to 0.5 for subsequent refinement, corresponding to a true racemic mixture. Short intermolecular contacts [C10*A*···C10*A*^{ii} = 2.502 (16) Å; symmetry code: (ii) $y-1, x+1, -z$] preclude the simultaneous presence of C10*A* in neighbouring molecules, but there are no constraints on the presence of C10*B*.

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. This principle has been further developed (Otto, 2001) into the concept of the 'effective cone angle', where the crystallographically determined metal–P bond length is used in the calculations. Using the Pt1—P2 bond distance obtained in this study and calculating the cone to the outermost H atoms (H11*A*, H19*A* and H25*A*) on C11, C19 and C25 results in a value of 146°. In addition, the cone angle is independent of the orientation of C10.

^{31}P NMR analysis of the reaction mixture indicated a number of species in solution corresponding to Pt complexes of both *cis* and *trans* geometry, as well as containing combinations of the different ligand isomers, *i.e.* (4*R*,4*R*), (4*S*,4*S*) and (4*R*,4*S*). Aside from the constraint observed for the intermolecular contacts involving C10*A*, the refined 50% disorder in the orientation of the C10 Me group is consistent with any of these combinations. Redissolving some of the single crystals obtained and recollecting the ^{31}P NMR spectrum confirmed that mixtures of this nature are indeed present in both the solid and solution states.

Based on high-pressure NMR experiments, it was previously shown that the 4*R* isomer coordinates preferentially during modified Co hydroformylation (Polas *et al.*, 2003; Dwyer *et al.*, 2004), and this observation was supported by modelling studies (Crause *et al.*, 2003). Considering, however, that the two isomers are electronically and sterically (as shown here) very similar, this behaviour is currently not well understood and may warrant further investigation.

Experimental

The Lim-Ph ligand (mixture of isomers) was prepared by adapting methods described previously (Bungu & Otto, 2007). 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*-cycloocta-1,5-diene) (200 mg, 0.53 mmol) was dissolved in dichloromethane (10 ml) and a dichloromethane solution of the ligand mixture (1.49 ml, 753 m*M*, 1.12 mmol) was subsequently added. The resulting reaction mixture was stirred overnight and a portion was subjected to ^{31}P NMR analysis. The spectra were quite complex, with both *cis* and *trans* Pt^{II} complexes present as mixtures of the two ligand isomers. Crystals of compound (I) suitable for single-crystal diffraction studies were obtained by addition of acetone to the dichloromethane reaction mixture followed by slow evaporation.

^{31}P ($CDCl_3$): *trans*-[$PtCl_2$(4*R*-Lim-Ph)$_2$] −8.82 p.p.m. (*t*, $^1J_{Pt-P}$ = 2378 Hz); *trans*-[$PtCl_2$(4*R*-Lim-Ph)(4*S*-Lim-Ph)] −9.83 (4*R*, *t*, $^1J_{Pt-P}$ = 2378 Hz) and −12.42 p.p.m. (4*S*, *t*, $^1J_{Pt-P}$ = 2383 Hz); *trans*-[$PtCl_2$(4*S*-Lim-Ph)$_2$] −13.58 p.p.m. (*t*, $^1J_{Pt-P}$ = 2384 Hz).

Crystal data

$[PtCl_2(C_{16}H_{23}P)_2]$
M_r = 758.62
Tetragonal, $P4_32_12$
a = 9.5909 (1) Å
c = 33.2924 (9) Å
V = 3062.41 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.88 mm^{-1}
T = 100 K
0.37 × 0.24 × 0.22 mm

Data collection

Bruker X8 APEXII 4K KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.273, T_{max} = 0.364
31409 measured reflections
3782 independent reflections
3209 reflections with $I > 2\sigma(I)$
R_{int} = 0.083

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.067
S = 1.15
3782 reflections
180 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.19 e Å^{-3}
$\Delta\rho_{min}$ = −1.42 e Å^{-3}
Absolute structure: Flack (1983), 1505 Friedel pairs
Flack parameter: 0.010 (10)

Table 1
Comparative data for *trans*-[$PtCl_2(P)_2$] complexes.

P	Pt—P (Å)	Pt—Cl (Å)	Reference
PEt_3	2.298 (18)	2.294 (9)	(i)
PPh_3	2.3164 (11)	2.2997 (11)	(ii)
PBz_3	2.3219 (12)	2.3092 (11)	(iii)
	2.3019 (10)	2.3053 (10)	(iii)
PCy_3	2.337 (2)	2.317 (2)	(iv)
PPh_2Fc	2.318 (2)	2.301 (2)	(v)
s-PhobPBu	2.3121 (11)	2.3059 (11)	(vi)
a_7PhobPBu	2.302 (4)	2.307 (4)	(vi)
	2.321 (5)	2.318 (4)	(vi)
1,2,6-tpp	2.3096 (12)	2.3118 (12)	(vii)

References: (i) Messmer & Amma (1966); (ii) Johansson & Otto (2000); (iii) Johansson *et al.* (2002); (iv) Del Pra & Zanotti (1980); (v) Otto & Roodt (1997); (vi) Carreira *et al.* (2009); (vii) Doherty *et al.* (2006).

The disorder of the methyl substituent on C4 of the Lim-Ph ligand was modelled as two orientations with occupancies summing to unity. Occupancies of 0.493 (18) and 0.507 (18) were obtained for C10*A* and C10*B*, respectively. Since these values do not differ significantly from 0.5, they were constrained to 0.5 for further refinement. The C4—C10*A* and C4—C10*B* distances were tightly restrained to 1.530 (5) Å. H atoms were placed geometrically with C—H distances of 1.00 Å for CH (alkyl), 0.95 Å for CH (aryl), 0.99 Å for CH_2 and 0.98 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. For the methyl groups, rotation was permitted about the C—C bond.

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, 2001); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BI3013). Services for accessing these data are described at the back of the journal.

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