

***trans*-Chloro(methyl)bis(tricyclohexylphosphine)platinum(II)**

Stefanus Otto

Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa, and Inorganic Chemistry 1, Chemical Centre, University of Lund, PO Box 124, SE-221 00 Lund, Sweden

Correspondence e-mail: stefanus.otto@inorg.lu.se

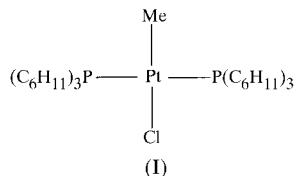
Received 5 March 2001

Accepted 6 April 2001

The crystal structure of the title compound, [PtCl(CH₃)(C₁₈H₃₃P)₂], is isostructural with various platinum(II) and palladium(II) complexes containing two bulky tricyclohexylphosphine ligands in a *trans* orientation. The Pt atom resides on an inversion centre, resulting in a 50% statistical disorder in the chloro and methyl positions. The most significant geometrical parameters are Pt—P 2.3431 (8), Pt—Cl 2.440 (4) and Pt—C1 2.179 (13) Å, and P—Pt—P 180, P—Pt—Cl 89.15 (12) and 90.85 (12), and C—Pt—Cl 172.7 (5)°. The effective and Tolman cone angles for the tricyclohexylphosphine ligands were calculated as 160 and 162°, respectively.

Comment

As part of a systematic investigation involving complexes with the general formula *trans*-[MMeCl(L)₂] (*M* = Pt or Pd; *L* = tertiary phosphine or arsine ligands), crystals of the title compound, (I), were obtained.

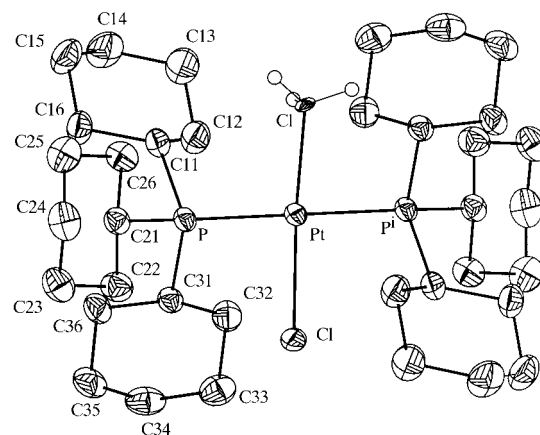


The Pt atom lies on an inversion centre, resulting in a 50% statistical disorder in the chloro and methyl positions, while the phosphine ligands are in a *trans* orientation with an 180° angle due to symmetry requirements. All angles within the Pt coordination sphere are close to those expected for an ideal square-planar environment, with P—Pt—Cl angles of 89.15 (12) and 90.85 (12)°, and P—Pt—C1 angles of 89.8 (4) and 90.2 (4)°. The C1—Pt—Cl angle of 172.7 (5)°, however, deviates quite substantially from 180°, while the angle between the disordered ligands, *i.e.* Cl—Pt—Cl' or C1—Pt—Cl', was determined as 7.3 (5)°. The Pt—P and Pt—Cl bond distances of 2.3431 (8) and 2.440 (4) Å are within normal ranges for a complex containing large phosphine ligands and a strong labilizing group, such as methyl, *trans* to the Cl ligand.

The Pt—Cl bond distance of 2.179 (13) Å is slightly longer than expected and may be an artifact of the disorder between the methyl and chloro ligands, a conclusion confirmed by the large uncertainty associated with this specific bond.

All three of the cyclohexyl (Cy) substituents of the phosphine ligands adopt the expected chair conformation for saturated six-membered rings and are exactly staggered with respect to the *trans* phosphine due to the inversion centre at the Pt position. The average tetrahedral angles around the P atom of 104.87 (16) and 113.65 (12)° for C—P—C and C—P—Pt, respectively, indicate that the substituents are slightly compressed towards each other as is normally encountered in coordinated phosphine ligands.

Measuring the spatial impact of a ligand in a coordination complex is an issue that has attracted much interest in the past and will continue to do so in future as the existing models are refined and new models are introduced. One such model and

**Figure 1**

The structure of the title complex with the atom-numbering scheme and 30% probability displacement ellipsoids. The disorder in the chloro and methyl positions is not indicated. The H atoms of the methyl group are of arbitrary size, while those of the cyclohexyl rings have been omitted for clarity.

probably the most generally recognized measure of steric size of phosphine ligands is the Tolman cone angle (Tolman, 1977). In this regard, it has been noted before that the flexibility of the PCy₃ ligand allows several conformers of the cyclohexyl groups to exist, leading to values for the Tolman cone angle ranging from 163° for *trans*-[PtI₂(PCy₃)₂] (Alcock & Leviston, 1974; Ferguson *et al.*, 1978) up to the 181° value determined in [Hg(NO₃)₂(PCy₃)₂] (Alyea *et al.*, 1977). In this study, the cone-angle calculations were performed based on Tolman's model using C—H bond distances of 0.97 Å and a van der Waals H-atom radius of 1.2 Å. The effective cone angle is calculated in a similar way to the Tolman cone angle but using the actual Pt—P bond distance determined from the crystallographic data, while a fixed distance of 2.28 Å is used for the Tolman cone-angle calculations. Values of 160 and 162° were calculated for the effective and Tolman cone angles, respectively. Both these values are very similar to the value of 163° determined for the isostructural *trans*-[PtI₂(PCy₃)₂] complex, as mentioned above.

In Table 2, the title compound is compared with other closely related Ni^{II}, Pd^{II} and Pt^{II} complexes from the literature containing two bulky tricyclohexylphosphine ligands in a *trans* orientation. The compound was found to be isostructural with several of these complexes, as indicated, showing that the crystal packing is predominantly determined by the tricyclohexylphosphine ligands and only when the metal core is drastically influenced as by the introduction of a phenyl or H ligand are the packing modes changed.

In Table 3, the title compound is compared with related *trans*-[MMeCl(L)₂] (*M* = Pd or Pt; *L* = P or As ligands) complexes, illustrating the effect of different phosphine and arsine ligands on the geometrical parameters. The Pt–P bond distance of 2.3431 (8) Å is comparably longer than the other *M*–P bond distances, even longer than in the PdPPh₂Fc complex (Fc is ferrocenyl) that also contains a bulky phosphine ligand. This can, in addition to the large size of PCy₃, also be due to the strong electron-donating capability of this ligand causing a mutual labilization when occupying positions *trans* to each other. The Pt–Cl bond distance of 2.440 (4) Å is also slightly longer than in the related complexes and is probably a combination of steric crowding and an electron-rich metal centre. Although the Pd–*L* bond lengths seem to be slightly longer than in the corresponding Pt–*L* complexes, this effect is not as evident in the *M*–Cl bonds.

Experimental

[PtMeCl(COD)] (COD is *cis,cis*-cycloocta-1,5-diene) was prepared according to literature procedures (Clark & Manzer, 1973). To a solution of [PtMeCl(COD)] (50 mg, 0.14 mmol) in dichloromethane (10 ml) was added PCy₃ (98 mg, 0.35 mmol) dissolved in dichloromethane (8 ml). Slow evaporation of this solution yielded colourless crystals suitable for X-ray analysis. ¹H NMR (CDCl₃): δ 0.28 (*t*, 3H, ³*J*_{P–H} = 11 Hz, ²*J*_{Pt–H} = 84 Hz), 2.6–1.2 (*m*, 66H). ³¹P NMR (CDCl₃): δ 21.9 (*t*, ¹*J*_{Pt–P} = 2822 Hz).

Crystal data

[PtCl(CH₃)(C₁₈H₃₃P)₂]
M_r = 806.40
 Triclinic, *P* $\bar{1}$
a = 10.654 (2) Å
b = 10.0701 (8) Å
c = 10.2620 (9) Å
 α = 91.4460 (8)°
 β = 109.639 (2)°
 γ = 112.649 (2)°
V = 941.7 (2) Å³
Z = 1
D_x = 1.422 Mg m^{−3}
 Mo *K*α radiation
 Cell parameters from 5952 reflections
 θ = 2.2–29.7°
 μ = 3.90 mm^{−1}
T = 293 (2) K
 Prism, colourless
 0.49 × 0.32 × 0.25 mm

Data collection

Siemens SMART CCD diffractometer
 ω scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
T_{min} = 0.093, *T_{max}* = 0.142
 10201 measured reflections
 5659 independent reflections
 5169 reflections with *I* > 2σ(*I*)
R_{int} = 0.027
 θ_{max} = 32.0°
h = −14 → 14
k = −14 → 14
l = −13 → 14
 first 50 frames repeated after data collection
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.034
wR(*F*²) = 0.076
S = 1.00
 5659 reflections
 198 parameters
 H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.0444*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.95 e Å^{−3}
 Δρ_{min} = −1.18 e Å^{−3}

Table 1

Selected geometric parameters (Å, °) for (I).

Pt–P	2.3431 (8)	P–C11	1.851 (3)
Pt–Cl	2.179 (13)	P–C21	1.864 (4)
Pt–Cl	2.440 (4)	P–C31	1.812 (3)
P–Pt–Cl	89.15 (12)	C11–Pt–P	90.2 (4)
P ¹ –Pt–Cl	90.85 (12)	C11–P–Pt	112.44 (11)
C1–Pt–Cl	172.7 (5)	C21–P–Pt	116.74 (10)
C1–Pt–P	89.8 (4)	C31–P–Pt	111.78 (12)

Symmetry code: (i) 1 − *x*, 1 − *y*, 1 − *z*.

Table 2

Comparative X-ray data for *trans*-[M(*X*)(*Y*)(PCy₃)₂] complexes.

<i>M</i> (<i>X</i>)(<i>Y</i>)	<i>M</i> –P (Å)	<i>M</i> – <i>X</i> (Å)	<i>M</i> – <i>Y</i> (Å)	Type ^a
Ni(Cl)(Cl) ⁱ	2.278	2.188	2.188	I
Pd(Cl)(Cl) ⁱⁱ	2.3628 (9)	2.3012 (9)	2.3012 (9)	I
Pt(Cl)(Cl) ⁱⁱⁱ	2.337 (2)	2.317 (2)	2.317 (2)	I
Pt(Br)(Br) ^{iv}	2.345 (1)	2.435 (1)	2.435 (1)	I
Pt(I)(I) ^v	2.371 (2)	2.612 (1)	2.612 (1)	I
Pt(Me)(Cl) ^{vi}	2.3431 (8)	2.179 (13)	2.440 (4)	I
Pd(Ph)(Cl) ^{vii}	2.343 (1)	2.004 (6)	2.403 (1)	NI
	2.347 (1)			
Pt(H)(H) ^{viii}	2.26 (1)			NI

Notes: (a) I = isostructural, NI = not isostructural; (i) Bellon *et al.* (1963), obtained from the Cambridge Structural Database without s.u.'s; (ii) Grushin *et al.* (1994); (iii) Del Pra & Zanotti (1980); (iv) Cameron *et al.* (1990); (v) Alcock & Leviston (1974); (vi) this work; (vii) Huser *et al.* (1989); (viii) Immirzi *et al.* (1975).

Table 3

Comparative X-ray data for *trans*-[MMeCl(L)₂] (*M* = Pd, Pt; *L* = tertiary phosphine or arsine ligand) complexes.

<i>M</i> (<i>L</i>)	<i>M</i> – <i>L</i> (Å)	<i>M</i> –C (Å)	<i>M</i> –Cl (Å)
Pt(PPh ₃) ^{ix}	2.295 (3)	2.08 (1)	2.431 (3)
	2.298 (3)		
Pt(PPh ₃) ^x	2.2955 (10)	2.02 (2)	2.415 (5)
Pt(PCy ₃) ^{xi}	2.3431 (8)	2.179 (13)	2.440 (4)
Pt(AsPh ₃) ^{xii}	2.3856 (9)	2.073 (8)	2.410 (2)
	2.3786 (9)		
PtAs(<i>p</i> -MePh) ₃ ^{xiii}	2.3883 (10)	2.111 (9)	2.397 (3)
	2.3875 (10)		
Pd(PPh ₃) ^{xiv}	2.3289 (7)	2.054 (2)	2.4227 (6)
	2.3224 (7)		
Pd(AsPh ₃) ^{xv}	2.3989 (5)	2.095 (4)	2.4086 (11)
	2.4067 (5)		
Pd(PPh ₂ Fc) ^{xvi}	2.3328 (10)	2.108 (10)	2.378 (3)

Notes: (ix) Bardi & Piazzesi (1981); (x) Otto *et al.* (1995); (xi) this work; (xii) Roodt *et al.* (1995); (xiii) Otto & Roodt (1996); (xiv) Otto (2001); (xv) Rath *et al.* (1995); (xvi) Otto *et al.* (2000).

H atoms were refined as riding (C–H = 0.96–0.98 Å). Both the minimum and maximum residual electron density lie within 1 Å of the Pt atom.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINTE* (Siemens, 1995); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1997); software used to prepare material for publication: *SHELXL97*.

Financial assistance from the South African FRD and the Research Fund of the University of the Free State is gratefully acknowledged. The Chemical Centre of the University of Lund, Sweden, is thanked for the use of their diffractometer for the data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1050). Services for accessing these data are described at the back of the journal.

References

- Alcock, N. W. & Leviston, P. G. (1974). *J. Chem. Soc. Dalton Trans.* pp. 1834–1836.
- Alyea, E. C., Diaz, S. A., Ferguson, G. & Restivo, R. J. (1977). *Inorg. Chem.* **16**, 2329–2334.
- Bardi, R. & Piazzesi, A. M. (1981). *Inorg. Chim. Acta*, **47**, 249–254.
- Bellon, P. L., Albano, V., Bianco, V. D., Pompa, F. & Scatturin, V. (1963). *Ric. Sci.* **3**, 1213–1220.
- Brandenburg, K. (1997). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Cameron, T. S., Clark, H. C., Linden, A. & Nicholas, A. M. (1990). *Polyhedron*, **9**, 1683–1688.
- Clark, H. C. & Manzer, L. E. (1973). *J. Organomet. Chem.* **59**, 411–428.
- Del Pra, A. & Zanotti, G. (1980). *Inorg. Chim. Acta*, **39**, 137–141.
- Ferguson, G., Roberts, P. J., Alyea, E. C. & Khan, M. (1978). *Inorg. Chem.* **17**, 2965–2967.
- Grushin, V. V., Bensimon, C. & Alper, H. (1994). *Inorg. Chem.* **33**, 4804–4806.
- Huser, M., Youinou, M.-T. & Osborn, J. A. (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 1386–1388.
- Immirzi, A., Musco, A., Carturan, G. & Belluco, U. (1975). *Inorg. Chim. Acta*, **12**, L23–24.
- Otto, S. (2001). *Acta Cryst.* **E57**, m75–77.
- Otto, S. & Roodt, A. (1996). *Acta Cryst.* **C52**, 1636–1638.
- Otto, S., Roodt, A. & Leipoldt, J. G. (1995). *S. Afr. J. Chem.* **48**, 114–119.
- Otto, S., Roodt, A. & Smith, J. (2000). *Inorg. Chim. Acta*, **303**, 295–299.
- Rath, N. P., Ladipo, F. T. & Anderson, G. K. (1995). *Acta Cryst.* **C51**, 1289–1290.
- Roodt, A., Otto, S. & Leipoldt, J. G. (1995). *Acta Cryst.* **C51**, 1105–1106.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1995). *SMART* and *SAINTE*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Tolman, C. A. (1977). *Chem. Rev.* **77**, 313–348.