

## *cis*-[1,2-Bis(diisopropylphosphino- $\kappa$ P)-1,2-dicarba-*closo*-dodecaborane]-dichloroplatinum(II) dichloromethane hemisolvate

Sari Paavola,<sup>a\*</sup> Francesc Teixidor,<sup>b</sup> Clara Viñas<sup>b</sup> and Raikko Kivekäs<sup>a</sup>

<sup>a</sup>Department of Chemistry, PO Box 55, FIN-00014 University of Helsinki, Finland, and <sup>b</sup>Institute of Material Sciences, Campus UAB, E-08193 Bellaterra, Spain  
Correspondence e-mail: sari.paavola@helsinki.fi

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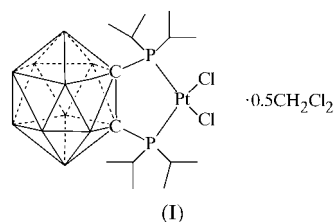
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The asymmetric unit of the title complex,  $[\text{PtCl}_2(\text{C}_{14}\text{H}_{38}\text{B}_{10}\text{P}_2)] \cdot 0.5\text{CH}_2\text{Cl}_2$  or *cis*- $[\text{PtCl}_2\{1,2-(\text{P}^i\text{Pr}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10}\}] \cdot 0.5\text{CH}_2\text{Cl}_2$ , contains one disordered solvent molecule and two molecules of the complex, in which each  $\text{Pt}^{\text{II}}$  atom displays slightly distorted square-planar coordination geometry. The P atoms connected to the cage C atoms are coordinated to the  $\text{Pt}^{\text{II}}$  atom. The Pt–P distances vary slightly [2.215 (3) and 2.235 (4) Å] and the Pt–Cl distances are equal [2.348 (3) and 2.353 (5) Å].

### Comment

We have previously synthesized and determined the crystal structures of several *o*-carborane derivatives bearing different substituents at the cage C atoms ( $\text{C}_c$  or C1 and C2) in order to study the elongation of the C1–C2 distance caused by the substituents (Kivekäs *et al.*, 1999; Sillanpää *et al.*, 1996). We are now investigating the use of these compounds as ligands, and have recently determined the crystal structures of  $[\text{PdCl}_2\{1,2-(\text{P}^i\text{Pr}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10}\}] \cdot \text{CHCl}_3$ , (II) (Sundberg *et al.*, 2002),  $[\text{PdCl}_2\{1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10}\}] \cdot \text{CH}_2\text{Cl}_2$ , (III) (Paavola *et al.*, 2000), and  $[\text{PdClMe}\{1,2-(\text{P}^i\text{Pr}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10}\}]$ , (IV), and



$[\text{PdClMe}\{1,2-(\text{PPh}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10}\}] \cdot \text{CH}_2\text{Cl}_2$ , (V) (Paavola *et al.*, 2002). Here, we describe the molecular structure of the title platinum complex,  $[\text{PtCl}_2\{1,2-(\text{P}^i\text{Pr}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10}\}] \cdot 0.5\text{CH}_2\text{Cl}_2$ , (I).

Complex (I) was synthesized using the same procedure as for the corresponding Pd complex, (II). A mixture of 1,2-bis-(diisopropylphosphino)-1,2-dicarba-*closo*-dodecaborane and  $[\text{MCl}_2(\text{cod})]$  (cod is cyclooctadiene) was refluxed in dichloromethane. However, whereas (II) was obtained in 96% yield after refluxing for 24 h (Paavola *et al.*, 2000), (I) could only be obtained as a mixture with  $[\text{PtCl}_2(\text{cod})]$ .

The symmetric unit of (I) consists of two  $[\text{PtCl}_2\{1,2-(\text{P}^i\text{Pr}_2)_2-1,2-\text{C}_2\text{B}_{10}\text{H}_{10}\}]$  complex units, labelled (IA) and (IB), and one disordered dichloromethane solvent molecule. Views of the complex units (IA) and (IB) are shown in Figs. 1 and 2, respectively, along with the atomic numbering schemes. In each complex unit, the  $\text{Pt}^{\text{II}}$  atom adopts a slightly distorted square-planar coordination sphere, where the P atoms connected to the  $\text{C}_c$  atoms are coordinated to  $\text{Pt}^{\text{II}}$  and the remaining two positions are occupied by two mutually *cis* Cl atoms.

As expected, the two complex units have similar coordination spheres. The Pt–Cl bond lengths [2.348 (3) and 2.353 (5) Å] are equal and the Pt–P distances [2.215 (3) and 2.235 (4) Å] are equal or differ only slightly. These distances are normal for Pt complexes, and the  $\text{C}_c$ – $\text{C}_c$  distances of 1.716 (16) Å in (IA) and 1.672 (16) Å in (IB) are typical of 1,2-diphosphino-*o*-carboranes (Paavola *et al.*, 2000, 2002). However, a difference in the P2–Pt–P1 angles is found between (IA) [93.13 (12)°] and (IB) [89.95 (12)°]. Comparison of the coordination spheres of (IA) and (IB) with that of the corresponding Pd complex, (II), reveals only minor differences; the M–Cl distances are equal within experimental error, and the M–P distances are equal or close to equal.

Two notable differences between (IA) and (IB) are found. Even though the crystallographic symmetry for both complex units is  $\text{C}_1$ , unit (IB) is more symmetric, adopting approximate  $\text{C}_s$  symmetry, with the pseudo-mirror plane perpendicular to the coordination plane and passing through atoms Pt1B, B3B, B6B, B8B and B10B, while in (IA), the mutual orientations of

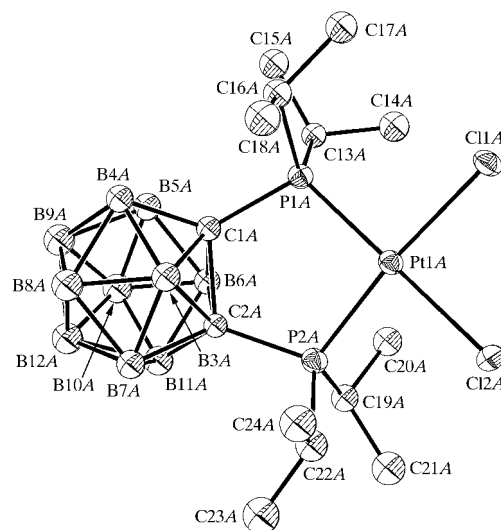


Figure 1

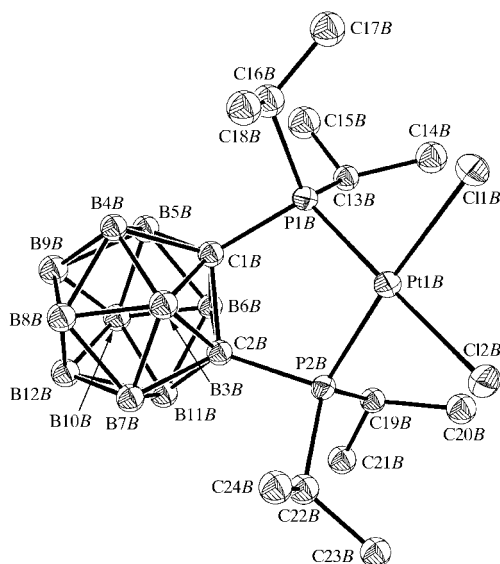
A view of the molecule of (IA) with 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

the <sup>i</sup>Pr groups are markedly different. Another molecular feature of interest in (IA) and (IB) is the appreciable difference in the conformation. The dihedral angle between the planes through atoms P1/Pt/P2 and P1/C1/C2/P2 is clearly larger in (IB) than in (IA) [28.1 (2) versus 11.7 (6)°]. Thus, the dihedral angles vary considerably, with the P atoms acting as hinges.

When dealing with solution chemistry, the above-mentioned dihedral angles do not differ very much from 0° and this suggests that the energy barrier needed to flip to the reciprocal conformer is low. Thus, in solution, these conformers can be expected to average to a complex where the C<sub>c</sub>, P, Cl and Pt atoms lie in a plane, resulting in average C<sub>2v</sub> symmetry for the molecule. Indeed, a 2:2:6 pattern in the <sup>11</sup>B NMR spectrum confirmed this. In the PdClMe complexes, (IV) and (V), the dihedral angles are 22.5 (3) and 25.25 (11)°, respectively, and these compounds also flip in solution to show an average C<sub>s</sub> symmetry in the <sup>11</sup>B NMR spectra.

In order to compare the influence of carborane and ethane backbones on the molecular geometry of PtCl<sub>2</sub> complexes, a literature search of the Cambridge Structural Database (October 2001 version; Allen & Kennard, 1993) was carried out. Unfortunately, no PtCl<sub>2</sub> complex of 1,2-bis(diisopropylphosphino)ethane was found. In dichloro[1,2-bis-(di-*tert*-butylphosphino)ethane]platinum(II), (VI) (Harada *et al.*, 1976), the M–P bond lengths are slightly longer than in (IA), (IB) and (II), but in dichloro[1,2-bis-(dicyclohexylphosphino)ethane]platinum(II), (VII) (Mague *et al.*, 1993), the M–P bond lengths are equal within experimental error or nearly equal. The Pt–Cl bond lengths are close to being equal in (IA), (IB), (VI) and (VII).

As expected, there are two notable differences in the five-membered chelate rings between the *o*-carborane complexes (IA), (IB) and (II), and the comparable complexes (VI) and (VII) with ethane backbones. The C<sub>c</sub>–C<sub>c</sub> distances are



**Figure 2**

A view of the molecule of (IB) with 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

significantly longer in (IA), (IB) and (II) than the corresponding C–C distances in (VI) and (VII), and the P–C–C–P torsion angles in (IA), (IB) and (II) are close to 0° [2.0 (10)–3.4 (11)°], while in (VI) and (VII), the angles are clearly larger [41.85 and 30.35°].

## Experimental

1,2-(P<sup>i</sup>Pr)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (Teixidor *et al.*, 1995) and [PtCl<sub>2</sub>(cod)] (cod is cyclooctadiene; McDermott *et al.*, 1976) were synthesized by the methods described in the literature. A mixture of 1,2-(P<sup>i</sup>Pr)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (0.10 g, 0.27 mmol) and [PtCl<sub>2</sub>(cod)] (0.10 g, 0.27 mmol) was dissolved in dry deoxygenated CH<sub>2</sub>Cl<sub>2</sub> (10 ml). The mixture was refluxed under argon for 24 h. After cooling, the solvent was evaporated *in vacuo* and the resulting solid was washed with dry ether. Crystals of (I) were grown from the insoluble solid in CH<sub>2</sub>Cl<sub>2</sub> layered with *n*-hexane. Spectroscopic analysis, FTIR ( $\nu$ , cm<sup>-1</sup>): 2583 (B–H); <sup>1</sup>H NMR (CD<sub>3</sub>CN,  $\delta$ , p.p.m.): 1.50–3.50 (*br*, BH), 1.66 (*m*, CH<sub>3</sub>, 24H), 3.09 (*m*, CH, 4H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN,  $\delta$ , p.p.m.): 20.6 [*d*, CH<sub>3</sub>, <sup>2</sup>J<sub>P–C</sub> = 83.1 Hz], 30.9 (*s*, CH); <sup>11</sup>B NMR (96.29 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ , p.p.m.): –1.0 (*d*, <sup>1</sup>J<sub>B–H</sub> = 154 Hz, 2B), –4.5 (*d*, <sup>1</sup>J<sub>B–H</sub> = 153 Hz, 2B), –11.2 (*d*, <sup>1</sup>J<sub>B–H</sub> = 154 Hz, 6B); <sup>31</sup>P{<sup>1</sup>H} NMR (121.48 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ , p.p.m.): 80.5 (*s*, <sup>1</sup>J<sub>Pt–P</sub> = 3617 Hz). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum clearly shows the appearance of satellites due to <sup>195</sup>Pt, with <sup>1</sup>J<sub>Pt–P</sub> = 3617 Hz. As one third of the Pt nuclei are <sup>195</sup>Pt with spin ½, and two thirds are <sup>196</sup>Pt having no spin, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum has three lines with an intensity ratio of *ca* 1:4:1.

## Crystal data

[PtCl <sub>2</sub> (C <sub>14</sub> H <sub>38</sub> B <sub>10</sub> P <sub>2</sub> )]·0.5CH <sub>2</sub> Cl <sub>2</sub>	$D_x = 1.688 \text{ Mg m}^{-3}$
$M_r = 684.94$	Mo $K\alpha$ radiation
Monoclinic, C2/c	Cell parameters from 23 reflections
$a = 42.785 (12) \text{ \AA}$	$\theta = 5.9\text{--}11.9^\circ$
$b = 10.320 (14) \text{ \AA}$	$\mu = 5.63 \text{ mm}^{-1}$
$c = 32.238 (11) \text{ \AA}$	$T = 193 (2) \text{ K}$
$\beta = 130.785 (12)^\circ$	Prismatic, colourless
$V = 10778 (15) \text{ \AA}^3$	$0.27 \times 0.20 \times 0.10 \text{ mm}$
$Z = 16$	

## Data collection

Rigaku AFC-7S diffractometer	$R_{\text{int}} = 0.053$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 25.3^\circ$
Absorption correction: $\psi$ scans (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 51$
$T_{\text{min}} = 0.295$ , $T_{\text{max}} = 0.570$	$k = 0 \rightarrow 12$
9888 measured reflections	$l = -38 \rightarrow 29$
9749 independent reflections	3 standard reflections
6434 reflections with $I > 2\sigma(I)$	every 150 reflections
	intensity decay: <1%

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 56.0903P]$
$R[F^2 > 2\sigma(F^2)] = 0.068$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.146$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 2.12 \text{ e \AA}^{-3}$
9749 reflections	$\Delta\rho_{\text{min}} = -1.69 \text{ e \AA}^{-3}$
324 parameters	
H-atom parameters constrained	

Attempted anisotropic refinement of the B and C atoms led to unsatisfactory outcomes. In order to avoid the use of an excessive number of ISOR restraints, these atoms were treated isotropically. The dichloromethane solvent molecule is disordered, assuming two orientations with site occupancies of 0.525 (18) for atoms C25A, H25A, H26A, C13A and C14A, and 0.475 (18) for atoms C25B, H25B,

**Table 1**Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Pt1A—P1A	2.227 (4)	Pt1B—P1B	2.235 (4)
Pt1A—P2A	2.215 (3)	Pt1B—P2B	2.220 (3)
Pt1A—C11A	2.351 (3)	Pt1B—C11B	2.348 (3)
Pt1A—C12A	2.350 (5)	Pt1B—C12B	2.353 (5)
P1A—C13A	1.848 (12)	P1B—C13B	1.855 (12)
P1A—C16A	1.844 (12)	P1B—C16B	1.844 (14)
P2A—C19A	1.875 (12)	P2B—C19B	1.847 (12)
P2A—C22A	1.831 (14)	P2B—C22B	1.836 (13)
P1A—C1A	1.880 (12)	P1B—C1B	1.879 (11)
P2A—C2A	1.861 (12)	P2B—C2B	1.872 (12)
C1A—C2A	1.716 (16)	C1B—C2B	1.672 (16)
P1A—Pt1A—C11A	92.47 (11)	P1B—Pt1B—C11B	91.69 (12)
P1A—Pt1A—C12A	178.97 (13)	P1B—Pt1B—C12B	178.93 (13)
P1A—Pt1A—P2A	93.13 (12)	P1B—Pt1B—P2B	89.95 (12)
P2A—Pt1A—C11A	173.27 (12)	P2B—Pt1B—C11B	174.20 (12)
P2A—Pt1A—C12A	86.57 (12)	P2B—Pt1B—C12B	90.98 (12)
C11A—Pt1A—C12A	87.78 (12)	C11B—Pt1B—C12B	87.33 (12)
C1A—C2A—P2A	113.2 (7)	C1B—C2B—P2B	113.3 (7)
C2A—C1A—P1A	114.4 (8)	C2B—C1B—P1B	113.0 (8)
P1A—C1A—C2A—P2A	−2.0 (10)	P1B—C1B—C2B—P2B	−3.0 (10)

H26B, C13B and C14B. The methyl groups were refined as rotating groups, with the H atoms at fixed distances from the C atoms. Other H atoms were refined using a riding model, starting from idealized positions, with B—H distances of 1.12  $\text{\AA}$  and C—H distances in the range 0.98–1.00  $\text{\AA}$ . The largest final residual electron-density peaks and holes found in the vicinity of Pt1A are 2.12 and  $-1.69 \text{ e \AA}^{-3}$ , respectively, while in the vicinity of Pt1B, they are 1.64 and  $-1.66 \text{ e \AA}^{-3}$ , respectively.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1993); program(s) used

to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990); 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: JZ1494). Services for accessing these data are described at the back of the journal.

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