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Bis(μ-phenylphosphido-κ^2P:P)bis{[1,2-(dicyclohexylphosphino)ethane-κ^2P,P']platinum(I)} dichloride bis(dichloromethane) hexane solvate

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Key indicators

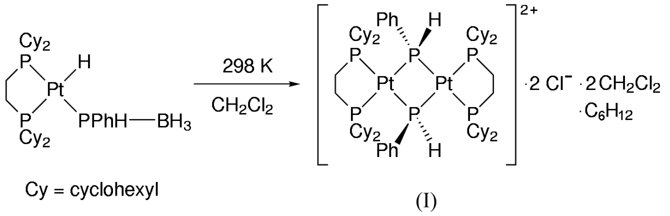
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.008 Å
Some non-H atoms missing
Disorder in solvent or counterion
R factor = 0.036
wR factor = 0.087
Data-to-parameter ratio = 23.5

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

In the title compound, $[Pt_2(C_6H_6P)_2(C_{26}H_{48}P_2)_2]Cl_2\cdot 2CH_2Cl_2\cdot C_6H_{14}$, the cation crystallizes as a phosphido-bridged Pt^I dimer [Pt(dcype)(μ-PPhH)]$_2$Cl$_2$, with crystallographic 2/m symmetry [dcype is 1,2-bis(dicyclohexylphosphino)ethane]. The Pt$_2$P$_2$ core forms a planar distorted square capped by chelating bisphosphine ligands, resulting in a distorted square-planar geometry for the Pt atoms. In the Pt$_2$P$_2$ core, the Pt—P bond length is 2.3403 (9) Å, with a narrow P—Pt—P angle of 76.87 (6)° and a wide Pt—P—Pt angle of 103.13 (6)°. The bite angle of the dcype ligand is 85.70 (6)°, with a Pt—P bond length of 2.2993 (11)°.

Comment

As part of our investigations into the mechanism of catalytic dehydrocoupling of phosphine–borane adducts using late transition metal catalysts (Jaska *et al.*, 2003), we explored the reaction of the platinum(II) dihydride complex *cis*-[PtH$_2$(dcype)] with various phenylated phosphines and phosphine–borane adducts bearing P—H bonds. The primary products from these reactions were the monosubstituted complexes *cis*-[PtH(PPh$R\cdot L$)(dcype)] (R = Ph, H; L = BH$_3$ or no substituent), formed *via* a dehydrocoupling reaction at the metal centre (Jaska *et al.*, 2004). In one case (for R = H, L = BH$_3$), however, a reaction between the hydride ligand and the chlorinated solvent CH$_2$Cl$_2$ was found to afford the title compound [Pt(dcype)(μ-PPhH)]2Cl$_2\cdot$2CH$_2$Cl$_2\cdot$C$_6$H$_{12}$, (I).



(I)

Similar complexes include [Pt(μ-PPhH)(PPh$_2$Me)$_2$]$_2$Cl$_2$, prepared from the reaction of (PPh)$_5$ with (PPh$_2$Me)$_2$PtCl$_2$ in CH$_2$Cl$_2$ (Parkin *et al.*, 1990), and [Pt(μ-MesPH)(dppe)]$_2$Cl$_2$, prepared by the reaction of [PtCl(MesPH$_2$)(μ-MesPH)]$_2$ (Mes is 2,4,6-trimethylphenyl) with dppe [dppe is 1,2-bis(diphenylphosphino)ethane] (Kourkine *et al.*, 1996).

The structure of the [Pt(dcype)(μ-PPhH)]$_2$ cation in (I) is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. The cation has 2/m symmetry at the centre of the Pt$_2$P$_2$ core with the twofold axis running through the two Pt atoms and the centre of both C—C bonds of the ethane linkages of the dcype ligands, while the mirror plane runs through the two bridging P atoms, all atoms of the central phenyl groups and the hydride atoms.

The Pt_2P_2 core forms a distorted square plane capped by chelating bis-phosphine ligands, resulting in a distorted square-planar geometry for the Pt atoms. In the Pt_2P_2 core, the Pt—P bond length is 2.3403 (9) Å, with a narrow P—Pt—P angle of 76.87 (6)° and a wide Pt—P—Pt angle of 103.13 (6)°. The bite angle of the dcype ligand is 85.70 (6)°, with a Pt—P bond length of 2.2993 (11)°.

Experimental

Under an atmosphere of N_2, a colourless solution of $PhPH_2 \cdot BH_3$ (0.007 g, 0.06 mmol) was added to a red–orange solution of *cis*-[PtH_2(dcype)] (0.035 g, 0.057 mmol; Jaska *et al.*, 2004) in toluene (5 ml). The solution was stirred for 24 h at 288 K, and the volatiles removed to yield the intermediate complex *cis*-[PtH($PPhH \cdot BH_3$)(dcype)]. The resulting solid was washed with hexanes (15 ml) and recrystallized from CH_2Cl_2/hexanes (5:1; 10 ml) by slow evaporation over 3–4 d at 288 K to afford colourless blocks of (I).

Crystal data

$[Pt_2(C_6H_6P)_2(C_{26}H_{48}P_2)_2]Cl_2 \cdot 2CH_2Cl_2 \cdot C_6H_{14}$
$M_r = 1780.43$
Monoclinic, $C2/m$
$a = 25.2586\ (9)$ Å
$b = 13.9813\ (5)$ Å
$c = 12.3080\ (5)$ Å
$\beta = 111.348\ (2)°$
$V = 4048.3\ (3)$ Å^3
$Z = 2$

$D_x = 1.461$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14 701 reflections
$\theta = 2.6$–$27.5°$
$\mu = 3.81$ mm^{-1}
$T = 150\ (1)$ K
Block, colourless
0.12 × 0.10 × 0.10 mm

Data collection

Nonius KapppaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.636$, $T_{\max} = 0.683$
14 701 measured reflections
4810 independent reflections

4223 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$
$\theta_{\max} = 27.5°$
$h = -32 \rightarrow 30$
$k = -16 \rightarrow 18$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.087$
$S = 1.09$
4810 reflections
205 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 2.26$ e Å^{-3}
$\Delta\rho_{\min} = -1.38$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.00110 (10)

Table 1
Selected geometric parameters (Å, °).

Pt1—P1	2.2993 (11)	H1P—P2	1.43 (6)
Pt1—P2	2.3403 (9)		
$P1^i$—Pt1—P1	85.70 (6)	$P2^i$—Pt1—P2	76.87 (6)
$P1^i$—Pt1—P2	166.11 (4)	$Pt1^{ii}$—P2—Pt1	103.13 (6)
P1—Pt1—P2	100.24 (4)		

Symmetry code: (i) $-x, y, 1-z$; (ii) $-x, -y, 1-z$.

During the structure refinement, a region of electron density was identified as a highly disordered molecule of hexane. Attempts to model this electron density as the hexane molecule were not successful due to the extent of the disorder. In the final structure model, the contribution of the electron density from the hexane molecule has been removed from the intensity data using the program *SQUEEZE* in *PLATON* (Spek, 2003). This greatly improved the precision of the refinement but did not affect the geometric parameters of the rest of the structure. The contribution from the hexane has been included in the empirical formula to give the correct calculated density, absorption coefficient and molecular weight. The Cl^- counter-ion is disordered over two sites, which are on twofold axes. Similarly, a twofold axis runs through the central CH_2 group of the dichloromethane solvent. The C atom and the two H atoms are all disordered over two sites on the twofold axis. All H atoms were placed in calculated positions, with C—H distances ranging from 0.95 to 1.00 Å, and included in the refinement in riding-model approximation, with $U_{\rm iso} = 1.2U_{\rm eq}$ of the carrier atom. The H atom bonded to P1 was refined independently with an isotropic displacement parameter. The highest residual peak in the final difference Fourier lies on a twofold axis, 0.84 Å from C1 (but is not chemically significant), while the deepest hole is 0.71 Å from Cl2

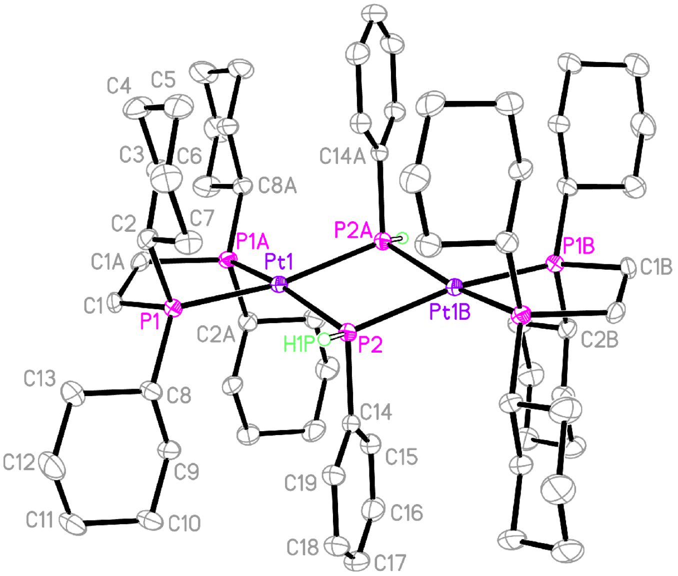


Figure 1
View of the cation in (I) with the atom-labelling scheme. The anions and solvent molecules are not shown, and H atoms have been omitted. Displacement ellipsoids are at the 30% probability level and atoms labelled with suffixes A and B are related by the symmetry codes ($-x$, y, $1-z$) and ($-x$, $-y$, $1-z$), respectively.

Data collection: *COLLECT* (Nonius, 1997–2002); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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