

Crystal structure of *trans*-dihydrido-bis[tris(dimethylamino)phosphane- κ P]-platinum(II)

Emma L. Downs, Lev N. Zakharov and David R. Tyler*

Department of Chemistry and Biochemistry, 1253 University of Oregon, Eugene, Oregon 97403-1253, USA. *Correspondence e-mail: dtyler@uoregon.edu

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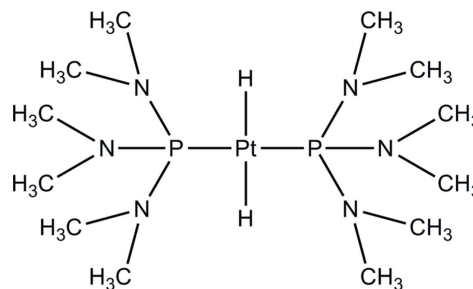
The molecule of the title compound, $[\text{PtH}_2(\text{C}_6\text{H}_{18}\text{N}_3\text{P})_2]$, has a centrosymmetric square-planar structure in which the Pt^{II} atom is bonded to two H and two P atoms in a mutually *trans* configuration. The Pt^{II} atom sits on an inversion center and thus the asymmetric unit contains only half the molecule. The Pt–P and Pt–H distances are 2.2574 (10) and 1.49 (7) Å, respectively.

Keywords: crystal structure; tris(dimethylamino)phosphane; platinum(II) complex; ligand-assisted hydration; nitrile hydration.

CCDC reference: 1051841

1. Related literature

For the synthesis of related compounds, see: Packett *et al.* (1985). For information on ligand-assisted hydration, see: Grotjahn (2005); Grotjahn *et al.* (2008*a,b*). For further information on nitrile hydration, see: García-Álvarez *et al.* (2011); Knapp *et al.* (2012, 2013*a,b*). For a review of the literature on nitrile hydration, see: Ahmed *et al.* (2011). For related structures, see: Packett *et al.* (1985); Robertson *et al.* (1986); Ferguson *et al.* (1979).



2. Experimental

2.1. Crystal data

$[\text{PtH}_2(\text{C}_6\text{H}_{18}\text{N}_3\text{P})_2]$	$\gamma = 60.652 (3)^\circ$
$M_r = 523.51$	$V = 514.8 (2) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 7.8871 (19) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 7.9499 (19) \text{ \AA}$	$\mu = 6.97 \text{ mm}^{-1}$
$c = 9.891 (2) \text{ \AA}$	$T = 173 \text{ K}$
$\alpha = 76.807 (4)^\circ$	$0.08 \times 0.06 \times 0.03 \text{ mm}$
$\beta = 73.241 (4)^\circ$	

2.2. Data collection

Bruker APEXII CCD area-detector diffractometer	5813 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1995)	2238 independent reflections
$T_{\text{min}} = 0.856$, $T_{\text{max}} = 1.000$	2238 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.020$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.059$	$\Delta\rho_{\text{max}} = 0.65 \text{ e \AA}^{-3}$
$S = 1.04$	$\Delta\rho_{\text{min}} = -0.69 \text{ e \AA}^{-3}$
2238 reflections	
101 parameters	

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: PK2545).

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Crystal structure of *trans*-dihydridobis[tris(dimethylamino)phosphane- κ P]platinum(II)

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S1. Comment

The hydration of nitriles using homogeneous catalysts is often too slow for practical applications (Ahmed *et al.*, 2011). Hydroxide is a much better nucleophile than water, and thus to increase the rate, many hydration reactions are carried out at high *pH*. When a ligand on the catalyst is capable of hydrogen bonding, the entering water nucleophile can be activated by hydrogen bonding interactions, avoiding the need for strongly basic solutions. Large rate accelerations in hydration reactions have been observed and attributed to this phenomenon, known as ligand assisted hydration or bifunctional catalysis (Grotjahn, 2005; Grotjahn *et al.*, 2008a,b). Complexes with phosphane ligands containing hydrogen bonding moieties, in particular tris(dimethylamino)phosphane (P(NMe₂)₃), have achieved excellent results in nitrile hydration reactions (García-Álvarez *et al.*, 2011; Knapp *et al.*, 2012, 2013a,b). In particular, we reported that the [RuCl₂(η^6 -*p*-cymene){P(NMe₂)₃}] complex is an excellent nitrile hydration catalyst (Knapp *et al.*, 2012). Unlike related catalysts, this complex was active under acidic conditions (*pH* 3.5), and the improved stability of cyanohydrins in an acidic medium yielded excellent results. Glycolonitrile (**1**) and lactonitrile (**2**) were hydrated fully to their corresponding amides and acetone cyanohydrin (**3**) was converted to 3-hydroxy-isobutyro nitrile (HIBAM) in 15% yield. Based on this result, we hypothesized that the tris(dimethylamino)phosphane ligand could be used in other homogeneous catalysts to enhance the rates of hydration. For this purpose, two new platinum complexes, Pt(H)(Cl)(P(NMe₂)₃)₂ and Pt(H)₂(P(NMe₂)₃)₂, were synthesized and tested for hydration activity with a variety of nitriles, including aromatic and aliphatic nitriles and cyanohydrins.

Pt(H)₂(P(NMe₂)₃)₂ was characterized by single-crystal X-ray diffraction methods. The molecule has a square planar structure (P(1)(1 - *x*, 2 - *y*, 1 - *z*)-Pt(1) (*x*, *y*, *z*)-P(1) (*x*, *y*, *z*) = 180.0 °). The Pt—P bond lengths (2.2572 (8) Å) are comparable to other Pt(H)₂(phosphane)₂ complexes: Pt(H)₂(PMe₃)₂, 2.259 (3) Å; Pt(PiPr₃)₂(H)₂, 2.252 (1) Å; Pt(H)₂(PtBu₃)₂, 2.276 (3) Å. (Packett *et al.*, 1985; Robertson *et al.*, 1986; Ferguson *et al.*, 1979). The P atom coordination environments are slightly distorted tetrahedral: N(3)—P(1)—N(1) = 110.86 (15)°; N(3)—P(1)—N(2) = 100.94 (14)°; N(1)—P(1)—N(2) = 98.70 (13)°; N(3)—P(1)—Pt(1) = 112.12 (10)°; N(1)—P(1)—Pt(1) = 113.82 (9)°; N(2)—P(1)—Pt(1) = 119.08 (9)°. The three NMe₂ groups bonded to each P atom have a staggered orientation with respect to the three NMe₂ groups on the other P atom. Consequently, the two Pt—P—N(2) angles, with atoms in the same plane as the Pt—H bonds, are significantly distorted (119.08 (9)°) from the tetrahedral angle.

S2. Experimental

Synthesis of Pt(H)₂(P(NMe₂)₃)₂. In an inert atmosphere, PtCl₂(COD) (0.1 g, 0.27 mmol) was dissolved in 10 ml dichloromethane. Two equivalents of P(NMe₂)₃ (0.1 ml, 0.54 mmol) were added dropwise with stirring. The solution turned from colorless to light yellow. The solution was stirred overnight. ³¹P NMR confirmed the formation of *cis*-PtCl₂(P(NMe₂)₃)₂: the free phosphane peak at 122 p.p.m. had disappeared and a peak with platinum satellites at 60 p.p.m. had appeared. The

solvent and COD were removed *in vacuo* and the resulting light yellow powder was redissolved in acetonitrile. Two equivalents (0.02 g, 0.54 mmol) of NaBH₄ were added with stirring. The solution was stirred for two hours and became bright orange; solids began to precipitate. The mixture was filtered through a celite plug to remove solids, and the solvent was removed. The brown solid was redissolved in minimal acetone and layered on top of water to precipitate brown crystals. ³¹P NMR: 129 p.p.m., Pt satellites at 138, 120 p.p.m.. $J_{\text{Pt-P}} = 1,891$ Hz. ¹H NMR: t, 2.8 p.p.m. ($J_{\text{P-H}} = 5.5$ Hz), tt, -3.5 ($J_{\text{P-H}} = 17.5$ Hz, $J_{\text{Pt-H}} = 405$ Hz).

S3. Refinement

The structure was solved using direct methods and refined with anisotropic thermal parameters for non-H atoms. The H atom bonded to the Pt atom was found in the residual density and refined with isotropic thermal parameters. H atoms in the Me groups were positioned geometrically and refined using a rigid group model: C—H = 0.98 Å, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

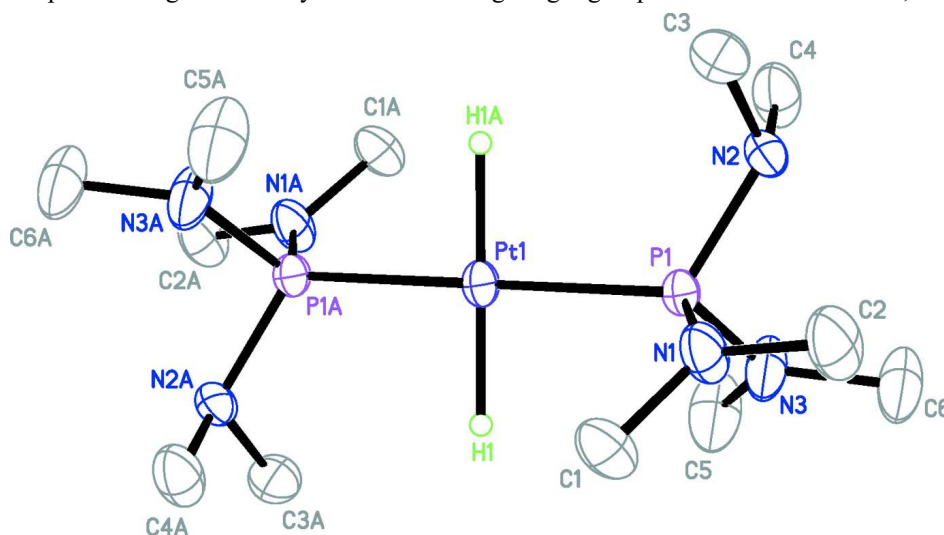


Figure 1

The crystal structure of *trans*-dihydrido-bis[tris(dimethylamino)phosphane]platinum(II) with 50% probability displacement ellipsoids. H atoms in the Me groups are omitted for clarity. [Symmetry code (A): 1 - x, 2 - y, 1 - z].

trans-Dihydrido-bis[tris(dimethylamino)phosphane-κP]platinum(II)

Crystal data

[PtH₂(C₆H₁₈N₃P)₂]

$M_r = 523.51$

Triclinic, $P\bar{1}$

$a = 7.8871$ (19) Å

$b = 7.9499$ (19) Å

$c = 9.891$ (2) Å

$\alpha = 76.807$ (4)°

$\beta = 73.241$ (4)°

$\gamma = 60.652$ (3)°

$V = 514.8$ (2) Å³

$Z = 1$

$F(000) = 260$

$D_x = 1.689$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3285 reflections

$\theta = 3.0$ – 26.9 °

$\mu = 6.97$ mm⁻¹

$T = 173$ K

Block, colorless

$0.08 \times 0.06 \times 0.03$ mm

Data collection

Bruker APEXII CCD area-detector
diffractometer
Radiation source: Sealed tube with triumph
monochromator
 φ and ω scans
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1995)
 $T_{\min} = 0.856$, $T_{\max} = 1.000$

5813 measured reflections
2238 independent reflections
2238 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$
 $\theta_{\max} = 27.0^\circ$, $\theta_{\min} = 2.2^\circ$
 $h = -10 \rightarrow 10$
 $k = -10 \rightarrow 10$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.059$
 $S = 1.04$
2238 reflections
101 parameters
0 restraints

Hydrogen site location: mixed
H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0425P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.65 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.69 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Pt1	0.5000	1.0000	0.5000	0.02501 (8)
P1	0.58089 (14)	0.80751 (13)	0.70124 (10)	0.02302 (18)
N1	0.8017 (5)	0.7594 (5)	0.7244 (4)	0.0332 (7)
N2	0.6130 (5)	0.5757 (4)	0.7200 (3)	0.0272 (6)
N3	0.4051 (6)	0.8932 (5)	0.8436 (4)	0.0405 (9)
C1	0.8862 (7)	0.8928 (6)	0.6632 (5)	0.0372 (9)
H1A	1.0160	0.8404	0.6880	0.056*
H1B	0.7971	1.0185	0.7007	0.056*
H1C	0.9028	0.9096	0.5597	0.056*
C2	0.9106 (7)	0.6069 (7)	0.8243 (5)	0.0433 (11)
H2A	1.0362	0.6085	0.8177	0.065*
H2B	0.9382	0.4808	0.8019	0.065*
H2C	0.8308	0.6284	0.9209	0.065*
C3	0.7765 (7)	0.4524 (6)	0.6164 (5)	0.0400 (10)
H3A	0.7849	0.3224	0.6347	0.060*
H3B	0.9016	0.4438	0.6244	0.060*
H3C	0.7529	0.5083	0.5205	0.060*
C4	0.4314 (7)	0.5651 (7)	0.7249 (5)	0.0433 (11)
H4A	0.4592	0.4288	0.7360	0.065*
H4B	0.3844	0.6298	0.6366	0.065*
H4C	0.3289	0.6295	0.8055	0.065*
C5	0.2224 (7)	1.0666 (8)	0.8357 (6)	0.0543 (14)

H5B	0.1401	1.0908	0.9314	0.081*
H5C	0.1509	1.0512	0.7769	0.081*
H5D	0.2511	1.1764	0.7935	0.081*
C6	0.4176 (8)	0.7934 (7)	0.9864 (5)	0.0488 (12)
H6C	0.2983	0.8692	1.0539	0.073*
H6D	0.5356	0.7789	1.0119	0.073*
H6A	0.4274	0.6649	0.9892	0.073*
H1	0.490 (10)	1.163 (10)	0.557 (7)	0.070 (19)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.03283 (12)	0.02060 (11)	0.02016 (11)	-0.01088 (8)	-0.01106 (8)	0.00457 (7)
P1	0.0288 (4)	0.0194 (4)	0.0196 (4)	-0.0097 (4)	-0.0092 (3)	0.0027 (3)
N1	0.0396 (18)	0.0315 (17)	0.0374 (19)	-0.0219 (15)	-0.0225 (15)	0.0127 (14)
N2	0.0358 (17)	0.0198 (15)	0.0279 (16)	-0.0138 (13)	-0.0115 (13)	0.0031 (12)
N3	0.043 (2)	0.0329 (19)	0.0202 (16)	-0.0017 (16)	-0.0033 (14)	0.0009 (14)
C1	0.037 (2)	0.034 (2)	0.047 (2)	-0.0233 (18)	-0.0090 (18)	0.0020 (18)
C2	0.047 (3)	0.042 (2)	0.048 (3)	-0.024 (2)	-0.030 (2)	0.017 (2)
C3	0.050 (3)	0.024 (2)	0.039 (2)	-0.0111 (18)	-0.0111 (19)	-0.0037 (17)
C4	0.052 (3)	0.050 (3)	0.042 (2)	-0.035 (2)	-0.023 (2)	0.014 (2)
C5	0.040 (2)	0.047 (3)	0.041 (3)	0.003 (2)	-0.003 (2)	-0.001 (2)
C6	0.054 (3)	0.043 (3)	0.024 (2)	-0.008 (2)	-0.0055 (19)	0.0046 (18)

Geometric parameters (Å, °)

Pt1—P1	2.2574 (10)	C2—H2A	0.9800
Pt1—P1 ⁱ	2.2574 (10)	C2—H2B	0.9800
Pt1—H1	1.49 (7)	C2—H2C	0.9800
P1—N3	1.660 (4)	C3—H3A	0.9800
P1—N1	1.664 (3)	C3—H3B	0.9800
P1—N2	1.705 (3)	C3—H3C	0.9800
N1—C1	1.450 (5)	C4—H4A	0.9800
N1—C2	1.451 (5)	C4—H4B	0.9800
N2—C3	1.460 (5)	C4—H4C	0.9800
N2—C4	1.462 (5)	C5—H5B	0.9800
N3—C5	1.432 (6)	C5—H5C	0.9800
N3—C6	1.458 (6)	C5—H5D	0.9800
C1—H1A	0.9800	C6—H6C	0.9800
C1—H1B	0.9800	C6—H6D	0.9800
C1—H1C	0.9800	C6—H6A	0.9800
P1—Pt1—P1 ⁱ	180.0	N1—C2—H2C	109.5
P1—Pt1—H1	90 (3)	H2A—C2—H2C	109.5
P1 ⁱ —Pt1—H1	90 (3)	H2B—C2—H2C	109.5
N3—P1—N1	110.9 (2)	N2—C3—H3A	109.5
N3—P1—N2	101.05 (19)	N2—C3—H3B	109.5
N1—P1—N2	98.82 (17)	H3A—C3—H3B	109.5

N3—P1—Pt1	112.10 (13)	N2—C3—H3C	109.5
N1—P1—Pt1	113.77 (12)	H3A—C3—H3C	109.5
N2—P1—Pt1	118.93 (12)	H3B—C3—H3C	109.5
C1—N1—C2	112.8 (3)	N2—C4—H4A	109.5
C1—N1—P1	121.1 (3)	N2—C4—H4B	109.5
C2—N1—P1	125.2 (3)	H4A—C4—H4B	109.5
C3—N2—C4	110.0 (4)	N2—C4—H4C	109.5
C3—N2—P1	114.7 (3)	H4A—C4—H4C	109.5
C4—N2—P1	113.4 (3)	H4B—C4—H4C	109.5
C5—N3—C6	114.0 (4)	N3—C5—H5B	109.5
C5—N3—P1	122.7 (3)	N3—C5—H5C	109.5
C6—N3—P1	123.1 (3)	H5B—C5—H5C	109.5
N1—C1—H1A	109.5	N3—C5—H5D	109.5
N1—C1—H1B	109.5	H5B—C5—H5D	109.5
H1A—C1—H1B	109.5	H5C—C5—H5D	109.5
N1—C1—H1C	109.5	N3—C6—H6C	109.5
H1A—C1—H1C	109.5	N3—C6—H6D	109.5
H1B—C1—H1C	109.5	H6C—C6—H6D	109.5
N1—C2—H2A	109.5	N3—C6—H6A	109.5
N1—C2—H2B	109.5	H6C—C6—H6A	109.5
H2A—C2—H2B	109.5	H6D—C6—H6A	109.5
N3—P1—N1—C1	-100.5 (4)	N3—P1—N2—C4	58.6 (3)
N2—P1—N1—C1	154.0 (3)	N1—P1—N2—C4	172.0 (3)
Pt1—P1—N1—C1	26.9 (4)	Pt1—P1—N2—C4	-64.5 (3)
N3—P1—N1—C2	67.7 (4)	N1—P1—N3—C5	130.0 (4)
N2—P1—N1—C2	-37.8 (4)	N2—P1—N3—C5	-126.0 (5)
Pt1—P1—N1—C2	-164.9 (3)	Pt1—P1—N3—C5	1.7 (5)
N3—P1—N2—C3	-174.0 (3)	N1—P1—N3—C6	-53.6 (5)
N1—P1—N2—C3	-60.5 (3)	N2—P1—N3—C6	50.4 (5)
Pt1—P1—N2—C3	62.9 (3)	Pt1—P1—N3—C6	178.1 (4)

Symmetry code: (i) $-x+1, -y+2, -z+1$.