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Structure of the Monohydrido Bridged Dinuclear Platinum(II) Dihydride [(PEt₃)₂PhPt(μ-H)PtH(PEt₃)₂][BPh₄]

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Abstract

The structure of the cationic complex μ-hydrido-1:2κ^2H-hydrido-2κH-phenyl-1κC-tetrakis(triethylphosphine)-1κ^2P,2κ^2P-diplatinum(II) consists of two platinum-containing units, which lie on reciprocally perpendicular planes. In each unit, the Pt atom is coordinated in a distorted square-planar arrangement. One hydride ligand is in a bridging position, while the other hydride is terminal on Pt(2). The Pt···Pt distance is 3.093 (1) Å.

Comment

In a preliminary communication, the preparation, characterization and the partially refined X-ray structure of the title compound were reported (Bracher, Grove, Venanzi, Bachechi, Mura & Zambonelli, 1978). The dihydrido-bridged isomer [(PEt₃)₂PhPt(μ-H)₂Pt(PEt₃)₂]⁺ has been studied also and its structure reported (Bachechi, Bracher, Grove, Kellenberger, Pregosin, Venanzi & Zambonelli, 1983).

The crystal structure contains discrete tetraphenylborate anions and dinuclear dihydridoplatinum(II) cations with no short contacts between atoms of different ions. The complex cation is shown in Fig. 1.

The structure of the cationic complex (I) consists of two Pt-containing units, which lie on almost perpendicular planes forming a dihedral angle of 82°. The hydride ligands were not located by X-ray analysis, but the coordination geometry of the Pt atoms is consistent with the NMR data (Bracher *et*
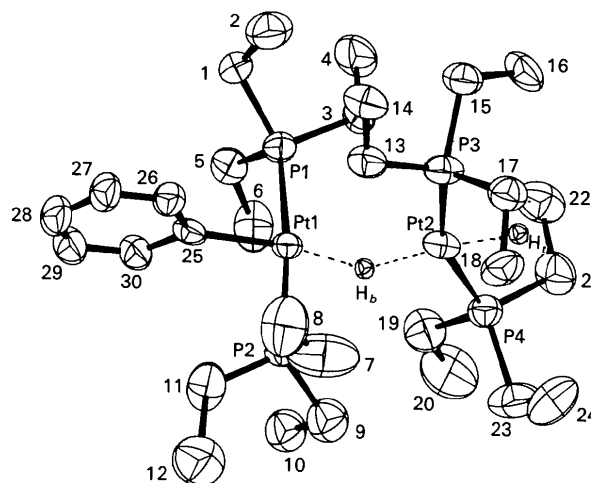

Fig. 1. Perspective view of the cationic complex with ellipsoids at the 30% probability level. In the core, the hydride ligands are placed at calculated sites.

al., 1978), which indicates the presence of one bridging and one terminal hydride ligand. In each unit, the Pt atom is coordinated in a distorted square-planar arrangement with apparent vacant sites. When these sites are considered occupied by the hydrides, one of them, *trans* to C(25), is bridging, while the other, bound to Pt(2), is terminal. The C(25)—Pt(1)···Pt(2) angle of 164.3 (4)° indicates that the bridging hydride is not collinear with the two metal centres.

$$\varphi(1) \wedge \varphi(2) = 82° \quad \varphi(1) \wedge \varphi(3) = 84° \quad \varphi(2) \wedge \varphi(3) = 14°$$


(I)
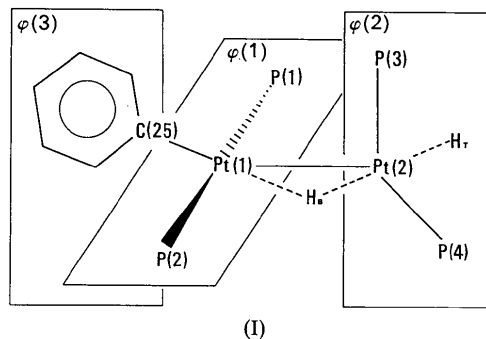
The probable positions of the hydride ligands were calculated using the program *HYDEX* (Orpen, 1980) at the potential energy minima and are represented in Fig. 1.

The Pt···Pt distance of 3.093 (1) Å is among the longest observed in Pt complexes with one hydrido bridge, together with those found in the trihydride [(PEt₃)₂HPt(μ-H)PtH(PEt₃)₂]⁺ [3.028 (1) Å (Bachechi, 1993)] and the monohydride [(PEt₃)₂PhPt(μ-H)PtPh(PEt₃)₂]⁺ [3.238 (1) Å (Carmona, Thouvenot, Venanzi, Bachechi & Zam-

bonelli, 1983)]. The PhP$_2$Pt unit is tetrahedrally distorted, with Pt(1) displaced 0.2 Å from the coordination plane and the angles at the metal atom being quite different from the theoretical values [P(1)—Pt(1)—P(2) = 169.5 (1), P(1)—Pt(1)—C(25) = 88.3 (3), P(2)—Pt(1)—C(25) = 87.6 (3)°]. In the P$_2$Pt unit, the two phosphine groups are strongly bent towards the terminal hydride [P(3)—Pt(2)—P(4) = 156.6 (2)°].

Experimental

Crystal data
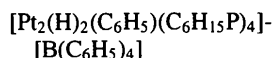
[Pt$_2$(H)$_2$(C$_6$H$_5$)(C$_6$H$_{15}$P)$_4$]- [B(C$_6$H$_5$)$_4$]
M_r = 1261.18
Monoclinic
$P2_1/n$
a = 14.297 (5) Å
b = 13.078 (3) Å
c = 30.301 (6) Å
β = 92.80 (2)°
V = 5659 (3) Å^3
Z = 4
D_x = 1.480 Mg m^{-3}
D_m = 1.45 (1) Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 15 reflections
θ = 20–25°
μ = 10.523 mm^{-1}
T = 293 K
Prism
0.32 × 0.14 × 0.12 mm
White

Data collection

Syntex $P2_1$ diffractometer
ω scans
Absorption correction: empirical (azimuthal scan; North, Phillips & Mathews, 1968)
T_{min} = 0.64, T_{max} = 1.00
8787 measured reflections
6450 independent reflections
5568 observed reflections [$I > 3\sigma(I)$]

R_{int} = 0.021
θ_{max} = 58°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 14$
$l = -33 \rightarrow 32$
3 standard reflections monitored every 100 reflections intensity variation: none

Refinement

Refinement on F
R = 0.059
wR = 0.066
S = 7.03
5568 reflections
345 parameters
H-atom parameters not refined

$w = 1/\sigma^2$
$(\Delta/\sigma)_{max}$ = 0.95
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = -0.28 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pt(1)	0.17321 (4)	0.12743 (4)	0.12722 (2)	0.0582 (2)
Pt(2)	0.35058 (5)	0.26119 (5)	0.12135 (2)	0.0770 (3)
P(1)	0.2040 (3)	0.0351 (3)	0.0652 (1)	0.073 (1)
P(2)	0.1397 (3)	0.1912 (3)	0.1954 (1)	0.069 (1)
P(3)	0.2730 (3)	0.3735 (3)	0.0762 (1)	0.085 (2)
P(4)	0.4776 (3)	0.1909 (3)	0.1593 (1)	0.085 (2)
B	0.2698 (12)	−0.0451 (13)	0.6288 (5)	0.08 (1)
C(1)	0.1163 (10)	0.0381 (11)	0.0180 (4)	0.08 (1)
C(2)	0.1041 (14)	0.1387 (14)	−0.0055 (6)	0.14 (1)
C(3)	0.3160 (10)	0.0632 (11)	0.0422 (4)	0.09 (1)
C(4)	0.3452 (12)	−0.0065 (14)	0.0046 (5)	0.12 (1)
C(5)	0.2067 (10)	−0.1016 (11)	0.0773 (4)	0.09 (1)
C(6)	0.2779 (11)	−0.1349 (12)	0.1131 (6)	0.12 (1)
C(7)	0.1208 (20)	0.3331 (21)	0.1971 (7)	0.23 (2)
C(8)	0.0287 (13)	0.3704 (17)	0.1814 (8)	0.17 (1)
C(9)	0.2382	0.1721	0.2349	0.20
C(10)	0.2418	0.0562	0.2417	0.20
C(9')	0.2353	0.2480	0.2263	0.20
C(10')	0.2280	0.2779	0.2744	0.20
C(11)	0.0447 (19)	0.1472 (32)	0.2192 (7)	0.39 (2)
C(12)	0.0194 (17)	0.1835 (27)	0.2660 (8)	0.15 (2)
C(13)	0.1431 (10)	0.3725 (11)	0.0747 (4)	0.09 (1)
C(14)	0.0932 (11)	0.4344 (12)	0.0387 (5)	0.10 (1)
C(15)	0.3002 (12)	0.3597 (12)	0.0186 (4)	0.10 (1)
C(16)	0.4048 (10)	0.3566 (14)	0.0111 (5)	0.11 (1)
C(17)	0.3014 (10)	0.5058 (11)	0.0898 (4)	0.10 (1)
C(18)	0.2859 (13)	0.5337 (13)	0.1367 (5)	0.12 (1)
C(19)	0.4655 (11)	0.0512 (14)	0.1730 (5)	0.12 (1)
C(20)	0.5450 (18)	−0.0004 (18)	0.1965 (8)	0.19 (1)
C(21)	0.5880 (11)	0.1950 (14)	0.1327 (6)	0.11 (1)
C(22)	0.5838 (14)	0.1446 (14)	0.0885 (6)	0.14 (1)
C(23)	0.5051 (13)	0.2464 (17)	0.2145 (6)	0.15 (1)
C(24)	0.4975 (14)	0.3613 (16)	0.2146 (7)	0.16 (1)
C(25)	0.0407 (8)	0.0728 (10)	0.1223 (4)	0.07 (1)
C(26)	−0.0347 (9)	0.1306 (11)	0.1040 (4)	0.08 (1)
C(27)	−0.1243 (9)	0.1001 (11)	0.1022 (5)	0.09 (1)
C(28)	−0.1448 (10)	0.0057 (14)	0.1178 (5)	0.11 (1)
C(29)	−0.0751 (10)	−0.0618 (12)	0.1347 (5)	0.10 (1)
C(30)	0.0148 (10)	−0.0268 (11)	0.1365 (4)	0.08 (1)
C(31)	0.3780 (5)	−0.0987 (7)	0.6296 (3)	0.095 (2)
C(32)	0.4283 (7)	−0.1166 (7)	0.6693 (2)	0.095 (2)
C(33)	0.5167 (7)	−0.1612 (7)	0.6692 (3)	0.095 (2)
C(34)	0.5548 (5)	−0.1880 (7)	0.6284 (3)	0.095 (2)
C(35)	0.5045 (7)	−0.1701 (7)	0.5897 (2)	0.095 (2)
C(36)	0.4161 (7)	−0.1255 (7)	0.5897 (3)	0.095 (2)
C(37)	0.2584 (7)	0.0395 (6)	0.5864 (3)	0.090 (2)
C(38)	0.3377 (5)	0.0922 (11)	0.5742 (3)	0.090 (2)
C(39)	0.3311 (6)	0.1617 (10)	0.5394 (3)	0.090 (2)
C(40)	0.2445 (7)	0.1784 (6)	0.5168 (3)	0.090 (2)
C(41)	0.1661 (5)	0.1257 (11)	0.5290 (3)	0.090 (2)
C(42)	0.1726 (6)	0.0563 (10)	0.5639 (3)	0.090 (2)
C(43)	0.2542 (7)	0.0148 (8)	0.6772 (3)	0.103 (2)
C(44)	0.2758 (7)	0.1181 (8)	0.6816 (3)	0.103 (2)
C(45)	0.2701 (7)	0.1660 (6)	0.7224 (4)	0.103 (2)
C(46)	0.2427 (7)	0.1104 (8)	0.7588 (3)	0.103 (2)
C(47)	0.2210 (7)	0.0070 (8)	0.7543 (3)	0.103 (2)
C(48)	0.2268 (7)	−0.0408 (6)	0.7135 (4)	0.103 (2)
C(49)	0.1874 (7)	−0.1395 (8)	0.6211 (3)	0.109 (2)
C(50)	0.0943 (8)	−0.1190 (6)	0.6293 (3)	0.109 (2)
C(51)	0.0261 (6)	−0.1934 (10)	0.6209 (3)	0.109 (2)
C(52)	0.0510 (7)	−0.2883 (8)	0.6044 (3)	0.109 (2)
C(53)	0.1441 (8)	−0.3088 (6)	0.5961 (3)	0.109 (2)
C(54)	0.2123 (6)	−0.2344 (10)	0.6044 (3)	0.109 (2)

Table 2. *Geometric parameters* (Å, °)

Pt(1)···Pt(2)	3.093 (1)	C(5)—C(6)	1.515 (22)
Pt(1)—P(1)	2.296 (4)	C(7)—C(8)	1.462 (34)
Pt(1)—P(2)	2.300 (3)	C(9)—C(10)	1.530
Pt(1)—C(25)	2.024 (12)	C(11)—C(12)	1.554 (35)
Pt(2)—P(3)	2.260 (4)	C(13)—C(14)	1.510 (20)
Pt(2)—P(4)	2.301 (4)	C(15)—C(16)	1.524 (22)
P(1)—C(1)	1.854 (14)	C(17)—C(18)	1.494 (21)
P(1)—C(3)	1.814 (14)	C(19)—C(20)	1.475 (29)
P(1)—C(5)	1.825 (14)	C(21)—C(22)	1.490 (25)
P(2)—C(7)	1.877 (28)	C(23)—C(24)	1.506 (30)
P(2)—C(9)	1.819	C(25)—C(26)	1.408 (18)
P(2)—C(11)	1.672 (29)	C(26)—C(27)	1.340 (18)
P(3)—C(13)	1.857 (15)	C(27)—C(28)	1.359 (23)
P(3)—C(15)	1.816 (14)	C(28)—C(29)	1.408 (22)
P(3)—C(17)	1.819 (15)	C(29)—C(30)	1.364 (20)
P(4)—C(19)	1.880 (18)	C(30)—C(25)	1.426 (19)
P(4)—C(21)	1.815 (17)	B—C(31)	1.698 (18)
P(4)—C(23)	1.836 (18)	B—C(37)	1.698 (18)

C(1)—C(2)	1.502 (23)	B—C(43)	1.694 (18)
C(3)—C(4)	1.533 (22)	B—C(49)	1.715 (20)
P(1)—Pt(1)—Pt(2)	93.4 (1)	Pt(2)—P(4)—C(23)	115.4 (7)
P(2)—Pt(1)—Pt(2)	93.1 (1)	C(19)—P(4)—C(21)	102.5 (8)
C(25)—Pt(1)—Pt(2)	164.3 (4)	C(19)—P(4)—C(23)	102.2 (8)
P(1)—Pt(1)—P(2)	169.5 (1)	C(21)—P(4)—C(23)	104.1 (8)
P(1)—Pt(1)—C(25)	88.3 (3)	P(1)—C(1)—C(2)	116.3 (11)
P(2)—Pt(1)—C(25)	87.6 (3)	P(1)—C(3)—C(4)	116.2 (11)
Pt(1)—Pt(2)—P(3)	91.3 (1)	P(1)—C(5)—C(6)	115.6 (10)
Pt(1)—Pt(2)—P(4)	112.0 (1)	P(2)—C(7)—C(8)	116.7 (18)
P(3)—Pt(2)—P(4)	156.6 (2)	P(2)—C(9)—C(10)	104.1
Pt(1)—P(1)—C(1)	118.0 (5)	P(2)—C(11)—C(12)	121.2 (23)
Pt(1)—P(1)—C(3)	114.5 (5)	P(3)—C(13)—C(14)	116.7 (10)
Pt(1)—P(1)—C(5)	110.7 (5)	P(3)—C(15)—C(16)	113.7 (10)
C(1)—P(1)—C(3)	106.1 (6)	P(3)—C(17)—C(18)	113.9 (11)
C(1)—P(1)—C(5)	100.5 (6)	P(4)—C(19)—C(20)	118.1 (14)
C(3)—P(1)—C(5)	105.4 (7)	P(4)—C(21)—C(22)	113.3 (12)
Pt(1)—P(2)—C(7)	114.8 (7)	P(4)—C(23)—C(24)	112.5 (13)
Pt(1)—P(2)—C(9)	110.7	C(25)—C(26)—C(27)	124.7 (13)
Pt(1)—P(2)—C(11)	118.2 (10)	C(26)—C(27)—C(28)	118.5 (13)
C(7)—P(2)—C(9)	103.0	C(27)—C(28)—C(29)	122.4 (13)
C(7)—P(2)—C(11)	101.9 (16)	C(28)—C(29)—C(30)	117.0 (14)
C(9)—P(2)—C(11)	106.7	C(29)—C(30)—C(25)	123.5 (13)
Pt(2)—P(3)—C(13)	118.1 (5)	C(30)—C(25)—C(26)	113.8 (1)
Pt(2)—P(3)—C(15)	113.3 (5)	C(31)—B—C(37)	109.4 (10)
Pt(2)—P(3)—C(17)	112.6 (5)	C(31)—B—C(43)	109.9 (10)
C(13)—P(3)—C(15)	103.7 (7)	C(31)—B—C(49)	108.9 (10)
C(13)—P(3)—C(17)	103.0 (7)	C(37)—B—C(43)	110.1 (10)
C(15)—P(3)—C(17)	104.9 (7)	C(37)—B—C(49)	108.9 (9)
Pt(2)—P(4)—C(19)	114.7 (5)	C(43)—B—C(49)	109.5 (10)
Pt(2)—P(4)—C(21)	116.2 (6)		

The structure was solved by Patterson and Fourier techniques and refined by least-squares methods. The thermal parameters of the P(2) ethyl groups were very high and some rotational disorder around the Pt(1)—P(2) bond was suspected. Difference Fourier maps revealed only two other peaks in the vicinities of C(9) and C(10). Thus, the ethyl group C(9)—C(10) was introduced in the refinement with two orientations [C(9), C(10), C(9′), C(10′)] having occupancy factors (0.66, 0.33) based on the relative heights of the Fourier peaks; the positions were not refined. The refinement was carried out with the phenyl rings of the tetraphenylborate anion treated as rigid groups and with the H atoms included at calculated positions.

All calculations were performed on a Data General Eclipse MV800011 computer, using local programs (Cerrini & Spagna, 1977). Probable hydride-ligand positions were calculated at the minima of the potential energy by the program *HYDEX* (Orpen, 1980).

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The Faulted Structures of [WCl$_2$(PhC$_2$Ph)(CH$_2$=CH$_2$)(PMe$_3$)$_2$] and [WCl$_2$(PhC$_2$Ph)$_2$(PMe$_3$)$_2$]

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Abstract

The crystal structures of dichloro(diphenyl-η^2-acetylene)(η^2-ethylene)bis(trimethylphosphine)-tungsten(IV) and dichlorobis(diphenyl-η^2-acetylene)-bis(trimethylphosphine)tungsten(IV) are described. The crystal structures are unusual in that they contain stacking faults leading to disordered structures. This has necessitated constrained restrained least-squares refinement.

Introduction

Details of the preparation and preliminary structural details for [WCl$_2$(PhC$_2$Ph)(CH$_2$=CH$_2$)(PMe$_3$)$_2$] have been published recently (Clark, Nielson, Rae & Rickard, 1992). During the initial structure solution and attempted refinement the presence of a stacking fault, in the crystal studied, became apparent. Preliminary investigations of the structure of [WCl$_2$-(PhC$_2$Ph)$_2$(PMe$_3$)$_2$] also indicated the presence of a stacking-fault. It was necessary to carry out a constrained restrained refinement of both structures to obtain a satisfactory convergence. Full details of the stacking-fault mechanisms and the refinement processes are presented.

The asymmetric unit of [WCl$_2$(PhC$_2$Ph)(CH$_2$=CH$_2$)(PMe$_3$)$_2$] contains three molecules. These three