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trans-Bromohydridobis(triphenylphosphine)-platinum(II)

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Key indicators

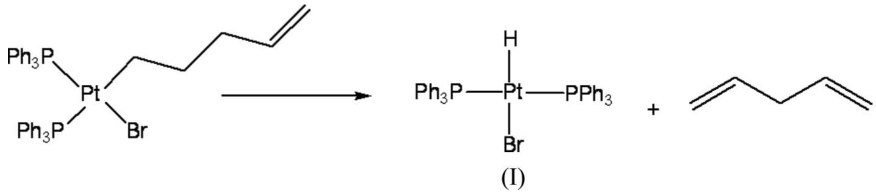
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.006 Å
R factor = 0.027
wR factor = 0.051
Data-to-parameter ratio = 16.7

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

The title compound, [PtBrH($C_{18}H_{15}P$)$_2$], has a square-planar environment around the Pt atom, with the hydride and bromide ligands being exactly collinear with Pt since they all lie on a crystallographic twofold rotation axis, and with mutually *trans* triphenylphosphine ligands with a P—Pt—P bond angle that is slightly bent towards the hydride [P—Pt—P = 170.81 (5)°]. The Pt—H distance (1.610 Å) is in good agreement with those found in structures determined by neutron diffraction.

Comment

The preparation of the title compound, *trans*-[HPtBr(PPh$_3$)$_2$], (I), was reported initially by Carr *et al.* (1985). It has also been prepared from the hydrolysis of either the platinum(II) boryl complex, *trans*-Pt(PPh$_3$)$_2$[B(Mes)Br]Br (Mes = 2,4,6-$Me_3C_6H_2$) (Aldridge *et al.*, 2003), or the alkoxycarbonyl, [PtX(COOR)(PPh$_3$)$_2$] (where R = Me or Et, X = halide), in the presence of a salt catalyst (NH$_4X$ or KX, X = halide), giving *trans*-[PtHX(PPh$_3$)$_2$] (Clark *et al.*, 1969). The X-ray single-crystal structures of the toluene monosolvated title compound (Habereder & Nöth, 2003) and of the toluene hemisolvated title compound (Aldridge *et al.*, 2003) were reported recently. We have now prepared and characterized the unsolvated title compound, (I) (Fig. 1), from decomposition of (PPh$_3$)$_2$Pt(1-pentenyl) (see equation below), and present the results here.



(I)

Compound (I) crystallizes in the space group $C2/c$ with Z = 4. The molecule is located at a special position at Wyckoff position e, with a twofold rotation axis running through the linear Br—Pt—H group. This results in *trans*-oriented triphenylphosphine ligands, with P—Pt—P [bond angle 170.81 (5)°] being slightly bent towards the hydride. The Pt—P distance of 2.2827 (9) Å and the Pt—Br distance of 2.5229 (6) Å are within the accepted ranges for similar platinum(II) complexes (Orpen *et al.*, 1989). The Pt—H distance is 1.61 Å. A search of the Cambridge Structural Database (CSD, Version 5.27 with August 2006 updates; Allen, 2002) for platinum(II) complexes with terminal hydrides gave rise to 65 hits. For all 65 complexes, Pt—H(terminal) distances range from 1.00 to 2.153 Å, with a median value of 1.626 Å and a mean value of 1.628 Å. In a search of all the platinum

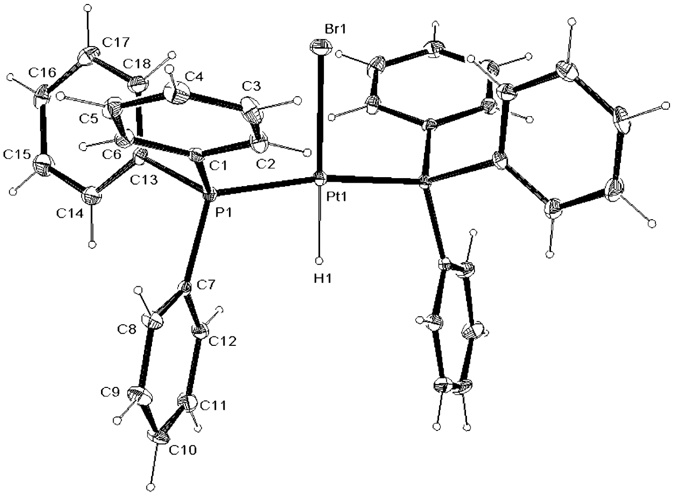


Figure 1
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary size.

complexes in the CSD, two structures with terminal hydrides had been determined by neutron diffraction and their Pt—H(terminal) distances are 1.549 Å (CSD refcode WAZPUI01; Albinati *et al.*, 1997) and 1.610 Å (CSD refcode CAKNEH01; Chiang *et al.*, 1984), respectively. Therefore, the Pt—H distance of 1.61 Å found for structure (I) is very reasonable. The salient bond lengths and angles are listed in Table 1.

Experimental

Compound (I) was prepared from a dichloromethane solution of *cis*-[Pt(1-pentenyl)Br(PPh$_3$)$_2$] on exposure to air (Sivaramakrishna & Moss, 2006). This is probably due to the breaking of the *M*—C bond through *β*-hydride elimination to form the Pt—H bond, and also isomerization from *cis* to *trans* (see scheme). ^{1}H NMR showed the Pt—H signals as a triplet at −14.8 p.p.m. with platinum satellites ($J_{\rm Pt-H}$ = 1240 Hz and $J_{\rm P-H}$ = 25.6 Hz). ^{31}P NMR indicated a singlet at 28.8 p.p.m. with platinum satellites ($J_{\rm Pt-P}$ = 2988 Hz). A solution containing *cis*-(PPh$_3$)$_2$Pt(CH$_2$CH$_2$CH$_2$CH=CH$_2$)Br (0.168 g, 0.193 mmol) in CH$_2$Cl$_2$ (20 ml) was exposed to air for three weeks. Removal of the solvent in high vacuum and recrystallization from a mixture of CH$_2$Cl$_2$ and *n*-hexane (1:1 *v*/*v*) led to the isolation of the title compound, (I), as colourless crystals (0.098 g, 63%).

Crystal data

[PtBrH(C$_{18}$H$_{15}$P)$_2$]
M_r = 800.55
Monoclinic, *C*2/*c*
a = 15.2835 (2) Å
b = 9.5241 (1) Å
c = 22.5045 (4) Å
β = 106.618 (1)°
V = 3138.97 (8) Å^3
Z = 4
D_x = 1.694 Mg m^{-3}
Mo *Kα* radiation
μ = 5.87 mm^{-1}
T = 173 (2) K
Needle, colourless
0.08 × 0.07 × 0.04 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and *ω* scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{\rm min}$ = 0.651, $T_{\rm max}$ = 0.799
37736 measured reflections
3048 independent reflections
2705 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.081
$\theta_{\rm max}$ = 26.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.051
S = 1.07
3048 reflections
183 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0152P)^2 + 11.9998P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 1.27 e Å^{-3}
$\Delta\rho_{\rm min}$ = −1.21 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.00053 (4)

Table 1
Selected geometric parameters (Å, °).

Pt1—P1	2.2827 (9)	P1—C1	1.817 (4)
Pt1—Br1	2.5229 (6)	P1—C7	1.833 (4)
Pt1—H1	1.61	P1—C13	1.825 (4)
P1—Pt1—P1$^{\rm i}$	170.81 (5)	C7—P1—Pt1	113.4 (1)
Br1—Pt1—H1	180	C13—P1—Pt1	115.5 (1)
P1—Pt1—Br1	94.60 (2)	C1—P1—C13	104.5 (2)
P1—Pt1—H1	85	C1—P1—C7	104.8 (2)
C1—P1—Pt1	113.3 (1)	C13—P1—C7	104.2 (2)

Symmetry code: (i) $-x, y, -z + \frac{3}{2}$.

Aromatic H atoms were placed in idealized positions in a riding model, with C—H = 0.95 Å, and refined with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The hydride atom (H1) was located in a difference electron-density map and refined with the constraint $U_{\rm iso}$(H1) = $U_{\rm eq}$(Pt1). The highest peak is located 0.65 Å from atom Pt1 and the deepest hole 0.03 Å from Pt1.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXL97*.

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