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## Structure Reports

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## trans-Bromohydridobis(triphenylphosphine)platinum(II)

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## Key indicators

Single-crystal X-ray study
$T=173 \mathrm{~K}$
Mean $\sigma(\mathrm{C}-\mathrm{C})=0.006 \AA$
$R$ factor $=0.027$
$w R$ 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.

[^0]The title compound, $\left[\mathrm{PtBrH}\left(\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{P}\right)_{2}\right]$, 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 $\mathrm{P}-\mathrm{Pt}-\mathrm{P}$ bond angle that is slightly bent towards the hydride $[\mathrm{P}-\mathrm{Pt}-\mathrm{P}$ $\left.=170.81(5)^{\circ}\right]$. The $\mathrm{Pt}-\mathrm{H}$ distance $(1.610 \AA)$ is in good agreement with those found in structures determined by neutron diffraction.

## Comment

The preparation of the title compound, trans- $\left[\mathrm{HPtBr}\left(\mathrm{PPh}_{3}\right)_{2}\right]$, (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 $-\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}[\mathrm{~B}(\mathrm{Mes}) \mathrm{Br}] \mathrm{Br} \quad(\mathrm{Mes}=2,4,6-$ $\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2}$ ) (Aldridge et al., 2003), or the alkoxycarbonyl, $\left[\mathrm{Pt} X(\mathrm{COOR})\left(\mathrm{PPh}_{3}\right)_{2}\right]($ where $R=\mathrm{Me}$ or $\mathrm{Et}, X=$ halide $)$, in the presence of a salt catalyst $\left(\mathrm{NH}_{4} X\right.$ or $\mathrm{K} X, X=$ halide $)$, giving trans-[ $\left.\mathrm{PtH} X\left(\mathrm{PPh}_{3}\right)_{2}\right]$ (Clark et al., 1969). The X-ray singlecrystal 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 $\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Pt}(1-$ pentenyl) (see equation below), and present the results here.

(I)

Compound (I) crystallizes in the space group $C 2 / c$ with $Z=$ 4. The molecule is located at a special position at Wyckoff position $e$, with a twofold rotation axis running through the linear $\mathrm{Br}-\mathrm{Pt}-\mathrm{H}$ group. This results in trans-oriented triphenylphosphine ligands, with $\mathrm{P}-\mathrm{Pt}-\mathrm{P}$ [bond angle $170.81(5)^{\circ}$ ] being slightly bent towards the hydride. The $\mathrm{Pt}-\mathrm{P}$ distance of 2.2827 (9) $\AA$ and the $\mathrm{Pt}-\mathrm{Br}$ distance of 2.5229 (6) $\AA$ are within the accepted ranges for similar platinum(II) complexes (Orpen et al., 1989). The $\mathrm{Pt}-\mathrm{H}$ distance is 1.61 A. 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, $\mathrm{Pt}-\mathrm{H}$ (terminal) distances range from 1.00 to $2.153 \AA$, with a median value of $1.626 \AA$ and a mean value of $1.628 \AA$. In a search of all the platinum

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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 PtH (terminal) distances are 1.549 A (CSD refcode WAZPUI01; Albinati et al., 1997) and $1.610 \AA$ (CSD refcode CAKNEH01; Chiang et al., 1984), respectively. Therefore, the $\mathrm{Pt}-\mathrm{H}$ distance of $1.61 \AA$ 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[ $\mathrm{Pt}\left(1\right.$-pentenyl) $\mathrm{Br}\left(\mathrm{PPh}_{3}\right)_{2}$ ] on exposure to air (Sivaramakrishna \& Moss, 2006). This is probably due to the breaking of the $M-\mathrm{C}$ bond through $\beta$-hydride elimination to form the $\mathrm{Pt}-\mathrm{H}$ bond, and also isomerization from cis to trans (see scheme). ${ }^{1} \mathrm{H}$ NMR showed the $\mathrm{Pt}-\mathrm{H}$ signals as a triplet at -14.8 p.p.m. with platinum satellites $\left(J_{\mathrm{Pt}-}\right.$ ${ }_{\mathrm{H}}=1240 \mathrm{~Hz}$ and $J_{\mathrm{P}-\mathrm{H}}=25.6 \mathrm{~Hz}$ ). ${ }^{31} \mathrm{P}$ NMR indicated a singlet at 28.8 p.p.m. with platinum satellites $\left(J_{\mathrm{Pt}-\mathrm{P}}=2988 \mathrm{~Hz}\right)$. A solution containing cis- $\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Pt}\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}=\mathrm{CH}_{2}\right) \mathrm{Br} \quad(0.168 \mathrm{~g}$, $0.193 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20 \mathrm{ml})$ was exposed to air for three weeks. Removal of the solvent in high vacuum and recrystallization from a mixture of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and $n$-hexane ( $1: 1 \mathrm{v} / \mathrm{v}$ ) led to the isolation of the title compound, (I), as colourless crystals ( $0.098 \mathrm{~g}, 63 \%$ ).

## Crystal data

$\left[\mathrm{PtBrH}\left(\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{P}\right)_{2}\right]$
$M_{r}=800.55$
Monoclinic, $C 2 / c$
$a=15.2835(2) \AA$
$b=9.5241(1) \AA$
$c=22.5045(4) \AA$
$\beta=106.618(1)^{\circ}$
$V=3138.97(8) \AA^{3}$

## $Z=4$

$D_{x}=1.694 \mathrm{Mg} \mathrm{m}^{-3}$
Mo K $\alpha$ radiation
$\mu=5.87 \mathrm{~mm}^{-1}$
$T=173$ (2) K
Needle, colourless
$0.08 \times 0.07 \times 0.04 \mathrm{~mm}$

## Data collection

Nonius KappaCCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2001) $T_{\text {min }}=0.651, T_{\text {max }}=0.799$

## Refinement

Refinement on $F^{2}$

$$
\begin{aligned}
& w=1 /\left[\sigma^{2}\left(F_{\mathrm{o}}^{2}\right)+(0.0152 P)^{2}\right. \\
& +11.9998 P \text { ] } \\
& \text { where } P=\left(F_{\mathrm{o}}{ }^{2}+2 F_{\mathrm{c}}{ }^{2}\right) / 3 \\
& (\Delta / \sigma)_{\max }=0.001 \\
& \Delta \rho_{\max }=1.27 \mathrm{e}^{-3}{ }^{-3} \\
& \Delta \rho_{\min }=-1.21 \mathrm{e}^{-3} \\
& \text { Extinction correction: SHELXL97 } \\
& \text { (Sheldrick, 1997) } \\
& \text { Extinction coefficient: } 0.00053 \text { (4) }
\end{aligned}
$$

Table 1
Selected geometric parameters ( $\mathrm{A},{ }^{\circ}$ ).

| $\mathrm{Pt} 1-\mathrm{P} 1$ | $2.2827(9)$ | $\mathrm{P} 1-\mathrm{C} 1$ | $1.817(4)$ |
| :--- | :---: | :--- | :--- |
| $\mathrm{Pt} 1-\mathrm{Br} 1$ | $2.5229(6)$ | $\mathrm{P} 1-\mathrm{C} 7$ | $1.833(4)$ |
| $\mathrm{Pt} 1-\mathrm{H} 1$ | 1.61 | $\mathrm{P} 1-\mathrm{C} 13$ | $1.825(4)$ |
|  |  |  |  |
| $\mathrm{P} 1-\mathrm{Pt} 1-\mathrm{P} 1^{\mathrm{i}}$ | $170.81(5)$ | $\mathrm{C} 7-\mathrm{P} 1-\mathrm{Pt} 1$ | $113.4(1)$ |
| $\mathrm{Br} 1-\mathrm{Pt} 1-\mathrm{H} 1$ | 180 | $\mathrm{C} 13-\mathrm{P} 1-\mathrm{Pt} 1$ | $115.5(1)$ |
| $\mathrm{P} 1-\mathrm{Pt} 1-\mathrm{Br} 1$ | $94.60(2)$ | $\mathrm{C} 1-\mathrm{P} 1-\mathrm{C} 13$ | $104.5(2)$ |
| $\mathrm{P} 1-\mathrm{Pt} 1-\mathrm{H} 1$ | 85 | $\mathrm{C} 1-\mathrm{P} 1-\mathrm{C} 7$ | $104.8(2)$ |
| $\mathrm{C} 1-\mathrm{P} 1-\mathrm{Pt} 1$ | $113.3(1)$ | $\mathrm{C} 13-\mathrm{P} 1-\mathrm{C} 7$ | $104.2(2)$ |
| Symmetry code: $(\mathrm{i})-x, y,-z+\frac{3}{2}$. |  |  |  |

Aromatic H atoms were placed in idealized positions in a riding model, with $\mathrm{C}-\mathrm{H}=0.95 \AA$, and refined with $U_{\text {iso }}(\mathrm{H})=1.2 U_{\text {eq }}(\mathrm{C})$. The hydride atom (H1) was located in a difference electron-density map and refined with the constraint $U_{\text {iso }}(\mathrm{H} 1)=U_{\text {eq }}(\mathrm{Pt} 1)$. The highest peak is located $0.65 \AA$ from atom Pt 1 and the deepest hole $0.03 \AA$ 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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## References

Albinati, A., Bracher, G., Carmona, D., Jans, J. H. P., Klooster, W. T., Koetzle, T. F., Macchioni, A. Ricci, J. S., Thouvenot, R. \& Venanzi, L. M. (1997). Inorg. Chim. Acta, 265, 255.
Aldridge, S., Coombs, D. \& Jones, C. (2003). Acta Cryst. E59, m584-m585.
Allen, F. H. (2002). Acta Cryst. B58, 380-388.
Barbour, L. J. (2001). J. Supramol. Chem. 1, 189-191.
Carr, S. W., Shaw, B. L. \& Thornton-Pett, M. (1985). J. Chem. Soc. Dalton Trans. pp. 2131-2137.
Chiang, M. Y., Bau, R., Minghetti, G., Bandini, A. L., Banditelli, G. \& Koetzle, T. F. (1984). Inorg. Chem. 23, 122.

Clark, H. C., Dixon, K. R. \& Jacobs, W. J. (1969). J. Am. Chem. Soc. 91, 13461350.

Habereder, T. \& Nöth, H. (2003). Appl. Organomet. Chem. 17, 525-538.
Nonius (2000). COLLECT. Nonius BV, Delft, The Netherlands.
Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. \& Taylor, R. (1989) J. Chem. Soc. Dalton Trans. pp. S1-83.

Otwinowski, Z. \& Minor, W. (1997). Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A, edited by C. W. Carter Jr \& R. M. Sweet, pp. 307-326. New York: Academic Press.
Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
Sheldrick, G. M. (2001). SADABS. Version 2.03. University of Göttingen, Germany.
Sivaramakrishna, A. \& Moss, J. R. (2006). In preparation.

## supporting information

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## S1. Comment

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Compound (I) crystallizes in the space group $C 2 / c$ with $Z=4$. The molecule is located at a special position at Wyckoff position e, with a twofold rotation axis running through the linear $\mathrm{Br}-\mathrm{Pt}-\mathrm{H}$ bond. This results in trans-orientated triphenylphosphine ligands, with $\mathrm{P}-\mathrm{Pt}-\mathrm{P}$ [bond angle $170.81(5)^{\circ}$ ] being slightly bent towards the hydride. The $\mathrm{Pt}-\mathrm{P}$ distance of 2.2827 (9) $\AA$ and the $\mathrm{Pt} — \mathrm{Br}$ distance of 2.5229 (6) $\AA$ are within the accepted ranges for similar platinum (II) complexes (International Tables for Crystallography, Vol. C). The Pt—H distance is $1.610 \AA$. 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, $\mathrm{Pt}-\mathrm{H}$ (terminal) distances range from 1.00 to $2.153 \AA$, with a median value of $1.626 \AA$ and a mean value of $1.628 \AA$. In a search of all the platinum complexes in the CSD, two structures with terminal hydrides had been determined by neutron diffraction and their $\mathrm{Pt}-\mathrm{H}$ (terminal) distances are $1.549 \AA$ (CSD Refcode WAZPUI01; Reference?) and $1.610 \AA$ (CSD Refcode CAKNEH01; Reference?), respectively. Therefore, the Pt -H distance of $1.610 \AA$ found for structure (I) is very reasonable. The salient bond lengths, angles and torsion angles are listed in Table 1.

## S2. Experimental

Compound (I) was prepared by the hydrolysis of a dichloromethane solution of cis-[ $\left.\mathrm{Pt}(1-\mathrm{pentenyl}) \mathrm{Br}\left(\mathrm{PPh}_{3}\right)_{2}\right]$ on exposure to air (Sivaramakrishna \& Moss, 2006). This is probably due to the breaking of the $M-\mathrm{C}$ bond through $\beta$-hydride elimination to form the $\mathrm{Pt}-\mathrm{H}$ bond, and also isomerization from cis to trans (see scheme). ${ }^{1} \mathrm{H}$ NMR showed the $\mathrm{Pt}-\mathrm{H}$ signals as a triplet at -14.8 p.p.m. with platinum satellites $\left(~_{\mathrm{P} t-\mathrm{H}}=1240 \mathrm{~Hz}\right.$ and $J_{\mathrm{P}-\mathrm{H}}=25.6 \mathrm{~Hz}$ ). ${ }^{31} \mathrm{P}$ NMR indicated a singlet at 28.8 p.p.m. with platinum satellites $\left(J_{\mathrm{Pt}-\mathrm{P}}=2988 \mathrm{~Hz}\right)$. A solution containing cis- $\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Pt}\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}=\mathrm{CH}_{2}\right) \mathrm{Br}(0.168 \mathrm{~g}, 0.193 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20 \mathrm{ml})$ was exposed to air for 3 weeks. Removal of the solvent in high vacuum and recrystallization from a mixture of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and n -hexane $(1: 1 \mathrm{v} / \mathrm{v})$ led to the isolation of the title compound, (I), as colourless crystals ( $0.098 \mathrm{~g}, 63 \%$ ). Analysis, calculated for $\mathrm{C}_{36} \mathrm{H}_{31} \mathrm{BrP}_{2} \mathrm{Pt}$ : C 54.01, H 3.90, C 53.82, H 3.84\%; Actual results?; $\left.M^{+}=800, \mathrm{Pt}^{( } \mathrm{PPh}_{3}\right)_{2}{ }^{+}=719$.

## S3. Refinement

Aromatic H atoms were placed in idealized positions in a riding model, with $\mathrm{C}-\mathrm{H}=0.95 \AA$, and refined with $U_{\text {iso }}(\mathrm{H})=$ $1.2 U_{\mathrm{eq}}(\mathrm{C})$. The hydride atom $(\mathrm{H} 1)$ was located in a difference electron-density map and refined with $U_{\mathrm{iso}}(\mathrm{H} 1)=U_{\mathrm{eq}}(\mathrm{Pt} 1)$.


## 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.

## trans-Bromohydridobis(triphenylphosphine)platinum(II)

## Crystal data

$\left[\mathrm{PtBrH}\left(\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{P}\right)_{2}\right]$
$M_{r}=800.55$
Monoclinic, $C 2 / c$
Hall symbol: -C 2 yc
$a=15.2835$ (2) $\AA$
$b=9.5241$ (1) $\AA$
$c=22.5045(4) \AA$
$\beta=106.618(1)^{\circ}$
$V=3138.97(8) \AA^{3}$
$Z=4$
$F(000)=1560$
$D_{\mathrm{x}}=1.694 \mathrm{Mg} \mathrm{m}^{-3}$
Melting point $=473-475 \mathrm{~K}$
Mo $K \alpha$ radiation, $\lambda=0.71073 \AA$
$\mu=5.87 \mathrm{~mm}^{-1}$
$T=173 \mathrm{~K}$
Needle, colourless
$0.08 \times 0.07 \times 0.04 \mathrm{~mm}$

## Data collection

Nonius KappaCCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$1.2^{\circ} \varphi$ and $\omega$ scans
Absorption correction: empirical (using intensity measurements)
(SADABS; Sheldrick, 2001)
$T_{\min }=0.651, T_{\text {max }}=0.799$

37736 measured reflections
3048 independent reflections
2705 reflections with $I>2 \sigma(I)$
$R_{\text {int }}=0.081$
$\theta_{\text {max }}=26.0^{\circ}, \theta_{\text {min }}=3.4^{\circ}$
$h=-18 \rightarrow 18$
$k=-11 \rightarrow 11$
$l=-27 \rightarrow 27$

## Refinement

Refinement on $F^{2}$
Least-squares matrix: full
$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right]=0.028$
$w R\left(F^{2}\right)=0.051$
$S=1.07$
3048 reflections
183 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

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Hydrogen site location: inferred from neighbouring sites
H -atom parameters constrained
\(w=1 /\left[\sigma^{2}\left(F_{0}^{2}\right)+(0.0152 P)^{2}+11.9998 P\right]\)
where \(P=\left(F_{\mathrm{o}}{ }^{2}+2 F_{\mathrm{c}}{ }^{2}\right) / 3\)
\((\Delta / \sigma)_{\text {max }}=0.001\)
\(\Delta \rho_{\text {max }}=1.27 \mathrm{e}^{\AA^{-3}}\)
\(\Delta \rho_{\text {min }}=-1.21 \mathrm{e} \AA^{-3}\)
Extinction correction: SHELXL97 (Sheldrick, 1997), \(\mathrm{Fc}^{*}=\mathrm{kFc}\left[1+0.001 \mathrm{xFc}^{2} \lambda^{3} / \sin (2 \theta)\right]^{-1 / 4}\)
Extinction coefficient: 0.00053 (4)
```


## Special details

Experimental. Half sphere of data collected using COLLECT strategy (Nonius, 2000). Crystal to detector distance $=30$ mm ; combination of $\varphi$ and $\omega$ scans of $1.2^{\circ}, 30 \mathrm{~s}$ per ${ }^{\circ}, 2$ iterations.
Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two 1.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.
Refinement. Refinement of $F^{2}$ against ALL reflections. The weighted $R$-factor $w R$ and goodness of fit $S$ are based on $F^{2}$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^{2}$. The threshold expression of $F^{2}>\sigma\left(F^{2}\right)$ is used only for calculating $R$-factors $(\mathrm{gt})$ etc. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^{2}$ are statistically about twice as large as those based on $F$, and $R$ - factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\hat{A}^{2}$ )

|  | $x$ | $y$ | $z$ | $U_{\mathrm{iso}} * / U_{\mathrm{eq}}$ |
| :--- | :--- | :--- | :--- | :--- |
| Pt1 | 0.0000 | $0.01637(2)$ | 0.7500 | $0.01499(9)$ |
| Br1 | 0.0000 | $-0.24853(6)$ | 0.7500 | $0.03449(17)$ |
| P1 | $0.11219(6)$ | $0.03558(9)$ | $0.84173(4)$ | $0.0140(2)$ |
| C7 | $0.1313(2)$ | $0.2163(4)$ | $0.87055(16)$ | $0.0155(8)$ |
| C12 | $0.1362(3)$ | $0.3214(4)$ | $0.82916(18)$ | $0.0206(9)$ |
| H12 | 0.1344 | 0.2974 | 0.7878 | $0.025^{*}$ |
| C2 | $-0.0015(3)$ | $-0.0986(4)$ | $0.90009(17)$ | $0.0216(9)$ |
| H2 | -0.0489 | -0.0743 | 0.8640 | $0.026^{*}$ |
| C6 | $0.1570(3)$ | $-0.1000(4)$ | $0.95768(17)$ | $0.0198(8)$ |
| H6 | 0.2187 | -0.0769 | 0.9610 | $0.024^{*}$ |
| C1 | $0.0882(2)$ | $-0.0625(4)$ | $0.90455(16)$ | $0.0154(8)$ |
| C4 | $0.0466(3)$ | $-0.2061(4)$ | $1.00064(18)$ | $0.0269(10)$ |
| H4 | 0.0323 | -0.2555 | 1.0333 | $0.032^{*}$ |
| C8 | $0.1358(3)$ | $0.2530(4)$ | $0.93120(18)$ | $0.0223(9)$ |
| H8 | 0.1346 | 0.1820 | 0.9606 | $0.027^{*}$ |
| C5 | $0.1358(3)$ | $-0.1705(4)$ | $1.00553(18)$ | $0.0236(9)$ |
| H5 | 0.1829 | -0.1944 | 1.0419 | $0.028^{*}$ |
| C9 | $0.1421(3)$ | $0.3932(4)$ | $0.9488(2)$ | $0.0282(10)$ |
| H9 | 0.1442 | 0.4177 | 0.9901 | $0.034^{*}$ |
| C3 | $-0.0222(3)$ | $-0.1697(4)$ | $0.94788(19)$ | $0.0289(10)$ |
| H3 | -0.0838 | -0.1936 | 0.9446 | $0.035^{*}$ |


| C13 | $0.2250(2)$ | $-0.0249(4)$ | $0.84063(15)$ | $0.0167(8)$ |
| :--- | :--- | :--- | :--- | :--- |
| C10 | $0.1453(3)$ | $0.4967(4)$ | $0.90715(19)$ | $0.0286(9)$ |
| H10 | 0.1486 | 0.5925 | 0.9194 | $0.034^{*}$ |
| C11 | $0.1439(3)$ | $0.4613(4)$ | $0.8472(2)$ | $0.0286(10)$ |
| H11 | 0.1481 | 0.5324 | 0.8186 | $0.034^{*}$ |
| C18 | $0.2372(3)$ | $-0.1661(4)$ | $0.82942(19)$ | $0.0259(10)$ |
| H18 | 0.1868 | -0.2287 | 0.8224 | $0.031^{*}$ |
| C14 | $0.2997(3)$ | $0.0649(4)$ | $0.8499(2)$ | $0.0292(10)$ |
| H14 | 0.2930 | 0.1619 | 0.8574 | $0.035^{*}$ |
| C17 | $0.3213(3)$ | $-0.2163(4)$ | $0.82838(19)$ | $0.0280(10)$ |
| H17 | 0.3288 | -0.3133 | 0.8212 | $0.034^{*}$ |
| C16 | $0.3943(3)$ | $-0.1264(4)$ | $0.83772(19)$ | $0.0282(10)$ |
| H16 | 0.4522 | -0.1612 | 0.8369 | $0.034^{*}$ |
| C15 | $0.3835(3)$ | $0.0132(5)$ | $0.8481(2)$ | $0.0360(11)$ |
| H15 | 0.4340 | 0.0752 | 0.8542 | $0.043^{*}$ |
| H1 | 0.0000 | 0.1854 | 0.7500 | $0.015^{*}$ |

Atomic displacement parameters $\left(\hat{A}^{2}\right)$

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Pt1 | $0.01540(12)$ | $0.01460(13)$ | $0.01317(12)$ | 0.000 | $0.00123(8)$ | 0.000 |
| Br1 | $0.0440(4)$ | $0.0169(3)$ | $0.0312(4)$ | 0.000 | $-0.0074(3)$ | 0.000 |
| P1 | $0.0142(5)$ | $0.0144(5)$ | $0.0125(5)$ | $0.0004(4)$ | $0.0023(4)$ | $0.0001(4)$ |
| C7 | $0.0106(18)$ | $0.0151(18)$ | $0.020(2)$ | $0.0009(15)$ | $0.0028(16)$ | $0.0013(16)$ |
| C12 | $0.024(2)$ | $0.018(2)$ | $0.016(2)$ | $0.0000(16)$ | $0.0009(17)$ | $-0.0009(16)$ |
| C2 | $0.020(2)$ | $0.028(2)$ | $0.016(2)$ | $-0.0023(17)$ | $0.0038(17)$ | $-0.0014(17)$ |
| C6 | $0.020(2)$ | $0.020(2)$ | $0.020(2)$ | $0.0008(16)$ | $0.0064(17)$ | $0.0006(16)$ |
| C1 | $0.018(2)$ | $0.0125(17)$ | $0.0154(19)$ | $-0.0010(15)$ | $0.0044(16)$ | $-0.0028(14)$ |
| C4 | $0.037(3)$ | $0.025(2)$ | $0.022(2)$ | $-0.0045(19)$ | $0.014(2)$ | $0.0047(18)$ |
| C8 | $0.028(2)$ | $0.019(2)$ | $0.021(2)$ | $-0.0038(16)$ | $0.0073(18)$ | $-0.0026(16)$ |
| C5 | $0.029(2)$ | $0.023(2)$ | $0.017(2)$ | $0.0047(18)$ | $0.0048(18)$ | $0.0050(16)$ |
| C9 | $0.036(3)$ | $0.024(2)$ | $0.027(2)$ | $-0.0051(19)$ | $0.012(2)$ | $-0.0097(18)$ |
| C3 | $0.027(2)$ | $0.037(2)$ | $0.024(2)$ | $-0.0137(19)$ | $0.010(2)$ | $-0.0016(19)$ |
| C13 | $0.0176(19)$ | $0.0220(19)$ | $0.0092(17)$ | $0.0030(16)$ | $0.0018(14)$ | $0.0026(15)$ |
| C10 | $0.029(2)$ | $0.015(2)$ | $0.040(3)$ | $-0.0067(18)$ | $0.0069(19)$ | $-0.0074(19)$ |
| C11 | $0.029(2)$ | $0.020(2)$ | $0.031(2)$ | $-0.0041(17)$ | $0.0008(19)$ | $0.0062(18)$ |
| C18 | $0.026(2)$ | $0.018(2)$ | $0.034(3)$ | $0.0017(17)$ | $0.009(2)$ | $0.0008(17)$ |
| C14 | $0.019(2)$ | $0.024(2)$ | $0.043(3)$ | $-0.0001(17)$ | $0.007(2)$ | $-0.0056(19)$ |
| C17 | $0.029(2)$ | $0.026(2)$ | $0.031(2)$ | $0.0096(19)$ | $0.013(2)$ | $0.0018(19)$ |
| C16 | $0.017(2)$ | $0.044(3)$ | $0.024(2)$ | $0.0111(19)$ | $0.0073(18)$ | $0.0023(19)$ |
| C15 | $0.019(2)$ | $0.036(3)$ | $0.054(3)$ | $-0.003(2)$ | $0.011(2)$ | $-0.007(2)$ |

Geometric parameters ( $\AA,{ }^{\circ}$ )

| $\mathrm{Pt} 1-\mathrm{P} 1$ | $2.2827(9)$ | $\mathrm{C} 8-\mathrm{C} 9$ | $1.389(5)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{Pt} 1-\mathrm{Br} 1$ | $2.5229(6)$ | $\mathrm{C} 8-\mathrm{H} 8$ | 0.9500 |
| $\mathrm{Pt} 1-\mathrm{H} 1$ | 1.610 | $\mathrm{C} 5-\mathrm{H} 5$ | 0.9500 |
| $\mathrm{P} 1-\mathrm{C} 1$ | $1.817(4)$ | $\mathrm{C} 9-\mathrm{C} 10$ | $1.370(6)$ |


| P1-C7 | 1.833 (4) |
| :---: | :---: |
| P1-C13 | 1.825 (4) |
| $\mathrm{Pt} 1-\mathrm{P} 1^{\mathrm{i}}$ | 2.2827 (9) |
| C7-C12 | 1.384 (5) |
| C7-C8 | 1.391 (5) |
| C12-C11 | 1.388 (5) |
| C12-H12 | 0.9500 |
| C2-C3 | 1.382 (5) |
| $\mathrm{C} 2-\mathrm{C} 1$ | 1.388 (5) |
| C2-H2 | 0.9500 |
| C6-C5 | 1.383 (5) |
| C6-C1 | 1.394 (5) |
| C6-H6 | 0.9500 |
| C4-C5 | 1.379 (6) |
| C4-C3 | 1.387 (6) |
| C4-H4 | 0.9500 |
| $\mathrm{P} 1-\mathrm{Pt} 1-\mathrm{P} 1^{\mathrm{i}}$ | 170.81 (5) |
| $\mathrm{Br} 1-\mathrm{Pt} 1-\mathrm{H} 1$ | 180.0 |
| $\mathrm{P} 1-\mathrm{Pt} 1-\mathrm{Br} 1$ | 94.60 (2) |
| $\mathrm{P} 1-\mathrm{Pt} 1-\mathrm{H} 1$ | 85.4 |
| $\mathrm{C} 1-\mathrm{P} 1-\mathrm{Pt} 1$ | 113.3 (1) |
| C7-P1-Pt1 | 113.4 (1) |
| C13-P1-Pt1 | 115.5 (1) |
| C1-P1-C13 | 104.5 (2) |
| C1-P1-C7 | 104.8 (2) |
| C13-P1-C7 | 104.2 (2) |
| $\mathrm{P} 1{ }^{\mathrm{i}}$-Pt1-Br1 | 94.60 (2) |
| $\mathrm{P} 1{ }^{\mathrm{i}}$ - $\mathrm{Pt} 1-\mathrm{H} 1$ | 85.4 |
| C12-C7-C8 | 118.8 (3) |
| C12-C7-P1 | 118.3 (3) |
| C8-C7-P1 | 122.7 (3) |
| C7-C12-C11 | 120.9 (4) |
| C7-C12-H12 | 119.6 |
| C11-C12-H12 | 119.6 |
| C3-C2-C1 | 120.4 (4) |
| C3-C2-H2 | 119.8 |
| $\mathrm{C} 1-\mathrm{C} 2-\mathrm{H} 2$ | 119.8 |
| C5-C6-C1 | 120.3 (4) |
| C5-C6-H6 | 119.8 |
| C1-C6-H6 | 119.8 |
| C2-C1-C6 | 119.0 (3) |
| $\mathrm{C} 2-\mathrm{C} 1-\mathrm{P} 1$ | 119.1 (3) |
| C6-C1-P1 | 121.9 (3) |
| C5-C4-C3 | 119.8 (4) |
| C5-C4-H4 | 120.1 |
| C3-C4-H4 | 120.1 |
| C9-C8-C7 | 120.0 (4) |


| C9-H9 | 0.9500 |
| :---: | :---: |
| C3-H3 | 0.9500 |
| C13-C18 | 1.391 (5) |
| C13-C14 | 1.393 (5) |
| C10-C11 | 1.384 (6) |
| C10-H10 | 0.9500 |
| C11-H11 | 0.9500 |
| C18-C17 | 1.378 (6) |
| C18-H18 | 0.9500 |
| C14-C15 | 1.384 (6) |
| C14-H14 | 0.9500 |
| C17-C16 | 1.375 (6) |
| C17-H17 | 0.9500 |
| C16-C15 | 1.368 (6) |
| C16-H16 | 0.9500 |
| C15-H15 | 0.9500 |
| C4-C5-C6 | 120.2 (4) |
| C4-C5-H5 | 119.9 |
| C6-C5-H5 | 119.9 |
| C10-C9-C8 | 120.7 (4) |
| C10-C9-H9 | 119.6 |
| C8-C9-H9 | 119.6 |
| C2-C3-C4 | 120.1 (4) |
| C2-C3-H3 | 119.9 |
| C4-C3-H3 | 119.9 |
| C18-C13-C14 | 118.3 (4) |
| C18-C13-P1 | 118.9 (3) |
| C14-C13-P1 | 122.8 (3) |
| C9-C10-C11 | 119.8 (4) |
| C9-C10-H10 | 120.1 |
| C11-C10-H10 | 120.1 |
| C10-C11-C12 | 119.7 (4) |
| C10-C11-H11 | 120.1 |
| C12-C11-H11 | 120.1 |
| C17-C18-C13 | 120.8 (4) |
| C17-C18-H18 | 119.6 |
| C13-C18-H18 | 119.6 |
| C15-C14-C13 | 120.2 (4) |
| C15-C14-H14 | 119.9 |
| C13-C14-H14 | 119.9 |
| C16-C17-C18 | 120.1 (4) |
| C16-C17-H17 | 119.9 |
| C18-C17-H17 | 119.9 |
| C15-C16-C17 | 119.9 (4) |
| C15-C16-H16 | 120.0 |
| C17-C16-H16 | 120.0 |
| C16-C15-C14 | 120.6 (4) |

supporting information

| C9-C8-H8 | 120.0 | C16-C15-H15 | 119.7 |
| :---: | :---: | :---: | :---: |
| C7-C8-H8 | 120.0 | C14-C15-H15 | 119.7 |
| Br1-Pt1-P1-C1 | -53.40 (13) | C3-C4-C5-C6 | -0.8 (6) |
| $\mathrm{Br} 1-\mathrm{Pt} 1-\mathrm{P} 1-\mathrm{C} 13$ | 67.11 (13) | C1-C6-C5-C4 | 1.0 (6) |
| $\mathrm{Br} 1-\mathrm{Pt} 1-\mathrm{P} 1-\mathrm{C} 7$ | -172.67 (13) | C7-C8-C9-C10 | -1.0 (6) |
| $\mathrm{C} 1-\mathrm{P} 1-\mathrm{C} 7-\mathrm{C} 12$ | -169.4 (3) | C1-C2-C3-C4 | -0.3 (6) |
| C13-P1-C7-C12 | 81.1 (3) | C5-C4-C3-C2 | 0.4 (6) |
| $\mathrm{Pt} 1-\mathrm{P} 1-\mathrm{C} 7-\mathrm{C} 12$ | -45.3 (3) | C1-P1-C13-C18 | 61.1 (3) |
| C1-P1-C7-C8 | 6.9 (4) | C7-P1-C13-C18 | 170.8 (3) |
| C13-P1-C7-C8 | -102.6 (3) | $\mathrm{Pt} 1-\mathrm{P} 1-\mathrm{C} 13-\mathrm{C} 18$ | -64.1 (3) |
| $\mathrm{Pt} 1-\mathrm{P} 1-\mathrm{C} 7-\mathrm{C} 8$ | 131.0 (3) | C1-P1-C13-C14 | -119.6 (3) |
| C8-C7-C12-C11 | -1.2 (6) | C7-P1-C13-C14 | -10.0 (4) |
| P1-C7-C12-C11 | 175.3 (3) | Pt1-P1-C13-C14 | 115.2 (3) |
| C3-C2-C1-C6 | 0.5 (6) | C8-C9-C10-C11 | -1.1 (6) |
| C3-C2-C1-P1 | -178.2 (3) | C9-C10-C11-C12 | 2.0 (6) |
| C5-C6-C1-C2 | -0.8 (5) | C7-C12-C11-C10 | -0.9 (6) |
| C5-C6-C1-P1 | 177.8 (3) | C14-C13-C18-C17 | 0.9 (6) |
| $\mathrm{C} 13-\mathrm{P} 1-\mathrm{C} 1-\mathrm{C} 2$ | -147.8 (3) | P1-C13-C18-C17 | -179.8 (3) |
| $\mathrm{C} 7-\mathrm{P} 1-\mathrm{C} 1-\mathrm{C} 2$ | 102.9 (3) | C18-C13-C14-C15 | -0.3 (6) |
| $\mathrm{Pt} 1-\mathrm{P} 1-\mathrm{C} 1-\mathrm{C} 2$ | -21.3 (3) | P1-C13-C14-C15 | -179.6 (3) |
| C13-P1-C1-C6 | 33.6 (3) | C13-C18-C17-C16 | -0.8 (6) |
| C7-P1-C1-C6 | -75.7 (3) | C18-C17-C16-C15 | 0.1 (6) |
| $\mathrm{Pt} 1-\mathrm{P} 1-\mathrm{C} 1-\mathrm{C} 6$ | 160.1 (3) | C17-C16-C15-C14 | 0.5 (7) |
| C12-C7-C8-C9 | 2.1 (6) | C13-C14-C15-C16 | -0.4 (7) |
| P1-C7-C8-C9 | -174.1 (3) |  |  |

Symmetry code: (i) $-x, y,-z+3 / 2$.


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