

Communication

# A Triple Cluster Platinaborane: $[(P_{(2)}Ph_3)Pt_{(1)}(\mu_2-B_{(11)}-(B_{(9)}-OC(CH_3)_3-B_{10}H_{10}))Pt_{(7)}(P_{(1)}Ph_3)]_2$

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The title platinaborane,  $[(P_{(2)}Ph_3)Pt_{(1)}(\mu_2-B_{(11)}-(B_{(9)}-OC(CH_3)_3-B_{10}H_{10}))Pt_{(7)}(P_{(1)}Ph_3)]_2$ , a triple cluster, which is a binuclear Pt complex dimer, was prepared. Single crystal X-ray diffraction analysis shows that a  $Pt_{(7)}$  atom served as a common vertex between cluster  $\{PtB_{10}\}$  and  $\{Pt_4\}$ . The  $\{Pt_4\}$  cluster is of parallelogram.

**Keywords**    platinaborane, metallaborane, triple cluster

In recent years synthesis and characterization of new metallaboranes and metallacarboranes have attracted much interest.<sup>1-3</sup> A wide variety of cluster complexes, in which coordination can be via B—H—M or (and)  $B_n$ —M bond ( $n = 1, 2, 3, 4, 5, 6$ ), have been synthesized and structurally characterized. The polyhedral borane dianion,  $[B_{10}H_{10}]^{2-}$ , has been extensively studied due to its extreme thermal, hydrolytic and oxidative stability. Recently we studied a series of reactions of  $PtCl_2(PPh_3)_2$  and  $(Et_4N)_2B_{10}H_{10}$  in various alcohols as solvent. It is very surprising that a new triple-cluster platinaborane was obtained. To our knowledge the metalla (hetero) borane triple clusters, reported in the literature, are quite limited. In 1985, Welch and co-workers<sup>4</sup> isolated a triple cluster metallaborane  $[(H_{12}B_{10}Au)(\mu-AuPEt_3)_4(AuB_{10}-H_{12})]$  containing two nido- $\{AuB_{10}\}$  and a  $\{Au_6\}$  clusters, in which an Au atom is shared by a  $\{AuB_{10}\}$  and a  $\{Au_6\}$  groups. Later Hawthorne and co-workers<sup>5</sup> reported another triple cluster anion,  $[Mo_2Cu_2(\mu-CO)_4(CO)_2(\mu-H)(C_2B_9H_{10})_2]^{2-}$ , and named it “clustered cluster”.

In this compound, the  $[Mo_2Cu_2]$  group is of parallelogram like the  $[Pt_4]$  group in the title triple cluster. It should be noted that platinaborane as a clustered cluster is not reported till now.

The title platinaborane was prepared by the reaction of  $PtCl_2(PPh_3)_2$  (0.317 g, 0.4 mmol) with  $(Et_4N)_2B_{10}H_{10}$  (0.304 g, 0.8 mmol) in *t*-BuOH (50 mL) by refluxing for 120 h under dry nitrogen. After filtration, the resulting yellow precipitation was dissolved in  $CH_2Cl_2$ , then the solution was reduced in volume and chromatographed using dichloromethane/light petroleum (4:1, *V/V*) as eluting medium to give the compound at  $R_f = 0.50$ . Then the product was recrystallized from *n*-hexane dichloromethane solution. The structure of the title compound has been confirmed by IR spectra and determined by single crystal X-ray diffraction analysis. IR  $\nu$ : 3060.24 (w), 2968.46 (w), 2924.48 (m), 2853.44 (w), 2497.44 (s), 2260.20 (w), 1629.94 (m), 1480.13 (s), 1435.24 (s), 1194.58 (m), 1118.87 (m), 1097.31 (m), 747.31 (m), 721.63 (m), 693.47 (s), 542.22 (m), 520.12 (m)  $cm^{-1}$ . This exhibits absorption characteristic of terminal B—H vibrations, the phenyl moiety and B—O stretching modes. Crystal data for the title compound are: *F. W.* = 2212.02, Monoclinic,  $C2/c$ ,  $a = 2.1656(4)$  nm,  $b = 1.4938(5)$  nm,  $c = 2.7101(6)$  nm,  $\beta = 99.64(2)^\circ$ ,  $V = 8.643(4)$  nm<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.700$  Mg/m<sup>3</sup>,  $\lambda$  (Mo  $K\alpha$ ) = 0.071069 nm. Measurements were carried out on a

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Rigaku AFC7R diffractometer. The structure was solved by direct methods and refined by full-matrix least squares method. The final  $R_1 = 0.0366$ ,  $wR_1 = 0.0900$  for 8032 observed reflections [ $I > 2\sigma(I)$ ] and  $R_2 = 0.0748$ ,  $wR_2 = 0.0997$  (for all data).

As shown in Fig. 1, the triple cluster is composed of two 11-vertex nido- $\{\text{PtB}_{10}\}$  and a  $\{\text{Pt}_4\}$  of parallelogram groups with a center of symmetry in the middle of Pt(1)—Pt(1)<sub>2</sub>. The Pt—Pt bond lengths indicate that Pt(1)—Pt(1)<sub>2</sub> [0.27209(9) nm] < Pt(1)—Pt(7) [0.29130(9) nm] < Pt(1)—Pt(7)<sub>2</sub> [0.30239(8) nm]. The Pt—Pt bond lengths are longer than those [0.25272(7)—0.25418(7) nm] in the platinum clusters of  $[\text{Pt}_4(\text{OOCMe}_3)_4(\text{pro})_4]$  ( $Hpro = L\text{-proline}$ )<sup>6</sup> and  $[\text{Pt}_4(\text{OOCMe}_3)_5\text{L}]$  (L = three hexadentate polyamine ligands)<sup>7</sup>, but fall in the range of 0.2634(1)—0.3077(2) nm in  $[\text{Pt}_7(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_{12}]$ <sup>8</sup>,  $[\text{Pt}_6(\mu_3\text{-HgI})_2(\mu\text{-CO})_6(\mu\text{-dppm})_3]$ <sup>9</sup> and  $[\text{Pt}_6(\mu_3\text{-AuPiPr}_3)_2(\mu\text{-CO})_6(\mu\text{-dppm})_3]^{2+}$  (dppm =  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ).<sup>10</sup> It shows that there exist metal bonds in  $\{\text{Pt}_4\}$  cluster. There are two B—H—Pt bonds in the title compound. These two B—H—Pt bonds strengthen the interactions between groups. The Pt atoms are unsaturatedly coordinated due to the steric effect of  $\text{B}_{10}$  cage.

For its asymmetry unit (Fig. 2), the  $\{\text{PtB}_{10}\}$  and  $\{\text{Pt}_4\}$  groups have a common vertex, Pt(7) atom. For  $\{\text{PtB}_{10}\}$ , Pt(7) atom is a point of the open  $\text{PtB}_4$  face and connected with one  $\text{PPh}_3$ , four B atoms and interacted with another Pt atom. The Pt—B bond lengths [0.2200(9)—0.2270(10) nm] are similar to those of reported Pt—B bonds, for example, 0.2214(5)—0.2301(6) nm in  $[7,7\text{-}(\text{PMe}_2\text{Ph})_2\text{-}7\text{-PtB}_{10}\text{H}_{12}]$ <sup>11</sup> and 0.2206(12)—2.342(13) nm in  $[8\text{-Cl-}7,7\text{-}(\text{PMe}_2\text{Ph})_2\text{-}7\text{-PtB}_{10}\text{H}_{11}]$ .<sup>12</sup> It can also be found that the distance of Pt(1)—B(11) [0.2048(9) nm] is significantly shorter than those of Pt—B in  $\{\text{PtB}_{10}\}$ . Due to the effect of OC-

$(\text{CH}_3)_3$ , the bond lengths of B(9)—B(10) [0.2092(14) nm] are slightly longer than those corresponding B—B bond in  $[(\text{PPh}_3)_2\text{PtB}_{10}\text{H}_{11}\text{-}8\text{-}(\text{OCH}_3)]$  [0.1929(12) nm],  $\{(\text{PPh}_3)_2\text{PtB}_{10}\text{H}_{11}\text{-}8\text{-}[\text{OCH}(\text{CH}_3)_2]\}$  [0.197(3) nm],  $\{(\text{PPh}_3)_2\text{PtB}_{10}\text{H}_{10}\text{-}9\text{-}[\text{OCH}(\text{CH}_3)_2]\}$  [0.2025(9) nm],<sup>13</sup>  $[(\text{PPh}_3)_2\text{PtB}_{10}\text{H}_{10}\text{-}8,10\text{-}(\text{OCH}_2\text{CH}_3)_2]$ .  $\text{CH}_2\text{Cl}_2$  [0.1990(9) nm], and  $\{(\text{PPh}_3)_2\text{PtB}_{10}\text{H}_{10}\text{-}8,10\text{-}[\text{OCH}(\text{CH}_3)_2]_2\}$  [0.2080(17) nm].<sup>14</sup> B—O bond lengths are similar to B—OR distances (0.1371—0.1409 nm) reported by Kennedy<sup>1</sup>, which is consistent with our previous works.<sup>13-14</sup>

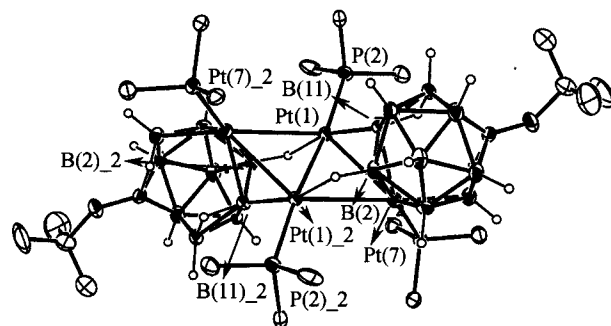


Fig. 1 Structure of the title compound.

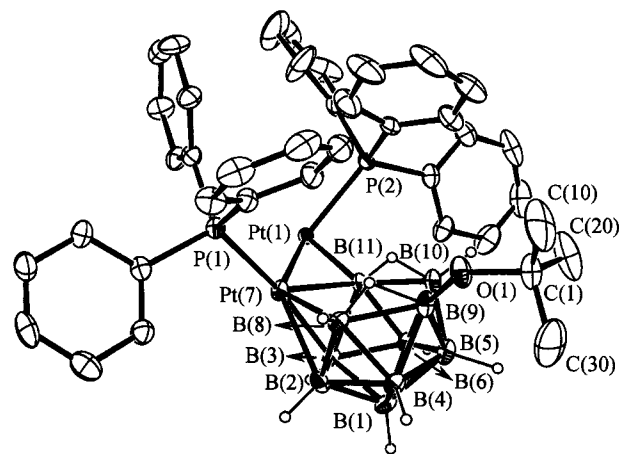


Fig. 2 Asymmetry unit of the title compound.

Table 1 Selected bond lengths (nm) and bond angles (deg)

bond lengths (nm)					
Pt(1)—Pt(7)	0.29130(9)	Pt(7)—Pt(1) <sub>2</sub>	0.30239(8)	B(8)—B(9)	0.1888(14)
Pt(1)—Pt(1) <sub>2</sub>	0.27209(9)	Pt(7)—P(1)	0.2333(2)	B(9)—B(10)	0.2092(14)
Pt(1)—Pt(7) <sub>2</sub>	0.30239(8)	Pt(7)—B(2)	0.2200(9)	B(10)—B(11)	0.1806(13)
Pt(1)—P(2)	0.2275(2)	Pt(7)—B(3)	0.2244(11)	B(8)—H(1U)	0.106(7)
Pt(1)—B(11)	0.2048(9)	Pt(7)—B(8)	0.2270(10)	B(9)—H(1U)	0.127(7)
Pt(1)—B(2) <sub>2</sub>	0.2555(9)	Pt(7)—B(11)	0.2233(9)	B(10)—H(2U)	0.105(8)
O(1)—B(9)	0.1386(11)	B(2)—Pt(1) <sub>2</sub>	0.2555(9)	B(11)—H(2U)	0.127(7)
O(1)—C(1)	0.1444(12)				

Continued

bond angles (deg)			
Pt(1) <sub>2</sub> -Pt(1)-Pt(7) <sub>2</sub>	60.666(19)	B(2)-Pt(7)-Pt(1) <sub>2</sub>	55.9(2)
Pt(1) <sub>2</sub> -Pt(1)-Pt(7)	64.82(2)	B(3)-Pt(7)-B(8)	46.9(4)
Pt(7)-Pt(1)-Pt(7) <sub>2</sub>	125.484(13)	B(3)-Pt(7)-P(1)	123.9(3)
Pt(1)-Pt(7)-Pt(1) <sub>2</sub>	54.516(13)	B(3)-Pt(7)-Pt(1)	123.2(3)
P(1)-Pt(7)-Pt(1)	112.71(6)	B(3)-Pt(7)-Pt(1) <sub>2</sub>	92.1(3)
P(1)-Pt(7)-Pt(1) <sub>2</sub>	126.02(6)	B(8)-Pt(7)-P(1)	90.7(3)
P(2)-Pt(1)-B(2) <sub>2</sub>	107.5(2)	B(8)-Pt(7)-Pt(1)	134.6(3)
P(2)-Pt(1)-Pt(1) <sub>2</sub>	169.69(6)	B(8)-Pt(7)-Pt(1) <sub>2</sub>	138.1(2)
P(2)-Pt(1)-Pt(7)	120.59(6)	B(11)-Pt(1)-P(2)	94.9(3)
P(2)-Pt(1)-Pt(7) <sub>2</sub>	113.27(6)	B(11)-Pt(1)-Pt(7)	49.8(3)
B(2) <sub>2</sub> -Pt(1)-Pt(7)	118.7(2)	B(11)-Pt(1)-Pt(7) <sub>2</sub>	120.0(3)
B(2) <sub>2</sub> -Pt(1)-Pt(1) <sub>2</sub>	74.6(2)	B(11)-Pt(1)-B(2) <sub>2</sub>	156.8(3)
B(2) <sub>2</sub> -Pt(1)-Pt(7) <sub>2</sub>	45.5(2)	B(11)-Pt(1)-Pt(1) <sub>2</sub>	82.3(3)
B(2)-Pt(7)-B(3)	47.7(4)	B(11)-Pt(7)-B(3)	85.2(4)
B(2)-Pt(7)-B(8)	84.6(3)	B(11)-Pt(7)-B(8)	92.5(4)
B(2)-Pt(7)-B(11)	48.5(4)	B(11)-Pt(7)-P(1)	140.0(3)
B(2)-Pt(7)-P(1)	170.7(3)	B(11)-Pt(7)-Pt(1)	44.5(2)
B(2)-Pt(7)-Pt(1)	76.1(2)	B(11)-Pt(7)-Pt(1) <sub>2</sub>	72.7(2)

$\cdot 2: -x + 1/2, -y + 1/2, -z + 1$

## References

- Kennedy, J. D. *Prog. Inorg. Chem.* **1986**, *34*, 211.
- Greenwood, N. N. *Pure Appl. Chem.* **1991**, *63*, 317.
- Kennedy, J. D. In *Advances in Boron Chemistry*, Ed: Siebert, W., Cambridge, Royal Society of Chemistry, **1997**, p. 451.
- Wynd, A. J.; Robins, S. E.; Welch, D. A.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1985**, 819.
- Do, Y.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1987**, *109*, 1853.
- Yamaguchi, T.; Shibata, A.; Ito, T. *J. Chem. Soc., Dalton Trans.* **1996**, 4031.
- Shibata, A.; Yamaguchi, T.; Ito, T. *Inorg. Chim. Acta* **1997**, *265*, 197.
- Yamamoto, Y.; Aoki, K.; Yamazaki, H. *Organometallics* **1983**, *2*, 1377.
- Hao, L. J.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Spivak, G. J.; Vittal, J. J.; Yufit, D. *Inorg. Chim. Acta* **1997**, *265*, 65.
- Spivak, G. J.; Vittal, J. J.; Puddephatt, R. J. *Inorg. Chem.* **1998**, *37*, 5474.
- Boocock, S. K.; Greenwood, N. N.; Kennedy, J. D. McDonald, W. S.; Staves, J. J. *Chem. Soc., Dalton Trans.* **1981**, 2573.
- Crook, J. E.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *J. Chem. Soc., Dalton Trans.* **1984**, 2487.
- Nie, Y.; Hu, C. H.; Li, X.; Yong, W.; Dou, J. M.; Sun, J.; Jin, R. S.; Zheng, P. J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2001**, *C56*, 897.
- Yong, W.; Hu, C. H.; Dou, J. M.; Sun, J.; Hu, K. J.; Jin, R. S.; Zheng, P. J. *Chin. J. Chem.* **2001**, *19*, 1162.

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