

# A New Type of Hexaosmium Boride Cluster, $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$ , That Does Not Conform to Electron Counting Rules

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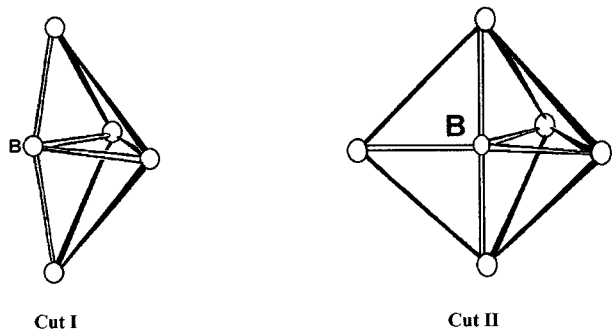
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A new type of hexaosmium boride cluster,  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$ , was produced in the thermolysis of  $\text{H}_3\text{Os}_3(\text{CO})_9(\text{BCO})$ . This complex is an 86 valence electron cluster, but the  $\text{Os}_6$  framework does not possess one of the geometries previously observed for  $\text{Os}_6$  clusters that have 86 valence electrons.  $[\text{HOs}_6(\text{CO})_{18}]^-$  and  $[\text{Os}_6(\text{CO})_{18}]^{2-}$  have octahedral frameworks while that of  $\text{H}_2\text{Os}_6(\text{CO})_{18}$  is a face-capped square pyramid. The  $\text{Os}_6$  framework of  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  can be viewed as being derived from a pentagonal bipyramid that is missing one equatorial vertex. It contains an interior boron atom. Alternatively, it can be viewed like the 84 valence cluster  $\text{Os}_6(\text{CO})_{18}$  as either a bicapped tetrahedron, with a boron atom residing on the edge of the tetrahedron that is common to the capped faces, or a face-capped trigonal bipyramid, with the boron atom on an equatorial edge of the bipyramid that is also an edge of the capped face.  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  was characterized by  $^1\text{H}$ , and  $^{11}\text{B}$ ,  $^{13}\text{C}$  NMR, IR, and mass spectroscopies and single-crystal X-ray diffraction analysis. The molecular structure was determined from two separate crystals. The analysis of each crystal yielded virtually identical structures, but their volumes differed by  $36 \text{ \AA}^3$  due to differences in packing in the unit cell. Data for crystal I of  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$ : monoclinic  $P2_1/n$ ,  $a = 9.954(2) \text{ \AA}$ ,  $b = 15.780(4) \text{ \AA}$ ,  $c = 16.448(3) \text{ \AA}$ ,  $\beta = 91.07(1)^\circ$ ,  $Z = 4$ . Data for crystal II of  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$ : monoclinic  $P2_1/n$ ,  $a = 9.927(2) \text{ \AA}$ ,  $\beta = 16.623(2) \text{ \AA}$ ,  $b = 16.0233(10) \text{ \AA}$ ,  $\beta = 97.78(1)^\circ$ ,  $Z = 4$ .

## Introduction

Within the past decade the preparation and study of molecular transition metal interstitial borides has produced a richly developed area of cluster chemistry.<sup>1</sup> While many interstitial boride clusters of the group 8 elements iron and ruthenium are now known,<sup>2–7</sup> only two osmaboride clusters have been reported.<sup>8</sup> These are the *arachno*-tetraosmaboride  $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$  which has a framework, **Cut I**, derived from an octahedron



with two adjacent equatorial vertexes removed and the *arachno*-

pentaosmaboride cluster  $\text{HOs}_5(\text{CO})_{16}\text{B}$ , **Cut II**, which has a framework that is based upon a pentagonal bipyramidal structure from which two nonadjacent equatorial vertexes have been removed. These borides were obtained from the thermolysis of  $\text{H}_3\text{Os}_3(\text{CO})_9(\text{BCO})$  in toluene.<sup>8</sup> From this thermolysis procedure we subsequently isolated a previously unidentified material that is now shown to be the osmaboride cluster  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$ , a boride cluster with a previously unobserved  $\text{M}_6\text{B}$  core. Reported here are the synthesis and structural characterization of this complex.

## Experimental Section

All reactions were carried out on a standard vacuum line or in a drybox under  $\text{N}_2$ . Toluene and  $\text{CDCl}_3$  (1% tetramethylsilane, Aldrich) were stirred over  $\text{P}_2\text{O}_5$  for several days and vacuum distilled into and stored in a sealed flask containing activated  $4 \text{ \AA}$  Linde molecular sieves. THF,  $\text{Me}_2\text{O}$ , and hexanes were dried over sodium benzophenone ketyl and were then vacuum distilled into storage flasks containing activated  $4 \text{ \AA}$  Linde molecular sieves.  $^{13}\text{C}$  (Isotec, 99.99%) was used without further purification. Thin-layer chromatography plates (J. T. Baker,  $250 \mu\text{m}$ , plastic-backed) were heated in a  $45^\circ\text{C}$  oven for 24 h before use. The cluster  $\text{H}_3\text{Os}_3(\text{CO})_9(\text{BCO})$  was prepared according to the published procedure.<sup>9</sup>  $^1\text{H}$  ( $\delta(\text{TMS}) = 0.00$  ppm),  $^{11}\text{B}$  ( $\delta(\text{BF}_3 \cdot \text{OEt}_2) = 0.00$  ppm), and  $^{13}\text{C}$  ( $\delta(\text{TMS}) = 0.00$  ppm) spectra were recorded on a Bruker AM-250 NMR. Infrared spectra were recorded on a Mattson Polaris Fourier transform spectrometer with  $2 \text{ cm}^{-1}$  resolution.

**Formation of  $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$  and  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  from the Thermolysis of  $\text{H}_3\text{Os}_3(\text{CO})_9(\text{BCO})$ .**  $\text{H}_3\text{Os}_3(\text{CO})_9(\text{BCO})$  (930 mg, 1.08 mmol) was added to a 100 mL flask equipped with a Kontes vacuum

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- (1) Housecroft, C. E. *Coord. Chem. Rev.* **1995**, *143*, 297.
- (2) (a) Wong, K. S.; Scheidt, W. R.; Fehlner, T. P. *J. Am. Chem. Soc.* **1982**, *104*, 1111. (b) Fehlner, T. P.; Housecroft, C. E.; Scheidt, W. R.; Wong, K. S. *Organometallics* **1983**, *7*, 2302.
- (3) (a) Harpp, K. S.; Housecroft, C. E.; Rheingold, A. L.; Shongwe, M. S. *J. Chem. Soc., Chem. Commun.* **1988**, 965. (b) Housecroft, C. E.; Rheingold, A. L.; Shongwe, M. S. *Organometallics* **1988**, *7*, 1885; **1989**, *8*, 2651. (c) Chipperfield, A. K.; Housecroft, C. E.; Rheingold, A. L. *Organometallics* **1990**, *9*, 681.
- (4) Khatter, R.; Puga, J.; Fehlner, T. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 1877.
- (5) (a) Hong, F.-E.; Coffy, T. J.; McCarthy, D. A.; Shore, S. G. *Inorg. Chem.* **1989**, *28*, 3284. (b) Draper, S. M.; Housecroft, C. E.; Keep, A. K.; Matthews, D. M.; Song, X.; Rheingold, A. L. *J. Organomet. Chem.* **1992**, *423*, 241. (c) McCarthy, D. A.; Krause-Bauer, J.; Oh, J. R.; Deng, H.; Liu, J.; Shore, S. G. *J. Organomet. Chem.* **1998**, *550*, 277.

- (6) Bandyopadhyay, A. K.; Khatter, R.; Puga, J.; Fehlner, T. P.; Rheingold, A. L. *Inorg. Chem.* **1992**, *31*, 465.
- (7) Housecroft, C. E.; Matthews, D. M.; Rheingold, A. L.; Song, X. *J. Chem. Soc., Chem. Commun.* **1992**, 842.
- (8) Chung, J. H.; Knoepfel, D.; McCarthy, D.; Columbie, A.; Shore, S. G. *Inorg. Chem.* **1993**, *32*, 3391.
- (9) (a) Shore, S. G.; Jan, D.-Y.; Hsu, L.-Y.; Hsu, W.-L. *J. Am. Chem. Soc.* **1983**, *105*, 5923. (b) Jan, D.-Y.; Workman, D. P.; Hsu, L.-Y.; Krause, J. A.; Shore, S. G. *Inorg. Chem.* **1992**, *31*, 5123.

adaptor, and then toluene (30 mL) was condensed into the flask at  $-78$  °C. The solution was stirred at  $110$  °C for 3 days. Solvent was removed by means of rotary evaporation, leaving a brown solid in the flask. Products were separated by preparative TLC on 2 mm silica using 1:4 toluene/hexane mixtures as an eluent. A light yellow band ( $R_f = 0.74$ ) was identified by NMR and IR spectroscopy as the previously<sup>8</sup> reported osmaboride HO<sub>8</sub>(CO)<sub>12</sub>BH<sub>2</sub> (49 mg, 0.044 mmol, 4.1% yield based on B in H<sub>3</sub>Os<sub>3</sub>(CO)<sub>9</sub>(BCO): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 30 °C)  $-9.5$  (q,  $J_{BH} = 65$  Hz, 2H),  $-24.3$  (s, 1H) ppm; <sup>11</sup>B NMR (CDCl<sub>3</sub>, 30 °C)  $119.7$  (t,  $J_{HB} = 65$  Hz) ppm; IR (C<sub>6</sub>H<sub>12</sub>,  $\nu_{CO}$ ) 2075 vs, 2054 m, 2028 ca, 2015 m, 2010 m, 1996 m cm<sup>-1</sup>.

A light brown band ( $R_f = 0.50$ ) in the preparative TLC on silica above was identified and characterized as H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B (40 mg, 0.025 mmol, 2.3% yield based on B in H<sub>3</sub>Os<sub>3</sub>(CO)<sub>9</sub>(BCO): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 30 °C)  $-9.5$  (t,  $J_{HH} = 5$  Hz, 1H),  $-16.9$  (d,  $J_{HH} = 5$  Hz, 5 Hz, 2H) ppm; <sup>11</sup>B NMR (CDCl<sub>3</sub>, 30 °C)  $188.4$  (s) ppm; IR (C<sub>6</sub>H<sub>12</sub>,  $\nu_{CO}$ ) 2080 m, 2062 s, 2035 m, 2026 m cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum of a crystal from which the molecular structure was determined was identical to the <sup>1</sup>H NMR spectrum of the bulk sample. In the FAB mass spectrum (*m*-nitrobenzyl alcohol matrix) of H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B, the parent mass *m/e* 1614 is not above background. The highest mass envelope observed has a maximum of *m/e* 1604, consistent with <sup>12</sup>C<sub>16</sub><sup>1</sup>H<sub>3</sub><sup>16</sup>O<sub>16</sub><sup>192</sup>Os<sub>6</sub> *m/e* 1603 and indicative of boron having been stripped from the molecule. Since the boron is not fully encapsulated by osmium atoms in the structure, the possibility for removal of boron in the fragmentation of the cluster in the mass spectrometer seems reasonable. Like most metal carbonyl clusters the lower mass envelopes indicate sequential loss of CO.

**Formation of H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B and HO<sub>8</sub>(CO)<sub>16</sub>B from the Thermolysis of HO<sub>8</sub>(CO)<sub>12</sub>BH<sub>2</sub>.** HO<sub>8</sub>(CO)<sub>12</sub>BH<sub>2</sub> (105 mg, 0.0945 mmol), which was obtained in the thermolysis of H<sub>3</sub>Os<sub>3</sub>(CO)<sub>9</sub>(BCO) in toluene,<sup>8</sup> was added to a 100 mL flask, and toluene (30 mL) was then condensed into the flask at  $-78$  °C. The solution was stirred at  $110$  °C for 2 days. The volatile components were removed to produce a deep brown residue. The products were separated by preparative TLC on 2 mm silica using a mixed-solvent toluene/hexanes as an eluent. A light brown band was identified from its NMR and IR spectra, as reported above, as H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B (40 mg, 0.0250 mmol, 27% yield based on B in HO<sub>8</sub>(CO)<sub>12</sub>BH<sub>2</sub>).

A brown band ( $R_f = 0.34$ ) was identified by NMR and IR spectra as the previously reported<sup>8</sup> osmaboride HO<sub>8</sub>(CO)<sub>16</sub>B (27 mg, 0.019 mmol, 20% yield based on B in HO<sub>8</sub>(CO)<sub>12</sub>BH<sub>2</sub>): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 30 °C)  $-21.2$  (s, 1H) ppm; <sup>11</sup>B NMR (CDCl<sub>3</sub>, 30 °C)  $184.4$  (s) ppm; IR (C<sub>6</sub>H<sub>12</sub>,  $\nu_{CO}$ ) 2137 w, 2083 s, 2060 s, 2054 s, 2026 m, 2018 m, 2015 m, 1975 w cm<sup>-1</sup>.

**Preparation of <sup>13</sup>CO-Enriched H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B.** Os<sub>3</sub>(CO)<sub>12</sub> (41% <sup>13</sup>CO) prepared by a published procedure<sup>10</sup> was the starting point in the preparation of <sup>13</sup>CO-enriched H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B. The enriched Os<sub>3</sub>(CO)<sub>12</sub> was converted to H<sub>2</sub>Os<sub>3</sub>(CO)<sub>10</sub> by hydrogenation<sup>11</sup> of the Os<sub>3</sub>(CO)<sub>12</sub>. In turn H<sub>2</sub>Os<sub>3</sub>(CO)<sub>10</sub> was converted to <sup>13</sup>CO-labeled H<sub>3</sub>Os<sub>3</sub>(CO)<sub>9</sub>(BCO) by reacting it with B<sub>2</sub>H<sub>6</sub>. Thermolysis of the H<sub>3</sub>Os<sub>3</sub>(CO)<sub>9</sub>(BCO) by the procedure described above yielded <sup>13</sup>CO-enriched H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B.

**Reaction of H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B with CO.** H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B (50 mg, 0.031 mmol) was placed in a Parr reactor, and toluene (30 mL) was added to the reactor. The reactor was flushed with prepurified CO, and the reactor was then charged with CO at 1 atm. The solution was stirred at  $110$  °C for 5 h. The solvent was removed by means of rotary evaporation, leaving behind a brown solid. This product was purified by means of preparative TLC on 2 mm silica using toluene/hexanes (1:4) as the eluent. It was identified as HO<sub>8</sub>(CO)<sub>16</sub>B (10 mg, 0.0071 mmol, 23% yield based on B in H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B) by means of <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy.

**X-ray Structure Determination of H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B.** Crystals of H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B were obtained from a CH<sub>2</sub>Cl<sub>2</sub> solution by slow evaporation of the solvent at room temperature. Crystals of suitable size were coated

**Table 1.** Crystal Data and Structure Refinement for Os<sub>6</sub>(CO)<sub>16</sub>BH<sub>3</sub>

	crystal I	crystal II
empirical formula	C <sub>16</sub> H <sub>3</sub> BO <sub>16</sub> Os <sub>6</sub>	C <sub>16</sub> H <sub>3</sub> BO <sub>16</sub> Os <sub>6</sub>
fm, amu	1603.20	1603.20
space group	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>
<i>T</i> , K	213(2)	213(2)
<i>a</i> , Å	9.954(2)	9.927(2)
<i>b</i> , Å	15.780(4)	16.623(2)
<i>c</i> , Å	16.448(3)	16.0233(10)
$\beta$ , deg	91.07(1)	97.78(1)
<i>V</i> , Å <sup>3</sup>	2583(1)	2619.8(6)
<i>Z</i>	4	4
$\rho$ (calcd) Mg/m <sup>3</sup>	4.122	4.065
radiation ( $\lambda$ , Å)	Mo K $\alpha$ (0.710 73)	Mo K $\alpha$ (0.710 73)
$\mu$ , mm <sup>-1</sup>	29.470	29.057
cryst size, mm	0.4 × 0.4 × 0.5	0.4 × 0.5 × 0.6
scan mode	$\omega-2\theta$	$\omega-2\theta$
2 $\theta$ limits, deg	2.37–22.48	2.28–22.46
$\pm h$	0, 10	0, 10
$\pm k$	16	0, 17
$\pm l$	17	–17, 16
no. rflns measd 6551	6551	3636
no. unique rflns [ $I > 2.0\sigma(I)$ ]	3285	2377
<i>R</i> <sub>int</sub>	0.048	0.058
no. of variables	353	343
<i>R</i> <sub>1</sub> indices [ $I > 2\sigma(I)$ ] <sup>a</sup>	0.0424	0.0452
w <i>R</i> <sub>2</sub> indices [ $I > 2\sigma(I)$ ] <sup>a</sup>	0.0968	0.1195
GoF	1.09	1.08

$$^a R_1 = \sum(F_o - F_c)/\sum(F_o); wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}.$$

with epoxy resin in the drybox and glued to the tips of glass fibers. Data sets were obtained from two crystals (I and II). All crystallographic data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K $\alpha$  radiation. Unit cell parameters were obtained by a least-squares refinement of the angular settings of 25 reflections, well distributed in reciprocal space and lying in a 2 $\theta$  range of 24–30°. All reflection data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied on the basis of measured  $\psi$  scans. Both specimens crystallized in the space group *P2<sub>1</sub>/n* (No. 14), with diffraction symmetry *C<sub>2h</sub>*, *2/m* and the systematic absences *h0l* for  $h + l = 2n + 1$  and *0k0* for  $k = 2n + 1$ .

From each data set the structure of H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B was solved by direct methods using SHELX86 and SHELX93 (difference electron density calculations, full-matrix least-squares refinements). For both structures an empirical absorption correction was applied. Because several atoms in structures I and II had nonpositive thermal parameters a spherical absorption correction was also applied to these data ( $\mu R = 6$ ). In the final refinement of structure I all thermal parameters were positive. The final refinement of structure II contained nonpositive anisotropic thermal parameters for C(41) and B(1). Therefore the refinement of structure I is preferred.

## Results and Discussion

**Formation and Properties of H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B.** Earlier,<sup>8</sup> we found that the thermolysis of H<sub>3</sub>Os<sub>3</sub>(CO)<sub>9</sub>(BCO) in toluene yields the tetra- and pentaosmaboride clusters HO<sub>8</sub>(CO)<sub>12</sub>BH<sub>2</sub> and HO<sub>8</sub>(CO)<sub>16</sub>B. An unidentified third product, the hexaosmaboride H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B cluster, has been isolated and identified in the present study. It was obtained in 2.3% yield along with HO<sub>8</sub>(CO)<sub>12</sub>BH<sub>2</sub> in 4.1% yield from the thermolysis of H<sub>3</sub>Os<sub>3</sub>(CO)<sub>9</sub>(BCO) in toluene at  $110$  °C for 3 days. Thermolysis of HO<sub>8</sub>(CO)<sub>12</sub>BH<sub>2</sub> in toluene at  $110$  °C for 2 days yielded H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B and HO<sub>8</sub>(CO)<sub>16</sub>B in 27% and 20% yields, respectively. These observations are consistent with the well-known<sup>12</sup>

(10) Bricker, J. C.; Payne, M. W.; Shore, S. G. *Organometallics* **1987**, *6*, 2545.

(11) Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, J. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942. 111.

(12) (a) Eady, C. R.; Johnson, B. F. G.; Lewis, J. J. *Organomet. Chem.* **1972**, *37*, C39. (b) Eady, C. R.; Johnson, B. F. G.; Lewis, J. J. *Chem. Soc., Dalton Trans.* **1975**, 2606. (c) Mingos, M. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall International Editions: New York, 1990; p 35.

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  (Structure I)

Os(1)–C(13)	1.87(3)	Os(1)–C(11)	1.91(2)	Os(5)–C(51)	1.93(2)	Os(5)–B(1)	2.32(2)
Os(1)–C(12)	1.93(2)	Os(1)–B(1)	2.04(2)	Os(5)–Os(6)	3.0203(11)	Os(6)–C(62)	1.92(2)
Os(1)–Os(2)	2.9695(11)	Os(1)–Os(3)	3.0070(12)	Os(6)–C(61)	1.95(2)	Os(6)–C(63)	1.96(3)
Os(1)–Os(4)	3.0428(12)	Os(1)–Os(5)	3.0474(13)	Os(6)–B(1)	2.01(2)	O(11)–C(11)	1.15(3)
Os(2)–C(21)	1.93(3)	Os(2)–C(23)	1.94(2)	O(12)–C(12)	1.14(3)	O(13)–C(13)	1.17(3)
Os(2)–C(22)	1.94(2)	Os(2)–B(1)	2.17(2)	O(21)–C(21)	1.12(3)	O(22)–C(22)	1.10(2)
Os(2)–Os(5)	2.8114(12)	Os(2)–Os(6)	2.9859(12)	O(23)–C(23)	1.12(3)	O(31)–C(31)	1.13(3)
Os(3)–C(32)	1.89(2)	Os(3)–C(31)	1.91(3)	O(32)–C(32)	1.18(3)	O(33)–C(33)	1.14(3)
Os(3)–C(33)	1.93(3)	Os(3)–B(1)	2.20(2)	O(41)–C(41)	1.16(3)	O(42)–C(42)	1.14(3)
Os(3)–Os(4)	2.7898(12)	Os(3)–Os(6)	2.9994(11)	O(51)–C(51)	1.10(3)	O(52)–C(52)	1.13(2)
Os(4)–C(41)	1.88(3)	Os(4)–C(42)	1.91(3)	O(61)–C(61)	1.12(2)	O(62)–C(62)	1.13(3)
Os(4)–B(1)	2.33(2)	Os(4)–Os(5)	2.6377(12)	O(63)–C(63)	1.11(3)		
Os(4)–Os(6)	3.0450(11)	Os(5)–C(52)	1.89(2)				
C(13)–Os(1)–C(11)	96.3(9)	C(13)–Os(1)–C(12)	95.6(10)	C(42)–Os(4)–Os(6)	178.3(7)	(1)–Os(4)–Os(6)	41.2(5)
C(11)–Os(1)–C(12)	92.8(9)	C(13)–Os(1)–B(1)	111.6(9)	Os(5)–Os(4)–Os(6)	63.74(3)	Os(3)–Os(4)–Os(6)	61.69(3)
C(11)–Os(1)–B(1)	125.8(10)	C(12)–Os(1)–B(1)	127.4(8)	Os(1)–Os(4)–Os(6)	83.14(3)	C(52)–Os(5)–C(51)	88.9(8)
C(13)–Os(1)–Os(2)	89.9(6)	C(11)–Os(1)–Os(2)	172.1(7)	C(52)–Os(5)–B(1)	134.2(8)	C(51)–Os(5)–B(1)	136.5(7)
C(12)–Os(1)–Os(2)	91.5(5)	B(1)–Os(1)–Os(2)	46.8(6)	C(52)–Os(5)–Os(4)	113.3(6)	C(51)–Os(5)–Os(4)	120.3(6)
C(13)–Os(1)–Os(3)	90.5(7)	C(11)–Os(1)–Os(3)	89.5(7)	B(1)–Os(5)–Os(4)	55.6(6)	C(52)–Os(5)–Os(2)	116.6(7)
C(12)–Os(1)–Os(3)	173.3(6)	B(1)–Os(1)–Os(3)	46.9(7)	C(51)–Os(5)–Os(2)	113.7(5)	B(1)–Os(5)–Os(2)	48.8(6)
Os(2)–Os(1)–Os(3)	85.60(3)	C(13)–Os(1)–Os(4)	145.1(7)	Os(4)–Os(5)–Os(2)	104.37(4)	C(52)–Os(5)–Os(6)	175.8(7)
C(11)–Os(1)–Os(4)	80.7(7)	C(12)–Os(1)–Os(4)	119.2(7)	C(51)–Os(5)–Os(6)	95.3(6)	B(1)–Os(5)–Os(6)	41.6(5)
B(1)–Os(1)–Os(4)	49.9(6)	Os(2)–Os(1)–Os(4)	91.48(3)	Os(4)–Os(5)–Os(6)	64.71(3)	Os(2)–Os(5)–Os(6)	61.47(3)
Os(3)–Os(1)–Os(4)	54.92(3)	C(13)–Os(1)–Os(5)	145.4(6)	C(52)–Os(5)–Os(1)	92.4(7)	C(51)–Os(5)–Os(1)	174.2(5)
C(11)–Os(1)–Os(5)	118.3(7)	C(12)–Os(1)–Os(5)	82.6(6)	B(1)–Os(5)–Os(1)	41.9(5)	Os(4)–Os(5)–Os(1)	64.24(3)
B(1)–Os(1)–Os(5)	49.5(6)	Os(2)–Os(1)–Os(5)	55.69(2)	Os(2)–Os(5)–Os(1)	60.75(3)	Os(6)–Os(5)–Os(1)	83.48(3)
Os(3)–Os(1)–Os(5)	90.74(3)	Os(4)–Os(1)–Os(5)	51.33(3)	C(62)–Os(6)–C(61)	94.8(9)	C(62)–Os(6)–C(63)	92.5(10)
C(21)–Os(2)–C(23)	92.3(9)	C(21)–Os(2)–C(22)	93.1(9)	C(61)–Os(6)–C(63)	93.8(9)	C(62)–Os(6)–B(1)	114.2(9)
C(23)–Os(2)–C(22)	96.3(9)	C(21)–Os(2)–B(1)	96.2(9)	C(61)–Os(6)–B(1)	123.1(9)	C(63)–Os(6)–B(1)	129.8(9)
C(23)–Os(2)–B(1)	130.4(8)	C(22)–Os(2)–B(1)	131.6(8)	C(62)–Os(6)–Os(2)	91.9(7)	C(61)–Os(6)–Os(2)	87.4(6)
C(21)–Os(2)–Os(5)	149.8(6)	C(23)–Os(2)–Os(5)	106.5(6)	C(63)–Os(6)–Os(2)	175.3(7)	B(1)–Os(6)–Os(2)	46.5(7)
C(22)–Os(2)–Os(5)	107.6(6)	B(1)–Os(2)–Os(5)	53.6(6)	C(62)–Os(6)–Os(3)	92.5(6)	C(61)–Os(6)–Os(3)	169.9(5)
C(21)–Os(2)–Os(1)	94.8(6)	C(23)–Os(2)–Os(1)	87.5(6)	C(63)–Os(6)–Os(3)	92.8(6)	B(1)–Os(6)–Os(3)	47.1(7)
C(22)–Os(2)–Os(1)	171.2(6)	B(1)–Os(2)–Os(1)	43.3(5)	Os(2)–Os(6)–Os(3)	85.45(3)	C(62)–Os(6)–Os(5)	147.1(7)
Os(5)–Os(2)–Os(1)	63.56(3)	C(21)–Os(2)–Os(6)	96.7(7)	C(61)–Os(6)–Os(5)	78.7(5)	C(63)–Os(6)–Os(5)	119.9(7)
C(23)–Os(2)–Os(6)	169.0(6)	C(22)–Os(2)–Os(6)	89.6(6)	B(1)–Os(6)–Os(5)	50.1(6)	Os(2)–Os(6)–Os(5)	55.82(3)
B(1)–Os(2)–Os(6)	42.2(5)	Os(5)–Os(2)–Os(6)	62.71(3)	Os(3)–Os(6)–Os(5)	91.41(3)	C(62)–Os(6)–Os(4)	146.9(7)
Os(1)–Os(2)–Os(6)	85.42(3)	C(32)–Os(3)–C(31)	98.2(10)	C(61)–Os(6)–Os(4)	118.2(6)	C(63)–Os(6)–Os(4)	84.3(7)
C(32)–Os(3)–C(33)	92.0(9)	C(31)–Os(3)–C(33)	91.3(10)	B(1)–Os(6)–Os(4)	49.9(6)	Os(2)–Os(6)–Os(4)	91.12(3)
C(32)–Os(3)–B(1)	127.7(9)	C(31)–Os(3)–B(1)	131.6(9)	Os(3)–Os(6)–Os(4)	54.97(3)	Os(5)–Os(6)–Os(4)	51.55(3)
C(33)–Os(3)–B(1)	100.5(9)	C(32)–Os(3)–Os(4)	109.0(6)	O(11)–C(11)–Os(1)	174(2)	O(12)–C(12)–Os(1)	175(2)
C(31)–Os(3)–Os(4)	101.0(7)	C(33)–Os(3)–Os(4)	153.6(6)	O(13)–C(13)–Os(1)	178(2)	O(21)–C(21)–Os(2)	178(2)
B(1)–Os(3)–Os(4)	54.1(6)	C(32)–Os(3)–Os(6)	169.2(7)	O(22)–C(22)–Os(2)	177(2)	O(23)–C(23)–Os(2)	178(2)
C(31)–Os(3)–Os(6)	91.0(7)	C(33)–Os(3)–Os(6)	93.4(6)	O(31)–C(31)–Os(3)	177(2)	O(32)–C(32)–Os(3)	178(2)
B(1)–Os(3)–Os(6)	42.0(5)	Os(4)–Os(3)–Os(6)	63.35(3)	O(33)–C(33)–Os(3)	173(2)	O(41)–C(41)–Os(4)	177(2)
C(32)–Os(3)–Os(1)	85.1(7)	C(31)–Os(3)–Os(1)	163.9(7)	O(42)–C(42)–Os(4)	177(2)	O(51)–C(51)–Os(5)	178(2)
C(33)–Os(3)–Os(1)	104.4(7)	B(1)–Os(3)–Os(1)	42.6(5)	O(52)–C(52)–Os(5)	178(2)	O(61)–C(61)–Os(6)	175(2)
Os(4)–Os(3)–Os(1)	63.19(3)	Os(6)–Os(3)–Os(1)	84.53(3)	O(62)–C(62)–Os(6)	178(2)	O(63)–C(63)–Os(6)	176(2)
C(41)–Os(4)–C(42)	89.8(9)	C(41)–Os(4)–B(1)	132.2(8)	Os(6)–B(1)–Os(1)	176.4(12)	Os(6)–B(1)–Os(2)	91.3(8)
C(42)–Os(4)–B(1)	137.2(8)	C(41)–Os(4)–Os(5)	120.2(7)	Os(1)–B(1)–Os(2)	89.9(8)	Os(6)–B(1)–Os(3)	90.9(9)
C(42)–Os(4)–Os(5)	116.1(6)	B(1)–Os(4)–Os(5)	55.2(6)	Os(1)–B(1)–Os(3)	90.5(8)	Os(2)–B(1)–Os(3)	137.1(11)
C(41)–Os(4)–Os(3)	108.6(7)	C(42)–Os(4)–Os(3)	117.0(7)	Os(6)–B(1)–Os(5)	88.3(8)	Os(1)–B(1)–Os(5)	88.6(8)
B(1)–Os(4)–Os(3)	49.8(6)	Os(5)–Os(4)–Os(3)	105.06(4)	Os(2)–B(1)–Os(5)	77.6(7)	Os(3)–B(1)–Os(5)	145.3(11)
C(41)–Os(4)–Os(1)	170.5(7)	C(42)–Os(4)–Os(1)	95.3(7)	Os(6)–B(1)–Os(4)	88.9(8)	Os(1)–B(1)–Os(4)	88.2(8)
B(1)–Os(4)–Os(1)	41.9(5)	Os(5)–Os(4)–Os(1)	64.43(3)	Os(2)–B(1)–Os(4)	146.8(11)	Os(3)–B(1)–Os(4)	76.1(7)
Os(3)–Os(4)–Os(1)	61.89(3)	C(41)–Os(4)–Os(6)	91.6(6)				

tendency for osmium carbonyl clusters to condense to higher nuclearity clusters upon thermolysis. The cluster  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  is an air-stable yellow solid at room temperature. It is stable in toluene at 110 °C for at least 2 days without apparent decomposition. It reacts with CO (1 atm) at 110 °C for 10 h in toluene to produce  $\text{HOS}_5(\text{CO})_{16}\text{B}$  in 20% yield.

**Molecular Structure and NMR Spectra of  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$ .** Single-crystal X-ray analyses were performed on data sets from two crystals of  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$ . The two data sets obtained (I and II) indicate that the  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  molecule crystallizes in two different cells belonging to the same space group,  $P2_1/n$ . Their volumes differ by 36 Å<sup>3</sup>, Table 1, but there is no significant difference Table 1 in their molecular structures. Differences between the two cells are attributed to differences in the packing of the molecules within the cells. Complete sets

of structural information obtained from crystals I and II are provided in the Supporting Information. Table 2 provides selected Os–C and C–O distances and selected bond angles obtained from crystal I.

The molecular structure of  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$ , derived from crystal I, is shown in Figure 1. All of the non-hydrogen atoms were located and refined. Hydrogen atoms could not be located, but the presence of three hydrogens is indicated from proton NMR spectra.

The hexaosmaboride  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  contains 86 valence electrons (7 skeletal electron pairs<sup>18</sup>). Its molecular structure has an Os<sub>6</sub> framework that can be viewed in several arbitrary ways if the electron count is not considered. A convenient view that reveals the positions of the ligands, Figure 1, is based upon

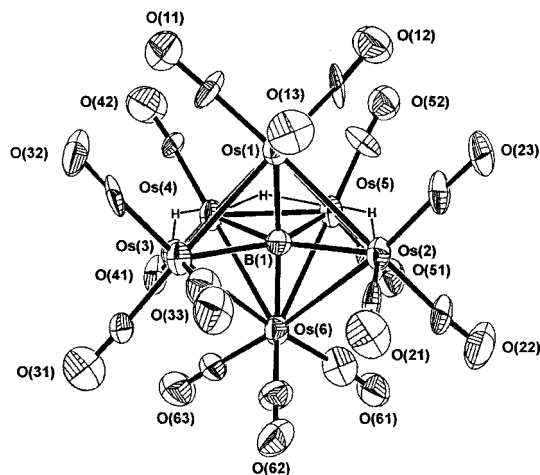
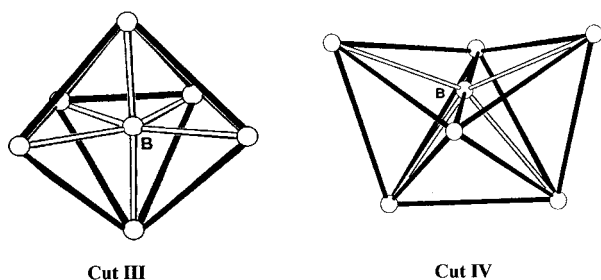


Figure 1. Molecular structure of H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B.

a pentagonal bipyramidal framework, **Cut II**, with an equatorial



vertex removed. It contains an interior boron atom. Alternatively, it can be viewed as either a bicapped tetrahedron, **Cut IV**, with a boron atom residing on the edge of the tetrahedron that is common to the capped faces or as a face-capped trigonal bipyramid with the boron atom on an equatorial edge of the bipyramid that is also an edge of the capped face. Bicapped tetrahedral core (face-capped trigonal bipyramidal) geometry is generally observed for 84 electron clusters,<sup>13</sup> as for example Os<sub>6</sub>(CO)<sub>18</sub>.<sup>14</sup>

The overall structure has approximate C<sub>2v</sub> symmetry. All sixteen carbonyl groups are terminally coordinated, three to each of four osmium atoms, Os(1), Os(2), Os(3), and Os(6), and two to each of two osmium atoms, Os(4) and Os(5). The boron atom is equidistant between Os(1) and Os(6) (Os(1)–B(1) = 2.04(2) Å; Os(6)–B(1) = 2.01(2) Å) in a close to linear arrangement (Os(1)–B(1)–Os(6) with an angle of 176.4(12)°). These Os–B distances and the associated Os–B–Os angle are close to those observed for the axial Os–B–Os arrangement shown in **Cut II** for HOs<sub>5</sub>(CO)<sub>6</sub>B.<sup>8</sup> These Os–B distances, however, are markedly shorter than other distances observed in this molecule and in HOs<sub>5</sub>(CO)<sub>6</sub>B.<sup>8</sup>

Due to the presence of the intervening boron atom, the Os(1)–Os(6) distance, 4.03(2) Å, is appreciably longer than the distance between corresponding atoms in Os<sub>6</sub>(CO)<sub>18</sub>.<sup>14</sup>

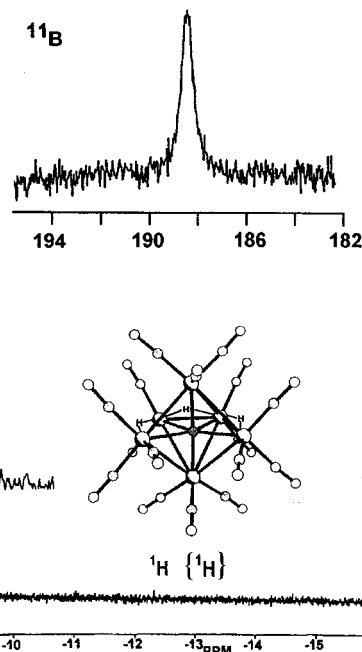


Figure 2. <sup>11</sup>B and <sup>1</sup>H NMR spectra of H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B.

Distances between the apical and equatorial osmium atoms (2.9695(11)–3.0474(13) Å) are significantly longer than the Os–Os distances in the equatorial plane due to B(1) being situated between Os(1) and Os(6). In the equatorial plane the distances Os(2)–Os(5) = 2.8114(12) Å and Os(3)–Os(4) = 2.7898(12) Å are in accord with the corresponding Os–Os connectivities in Os<sub>6</sub>(CO)<sub>18</sub>.<sup>14</sup> However, the distance Os(4)–Os(5) = 2.6377(12) Å is significantly shorter than the corresponding Os–Os connectivity (2.732 Å), which is the shortest Os–Os distance, in Os<sub>6</sub>(CO)<sub>18</sub>.<sup>14</sup>

The <sup>11</sup>B NMR spectrum of H<sub>3</sub>Os<sub>6</sub>(CO)<sub>16</sub>B, Figure 2, consists of a sharp singlet at 188.4 ppm which is consistent with the large downfield chemical shifts observed for metal borides.<sup>2–8</sup> The <sup>11</sup>B{<sup>1</sup>H} NMR spectrum shows no noticeable sharpening compared to that of the coupled <sup>11</sup>B NMR spectrum. The <sup>1</sup>H NMR spectrum consists of a triplet [–9.5 ppm (t, J<sub>HH</sub> = 5 Hz)] and a doublet [–16.9 ppm (d, J<sub>HH</sub> = 5 Hz)] in the area ratio of 1:2, Figure 2. Proton NMR spectra from 25 to 65 °C showed no apparent coalescence of the multiplets, but at 65 °C broadening of the signals was just noticeable.

In view of the proton couplings observed, in view of an examination of space filling models, in the manner of Henrick, McPartlin, and Morris,<sup>15</sup> and on the basis of the single-crystal X-ray analysis, the three hydrogens are believed to be located in bridge positions along the perimeter of the equatorial plane. The chemical shift (–16.9 ppm) of the proton signal of area 2 is assigned to the hydrogen in Os(3)–H–Os(4) and Os(2)–H–Os(5). The proton signal of area 1 (–9.5 ppm) is assigned to the Os(4)–H–Os(5) bridge with a “short” Os–Os distance (2.6377(12) Å). This signal is significantly downfield from that generally observed for Os–H–Os bridges. Interestingly, the 46 valence electron unsaturated cluster H<sub>2</sub>Os<sub>3</sub>(CO)<sub>10</sub> produces a proton chemical shift (–10.7 ppm in CD<sub>2</sub>Cl<sub>2</sub>)<sup>16</sup> that is significantly downfield from that usually observed for Os–H–Os hydrogen and it has a “short” Os–Os distance 2.683(1) Å.<sup>17</sup>

Variable-temperature <sup>13</sup>C NMR spectra can be partially assigned, consistent with the proposed arrangement of hydrogen atoms. Figure 3 reveals a spectrum at –60 °C that consists of five resonances in the ratio 4:4:4:2:2. The doublet signal at 166.3 ppm, J(<sup>13</sup>CH = 10 Hz), is assigned to atoms C(21) and C(33)

(13) (a) Mingos, M. P.; May, A. S. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH Publishers: New York, 1990; p 48.

(14) Mason, R.; Thomas, K. H.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1973**, *95*, 3802.

(15) Henrick, K.; McPartlin, M.; Morris, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 853.

(16) Johnson, B. F. G.; Lewis, J.; Kilty, P. A. *J. Chem. Soc. A* **1968**, 2859.

(17) (a) Broach, R. W.; Williams, J. M. *Inorg. Chem.* **1979**, *18*, 314. (b) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2697.

(18) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

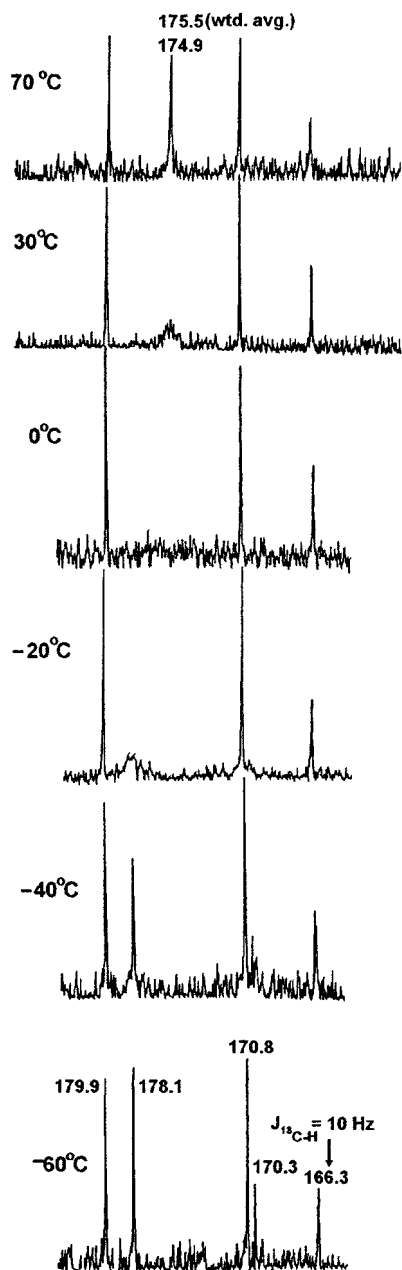


Figure 3.  $^{13}\text{C}$  NMR spectra of  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$ .

since they are trans to the proposed hydrogen arrangement. This signal and the two at 179.9 and 170.8 ppm are independent of temperature in the range studied. With increasing temperature the signals at 178.1 and 170.3 ppm merge to give a single signal at 174.9 ppm at 70 °C. The weighted average of the two signals is 175.5 ppm. These two signals are assigned to the carbons of the apical  $\text{Os}(\text{CO})_3$  groups C(11), C(12), C(61), C(61) and

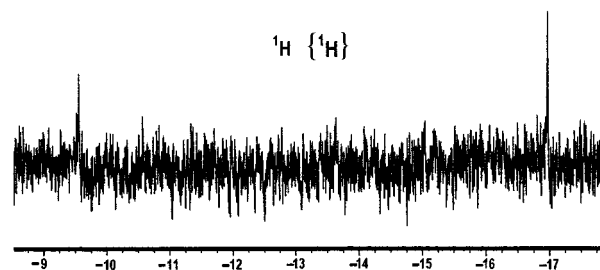


Figure 4. Proton NMR spectrum obtained from crystal I, from which X-ray data were collected for the structural analysis of  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  (1000 scans).

C(13), C(62), respectively, which could average through rotation of these groups as the temperature of the NMR sample is increased.

While the complex  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  is an 86 valence electron cluster with seven skeletal electron pairs,<sup>18</sup> the  $\text{Os}_6$  core does not possess the geometries previously observed for  $\text{Os}_6$  clusters that have the same number of valence electrons.<sup>19</sup>  $[\text{Os}_6(\text{CO})_{18}]^-$  and  $[\text{Os}_6(\text{CO})_{18}]^{2-}$  have octahedral frameworks while that of  $\text{H}_2\text{Os}_6(\text{CO})_{18}$  is a triangular face-capped square pyramid. The  $\text{Os}_6$  framework of  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  mimics that of  $\text{Os}_6(\text{CO})_{18}$ , an 84 electron cluster, except for the presence of the boride atom that resides between Os(1) and Os(6). The possibility was considered that the crystals from which the X-ray data were obtained did not represent the bulk sample from which NMR data were obtained but were composed of the 84 electron cluster  $\text{HOs}_6(\text{CO})_{16}\text{B}$ . To test this possibility, the proton NMR spectrum of crystal I was obtained. Although the resolution of the spectrum was poor due to the highly dilute nature of the solution, the spectrum showed two signals in accord with the spectrum obtained from the bulk solution, Figure 4, thereby eliminating the possibility that the crystals from which the structure was determined contained only one hydrogen and were composed of the as yet unknown 84 electron  $\text{HOs}_6(\text{CO})_{16}\text{B}$  cluster.

Electron counting rules can be very useful in predicting shapes of cluster frameworks. But exceptions to the rules are not uncommon. The hexaosmaboride  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  appears to be such an exception, and perhaps only a detailed theoretical analysis will provide the reason for this apparent exception.

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**Supporting Information Available:** Tables of crystallographic data, positional and thermal parameters, and interatomic distances and angles for structures I and II and an ORTEP diagram. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(19) McPartlin, M.; Eady, C. R.; Johnson, B. F. G.; Lewis, J. *Chem. Soc., Chem. Commun.* **1976**, 883.