

단 신

테트라- 그리고 헥사 오스뮴 카보닐 붕소 클러스터,  $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$ ,  
 $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$ 의 효율적 합성 방법 연구

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Improved Synthesis of Tetra- and Hexaosmium Carbonyl Boride Cluster  
 $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$  and  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$

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The area of the transition metal interstitial boride cluster chemistry has been richly developed for the past decade.<sup>1</sup> However, of many interstitial boride clusters of the group 8 elements, only three osmium carbonyl interstitial boride cluster have been reported.<sup>2-5</sup> These are tetra-, penta-, and hexaosmium carbonyl boride clusters,  $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$ ,<sup>6</sup>  $\text{HOs}_5(\text{CO})_{16}\text{B}$ ,<sup>6</sup> and  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$ .<sup>7</sup> While *arachno* tetraosmium carbonyl boride cluster has a framework derived from an octahedron with two adjacent equatorial vertexes removed and another *arachno* pentaosmium carbonyl boride cluster has a framework that is based upon a pentagonal bipyramidal structure from which two nonadjacent equatorial vertexes have been removed, the framework of hexaosmium boride cluster which does not confirm to electron counting rule can be viewed as being derived from a pentagonal bipyramid with one equatorial vertex removed. However, these clusters were obtained from the thermolysis of  $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu\text{-BCO})$  in very low yields and thus the synthetic procedure has been investigated.

Reported here are improved synthesis of the previously reported tetra-osmium  $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$  and

hexa-osmium carbonyl boride cluster  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  and proposed reaction pathways for the formation of  $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$ .

EXPERIMENTAL SECTION

General Data

All reactions were performed under inert atmosphere conditions. Standard vacuum line and inert-atmosphere techniques were employed.<sup>8</sup>  $\text{Os}_3(\text{CO})_{12}$  (Strem) was used as received.  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$  was prepared according to the literature method.<sup>9</sup>  $\text{BH}_3 \cdot \text{N}(\text{C}_2\text{H}_5)_3$  (Aldrich) was stored in a glovebox refrigerator and used as received. Solvents were dried with  $\text{P}_2\text{O}_5$  or Na, distilled and stored in a sealed flask. Thin-layer chromatography plates (J.T. Baker, 250 m) were activated at 45 °C for 24 hours before use. <sup>1</sup>H and <sup>11</sup>B NMR spectra were obtained using a brucker AM-300. NMR chemical shifts are referenced to  $\text{Si}(\text{CH}_3)_4$  (<sup>1</sup>H,  $\delta=0.00$  ppm) and  $\text{BF}_3 \cdot \text{OEt}_2$  (<sup>11</sup>B,  $\delta=0.00$  ppm). Infrared spectra were recorded on a Mattson Polaris Fourier transition spectrometer with 2 cm<sup>-1</sup> 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 reaction of  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$  with  $\text{BH}_3 \cdot \text{NEt}_3$**

$(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$  (300 mg, 0.353 mmol) was placed in a 100 mL flask equipped with a Kontes vacuum adaptor and 30 mL volume of hexane was condensed into the flask at  $-78^\circ\text{C}$ . In the glovebox, borane complex  $\text{BH}_3 \cdot \text{NEt}_3$  (1.00 mmol) was added to the flask via syringe. The contents of the flask were frozen and the flask was evacuated several times to ensure that no nitrogen from the glovebox atmosphere remained. After being warmed to room temperature, the solution was stirred at  $70^\circ\text{C}$  for 1 h during which time the solution became yellow. The volatile components were removed by means of dynamic high vacuum leaving brown residue. The products were separated by preparative TLC on 2 mm silica using a mixed solvent toluene/hexane as an eluent. A light yellow band ( $R_f = 0.74$ ) was identified by NMR and IR spectroscopy as the previously reported tetraosmium carbonyl boride cluster  $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$  (98 mg, 0.088 mmol, 33% yield based on  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ :  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $30^\circ\text{C}$ )  $-9.5$  (q,  $J_{\text{BH}}=65$  Hz),  $-24.3$ (s) ppm;  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ,  $30^\circ\text{C}$ )  $119.7$  (t,  $J_{\text{HB}}=65$  Hz) ppm; IR ( $\text{C}_6\text{H}_{12}$ ,  $\nu_{\text{CO}}$ ) 2075 vs, 2054 m, 2028 m, 2015 m, 2010 m, 1996  $\text{cm}^{-1}$ .

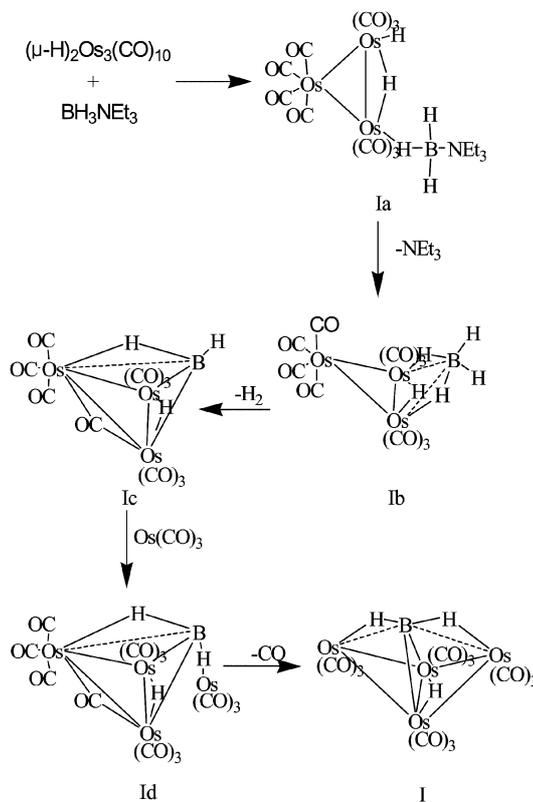
A light brown band ( $R_f = 0.50$ ) in the preparative TLC on silica above was identified by NMR and IR spectroscopy as hexaosmium carbonyl boride cluster  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  (63 mg, 0.039 mmol, 21% yield based on  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ :  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $30^\circ\text{C}$ )  $-9.5$  (t,  $J_{\text{BH}}=5$  Hz),  $-16.9$  (d,  $J_{\text{BH}}=5$  Hz) ppm;  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ,  $30^\circ\text{C}$ )  $188.4$  (s) ppm; IR ( $\text{C}_6\text{H}_{12}$ ,  $\nu_{\text{CO}}$ ) 2080 m, 2062 s, 2035 m, 2026  $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSIONS

Earlier, we found that the thermolysis of  $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu\text{-BCO})$  in toluene at  $110^\circ\text{C}$  for 3 days produced the tetra- and hexaosmium carbonyl boride clusters,  $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$ <sup>6</sup> and  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$ <sup>7</sup> in 4.1% and 2.3% yields, respectively. These observations are consistent with the well-known tendency for osmium carbonyl clusters to condense to higher nuclearity clusters upon thermolysis.<sup>10</sup> However, the synthetic method is required to improve the very low yields. The previously reported clus-

ters  $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$  and  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  are formed in 33% and 21% yields when the reaction of  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$  with  $\text{BH}_3 \cdot \text{NEt}_3$  occurs at  $70^\circ\text{C}$  for 1 h. This new procedure is superior to the previous one in that the latter guarantees higher yields with reduced reaction time is required and the yields are much higher.

The observation of the intermediates in the formation of  $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$  was not successful. However, the reaction pathways for the formation of  $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$  can be proposed as shown in Scheme 1 based on known chemistry of boranes and the product obtained.  $\text{BH}_3 \cdot \text{NEt}_3$  can function as an electron pair donor through a B-H bond, adding to the unsaturated cluster  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$  by forming as Os-H-B bond and then the formation of the initial adduct Ia occurs. The ability of  $\text{BH}_3 \cdot \text{L}$  ( $\text{L}=\text{Lewis base}$ ) type complexes to add to transition

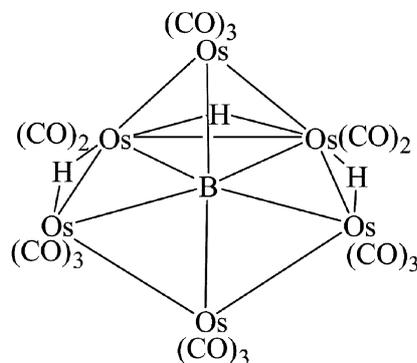


Scheme 1. Proposed reaction pathways for the formation of  $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$ .

metals through the formation of metal-H-B bonds is well-known.<sup>11</sup>  $\text{BH}_3 \cdot \text{NEt}_3$  is significantly dissociated at 70 °C, thereby inducing the formation of intermediate Ib with two Os-H-B bonds. The initial adducts occurring through the formation of Os-H-B in the *Scheme 1* are based on the reaction pathways for the formation of triosmium carbonyl borylidyne cluster  $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu\text{-BCO})$  in the reaction of  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$  with  $\text{B}_2\text{H}_6$  and  $\text{BH}_3 \cdot \text{NEt}_3$  at room temperature.<sup>12</sup> The proposed intermediate Ib is similar in structure to that assigned to its analogue  $\text{Os}_3(\text{CO})_{10}\text{CH}_4$ .<sup>13</sup>

While insertion of boron atom into an osmium-carbonyl bond of the  $\text{Os}(\text{CO})_4$  unit with concomitant reductive elimination of  $\text{H}_2$  produces  $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu\text{-BCO})$ , the complex is not observed in this reaction. This result shows the insertion of boron atom into the osmium-carbonyl bond does not occur in the reaction. Instead, reductive elimination of  $\text{H}_2$  from the intermediate Ib would lead to intermediate Ic which has a bridge B-H-Os hydrogen and a bridge Os-CO-Os carbonyl. The intermediate Ic combines with  $\text{Os}(\text{CO})_3$ , which is a fragment of  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ , through the formation of B-H-Os bond and a Os-Os bond between two electron deficient  $\text{Os}(\text{CO})_3$  units. Although intermediate Ic was not observed, Fehlner has prepared the iron analogue of Ic.<sup>14</sup> Finally, the dissociation of the Os-CO-Os bridge carbonyl induces the formation of another Os-Os bond to produce tetraosmium carbonyl boride cluster  $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$ .

Hexaosmium carbonyl boride cluster  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  contains 86 valence electrons with seven skeletal electron pairs.<sup>15</sup> However, the cluster does not possess one of the geometries previously observed for  $\text{Os}_6$  cluster with 86 valence electrons which conform to electron counting rule.<sup>16</sup> 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 in *Fig. 1*. It contains an interstitial boron atom. Many high nuclearity clusters were originally prepared by unplanned routes or by-products. Meanwhile,  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  was formed efficiently in the reaction of  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$  with  $\text{BH}_3 \cdot \text{NEt}_3$  in high yield. Although the system-



*Fig. 1.* Molecular structure of  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$ .

atic procedures for the formation of the cluster are too complicated, it can be deduced that  $\text{Os}_3\text{B}$  unit such as intermediate Ic in *Scheme 1* combines with an electron deficient  $\text{Os}_3$  unit to produce  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  through dissociation of CO and reductive elimination of  $\text{H}_2$ .

In summary, the clusters  $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$  and  $\text{H}_3\text{Os}_6(\text{CO})_{16}\text{B}$  were produced in the reaction of  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$  with  $\text{BH}_3 \cdot \text{NEt}_3$  at 70 °C for 1 hour which is superior to previous one because significantly less reaction time is required and the yields are much higher. The reaction pathways for the formation of  $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$  can be proposed as shown in *Scheme 1*.

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