

## Coordination Chemistry

# Cage Opening of a Carborane Ligand by Metal Cluster Complexes

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**Abstract:** The reaction of  $Os_3(CO)_{10}(NCMe)_2$  with closo-o-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> has yielded two interconvertible isomers Os<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ -4,5,9-C<sub>2</sub>B<sub>10</sub>H<sub>8</sub>)( $\mu$ -H)<sub>2</sub> (**1 a**) and Os<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ -3,4,8-C<sub>2</sub>B<sub>10</sub>H<sub>8</sub>)( $\mu$ -H)<sub>2</sub> (**1 b**) formed by the loss of the two NCMe ligands and one CO ligand from the Os<sub>3</sub> cluster. Two BH bonds of the *o*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> were activated in its addition to the osmium cluster. A second triosmium cluster was added to the **1a/1b** mixture to yield the complex Os<sub>3</sub>(CO)<sub>9</sub>( $\mu$ -H)<sub>2</sub>( $\mu_3$ -4,5,9- $\mu_3$ -7,11,12-C<sub>2</sub>B<sub>10</sub>H<sub>7</sub>)Os<sub>3</sub>(CO)<sub>9</sub>( $\mu$ -H)<sub>3</sub> (**2**) that contains two triosmium triangles attached to the same carborane cage. When heated, **2** was transformed to the complex Os<sub>3</sub>(CO)<sub>9</sub>( $\mu$ -H)(**3**) by a novel opening of the carborane cage with loss of H<sub>2</sub>.

Cage stability is one of the hallmarks of the closo polyhedral boranes and carboranes.<sup>[1–2]</sup> The stability is created by electron delocalization manifested in their highly delocalized bonding molecular orbitals. Carboranes are structures in which some of the BH groups of the boranes are replaced by CH groups.<sup>[2]</sup> These substitutions lead to inequivalences and differences in reactivity of the remaining BH groups.<sup>[3]</sup> Studies have shown the strong bases can attack the most electron deficient BH groups leading to cage rupture including, in many cases, complete removal (deboronation) of a BH group from the cage.<sup>[4]</sup>

Two products,  $Os_3(CO)_9(\mu_3-4,5,9-C_2B_{10}H_8)(\mu-H)_2$  (**1 a**) and  $Os_3(CO)_9(\mu_3-3,4,8-C_2B_{10}H_8)(\mu-H)_2$  (**1 b**) were obtained from the reaction of  $Os_3(CO)_{10}(NCMe)_2$  with closo-o- $C_2B_{10}H_{10}$  in toluene solvent at 110°C for 1.5 h. ORTEP diagrams of the molecular structures **1a** and **1b** are shown in Figures 1 and 2. Compounds **1a** and **1b** are isomers formed by the loss of the two NCMe ligands and one CO ligand from the  $Os_3(CO)_{10}(NCMe)_2$ , and the addition of one equivalent of  $closo-C_2B_{10}H_{10}$  to the triosmium cluster. The carborane is a triply bridging ligand containing two direct Os –B bonds, and one agostically-coordinated BH group to the third metal atom in each isomer. The distances of the direct Os–B bonds, Os(1)–B(5)=2.168(10), Os(3)–B(4)=2.181(10) Å for **1a**, and Os(1)–B(3)=2.189(11), Os(3)-

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**Figure 1.** An ORTEP diagram of the molecular structure of  $Os_3(CO)_5(\mu_3-4,5,9-C_2B_{10}H_{10})(\mu-H)_2$  (**1 a**) showing 30% thermal ellipsoid probability. Selected interatomic bond distances [Å] are as follows: Os(1)-B(5) = 2.168(10), Os(3)-B(4) = 2.181(10), Os(2)-B(9) = 2.624(10), Os(2)-H(9a) = 1.64(16), B(9)-H(9a) = 1.41(16), and C(1)-C(2) = 1.594(13).



**Figure 2.** An ORTEP diagram of the molecular structure of  $Os_3(CO)_9(\mu_3-3,4,8-C_2B_{10}H_{10})(\mu-H)_2$  (**1 b**) showing 30% thermal ellipsoid probability. Selected interatomic bond distances [Å] are as follows: Os(1)-B(3) = 2.189(11), Os(3)-B(4) = 2.176(12), Os(2)-B(8) = 2.629(13), Os(2)-H(8a) = 1.70(18), B(8)-H(8a) = 1.03(18), and C(1)-C(2) = 1.645(15).

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B(4) = 2.176(12) Å for **1 b**, are considerably shorter than the distance to the agostically coordinated BH groups, B(9)-H(9a) bond, B(9)-H(9a) = 1.41(16), Os(2)-B(9) = 2.624(10), and Os(2)-H(9a) = 1.64(16) Å, in **1a**, and B(8)–H(8a) = 1.03(18), Os(2)– B(8) = 2.629(13), and Os(2)–H(8a) = 1.70(18) Å for **1 b**. Agostically coordinated B-H bonds exhibit characteristically longer M-B distances.<sup>[7]</sup> Two B–H bonds were cleaved from the cage in the ligation process and the hydrogen atoms were shifted to the metal atoms to become bridging hydrido ligands as shown in Figures 1 and 2: <sup>1</sup>H NMR:  $\delta = -17.90$  (s, 1 H), -20.25 ppm (s, 1 H) for **1a** and  $\delta = -17.93$  (s, 1 H), -20.22 ppm (s, 1 H) for **1b**. The boron atoms from the cleaved B-H bonds are the ones coordinated directly to the metal atoms. The hydrogen atoms of the agostically coordinated BH groups are also characteristically shifted upfield and appear as a quartet due to  $^{1}J$  coupling to the neighboring boron atom: for **1a**:  $\delta = -9.97$  ppm (g, br, B–H $\rightarrow$ Os), <sup>1</sup>J<sub>B–H</sub>=76 Hz; for **1b**:  $\delta$ =-9.91 ppm (q, br, B–H $\rightarrow$ Os),  ${}^{1}J_{B-H} = 78$  Hz.<sup>[8]</sup> Isomers **1a** and **1b** differ principally by the B<sub>3</sub> triangle through which the carborane is coordinated to the Os<sub>3</sub> triangle. For **1a** it is coordinated to the 4,5,9 triangle, but for 1b it is coordinated to the 3,4,8 triangle. The locations of the carbon atoms in each carborane ligand were identified by their characteristically short C-C bond distance.

Compounds **1a** and **1b** can be interconverted thermally. The equilibrium ratio 1a/1b = 0.63 in toluene solvent was achieved by heating **1a** at 108 °C for 48 h. In the transformation of **1a** to **1b**, the carborane cage must shift by two B<sub>3</sub> triangles and must involve the addition of a hydrogen atom to B5 and a cleavage of the hydrogen atom from B3. It is likely that the hydrido ligands on the metal cluster participate in these hydrogen exchanges, but details of the mechanism are not available at this time.

Interestingly, **1a** and **1b** react with a second equivalent of  $Os_3(CO)_{10}(NCMe)_2$  at 97 °C to yield two new hexaosmium compounds:  $Os_3(CO)_9(\mu-H)_2(\mu_3-4,5,9-\mu_3-7,11,12-C_2B_{10}H_7)Os_3(CO)_9(\mu-H)_3$  (**2**) (38% yield) and  $Os_3(CO)_9(\mu-H)(\mu_3-3,4,8-\mu_3-7,11,12-C_2B_{10}H_8)Os_3(CO)_9(\mu-H)$  (**3**) (5% yield). Compound **2** can be converted to **3** in 15% yield by heating a solution of **2** in nonane solvent to reflux for 1.25 h. Compounds **2** and **3** have both been characterized by a combination of IR, NMR and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **2** is shown in Figure 3.

Compound **2** contains a  $C_2B_{10}H_7$  cage sandwiched between two triangular triosmium carbonyl clusters. The metal clusters bridge the 4,5,9 and 7,11,12 B<sub>3</sub> triangles of the closo- $C_2B_{10}H_7$ cage. Two boron atoms, Os(1)-B(4) = 2.169(11), Os(3)-B(5) =2.188(11) Å, and one agostically coordinated BH group, Os(2)-B(9) = 2.593(11), Os(2)-H(9 A) = 1.86(10) Å, <sup>1</sup>H NMR  $\delta =$ -9.70 ppm (q, 1 H), <sup>1</sup> $J_{B-H} = ~82$  Hz, are bonded to the Os(1)-Os(2)-Os(3) triangle. The Os(1)-Os(2)-Os(3) triangle also contains two bridging hydrido ligands that were presumably transferred to the cluster from the two boron atoms that are directly bonded to the osmium atoms. Three boron atoms, Os(4)-B(11) = 2.189(11), Os(5)-B(7) = 2.185(11), and Os(6)-B(11) =2.211(11) Å are directly coordinated to the Os(4)-Os(5)-Os(6) triangle. Accordingly, this Os<sub>3</sub> triangle contains three hydrido ligands with one bridging each of the three Os–Os bonds.



**Figure 3.** An ORTEP diagram of the molecular structure of  $Os_3(CO)_9(\mu-H)_2(\mu_3-4,5,9-\mu_3-7,11,12-C_2B_{10}H_7)Os_3(CO)_9(\mu-H)_3$  (**2**) showing 25% thermal ellipsoid probability. Selected interatomic bond distances [Å] are as follows: Os(1)-B(4) = 2.169(11), Os(2)-B(9) = 2.593(11), Os(3)-B(5) = 2.188(11), Os(4)-B(11) = 2.189(11), Os(5)-B(7) = 2.185(11), Os(6)-B(11) = 2.211(11), Os(2)-H(9A) = 1.30(9), and C(1)-C(2) = 1.603(14).

Except for the presence of one of the bridging hydrido ligands, H(2), on the Os(1)-Os(2)-Os(3) triangle, compound **2** contains overall an approximate reflection symmetry with the symmetry plane passing through the cage atoms C(1), C(2), B(9), and B(12).

An ORTEP diagram of the molecular structure of 3 is shown in Figure 4. Compound 3 also contains two triangular triosmium clusters that are coordinated to a significantly ruptured C<sub>2</sub>B<sub>10</sub>H<sub>8</sub> cage. Each triosmium cluster contains two directly-coordinated boron atoms, one triply-bridging agostic BH group and one bridging hydrido ligand. The Os-B distances to the triply-bridging agostic BH groups, B(3) and B(7), are significantly shorter, Os(1)-B(3) = 2.132(10), Os(2)-B(3) = 2.200(10), Os(3)-B(3) = 2.199(10), Os(1)-H(3A) = 1.85(15), Os(5)-B(7) = 2.150(11),Os(4)-B(7) = 2.235(10), Os(6)-B(7) = 2.191(11) Å, than those to the agostically coordinated BH groups that are coordinated to only one metal atom as found in compounds 1a, 1b, and 2. The resonances of the triply bridging agostic BH groups are shifted to slightly higher field values,  $\delta = -11.83$  (br, 1 H), and -13.56 ppm (br, 1H), than those of 1a, 1b, and 2. The osmium triangle Os(4)-Os(5)-Os(6) is bonded to the same group of boron atoms, 7,11,12, as found in 2, but the Os(1)-Os(2)-Os(3) group is bonded instead to the B<sub>3</sub> group 3,4,8 and thus was shifted in the course of the conversion of 2 to 3.

We have analyzed the transformation of **2** into **3** in terms a two-step mechanism as shown in Scheme 1. The process begins with a shift of the Os(1)-Os(2)-Os(3) cluster from the 4,5,9  $B_3$ -triangle to the 3,4,8  $B_3$ -triangle. In the process, a hydrogen atom is shifted to B(5) and one is cleaved from B(3). This step would lead to the formation of an intermediate represent-

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Scheme 1. A proposed mechanism for the transformation of 2 to 3. The red lines in the Intermediate 2a indicate the cage bonds that must be cleaved in the cage-opening process.



Figure 4. An ORTEP diagram of the molecular structure of  $Os_3(CO)_9(\mu-H)(\mu_3-3,4,8-\mu_3-7,11,12-C_2B_{10}H_8)Os_3(CO)_9(\mu-H)$  (3) showing 20% thermal ellipsoid probability. Selected interatomic bond distances [Å] are as follows Os(1)-B(3)=2.132(10), Os(2)-B(3)=2.200(10), Os(3)-B(3)=2.199(10), Os(1)-H(3A)=1.85(15), Os(2)-B(4)=2.291(11), Os(3)-B(8)=2.304(10), Os(5)-B(7)=2.150(11), Os(4)-B(7)=2.235(10), Os(6)-B(7)=2.191(11), Os(4)-B(11)=2.307(10), Os(6)-B(12)=2.335(10), and C(1)-C(2)=1.446(14).

ed as **2a** in Scheme 1. This step of the rearrangement is formally equivalent to the isomerization of **1a** to **1b** described above. The opening of the  $C_2B_{10}$  cage requires the cleavage of five cage bonds, B(3)–B(7), B(3)–C(1), B(3)–C(2), B(7)–C(2), and B(7)–B(8). The sequence of these cleavages is not known at present, but we are willing to speculate that the process begins with cleavage of the bonds between B(3) and the two carbon atoms, C(1) and C(2), because previous studies have shown that these B(3)–C cage bonds are the first to cleave upon the addition of bases to  $1,2-C_2B_{10}H_{12}$ .<sup>[4]</sup> Hydrogen atoms, presumably from the metal atoms, are added to the boron atoms B(3) and B(7). These additions would facilitate cleavage of the bonds to B(7), particularly B(3)–B(7), and also B(7)–C(2) and B(7)–B(8), to complete the cage opening process. Two hydrogen atoms were eliminated, presumably as  $H_2$ , in the transformation of **2** to **3**.

The metalated boron cages reported herein are the rare examples of the unsupported metal-boryl complexes of unsubstituted icosahedral carboranes. The formation of transition-metal B-carboranyl bonds by nondirected B–H activation has been reported only for the reaction of  $o-C_2B_{10}H_{12}$  and  $[Ir(PPh_3)_3CI]$  or  $[Ir(AsPh_3)_3CI]$ .<sup>[9]</sup> Furthermore, compound **2** is the first example of the complex containing a total of five metal-boryl bonds on a single icosahedral carborane cage.

It is anticipated that similar cluster-induced cage-opening reactions can be obtained with other carboranes and by using clusters of different transition metals. Indeed, Du et al. have shown that reaction of the carborane, closo-4-CB<sub>8</sub>H<sub>9</sub>, with [Ru<sub>3</sub>(CO)<sub>12</sub>] proceeds by formation of an Ru<sub>6</sub> raft from which three of the ruthenium atoms have been inserted into the carborane cage to form a 12-vertex triruthenacarborane.<sup>[10]</sup> It will be interesting to see if carboranes will also open when they are deposited on clean metal surfaces and, if so, could carboranes serve as precursors to "carborene" hybrids of graphenes<sup>[11]</sup> and borophenes<sup>[12]</sup> on metal surfaces?

#### **Experimental Section**

#### Synthesis of 1 a and 1 b

 $C_2B_{10}H_{12}$  (7.4 mg, 0.0513 mmol) was added to  $Os_3(CO)_{10}(NCMe)_2$  (48.0 mg, 0.0515 mmol) dissolved in toluene (30 mL) and then heated to reflux for 1.5 h. After removal of the solvent in vacuo, TLC analysis was performed on alumina which provided **1a** and **1b** in yields of 26 and 9%, respectively.

#### Synthesis of 2 and 3

Complex 1 (27.0 mg, 0.0279 mmol) was added to  $Os_3(CO)_{10}(NCMe)_2$  (22.5 mg, 0.0241 mmol) dissolved in heptane (30 mL) and then heated to reflux for 1.25 h. After removal of solvent in vacuo, TLC analysis was performed on silica which provided **2** and **3** in yields of 38 and 5 %, respectively.

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#### Interconversion of 1 a/1 b

Conversion of **1a** to **1b** and vice versa was performed by dissolving either **1a** or **1b** in  $[D_8]$ toluene and heating at 108 °C for 43 h. The ratio of the two isomers was then measured by NMR spectroscopic integration. Conversion of **2** to **3** was performed by simply heating **2** in a nonane solution at reflux for 1.25 h.

#### Single-crystal structure determination

The intensity data were collected by using a Bruker SMART APEX CCD-based diffractometer with Mo<sub>Ka</sub> radiation ( $\lambda = 0.71073$  Å) at 294 K. All nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-square refinements.

**Crystal data for 1 a:**  $Os_3O_9C_{11}B_{10}H_{12}$  monoclinic;  $P2_1/n$ ;  $M_r$ = 966.91 g mol<sup>-1</sup>; a=8.1347(12), b=20.133(3), c=13.984(2) Å; a= 90.00,  $\beta$ =94.286(3),  $\gamma$ =90.00°; V=2283.9(6) Å<sup>3</sup>; Z=4;  $\rho_{calcd}$ = 2.812 g cm<sup>-3</sup>;  $\mu$ =16.690 mm<sup>-1</sup>;  $2\theta_{max}$ =56.70°; F(000)=1712;  $R_{int}$ = 0.0560; no. collected/unique/ $I_o$ >2 $\sigma I_o$  data=22609/4016/3738; R1/WR2 (alldata)=0.0528/0.1331;  $R1/WR2(I_o$ >2 $\sigma I_o)$ =0.0509/0.1307; max/min. electron density=4.105/-3.346 e-Å<sup>-3</sup>.

**Crystal data for 1b**:  $Os_3O_9C_{11}B_{10}H_{12}$  monoclinic;  $P2_1/n$ ;  $M_r$ = 966.91 g mol<sup>-1</sup>; a=8.2829(8), b=19.6941(19), c=14.0536(14) Å;  $\alpha$ =90.00,  $\beta$ =96.960(2),  $\gamma$ =90.00°; V=2275.6(4) Å<sup>3</sup>; Z=4;  $\rho_{calcd}$ = 2.822 g cm<sup>-3</sup>;  $\mu$ =16.750 mm<sup>-1</sup>;  $2\theta_{max}$ =52.18°; F(000)=1712;  $R_{int}$ = 0.0804, no.collected/unique/ $I_o$ >2 $\sigma I_o$  data=23765/4015/3342; R1/wR2 (alldata)=0.0464/0.0905;  $R1/wR2(I_o$ >2 $\sigma I_o$ )=0.0362/0.0849; max/min. electron density=1.697/-1.199 e-Å<sup>-3</sup>.

**Crystal data for 2**:  $Os_6O_{18}C_{20}B_{10}H_{12}$  monoclinic;  $P2_1/n$ ,  $M_r$ = 1789.79 g mol<sup>-1</sup>; a=9.6636(2), b=15.4422(4), c=25.6755(6) Å; a= 90.00,  $\beta$ =90.5760(10),  $\gamma$ =90.00°; V=3831.29(16) Å<sup>-3</sup>; Z=4;  $\rho_{calcd}$ = 3.103 g cm<sup>-3</sup>;  $\mu$ =19.888 mm<sup>-1</sup>;  $2\theta_{max}$ =56.67°; F(000)=3128;  $R_{int}$ = 0.0740; no.collected/unique/ $l_o$ >2 $\sigma l_o$ data=45720/6784/5836; *R*1/*wR*2 (alldata)=0.0450/0.1017; *R*1/*wR*2( $l_o$ >2 $\sigma l_o$ )=0.0378/0.0961; max/min. electron density=2.068/-1.741 e-Å<sup>-3</sup>.

**Crystal data for 3**:  $Os_6O_{18}C_{20.5}B_{10}CIH_{10}$  monoclinic, C2/c,  $M_r = 1808.31 \text{ gmol}^{-1}$ ; a = 19.2832(13), b = 18.0798(12), c = 23.6626(16) Å; a = 90.00,  $\beta = 108.5790(10)$ ,  $\gamma = 90.00^{\circ}$ ; V = 7819.7(9) Å<sup>3</sup>; Z = 8;  $\rho_{calcd} = 3.072 \text{ gcm}^{-3}$ ;  $\mu = 19.523 \text{ mm}^{-1}$ ;  $2\theta_{max} = 56.78^{\circ}$ ; F(000) = 6332;  $R_{int} = 0.0551$ ; no.collected/unique/ $l_o > 2\sigma l_o$  data = 41237/6912/ 6178; R1/wR2 (alldata) = 0.0372/0.0849;  $R1/wR2(l_o > 2\sigma l_o) = 0.0319/$ 0.0823; max/min. electron density = 1.456/-1.516 e-Å^{-3}.

CCDC 1448072 (1 a), 1448073 (1 b), 1448074 (2) and 1448075 (3) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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