Inorg. Chem. 1993, 32, 3391–3392

Preparation and Structures of the Osmaborides $HOs_5(CO)_{16}B$ and $HOs_4(CO)_{12}BH_2$[†]

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Received March 17, 1993

Although several metal-rich iron[1–3] and ruthenium[4,5] carbonyl clusters containing boron are known, $H_3Os_3(CO)_9BCO$ is the only reported example of an osmium-rich carbonyl cluster containing boron.[6] The boron atom caps a triangle of osmium atoms and is bonded to a carbonyl group. This carbonyl borylidyne cluster is prepared by hydroborating the unsaturated cluster $H_2Os_3(CO)_{10}$. The possibility of preparing other osmium-rich cluster complexes containing boron is of continuing interest to us, and we find that $H_3Os_3(CO)_9BCO$ can serve as a precursor to such clusters.

Reported here are syntheses and structural characterizations of the osmaborides $HOs_5(CO)_{16}B$, the first example of a pentametal boride with an encapsulated boron, and $HOs_4(CO)_{12}BH_2$. These complexes were obtained through the following thermolysis reaction:

$$H_3Os_3(CO)_9BCO \xrightarrow[110\,°C]{\text{toluene}} HOs_4(CO)_{12}BH_2 + HOs_5(CO)_{16}B \qquad (1)$$

$H_3Os_3(CO)_9BCO$ (930 mg, 1.08 mmol) 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 6 days, and solvent was removed by means of rotary evaporation, leaving a brown solid in the flask. The products were separated by prep-TLC on silica using a 1:4 toluene:hexanes mixtures as an eluent. A light yellow band was identified as $HOs_4(CO)_{12}BH_2$ (54 mg, 0.0486 mmol, 4.5% yield based on $H_3Os_3(CO)_9BCO$), and a reddish brown band was identified as $HOs_5(CO)_{16}B$ (32 mg, 0.0227 mmol, 3.4% yield based on $H_3Os_3(CO)_9BCO$). These osmaborides were characterized by single-crystal X-ray analysis[7] and NMR, IR, and mass spectroscopy.

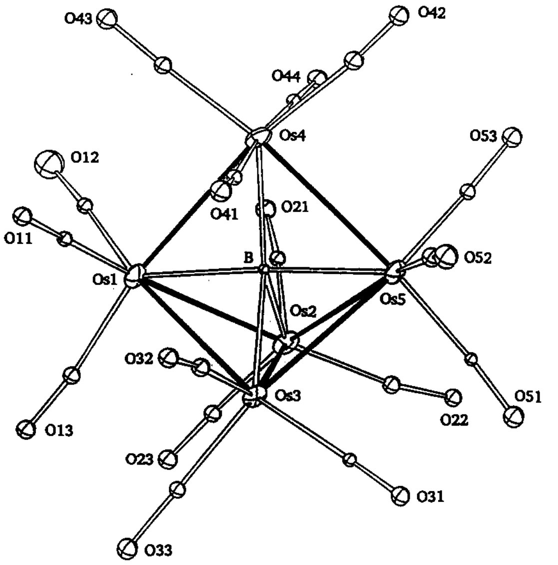

Figure 1. ORTEP plot of the molecular structure of $HOs_5(CO)_{16}B$. Selected bond distances (Å): Os(1)–Os(2) = 2.962(1), Os(1)–Os(3) = 2.957(1), Os(1)–Os(4) = 3.040(1), Os(2)–Os(3) = 2.903(1), Os(2)–Os(5) = 2.979(1), Os(3)–Os(5) = 2.943(1), Os(4)–Os(5) = 2.997(1), Os(1)–B = 2.06(2), Os(2)–B = 2.16(2), Os(3)–B = 2.23(2), Os(4)–B = 2.17(2), Os(5)–B = 2.01(2).

The molecular structure of $HOs_5(CO)_{16}B$ is shown in Figure 1. The five Os atoms define a bridged butterfly metal framework. The boron atom is encapsulated in the cluster, bonded to all five metal atoms. While the hydrogen atom was not located, it is believed to be on the surface of the Os_5 core, perhaps bridging Os(2)–Os(3) or fluxional at room temperature. All sixteen carbonyl groups are terminally coordinated, four to the bridging Os atom and three each to the other four Os atoms. The overall molecular geometry of $HOs_5(CO)_{16}B$ closely resembles those of the pentaosmium carbonyl carbide cluster $Os_5C(CO)_{16}$,[8] containing a carbon atom encapsulated in the Os_5 core, and the related ruthenium–acetonitrile adduct $Ru_5C(CO)_{15}(NCMe)$.[9] The only other reported example of a pentametal boride is a gold derivative of a square pyramidal ruthenaboride which has the boron residing on the square face:[10] $Ru_5(CO)_{15}B(AuPh_3)$. $HOs_5(CO)_{16}B$, like $Os_5C(CO)^{16}$, is a 76-valence-electron system. On the basis of Wade–Williams–Rudolph[11] electron-counting rules, it can be considered to be an *arachno* cluster derived from a pentagonal bipyramid from which nonadjacent equatorial vertices are removed. Selected bond

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[†] Dedicated to Professor Heinrich Nöth in honor of his 65th birthday.

[‡] Deceased.

(1) (a) Harpp, K. S.; Housecroft, C. E.; Rheingold, A. L.; Shongwe, M. S. *J. Chem. Soc., Chem. Commun.* **1988**, 965. (b)Khattar, R.; Puga, J.; Fehlner, T. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 1877.

(2) Vites, J. C.; Housecroft, C. E.; Jacobsen, G. B.; Fehlner, T. P. *Organometallics* **1984**, *3*, 1591.

(3) (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.

(4) (a) Hong, F.-E.; McCarthy, D. A.; White, J. P., III; Cottrell, C. E.; Shore, S. G. *Inorg. Chem.* **1990**, *29*, 2874. (b) Hong, F.-E.; Coffy, T. J.; McCarthy, D. A.; Shore, S. G. *Inorg. Chem.* **1989**, *28*, 3284.

(5) (a) Chipperfield, A. K.; Housecroft, A. E.; Rheingold, A. L. *Organometallics* **1990**, *9*, 681. (b) Chipperfield, A. K.; Housecroft, C. E.; Raithby, P. R. *Organometallics* **1990**, *9*, 479. (c) Chipperfield, A. K.; Housecroft, C. E.; Mathews, D. M. *J. Organomet. Chem.* **1990**, *384*, C38. (d) Chipperfield, A. K.; Housecroft, A. E.; Rheingold, A. L. *J. Organomet. Chem.* **1988**, *349*, C17.

(6) (a) Jan, D.-Y.; Workman, D. P.; Hsu, L.-Y.; Krause, J. A.; Shore, S. G. *Inorg. Chem.* **1992**, *31*, 5123. (b) Shore, S. G.; Jan, D.-Y.; Hsu, L.-Y.; Hsu, W.-L. *J. Am. Chem. Soc.* **1983**, *105*, 5923.

(7) Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. All data were corrected for Lorentz and polarization effects. An empirical absorption correction (ψ-scans) was applied. Crystallographic computations were carried out on a DEC Vax Station 3100 computer, using the Structure Determination Package (SDP). The structure was solved by the direct method Multan 11/82 and difference Fourier synthesis. Full-matrix least-squares procedures were employed. Crystal data for $HOs_5(CO)_{16}B$ (−60 °C): space group $P2_1/n$ (No. 14), a = 8.983(2) Å, b = 18.572(4) Å, c = 15.634(9) Å, β = 93.27(2)°, V = 2604 Å^3, fw = 1410.98, ρ(calcd) 3.599 g/cm^3, Z = 4, μ = 244.2 cm^{-1}; R_f = 0.061, R_{wF} = 0.082, and GOF = 2.958 with 309 variables (including secondary extinction coefficient refined to 3.45 × 10^{-8}) refined for 3538 unique observations [$I \geq 3.0\sigma(I)$] refined of 4930 reflections collected over the 2θ range $4° \leq 2\theta \leq 50°$. Crystal data for $HOs_4(CO)_{12}BH_2$ (−60 °C): space group $P2_1/n$ (No. 14), a = 9.215(2) Å, b = 14.129(4) Å, c = 15.438(2) Å, β = 92.25(1)°, V = 2008.6 Å^3, fw = 1110.76, ρ(calcd) = 3.673 g/cm^3, Z = 4, μ = 253.2 cm^{-1}; R_f = 0.062, R_{wF} = 0.082, and GOF = 2.705 with 228 variables (including secondary extinction coefficient refined to 1.19 × 10^{-7}) refined for 2517 unique observations [$I \geq 3.0\sigma(I)$ of 3518 reflections collected over the 2θ range $4° \leq 2\theta \leq 50°$.

(8) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Nicholls, J. N.; Puga, J.; Rathby, P. R.; Rosales, M. J.; Schroder, M.; Vargas, M. D. *J. Chem. Soc., Dalton Trans.* **1983**, 2447.

(9) Johnson, B. F. G.; Lewis, J.; Nicholls, J. N.; Puga, P. R.; Raithby, P. R.; Rosales, M. J.; McPartlin, M.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1983**, 277.

(10) Housecroft, C. E.; Matthews, D. M.; Rheingold, A. L. *Organometallics* **1992**, *11*, 2959.

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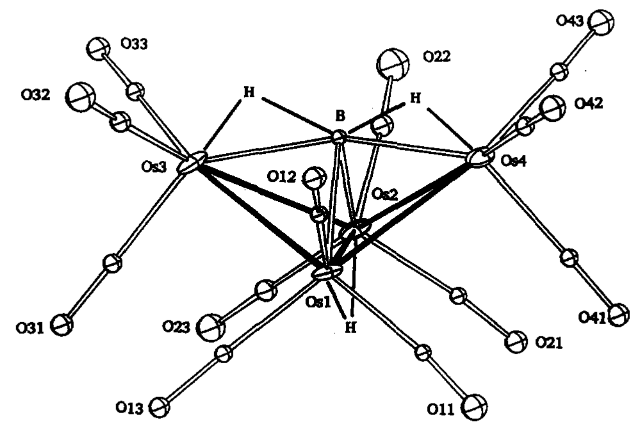

Figure 2. ORTEP plot of the molecular structure of $HOs_4(CO)_{12}BH_2$. Selected bond distances (Å): Os(1)–Os(2) = 2.909(1), Os(1)–Os(3) = 2.867(1), Os(1)–Os(4) = 2.878(1), Os(2)–Os(3) = 2.886(1), Os(2)–Os(4) = 2.884(1), Os(1)–B = 2.26(2), Os(2)–B = 2.21(2), Os(3)–B = 2.09(2), Os(4)–B = 2.11(2).

distances are shown in Figure 1. The dihderal angle between the butterfly wings, the Os(1)Os(2)Os(3) and Os(2)Os(3)Os(5) planes, is 104°. It corresponds well with the value observed for $Os_5C(CO)_{16}$ (101°). ^{11}B NMR ($CDCl_3$, 30 °C): 184.4 ppm (s), 43.6 Hz full width at half maximum. ^1H NMR ($CDCl_3$, 30 °C): −21.19 ppm (s). ^1H NMR ($CDCl_3$, −63 °C): −21.49 ppm (s). IR (ν_{CO}, C_6H_{12}): 2091 m, 2083 m 2073 s, 2059 sh, 2054 s, 2006 m cm^{-1}. MS (FAB): highest intensity peak in the parent envelope calculated for $HBC_{16}O_{16}Os_5$ m/e = 1411; found m/e = 1412. The parent envelope and the distribution of peak intensities in the envelope are in accord with those predicted[13] for natural-abundance isotopic distribution.

The molecular structure of $HOs_4(CO)_{12}BH_2$ is shown in Figure 2. It consists of four $Os(CO)_3$ groups arranged in a butterfly configuration, with the boron atom residing midway between the osmium atoms that define the wing tips. A crystallographically imposed mirror plane passes through Os(3), B, and Os(4). This molecule is isostructural with $HRu_4(CO)_{12}BH_2$[5] and $HFe_4(CO)_{12}BH_2$[3] and accordingly can be considered to be an *arachno*, four-atom cluster with an interstitital boron or alternatively a 62-valence-electron complex in which the BH_2 ligand contributes five electrons on the basis of the skeletal electron-pair theory.[11] Selected bond distances are shown in Figure 2. The dihedral angle between the butterfly wings is 113°. It corresponds well with the values observed for $HRu_4(CO)_{12}BH_2$ (118°) and $HFe_4(CO)_{12}BH_2$ (114°), and it is also consistent with the ideal dihedral angle, 109°, for a four-atom, butterfly, *arachno* cluster derived from an octahedron.

^1H and ^{11}B NMR spectra are consistent with the solid-state molecular structure of $HOs_4(CO)_{12}BH_2$. The ^{11}B NMR spectrum ($CDCl_3$, 30 °C) consists of a triplet [119.7 ppm (t, J_{BH} = 63 Hz), 43.6 Hz full width at half-maximum] reflecting coupling with two bridging hydrogens. The ^1H NMR spectrum ($CDCl_3$, 30 °C) consists of a quartet and a sharp singlet [−9.5 (q, 1:1:1:1, J_{BH} = 65 Hz, B–H–Os), −20.5 ppm (s, Os–H,Os)]. Bridge hydrogens in the neutral molecule do not appear to be fluxional at room temperature. IR (ν_{CO}, C_6H_{12}): 2075 vs, 2067 vs, 2054 m, 2028 vs, 2015 m, 2010 m, 1996 m cm^{-1}. MS (FAB): highest intensity peak in the parent envelope calculated for $H_3BC_{12}O_{12}Os_4$ m/e = 1112; found m/e = 1109. The parent envelope and the distribution of peak intensities in the envelope in general are in accord with those predicted[13] for natural-abundance isotopic distribution.

Removal of an Os–H–B hydrogen occurs in the reaction of an equimolar amount of KH with $HOs_4(CO)_{12}BH_2$ in Me_2O at −78 °C over a period of 12 h to give $K[HOs_4(CO)_{12}BH]$, a brownish yellow solid that was shown from its NMR spectra to possess a remaining Os–H–B hydrogen and an Os–H–Os bond. ^{11}B NMR (glyme-d_{10}, 30 °C): 129.9 ppm (partially collapsed doublet, J_{BH} = 88 Hz). ^1H NMR (glyme-d_{10}, 30 °C): −8.7 (partially collapsed quartet, br, Os–H–B), −20.3 ppm (s, Os–H–Os). IR (ν_{CO}, C_6H_{12}): 2068 s, 2048 m, 2035 w, 2020 s, 1999 w, 1991 w cm^{-1}. Reaction of $HOs_4(CO)_{12}BH_2$ with excess KH in THF at room temperature for 2 days results in deprotonation of both Os–H–B bonds to form $K_2[HOs_5(CO)_{12}B]$. ^{11}B NMR (THF-d_8, 30 °C): 142 ppm (s). ^1H NMR (THF-d_8, 30 °C): −18.9 ppm (s, Os–H–Os). IR (ν_{CO}, C_6H_{12}): 2035 s, 2017 s, 2008 m, 1993 s, 1967 s, 1961 m cm^{-1}. The removal of two bridge hydrogens is in accord with deprotonation studies of $HRu_4(CO)_{12}BH_2$[4a] and also further confirms Fehlner's[12] prediction that although the first two protons removed from $HFe(CO)_{12}BH_{12}$ are from Fe–H–B and Fe–H–Fe bonds, the first two protons to be removed from the ruthenium and osmium analogues would come from the Ru–H–B and Os–H–B bonds.

Attempted deprotonation of $HOs_5(CO)^{16}B$ resulted in decomposition of the cluster.

Acknowledgment. We thank the National Science Foundation for support of this work through Grant CHE91-04035. FAB mass spectra and NMR spectra were obtained at the Ohio State University Chemical Instrumentation Center (funded in part by National Science Foundation Grant No. 79-10019 and National Institutes of Health Grant No. 1 S10 PRO140518-01A).

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances, bond angles, and anisotropic displacement parameters (14 pages). Ordering information is given on any current masthead page.

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(11) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976,** *18,* 1. Williams, R. E. *Inorg. Chem.* **1971,** *10,* 210. Rudolph, R. W.; Pretzer, W. R. *Inorg. Chem.* **1972,** *11,* 1974.

(12) (a) Fehlner, T. P. *Polyhedron* **1990,** *9,* 1955. (b) Fehlner, T. P. *Comments on Inorganic Chemistry*; Gordon & Breach Science Publishers, Inc.: London, 1988; Vol. 7, No. 6, p 326.

(13) Calculated from a program developed by J. Norton and C. Scott, Colorado State University, Ft. Collins, CO.