Hydroboration of $(\mu\text{-H})_2Os_3(CO)_{10}$: Formation of the Borylidyne Cluster $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$. An Improved Synthesis of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})^{\dagger}$

Jang-Hoon Chung, Edwin P. Boyd, Jianping Liu, and Sheldon G. Shore*

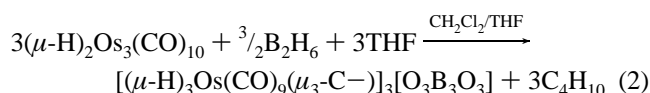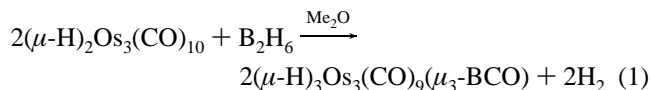Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

At room temperature, the reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ with $BH_3S(CH_3)_2$ produces the new borylidyne cluster $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$, a methylidyne cluster analog. At 65 °C the previously reported ketenylidene cluster analog $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ is formed. The complex $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$ was characterized by ^1H NMR, ^{11}B NMR, and infrared spectroscopies as well as mass spectrometry. Its molecular structure was determined from a single-crystal X-ray analysis. The molecule is of approximate C_s symmetry. It consists of a tetrahedral Os_3B core with a terminal B−H bond, two Os−H−B, hydrogen bridge bonds, and three $Os(CO)_3$ units. A similar structure has been proposed for one of the isomers of a ruthenium analog, $(\mu\text{-H})_2Ru_3(CO)_9(\mu\text{-H})_2BH$, but it differs from the related iron complex $(\mu\text{-H})Fe_3(CO)_9(\mu\text{-H})_3BH$ which has three Fe−H−B bridge bonds. Crystal data for $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$: triclinic space group $P\bar{1}$, $a = 9.501(4)$ Å, $b = 9.525(4)$ Å, $c = 10.070(2)$ Å, $\alpha = 87.72(3)$ $\beta = 88.32(3)°$, $\gamma = 61.45(3)°$, $Z = 2$.

Introduction

In earlier reports[1] we described the first examples of the hydroboration of the unsaturated metal−metal bond in $(\mu\text{-H})_2Os_3(CO)_{10}$. Hydroboration products depend upon reaction conditions employed (reactions 1 and 2). These products show

$$2(\mu\text{-H})_2Os_3(CO)_{10} + B_2H_6 \xrightarrow{Me_2O}$$
$$2(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO}) + 2H_2 \quad (1)$$

$$3(\mu\text{-H})_2Os_3(CO)_{10} + {}^3/_2B_2H_6 + 3THF \xrightarrow{CH_2Cl_2/THF}$$
$$[(\mu\text{-H})_3Os(CO)_9(\mu_3\text{-C}-)]_3[O_3B_3O_3] + 3C_4H_{10} \quad (2)$$

interesting derivative chemistry. The complex $[(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-C}-)]_3[O_3B_3O_3]$ reacts with BX_3 (X = Cl, Br) to give halomethylidyne clusters $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CX})$,[1a,c] but in benzene in the presence of BF_3 a Friedel−Crafts type reaction occurs to form the phenylmethylidyne cluster $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CPh})$. This type of Friedel−Crafts reaction is also observed in the reaction of $[(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-C}-)]_3[O_3B_3O_3]$ with the boron hydride B_5H_9 and the carborane $1,2\text{-}C_2B_{10}H_{12}$.[1e] The CO of the BCO unit in $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ can be reduced by BH_3THF to produce the vinylidene cluster analog $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-BCH}_2)$.[2a] Pyrolysis of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ yields the osmaboride clusters $HOs_4(CO)_{12}BH$,[2b] $HOs_5(CO)_{16}B$,[2b] and $H_3Os_6(CO)_{16}B$.[2c]

Reported here are results of studies of the reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ with $BH_3S(CH_3)_2$ which led to the preparation of the new borylidyne cluster $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$, a methylidyne cluster analog, and an improved synthesis of the previously reported ketenylidene cluster analog $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$.[1a,b]

Results and Discussion

$(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$. The borylidyne cluster $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$ is produced in 45% yields from the reaction of $H_2Os_3(CO)_{10}$ with $BH_3S(CH_3)_2$ for 1 week at room temperature. A minute amount of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ identified by a very weak signal in the ^1H spectrum is also formed. Boron-11 and proton NMR spectra were obtained from solutions of a crop of single crystals that also provided the single crystal for the X-ray structure determination. The ^{11}B resonance is a broad signal that occurs at 18.5 ppm which narrows considerably upon proton decoupling. The ^1H NMR spectrum consists of three signals: 4.7 ppm (broad, BH), −13.6 ppm (broad, Os−H−B), −20.5 ppm (sharp, Os−H−Os). These NMR results are consistent with the NMR spectra obtained from iron[4] and ruthenium[5] borylidyne clusters. The ^1H NMR spectrum of $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$ shows no changes in chemical shifts in the temperature range 233 to 363 K, but the signals are noticeably broadened with increasing temperature.

The previously reported ketenylidene cluster analog $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$[1a,b] is formed in 85% yield when the reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ with BH_3SMe_2 occurs at 65 °C for 1 h. A small amount of $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$ was detected in the ^1H NMR spectrum. Although the yield is equivalent to that obtained in the earlier synthetic procedure, this new procedure is superior to that described previously[1b] because significantly less reaction time is required.

Although it is conceivable that $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ is an intermediate in the formation of $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$,

---

† This work is dedicated to Prof. Dr. G. Huttner in honor of his 60th birthday.
⊗ Abstract published in *Advance ACS Abstracts,* September 15, 1997.
(1) (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, W.-L. *J. Am. Chem. Soc.* **1983,** *105,* 5923. (c) Shore, S. G.; Jan, D.-Y.; Hsu, L.-Y.; Kennedy, S.; Hoffman, J. C.; Lin Wang, T.-C.; Marshall, A. G. *J. Chem. Soc., Chem. Commun.* **1984,** 392. (d) Shore, S. G. In *Inorganic Chemistry Toward the 21st Century*; Chisholm, M., Ed.; ACS Symposium Series 211; American Chemical Society: Washington, DC, 1983; p 399. (e) Wermer, J. R.; Jan, D.-Y; Getman, T. D.; Moher, E.; Shore, S. G. *Inorg. Chem.* **1988,** *27,* 4274.
(2) (a) Jan, D.-Y.; Shore, S. G. *Organometallics* **1987,** *6,* 428. (b) Chung, J.-H.; Knoeppel, D.; McCarthy, D.; Columbie, A.; Shore, S. G. *Inorg. Chem.* **1993,** *32,* 3391. (c) Chung, J.-H Doctoral Dissertation, The Ohio State University, 1994.

(3) Wade, K. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980; p 193.
(4) Vites, J. C.; Eigenbrot, C.; Fehlner, T. P. *J. Am. Chem. Soc.* **1984,** *106,* 4633.
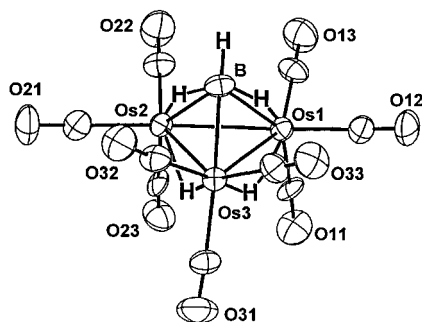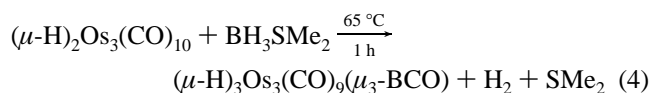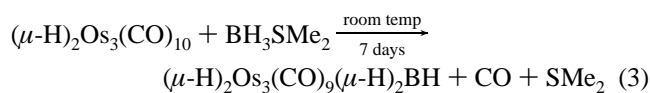(5) Chipperfield, A. K.; Housecroft, C. E. *J. Organomet. Chem.* **1988,** *349,* C17.

Figure 1. Molecular structure of $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$ (50% probablility thermal ellipsoids).

Figure 2. Arrangement of bridge hydrogens in isomers of $H_4M_3(CO)_9$-BH (M = Fe, Ru, Os).

no evidence could be obtained to demonstrate this possibility. Under the conditions described above for the formation of $(\mu\text{-}H)_2Os_3(CO)_9(\mu\text{-H})_2BH$ from the reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ with BH_3SMe_2, there was no apparent reaction of $(\mu\text{-H})_3$-$Os_3(CO)_9(\mu_3\text{-BCO})$ with BH_3SMe_2 to form $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-}H)_2BH$. Therefore we believe that $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$ and $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ are formed independently of each other. At room temperature the former product is favored (reaction 3), while the latter product is favored at 65 °C (reaction 4).

$$(\mu\text{-H})_2Os_3(CO)_{10} + BH_3SMe_2 \xrightarrow[\text{7 days}]{\text{room temp}}$$
$$(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH + CO + SMe_2 \quad (3)$$

$$(\mu\text{-H})_2Os_3(CO)_{10} + BH_3SMe_2 \xrightarrow[\text{1 h}]{\text{65 °C}}$$
$$(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO}) + H_2 + SMe_2 \quad (4)$$

Our earlier study of the preparation of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3$-BCO) indicates that formation of this complex is favored when a weakly coordinating solvent such as Me_2O is employed in the reaction of B_2H_6 with $(\mu\text{-H})_2Os_3(CO)_{10}$. That the formation of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ is favored at elevated temperature in reaction 4 is consistent with this observation since the extent of dissociation of BH_3SMe_2 is expected to increase with increasing temperature.

The molecular structure of $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$, determined by a single-crystal X-ray analysis, is shown in Figure 1. Although the hydrogen atoms could not be located, their existence and positions are inferred from the NMR spectra and the structural information provided by the non-hydrogen atoms. The molecule has *pseudo C_s* symmetry with a tetrahedral Os_3B core. Each osmium is bound to three terminal CO's, and the boron atom is bound to a terminal hydrogen. Evidence for a terminal B—H bond is given by the ^{11}B and ^1H NMR spectra. The Os_1—B and Os_2—B bonds (2.34(2) and 2.36(2) Å, respectively) are approximately 0.1 Å longer than the Os_3—B bond (2.23(2) Å) indicating that the former two bonds each contain a bridging hydrogen atom. This is also reflected in the greater B—Os—CO bond angles where B—H—Os bonds are said to exist: C_{13}—Os_1—B (104.4(7)°), C_{12}—Os_1—B (111.5(7)°), C_{22}—Os_2—B (104.1(7)°), and C_{21}—Os_2—B (115.0(7)°) as opposed to C_{33}—Os_3—B (91.3(7)°) and C_{32}—Os_3—B (88.4(7)°). The Os_1—Os_3 (2.898(1) Å) and Os_2—Os_3 (2.923(1) Å) distances are approximately 0.12 Å longer than the Os_1—Os_2 (2.779(1) Å) distance, suggesting that the bridging hydrogen atoms are located at Os_1—H—Os_3 and Os_2—H—Os_3 bonds, respectively. The distances for bridged and unbridged Os—Os bonds are consistent with the reported values.[6] The presence of these hydrogen bridge bonds is also inferred by the greater angles of Os_3—Os_1—C_{12} (104.9(5)°) and Os_3—Os_2—C_{21} (105.2(5)°) compared
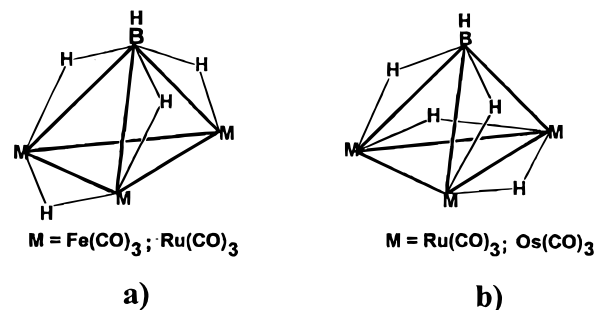
to Os_2—Os_1—C_{13} (94.1(6)°) and Os_1—Os_2—C_{22} (95.5(5)°). Furthermore, the angles of Os_1—Os_3—C_{33} (94.2(5)°) and Os_2—Os_3—C_{32} (96.8(5)°) are greater than C_{32}—Os_3—C_{33} (91.8(8)°), indicative of the existence of bridging hydrogen atoms. The single ^1H resonance in the NMR signal that is assigned to the Os-H—Os bonds is also consistent with the apparent C_s symmetry of the molecule.

The borylidyne cluster $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$ completes the series of group VIII methylidyne analogs of composition $H_4M_3(CO)_9BH$ (M = Fe, Ru, Os).[4,5] While the structures of all these complexes are based upon a tetrahedral core M_3B with a terminal BH bond, the positions of the bridging hydrogens depend upon the transition metal. Two types of structures have been reported (Figure 2). Structure **a** is observed in the complex $(\mu\text{-H})Fe_3(CO)_9(\mu\text{-H})_3BH$.[4] On the basis of ^1H NMR spectra, the ruthenium methylidyne analog has been reported to exist in two isomeric forms **a** and **b** at room temperature: $(\mu\text{-H})$-$Ru_3(CO)_9(\mu\text{-H})_3BH$ and $(\mu\text{-H})_2Ru_3(CO)_9(\mu\text{-H})_2BH$, respectively.[5] At elevated temperature (*ca.* 100 °C) the **b** isomer is favored. In the present investigation only structural type **2b** was observed. On the basis of the proton NMR spectrum, there is no apparent conversion to another isomeric form at elevated temperature (*ca.* 90 °C). The Os—H—Os ^1H NMR resonance is quite sharp unlike the Ru—H—Ru ^1H NMR resonance which is broad at room temperature.[5] Housecroft offers rationale for this trend in structural type based upon increased metal—metal hydrogen bond strength (*i.e.* E(Os—H) > E(Ru—H) > E(Fe—H)) or alternatively optimization of metal to boron atom bonding.[5,7]

Experimental Section

A. General Data. All manipulations were performed under inert-atmosphere conditions. Standard vacuum line and inert-atmosphere techniques were employed.[8] $(\mu\text{-H})_2Os_3(CO)_{10}$ was prepared according to the literature method.[9] $H_3BS(CH_3)_2$ (Aldrich) was stored in a glovebox refrigerator and used as received. Methylene chloride (Mallinkrodt) was degassed and stirred over P_2O_5 while hexane (Mallinkrodt) was first stirred over H_2SO_4 for 2 days, washed with water, and then degassed and stirred over CaH_2 for several days. Toluene (Mallinckrodt) was degassed and refluxed over sodium for several days. Solvents were vacuum transferred to storage flasks containing activated 13x Linde molecular sieves. $CDCl_3$ (1% tetramethylsilane, Aldrich) was degassed, stirred over P_2O_5 for several days,

(6) (a) Churchill, M. R.; DeBore, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843. (b) Churchill, M. R. *Adv. Chem. Ser.* **1978**, *No. 67*, 36.
(7) (a) Lynam, M. M.; Chipman, D. M.; Barreto, R. D.; Fehlner, T. P. *Organometallics* **1987**, *6*, 2405. (b) Barreto R. D.; Fehlner, T. P.; Hsu, L.-Y.; Jan, D.-Y.; Shore, S. G. *Inorg. Chem.* **1986**, *25*, 3572. (c) Sherwood, D. E.; Hall, M. B. *Organometallics* **1982**, *1*, 1519.
(8) Shriver, D. F. and Drezdzon, M. A. *The Manipulation of Air Sensitive Compounds*; 2nd ed.; John Wiley & Sons: New York, 1986.
(9) Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942.

Table 1. Crystallographic Data for $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$

empirical formula	$C_9H_5BO_9Os_3$
fw	838.54
space group	$P\bar{1}$
a, Å	9.501(4)
b, Å	9.525(4)
c, Å	10.070(2)
α, deg	87.72(3)
β, deg	88.32(3)
γ, deg	61.45(3)
V, Å^3	799.8
Z	2
ρ(calcd), g cm^{-3}	3.482
T, °C	25
radiation (λ, Å)	Mo Kα (0.710 73)
μ, cm^{-1}	23.808
transm coeff, %	17.3−95.2
$R_1{}^a$ [$I > 2\sigma(I)$]	0.047
$wR_2{}^b$ (all data)	0.141

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

Table 2. Atomic Coordinates ($\times 10^{-4}$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$

atom	x	y	z	U(eq)^a
Os(1)	2280(1)	8172(1)	7497(1)	31(1)
Os(2)	3284(1)	10441(1)	7807(1)	31(1)
Os(3)	5693(1)	7081(1)	7608(1)	31(1)
C(11)	1626(20)	8168(18)	9268(18)	38(4)
O(11)	1290(17)	8142(17)	10378(17)	61(4)
C(12)	2109(21)	6326(20)	7003(20)	43(4)
O(12)	2006(20)	5276(16)	6678(17)	66(4)
C(13)	170(21)	9712(22)	6953(18)	42(4)
O(13)	−1083(17)	10625(17)	6618(18)	68(4)
C(21)	4478(19)	11592(19)	7856(21)	43(4)
O(21)	5188(17)	12294(15)	7874(18)	67(4)
C(22)	1324(21)	12221(19)	7260(18)	41(4)
O(22)	151(17)	13291(16)	6925(19)	70(5)
C(23)	2618(19)	10745(18)	9623(17)	34(3)
O(23)	2133(17)	10933(17)	10665(15)	58(3)
C(31)	6956(19)	5999(18)	9164(18)	41(4)
O(31)	7686(20)	5434(17)	10075(17)	76(5)
C(32)	7303(21)	7440(21)	6743(20)	47(4)
O(32)	8223(18)	7721(19)	6178(17)	70(4)
C(33)	6264(20)	5215(21)	6602(21)	45(4)
O(33)	6528(17)	4133(15)	6012(16)	64(4)
B	3983(22)	8650(20)	6046(19)	36(4)

^{a} U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

and vacuum transferred to a storage flask containing activated 13x Linde molecular sieves. ^{13}CO (Isotec, 99.99%) was used without further purification. Thin-layer chromatography plates (J. T. Baker, 250 μm, plastic-backed) were heated in a 45 °C oven for 24 h before use.

IR spectra were recorded with 2 cm^{-1} resolution using a Mattson Polaris FT-IR spectrometer. ^{1}H, ^{11}B, and ^{13}C NMR spectra were obtained using a Bruker AM-250 spectrometer. ^{11}B NMR spectra were referenced to BF$_3$OEt$_2$ ($\delta = 0.00$ ppm). Gas mass spectra were obtained from a Balzers 112 quadrupole, mass spectrometer while FAB, EI, and CI mass spectra were obtained on VG 70-250s, Nicolet FTMS-2000, or Finnigan Mat-900 mass spectrometers.

B. X-ray Crystal Structure Determination. Pale yellow crystals for single-crystal X-ray analysis were obtained from concentrated solutions in CHCl$_3$ by slow evaporation. X-ray data were collected at room temperature with a Enraf-Nonius CAD4 diffractometer on a single crystal in a sealed glass capillary and examined with graphite-monochromated Mo Kα radiation. Cell dimensions were obtained from 25 reflections measured in the range $24° < 2\theta < 30°$. Intensity data were collected in the $\omega-2\theta$ scan mode. All data were corrected for Lorentz and polarization effects. An empirical absorption correction based on the crystal orientation and measured ψ-scans was made. The structure was solved by direct methods and refined using SHELXTL.[10] All non-hydrogen atoms were refined anisotropically.

Table 3. Bond Lengths (Å) and Angles (deg) for $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$

Bond Lengths			
Os(1)−C(11)	1.87(2)	Os(3)−C(33)	1.92(2)
Os(1)−C(13)	1.91(2)	Os(3)−C(31)	1.94(2)
Os(1)−C(12)	1.93(2)	Os(3)−B	2.23(2)
Os(1)−B	2.34(2)	C(11)−O(11)	1.16(2)
Os(1)−Os(2)	2.779(1)	C(12)−O(12)	1.11(2)
Os(1)−Os(3)	2.898(1)	C(13)−O(13)	1.14(2)
Os(2)−C(22)	1.90(2)	C(21)−O(21)	1.16(2)
Os(2)−C(23)	1.91(2)	C(22)−O(22)	1.14(2)
Os(2)−C(21)	1.92(2)	C(23)−O(23)	1.12(2)
Os(2)−B	2.36(2)	C(31)−O(31)	1.12(2)
Os(2)−Os(3)	2.923(1)	C(32)−O(32)	1.16(2)
Os(3)−C(32)	1.90(2)	C(33)−O(33)	1.13(2)

Angles			
C(11)−Os(1)−C(13)	92.5(7)	C(11)−Os(1)−Os(2)	95.4(5)
C(11)−Os(1)−C(12)	96.1(8)	C(13)−Os(1)−Os(2)	94.1(6)
C(13)−Os(1)−C(12)	95.7(8)	C(12)−Os(1)−Os(2)	164.5(6)
C(11)−Os(1)−B	145.5(7)	B−Os(1)−Os(2)	54.2(5)
C(13)−Os(1)−B	104.4(7)	C(11)−Os(1)−Os(3)	105.1(5)
C(12)−Os(1)−B	111.5(7)	C(13)−Os(1)−Os(3)	151.0(6)
C(12)−Os(1)−Os(3)	104.9(5)	C(33)−Os(3)−B	91.3(7)
B−Os(1)−Os(3)	49.1(4)	C(31)−Os(3)−B	170.5(6)
Os(2)−Os(1)−Os(3)	61.93(3)	C(32)−Os(3)−Os(1)	140.3(5)
C(22)−Os(2)−C(23)	91.3(7)	C(33)−Os(3)−Os(1)	94.2(5)
C(22)−Os(2)−C(21)	96.0(7)	C(31)−Os(3)−Os(1)	122.6(5)
C(23)−Os(2)−C(21)	95.4(8)	B−Os(3)−Os(1)	52.3(5)
C(22)−Os(2)−B	104.1(7)	C(32)−Os(3)−Os(2)	96.8(5)
C(23)−Os(2)−B	143.6(6)	C(33)−Os(3)−Os(2)	142.3(5)
C(21)−Os(2)−B	115.0(7)	C(31)−Os(3)−Os(2)	118.2(5)
C(22)−Os(2)−Os(1)	95.5(5)	B−Os(3)−Os(2)	52.5(5)
C(23)−Os(2)−Os(1)	93.0(4)	Os(1)−Os(3)−Os(2)	57.02(3)
C(21)−Os(2)−Os(1)	165.6(5)	O(11)−C(11)−Os(1)	177(2)
B−Os(2)−Os(1)	53.4(5)	O(12)−C(12)−Os(1)	178(2)
C(22)−Os(2)−Os(3)	150.7(6)	O(13)−C(13)−Os(1)	179(2)
C(23)−Os(2)−Os(3)	106.3(5)	O(21)−C(21)−Os(2)	179(2)
C(21)−Os(2)−Os(3)	105.2(5)	O(22)−C(22)−Os(2)	180(2)
B−Os(2)−Os(3)	48.6(4)	O(23)−C(23)−Os(2)	175(2)
Os(1)−Os(2)−Os(3)	61.05(3)	O(31)−C(31)−Os(3)	177(2)
C(32)−Os(3)−C(33)	91.8(8)	O(32)−C(32)−Os(3)	177(2)
C(32)−Os(3)−C(31)	95.4(8)	O(33)−C(33)−Os(3)	177(2)
C(33)−Os(3)−C(31)	97.3(7)	Os(3)−B−Os(1)	78.6(6)
C(32)−Os(3)−B	88.4(7)	Os(3)−B−Os(2)	78.9(6)
Os(1)−B−Os(2)	72.4(5)		

Table 1 gives crystallographic data for $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$. Atomic coordinates and bond lengths and angles for $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$ are given in Tables 2 and 3.

C. Preparation of $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$. $(\mu\text{-H})_2Os_3(CO)_{10}$ (135.0 mg, 0.1583 mmol) was weighed into a 50 mL long-neck flask containing a stirbar. A 6.0 mL volume of BH$_3$S(CH$_3$)$_2$ was added to the flask via syringe. The flask was topped with a vacuum line adaptor and removed from the glovebox. 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 for 7 days during which time the $(\mu\text{-H})_2Os_3(CO)_{10}$ dissolved and a slightly cloudy, yellow solution formed. The contents were frozen at −196 °C, and a check for noncondensible gas showed that none had formed. Excess BH$_3$S(CH$_3$)$_2$ was removed under vacuum to give a yellow-brown solid. The flask was returned to the glovebox where an extractor and receiver flask were attached. The extraction apparatus was removed from the glovebox and evacuated on the vacuum line. A 25 mL volume of hexane was then vacuum transferred onto the solid, and the contents of the flask were stirred at room temperature for 1 h. The solution was filtered to give a yellow filtrate. The solid left on the frit was then extracted three more times with hexane. The filtrate was then evaporated to dryness, and the yellow-brown residue was dissolved in 2 mL of CH$_3$Cl and recrystallized. The yield of product is 59.6 mg (0.0711 mmol of $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$), a 44.9% yield based on

(10) SHELXTL (version 5), Siemens Energy & Automation, Inc., 1994 (used to solve and refine crystal structures from diffraction data).

$(\mu\text{-H})_2Os_3(CO)_{10}$. $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$: ^1H NMR (CD$_2Cl_2$, 30 °C) δ 4.7 (br, 1 B−H), −13.6 (br, 2 B−H−Os), −20.46 (s, 2 μ-H) ppm; ^{11}B NMR (CD$_2$Cl$_2$, 30 °C) δ 18.5 (br, fwhm = 324 Hz) ppm; $^{11}B\{^1H\}$ NMR (CD$_2$Cl$_2$, 30 °C) δ 18.5 (br, fwhm = 174 Hz) ppm; IR (ν_{CO}) (CH$_2$Cl$_2$) 2112 w, 2080 vs, 2073 vs, 2056 w, sh, 2027 s, 2012 s cm^{-1}; EI mass spectrum (parent ion peak) calculated *m/e* 844, found *m/e* 844.

D. Preparation of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$. $(\mu\text{-H})_2Os_3(CO)_{10}$ (105 mg, 0.124 mmol) was placed in a 50 mL flask in air. The flask was then transferred to the glovebox, and BH$_3$S(CH$_3$)$_2$ (0.5 mL) was added to it *via* a syringe. The flask was then connected to the vacuum line and evacuated, and then 25 mL of CH$_2$Cl$_2$ was vacuum distilled into it at −78 °C. After the contents of the flask were warmed to room temperature, the flask was stirred at 65 °C for 1 h during which time the solution became yellow in color. Methylene chloride was then vacuum distilled from the flask leaving a yellow residue. The product was recrystallized in methylene chloride to give a bright yellow solid (yield 89.3 mg, 85.0% based on $(\mu\text{-H})_2Os_3(CO)_{10}$) that was identified as $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ by ^1H and ^{11}B NMR and IR spectroscopies.

E. Reaction of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ with BH$_3$SMe$_2$. $(\mu\text{-H})_3$-Os$_3$(CO)$_9(\mu_3$-BCO) (174 mg, 0.200 mmol) was placed in a 50 mL flask

in air. The flask was then transferred to the glovebox, and BH$_3$SMe$_2$ (0.5 mL) was added to it *via* a syringe. A 25 mL volume of CH$_2$Cl$_2$ was vacuum distilled into it at −78 °C. After the contents of the flask were warmed to room temperature, the solution was stirred at room temperature for 1 week. The yellow color of the solution did not change. CH$_2$Cl$_2$ was then vacuum removed from the flask leaving a yellow residue. The yellow residue was identified as the starting material $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ by ^1H and ^{11}B NMR spectroscopy. There was no evidence for $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-H})_2BH$ in this reaction.

Supporting Information Available: Tables of crystallographic data (Table S1), atomic coordinates (Table S2), complete bond lengths and angles (Table S3), and anisotropic thermal parameters (Table S4) (5 pages). Ordering information is given on any current masthead page.

IC970683S