gift of Q1 catalyst, and Martin Stiles for helpful discussions.

Supplementary Material Available: Listings of positional and thermal atomic parameters for nongroup atoms (Table II), group atoms (Table III), and hydrogen atoms (Table IV) and experimental and calculated structure factors (Table V) (39 pages). Ordering information is given on any current masthead page.

Insertion of Boron into an Osmium–Carbonyl Bond. Preparation and Structure of the Carbonyl Borylidyne $(\mu\text{-H})_3(CO)_9Os_3BCO$

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From the hydroboration of the unsaturated cluster $(\mu\text{-H})_2Os_3(CO)_{10}$, the first example of a carbonyl borylidyne transition-metal cluster $(\mu\text{-H})_3(CO)_9Os_3BCO$ (I) has been prepared through the insertion of boron into a metal–carbonyl bond. Compound I is an analogue of the known carbonyl methylidyne complexes $(\mu\text{-H})_2(CO)_9Os_3CCO$, $(\mu\text{-H})_3(CO)_9Os_3CCO^+$, and $(CO)_9Co_3CCO^+$.[1-3] The arrangement of non-hydrogen atoms in the molecular structure of $(\mu\text{-H})_3(CO)_9Os_3BCO$ (Figure 1) is like that of $(\mu\text{-H})_2(CO)_9Os_3CCO$.[1]

Compound I was prepared according to reaction 1. No apparent reaction occurred unless both BH_3NEt_3 and B_2H_6 were present.

$$(\mu\text{-H})_2Os_3(CO)_{10} + {}^1/_2B_2H_6 \xrightarrow[CH_2Cl_2]{BH_3NEt_3} (\mu\text{-H})_3(CO)_9Os_3BCO + H_2 \quad (1)$$

Scheme I accounts for this requirement. In this scheme an initial adduct, **1**, of BH_3NEt_3 to $(\mu\text{-H})_2Os_3(CO)_{10}$ is believed to occur through the formation of a B–H–Os bond. Abstraction of NEt_3 by the free B_2H_6 in the system would allow formation of the metalloboranes **2a** and **2b** followed by an irreversible step involving insertion of boron into an osmium–carbonyl bond of the $Os(CO)_4$ unit with concomitant reductive elimination of H_2. The proposed intermediate **2b** is similar in structure to that assigned to its analogue $Os_3(CO)_{10}CH_4$.[4,5]

According to Scheme I, BH_3NEt_3 is regenerated as reaction 1 proceeds to completion. To test this point, reaction 1 was followed by ^1H NMR spectroscopy. No apparent diminution in BH_3NEt_3 concentration was observed even as the reaction approached completion.

In a typical synthesis, I was prepared from a mixture of $(\mu\text{-H})_2Os_3(CO)_{10}$ (0.164 mmol), B_2H_6 (0.082 mmol), and BH_3NEt_3 (0.164 mmol) in 12 mL of CH_2Cl_2, stirred for 3 days at room temperature. It was obtained in 85% yield (0.139 mmol) as a bright yellow solid [Infrared in cyclohexane (ν_{CO}): 2120 w, 2094 s, 2040 s, 2015 m, 1969 w(br) cm^{-1}] and H_2 was produced in 91% yield (0.149 mmol). It was also obtained when THF replaced NEt_3. However when excess THF was used, another cluster system formed, $[(\mu\text{-H})_3Os_3(CO)_9]_3(B_3O_3)$.[6]

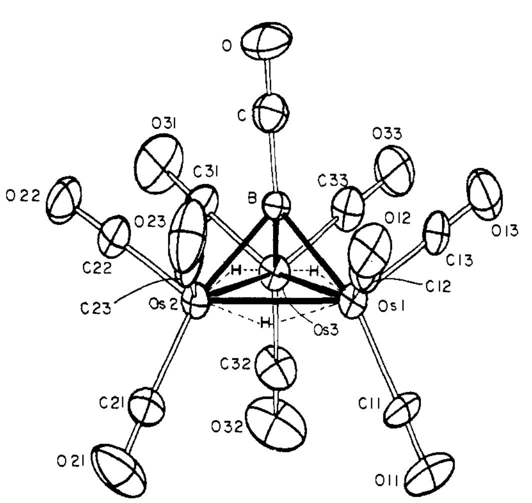
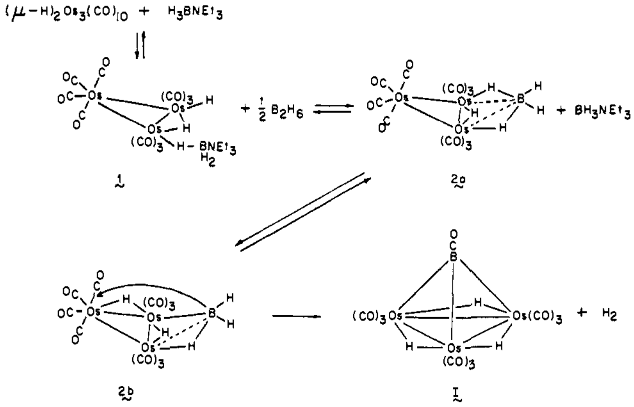


Figure 1. Molecular structure of $(\mu\text{-H})_3(CO)_9Os_3BCO$.

Scheme I



The ^{13}C NMR spectrum of $(\mu\text{-H})_3(CO)_9Os_3BCO$ is consistent with its molecular structure (Figure 1) in that three different types of carbon are present in the ratio of about 1:3:6. Three hydrogens in this compound are revealed by the ^{11}B NMR spectrum[8], which is a quartet (1:3:3:1), and the ^1H NMR signal has a chemical shift consistent with the presence of Os–H–Os bridges.[9]

Compound I is stable in air. It sublimes in vacuum (60 °C). There is no apparent ^{13}CO–^{12}CO exchange between ^{13}CO (1 atm) over a solution of $(\mu\text{-H})_3(CO)_9Os_3BCO$ in CH_2Cl_2 (2 days, 25 °C). However, CO is quantitatively displaced from boron by 1 equiv of $P(CH_3)_3$ in CH_2Cl_2 (1 day, 25 °C) to form $(\mu\text{-H})_3(CO)_9Os_3BP(CH_3)_3$ (**II**) (reaction 2). The ^{11}B NMR spectrum,[10] a doublet, and the ^{31}P NMR spectrum,[11] a quartet (1:1:1:1), indicate that the $P(CH_3)_3$ group is bound to boron.

$$(\mu\text{-H})_3(CO)_9Os_3BCO + P(CH_3)_3 \rightarrow (\mu\text{-H})_3(CO)_9Os_3BP(CH_3)_3 + CO \quad (2)$$

The molecular structure of $(\mu\text{-H})_3(CO)_9Os_3BCO$[12] has approximate C_{3v} symmetry (Figure 1). Although the three hydrogens

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[7] ^{13}C NMR spectrum (CH_2Cl_2, 50% ^{13}CO enriched, 25 °C) δ 193.3 (1, CO, quartet 1:1:1:1), $J_{B-C} = 88$ Hz), 171.5 (3, CO, s), 168.2 (6, CO, d, $J_{C-H} = 8.5$ Hz), 0.00 (Me_4Si).

[8] ^{11}B NMR spectrum (CD_2Cl_2, 25 °C) δ 19.4 [quartet (1:3:3:1), $J_{B-H} = 3$ Hz] 0.00 (BF_3OEt_2).

[9] ^1H NMR spectrum (CD_2Cl_2, 25 °C) τ 29.8, 10.00 (Me_4Si).

[10] ^{11}B NMR spectrum ($CDCl_3$, 25 °C) δ 60.9 (d, $J_{B-P} = 118$ Hz).

[11] ^{31}P NMR spectrum (CH_2Cl_2, 25 °C) δ 16.3 [quartet (1:1:1:1), $J_{BP} = 118$] 0.00 (H_3PO_4).

[12] Crystal data for $(\mu\text{-H})_3(CO)_9OsBCO$: Space group $P\bar{1}$, $a = 9.203$ (2) Å, $b = 12.608$ (2) Å, $c = 8.188$ (2) Å, $\alpha = 80.93$ (2)°, $\beta = 111.43$ (2)°, $\gamma = 87.73$ (2)°, $V = 833.2$ (6) Å^3, ρ(calcd) = 3.44 g cm^{-3} for M_r 864.41, $Z = 2$. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer. Crystallographic computations were carried out on a PDP 11/44 computer using the SDP (structure determination package). The structure was solved by interpreting the Patterson map, difference Fourier syntheses, and full-matrix least-squares refinement. $R_F = 0.077$ and $R_{WF} = 0.095$ for 4083 reflections [$I > 3.0\sigma(I)$] of 5366 reflections collected in the range of $4° \leq 2\theta \leq 60°$ (Mo Kα radiation).

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were not located, they are probably bridging the basal osmium atoms since observed Os–Os distances are appropriate for such an arrangement: Os(1)–Os(2) = 2.913 (1) Å, Os(1)–Os(3) = 2.917 (1) Å, Os(2)–Os(3) = 2.919 (1) Å.[13-18]

A nearly linear BCO unit [∠178.0 (2)°] is present in I and the CO distance, 1.145 (15) Å, is typical for a carbonyl group. The BC distance, 1.469 (15) Å, is short compared to the B–C distances in BH_3CO, $B_2H_4(CO)_2$, and B_3H_7CO (1.52–1.57 Å),[19-21] compounds that tend to lose CO with relative ease compared to I. This could reflect significant back bonding between the e orbitals of boron and the e* orbitals of CO, with electron density being furnished by the Os_3B cluster unit. However, if such back bonding is significant, it is not reflected in the CO stretching frequency of the unique carbonyl on boron, 2120 cm^{-1} (tentatively assigned), since this value is larger than expected[19] but is below the stretching frequencies observed in the borane carbonyls (2163–2140 cm^{-1}) cited above.

Work on $(\mu\text{-}H)_3(CO)_9Os_3BCO$ with respect to examining its derivative chemistry is in progress.

Acknowledgment. We thank NSF for support of this work (Grant CHE79-18149). We also thank J. R. Shapley for helpful conversations.

Supplementary Material Available: Tables of selected bond distances, bond angles, positional parameters, thermal parameters, and observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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$Mo_2(SC_6H_2Me_3)_6$. The First Example of a Compound Containing a Mo–Mo Triple Bond Supported by Six Mercaptido Ligands

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Homoleptic compounds of formula $X_3Mo\equiv MoX_3$ are known for X = bulky β-elimination-stabilized alkyls (CH_2CMe_3, CH_2SiMe_3), NMe_2, and OR (R = a bulky alkyl or trialkylsilyl group, e.g., *t*-Bu, *i*-Pr, CH_2-*t*-Bu, $SiMe_3$, $SiEt_3$, etc.).[1,2] We have wondered for some time whether this series could be extended to include mercaptido, SR, ligands. Though there was no reason to believe that such compounds could not exist, our initial synthetic attempts were thwarted by problems arising from molybdenum's high affinity toward sulfur, facile C–S bond cleavage, polymerization by μ-SR formation, and oxidation of the Mo_2^{6+} center.[3]

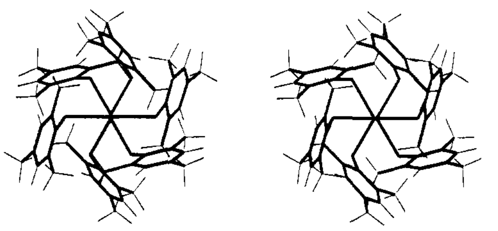

Figure 1. Stereoview of the $Mo_2(SC_6H_2Me_3)_6$ molecule viewed down the Mo–Mo bond. Pertinent distances (Å) and angles (deg) are Mo–Mo = 2.228 (1), Mo–S = 2.325 (2), S–C = 1.792 (5), ∠Mo–Mo–S = 96.6 (1), ∠Mo–S–C = 110.1 (2), and the torsion angle Mo–Mo–S–C = 25.5 (2).

We wish here to report a successful synthesis and our characterization of the first mercaptido member of the $X_3Mo\equiv MoX_3$ class.

Recognizing the problems associated with facile C–S bond cleavage and μ-SR formation, we chose to work with the bulky aromatic thiol, 2,4,6-trimethylbenzenethiol.[4] Reaction between hydrocarbon solutions of $Mo_2(NMe_2)_6$ and $C_6H_2Me_3SH$ (≥6 equiv) at room temperature gives an orange crystalline compound of formula $Mo_2(NMe_2)_2(SC_6H_2Me_3)_4$. Similarly, $Mo_2(OR)_6$ and $C_6H_2Me_3SH$ (≥6 equiv) yield $Mo_2(OR)_2(SC_6H_2Me_3)_4$, where R = *t*-Bu and *i*-Pr.[5] The inability to replace completely the dimethylamido and alkoxy groups is interesting and could be due to steric factors, electronic factors or both. However, we find that by first introducing two *t*-BuS ligands to the dimetal center, 1,2-$Mo_2Cl_2(NMe_2)_4$ + 2LiS-*t*-Bu → 1,2-Mo_2(S-*t*-Bu)$_2$(NMe_2)$_4$,[6] followed by reaction with $C_6H_2Me_3SH$ (≥6 equiv), we obtain the orange-red crystalline compound $Mo_2(SC_6H_2Me_3)_6$, along with an as yet uncharacterized yellow powder that is insoluble in all common hydrocarbon solvents. The latter shows bands in the IR spectrum characteristic of the $SC_6H_2Me_3$ ligand.

The compound $Mo_2(SC_6H_2Me_3)_6$ is diamagnetic and hydrocarbon soluble and shows a simple ^1H NMR spectrum.[7] The molecular structure deduced from an X-ray study[8] confirmed that this compound is a member of the $X_3Mo\equiv MoX_3$ class of compounds.[9] There is an unbridged Mo–Mo bond of distance 2.228 (1) Å, essentially the same as that found in $Mo_2(OCH_2\text{-}t\text{-}Bu)_6$, 2.222 (1) Å.[10] The molecule has crystallographically imposed symmetry, S_6, which yields a beautiful view down the Mo–Mo bond as shown in Figure 1. The Mo–S distance, 2.325 (2) Å, is similar to that seen in Mo_2(S-*t*-Bu)$_2$(NMe_2)$_4$.[6]

We conclude that by appropriate choice of thiol and synthetic strategy, it should be possible to prepare $Mo_2(SAr)_6$ compounds in sufficient number and quantity so that their chemistry may be explored in a manner akin to that for $Mo_2(OR)_6$ compounds.[11]

Further studies are in progress.[12]

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