

Borane-osmium cluster chemistry

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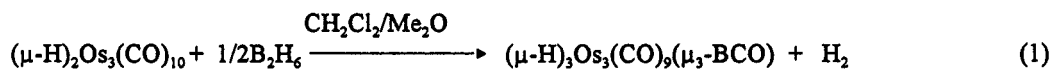
Abstract Triosmium carbonyl borylidyne clusters $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-BCO})$, **I**, $(\mu\text{-H})_3\text{Os}_3(\text{CO})_8(\text{PPh}_3)(\mu_3\text{-BCO})$, **II**, and the boroxin supported triosmium oxomethylidyne cluster system $[(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CO})]_3[\text{B}_3\text{O}_3]$, **III**, are produced in the hydroboration of the unsaturated clusters $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$, and $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{PPh}_3)$. Reactions of these complexes are described. Investigations include kinetic studies of the displacement of the unique carbonyl in **I** and **II** by PMe_3 ; the conversion of **I** and **II** into boron containing analogues of vinylidene and alkyne clusters through reactions with THFBH_3 and boron halides; and the thermal conversion of **I** into osmaboride clusters. Reactions of **III** with boron halides to form triosmium chloro and bromomethylidene clusters are described. Friedel-Crafts type reactions of **III** in the presence of BF_3 to form triosmium phenyl, pentaboranyl and icosacarboranylmethylidyne clusters are also discussed.

I. INTRODUCTION

While hydroboration of unsaturated organic compounds by boranes is a well established synthetic tool in organic chemistry (1), the hydroboration of organometallic complexes containing unsaturated metal-metal (2) or metal-ligand (3) bonds is relatively recent. In this laboratory we have shown (2) that two different cluster systems can be produced by means of appropriate choice of reaction conditions for the hydroboration of the unsaturated cluster $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$, a triangular molecule in which two of the osmium atoms are doubly hydrogen bridged. This molecule is electron deficient. It contains 46 instead of the 48 valence electrons required for an electron precise triangular molecule of the iron sub-group.

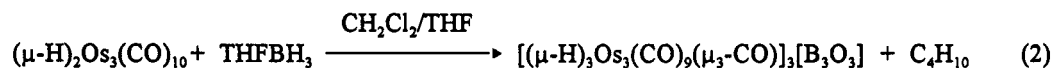
II. HYDROBORATION REACTIONS

The carbonyl borylidyne cluster $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-BCO})$, **I**, is produced (2a, c) in the following hydroboration reaction, Reaction (1). It is an analogue of the ketylidene cluster $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-CCO})$.



The molecular structure of **I** (Fig. 1a) is tetrahedral, in which the Os_3 face is capped by a nearly linear BCO unit that is tilted 6.4° from perpendicularity with respect to the Os_3 triangle. In the formation of **I**, a BH_3 unit adds to the Os_3 triangle, transfers hydrogen to it and effectively inserts into the OsCO bond in the process of capping the Os_3 unit. The B-C distance is $1.469(15) \text{ \AA}$. A related carbonyl borylidyne $(\mu\text{-H})_3\text{Os}_3(\text{CO})_8(\text{PPh}_3)(\mu_3\text{-BCO})$, **II**, is obtained (2c) from the hydroboration of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{PPh}_3)$; it is structurally similar to **I** (Fig. 1b).

On the other hand the hydroboration of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ by THFBH_3 in CH_2Cl_2 solution with the ratio $\text{THF}:\text{B}_2\text{H}_6 > 2:1$ produces the boroxin supported triosmium oxomethylidyne cluster system $[(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CO})]_3[\text{B}_3\text{O}_3]$, **III**, (2b, c) (Reaction (2)). Its structure (Fig. 2a) consists of three



oxomethylidyne cluster units, $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CO})$, linked to a boroxin (B_3O_3) ring *via* oxygen

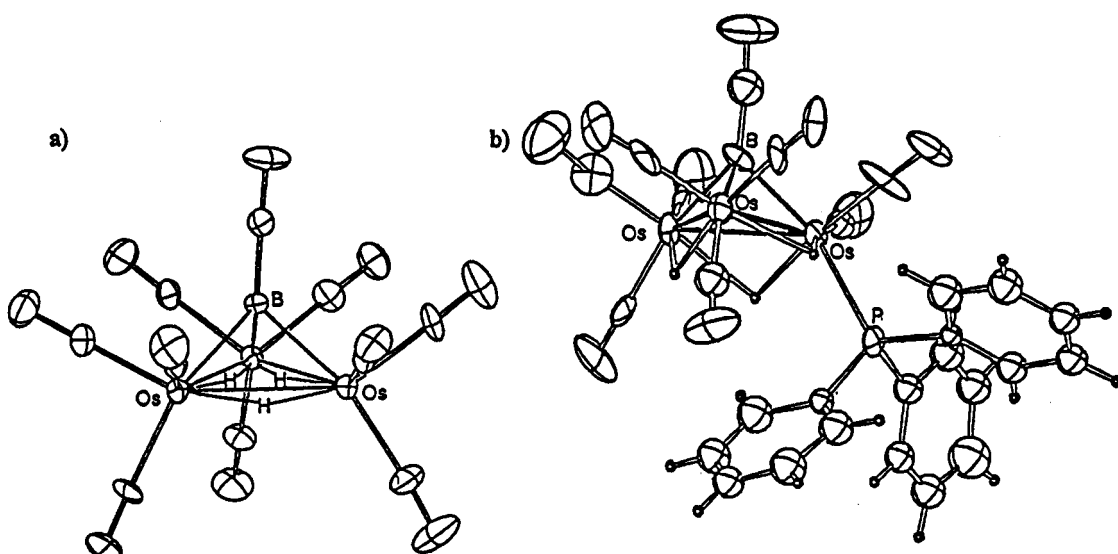
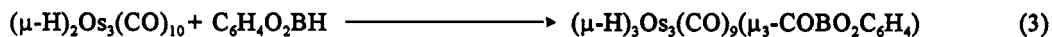


Fig. 1. a) Molecular structure of $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-BCO})$, I
 b) Molecular structure of $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\text{PPh}_3)(\mu_3\text{-BCO})$, II

bridges. In the formation of this complex it appears that one hydrogen of the THFBH_3 is transferred to the Os_3 triangle whereas the resulting BH_2THF unit binds to a terminal carbonyl causing it to move to a capping position over the Os_3 unit. Subsequent transfer of the remaining BH hydrogens of BH_2THF to the THF ring results in the formation of C_4H_{10} and a BO unit linked to the triosmium carbonyl methylidyne via an oxygen bridge. Trimerization of these BO units results in the boroxin supported cluster system II. Experimental evidence and details for schemes for the proposed reaction pathways for the formation of I and II are described elsewhere (2c).

Hydroboration of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ by catechol borane gives the oxomethylidyne cluster $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-COBO}_2\text{C}_6\text{H}_4)$, IV, (Reaction (3)). Its proposed structure (Fig. 2b) is based upon spectro-



scopic data (MS, IR, ^1H , ^{11}B , and ^{13}C NMR), elemental analysis, and its derivative chemistry (2c).

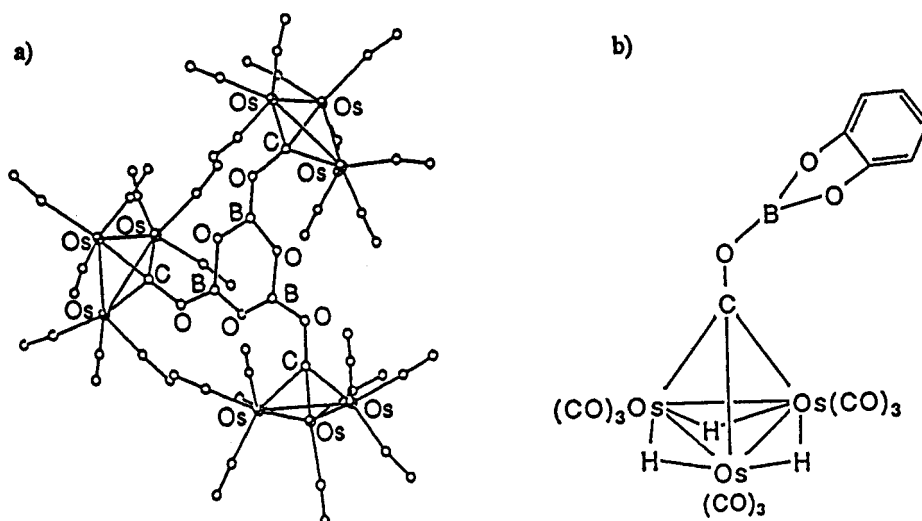
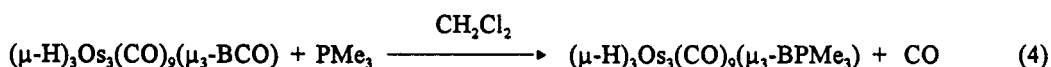


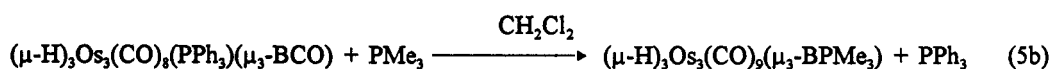
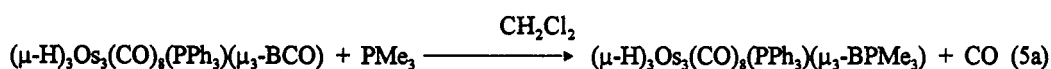
Figure 2. a) Molecular structure of $[(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CO})]_3[\text{B}_3\text{O}_3]$, III
 b) Proposed molecular structure of $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-COBO}_2\text{C}_6\text{H}_4)$, IV.

III. DISPLACEMENT OF CARBON MONOXIDE FROM CARBONYL BORYLIDYNES

Complexes **I** and **II** are remarkable molecules. Unlike many transition metal carbonyl clusters, they are not fluxional on the NMR time-scale up to their decomposition temperatures, *ca* 90 °C (2a, c, 4). Furthermore, no detectable exchange of carbon monoxide gas with carbon monoxide in ¹³C enriched **I** and **II** occurs up to 1,000 psi and 50 °C for three days. On the other hand the carbonyl on the boron site is readily displaced by PMe₃ at room temperature. In the case of **I** the carbon monoxide at the apical site is exclusively replaced by PMe₃ to form (μ-H)₃Os₃(CO)₉(μ₃-BPMe₃), **V**, at room temperature within 1 day when the molar ratio PMe₃:**I** is ≤ 1:1 (Reaction 4).



The reaction of **II** with PMe₃, however, gives a mixture of **V** and (μ-H)₃Os₃(CO)₈(PPh₃)(μ₃-BPMe₃), **VI**, in a ratio of 1.5:1 - 2.0:1 over the temperature range 15 - 40 °C. These products are formed in parallel, concurrent reactions and the products are produced in a constant ratio as the reaction progresses (Reactions 5a and 5b) (4).



Studies of kinetics of reactions of PMe₃ with **I** and **II** indicate that they are associative in nature, being first order in cluster and first order in PMe₃. Rate constants and activation parameters are summarized in Table I. Several pathways have been considered as possible routes for substitution Reactions (4), (5a), and (5b). Since no experimental method appears to be available for preferentially labeling complexes **I** and **II** with ¹³CO, additional experimental information that might assist in choosing a mechanistic pathway is not available.

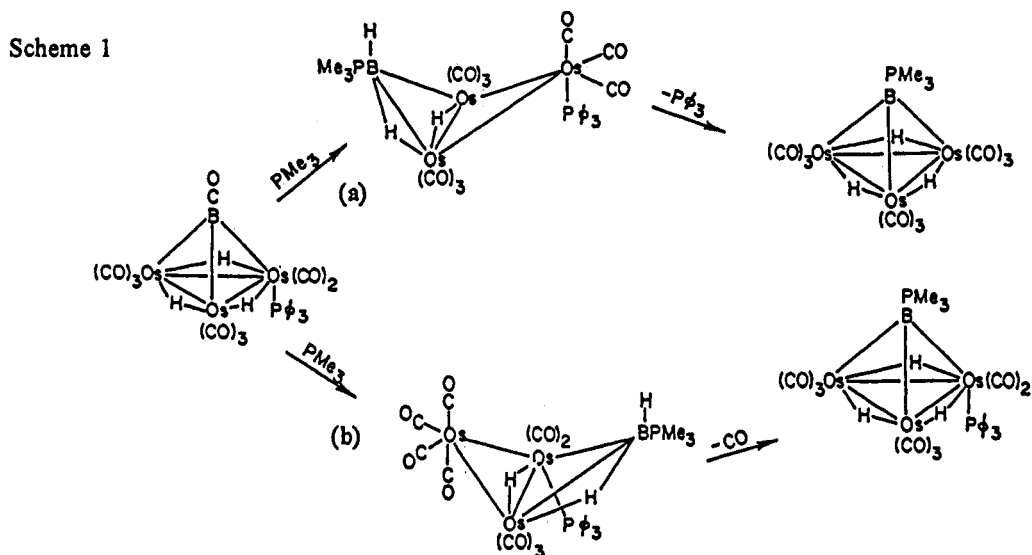
TABLE 1. Rate Constants and Activation Parameters for Reactions (4) and (5) at 293 °K

Reaction	k, M ⁻¹ s ⁻¹ × 10 ³	ΔH [‡] , kcal/mol	ΔS [‡] , cal/mol-deg
(3)	2.56 ± 0.17	18.0 ± 0.8	-8.8 ± 2.6
(4a)	2.27 ± 0.05	19.1 ± 0.8	-5.3 ± 2.6
(4b)	1.42 ± 0.03	17.8 ± 0.6	-11.0 ± 2.0

One pathway that has been considered and rejected involves addition of PMe₃ to a basal osmium atom followed by migration of the PMe₃ to the boron atom, displacing the apical CO. This pathway is considered to be unlikely in the present case, since the enthalpies of activation for Reactions (4), (5a), and (5b) are not significantly different. The position of PPh₃ at an axial position on an osmium atom (Figure 1b) is expected to significantly hinder the approach of PMe₃, with consequent increase in the enthalpy's of activation for Reactions (5a) and (5b) compared to that for Reaction (4).

A second pathway that has been considered and rejected involves initial attack of the PMe₃ at the carbon atom of the carbonyl attached to boron to form an adduct followed by a concerted exchange between CO and PMe₃. One difficulty with this proposal resides in the substantial steric hindrance caused by the arrangement of six of the nine carbonyls that are disposed upward in the direction of the apical boron (Figures 1a and 1b). Furthermore, the low entropy of activation observed compared to that observed for mononuclear substitution reactions with a transition state of higher coordination number than that of the ground state (*ca* -25 cal/mol-deg) suggests that there is appreciable rearrangement in the structure of the activated complex in the current system (5).

A reaction pathway that we favor involves a cluster-opening step by adding PMe_3 to I or II to form an intermediate with a "butterfly" structure followed by a subsequent cluster reclosing step to eject CO with the formation of V or VI. If PPh_3 is eliminated in the cluster reclosing step, VI is formed. Scheme 1 represents these pathways for the formation of V and VI in the reaction of II with PMe_3 (Reactions (5a) and (5b)). In this scheme PMe_3 adds to the cluster to form one of two possible isomeric "butterfly" intermediates. In the reformation of the Os_3B tetrahedral core either CO or PPh_3 is eliminated to yield respectively either V or VI. Statistically it is twice as favorable to eliminate CO than PPh_3 , thereby accounting for a ratio of V:VI that approaches 2:1 with increasing temperature. Route (b) shown in this scheme is also applicable to the formation V in the reaction of I with PMe_3 .

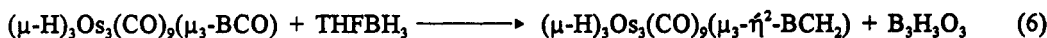


A reaction pathway with an intermediate of "butterfly geometry" has also been proposed in the CO substitution reaction of $\text{Ir}_2(\text{CO})_{12}$ by trialkyl phosphines (6). This reaction pathway appears to be operative in several systems in which intermediates with open structures have been isolated or detected (7).

IV. REACTIONS OF I WITH LEWIS ACIDS

A. Vinylidene cluster analogues

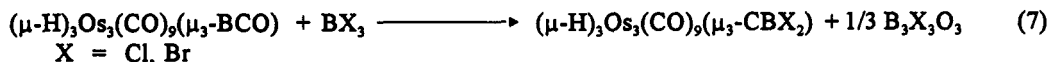
1. **Reaction of I with THFBH_3 .** The unique carbonyl in I is reduced to a methylene group by THFBH_3 to form $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-BCH}_2)$, VII, (Reaction (6) (8a, b). Its structure (Figure 3a)



resembles that of the vinylidene cluster $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CCH}_2)$ (9). However the B-C bond is canted 60° from the perpendicular with respect to the Os_3 plane which is significantly larger than observed for the analogous C-C bond in structurally characterized vinylidene clusters ($40\text{-}50^\circ$) (10). The two B-H-Os bridges in the structure probably force the BCH_2 unit to an extreme tilt angle compared to the vinylidene complexes. The extreme tilt angle implies that the compound could also be described as a methylene-bridged complex. However, the "short" B-C distance, 1.498 (15) Å, compared to observed B-C single bond distances that are *ca.* 0.1 Å longer (11a, b) suggest partial double bond character and the relatively long Os-C distance, 2.325 (17) Å, favor the vinylidene analogy.

Formation of VII is believed to occur through initial coordination of BH_3 to the oxygen atom of the carbonyl to give $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-BCOBH}_3)$ followed by transfer of two BH hydrogens to the carbon atom. Elimination of H-B-O as the boroxine trimer, $\text{B}_3\text{H}_3\text{O}_3$, would then result in the formation of VII. Deuterium-labeling experiments indicate that reduction of the CO occurs with no apparent scrambling of B-H, C-H, and Os-H-Os hydrogen atoms.

2. Reaction of I with Boron Trihalides. Boron trihalides react with I to form vinylidene cluster analogues $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CBX}_2)$ ($X = \text{Cl, Br}$), **VIII**, in which the boron and carbon have exchanged positions (Reaction (7)) (8b, c). The reaction of $^{10}\text{BCl}_3$ with I does not involve interchange of ^{10}B with the



^{11}B in the cluster. Therefore, the formation of **VIII** appears to involve intramolecular exchange of the boron and carbon atoms of I. The structure of **VIII** (Figure 3b) differs from that of **VII** not only in that the

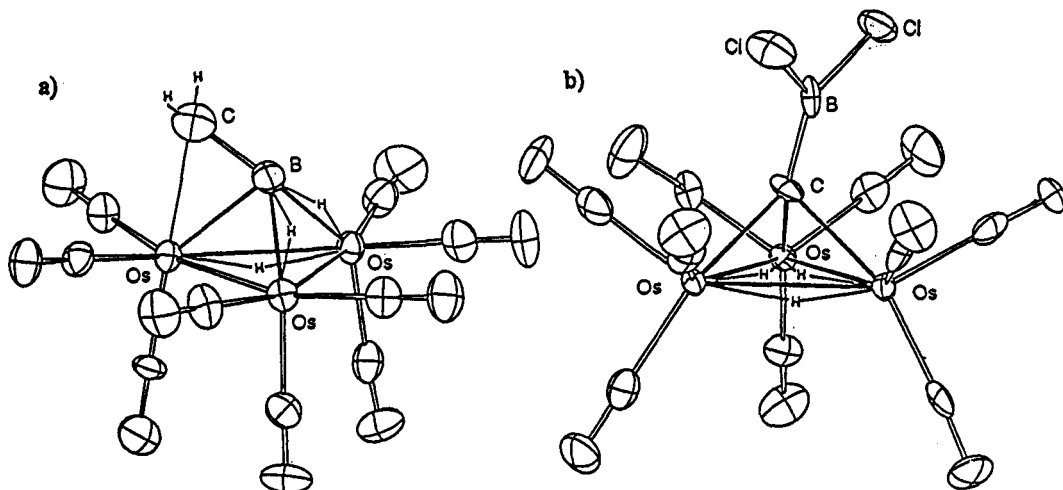
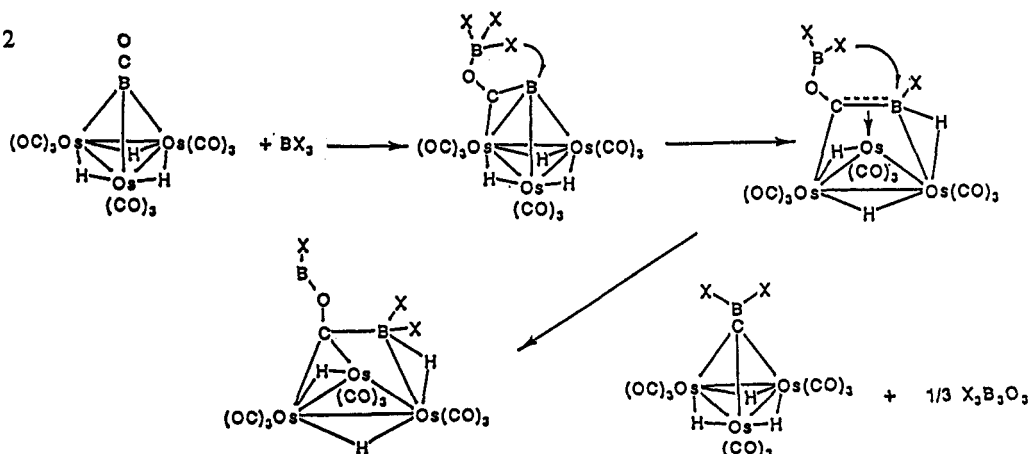


Fig. 3. a) Molecular structure of $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-BCH}_2)$, **VII**
 b) Molecular structure of $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CBX}_2)$ ($X = \text{Cl, Br}$), **VIII**

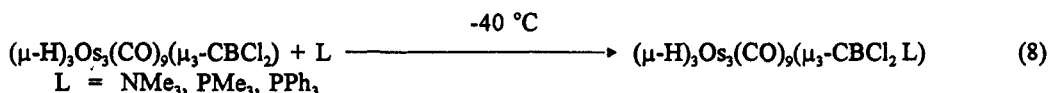
carbon positions are reversed but also the C-B bond in **VIII** is canted only 15° from perpendicularity to the Os_3 plane. As in the case **VII**, the B-C distance $1.47(2) \text{ \AA}$ is "short" compared to observed (11) single bond B-C distances.

Scheme 2 presents a proposed pathway by which **VIII** is formed. Upon interacting with the unique carbonyl oxygen, the boron trihalide is a sufficiently strong electron withdrawing agent to reduce the bond order of the carbon oxygen bond causing it to move to a bridging site. Movement of the carbonyl ligand into the μ_3 site exposes the boron and results in successive halogen atom transfer from the reagent boron to the cluster boron. Compound **VIII** is produced when X-B-O is eliminated as $\text{B}_3\text{X}_3\text{O}_3$. That reaction of I with BH_3 differs from its reactions with boron trihalides is attributed (8b) to the relatively stronger Lewis acidities of the trihalides toward oxygen donors than BH_3 (12).

Scheme 2



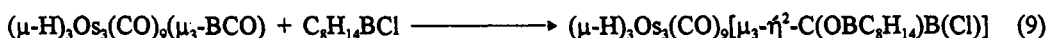
The tricoordinate boron in VIII can accept donor molecules to form Lewis acid-base adducts $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CBCl}_2\text{L})$, IX, (L = NMe₃, PMe₃, PPh₃) (Reaction (8)) (8b). However above -10 °C



the trimethylene adduct is transformed to the salt $[\text{NMe}_3\text{H}][(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-CBCl}_2)]$ through deprotonation of the cluster by the amine.

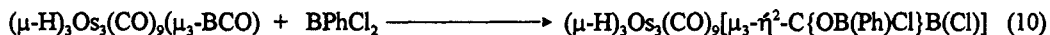
B. Alkyne cluster analogues

1. Reaction of I with B-Cl-9BBN and BPhCl₂. An alkyne cluster analogue $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9[\mu_3\text{-}\eta^2\text{-C}(\text{OBC}_8\text{H}_{14})\text{B}(\text{Cl})]$, X, is formed from the reaction I with B-Cl-9BBN (C₈H₁₄BCl) (Reaction (9)) (8b, d). The structure of X (Fig. 4a) reveals that in the formation of this compound the



unique carbonyl of I moves to a μ_3 -site that caps two osmium atoms and the boron atom whereas the chlorine atom of the B-Cl-9BBN moves to the boron of the cluster. This compound is an alkyne cluster analogue in which a BH group takes the place of a carbon atom. The B-C bond is oriented nearly parallel (within 10°) to an Os-Os bond. It adopts the $\mu^3\text{-}\eta^2$ bonding mode that occurs for the C-C bond in alkyne cluster analogues (13). The bond distance is 1.46 (2) Å, comparable to that in I, VII, and VIII and between the values for a B-C single bond, ca 1.6 Å (11a, b) and a B-C double bond, 1.361 (5) Å, (11c).

Another alkyne cluster analogue $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9[\mu_3\text{-}\eta^2\text{-C}\{\text{OB}(\text{Ph})\text{Cl}\}\text{B}(\text{Cl})]$, XI, is formed in the reaction of I with BPhCl₂ (Reaction (10)) (8b). The proposed structure of XI (Fig. 4b) is related to that



of X and is based upon spectroscopic data (IR, NMR).

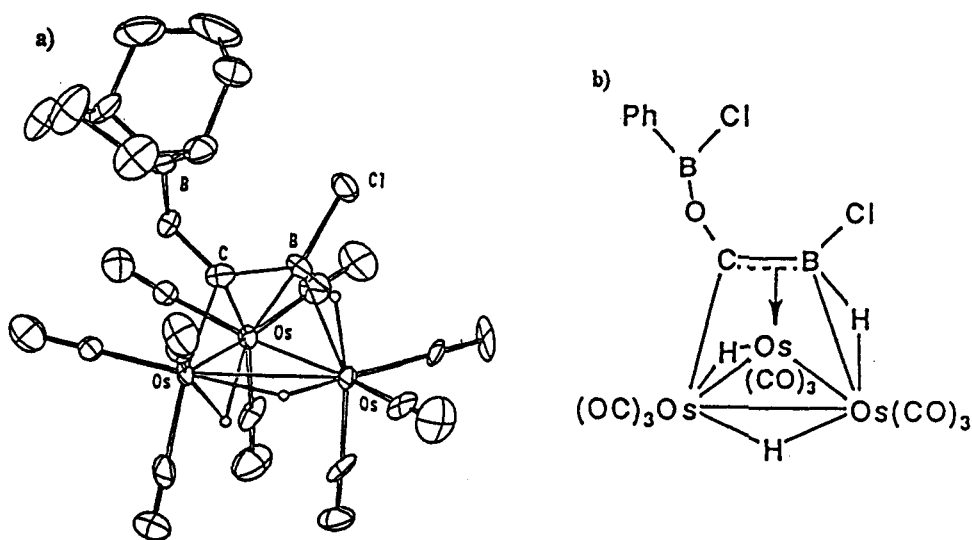
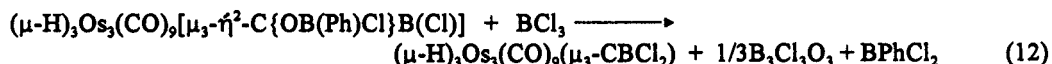
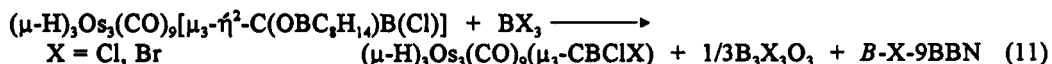
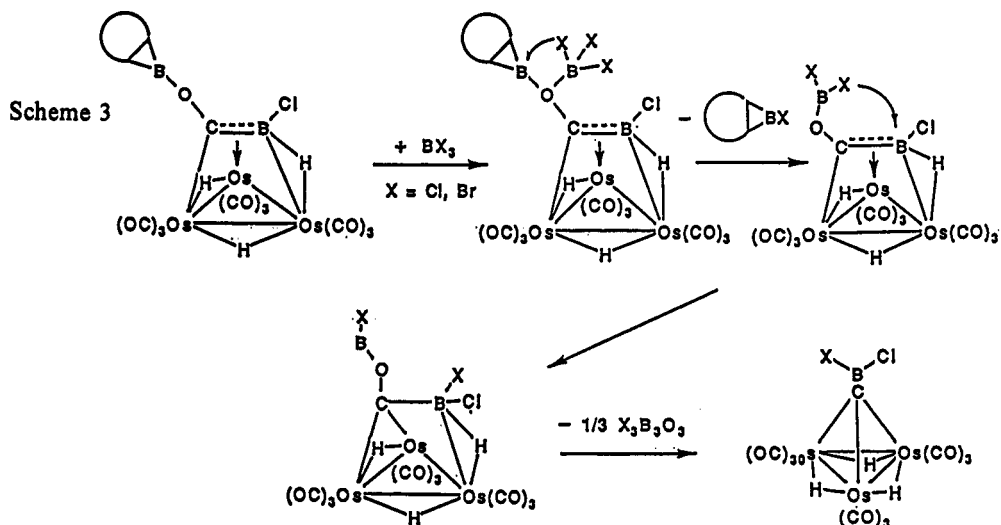


Fig. 4 a) Molecular structure of $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9[\mu_3\text{-}\eta^2\text{-C}(\text{OBC}_8\text{H}_{14})\text{B}(\text{Cl})]$, X.
b) Proposed structure of $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9[\mu_3\text{-}\eta^2\text{-C}\{\text{OB}(\text{Ph})\text{Cl}\}\text{B}(\text{Cl})]$, XI

2. Reactions of X and XI with Boron Trihalides. Complexes X and XI are related to the proposed intermediate in Scheme 2 in the reaction of I with BX_3 ($X = Cl, Br$). They react with boron trihalides to form compounds of type VIII, vinylidene cluster analogues (Reactions (11) and (12)) (8b).



In scheme 2 the initial intermediate is an alkyne cluster analogue like X and XI. In subsequent steps halogen is transferred to the boron atom of the cluster. In Reactions (11) and (12) the boron halide provides the additional halogen. A proposed sequence is given in Scheme 3.



V. FORMATION OF OSMABORIDE CLUSTERS FROM I

The first examples of osmaboride clusters, $\text{HOs}_5(\text{CO})_{16}\text{B}$, XII, and $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$, XIII, were produced through the thermolysis of I at 110° (15a). In the structure of XII (Fig. 5a) the five Os atoms

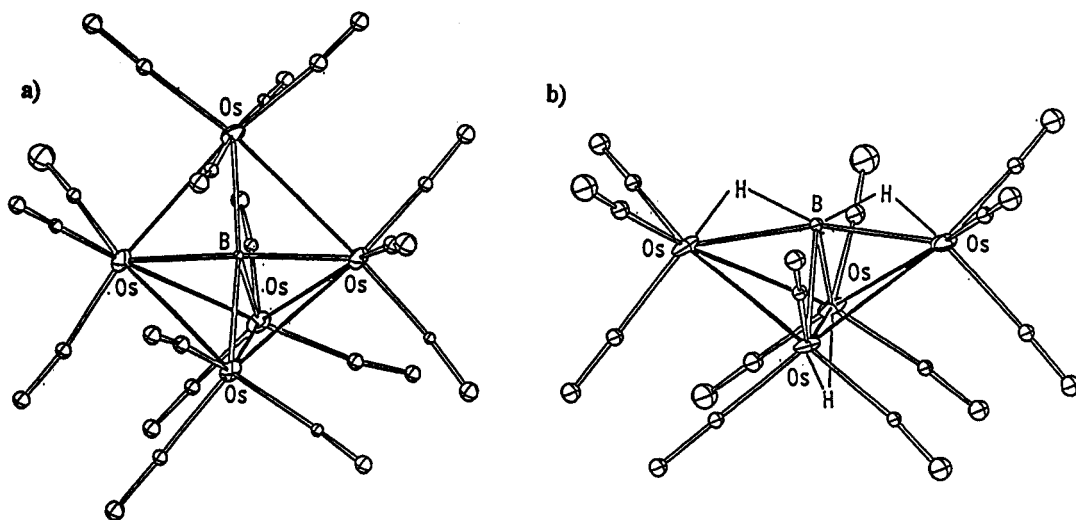
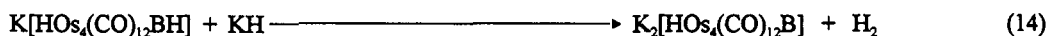
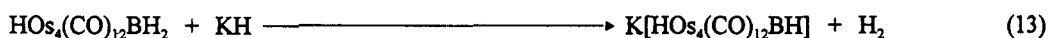


Fig. 5 a) Molecular structure of $\text{HOs}_5(\text{CO})_{16}\text{B}$, XII
 b) Molecular structure of $\text{HOs}_4(\text{CO})_{12}\text{BH}_2$, XIII

define a bridged "butterfly" metal framework and the boron atom is encapsulated in the cluster, bonded to all five osmium atoms. The hydrogen atom was not located, but it is believed to be on the cluster surface, possibly bridging the two osmium atoms that form the hinge of the "butterfly". The overall molecular geometry of this cluster resembles the pentaosmium carbonyl carbide cluster $\text{Os}_5(\text{CO})_{16}\text{C}$ (14b) containing a carbon atom encapsulated in the Os_5 core. Complex XII like $\text{Os}_5(\text{CO})\text{C}$ is a 76 valence electron system. From the Wade, Williams, and Rudolph electron counting rules (15 a, b, c), this compound can be considered to be an *arachno* cluster that is derived from a pentagonal bipyramid from which non-adjacent equatorial vertices are removed.

The molecular structure of XIII (Fig. 5b) contains four Os atoms forming a "butterfly" cluster core with the boron atom residing midway between the osmium atoms that define the wing tips. This molecule is isostructural with ruthenium (16a) and iron (16b) analogues and is considered to be an *arachno*, four atom cluster with an interstitial 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 (15a). Although the bridging hydrogens were not located from the X-ray data, ^{11}B and ^1H NMR spectra indicate that they are located at the positions shown in Fig. 5b. Complex XIII is deprotonated by KH in ether solvents (Reactions (13) and (14)) (14a). In these reactions, deprotonation occurs at the Os-H-B bridges, which is

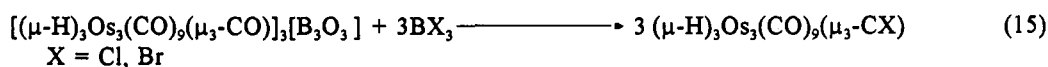


consistent with results from deprotonation studies of $\text{HRu}_4(\text{CO})_{12}\text{BH}_2$ (16a) and confirms, further, the predictions of Fehlner (17) concerning the deprotonation of these clusters.

VI. TRIOSMIUM METHYLIDYNE CLUSTER DERIVATIVES OF III

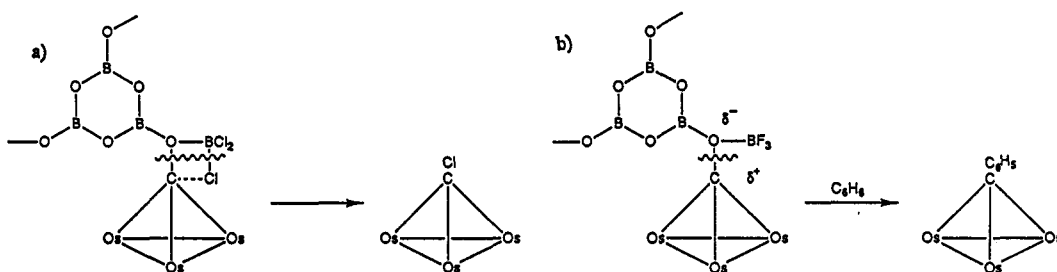
A. Reactions with boron trihalides

The boroxin supported triosmium oxomethylidyne cluster, III, (Figure 2a) is a useful reagent in the preparation of methylidyne cluster derivatives. Boron trichloride and boron tribromide react with III to produce triosmium chloro and bromomethylidyne clusters, $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CX})$ ($\text{X} = \text{Cl}, \text{Br}$), XIV, (Reaction (15)) (2a, 8b). In this reaction it is believed that the boron halide coordinates to the oxygen atom

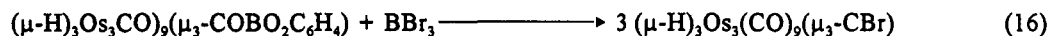


of the C-O-B unit followed by transfer of a halogen atom to the methylidyne carbon atom with rupture of the carbon-oxygen bond (2a, 8b), as indicated in Scheme 4a.

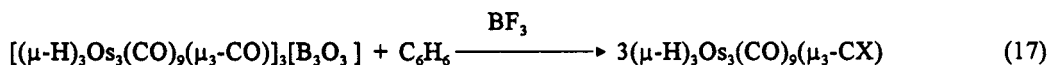
Scheme 4



Complex IV contains a C-O-B bond (Fig. 2b) and it also reacts with BBr_3 to form XIV (Reaction 16) (8b).



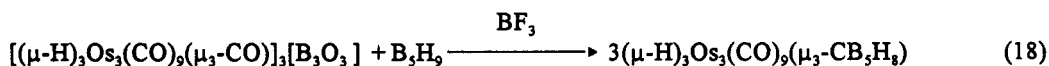
Boron trifluoride reacts with **III** in CH_2Cl_2 to give an uncharacterized highly air and moisture-sensitive product. However, when the reaction is undertaken in benzene, the triosmium phenylmethylidyne cluster $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CPh})$, **XV**, is produced (Reaction (17)) (2a, 8b). As in Reactions (15) and (16),



the boron trihalide is believed to coordinate to the methylidyne oxygen. But in this case unlike the BCl_3 and BBr_3 adducts, fluorine is not transferred to the methylidyne carbon. Instead, either hetrolytic cleavage of the C-O bond to produce a triosmium methylidyne carbonium ion or perhaps extreme polarization of the C-O bond occurs as indicated in Scheme 4b to form an intermediate capable of electrophilic attack of the benzene solvent (19), thereby facilitating a Friedel-Crafts type of Reaction (18).

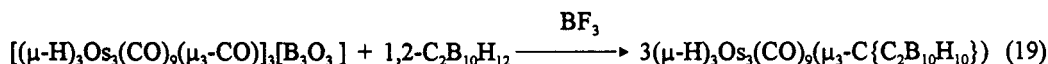
B. "Alkylation" of pentaborane(9) and 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$

That several boron hydrides (20) and carboranes (21) undergo Friedel Crafts type reactions resulting in electrophilic displacement of a B-H hydrogen, prompted attempts to link a borane or a carborane cage to a triosmium methylidyne unit through the formation of a B-C bond (19). In the presence of BF_3 pentaborane(9) reacts with **III** to produce $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CB}_5\text{H}_9)$, **XVII**, (Reaction (18)) (22). The



proposed structure of **XVI** (Fig. 6a) is readily deduced from NMR and mass spectra. The pentaborane(9) is substituted at the apex which is consistent with other examples of electrophilic substitution of this molecule (20) and supports a Friedel-Crafts type reaction where electrophilic attack is expected at the most negative boron atom (20e), the apical atom of B_5H_9 .

In the presence of BF_3 1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ reacts with **III** to produce $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-C}\{\text{C}_2\text{B}_{10}\text{H}_{10}\})$, **XVII** (Reaction (19)) (22). The proposed structure for **XVII** (Fig. 6b) is based on the observation



that electrophilic substitution occurs predominantly at the boron atom farthest from the carbons of the carborane structure (21).

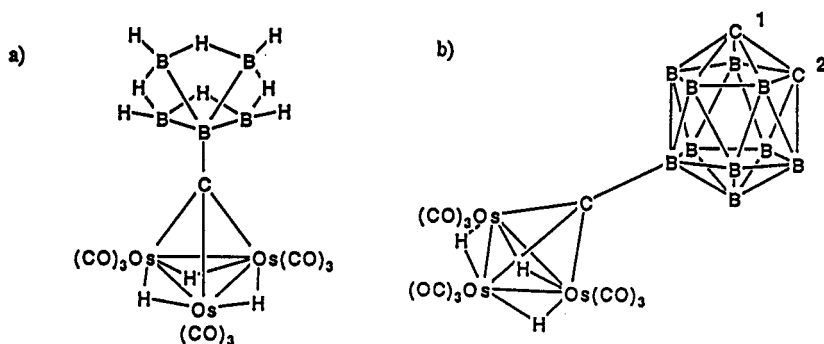


Fig. 6 a) Proposed structure of $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CB}_5\text{H}_9)$.

b) Proposed structure of $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-C}\{\text{C}_2\text{B}_{10}\text{H}_{10}\})$.

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