Borane-osmium cluster chemistry

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Abstract Triosmium carbonyl borylidyne clusters (µ-H)₃Os₃(CO)₁₀(µ₁-BCO), I, (µ-H)₃-
Os₃(CO)₁₀(PPh₃)(µ₂-BCO), II, and the boroxin supported triosmium oxomethylidyne
cluster system [(µ-H)₃Os₃(CO)₉(µ₂-CO)]₃[B₂O₃], III, are produced in the hydroboration
of the unsaturated clusters (µ-H)₂Os₃(CO)₁₀, and (µ-H)₂Os₃(CO)₁₀(PPh₃). Reactions of
these complexes are described. Investigations include kinetic studies of the
replacement of the unique carbonyl in I and II by PMe₃; the conversion of I and II,
into boron containing analogues of vinylidene and alkyne clusters through reactions
with THF:BH₃ and boron halides; and the thermal conversion of I into osmaboride
clusters. Reactions of III with boron halides to form triosmium chloro and bromo-
methylidyne clusters are described. Friedel-Crafts type reactions of III in the presence
of BF₃ to form triosmium phenyl, pentaboranyl and icosacarboranyl methylidyne
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 (µ-H)₂Os₃(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 (µ-H)₃Os₃(CO)₁₀(µ₁-BCO), I, is produced (2a, c) in the following
hydroboration reaction, Reaction (1). It is an analogue of the ketenylidene cluster (µ-H)₃Os₃(CO)₁₀(µ₁-CCO).

\[
\text{CH}_2\text{Cl}_2/\text{Me}_2\text{O} \quad \text{I} \quad \text{II} \quad \text{III}
\]

The molecular structure of I (Fig. 1a) is tetrahedral, in which the Os₃ face is capped by a nearly linear
BCO unit that is tilted 6.4° from perpendicularity with respect to the Os₃ triangle. In the formation of I,
a BH₃ unit adds to the Os₃ triangle, transfers hydrogen to it and effectively inserts into the OsCO bond in
the process of capping the Os₃ unit. The B-C distance is 1.469 (15) Å. A related carbonyl borylidyne
(µ-H)₃Os₃(CO)₁₀(PPh₃)(µ₂-BCO), II, is obtained (2c) from the hydroboration of (µ-H)₂Os₃(CO)₁₀(PPh₃); it
is structurally similar to I (Fig. 1b).

On the other hand the hydroboration of (µ-H)₂Os₃(CO)₁₀ by THF:BH₃ in CH₂Cl₂ solution with the
ratio THF:B₂H₆ > 2:1 produces the boroxin supported triosmium oxomethylidyne cluster system
[(µ-H)₂Os₃(CO)₉(µ₂-CO)]₃[B₂O₃], III, (2b, c) (Reaction (2)). Its structure (Fig. 2a) consists of three

\[
\text{CH}_2\text{Cl}_2/\text{THF} \quad \text{III}
\]

oxomethylidyne cluster units, (µ-H)₂Os₃(CO)₁₀(µ₁-CO), linked to a boroxin (B₂O₃) ring via oxygen
bridges. In the formation of this complex it appears that one hydrogen of the THFBH₃ is transferred to the Os₃ triangle whereas the resulting BH₂THF unit binds to a terminal carbonyl causing it to move to a capping position over the Os₃ unit. Subsequent transfer of the remaining BH hydrogens of BH₂THF to the THF ring results in the formation of C₆H₁₀ 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 (μ-H)₂Os₃(CO)₁₀ by catechol borane gives the oxomethylidyne cluster (μ-H)₂Os₃(CO)₉(μ₁-COBO₂C₆H₄), IV, (Reaction (3)). Its proposed structure (Fig. 2b) is based upon spectroscopic data (MS, IR, ¹H, ¹¹B, and ¹³C NMR), elemental analysis, and its derivative chemistry (2c).

The reaction is shown in the following equation:

(μ-H)₂Os₃(CO)₁₀ + C₆H₄O₂BH → (μ-H)₂Os₃(CO)₉(μ₁-COBO₂C₆H₄)  (3)

Figure 2. a) Molecular structure of [(μ-H)₂Os₃(CO)₇(μ₁-CO)]₃[B₂O₃], III
b) Proposed molecular structure of (μ-H)₂Os₃(CO)₉(μ₁-COBO₂C₆H₄), 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 \((\mu-H)O_5s(CO)_9(\mu_3-BPMe_3), V\), at room temperature within 1 day when the molar ratio PMe3/I is ≤ 1:1 (Reaction 4).

\[
\begin{align*}
\text{CH}_2\text{Cl}_2 & \\
(\mu-H)_3O_5s(CO)_9(\mu_3-BCO) + \text{PMe}_3 & \rightarrow (\mu-H)_3O_5s(CO)_9(\mu_3-BPMe_3) + \text{CO} \quad (4)
\end{align*}
\]

The reaction of II with PMe3, however, gives a mixture of V and \((\mu-H)_3O_5s(CO)_9(\mu-PPh_3)(\mu_3-BPMe_3), VI\), 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).

\[
\begin{align*}
\text{CH}_2\text{Cl}_2 & \\
(\mu-H)_3O_5s(CO)_9(\mu-PPh_3)(\mu_3-BCO) + \text{PMe}_3 & \rightarrow (\mu-H)_3O_5s(CO)_9(\mu-PPh_3)(\mu_3-BPMe_3) + \text{CO} \quad (5a)
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{Cl}_2 & \\
(\mu-H)_3O_5s(CO)_9(\mu-PPh_3)(\mu_3-BCO) + \text{PMe}_3 & \rightarrow (\mu-H)_3O_5s(CO)_9(\mu-PPh_3)(\mu_3-BPMe_3) + \text{PPh}_3 \quad (5b)
\end{align*}
\]

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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>k, M⁻¹s⁻¹ x 10⁹</th>
<th>(\Delta H^\ddagger), kcal/mol</th>
<th>(\Delta S^\ddagger), cal/mol-deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3)</td>
<td>2.56 ± 0.17</td>
<td>18.0 ± 0.8</td>
<td>-8.8 ± 2.6</td>
</tr>
<tr>
<td>(4a)</td>
<td>2.27 ± 0.05</td>
<td>19.1 ± 0.8</td>
<td>-5.3 ± 2.6</td>
</tr>
<tr>
<td>(4b)</td>
<td>1.42 ± 0.03</td>
<td>17.8 ± 0.6</td>
<td>-11.0 ± 2.0</td>
</tr>
</tbody>
</table>

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\textsubscript{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\textsubscript{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\textsubscript{3} (Reactions (5a) and (5b)). In this scheme PMe\textsubscript{3} adds to the cluster to form one of two possible isomeric "butterfly" intermediates. In the reformation of the Os\textsubscript{2}B tetrahedral core either CO or PPh\textsubscript{3} is eliminated to yield respectively either V or VI. Statistically it is twice as favorable to eliminate CO than PPh\textsubscript{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\textsubscript{3}.

Scheme 1

A reaction pathway with an intermediate of "butterfly geometry" has also been proposed in the CO substitution reaction of Ir\textsubscript{5}(CO)\textsubscript{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. Vinylimide cluster analogues

1. Reaction of I with THFBH\textsubscript{3}. The unique carbonyl in I is reduced to a methylene group by THFBH\textsubscript{3} to form (μ-H)\textsubscript{2}Os\textsubscript{3}(CO)\textsubscript{9}(μ\textsubscript{2}-η\textsuperscript{2}-BCH\textsubscript{2}), VII, (Reaction (6) (8a, b). Its structure (Figure 3a)

\[
(μ-H)\textsubscript{2}Os\textsubscript{3}(CO)\textsubscript{9}(μ\textsubscript{2}-BCO) + THFBH\textsubscript{3} \rightarrow (μ-H)\textsubscript{2}Os\textsubscript{3}(CO)\textsubscript{9}(μ\textsubscript{2}-η\textsuperscript{2}-BCH\textsubscript{2}) + B\textsubscript{3}H\textsubscript{6}O\textsubscript{3}
\]  

(6)

resembles that of the vinylimide cluster (μ-H)\textsubscript{2}Os\textsubscript{3}(CO)\textsubscript{9}(μ\textsubscript{2}-η\textsuperscript{2}-CCH\textsubscript{2}) (9). However the B-C bond is canted 60° from the perpendicular with respect to the Os\textsubscript{3} plane which is significantly larger than observed for the analogous C-C bond in structurally characterized vinylimide clusters (40-50°) (10). The two B-H-Os bridges in the structure probably force the BCH\textsubscript{2} unit to an extreme tilt angle compared to the vinylimide 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 vinylimide analogy.

Formation of VII is believed to occur through initial coordination of BH\textsubscript{3} to the oxygen atom of the carbonyl to give (μ-H)\textsubscript{2}Os\textsubscript{3}(CO)\textsubscript{9}(μ\textsubscript{2}-BCOHB\textsubscript{3}) followed by transfer of two BH hydrogens to the carbon atom. Elimination of H-B-O as the boroxine trimer, B\textsubscript{3}H\textsubscript{6}O\textsubscript{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 \((\mu-H)Os_5(\text{CO})_9(\mu_2-\text{CBX}_2)\) \((X = \text{Cl, Br})\), VIII, in which the boron and carbon have exchanged positions (Reaction (7)) (8b, c). The reaction of \(^{11}\text{BCl}_3\) with I does not involve interchange of \(^1\text{B}\) with the \[^{11}\text{B}\] 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 carbon positions are reversed but also the C-B bond in VIII is canted only 15° from perpendicularity to the Os₅ plane. As in the case VII, the B-C distance 1.47 (2) Å 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 \(\mu_3\) 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 B₃X₃O₃. That reaction of I with BH₃ differs from its reactions with boron trihalides is attributed (8b) to the relatively stronger Lewis acidities of the trihalides toward oxygen donors than BH₃ (12).

![Diagram of molecular structures](image-url)
The tricoordinate boron in VIII can accept donor molecules to form Lewis acid-base adducts $(\mu$-$H)_2$Os$_5$(CO)$_9$(μ$_2$-CBCl$_2$ L), IX, ($L = \text{NMe}_3, \text{PMe}_3, \text{PPh}_3$) (Reaction (8)) (8b). However above -10 °C

\[
-40 ^\circ \text{C} \quad \xrightarrow{} \quad (\mu$-$H)_2$Os$_5$(CO)$_9$(μ$_2$-CBCl$_2$ L) \quad \xrightarrow{L = \text{NMe}_3, \text{PMe}_3, \text{PPh}_3} \quad (\mu$-$H)_2$Os$_5$(CO)$_9$(μ$_2$-CBCl$_2$ L)
\]

the trimethylene adduct is transformed to the salt $[\text{NMe}_3\text{H}] [(\mu$-$H)_2$Os$_5$(CO)$_9$(μ$_2$-CBCl$_2$)] through deprotonation of the cluster by the amine.

B. Alkyne cluster analogues

1. Reaction of I with B-Cl-9BBN and BPhCl$_2$. An alkyne cluster analogue $(\mu$-$H)_2$Os$_5$(CO)$_9$(μ$_2$-$\eta^2$-C(BO$_2$H)$_2$B(Cl)), X, is formed from the reaction I with B-Cl-9BBN (C$_6$H$_4$BCl) (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$_2$-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 μ$_2$-$\eta^2$ 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 $(\mu$-$H)_2$Os$_5$(CO)$_9$(μ$_2$-$\eta^2$-C(OBPhCl)B(Cl)), XI, is formed in the reaction of I with BPhCl$_2$ (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 $(\mu$-$H)_2$Os$_5$(CO)$_9$(μ$_2$-$\eta^2$-C(BO$_2$H)$_2$B(Cl)), X.

b) Proposed structure of $(\mu$-$H)_2$Os$_5$(CO)$_9$(μ$_2$-$\eta^2$-C(OBPhCl)B(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 BX₃ (X = Cl, Br). They react with boron trihalides to form compounds of type VIII, vinylidene cluster analogues (Reactions (11) and (12)) (8b).

\[
\begin{align*}
(\mu-H)\text{Os}_{2}(CO)_{6}[\mu_{3}-\eta^2-C(\text{OBC}_{2}H_{5})B(Cl)] + BX_{3} & \rightarrow (\mu-H)\text{Os}_{2}(CO)_{6}[\mu_{3}-\text{CBClX}] + 1/3B_{2}X_{3}O_{3} + B-X-9BBN \quad (11) \\
(\mu-H)\text{Os}_{2}(CO)_{6}[\mu_{3}-\eta^2-C(\text{OBPhCl})B(Cl)] + BCl_{3} & \rightarrow (\mu-H)\text{Os}_{2}(CO)_{6}[\mu_{3}-\text{CBCl}_{2}] + 1/3B_{2}Cl_{3}O_{3} + BPhCl_{2} \quad (12)
\end{align*}
\]

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, HOs₅(CO)₆B, XII, and HOs₅(CO)₁₂BH₂, 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 HOs₅(CO)₆B, XII.

b) Molecular structure of HOs₅(CO)₁₂BH₂, 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 Os₅(CO)₅C (14b) containing a carbon atom encapsulated in the Os₅ core. Complex XII like Os₅(CO)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 BH₂ 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, ¹¹B 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 HRu₅(CO)₅BH₂ (16a) and confirms, further, the predictions of Fehlner (17) concerning the deprotonation of these clusters.

VI. TRIOSMlUM METHYLDYNE 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, (p-H)₃Os₃(CO)₃(p-CX) (X = Cl, 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 BBr₃ to form XIV (Reaction 16) (8b).

\[(\mu-H)_3Os_3(CO)_3(\mu_3-COBO_2C_2H_4) + BBr_3 \rightarrow 3(\mu-H)_3Os_3(CO)_3(\mu_3-CBr)\]
Boron trifluoride reacts with \( \text{III} \) in \( \text{CH}_2\text{Cl}_2 \) to give an uncharacterized highly air and moisture-sensitive product. However, when the reaction is undertaken in benzene, the triosmium phenylmethylidyne cluster (\( \mu\)-H)\(_2\)Os\(_5\)(CO)\(_5\)(\( \mu_2\)-CPh), \( \text{XV} \), is produced (Reaction (17)) (2a, 8b). As in Reactions (15) and (16),

\[
\text{BF}_3 \quad \xrightarrow{[\text{C}_6\text{H}_6]} \quad (\mu\text{-H})_3\text{Os}_5(\text{CO})_5(\mu_2\text{-CX})
\]

the boron trihalide is believed to coordinate to the methylidyne oxygen. But in this case unlike the BCl, and BBr, adducts, fluorine is not transferred to the methylidyne carbon. Instead, either heterolytic 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-C\(_2\)B\(_{10}\)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 \( \text{III} \) to produce (\( \mu\)-H)\(_2\)Os\(_5\)(CO)\(_5\)(\( \mu_2\)-CB\(_5\)H\(_8\)), \( \text{XVII} \), (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\(_5\)H\(_9\).

In the presence of BF\(_3\), 1,2-C\(_2\)B\(_{10}\)H\(_{12}\) reacts with \( \text{III} \) to produce (\( \mu\)-H)\(_2\)Os\(_5\)(CO)\(_5\)(\( \mu_2\)-C(C\(_2\)B\(_{10}\)H\(_{12}\))), \( \text{XVII} \) (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).

\[
\text{BF}_3 \quad \xrightarrow{[\text{C}_6\text{H}_6]} \quad 3(\mu\text{-H})_2\text{Os}_5(\text{CO})_5(\mu_2\text{-CB}_{10}\text{H}_{12})
\]

Acknowledgement

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REFERENCES