(5) the three isotopically shifted imidazole proton NH signals due to the coordinated histidines in the zinc site of $Cu^I_2Co^{II}_2SOD$[51,52] and $Cu^I_2Ni^{II}_2SOD$,[53] where one of the NH signals is due to the protonated formerly bridging His-61, and (6) the similarity of the X-ray absorption edge spectra of Zn^{II} in both oxidized and reduced Cu_2Zn_2SOD, suggesting that the imidazole ring of histidine-61 is coordinated to zinc in both species.[32,54]

The configuration of the Cu binding site in $Cu^I_2Zn^{II}_2SOD$ is still not known. In general, cuprous ion can form either linear, trigonal, or tetrahedral complexes.[55] It seems likely from ^1H NMR studies of reduced native protein that histidine-44, -46 and -118 remain coordinated to Cu^I.[20,30,36] It was previously proposed that there was a coordination site available on Cu^I in the reduced native protein and that this was thought to be the site that bound anions as well as the substrate, superoxide.[8,9,11] It was therefore proposed[8] that reduction of superoxide by $Cu^I_2Zn^{II}_2SOD$ requires binding of O_2^- to the Cu^I ion prior to electron transfer. This mechanism avoids the formation of the energetically unstable O_2^{2-} ion, since a proton can be readily donated by histidine-61 to the coordinated O_2^{2-} ion and the imidazolate bridge reformed. In this paper, we show evidence suggesting that Arg-141 plays a major role in enhancing chloride binding to the active-site region in reduced native Cu_2Zn_2SOD, and therefore we propose that electrostatic interactions between the substrate O_2^- and the positively charged side chain of Arg-141 are present not only in the oxidized form[6,7,13-16] but also in the reduced form of native Cu_2Zn_2SOD. This anion binding scheme for the reduced protein is in agreement with that proposed in two recent theoretical studies.[56,57] In these two studies, it was suggested that the close proximity of Arg-141 to the metal center leads to the formation of a stable superoxide–Cu^{II} intermediate that can oxidize another superoxide to oxygen with a simultaneous reduction of the Cu center. According to the mechanism proposed by Osman and Basch,[56] the resulting reduced form of the complex accepts a proton from Arg-141 and undergoes a charge distribution that leads to a new complex between Cu^{II} and a hydroperoxide anion. Addition of a second proton from the bridging histidine residue leads to release of the hydroperoxide anion in the form of hydrogen peroxide. Bertini's proposed mechanism[57] for superoxide reduction is different in that two protons (one from Arg-141 and the other from the bridging histidine residue) are added to the reduced form of the superoxide–enzyme complex causing an increase in the Cu–O distance prior to electron transfer. Both of these models of enzyme action suggest the importance of Arg-141 in the reduced form of native Cu_2Zn_2SOD. Our NMR data provide direct evidence that anion, and presumably substrate, binding to reduced Cu_2Zn_2SOD involves the Arg-141 residue.

Acknowledgment. This work was supported by USPHS Grant GM 28222 (J.S.V.).

Registry No. SOD, 9054-89-1; Cl^-, 16887-00-6; PO_4^{3-}, 14265-44-2; Arg, 74-79-3; Lys, 56-87-1; Cu, 7440-50-8; His, 71-00-1.

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Contribution from the Department of Chemistry,
The Ohio State University, Columbus, Ohio 43210

Activation of the BCO Unit in the Ketenylidene Analogue $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ by Electrophiles: Syntheses of Vinylidene and Alkyne Analogues

David P. Workman, Deng-Yang Jan, and Sheldon G. Shore*

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The Lewis acids BX_3 (X = Cl, Br), BH_3, *B*-Cl-9-BBN, and $PhBCl_2$ react with $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ (I), a ketenylidene analogue, apparently through electrophilic attack at the oxygen of the unique carbonyl. Reactions of I with BX_3 (X = Cl, Br) result in an exchange of B and C atom positions in the BCO unit to form a vinylidene analogue, $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBX}_2)$. Boron-10-labeling experiments indicate that this transformation occurs through an intramolecular interchange of the boron and carbon atom positions. The ketenylidene analogue $(\mu\text{-H})_3Os_3(CO)_8(PPh_3)(\mu_3\text{-BCO})$ reacts similarly with BCl_3 to produce $(\mu\text{-H})_3Os_3(CO)_8(PPh_3)(\mu_3\text{-CBCl}_2)$. The nucleophiles PMe_3, PPh_3, and NMe_3 add to the tricoordinate boron of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$. Above −10 °C the NMe_3 adduct is converted to the salt $[NMe_3H][(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-CBCl}_2)]$ and the PMe_3 adduct dissociates. The PPh_3 adduct decomposes above 30 °C. The reaction of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ with $THF{\cdot}BH_3$ produces $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCH}_2)$, a second type of vinylidene analogue. In this case the boron and carbon atoms do not change positions. Alkyne analogues, $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C(OBC}_8H_{14})B(Cl)]$ and $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C\{OB(Ph)Cl\}B(Cl)}]$ are obtained from reactions of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ with *B*-Cl-9-BBN and $PhBCl_2$. These compounds react with BCl_3 to produce $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$. They also react with HCl to produce $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CH})$.

Introduction

Metal ketenylidene clusters possess a rich and diverse chemistry. Cationic,[1,2] $[Co_3(CO)_9(\mu_3\text{-CCO})]^+$, $[CpMoCo_2(CO)_9(\mu_3\text{-CCO})]^+$, and neutral,[3,4] $(\mu\text{-H})_2M_3(CO)_9(\mu_3\text{-CCO})$ (M = Ru, Os), ketenylidenes react with nucleophilic reagents. The most extensively studied of these clusters, $[Co_3(CO)_9(\mu_3\text{-CCO})]^+$, has been shown by Seyferth and co-workers[1] to undergo nucleophilic attack exclusively at the β-carbon atom of the CCO unit. Monoanionic ketenylidenes, $[Fe_2Co(CO)_9(\mu_3\text{-CCO})]^-$ and $[(\mu\text{-H})Ru_3(CO)_9(\mu_3\text{-CCO})]^-$, exhibit similar reactivity.[5,6]

Shriver and co-workers[6-9] have demonstrated that the group VIII dianionic ketenylidenes $[M_3(CO)_9(\mu_3\text{-CCO})]^{2-}$ (M = Fe,

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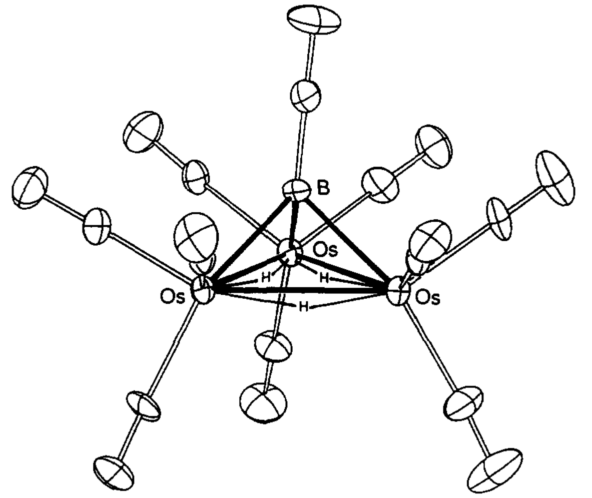

Figure 1. Molecular structure of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ (I).[10]

Ru, Os) react with protons and carbon-based electrophiles. Electrophilic attack can occur at the α-carbon or the oxygen atom of the CCO unit or at the metal atom, depending upon the specific metal ketenylidene and electrophile used. For the Fe- and Os-based clusters, bulky carbocations attack the oxygen of the CCO unit to give acetylide complexes, while the methyl cation appears to attack the α-carbon, resulting in scission of the carbon–carbon bond to form CH_3 and CO ligands. Protonic acids also appear to attack the α-carbon of the CCO unit of the Fe-based ketenylidene dianions to produce CH and CO ligands.

The triosmium carbonyl borylidyne $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$[10] (I) (Figure 1) is an analogue of $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-CCO})$ in which the α-carbon atom of the CCO fragment is replaced by a boron atom and a hydrogen atom. The boron atom occupies the capping μ_3-site on the triosmium framework, and on the basis of Os–Os distances[10] and NMR spectra,[18] the hydrogen atom bridges two osmium atoms. The BCO unit in I is nearly linear ($\angle$B–C–O = 178 (2)°); it is tilted only 6.4° from being perpendicular to the triosmium plane. Photoelectron spectroscopy combined with Fenske–Hall molecular orbital calculations[11] indicates that the electronic structure and bonding of I are similar to those of $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-CCO})$. These calculations indicate that the oxygen of the unique carbonyl has the largest negative Mulliken atomic charge (−0.246e) of any of the oxygens in the molecule. Preliminary communications from this laboratory describe reactions of electrophilic reagents with I[12–14] which indicate that electrophilic attack occurs at this oxygen. We report herein details of this work and provide results that represent extensions of our earlier studies.

Results and Discussion

Although the acid-catalyzed reaction of $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-CCO})$ with H_2O produces the cluster carboxylic acid $[(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CCOOH})]_2$,[15] an analogous reaction involving I does not appear to take place. In general, I does not seem to react with proton sources or methylating agents ($CH_3OSO_2CF_3$ or CH_3OSO_2F). It does react, however, with molecular Lewis acids as described below.

Table I. NMR Data for Vinylidene Analogues[a]

^{1}H NMR	^{11}B NMR	^{13}C NMR
$(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$ (II) (30 °C)		
−19.43 (3 Os–H–Os, s)	57.4 (br s)	167.41 (3 CO, s)
		165.26 (6 CO, d, J_{CH} = 11.3 Hz)
		132.50 (1 C, br)
$(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBBr}_2)$ (II) (30 °C)		
−19.36 (3 Os–H–Os, s)	52.5 (br s)	166.83 (3 CO, s)
		164.55 (6 CO, d, J_{CH} = 12.5 Hz)
		138.45 (1 C, br)
$(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-BCH}_2)$ (VI) (30 °C)		
3.74 (1 H, m)	53.5 (br s)	178.98 (1 CO, d, J_{CH} = 12.6 Hz)
3.49 (1 H, m)		169.74 (1 CO, d, J_{CH} = 9.5 Hz)
−12.26 (1 Os–H–B, br)		174.05 (1 CO, d, J_{CC} = 15.6 Hz)
−13.45 (1 Os–H–B, br)		172.96 (1 CO, s)
−20.39 (1 Os–H–Os, s)		172.59 (1 CO, s)
		172.13 (1 CO, s)
		167.96 (1 CO, d, J_{CH} = 9.3 Hz)
		167.60 (1 CO, d, J_{CH} = 4.6 Hz)
		165.49 (1 CO, d, J_{CH} = 9.3 Hz)
		47.71 (CH_2, br s)

[a] In CD_2Cl_2.

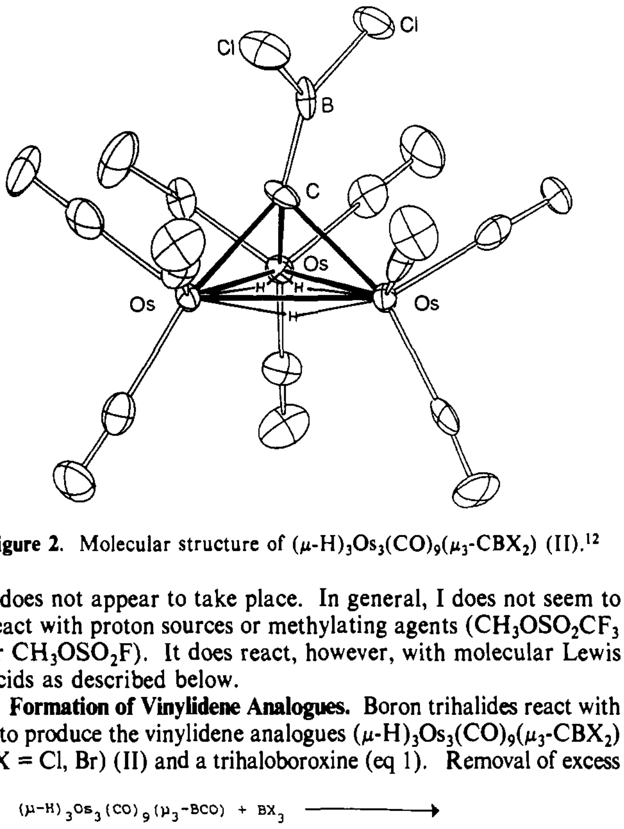

Figure 2. Molecular structure of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBX}_2)$ (II).[12]

Formation of Vinylidene Analogues. Boron trihalides react with I to produce the vinylidene analogues $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBX}_2)$ (X = Cl, Br) (II) and a trihaloboroxine (eq 1). Removal of excess

$$\underset{\text{I}}{(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})} + BX_3 \longrightarrow \underset{\text{II}}{(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBX}_2)} + {}^1/_3\ B_3X_3O_3 \qquad (1)$$

BX_3 results in disproportionation of the trihaloboroxine $B_3X_3O_3$ to BX_3 and B_2O_3.[16] Chemical confirmation of the Os_3C core of II is provided by hydrolysis to $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CH})$ and boric acid. NMR data from II are presented in Table I.

The molecular structure of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$ has been determined by means of a single-crystal X-ray analysis (Figure 2).[12] Its Os_3C core is structurally similar to that of the methylidyne clusters $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CX})$ (X = H, Cl, Br, Ph).[17–19] The B–C vector is tilted 15° from being perpendicular to the triosmium plane. The two Cl–B–C bond angles (123 (1), 121 (1)°) and the Cl–B–Cl bond angle (116 (1)°) around the tricoordinate boron atom are consistent with its being sp^2 hybridized. The B–C distance, 1.47 (2) Å, is intermediate between

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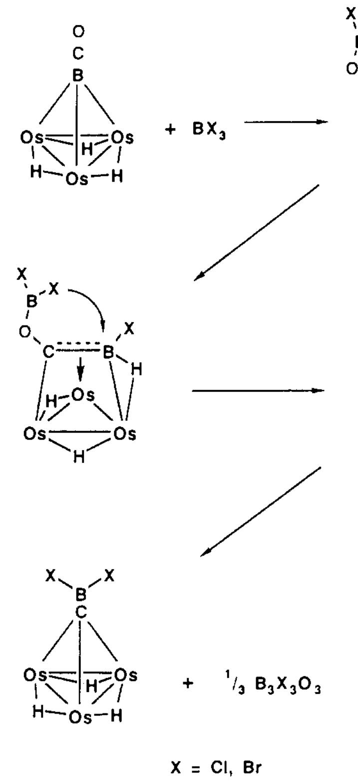
Scheme I



the observed boron–carbon double-bond distance, 1.361 (5) Å,[20a] and observed boron–carbon single-bond distances (ca. 1.6 Å).[20b,c] It is indicative of partial double-bond character, which could reflect π-interaction between the empty p orbital on the boron and the filled e set of cluster orbitals centered on the capping carbon atom.[21] Similar bonding interaction between the carbido carbon and the tricoordinate boron in $HFe_4(CO)_{12}CBH_2$ has been proposed by Fehlner and co-workers.[22]

The vinylidene analogues, $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}CBX_2)$ (X = Cl, Br), produce simple NMR spectra (Table I). Proton NMR spectra consist of a singlet at high field corresponding to equivalent hydrogen atoms that bridge osmium–osmium bonds. Boron-11 NMR spectra show a broad singlet. The three axial carbonyl ligands give rise to a single singlet in the ^{13}C NMR spectra, while the six radial carbonyls produce a single doublet. The doublet character of the radial carbonyls' signal and its magnitude ($J_{CH} \sim 10$ Hz) indicate that they are trans to the hydrogen bridges. A broad singlet in each spectrum is assigned to the capping carbon of the cluster. It falls in the range reported for other methylidyne clusters.[23]

Table II. NMR Data for $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}BCl_2(L))^a$

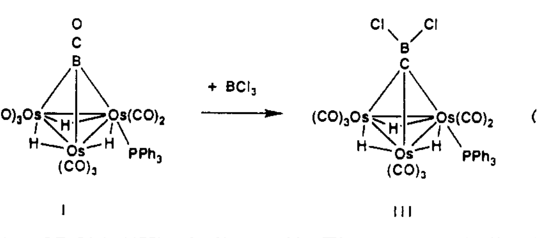
^1H NMR	^{11}B NMR
L = NMe_3 (−40 °C)	
3.18 (9 H, s)	21.0 (s)
−18.98 (3 Os-H-Os, s)	
L = PMe_3 (−40 °C)	
1.62 (9 H, d, J_{PH} = 105 Hz)	13.1 (br s)
−19.07 (3 Os-H-Os, s)	
L = PPh_3 (30 °C)	
7.32 (3 H, m)	3.98 (d, J_{BP} = 154 Hz)
7.11 (6 H, d, J_{HH} = 5.0 Hz)	
6.99 (6 H, d, J_{HH} = 5.2 Hz)	
−19.00 (3 Os-H-Os, s)	

[a] In CD_2Cl_2.

The formation of II from the reaction of I with BCl_3 (eq 2) involves interchange of the boron and carbon atom positions. This transformation was studied by examining the products of the synthesis using ^{10}B-labeled reactants. From the reaction of $^{10}BCl_3$ with I (normal boron isotopic abundance), the ^{11}B NMR spectrum exhibits a signal of normal intensity for II (57.4 ppm), while no signal is observed for $B_3Cl_3O_3$ or its decomposition products. On the other hand, the ^{11}B NMR spectrum from the reaction of I (^{10}B labeled) with BCl_3 (normal boron isotopic distribution) reveals only the presence of $B_3Cl_3O_3$. These observations indicate that there is no detectable interchange between the boron in BCl_3 and the boron of $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}BCO)$ in the formation of $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}CBCl_2)$. Thus the formation of II appears to occur through intramolecular exchange of the boron and carbon atoms of I. However, on a much slower time scale than that of the formation of II (10 min vs 2 days), $^{10}BCl_3$ reacts with II to noticeably enrich II with the ^{10}B isotope.

A proposed reaction pathway for the formation of II is given in Scheme I. This scheme is similar to but differs in detail from that proposed in a preliminary communication[12] and is influenced by the structure of $(\mu\text{-}H)_3Os_3(CO)_9[\mu^3\text{-}\eta^2\text{-}C(OC_8H_{14})BCl]$, which is described later in this report. In Scheme I the formation of II is initiated through electrophilic attack of BX_3 at the oxygen of the unique carbonyl. The resulting reduction of the CO bond order induces a shift of this carbonyl from the terminal position to a bridging site.[24] Movement of the carbonyl ligand into the μ_3-site exposes the boron vertex and results in successive halogen atom transfer from the reagent boron to the cluster boron. With the elimination of X–B–O as trihaloboroxine, $B_3X_3O_3$, cluster II is produced.

A triphenylphosphine derivative of I has been prepared:[18] $(\mu\text{-}H)_3Os_3(CO)_8(PPh_3)(\mu_3\text{-}BCO)$. Its structure, determined from a single-crystal X-ray analysis,[25] is like that of I (Figure 1) except that an axial carbonyl group bound to an osmium atom is replaced by an axial PPh_3 group. The reaction of this cluster with BCl_3 was studied in order to determine if an analogue of a vinylidene cluster would be formed or whether the BCl_3 would abstract the PPh_3 group from the cluster. The observed reaction (equation 2) produced the vinylidene analogue $(\mu\text{-}H)_3Os_3(CO)_8(PPh_3)(\mu_3\text{-}CBCl_2)$ (III), similar to II. There was no indication of abstraction of PPh_3 to form Ph_3PBCl_3. The ^{11}B NMR spectrum, a broad singlet at 53.4 ppm, correlates well with that of II. The proton NMR spectrum in CD_2Cl_2 at 30 °C (7.42 (m, 15 H), −18.41 (d, 2 H, J_{PH} = 10.8 Hz), −19.63 ppm (s, 1 H)) is consistent with a structure in which the PPh_3 ligand is in an axial position cis to the bridging hydrogens. The P–H coupling constant observed is in accord with previously reported values for



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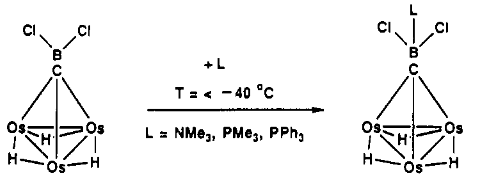
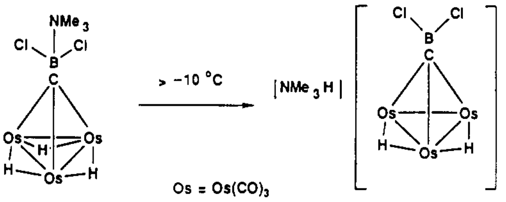
cis P–H coupling[26] between an axial phosphorus and a bridge proton. This compound is very sensitive to moisture; it is hydrolyzed quantitatively to $(\mu\text{-H})_3Os_3(CO)_8(PPh_3)(\mu_3\text{-CH})$ and boric acid.

Reactions of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$ with Nucleophiles. The Lewis bases NMe_3, PMe_3, and PPh_3 add to the tricoordinate boron of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$ (II) (equation 3a). NMR data from the adducts are given in Table II. Boron-11 chemical shifts of the adducts are 30–50 ppm upfield of the chemical shift of II (57.4 ppm). Above −10 °C the NMe_3 adduct is converted to the salt $[NMe_3H][(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-CBCl}_2)]$ through deprotonation of II by the amine (equation 3b). NMR spectra in CD_2Cl_2 at 30 °C are as follows. $[NMe_3H]^+$: $\delta(^1H)$ 11.79 (br s, 1 H), 2.87 ppm (s, 9 H). $[(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-CBCl}_2)]^-$: $\delta(^1H)$ −19.23 ppm (s, 2 H); $\delta(^{11}B)$ 45.0 ppm (br s). Similarly $HFe_4(CO)_{12}CBH_2$, a cluster-substituted monoborane, was shown by Fehlner and co-workers[22b] to be deprotonated by NMe_3 to form $[NMe_3H][Fe_4(CO)_{12}CBH_2]$.



II

(3a)

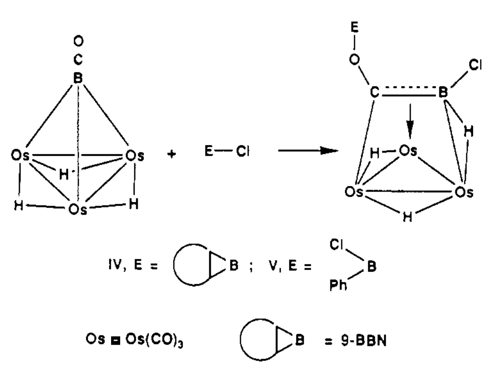


(3b)

Above −10 °C, the PMe_3 adduct is unstable. The PPh_3 adduct is sufficiently stable at 30 °C to obtain its NMR spectrum. Above this temperature, the presence of free PPh_3 is noted in the ^{31}P NMR spectrum.

Formation of Alkyne Analogues. In an attempt to isolate compounds that would relate to proposed intermediates in the reaction of I with BX_3 (Scheme I) to produce II (equation 2), reactions of I with the mono- and dichloroborane reagents *B*-chloro-9-borabicyclo(3.3.1)nonane (*B*-Cl-9-BBN)[27] and phenylboron dichloride were studied.

B-Cl-9-BBN reacts with I to produce $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C(OBC}_8H_{14})B(Cl)]$ (IV) (eq 4). The molecular structure of IV has been determined by means of a single-crystal X-ray analysis (Figure 3).[13] In the formation of IV, the unique carbonyl of I is shifted to a μ_3-site capping two osmiums and the boron atom, while the chlorine atom of *B*-Cl-9-BBN is transferred to the μ_3-boron of the cluster.



(4)

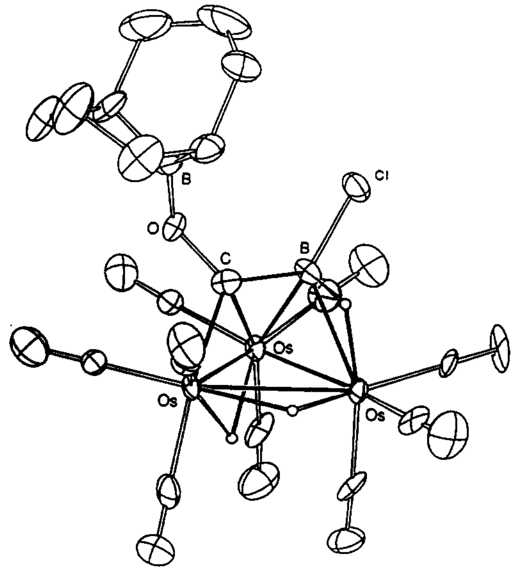


Figure 3. Molecular structure of $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C(OBC}_8H_{14})B(Cl)]$ (IV).[13]

Compound IV is considered to be an alkyne analogue, having a carbon atom replaced by a BH group. The B–C unit along with the H atom bridging Os–B donates 4 electrons to the cluster through a π-interaction with an Os atom, an Os–C σ-bond, and a hydrogen-bridged Os–H–B bond. The B–C unit adopts the $\mu_3\text{-}\eta^2$ bonding mode observed for the C–C bond in alkyne analogues.[28] It is oriented nearly parallel, within 10°, to an Os–Os bond. Analogously, alkyne products result from electrophilic attack at the oxygen atom of the CCO unit of iron and osmium ketenylidene dianions[7,8] and a mononuclear tungsten complex.[29] The B–C distance in IV, 1.46 (2) Å, is comparable to B–C distances observed in $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ (I),[10] $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$ (II),[12] and the ditungsten alkyne analogue $W_2[\mu\text{-MeCB(H)Et}](CO)_4(\eta^5\text{-}C_5H_5)_2$[30] (1.469 (15), 1.47 (2), and 1.46 (1) Å respectively).

Phenylboron dichloride, $PhBCl_2$, reacts with I to produce the alkyne analogue $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C\{OB(Ph)Cl\}B(Cl)}]$ (V) (equation 4). This complex is slowly converted to $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$ (II) at room temperature. The proposed structure of V is related to that of IV. Infrared spectra of IV and V (Figure 4) show strong similarities. NMR data (Table III) from the cluster components of IV and V are also very similar.

Boron-11 NMR spectra of IV and V consist of a broad downfield resonance due to the oxygen-substituted borons and a sharper upfield signal for the cluster borons. Assignment of the oxygen-substituted borons is based upon reported values for 9-BBN phenylboron alkoxide derivatives.[31] Proton NMR spectra from IV and V have downfield signals for the organic fragments and three distinct hydride signals. Broad singlets at −11.75 ppm from IV and −11.69 ppm from V sharpen with ^{11}B decoupling or upon reducing the temperature (−30 °C) and are attributed to Os–H–B interactions. The remaining hydride resonances are assigned to hydrogen atoms bridging along the osmium framework.

The $^{13}C\{^1H\}$ NMR spectrum at 30 °C from IV has signals for the bicyclic ring carbons and the nine terminal carbonyl ligands.

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Table III. NMR Data for Alkyne Analogues[a]

^1H NMR	^{11}B NMR	$^{13}C\{^1H\}$ NMR			
	$(\mu\text{-}H)_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C(OBC_8H_{14})B(Cl)]$ (IV) (30 °C)				
1.90 (4 H, m)	58.8 (B–O, br s)	CO	175.03	174.42	172.75
1.82 (8 H, m)	18.5 (B–Cl, s)		169.06	168.26	167.95
1.39 (2 H, m)			166.06	165.93	162.51
−11.75 (1 B–H–Os, br)		C–B	138.03 (br s)		
−16.18 (1 Os–H–Os, br)		9-BBN	33.79	33.52	
−21.87 (1 Os–H–Os, br)			24.96 (br)	23.42	
	$(\mu\text{-}H)_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C\{OB(Ph)Cl\}B(Cl)]$ (V) (−85 °C)				
7.96 (2 H, d, J_{HH} = 3 Hz)	37.5 (B–O, br s)	CO	174.70	173.53	171.07
7.54 (2 H, m)	20.4 (B–Cl, s)		168.61	167.95	167.16
7.42 (1 H, t, J_{HH} = 3 Hz)			165.65	164.99	162.15
−11.69 (1 B–H–Os, br)		C–B	129.74 (br s)		
−16.69 (1 Os–H–Os, s)		phenyl	134.42	132.27	
−21.71 (1 Os–H–Os, s)			131.68 (br)	127.51	

[a] In CD_2Cl_2.

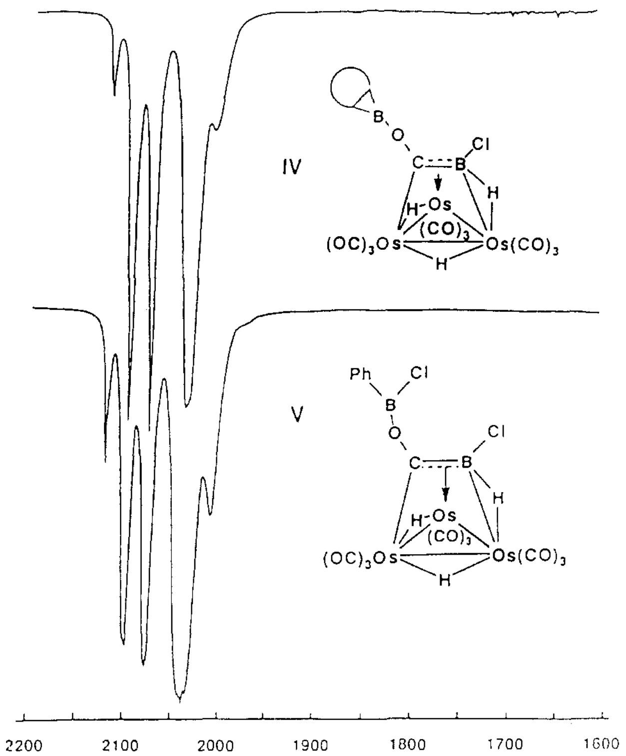


Figure 4. Infrared spectra of $(\mu\text{-}H)_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C(OBC_8H_{14})B(Cl)]$ (IV) and $(\mu\text{-}H)_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C\{OB(Ph)Cl\}B(Cl)]$ (V).

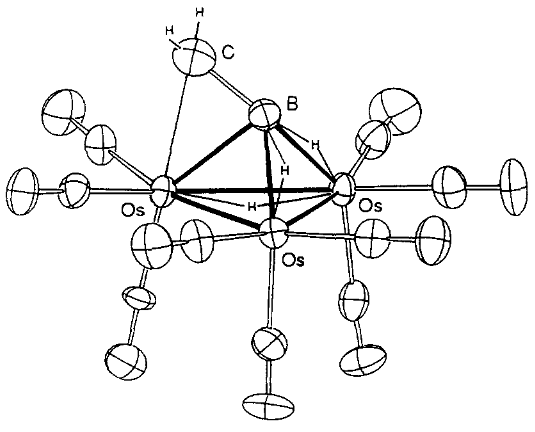
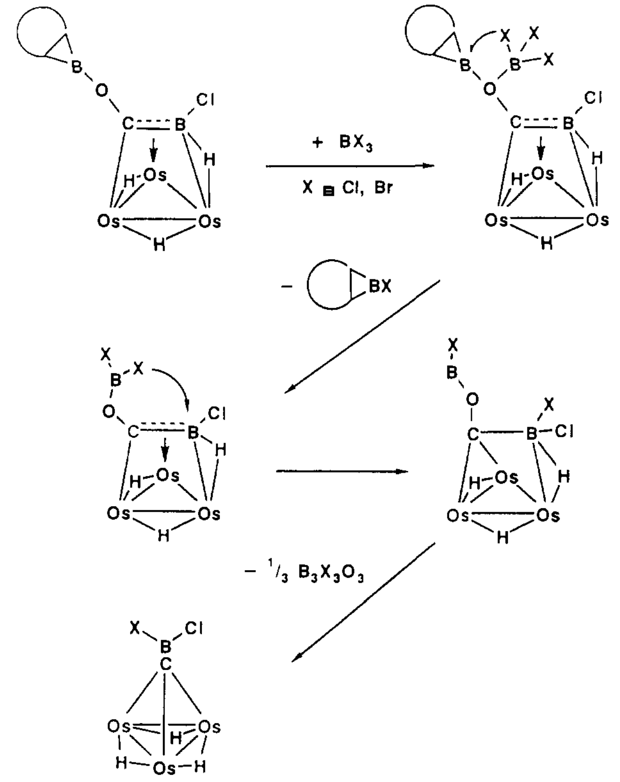


Figure 5. Molecular structure of $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CCH_2)$ (VI).[14]

The alkyne carbon signal occurs as a broad singlet at 138.03 ppm. The $^{13}C\{^1H\}$ NMR (30 °C) spectrum from V has signals for the phenyl group and the carbonyl ligands but not the two carbons bonded to boron atoms (alkyne carbon and phenyl ipso carbon).

Scheme II



However, two new broad signals at 131.68 and 129.74 ppm are observed in the low-temperature (−85 °C) $^{13}C\{^1H\}$ NMR spectrum. Low-temperature NMR spectroscopy has been used previously to obtain ^{13}C NMR data for phenylboron derivatives.[32] Since the cluster carbons are ^{13}C enriched (30–35%) while the phenyl carbons are not, the signal of higher intensity, 129.74 ppm, is assigned to the alkyne carbon.

The reaction of $(\mu\text{-}H)_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C(OBC_8H_{14})B(Cl)]$ with BCl_3 produces $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}CBCl_2)$ (II), while the reaction with BBr_3 gives evidence for the formation of the mixed-halo complex $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}CBClBr)$ (equation 5). Boron-11 NMR studies of this reaction show rapid formation of *B*-X-9-BBN. Initial coordination of BX_3 to the oxygen atom of the C–O–B unit (Scheme II) followed by halogen atom transfer to the 9-BBN boron could cause rupture of the B–O bond with elimination of *B*-X-9-BBN to produce the proposed intermediate for the reaction of $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}BCO)$ with BX_3 (Scheme I). A similar step has been proposed for the reaction of BX_3 (X

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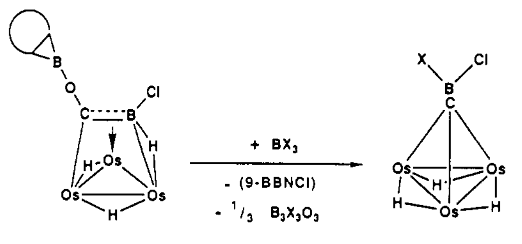


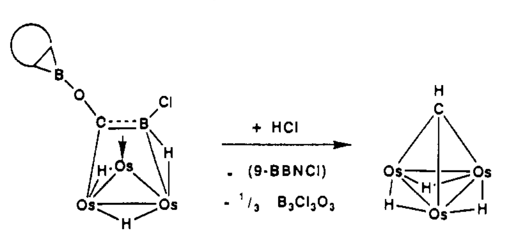
(5)

IV

X = Cl, Br Os = Os(CO)$_3$

= Cl, Br) with the boroxin-supported methylidyne cluster [(μ-H)$_3$Os$_3$(CO)$_9$(μ_3-C)]$_3$[O$_3$B$_3$O$_3$][17] and for the reaction of BX$_3$ (X = Cl, Br) with the methylidyne clusters (μ-H)$_3$M$_3$(CO)$_9$(μ_3-COMe) (M = Ru, Os).[33] In a reaction analogous to that given by eq 5, V reacts with BCl$_3$ to form II, PhBCl$_2$, and B$_3$Cl$_3$O$_3$.

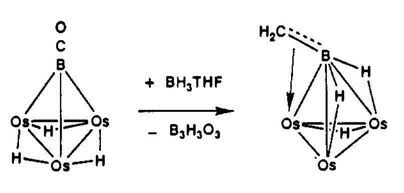
The methylidyne complex (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-CH) is formed in nearly quantitative yield in the reaction of IV with HCl (eq 6). It is formed in reduced yield (25%) in the reaction of V with HCl.



(6)

IV Os = Os(CO)$_3$

Reduction of the Unique Carbonyl in (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-BCO) with BH$_3$·THF. The unique carbonyl of I is reduced to a CH$_2$ group by THF·BH$_3$ to produce the vinylidene analogue (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-η^2-BCH$_2$) (VI)[14] (eq 7), a process that could occur through initial coordination of BH$_3$ to the oxygen atom of the carbonyl to give (μ-H)$_3$(CO)$_9$Os$_3$(μ_3-BCOBH$_3$) followed by transfer of two BH hydrogens to the carbon atom. Elimination of H–B–O as the boroxine trimer, B$_3$H$_3$O$_3$, would then result in the formation of VI. The boroxine trimer decomposes into B$_2$O$_3$ and B$_2$H$_6$.[34] Deuterium-labeling experiments indicate that reduction of the CO occurs with no apparent scrambling of B–H and Os–H–Os hydrogen atoms. Reaction of (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-BCO) with BD$_3$·THF gives (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-η^2-BCD$_2$), while reaction of (μ-D)$_3$Os$_3$(CO)$_9$(μ_3-BCO) with BH$_3$·THF gives (μ-D)$_3$Os$_3$(CO)$_9$(μ_3-η^2-BCH$_2$). The electrophile BH$_3$ is a weaker Lewis acid toward oxygen bases than the trihaloboranes, BX$_3$ (X = F, Cl, Br).[35] It is probably not sufficiently electrophilic to induce a shift of the unique carbonyl ligand from its terminal position to a bridging site,[24] which would account for the fact that interchange of boron and carbon atom positions does not occur as in the formation of II from the reaction of I with BCl$_3$.



(7)

I Os ≡ Os(CO)$_3$ VI

The molecular structure of VI has been determined by a single-crystal X-ray analysis (Figure 5).[14] The basic structure resembles that of (μ-H)$_2$Os$_3$(CO)$_9$(μ_3-η^2-CCH$_2$),[36] a vinylidene cluster. The B–C distance, 1.498 (15) Å, is approximately 0.1 Å shorter than observed B–C single-bond distances.[20b,c] The BCH$_2$ fragment can be considered to be bound to the triosmium framework through two hydrogen-bridged bonds between Os and B atoms and through interaction of the B–CH$_2$ π-system with an Os atom. This π-interaction results in a tilt of the BCH$_2$ unit toward the Os atom. The tilt (60° from the perpendicular) is significantly larger than observed in structurally characterized vinylidene clusters (40–50°).[37] 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. While the extreme tilt angle implies that the compound could also be described as a methylene-bridged complex, the "short" B–C distance and the relatively long Os–C distance, 2.325 (17) Å, favor the vinylidene analogy.

The proton NMR spectrum of VI (Table I) indicates that VI is an asymmetric molecule. Five signals are observed. Two signals are assigned to the CH$_2$ protons, and three signals are assigned to the bridging hydrides. Two of the bridge signals are broad; they sharpen upon ^{11}B decoupling and also upon decreasing the temperature (−30 °C). These signals are assigned to Os–H–B interactions. The remaining bridge signal is assigned to the proton in the Os–H–Os bridge. The ^{1}H NMR spectrum of IV gives no evidence for fluxional character, up to the decomposition temperature of 90 °C in toluene. On the other hand the analogue (μ-H)$_2$Os$_3$(CO)$_9$(μ_3-η^2-CCH$_2$) is fluxional above room temperature; singlets due to the CH$_2$ protons coalesce to a single signal at 72 °C.[36a]

The ^{11}B NMR spectrum of VI consists of a broad singlet at 53.5 ppm. A boron–carbon coupling constant of 51 Hz was obtained from the boron-11 NMR spectrum of a ^{13}C-enriched (30–35%) sample of VI. The ^{13}C NMR spectrum (Table I) of VI also implies that the molecule is asymmetric. Upon proton decoupling, the nine terminal carbonyl ligands produce eight singlets and a doublet (J_{CC} = 15.6 Hz). The doublet is attributed to coupling of the methylene carbon with the carbonyl ligand trans to it. A broad singlet at 47.7 ppm is assigned to the methylene carbon.

Experimental Section

General Data. All manipulations were performed with standard high-vacuum-line techniques or in a drybox under an atmosphere of prepurified N$_2$. All solvents were dried, degassed, and then distilled into storage bulbs equipped with 4-mm Kontes Teflon stopcocks. Methylene chloride was dried over P$_2$O$_5$, while hexanes, pentanes, and toluene were dried over sodium benzophenone ketyl. BBr$_3$ (Aldrich Chemical Co.) and BCl$_3$ (Matheson Scientific Products) were fractionated on a high-vacuum line to remove any HBr or HCl impurities. ^{10}BF$_3$ (92% ^{10}B) was obtained by heating the ^{10}BF$_3$·CaF$_2$ adduct (Eagle-Pitcher Industries Inc.) to 200 °C for 4 h. The ^{10}BF$_3$ was collected at −196 °C and fractionated through a −140 °C trap (low-boiling petroleum ether/liquid N$_2$) to remove any impurities. B$_2$H$_6$ was prepared through published methods.[38,39] B$_2$D$_6$ was prepared by using LiAlD$_4$ instead of LiAlH$_4$, while ^{10}B$_2$H$_6$ was prepared by using ^{10}BF$_3$.[38] LiAlH$_4$, LiAlD$_4$ (95% d_4), and borabicyclo(3.3.1)nonane (9-BBN) were obtained from Aldrich Chemical Co. and used as received. *B*-Cl-9-BBN was prepared by the published procedure and was purified by sublimation.[27] A 10-g sample of PhBCl$_2$ (Alfa Products) was dissolved in 100 mL of hexanes in a volumetric flask equipped with a 9-mm Fisher-Porter solv-seal joint and stored until use. PPh$_3$ (Alfa Products) was recrystallized from hot C$_2$H$_5$OH and dried under high vacuum. Os$_3$(CO)$_{12}$ (Strem Inc.) was used as received. (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-BCO) was prepared by hydroboration of (μ-H)$_2$Os$_3$(CO)$_{10}$.[10] (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-^{10}BCO) was prepared by using ^{10}B$_2$H$_6$[10] as the ^{10}B source. (μ-H)$_3$Os$_3$(CO)$_8$(PPh$_3$)(μ_3-BCO) was prepared by

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hydroboration of $(\mu\text{-H})_2Os_3(CO)_9(PPh_3)$.[18]

Boron-11 NMR [$\delta(Et_2O{\cdot}BF_3) = 0.00$ ppm)] and proton NMR spectra [δ(TMS) = 0.00 ppm] were obtained on either a Bruker MSL-300 NMR spectrometer operating at 96.3 and 300 MHz or a Bruker AM-250 NMR spectrometer operating at 80.2 and 250 MHz, respectively. Carbon-13 NMR spectra were obtained on either a Bruker AM-500 spectrometer (125.7 MHz) or a Bruker AM-250 spectrometer (62.9 MHz). Infrared spectra were obtained with a Mattson Cygnus-25 FT spectrometer.

Attempted Reactions of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ with Proton Sources and Methylating Agents. No change in the IR, ^{1}H NMR, and ^{11}B NMR spectra of $(\mu\text{-H})_3Os_3(CO)_9(\mu^3\text{-BCO})$ was observed upon attempting reactions with proton sources (HCl, HBr, and CF_3COOH) or methylating agents ($CH_3OSO_2CF_3$ and CH_3OSO_2F) in CH_2Cl_2 and in toluene at 30–70 °C using 1–20 equiv of the electrophile.

Preparation of $^{10}BCl_3$. $^{10}BF_3$ (1 mmol) was condensed into a 250-mL flask containing $AlCl_3$ (625 mg, 4.69 mmol). The mixture was heated to 200 °C for 2 h to produce $^{10}BCl_3$ and AlF_3. The $^{10}BCl_3$ was purified by fractionation through a series of traps at −45, −110, and −196 °C. It was collected in the −110 °C trap. Impurities and any unreacted $^{10}BF_3$ were collected in the remaining traps.

Preparation of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBX}_2)$ (X = Cl, Br). Into a 25-mL reaction flask was condensed onto a CH_2Cl_2 solution (6 mL) of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ (130 mg, 0.150 mmol) an excess amount of BX_3 (X = Cl, Br). The reaction mixture was allowed to warm to room temperature and stirred for 30 min. Volatile components were removed, and fresh CH_2Cl_2 was added to the reaction residue. The solution was filtered through a frit in an extractor, leaving an insoluble solid (B_2O_3) and a pale yellow solution. Solvent CH_2Cl_2 was pumped away from the filtrate, and the residue was washed with hexanes to produce white $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBX}_2)$. The yield is 93% for X = Cl (120 mg, 0.140 mmol) and 87% for X = Br (132 mg, 0.131 mmol). NMR data are listed in Table I. IR spectrum of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$ (ν_{CO}; CH_2Cl_2: 2020 (s, br), 2089 cm^{-1} (s). IR spectrum of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBBr}_2)$ (ν_{CO}; CH_2Cl_2): 2029 (br, s), 2091 cm^{-1} (s). Mass spectrum (EI): calc for $^{12}C_{10}{}^1H_3{}^{11}B^{81}Br_2{}^{16}O_9{}^{192}Os_3$, m/e = 1016; obs, $m/e(M - 1)$ = 1015. Anal. Calc for $C_{10}H_3B_1Br_2O_9Os_3$: C, 11.90; H, 0.30. Found: C, 11.75; H, 0.32.

Preparation of $(\mu\text{-H})_3Os_3(CO)_8(PPh_3)(\mu_3\text{-CBCl}_2)$. BCl_3 (0.300 mmol) was condensed into a 25-mL flask containing a CH_2Cl_2 solution (8 mL) of $(\mu\text{-H})_3Os_3(CO)_8(PPh_3)(\mu_3\text{-BCO})$ (114.5 mg, 0.104 mmol). The reaction mixture was stirred at room temperature for 30 min, and then the volatile components were removed. Fresh CH_2Cl_2 was added and the solution was filtered through a frit on an extractor, leaving an insoluble white precipitate of B_2O_3. The yellow solid, produced from the filtrate, was washed with hexanes to give $(\mu\text{-H})_3Os_3(CO)_8(PPh_3)(\mu_3\text{-CBCl}_2)$ in 78% yield (90.9 mg, 0.078 mmol). NMR spectra (CD_2Cl_2, 30 °C): $\delta(^1H)$ 7.42 (15 H, m), −18.41 (2 H, d, J_{PH} = 10.5 Hz), −19.63 ppm (1 H, s); $\delta(^{11}B)$ 53.4 ppm (br s); $\delta(^{31}P)$ −10.83 ppm (m). IR spectrum (ν_{CO}; CH_2Cl_2): 1968 (w), 2013 (s), 2034 (s), 2082 (vs), 2101 cm^{-1} (w).

Hydrolysis of Vinylidene Analogues. (a) $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBX}_2)$ (X = Cl, Br) To Produce $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CH})$. Complexes containing Cl or Br were hydrolyzed by the following general procedure. Excess H_2O (ca. 2 mL) was condensed onto a CH_2Cl_2 solution (5 mL) of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBX}_2)$ (ca. 0.050 mmol) at −78 °C. The reaction mixture was stirred for 24 h, and then the volatile components were pumped away to leave a light yellow residue. In an extractor the residue was treated with CH_2Cl_2. Solvent was pumped from the extract, leaving behind solid $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CH})$ in 95% yield. It was identified by comparison with its reported ^{1}H NMR, ^{13}C NMR, IR, and mass spectra.[40] The remaining white residue on the extractor frit was boric acid.

(b) $(\mu\text{-H})_3Os_3(CO)_8(PPh_3)(\mu_3\text{-CBCl}_2)$ To Produce $(\mu\text{-H})_3Os_3(CO)_8(PPh_3)(\mu_3\text{-CH})$. Excess H_2O (ca. 2 mL) was condensed onto a solution of 48.5 mg (0.042 mmol) of $(\mu\text{-H})_3Os_3(CO)_8(PPh_3)(\mu_3\text{-CBCl}_2)$ in 5 mL of CH_2Cl_2 at −78 °C. The reaction mixture was stirred for 24 h, and then the volatile components were removed to leave behind the yellow residue. In an extractor the residue was treated with CH_2Cl_2. Solvent was pumped from the extract to give $(\mu\text{-H})_3Os_3(CO)_8(PPh_3)(\mu_3\text{-CH})$ in 94% yield (41.8 mg, 0.039 mmol). NMR spectrum: $\delta(^1H)$ 9.82 (1 H, s), 7.33 (15 H, m), −18.42 (2 H, d, J_{PH} = 10.0 Hz), −19.58 ppm (1 H, s). Mass spectrum: calc for $^{12}C_{27}{}^1H_{19}{}^{16}O_8{}^{31}P^{192}Os_3$, m/e = 1078; obs, m/e = 1078.

Boron-10-Labeled Reactions. (a) Reaction of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ with $^{10}BCl_3$. In a reaction flask equipped with an NMR tube side arm, $^{10}BCl_3$ (0.100 mmol) was condensed at −196 °C onto a CH_2Cl_2 solution (0.5 mL) of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ (86.4 mg, 0.100 mmol). The reaction mixture was stirred for 10 min at room temperature, and then the volatiles were pumped away. The ^{11}B NMR spectrum of the reaction mixture revealed only the presence of the signal for $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$, 57.4 ppm (br s).

(b) Reaction of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-}^{10}BCO)$ with BCl_3. In an experiment carried out under the same conditions as above except that $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-}^{10}BCO)$ was allowed to react with BCl_3, only ^{11}B signals for $B_3Cl_3O_3$, 26.6 ppm (s), and its decomposition product B_2O_3, 32.3 ppm (br s), were observed.

(c) ^{10}B–^{11}B Exchange Reaction between $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$ and $^{10}BCl_3$. In a series of experiments, $^{10}BCl_3$ (0.2 mmol) was condensed onto a CD_2Cl_2 solution (0.5 mL) of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$ (65 mg, 0.070 mmol) in a reaction flask equipped with an NMR tube side arm. For each experiment, the reaction mixture was stirred at room temperature for a different period from 6 h to 2 days, after which the mixture was decanted into the NMR tube and sealed off at −196 °C. The ^{11}B NMR spectrum after 2 days was the only one that showed a significant amount of exchange by revealing the presence of a $^{11}BCl_3$ signal at 46.8 ppm (s).

Reaction of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$ with Nucleophiles. The Lewis bases studied react with $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$ in 1:1 molar ratios without evolution of CO. In order to obtain NMR data and to establish stabilities of adducts, 1 equiv of Lewis base was added to (PPh_3) or condensed into (NMe_3 and PMe_3) an NMR tube containing a CD_2Cl_2 (0.5 mL) solution of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$ (115 mg, 0.100 mmol) at −196 °C. The NMR tube was sealed off at −196 °C. To initiate the reactions, the contents of the NMR tube was thawed and shaken twice. The NMR tube was then placed into a precooled NMR probe and allowed to equilibrate for 5 min before spectra were collected. The NMR data from the adducts and their stabilities are reported in Table II and under Results and Discussion.

The salt $[NMe_3H][(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-CBCl}_2)]$ was prepared and isolated as follows. NMe_3 (0.052 mmol) was condensed at −196 °C into a reaction flask that contained $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$ (47.8 mg, 0.052 mmol) in CH_2Cl_2 (8 mL). The reaction mixture was stirred at room temperature for 1 h. Volatiles were then pumped away, leaving behind $[NMe_3H][(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-CBCl}_2)]$ as a white solid, which was washed with 2 mL of Et_2O. A 90% yield (38.7 mg, 0.047 mmol) was obtained. NMR spectra are reported under Results and Discussion. IR spectrum (ν_{CO}; CH_2Cl_2, 30 °C): 2013 (s), 2083 cm^{-1} (br). The cation and anion were identified by comparison of the ^{1}H and ^{11}B NMR spectra of the product with the ^{1}H NMR spectrum of $[NMe_3H]Cl$ and the ^{1}H NMR, ^{11}B NMR, and IR spectra of $K[(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-CBCl}_2)]$. $K[(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-CBCl}_2)]$ was generated from the reaction of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$ with excess KH in the presence of BMe_3 (10%) in THF at room temperature. The reaction gives off 1 mol of H_2/mol of cluster. NMR spectra (CD_2Cl_2, 30 °C): $\delta(^1H)$ −19.42 ppm; $\delta(^{11}B)$ 46.2 ppm (br s). IR spectrum (γ_{CO}; CH_2Cl_2, 30 °C): 2013 (s), 2083 cm^{-1} (br).

Preparation of $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C(OBC}_8H_{14})B(Cl)]$. In the drybox, *B*-Cl-9-BBN (74.3 mg, 0.474 mmol) was weighed into a vial. The vial was rinsed with CH_2Cl_2 (6–8 mL) into a 25-mL reaction flask containing $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ (82.1 mg, 0.0950 mmol). The reaction mixture was then degassed at −78 °C and stirred at ambient temperature for 1 h. Volatile components, including the excess *B*-Cl-9-BBN, were removed resulting in an oily residue. Pentanes were added to the residue, and the mixture was stirred for 30 min, resulting in the formation of a pale yellow precipitate. Volatiles were removed and fresh pentanes added. The precipitate was filtered out, washed with additional pentanes, and isolated as $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C(OBC}_8H_{14})B(Cl)]$ in 75% yield (72.7 mg, 0.071 mmol). NMR data are listed in Table II. IR spectrum (ν_{CO}; CH_2Cl_2): 2010 (m, sh), 2035 (s), 2075 (s), 2095 (s), 2117 cm^{-1} (w). Mass spectrum (EI): calcd for $^{12}C_{18}{}^1H_{17}{}^{11}B_2{}^{37}Cl^{16}O_{10}{}^{192}Os_3$, m/e = 1028; obs, $m/e(M - 1) - 1027$. Anal. Calc for $C_{18}H_{17}B_2Cl_1O_{10}Os_3$: C, 21.16; H, 1.67. Found: C, 20.90; H, 1.47.

Reaction of $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C(OBC}_8H_{14})B(Cl)]$ with BX_3 (X = Cl, Br). Into a reaction flask equipped with an NMR tube side arm was condensed excess BX_3 (X = Cl, Br) onto a CD_2Cl_2 solution (0.5 mL) of $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C(OBC}_8H_{14})B(Cl)]$ (86.8 mg, 0.085 mmol). The reaction mixture was stirred at room temperature for 2 h, and then it was decanted into the NMR tube, which was cooled to −196 °C and sealed. ^{11}B NMR spectra (CD_2Cl_2, 30 °C): X = Cl, 82.0 (s, *B*-Cl-9-BBN), 57.4 (br s, $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$), 26.6 ppm (s, $B_3Cl_3O_3$); X = Br; (s, *B*-Br-9-BBN), 55.4 (br s, $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBClBr})$), 23.8 ppm (br s, $B_3Br_3O_3$).

Reaction of $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C(OBC}_8H_{14})B(Cl)]$ with HCl. Anhydrous HCl (0.092 mmol) was condensed onto a CD_2Cl_2 solution (0.5 mL) of $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C(OBC}_8H_{14})B(Cl)]$ (94.0 mg, 0.092 mmol) in a reaction flask equipped with an NMR tube side arm. The reaction mixture was stirred for 2 h at room temperature, and a small amount of a white precipitate formed. The mixture was then decanted

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into the NMR tube, which was cooled to −196 °C and then sealed. The product $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CH})$ was identified by its ^1H NMR, ^{13}C NMR, IR, and mass spectra.[40]

Preparation of $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C\{OB(Ph)Cl\}B(Cl)}]$. $PhBCl_2$ (100 mg (0.630 mmol) in 1 mL of hexane) was pipetted into a 30-mL reaction vessel containing $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ (77.8 mg, 0.0900 mmol) in the drybox. The reaction mixture was degassed at −78 °C, and CH_2Cl_2 (8 mL) was added. The mixture was stirred for 1 h, resulting in a color change from bright yellow to colorless. After removal of the volatile components, the residue was washed with hexanes to give white $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C\{OB(Ph)Cl\}B(Cl)}]$ in 92% yield (84.7 mg, 0.083 mmol). NMR data are listed in Table II. IR spectrum (ν_{CO}; CH_2Cl_2): 2010 (m), 2034 (vs, br), 2075 (s), 2097 (s), 2118 cm^{-1} (w). Mass spectrum (El): calc for $^{12}C_{16}{}^1H_8{}^{11}B_2{}^{37}Cl_2{}^{16}O_{10}{}^{192}Os_3$, $m/e = 1032$; obs, $m/e = 1032$.

Reaction of $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C\{OB(Ph)Cl\}B(Cl)}]$ with BCl_3. Excess BCl_3 (0.235 mmol) was condensed into a reaction flask containing a CD_2Cl_2 solution (0.5 mL) of $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C\{OB(Ph)Cl\}B(Cl)}]$ (79.6 mg, 0.778 mmol). The reaction vessel was equipped with an NMR tube side arm. The reaction mixture was stirred for 1 h, and then it was decanted into the NMR tube, which was cooled to −196 °C and then sealed. ^{11}B NMR spectrum: 57.4 (br s, $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$), 54.8 ($PhBCl_2$), 26.6 ppm ($B_3Cl_3O_3$).

Preparation of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-BCH}_2)$. Diborane (0.858 mmole) was condensed at −196 °C into a 25-mL reaction flask containing a THF solution (7 mL) of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ (93.3 mg, 0.108 mmol). The reaction mixture was warmed to room temperature and stirred for 30 min, with formation of a white precipitate. Volatiles were pumped away, and the residue was extracted with toluene, leaving behind solid B_2O_3. Volatiles were pumped away from the extract to yield a light yellow solid. Recrystallization from diethyl ether produced $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCH}_2)$ in 80% yield (73.5 mg, 0.086 mmol) based on the cluster starting material. NMR data are listed in Table I. IR spectrum (ν_{CO}; C_6H_{12}): 1985 (m), 1993 (w), 2015 (s), 2034 (s), 2054 (s), 2076 (s), 2107 cm^{-1} (m).

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Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77204-5641

Preparation and Characterization of Tris(trimethylsilyl)silyl Derivatives of Tin. X-ray Crystal Structure of $Cl_2Sn[Si(Si(CH_3)_3)_3]_2$

S. P. Mallela and R. A. Geanangel*

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Six new [tris(trimethylsilyl)silyl]tin(IV) compounds, $R_{4-x}Sn[Si(SiMe_3)_3]_x$ ($R = Me$, $x = 1, 2$; $R = n\text{-Bu}$, $x = 1, 2$; $R = Cl$, $x = 1, 2$) have been prepared and characterized, including ^1H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra, which were consistent with the expected structures. An X-ray structure determination of $Cl_2Sn[Si(SiMe_3)_3]_2$ revealed a pronounced distortion of the tetrahedral geometry around tin induced by the large steric requirements of the $Si(SiMe_3)_3$ groups. Crystals of $C_{18}H_{54}Cl_2Si_8Sn$ were monoclinic, $C2/c$, with $a = 16.050$ (4) Å, $b = 10.014$ (2) Å, $c = 47.289$ (10) a, $\beta = 90.17°$, $V = 7600$ Å^3, and $Z = 8$. The compound was more stable toward atmospheric moisture than comparable organotin dichlorides. Attempts to make the germanium analogue of the dichlorostannane via reaction of $GeCl_4$ with 2 equiv of $(THF)_3LiSi(Si(CH_3)_3)_3$ gave the dimer $[Cl_2GeSi(SiMe_3)_3]_2$ instead.

Introduction

Several reports have described the preparation of metal compounds bearing the tris(trimethylsilyl)methyl and tris(trimethylsilyl)silyl substituents. Derivatives of the former involving Hg,[1] Au,[1] Ge,[1,2] and Sn[1-4] have been described along with examples involving a number of d-block metal compounds[5-10] and one tin compound[11] incorporating the latter. Our interest in these substituents derives from their exceptionally large steric demands, which, in some cases, appear to convey improved thermal stability to their compounds, compared to analogous trimethylsilyl-bearing structures.[7,12] Except in the case of the linear MR_2 compounds ($M = Zn$, Cd, Hg; $R = Si(SiMe_3)_3$), where steric interactions between substituents should be minimal, and $[(Me_3Si)Si]_2Sn(\mu\text{-Cl})Li(THF)_3$, where the Si–Sn–Si bond angle is unusually large at 114.2°, there are no other structurally characterized examples of tris(trimethylsilyl)silyl derivatives that contain more than one such group. It is not clear whether this is due to destabilizing intramolecular steric interactions when more than one large substituent is present or to other factors. Since the utility of bulky substituents in the stabilization of unusual structural and bonding features is well-known, we elected to attempt the synthesis of selected tris(trimethylsilyl)silyl–tin compounds in order to better understand the effect of the bulky group on the behavior and thermal stability of such compounds. We wish to report here the preparation and characterization of new tin(IV) derivatives, $R_{4-x}Sn[Si(SiMe_3)_3]_x$ ($R = Me$, $x = 1, 2$; $R = n\text{-Bu}$, $x = 1, 2$; $R = Cl$, $x = 1, 2$), and X-ray structure determination on Cl_2Sn-

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