Coordination Chemistry Reviews, 121 (1992) 131–154
Elsevier Science Publishers B.V., Amsterdam

Oxyligand derivatives of triosmium dodecacarbonyl

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(Received 7 January 1992)

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A. INTRODUCTION

The rich chemistry of triosmium dodecacarbonyl ($Os_3(CO)_{12}$) is dominated by derivatives containing either soft and/or π-accepting ligands, such as phosphines [1–3], alkynes [4] and nitriles [5], or small hydrocarbon fragments and molecules, such as ethylidyne [6] and benzene [7] (see refs. 8–10 for recent reviews). However, clusters containing "hard" oxygen donor atom ligands [11] such as alkoxides,

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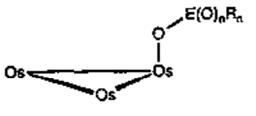
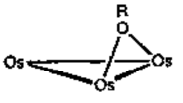
carboxylates and oxyanions are becoming both abundant and increasingly important. For the purpose of this review, oxyligands refers to ligands that are coordinated only through oxygen donor atoms.

Owing to the durability of its metal core, $Os_3(CO)_{12}$ has been found to be a fruitful framework upon which to examine the coordination chemistry of "hard" oxyligands with the formally low-valent transition metal centers found in carbonyl cluster compounds. Among the various complexes known, one particularly interesting group contains triply bridging tridentate oxyligands, such as sulfate [12] and phosphonate [13]. The utility of $Os_3(CO)_{12}$ oxyligand derivatives extends beyond aspects of unusual coordination modes and into the role of model compounds for phenomena such as the chemisorption of oxyligands to metal surfaces [14] and of metal clusters to oxide supports [15–17]. Other derivatives have served as synthetic intermediates [18–20].

The known types of oxyligand derivatives of $Os_3(CO)_{12}$ are shown below. For each given type, the known examples are discussed herein with emphasis on synthetic routes, reactivity, and crystallographic studies. Compilations of hydride ligand chemical shifts, and selected bond distances and angles appear in Sect. D.



Type A



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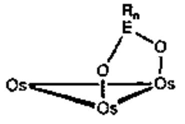

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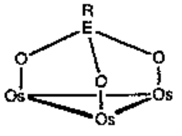

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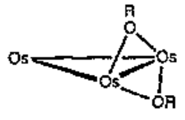
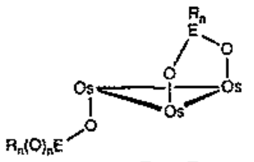


Type E



Type F

In the discussion that follows, oxyligand derivatives that otherwise contain only carbonyl and hydride ligands are referred to as "unsubstituted" and those for which one or more CO/H ligands have been replaced are called "substituted".

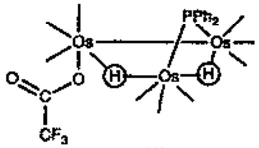
B. COMPLEXES CONTAINING ONE OXYLIGAND

(i) η^1-$OE(O)_nR_n$ ligands (type A)

Two unsubstituted type A clusters have been prepared and characterized by spectroscopic methods: $(\mu\text{-H})Os_3(CO)_{11}(\eta^1\text{-}OC(O)CF_3)$ [20] and $(\mu\text{-H})Os_3(CO)_{11}$-

(η^1-$OReO_3$) [21]. The former complex was synthesized by oxidative addition of F_3CCO_2H to the substitutionally labile cluster $Os_3(CO)_{11}(NCCH_3)$. The unidentate nature of the trifluoroacetate group is evidenced by ν_{COO} vibrations at 1694 and 1413 cm^{-1}. Carbonyl stretching frequencies and ^1H NMR data suggest that this cluster is isostructural with the halogen derivatives (μ-H)$Os_3(CO)_{11}X$ (X = Cl, Br) [22]; however, neither of these clusters has been examined crystallographically. Consequently, the axial orientation of the halogen or trifluoroacetate ligands, presumed using electronic arguments (minimization of the number of good π-acceptors trans to one another), has not been proven. The latter compound, (μ-H)$Os_3(CO)_{11}$(η^1-$OReO_3$), was prepared by reaction of (μ-H)$Os_3(CO)_{11}Br$ with $AgReO_4$. Consistent with η^1 coordination leading to approximate C_{3v} symmetry for the perrhenate group, this complex exhibits three Re–O stretches (940, 914 and 887 cm^{-1}).

Protonation of the cyclometallated cluster [(μ-H)$_2Os_3(CO)_9\{P(C_6H_4)Ph\}$] with F_3CCO_2H is followed by coordination of the $F_3CCO_2^-$ anion to give the substituted type **A** cluster (μ-H)$_2Os_3(CO)_9$(η^1-$OC(O)CF_3$) (μ-PPh_2) (**1**) [23]. Complex **1** was structurally characterized. The $F_3CCO_2^-$ ligand is axially bound and on the opposite side of the Os_3 framework relative to the μ-PPh_2 group.



(1)

(ii) μ-OR ligands (type **B**)

If substitution of a single carbonyl ligand in $Os_3(CO)_{12}$ by OR^- were to occur, an anionic cluster of formula $[Os_3(CO)_{11}(OR)]^-$ would result. Though such a species, or its hydride equivalent $HOs_3(CO)_{11}(OR)$, is a likely intermediate in the reaction of $Os_3(CO)_{12}$ with alcohols, no isolated examples with terminal OR^- ligands have been reported. Instead, the known alkoxide and hydroxide derivatives of $Os_3(CO)_{12}$ all contain bridging OR^- ligands (types **B** and **E**). Type **B** clusters are discussed in this section and type **E** clusters are discussed in Sect. C.

(a) Unsubstituted complexes

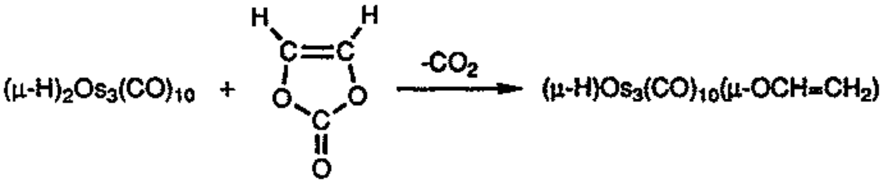
This class of compounds is extensive and alkoxy, phenoxy, siloxy, and vinyloxy derivatives are known. The first type **B** compounds reported, (μ-H)$Os_3(CO)_{10}$(μ-OH) and (μ-H)$Os_3(CO)_{10}$(μ-OMe), were obtained as low-yield by-products (1.6 and 0.2%, respectively) in the synthesis of $Os_3(CO)_{12}$ from OsO_4 and CO in methanol [24,25]. Since this first report, several strategies have been found successful for the synthesis of such clusters in high yields. Direct reaction of $Os_3(CO)_{12}$ with alcohols at elevated temperatures (typically 140–170°C) yields (μ-H)$Os_3(CO)_{10}$(μ-OR) derivatives (R = H

[26]; R = Me, Ph, 2-naphthyl, CH_2Ph, $CHMe_2$, CHMePh, and CMe_2Ph [27]; and R = $SiPh_3$ [28,29]) in variable yields (trace to 81%) (Scheme 1). Using synthetic

$$Os_3(CO)_{12} \xrightarrow{ROH,\ -2CO} (\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OR})$$

Scheme 1.

intermediates such as $Os_3(CO)_{10}(C_6H_8)$ and $Os_3(CO)_{10}(NCCH_3)_2$, less severe conditions (refluxing cyclohexane) are required for reaction with alcohols, and clusters prepared from these intermediates include those with R = H, Et, C_6H_{11}, Ph, and $SiEt_3$ [5,17,30]. The triethylsiloxy derivative $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OSiEt}_3)$ can also be prepared from $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ and Et_3SiOH, presumably with liberation of methane [16,31]. In the presence of ethereal HBF_4 and the weak acids water, methanol, or ethylene glycol, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-N=CHNMe}_2)$ reacts to give $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OR})$ (R = H, Me and CH_2CH_2OH) clusters in good yields (60–75%) [32]. Clusters containing bridging vinyloxy groups, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OCH=CR}_2)$ (R = H, Me, and Ph), have been prepared from reaction of the unsaturated cluster $(\mu\text{-H})_2Os_3(CO)_{10}$ and the appropriate substituted ketene ($R_2C{=}C{=}O$) [33,34]. An improved procedure for the synthesis of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OCH=CH}_2)$ from $(\mu\text{-H})_2Os_3(CO)_{10}$ uses vinylene carbonate rather than ketene [35] (Scheme 2).



Scheme 2.

The seemingly ubiquitous hydroxy compound $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OH})$ has also been obtained from the reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ with dioxygen in the presence of CO and base [36]. Scheme 3 was proposed to account for this reaction, but O_2 was not confirmed as the oxygen atom source by means such as a labeling study.

$$(\mu\text{-H})_2Os_3(CO)_{10} \xrightarrow{CO} (\mu\text{-H})_2Os_3(CO)_{11} \xrightarrow{base,\ -H^+}$$

$$(\mu\text{-H})Os_3(CO)_{11}^- \xrightarrow{O_2,\ -CO_2} (\mu\text{-H})Os_3(CO)_{10}(\mu\text{-O})^- \xrightarrow{H^+} (\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OH})$$

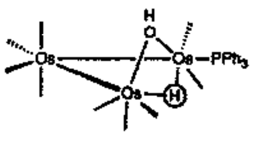
Scheme 3.

Others have noted conversion of $(\mu\text{-H})_2Os_3(CO)_{10}$ to $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OH})$ in wet acetone, suggesting reaction with water rather than O_2 [37]. Recently, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OH})$ was obtained in good yield by reaction of $Os_3(CO)_{10}$ chemisorbed onto silica with HF followed by hydrolysis [38]. The structural nature of $Os_3(CO)_{10}$ chemisorbed on silica is discussed below.

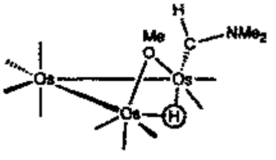
(b) Substituted complexes

The majority of substituted type **B** clusters have been synthesized directly from unsubstituted alkoxy precursors. There are four important reactions for the alkoxy derivatives: (a) substitution of a bridgehead carbonyl(s) ligand, (b) hydride replacement, (c) acid-induced displacement of OR^-, and (d) base-induced displacement of OR^-. Reactions (a) and (b) give substituted alkoxy derivatives and are discussed in this section. Reactions (c) and (d) have been used to prepare other derivatives of $Os_3(CO)_{12}$, including carboxylate complexes that are discussed later.

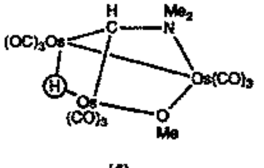
The hydroxy derivative $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OH})$ reacts with PPh_3 under very mild conditions (20°C) with loss of CO to give high yields (93%) of the bridgehead substituted cluster $(\mu\text{-H})Os_3(CO)_9(PPh_3)$ $(\mu\text{-OH})$ (**2**) [39,40]. Its structure was confirmed by X-ray crystallography. No intermediate species having a terminal OH group was reported. Under slightly more vigorous conditions (refluxing hexane) and using diphenylphosphinomethane (dppm), $(\mu\text{-H})Os_3(CO)_8(\mu\text{-OH})$ $(\mu,\eta^2\text{-dppm})$ has been prepared [41]. $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OMe})$ reacts with $CH_2(NMe_2)_2$ in heptane at reflux to give two isomeric clusters of general formula $(\mu\text{-H})Os_3(CO)_9(C(H)NMe_2)$-$(\mu\text{-OMe})$ (**3** and **4**) [42]. Both **3** and **4** were studied by X-ray crystallography.



(**2**)



(**3**)



(**4**)

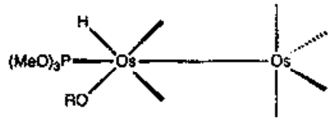
Oxidative decarbonylation, as opposed to thermally induced decarbonylation, has also been used to prepare bridgehead substituted clusters. Derivatives prepared by oxidative decarbonylation of unsubstituted type **B** precursors with Me_3NO in acetonitrile include those with the general formula $(\mu\text{-H})Os_3(CO)_9(L)$ $(\mu\text{-OR})$ (R = H, Me, Et, and Ph; L = $NCCH_3$) (Scheme 4) [43]. Reaction of the acetonitrile derivatives with trimethylphosphite generates stereochemical isomers of formula $(\mu\text{-H})Os_3$-$(CO)_9(L)$ $(\mu\text{-OR})$ (R = H, Me, Et, and Ph; L = $P(OMe)_3$). Spectroscopic evidence suggests that these isomers differ in the positioning of the phosphite ligand on a bridgehead osmium atom, i.e. cis or trans to the hydride ligand as in **5** or **6**,

$$(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OR}) + Me_3NO \xrightarrow{NCCH_3}$$

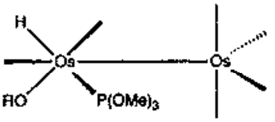
$$(\mu\text{-H})Os_3(CO)_9(NCCH_3)(\mu\text{-OR}) + CO_2 + Me_3N$$

Scheme 4.

respectively. Tetrametal clusters of formula $(\mu\text{-H})_2Os_3(CO)_9[OsH(CO)_4]$ $(\mu\text{-OR})$

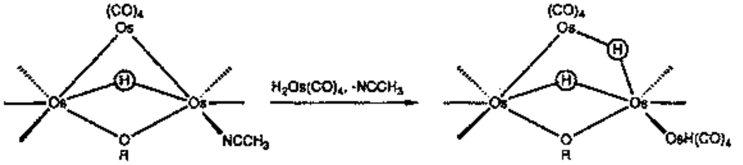


(5)



(6)

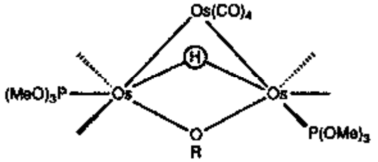
(7) (R = Me, Ph) have been prepared by reaction of $(\mu\text{-H})Os_3(CO)_9(NCCH_3)$ $(\mu\text{-OR})$ and $H_2Os(CO)_4$ [44] (Scheme 5).



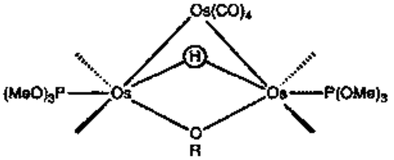
(7)

Scheme 5.

Clusters with two $P(OMe)_3$ ligands ($(\mu\text{-H})Os_3(CO)_8(P(OMe)_3)_2(\mu\text{-OR})$ (R = H, Me and Ph)) are obtained by reaction of the appropriate unsubstituted precursor with slightly more than two equivalents of Me_3NO in acetonitrile and the subsequent addition of excess phosphite ligand. In these clusters, the phosphite ligands are disposed to separate bridgehead osmium atoms in the final products and stereochemical isomers were again noted (**8** and **9**). Similarly, a tetrametal cluster of formula

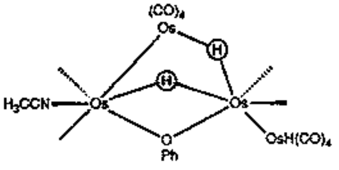


(8)

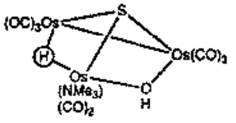


(9)

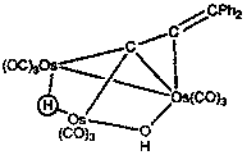
$(\mu\text{-H})_2Os_3(CO)_8(NCCH_3)$ $[OsH(CO)_4]$ $(\mu\text{-OPh})$ (**10**) has been prepared by reaction of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OPh})$ and $H_2Os(CO)_4$ after "activation" with 2.2 equivalents of Me_3NO [45].



(10)



(11)



(12)

Reaction of $Os_3(CO)_{10}(\mu_3\text{-S})$ with two equivalents of $Me_3NO\cdot 2H_2O$ gives $(\mu\text{-H})Os_3(CO)_8(NMe_3)$ $(\mu\text{-OH})$ $(\mu_3\text{-S})$ (**11**) [46]. Acid (F_3CCO_2H)-induced isomerization of (μ-H)$Os_3(CO)_9$(μ_3-$CCCPh_2OH$) gives (μ-H)$Os_3(CO)_9$(μ-OH)(μ_3-C=C=CPh_2) (**12**) as a result of hydroxyl group migration from the carbon atom to the metal framework [47]. Each of these clusters was characterized by X-ray crystallography.

Replacement of a bridging hydride ligand in a type **B** cluster by the isolobal $Au(PPh_3)^+$ moiety has been achieved in low yield (7%) following the procedure outlined in Scheme 6 [48].

$$(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OH}) \xrightarrow{Li(NPr^i_2),\ -78°C,\ -H^+} \xrightarrow{Au(PPh_3)Cl,\ Tl(PF_6),\ -TlCl}$$

$$\xrightarrow{\text{warm to } 20°C} (\mu\text{-AuPPh}_3)Os_3(CO)_{10}(\mu\text{-OH})$$

Scheme 6.

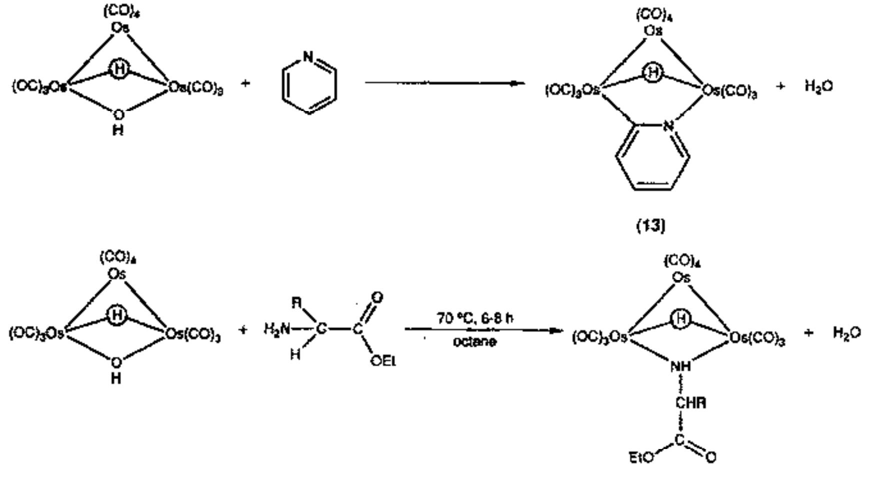
(c) *Additional reactions*

Acid-induced displacement of hydroxide from (μ-H)$Os_3(CO)_{10}$(μ-OH) has been achieved with carboxylic acids (formic, acetic, trifluoroacetic, and (η^5-$C_5H_4CO_2H$)$Mn(CO)_3$), giving carboxylate-bridged species [18,49]. These derivatives are discussed later. Reaction of (μ-H)$Os_3(CO)_{10}$(μ-OH) with HBF_4 in acetonitrile gives the cluster cation $[(\mu\text{-H})Os_3(CO)_{10}(NCCH_3)_2]^+$ [50]. These reactions have been suggested to proceed by protonation of the bridging hydroxyl group and its displacement as water by a conjugate base or solvent molecules. In contrast, (μ-H)$Os_3(CO)_{10}$(μ-OPh) is relatively stable towards substitution of the μ-OPh group by carboxylate ligands and in acid media (F_3CCO_2H) a species reversibly protonated at a metal–metal bond is obtained [18,19]. This protonated species only slowly converts to (μ-H)$Os_3(CO)_{10}$(μ,η^2-O_2CCF_3).

At low temperature (−45°C), HCl and F_3CCO_2H react with (μ-H)$Os_3(CO)_{10}$-(μ-OCH=CH_2) by addition across the vinyloxy group to give (μ-H)$Os_3(CO)_{10}$-(μ-$OCHXCH_3$) (X = Cl and OC(O)CF_3) [35]. When warmed to room temperature, β-elimination occurs, giving acetaldehyde and the clusters (μ-H)$Os_3(CO)_{10}$(μ-Cl) and (μ-H)$Os_3(CO)_{10}$(μ,η^2-O_2CCF_3), respectively. Protonation of (μ-H)$Os_3(CO)_{10}$-(μ-OCH=CH_2) with ethereal HBF_4 at −78°C in dichloromethane followed by the addition of (Et_4N)X salts (X = Cl, Br, or I) and warming gives (μ-H)$Os_3(CO)_{10}$(μ-X) complexes in good yields (65, 55, and 81% for X = Cl, Br, and I, respectively). A similar protonation reaction in methanol solvent, followed by deprotonation with (Bu_4N)OH, gives (μ-H)$Os_3(CO)_{10}$(μ-OMe) (57%).

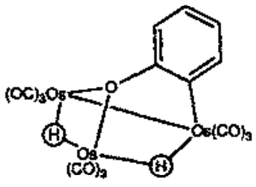
Base-induced hydroxide displacement has been reported for (μ-H)$Os_3(CO)_{10}$-(μ-OH). Reaction with pyridine affords the pyridyl-bridged cluster (μ-H)$Os_3(CO)_{10}$-(μ-C_5H_4N) (**13**) [51]. Reaction with esterified α-amino acids gives amide-bridged clusters (**14**) [52].

Intramolecular metallation of a phenyl ring occurs upon thermolysis (refluxing nonane) of (μ-H)$Os_3(CO)_{10}$(μ-OR) derivatives when R is an aromatic group [27]. For R = Ph, it was originally proposed that the product, $(\mu\text{-H})_2Os_3(CO)_9$($\mu$-$OC_6H_4$),

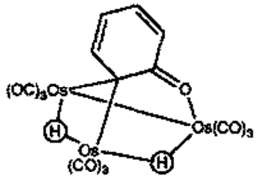


Scheme 7.

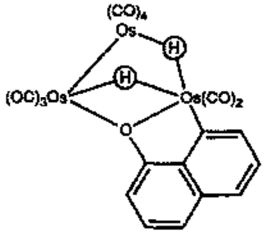
had the structure **15a**. Later, a diffraction study showed that the correct structure was **15b** [53]. For R = 1-naphthyl, o-hydroxyphenyl, 2-phenylisopropyl, and 1-phenylethyl, nonacarbonyl compounds of formula $(\mu\text{-H})_2Os_3(CO)_9(\mu\text{-OR})$ have also been isolated, but, in contrast to their phenyl counterparts; aromatic groups in these derivatives are metallated at a γ position and the cluster is substituted at a bridgehead metal center (**16**).



(15a)



(15b)



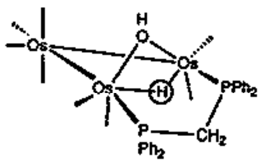
(16)

(d) Structurally characterized complexes

Structurally characterized triosmium carbonyl clusters containing a single μ-OR moiety include $(\mu\text{-H})Os_3(CO)_8(NMe_3)(\mu\text{-OH})(\mu_3\text{-S})$ (**11**) [46], $(\mu\text{-H})Os_3(CO)_9(\mu\text{-OMe})(\mu_3,\eta^2\text{-C(H)NMe}_2)$ (**4**) [42], $(\mu\text{-H})Os_3(CO)_9(\mu\text{-OH})(\mu_3\text{-C=C=CPh}_2)$ (**12**) [47], $(\mu\text{-H})Os_3(CO)_9(L)(\mu\text{-OR})$ (R = H, L = PPh_3 (**2**) [39] and PMe_2Ph [55]; R = Me, L = C(H)NMe$_2$ (**3**) [42]), $(\mu\text{-H})Os_3(CO)_8(\mu\text{-OH})(\mu,\eta^2\text{-dppm})$ (**17**) [41], and $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OR})$ (R = Me (**18**) [54] and $SiEt_3$ [17]).

Each of the clusters containing triply bridging ligands (**4**, **11**, and **12**) have several common structural features: (i) nine terminal two e^- donors, (ii) a non-metal–

metal bonding Os—Os edge bridged by a μ-OR group (Os—Os distances of 3.492, 3.3707, and 3.373 Å, respectively), (iii) μ-H and μ-OR groups bridging different Os—Os edges, (iv) elongated μ-H bridged Os—Os edge (μ-H bridged Os—Os edge (Å)/Os—Os edge not bridged by H or OR (Å): 2.873/2.793, 2.9018/2.7869, and 2.903/2.865, respectively).



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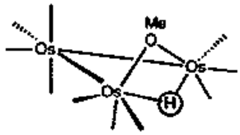


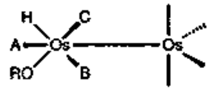
(18)

In the remaining structurally characterized (μ-OR) (μ-H) derivatives, the μ-OR and μ-H ligands bridge the same Os—Os edge. The cluster $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OMe})$ (**18**), whose structure has been fully described [54], serves to illustrate this and other features. Unlike **4**, **11** and **12**, all of the Os—Os distances for **18** are within normal bonding distance (2.812, 2.813, and 2.822 Å). On the basis of simple electron counting, this distinction is expected. The μ-OMe group is disposed at 106.42° relative to the triosmium plane, and symmetrically bridges an Os—Os edge (Os—O distances of 2.112 and 2.093 Å). The hydride ligand bridges the same Os—Os edge as the methoxy group and the Os_3 and Os—H—Os planes form an angle of 123.32°. Selected structural parameters for the entire group of unsubstituted type **B** clusters are given in Sect. D. (Table 2). Note that the double-edge bridged Os—Os distances are all slightly shorter than their unbridged counterparts. Since hydride-bridged Os—Os bonds are normally longer than their unbridged counterparts [56–58], this suggests a contracting influence by the μ-OR group.

For the substituted clusters, the non-carbonyl ligands occupy bridgehead sites. They are cis to the hydride in $(\mu\text{-H})Os_3(CO)_9(PMe_2Ph)$ $(\mu\text{-OH})$ [55] and $(\mu\text{-H})Os_3(CO)(PPh_3)$ $(\mu\text{-OH})$ (**2**) [39] and trans to the hydride in $(\mu\text{-H})Os_3(CO)(C(H)NMe_2)$-$(\mu\text{-OMe})$ (**3**) [42]. For the chelating phosphine in $(\mu\text{-H})Os_3(CO)_8(\mu\text{-OH})$ $(\mu,\eta^2\text{-dppm})$ (**17**) [41], the ligand is coordinated diequatorially.

(e) ^1H NMR data for (μ-H) (μ-OR) complexes

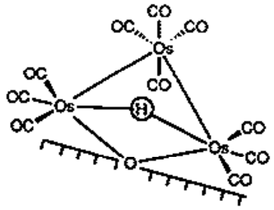
^1H NMR data for the bridging hydride ligands in double edge bridged type **B** clusters are summarized in Sect. D (Table 1). Hydride resonances for unsubstituted clusters fall in the range $\delta -11.25$ to $\delta -12.84$ and all are singlets. For μ-OH complexes, no hydride–hydroxyl proton coupling has been observed. For the substituted compounds, the hydride ligand chemical shifts range from $\delta -11.32$ to $\delta -13.12$. When the hetero ligand is a phosphine, two-bond phosphorus–hydrogen coupling is seen. The magnitude of this coupling is small for cis configurations (position A in **19**) (7.0–11.9 Hz) and large for trans configurations (position B in **19**) (58–65 Hz). In the instance of $P(OMe)_3$ substitution, there is little difference between the hydride ligand chemical shifts for cis or trans configurations.



(19)

(f) $Os_3(CO)_{10}$ *on silica*

Reaction of $Os_3(CO)_{12}$ or the "lightly stabilized" complex $Os_3(CO)_{10}(NCCH_3)_2$ with silica or alumina results in a surface-grafted triosmium carbonyl species [28,29,59]. The formulation of this species as a chemisorbed $Os_3(CO)_{10}$ cluster is based on the observation that two equivalents of CO are released upon reaction [28,29,59], and the results of various spectroscopic measurements such as Raman [60,61], IR [28,29,59,61–63], and EXAFS [29,59,61,64–66].



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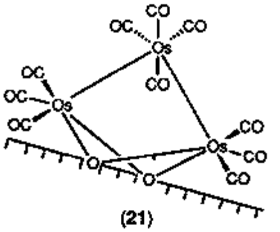

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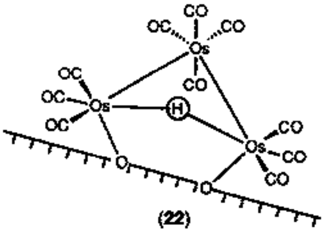


(22)

In principle, an $Os_3(CO)_{10}$ moiety can bond to an oxide support in three distinct modes: **20**, **21**, and **22**. For each of these modes, a clear molecular analogue exists, and much of the inference as to the structure of the grafted cluster has been derived from spectral comparisons with molecular model compounds. Mode **21** can be eliminated as a possibility because an Os–H vibration has been observed by IR [67]. Distinguishing between the two remaining possibilities has been most clearly demonstrated by comparison of magic-angle-spinning ^{13}C NMR for the supported cluster with solution ^{13}C NMR spectra for model compounds such as $(\mu\text{-H})Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CH)$, $Os_3(CO)_{10}(\mu\text{-OMe})_2$, and $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OSiEt}_3)$ [15,16]. By this and other methods it is now evident that the supported cluster is bound as shown by **20**. Thus, the formulation of the supported cluster can be written as $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OSi}\equiv)$. Two model compounds for this type of interaction have been structurally characterized: $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OSiEt}_3)$ [17] and $(\mu\text{-H})Os_3(CO)_{10}[(\mu\text{-O})Si_7O_{10}(C_6H_{11})_7]$ [68].

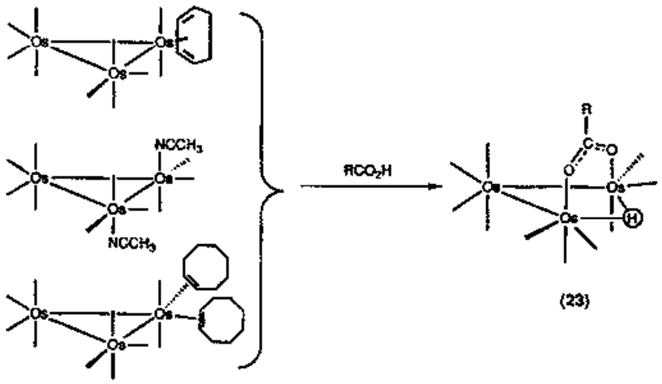
(iii) $\mu,\eta^2\text{-}O_2ER_n$ *ligands (type* **C***)*

Oxyligands with more than one oxygen donor atom can potentially bond to the triosmium cluster framework by replacing two or more carbonyl ligands. For carboxylate ligands, the bridging didentate mode (type C) is common, but chelation to a single metal center is unknown. As compared with the μ-OR derivatives, μ,η^2 carboxylate ligands adopt more nearly axial coordination to the Os_3 framework.

(a) Unsubstituted complexes

Though many unsubstituted type C clusters exist, no synthetic procedures involving direct thermal reaction of $Os_3(CO)_{12}$ with carboxylic acids are known to give carboxylate triosmium clusters in high yield. The complex $(\mu\text{-H})Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CCH_3)$ has been obtained as a minor product from the reaction of $Os_3(CO)_{12}$ and acetic acid in *n*-octane at reflux and in the presence of PhCN, but the two major products were non-oxyligand compounds [69]. However, several decacarbonyl species have been found to be excellent synthetic intermediates.

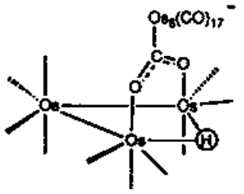
$Os_3(CO)_{10}(C_6H_8)$ reacts readily in refluxing cyclohexane with carboxylic acids to give $(\mu\text{-H})Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CR)$ (23) (R = H, Me, CF_3, Et, Ph, *p*-chlorophenyl, *p*-nitrophenyl, or CO_2Et) clusters in generally excellent yields (ca. 90%) [30] (Scheme 8).



Scheme 8.

Only the formate complex was obtained in poor yield (20%). Using $Os_3(CO)_{10}(C_8H_{14})_2$ instead, the formate derivative can be isolated in 61% yield [14]. The μ-hydroxy compound $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OH})$ reacts with carboxylic acids (R = H, Me, and CF_3) to give type C complexes under mild conditions (room temperature to 40°C) (yields: 68, 100, and 97% for $(\mu\text{-H})Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CR)$ (R = H, Me, and CF_3 respectively)) [18]. When the unusual carboxylic acid $(\eta^5\text{-}C_5H_4CO_2H)Mn(CO)_3$ is reacted with $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OH})$, the heterometallic cluster $(\mu\text{-H})Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CC_5H_4Mn(CO)_3)$ can be obtained after prolonged reflux (80 h) in THF (48% yield) [49]. Reaction of either $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CH=CH}_2)$ [70], $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-N=CHNMe}_2)$ [32] or $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OCH=CH}_2)$ [35] with excess F_3CCO_2H gives $(\mu\text{-H})Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CCF_3)$. Reaction of $(\mu\text{-H})Os_3$-

$(CO)_{10}(\mu\text{-}N{=}CHNMe_2)$ with acetic acid in the presence of the strong acid $HBF_4 \cdot Et_2O$ gives $(\mu\text{-}H)Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CCH_3)$ (97%) [32].



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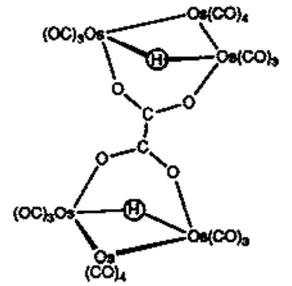

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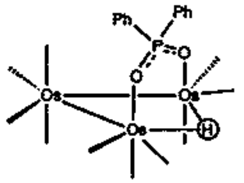


(26)

The unusual cluster anion $[(\mu\text{-}H)Os_3(CO)_{10}\{\mu,\eta^2\text{-}O_2C(Os_6(CO)_{17})\}]^-$ **(24)** is obtained from reaction of $Os_6(CO)_{18}$ and $HOs_3(CO)_{11}^-$ in dichloromethane in a rapid room temperature reaction [71,72]. It was isolated as the PPN salt in 70–80% yield and structurally characterized (see below). An oxylate bridged "dimer" **(25)** has been obtained by reaction of $Os_3(CO)_{10}(NCCH_3)_2$ and oxalic acid [73].

Bridging bidentate coordination of diphenylphosphinate is found in $(\mu\text{-}H)Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2PPh_2)$ **(26)** [74]. This cluster was prepared in 57–65% yield by reaction of $Os_3(CO)_{10}(NCCH_3)_2$ or $Os_3(CO)_{10}(C_8H_{14})_2$ with Ph_2PO_2H and was structurally characterized.

(b) Reactions

Only a few studies on the reactivity of type **C** clusters have been reported. $(\mu\text{-}H)Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CCH_3)$ reacts rapidly with BH_4^- at −40°C in CD_2Cl_2 [75]. ^1H NMR spectra suggested that an anionic formyl complex, $[(\mu\text{-}H)Os_3(CO)_9(C(O)H)(\mu,\eta^2\text{-}O_2CCH_3)]^-$, had formed. Warming to 0°C, hydride migration from the formyl group to the metal was proposed to occur giving the dihydride $[(\mu\text{-}H)_2Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CCH_3)]^-$. Upon acidification, the starting cluster was obtained. These results are summarized in Scheme 9.

$$(\mu\text{-}H)Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CMe) \xrightarrow{BH_4^-}$$

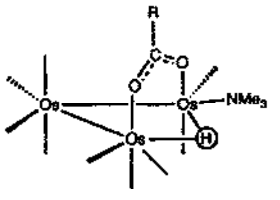
$$[(\mu\text{-}H)Os_3(CO)_9(C(O)H)(\mu,\eta^2\text{-}O_2CMe)]^- \xrightarrow{0^\circ C}$$

$$[(\mu\text{-}H)_2Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CMe)]^- \xrightarrow{H^+,\ -H_2}$$

$$(\mu\text{-}H)Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CMe)$$

Scheme 9.

Reactions of $(\mu\text{-}H)Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CR)$ (R = H, Me, and Ph) with Me_3NO give the bridgehead substituted clusters $(\mu\text{-}H)Os_3(CO)_9(NMe_3)(\mu,\eta^2\text{-}O_2CR)$ **(27)** in good yields (70, 70, and 55% for R = H, Me, and Ph, respectively) [76]. Further reaction of these trimethylamine complexes with $P(OMe)_3$ give the analogous phosphite-substituted clusters. ^1H NMR data, especially a $^2J_{PH}$ value of ~10 Hz, are consistent with the $P(OMe)_3$ ligand being coordinated to a bridgehead osmium atom and cis to the bridging hydride (**28**).



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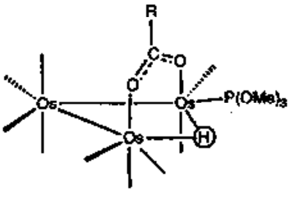

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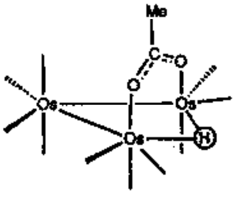


(29)

(c) Structurally characterized complexes

The structurally characterized type **C** clusters are listed in Sect. D (Table 2). In all instances, the carboxylate moiety is bridging bidentate and very near to truly axial ligation (O—Os—Os—O "coordination plane"/Os_3 plane dihedral angles range from 97.0 to 100.5°). The hydride ligand, located directly for R = Me and with an apparent position for the others, bridges the same Os—Os edge and lies nearly in the triosmium plane. For example, in $(\mu\text{-}H)Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CMe)$ (**29**) the Os_3 plane/Os—H—Os plane dihedral angle is 167° [69]. The double edge-bridged Os—Os bonds are all somewhat longer than their unbridged counterparts. Hydrogen bridging generally elongates Os—Os bonds by ~0.15 Å [58]. That the lengthening is less than expected for these compounds results from the opposing effect of the carboxylate ligand and its small "bite". Acute Os—Os—O angles (e.g. 81.2 (ave)° in $(\mu\text{-}H)Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CH)$) provide support for this contention. Compared with the carboxylate derivatives, the phosphinate ligand in $(\mu\text{-}H)Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2PPh_2)$ (**26**) is much closer to being normal to the Os_3 plane as evidenced by an O—Os—Os—O "coordination plane" angle of 93.91 (ave)° and Os—Os—O angles of 84.5 (ave)° [74].

The compound $[(\mu\text{-}H)Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2C(Os_6(CO)_{17}))]^-$ (**24**) differs from the other carboxylate derivatives in two significant respects: the C—O distances for the $\mu,\eta^2\text{-}O_2C$ moiety are longer (1.299 vs. ~1.25 Å) and the O—C—O angle (112.4° vs. ~128°) is smaller [71,72]. An alternative to viewing this cluster as the "carboxylate" ligand $O_2C(Os_6(CO)_{17})$ bound to a $(\mu\text{-}H)Os_3(CO)_{10}$ fragment is to consider the $Os\text{—}CO_2$ unit as a carbene. Simple electron counting suggests this is a reasonable possibility. For a carbene unit, the C—O bond orders should be close to one and, hence, the C—O distances should be longer than for a carboxylate moiety (formal bond order 1.5). Indeed, parameters for the $Os\text{—}CO_2$ moiety in the **24** unit compare favorably with the carbene ligand in $(\mu\text{-}H)Os_3(CO)_9(\eta^1\text{-}C(OMe)_2)$ $(\mu_3\text{-}CPh)$ (C—O = 1.299 (ave) and 1.315 (ave) Å, Os—C(carbene) = 2.009 and 2.039 Å, O—C—O angle = 112.4° and 109.0°) [77].

(d) ^{1}H NMR data for (μ-H) (μ,η^2-O_2ER_n) complexes

^{1}H NMR chemical shifts for hydride ligands in type **C** clusters are summarized in Sect. D. Hydride resonances for the unsubstituted carboxylate compounds fall in a very narrow range: $\delta -10.10$ to $\delta -10.42$. Bridgehead substitution of CO by NMe_3 causes a downfield shift of about 1 ppm. For $P(OMe)_3$ substitution, little effect on the chemical shift of the resonance is observed, and the hydride signal is split into a doublet with the magnitude of the coupling ($^2J_{PH} = 12.2$ Hz) consistent with phosphite coordination to an equatorial site cis to the bridging hydride. The phosphinate cluster $(\mu\text{-H})Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2PPh_2)$ exhibits a doublet ($^3J_{PH} = 8.7$ Hz) for the hydride ligand at $\delta -10.49$ [74].

*(iv) μ_3,η^3-O_3ER ligands (type **D**)*

Type **D** clusters of the general formula $(\mu\text{-H})_2Os_3(CO)_9(\mu_3,\eta^3\text{-}O_3ER)$ (E = S, R = O; E = P, R = OH, Me, Ph; E = As, R = Ph) have been prepared by reaction of

$$(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CH}) \xrightarrow{H_2SO_4,\ -CH_4} \xrightarrow{H_2O} (\mu\text{-H})_2Os_3(CO)_9(\mu_3,\eta^3\text{-}O_3SO)$$

(30)

$$(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CH}) \xrightarrow{F_3CSO_3H,\ -CH_4} \xrightarrow{RPO_3H_2 \text{ or } RAsO_3H_2} \xrightarrow{H_2O}$$

$$(\mu\text{-H})_2Os_3(CO)_9(\mu_3,\eta^3\text{-}O_3ER)$$

Scheme 10.

$(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CH})$ with strong acids (Scheme 10) [12,13,21,78]. Both the sulfate (**30**) [12] and phenylphosphonate [13] derivatives have been structurally characterized. The IR spectra of these derivatives very clearly show important oxyligand vibrational modes. As shown in Fig. 1, the IR spectrum of $(\mu\text{-H})_2Os_3(CO)_9$-

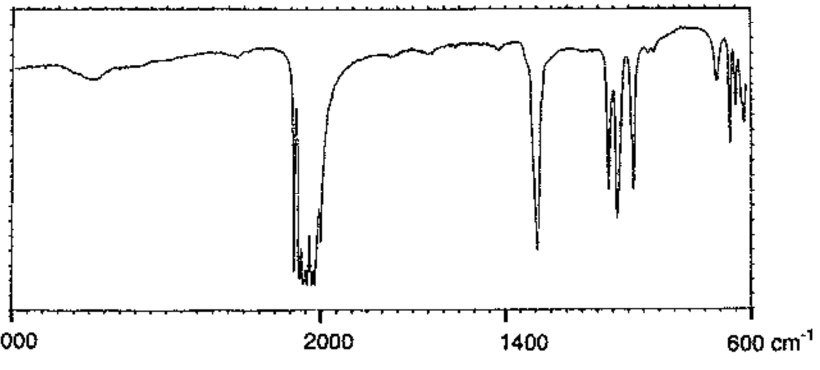
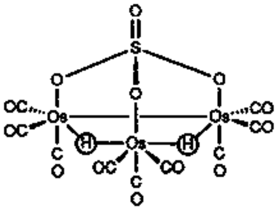


Fig. 1. IR spectrum of **30** dispersed in KBr. (Reproduced with permission from ref. 21.)

(μ_3,η^3-O_3SO) exhibits four strong and well-resolved ν_{SO} bands (1275, 1048, 1020 and 966 cm^{-1}) consistent with a SO_4 ligand having approximate C_s symmetry. Fluxional behavior consistent with hydride migration about the Os_3 framework has been observed for the phenylphosphonate complex [13]. These complexes react reversibly with methoxide to give base adducts of formula $[(\mu\text{-H})_2Os_3(CO)_9(C(O)OMe)(\mu_3,\eta^3\text{-}O_3ER)]^-$ [79]. On the basis of spectroscopic evidence, the site of adduct formation is an equatorial CO ligand on the unique Os atom (**31**).



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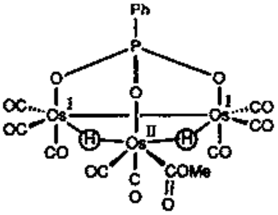


(31)

C. COMPLEXES CONTAINING TWO OXYLIGANDS

*(i) (μ-OR)$_2$ complexes (type **E**)*

This class is represented only by double edge-bridged bis-alkoxy compounds of the general formula $Os_3(CO)_{10}(\mu\text{-OR})_2$. Preparative routes for only the bis-methoxy derivative have been described in detail. Originally obtained as a co-product in the high-pressure synthesis of $Os_3(CO)_{12}$ from OsO_4 and CO in methanol solvent in low yield (~5%) [24,25], subsequent methods include its synthesis by reaction of $Os_3(CO)_{12}$ and methanol at 160–170°C for 19 h (13% yield) [27], and (μ-H)$Os_3(CO)_{10}(\mu\text{-OMe})$ and methanol at 145°C for 12 h (19%) [16]. The latter procedure possibly proceeds via the mechanism described in Scheme 11. Bis-ethoxy [80,81] and phenoxy [28,29,53] species have been mentioned in the literature, but few details on their preparation or properties were provided.

$$(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OMe}) + MeOH \rightarrow$$
$$H_2Os_3(CO)_{10}(OMe)_2 \xrightarrow{-H_2} Os_3(CO)_{10}(\mu\text{-OMe})_2$$

Scheme 11.

(32)

The cluster $Os_3(CO)_{10}(\mu\text{-}OMe)_2$ (**32**) has been structurally characterized [82]. The doubly bridged edge is much longer than the other Os—Os edges (3.078(3) vs. 2.819(ave) Å), suggesting the absence of a metal–metal bond. Formal electron counting is consistent with this observation though, as discussed below, the electronic properties of these clusters are more complex and not amenable to a simple description. The methoxy groups are symmetrically disposed, forming angles of 117° and 110° relative to the triosmium plane.

(a) Bonding in $(\mu\text{-}OR)_2$ complexes

To satisfy the 18 electron rule, formal electron counting would suggest metal–metal bond orders of two, one, and zero for the double edge-bridged clusters $(\mu\text{-}H)_2Os_3(CO)_{10}$, $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}OMe)$, and $Os_3(CO)_{10}(\mu\text{-}OMe)_2$, respectively. Increasing metal–metal distances of 2.670, 2.863, and 3.078 Å support this suggestion and Mason and Mingos provided a qualitative description of the bonding in these clusters based upon it [83]. However, Broach and Williams, in their neutron diffraction study of $(\mu\text{-}H)_2Os_3(CO)_{10}$, described the Os_2H_2 moiety in terms of a four-center, four-electron bond (alternatively two three-center, two-electron bonds as in diborane) [84]. Further work on the electronic properties of (μ-X) (μ-Y) clusters (X = H, Y = H, halogen, OR; X = Y = halogen, OR) by Sherwood and Hall [85], Chesky and Hall [86], and Granozzi et al. [81], are in agreement with such a description and they proposed no significant direct Os—Os bonding for the bridged edges. Only a weak "t_{2g}–t_{2g}" interaction, of diminishing importance going from the dihydride to methoxy hydride to dimethoxy compounds, which is bonding for $(\mu\text{-}H)_2Os_3(CO)_{10}$ and weakly antibonding for $Os_3(CO)_{10}(\mu\text{-}OMe)_2$, was proposed. Additional lengthening influences for $3e^-$ donor-substituted species result from interactions of the p orbitals on the donor ligands with a low-lying unoccupied MO which is antibonding with respect to the Os atoms.

(ii) Complexes containing one $\eta^1\text{-}OE(O)_nR_n$ and one $\mu,\eta^2\text{-}O_2ER_n$ ligand (type **F**)

Reaction of $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}CH)$ with F_3CSO_3H, followed by careful layering of the reaction solution with diethyl ether, gives $(\mu\text{-}H)_2Os_3(CO)_9(O_3SCF_3)_2$ (**33**) in good yield (76%) [20]. From **33**, other type **F** clusters can be prepared by reaction with neat carboxylic acids (Scheme 12). Reaction of **33** with neat $NCCH_3$ gives the cationic cluster $[(\mu\text{-}H)_2Os_3(CO)_9(NCCH_3)_3]$ $(O_3SCF_3)_2$ in high yield (79%).

The mixed oxyligand cluster $(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CMe)$ $(\eta^1\text{-}OS(O)_2CF_3)$ (**34**), which has been structurally characterized, shows remarkable stability towards substitution of its triflate ligand as evidenced by its lack of reactivity with potential ligands such as THF and $NCCH_3$. Structural data, especially the long S—O(Os) distance (1.50(1) Å), provide further evidence that the triflate ligand in **34** is tightly bound compared with other transition metal triflate complexes. Some substitution

$$(\mu\text{-H})_2Os_3(CO)_9(O_3SCF_3)_2 \xrightarrow{RCO_2H,\,-F_3CSO_3^-\;<30\,min}$$

(33)

$$(\mu\text{-H})_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CR)(\eta^1\text{-}OS(O)_2CF_3)$$

$R = H$, Me **(34)**, CF_3

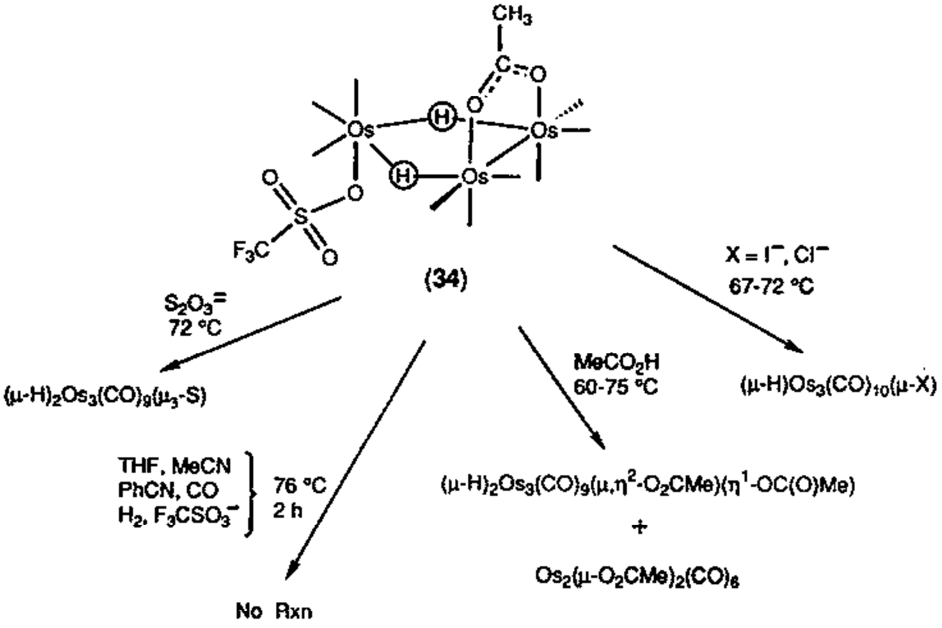
$$(\mu\text{-H})_2Os_3(CO)_9(O_3SCF_3)_2 \xrightarrow{RCO_2H,\,-2F_3CSO_3^-\;>2\,h}$$

(33)

$$(\mu\text{-H})_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CR)(\eta^1\text{-}OC(O)R)$$

$R = H, CF_3$

Scheme 12.



Scheme 13.

chemistry has been reported for **34** at elevated temperature (60–80°C) (Scheme 13), but most of the products isolated did not result from replacement of only the triflate ligand.

D. COMPILATIONS OF HYDRIDE LIGAND CHEMICAL SHIFTS, AND SELECTED BOND DISTANCES AND ANGLES FOR OXYLIGAND DERIVATIVES OF $Os_3(CO)_{12}$

TABLE 1

Chemical shifts for bridging hydride ligands in oxyligand derivatives of $Os_3(CO)_{12}$

Complex			Solvent	δ μ-H	Ref.
R	L/*n*	ER			
(μ-H)$Os_3(CO)_{10-n}(L)_n(\mu$-OR)					
H	CO/1		CCl_4	−12.6 (s)	40
Et	CO/1		$CDCl_3$	−11.40 (s)	30
C_6H_{11}	CO/1		$CDCl_3$	−11.25 (s)	30
$CHMe_2$	CO/1		$CDCl_3$	−12.84 (s)	27
CH_2CH_2OH	CO/1		CD_2Cl_2	−12.51 (s)	32
$CHClCH_3$	CO/1		$CDCl_3$	−12.81 (s)	35
$CH(OC(O)CF_3)CH_3$	CO/1		$CDCl_3$	−12.54 (s)	35
CH_2PH	CO/1		$CDCl_3$	−12.42 (s)	27
CHMePh	CO/1		$CDCl_3$	−12.67 (s)	27
Ph	CO/1		$CDCl_3$	−12.20 (s)	27
2-Naphthyl	CO/1		$CDCl_3$	−11.97 (s)	27
$CH{=}CH_2$	CO/1		$CDCl_3$	−12.35 (s)	34
$CH{=}CMe_2$	CO/1		$CDCl_3$	−11.94 (s)	34
$CH{=}CPh_2$	CO/1		$CDCl_3$	−11.83 (s)	34
$SiEt_3$	CO/1		$CDCl_3$	−12.37 (s)	17
$SiPh_3$	CO/1		$CDCl_3$	−11.36 (s)	17
$Si_7O_{10}(C_6H_{11})_7$	CO/1		$CDCl_3$	−12.56 (s)	68
H	MeCN/1		$CDCl_3$	−11.54 (s)	43
Me	MeCN/1		$CDCl_3$	−11.32 (s)	43
Et	MeCN/1		$CDCl_3$	−11.33 (s)	43
H (A)[a]	$P(OMe)_3/1$		$CDCl_3$	−13.12 (d, 8.6 z)	43
Me (A)[a]	$P(OMe)_3/1$		$CDCl_3$	−12.55 (d, 7.9 Hz)	43
Et (A)[a]	$P(OMe)_3/1$		$CDCl_3$	−12.65 (d, 7.0 Hz)	43
Ph (A)[a]	$P(OMe)_3/1$		$CDCl_3$	−12.24 (d, 8.4 Hz)	43
H (A)[a]	$PMe_2Ph/1$		$CDCl_3$	−12.65 (d, 8.7 Hz)	55
H (A)[a]	$PPh_3/1$		CCl_4	−12.5 (d, 7.6 Hz)	39,40

Me (B)[a]	$C(H)NMe_2$/1		$CDCl_3$	−12.92 (s)	42
Me (B)[a]	$P(OMe)_3$/1		$CDCl_3$	−12.67 (d, 58 Hz)	43
Et (B)[a]	$P(OMe)_3$/1		$CDCl_3$	−12.79 (d, 58 Hz)	43
Ph (B)[a]	$P(OMe)_3$/1		$CDCl_3$	−12.25 (d, 59 Hz)	43
H (A, A)[a]	$P(OMe)_3$/2		$CDCl_3$	−12.95 (t, 9 Hz)	43
Ph (A, A)[a]	$P(OMe)_3$/2		$CDCl_3$	−11.60 (t, 8.6 Hz)	43
H (A, A)[a]	dppm/2[b]		$CDCl_3$	−11.68 (t, 11.9 Hz)	41
Me (A, B)[a]	$P(OMe)_3$/2		$CDCl_3$	−12.82 (dd, 8, 65 Hz)	43
$(\mu\text{-}H)Os_3(CO)_{10-n}(L)_n(\mu,\eta^2\text{-}O_2CR)$					
H	CO/1		$CDCl_3$	−10.28 (s)	30
Me	CO/1		$CDCl_3$	−10.42 (s)	30
Et	CO/1		$CDCl_3$	−10.35 (s)	30
CF_3	CO/1		$CDCl_3$	−10.30 (s)	30
Ph	CO/1		$CDCl_3$	−10.30 (s)	30
$p\text{-}C_6H_4Cl$	CO/1		$CDCl_3$	−10.15 (s)	30
$p\text{-}C_6H_4NO_2$	CO/1		$CDCl_3$	−10.10 (s)	30
CO_2Et	CO/1		$CDCl_3$	−10.29 (s)	30
$(C_5H_4)Mn(CO)_3$	CO/1		CCl_4	−10.3 (s)	49
$[Os_6(CO)_{17}]^-$	CO/1		CD_2Cl_2	−10.24 (s)	71
H	NMe_3/1		$CDCl_3$	−9.38 (s)	76
H	$P(OMe)_3$/1		$CDCl_3$	−10.57 (d, 12.2 Hz)	76
Me	NMe_3/1		$CDCl_3$	−9.35 (s)	76
Me	$P(OMe)_3$/1		$CDCl_3$	−10.56 (d, 12.2 Hz)	76
Me	$[C(O)H]^-$/1		CD_2Cl_2	−10	75
Ph	NMe_3/1		$CDCl_3$	−9.13 (s)	76
Ph	$P(OMe)_3$/1		$CDCl_3$	−10.34 (d, 12.2 Hz)	76
$(\mu\text{-}H)_2Os_3(CO)_9(\mu_3,\eta^3\text{-}O_3ER)$					
		SO	$(CD_3)_2CO$	−12.04 (s)	12
		POH	$(CD_3)_2CO$	−12.45 (d, 3.2 Hz)	12
		PPh	CD_2Cl_2	−12.57 (d, 3 Hz)	13
		PMe	CD_2Cl_2	−12.68 (d, 3 Hz)	13
		AsPh	CD_2Cl_2	−12.25 (s)	13
$[(\mu\text{-}H)_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3ER)]^-$					
		SO	CD_2Cl_2	−10.25 (d, 1.5 Hz) −12.79 (d, 1.5 Hz)	79

TABLE 1 (*continued*)

Complex			Solvent	δ μ-H	Ref.
R	L/*n*	ER			
		PPh	CD_2Cl_2	−10.37 (dd, 2, 3 Hz) −12.23 (dd, 2, 2.7 Hz)	79
$(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CR)$ $(\eta^1\text{-}OC(O)R)$					
H			CD_2Cl_2	−12.50 (s)	20
Me			CD_2Cl_2	−12.46 (s)	20
CF_3			CD_2Cl_2	−12.29 (s)	20
$(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CR)$ $(\eta^1\text{-}OS(O)_2CF_3)$					
H			CD_2Cl_2	−11.88 (s)	20
Me			CD_2Cl_2	−11.80 (s)	20
CF_3			CD_2Cl_2	−11.84 (s)	20
Others					
$(\mu\text{-H})Os_3(CO)_{11}$ $(\eta^1\text{-OC(O)CF}_3)$			CD_2Cl_2	−15.29 (s)	20
$(\mu\text{-H})Os_3(CO)_{10}$ $(\mu,\eta^2\text{-O}_2\text{PPh}_2)$			$CDCl_3$	−10.49 (d, 8.7 Hz)	74
$(\mu\text{-H})Os_3(CO)_8(NMe_3)(\mu\text{-OH})(\mu_3\text{-S})$			$CDCl_3$	−19.43 (s)	46
$(\mu\text{-H})Os_3(CO)_9(\mu\text{-OMe})(\mu_3,\eta^2\text{-C(H)NMe}_2)$			$CDCl_3$	−11.37 (d, 1.33 Hz)	42
$[\{(\mu\text{-H})Os_3(CO)_{10}\}_2(C_2O_4)]$			CD_2Cl_2	−10.41 (s)	73
$[(\mu\text{-H})_2Os_3(CO)_{10}(\mu,\eta^2\text{-O}_2\text{CMe})]^-$			CD_2Cl_2	−10.08, −15.91	75
$(\mu\text{-H})_2Os_3(CO)_9[OsH(CO)_4](\mu\text{-OMe})$			$CDCl_3$	−10.8, −14.2	44
$(\mu\text{-H})_2Os_3(CO)_9[OsH(CO)_4](\mu\text{-OPh})$			$CDCl_3$	−10.2, −13.4	44
$(\mu\text{-H})_2Os_3(CO)_8(NCCH_3)[OsH(CO)_4](\mu\text{-OPh})$			$CDCl_3$	−8.0 (s), −9.3 (s)	45
$(\mu\text{-H})_2Os_3(CO)_8(P(OMe)_3)[OsH(CO)_4](\mu\text{-OPh})$			$CDCl_3$	−10.6 (d, 3.8 Hz) −13.6 (d, 6.6 Hz)	45
$(\mu\text{-H})_2Os_3(CO)_9(\eta^1\text{-OC(O)CF}_3)(\mu\text{-PPh}_2)$			CD_2Cl_2	−15.95 (dd, 1, 11 Hz) −17.09 (dd, 1, 5 Hz)	23
$(\mu\text{-H})_2Os_3(CO)_9(\eta^1\text{-OS(O)}_2\text{CF}_3)(\mu\text{-OH})$			$(CD_3)_2CO$	−12.46 (d, 1 Hz) −13.48 (d, 1 Hz)	21

[a] Letter (A) indicates that L is cis to the bridging hydride ligand and letter (B) that L is trans.

[b] $(\mu\text{-H})Os_3(CO)_8(\mu\text{-OH})(\mu,\eta^2\text{-dppm})$.

TABLE 2

Selected bond distances (Å) and angles (deg) for oxyligand derivatives of $Os_3(CO)_{12}$
The ligand for which the data are listed is highlighted.

Complex	Os—O distance	Oxyligand bridged Os—Os distance	Oxyligand/Os_3 "coordination plane" angle	O—E—O "bite angle" for μ,η^2-O_2ER_n complexes or Os—O—Os angle for μ-OR complexes	Ref.
η^1-OE(O)$_n$R$_n$					
$(\mu\text{-H})_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CCH_3)(\boldsymbol{\eta^1}\textbf{-OS(O)}_\mathbf{2}\mathbf{CF_3})$	2.146(10)				20
$(\mu\text{-H})_2Os_3(CO)_9(\boldsymbol{\eta^1}\textbf{-OC(O)CF}_\mathbf{3})(\mu\text{-}PPh_2)$	2.149(21)				23
μ-OR					
$(\mu\text{-H})Os_3(CO)_{10}(\boldsymbol{\mu}\textbf{-OMe})$	2.103(ave)	2.812	106.42	83.9	54
$(\mu\text{-H})Os_3(CO)_{10}(\boldsymbol{\mu}\textbf{-OSiEt}_\mathbf{3})$	2.118(ave)	2.777(1)		81.9(2)	17
$(\mu\text{-H})Os_3(CO)_{10}[(\boldsymbol{\mu}\textbf{-O)Si}_\mathbf{7}\mathbf{O_{10}})(\mathbf{C_6H_{11}})_7]$	2.12(ave)	2.789(2)			68
$(\mu\text{-H})Os_3(CO)_9(PPh_3)(\boldsymbol{\mu}\textbf{-OH})$	2.12(ave)	2.808		82	39,40
$(\mu\text{-H})Os_3(CO)_9(PMe_2Ph)(\boldsymbol{\mu}\textbf{-OH})$	2.127(ave)	2.801(0)		82.4(2)	55
$(\mu\text{-H})Os_3(CO)_9[C(H)NMe_2](\boldsymbol{\mu}\textbf{-OMe})$		2.7880(9)			42
$(\mu\text{-H})Os_3(CO)_8(NMe_3)(\boldsymbol{\mu}\textbf{-OH})(\mu_3\text{-S})$	2.142(ave)	3.3707(6)		103.7(3)	46
$(\mu\text{-H})Os_3(CO)_9(\boldsymbol{\mu}\textbf{-OH})(\mu_3\text{-C=C=CPh}_2)$	2.13(ave)	3.373(ave)		106(1)	47
$(\mu\text{-H})Os_3(CO)_9(\boldsymbol{\mu}\textbf{-OMe})[(\mu_3,\eta^2\text{-C(H)NMe}_2]$		3.492(1)			42
$(\mu\text{-H})Os_3(CO)_8(\boldsymbol{\mu}\textbf{-OH})(\mu,\eta^2\text{-dppm})$	2.162(ave)	2.774(1)			41
$Os_3(CO)_{10}(\boldsymbol{\mu}\textbf{-OMe})_2$	2.09(ave)	3.078(3)	113(ave)	95.1(ave)	82
μ,η^2-O$_2$ER$_n$					
$(\mu\text{-H})Os_3(CO)_{10}(\boldsymbol{\mu,\eta^2}\textbf{-O}_\mathbf{2}\textbf{CH})$	2.151(ave)	2.909(ave)	98.6(ave)	127.8(ave)	14
$(\mu\text{-H})Os_3(CO)_{10}(\boldsymbol{\mu,\eta^2}\textbf{-O}_\mathbf{2}\textbf{CCH}_\mathbf{3})$	2.13(1)	2.909(10)	97.0	127.6(7)	69
$(\mu\text{-H})Os_3(CO)_{10}\{\boldsymbol{\mu,\eta^2}\textbf{-O}_\mathbf{2}\textbf{CC}_\mathbf{5}\textbf{H}_\mathbf{4}\textbf{Mn(CO)}_\mathbf{3}\}$	2.14(ave)	2.911(1)	98.6	129(1)	49
$(\mu\text{-H})_2Os_3(CO)_9(\boldsymbol{\mu,\eta^2}\textbf{-O}_\mathbf{2}\textbf{CCH}_\mathbf{3})(\eta^1\text{-OS(O)}_2CF_3)$	2.11(ave)	2.7713(9)	89.84	125(1)	20
$[\{(\mu\text{-H})Os_3(CO)_{10}\}_2(\mathbf{C_2O_4})]$	2.15(ave)	2.918(2)		126(1)	73
$(\mu\text{-H})Os_3(CO)_{10}(\boldsymbol{\mu,\eta^2}\textbf{-O}_\mathbf{2}\textbf{PPh}_\mathbf{2})$	2.15(ave)	2.945(ave)	93.91(ave)	113.8(ave)	74
$[(\mu\text{-H})Os_3(CO)_9(\boldsymbol{\mu,\eta^2}\textbf{-O}_\mathbf{2}\textbf{COs}_\mathbf{6}\textbf{(CO)}_\mathbf{17})]^-$	2.153(ave)	2.895	100.5	112.4	71,72
μ_3, η^3-O$_3$ER					
$(\mu\text{-H})_2Os_3(CO)_9(\boldsymbol{\mu_3,\eta^3}\textbf{-O}_\mathbf{3}\textbf{SO})$	2.13(ave)	2.966(ave)			12
$(\mu\text{-H})_2Os_3(CO)_9(\boldsymbol{\mu_3,\eta^3}\textbf{-O}_\mathbf{3}\textbf{PPh})$	2.10(ave)	2.968(ave)			13

ACKNOWLEDGEMENT

The author wishes to thank Professor John R. Shapley for financial support and helpful discussions.

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