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Attack at coordinated carbon monoxide in a set of dihydrido triosmium carbonyl clusters

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Abstract

Methoxide reacts with triosmium carbonyl clusters of formula $(\mu\text{-H})_2Os_3(CO)_9(\mu_3,\eta^3\text{-}O_3ER)$ (E = S, R = O (**1**); E = P, R = OH (**2**), Ph (**3**); E = As, R = Ph (**4**)) at a coordinated CO ligand to form methoxycarbonyl adducts. For the sulfate (**1**), phenylphosphonate (**3**), and phenylarsonate (**4**) compounds one equivalent of base is consumed to give anionic clusters of formula $[(\mu\text{-H})_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3ER)]^-$. For the hydrogen phosphate cluster (**2**) two equivalents of base are consumed to give the dianion $[(\mu\text{-H})_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3PO)]^{2-}$. The salts of two adducts, $[^nBu_4N][(\mu\text{-H})_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3SO)]$ (**5**) and $[PPN][(\mu\text{-H})_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3PPh)]$ (**6**), were isolated. A proposed site of adduct formation, based on ^{13}C NMR spectra, is presented.

Introduction

Previously we suggested that triosmium carbonyl cluster compounds for formula $(\mu\text{-H})_2Os_3(CO)_9(\mu_3,\eta^3\text{-}O_3ER)$ (E = S, R = O (**1**); E = P, R = OH (**2**), Ph (**3**); E = As, R = Ph (**4**)) contain a highly electronegative metal core, based, in part, on the observation of some relatively high energy (> 2125 cm^{-1}) carbonyl stretching frequencies for them [1]. Such high energy $\nu(CO)$ frequencies are consistent with poor π-donation from osmium to CO. As a further consequence of their electronegative core, the hydride ligands of clusters **1–4** might have substantial acidity. The acidity of bridging hydride ligands has been demonstrated previously for $H_4Os_4(CO)_{12}$ ($pK_a = 12.0$ in methanol) [2]. In addition, Lewis, and others, have shown that the dihydrido cluster $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-S})$ reacts with methanolic KOH to give the monohydrido anionic cluster $[(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-S})]^-$ [3]. This cluster was isolated as its PPN salt and structurally characterized [4].

With the above results in mind, a study of the reaction of clusters **1–4** with base was undertaken. The products initially expected were monohydrido cluster anions analogous to $[(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-S})]^-$. However, instead of deprotonated species, this reaction afforded base (methoxide) adducts of formula $[(\mu\text{-H})_2Os_3(CO)_8(C(O)$-

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$OMe)(\mu_3,\eta^3\text{-}O_3ER)]^-$. Nucleophilic attack at coordinated CO to give an adduct is a well established phenomenon [5], and the simplest triosmium cluster, $Os_3(CO)_{12}$ undergoes such a reaction [6*]. Nevertheless, the formation of such adducts from **1**–**4** by direct reaction with base is surprising given the precedence for deprotonation of bridging hydride ligands cited above. Thus, these adducts may represent an important intermediate stage in the deprotonation reactions of carbonyl cluster compounds containing bridging hydride ligands.

Results and discussion

Syntheses

Clusters **1**–**4**, when dissolved or suspended in methanol, react cleanly with methanolic base (KOH or $(^nBu_4N)OH$) to give solutions with similar IR spectral patterns (see Fig. 1). For compounds **1**, **3**, and **4**, one equivalent of base was required to completely consume the neutral starting clusters. In the reaction of $(\mu\text{-}H)_2Os_3(CO)_9(\mu_3,\eta^3\text{-}O_3POH)$ (**2**), though one equivalent of base consumed the starting material, two equivalents of base were required before a spectral pattern recognizably similar to those for the adducts of **1**, **3**, and **4** was obtained. The salts of two adducts, $[^nBu_4N][(\mu\text{-}H)_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3SO)]$ (**5**) and $[PPN][(\mu\text{-}H)_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3PPh)]$ (**6**), were isolated from their respective reaction solutions.

Characterization of 5 and 6

The negative ion FAB mass spectra of both **5** and **6** showed ions at 957 and 1017 amu, respectively, which correspond to their $[(\mu\text{-}H)_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3ER)]^-$ anions (see Fig. 2 for the spectrum of **6**). Also observed were ions resulting from loss of methanol and sequential loss of several CO ligands from these moieties. Some unexpected ions were seen and these are discussed below.

The ^1H NMR spectrum of **5**, rather than showing only one hydride resonance as would be expected if deprotonation occurred, exhibited two signals in this region. They appeared as equally intense doublets at δ −10.25 and −12.03 and integrated (relative to resonances for $^nBu_4N$) to one hydrogen each [7*]. The coupling constants are the same for each signal (1.5 Hz) and of the magnitude expected for coupling of inequivalent bridging hydrides in triosmium clusters [8]. Also observed was a resonance at δ 3.71 (3H) which can be assigned to hydrogens of the methoxycarbonyl moiety. Upon addition of acid (F_3CCO_2H) to a solution of **5** in dichloromethane-d_2 two observations were made: (i) the methoxycarbonyl resonance disappeared and was replaced by a signal for free methanol (δ 3.46), and (ii) the hydride resonances for **5** disappeared and were replaced by the singlet for the neutral cluster **1**.

The ^1H NMR spectrum of **6** is similar to that for **5**, but with the added effect of PH coupling. The hydride resonances, which are observed at δ −10.37 (1H) and −12.23 (1H), rather than being doublets, as for **5**, are doublet of doublets with $J(HH) = 2.1$ and $J(PH) = 3$ Hz. A resonance at δ 3.67 (3H) can be assigned to the

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* Reference number with asterisk indicates a note in the list of references.

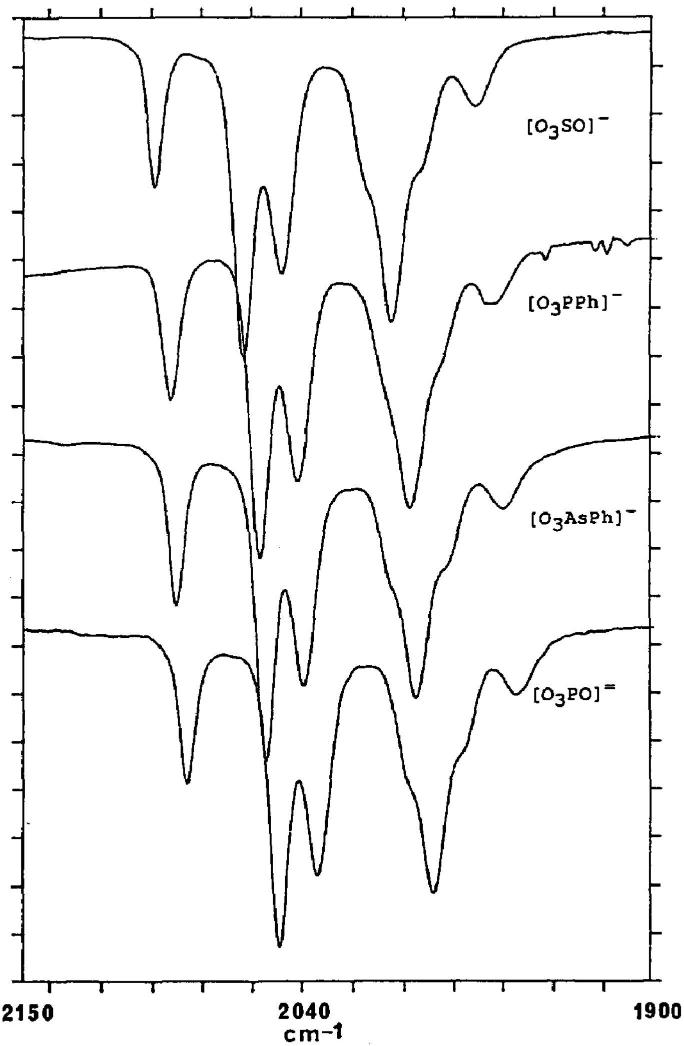


Fig. 1. Carbonyl region IR spectra for the base adducts prepared by reaction of **1**–**4** with methanolic KOH. Capping ligand and total charge of the adduct are indicated. Spectra for isolated **5** and **6** were identical to those for their respective adducts generated in situ.

hydrogens of the methoxycarbonyl moiety in **6**. As we observed for **5** above, the addition of acid (F_3CCO_2H) to the anion in **6** in dichloromethane-d_2 liberated methanol from the methoxycarbonyl moiety, and cleanly generated the neutral cluster **3**. Two additional weak multiplets seen in the hydride region which are not attributable to **6**, are believed to result from hydrolysis of **6** (see below).

Additional evidence for a C(O)OMe moiety in **5** and **6** is the presence of bands in their IR spectra at 1644 (m) cm^{-1} and 1648 (m) cm^{-1}, respectively. These bands are in the range expected for ν(C=O) in η^1 alkoxycarbonyls (1580–1703 cm^{-1}) [5] and compare favorably with the band observed for $Os_3(CO)_{11}(C(O)OMe)^-$ (1631 (w) cm^{-1}) [9]. Bands for **5** observed at 1256 (s), 1044 (s), 1028 (sh), 972 (m) cm^{-1} have been assigned as ν(S–O). These bands are shifted somewhat from values for the neutral cluster **1** (1275 (vs), 1048 (s), 1020 (s), and 966 (s) cm^{-1}) [1]. Qualitatively,

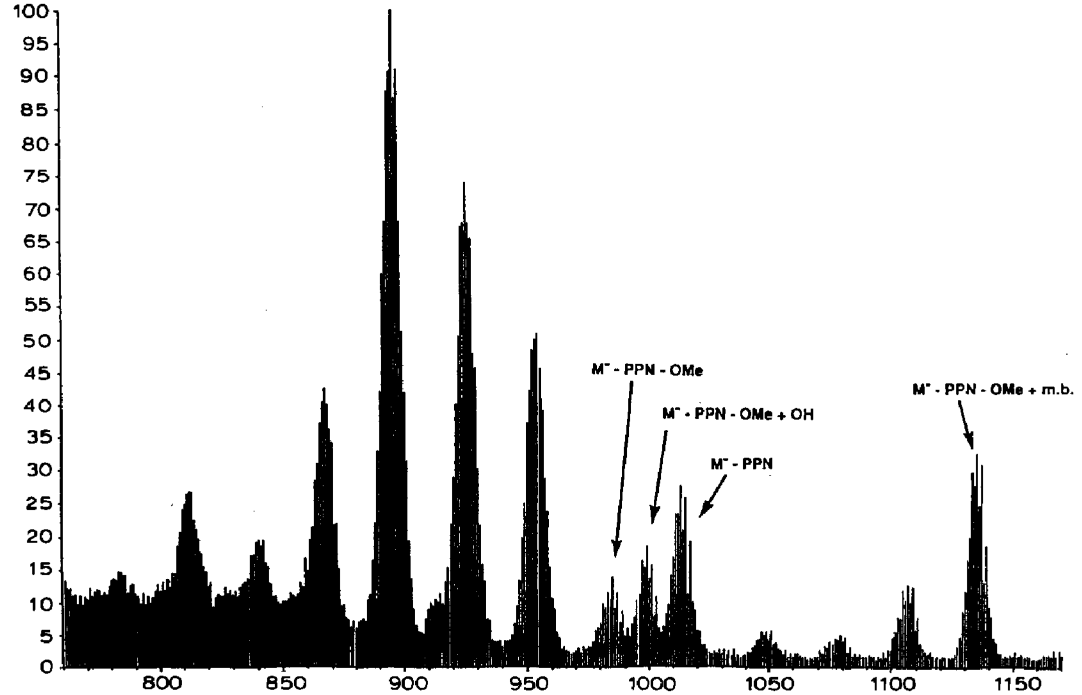


Fig. 2. Negative ion fast atom bombardment mass spectrum for [PPN][(μ-H)$_2$Os$_3$(CO)$_8$(C(O)OMe)(μ_3, η^3-O$_3$PPh)] (6) in matrix of dithioerythritol and dithiothreitol. The matrix anion is abbreviated m.b. (after magic bullet). The mass envelopes observed have the intensity pattern expected for ions containing Os$_3$ moieties.

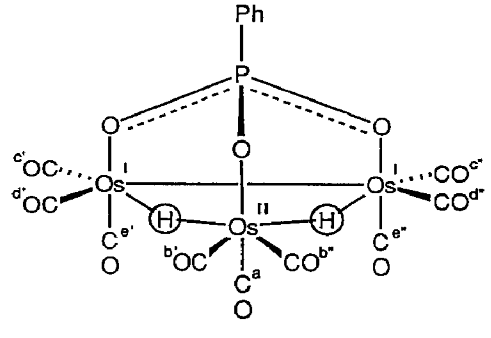
any influence which increases the electron density of the triosmium core, such as base adduct formation, should, through inductive effects, tend to reduce the electronegativity of sulfur with a concomitant reduction in the S=O bond strength. For 5, three ν(S–O) bands are shifted to lower frequency and one to higher frequency. The complexity of the spectrum for 6 between 1300 and 800 cm^{-1} precluded assignment of its ν(P–O) bands.

The elemental analysis for 5 was only marginal; low values for C, H, and N were obtained. These low values clearly result from contamination with the neutral precursor 1. Evidence for this includes weak bands attributable to 1 in the solution IR spectrum of 5 (recorded in methanol) and a weak signal for 1 in the ^{1}H NMR spectrum of 5 at δ −12.5. Attempts at removing this impurity by further recrystallization were not successful owing to the low solubility of 1 in common organic solvents. This low solubility provides a driving force for the formation of 1 from solutions of 5. The elemental analysis for 6 was satisfactory.

Site of adduct formation

In an attempt to establish the carbonyl ligand where methoxide attack occurs, we prepared ^{13}C-enriched 6 (in methanol-d_4 solution by reaction of ^{13}C-enriched 3 with methanolic (^{n}Bu$_4$N)OH) and recorded the ^{13}C NMR spectrum at −35 °C (see Fig. 3).

Though we cannot unambiguously identify the carbonyl which has undergone nucleophilic attack, we can make a reasonable and well supported suggestion. In the



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absence of steric factors, adduct formation with methoxide should occur at the most electrophilic carbonyl. For **3**, this is probably CO$^{b'}$ or CO$^{b''}$ since they are coordinated to the Os with the highest formal charge (see I). Nucleophilic attack at either of these carbonyls would yield a low symmetry (C_1) species. The observed ^{13}C NMR spectrum which shows a 1 : 1 : 1 : 1 : 1 : 1 : 1 : 1 : 1 pattern for the nine CO ligands, is consistent with such a low symmetry (C_1) species. Attack at CO^{a} is unlikely since this would, assuming a low rotational barrier for the C(O)OMe group, result in a species of approximate C_s symmetry and a 2 : 2 : 2 : 2 : 1 pattern for the CO ligands. A species with C_s symmetry is also at variance with the ^{1}H NMR spectrum for **6** (see above).

The following assignment is proposed for the ^{13}C NMR spectrum of **6**: δ 182.54 (m, CO$^{b'}$), 179.81 (d, ^2J(CH) = 13.3 Hz, CO$^{c'}$ or CO$^{c''}$), 179.22 (d, ^2J(CH) = 13.4 Hz, CO$^{c'}$ or CO$^{c''}$), 178.79 (m, CO$^{b''}$), 176.23 ("t", ^3J(PC) = 6.6 Hz, CO$^{d'}$ or CO$^{d''}$, unresolved CH coupling), 175.64 (dd, ^3J(PC) = 6.7 Hz, ^2J(CH) = 4.5 Hz CO$^{d'}$ or CO$^{d''}$), 175.44 (d, ^2J(CH) = 2.4 Hz, CO^{a}, CO$^{e'}$, or CO$^{e''}$), 175.28 (CO^{a}, CO$^{e'}$, or CO$^{e''}$), and 175.20 (CO^{a}, CO$^{e'}$, or CO$^{e''}$). The resonance at δ 182.54 is assigned to the carbonyl where adduct formation has occurred (CO$^{b'}$) owing to its position farthest downfield. Also, this resonance, appears significantly broader in the proton coupled spectrum, indicating coupling to one or both hydride ligands, but its multiplicity could not be established. Small coupling to phosphorus (< 2 Hz) is also seen. Resonances at δ 179.81 and 179.22 are assigned to carbonyls CO$^{c'}$ and CO$^{c''}$ which are *trans* to hydride ligands, consistent with the large CH coupling observed (^2J(CH) = 13 Hz). The resonance at δ 178.79, which appears as a non-descript multiplet in the ^{1}H coupled spectrum (much as do ligands CO$^{b'}$ and CO$^{b''}$ in the spectrum of **3**), is assigned to CO$^{b''}$ as it shows strong coupling to the *trans* hydride ligand as well as probable *cis* coupling to the other hydride and weak PC coupling (< 2 Hz). Resonances at δ 176.23 and 175.64, assigned to CO$^{d'}$ and CO$^{d''}$, appear as a "triplet" and doublet of doublet, respectively, due to three bond coupling to phosphorus (6.6 and 6.7 Hz respectively) and two bond coupling to a *cis* hydride of similar magnitude (ca. 4.5 Hz). The remaining signals (δ 175.44, 175.28, and 175.20) are assigned to the three axial carbonyls CO^{a}, CO$^{e'}$ and CO$^{e''}$. They each show weak CH coupling and no PC coupling.

Evidence for facile nucleophile exchange

The additional weak multiplets in the hydride region of the spectrum of **6** are

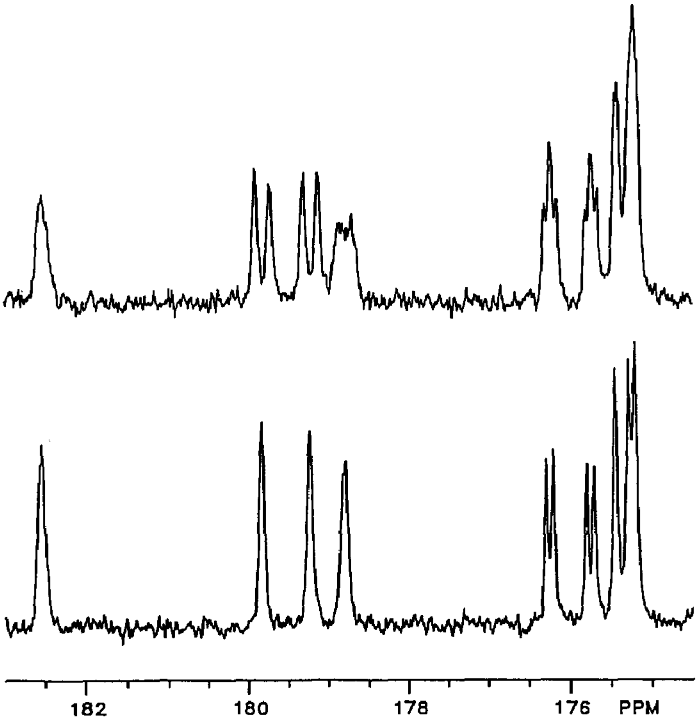

Fig. 3. ^{13}C NMR spectra for ^{13}C-enriched **6** prepared in methanol-d_4 by reaction of ^{13}C-enriched **2** and methanolic KOH. Top spectrum is proton coupled. Bottom spectrum is $\{^1H\}$. Spectra were recorded at −35°C.

believed due to $[(\mu\text{-H})_2Os_3(CO)_8(C(O)OH)(\mu_3,\eta^3\text{-}O_3PPh)]^-$. This product presumably arises from hydrolysis of **6**. Further evidence for this product is also provided by the FAB MS spectum of **6** which showed a weak ion for such a species at 1003 amu (see Fig. 2).

Additional evidence in support of methoxide/hydroxide exchange in these base adducts was provided by an experiment with crude **5**. The ^{1}H NMR spectrum (in dichloromethane-d_2) of crude **5**, recovered from the mother liquor after crystallization of **5** from diethylether, showed, in addition to signals for **5**, a second set of doublets in the hydride region at δ −10.37 and −12.07. These signals are assigned to a hydroxy species of formula $[(\mu\text{-H})_2Os_3(CO)_8(C(O)OH)(\mu_3,\eta^3\text{-}O_3SO)]^-$. When excess methanol was added, these signals disappeared, and only those due to **5** remained. Such nucleophile exchange reactions are known for base adducts of coordinated CO [5].

The apparent facility with which methoxide/hydroxide exchange occurs allows us to assign several unexpected ions in the negative ion FAB MS spectra of **5** and **6**. In the case of **5**, these occur at 1079, 1051, 1023, and 995 amu. The 1079 envelope is the most intense of these, and is assigned to a base adduct derived from exchange of the methoxy group (31 amu) in **5** by the conjugate base of dithioerythritol or dithiothreitol (each 153 amu). Dithioerythritol and dithiothreitol were used as the matrix for the FAB experiment. The remaining ions (1051, 1023, and 995 amu) are due to successive CO loss from the dithioerythritoxy or dithiothreitoxy adduct. In

Table 1

Carbonyl stretching frequencies (cm^{-1}) for the base adducts generated in methanol solution

5	2099 (m)	2063 (vs)	2048 (s)	2004 (s)	1971 (w)
6	2091 (m)	2056 (vs)	2040 (s)	1995 (s)	1961 (w)
7	2090 (m)	2054 (vs)	2039 (s)	1995 (s)	1959 (w)
8	2086 (m)	2049 (vs)	2035 (s)	1988 (s)	1955 (w)

the FAB MS spectrum of **6** (Fig. 2), a mass envelope is also observed for a dithioerythritoxy or dithiothreitoxy adduct, derived from exchange of methoxide, at 1139 amu. An envelope at 1111 amu corresponds to CO loss from this species.

Reaction of 2 with methoxide

It was noted earlier that the reaction of **2** with base required two equivalents before an IR spectrum similar to those for the monoanions $[(\mu\text{-H})_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3SO)]^-$ (**5**), $[(\mu\text{-H})_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3PPh)]^-$ (**6**), and $[(\mu\text{-H})_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3AsPh)]^-$ (**7**), derived from **1**, **3**, and **4**, respectively, was achieved (see Fig. 1). We suggest that, for **2**, the cluster derived from this reaction is a dianion of formulation $[(\mu\text{-H})_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3PO)]^{2-}$ (**8**). Support for this suggestion is provided by the systematically lower $\nu(CO)$ bands for the cluster **8** compared to the monoanions **5**–**7** (see Table 1). We noted for their neutral precursors **1**–**4** a good correlation between the basicity of the oxyligand and the carbonyl stretching frequencies [1]. If a similar correlation is assumed for the anions, the $\nu(CO)$ bands for **8** are too low in energy to be accounted for by a monoanionic cluster containing a capping $HOPO_3^{2-}$ moiety, since hydrogen phosphate is roughly as basic as phenylphosphonate and phenylarsonate. If instead the more basic PO_4^{3-} moiety is present, the CO stretches should occur at lower energy, and this is what we observe.

Only one equivalent of base was required for consumption of **2**, as evidenced by the disappearance of IR bands for it (see Fig. 4). Intermediate IR spectra were sufficiently complex that a mixture was probably present. The presence of three bands with increasing intensities at 2130 (w), 2093 (s), and 2065 (vs) cm^{-1} suggests that one intermediate species present in this mixture may be the anion resulting from deprotonation of the hydrogen phosphate group (i.e. $[(\mu\text{-H})_2Os_3(CO)_9(\mu_3,\eta^3\text{-}O_3\text{-}O_3PO)]^-$. A similar spectral pattern was noted for all the neutral clusters **1**–**4** [1]. For comparison, the three highest frequency bands for $(\mu\text{-H})_2Os_2(CO)_9(\mu_3,\eta^3\text{-}O_3POH)$ (**2**) occur at 2135 (w), 2100 (s), and 2073 (vs) cm^{-1} in methanol. A second intermediate species present may be the adduct $[(\mu\text{-H})_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3POH)]^-$. The addition of the second equivalent of base to either of these intermediates can generate **8** by either nucleophilic attack at CO or deprotonation of the POH group.

We have also studied the reaction of **2** with base in methanol-d_4 by ^1H NMR spectroscopy. After the addition of 0.3 equiv. of base (methanolic $(Et_4N)OH$) (see Fig. 5), two equally intense new signals are seen in the hydride region at δ -10.60 and -12.48. Both of these signals appear as a doublet of doublets, indicating HH and PH coupling, similar to that observed for **6**, and are assigned to a methoxycarbonyl species. At this point, such a species is probably the monoanion $[(\mu\text{-H})_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3POH)]^-$. Resonances for the other intermediate

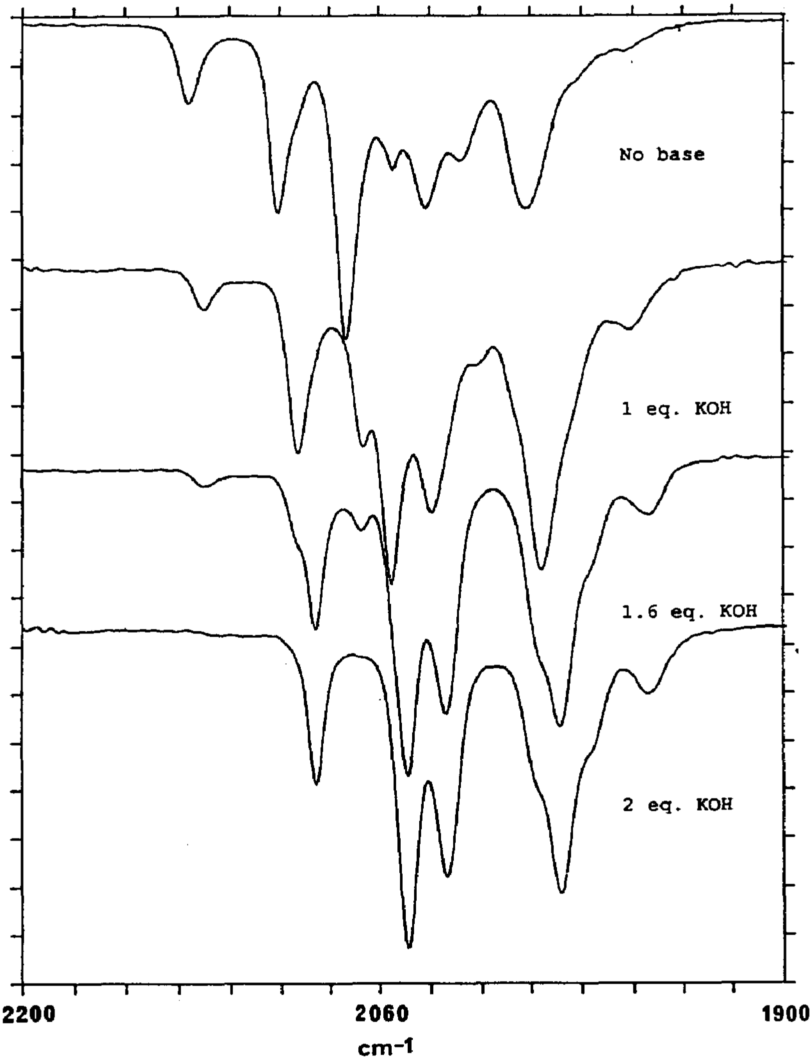

Fig. 4. Carbonyl region IR spectra for the reaction of 2 with base.

suggested by the IR study above, $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3,\eta^3\text{-O}_3\text{PO})]^-$, are not evident; possibly because of fast exchange with solvent protons to give the starting cluster **2**. Further addition of base results in an increase in the new hydride signals, and a corresponding decrease in the intensity of doublet for **2**. After addition of 2.1 equiv. of base, no **2** could be detected. The multiplets for the methoxycarbonyl species shifted slightly to δ -10.48 and -12.51, respectively. At this point the cluster dianion $(\mu\text{-H})_2\text{Os}_3(\text{CO})_8(\text{C(O)OMe})(\mu_3,\eta^3\text{-O}_3\text{PO})^{2-}$ is present. During the course of reaction the doublet for **2** also shifts slightly. Initially at δ -12.593, it is located at -12.549 after addition of 1.5 equiv. of base. This shift is consistent with the rapid interchange of **2** and $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3,\eta^3\text{-O}_3\text{PO})]^-$, providing the resonance for the deprotonated cluster is around δ -12.5. The two multiplets at δ -10.85 and -12.54, both doublet of doublets, which are first observed after addition of 1.5 equiv. of base, are believed to result from hydrolysis of the

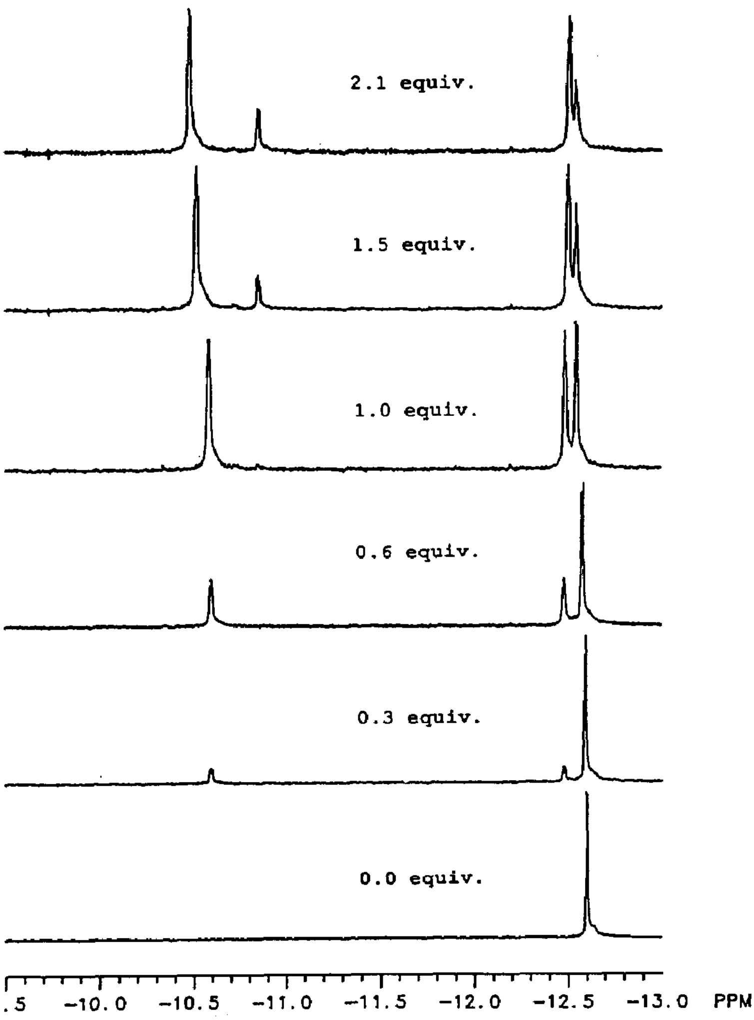

Fig. 5. ^{1}H NMR spectra for the reaction of **2** with base in methanol-d_4.

methoxycarbonyl species. Only a small change in the intensity of these multiplets, relative to those assigned to the methoxycarbonyl cluster, are seen when more base is added (3.5 equivalents total).

Experimental

General

Compounds **1**–**4** were prepared according to the literature method [1]. Bis(triphenylphosphine)iminium chloride (PPN)Cl) (Aldrich) was used as received. Titers of methanolic (^{n}Bu$_4$N)OH (0.0597 *M*), prepared by dilution of concentrated (^{n}Bu$_4$N)OH (Aldrich, 40% in water), and methanolic KOH (0.0657 *M*) were determined by titration of potassium acid phthalate to the phenolphthalein end point. Elemental analyses were performed by the staff of the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained on a GE QE-300 spectrometer and were referenced to solvent resonances. IR spectra were recorded on a Perkin-Elmer 1750 Fourier transform IR spectrometer. Negative ion fast atom bombardment (FAB) mass spectra were obtained by the staff of the Mass Spectroscopy Laboratory of the School of Chemical Sciences at the University of Illinois using a Varian ZAB-SE and a matrix of dithioerythritol/dithiothreitol.

Reactions with methoxide

The cluster monoanions $[(\mu\text{-H})_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3SO)]^-$ (**5**), $[(\mu\text{-H})_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3PPh)]^-$ (**6**), and $[(\mu\text{-H})_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3AsPh)]^-$ (**7**); and the cluster dianion $[(\mu\text{-H})_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3PO)]^{2-}$ (**8**), were generated in methanol solution by titration of their neutral parent clusters with methanolic KOH (0.0657 *M*) or (^{n}Bu$_4$N)OH (0.0597 *M*). The base solutions were added slowly via syringe to stirred suspensions or solutions of the clusters in methanol (2–5 mL). Reactions were monitored to completion by IR. A slight color change from very pale yellow to essentially colorless was noted for each reaction. Tabulated below are the relevant starting and titrant quantities. ν(CO) frequencies for the adducts are listed in Table 1.

Starting cluster	Weight (mg)/ mmol ($\times 10^3$)	Titrant	Titrant vol (μL)/ mmol ($\times 10^3$)	Equiv. base
1	7.07/7.68	(^{n}Bu$_4$N)OH	129/7.70	1.0
3	4.8/4.9	KOH	81/5.3	1.1
4	8.63/8.42	(^{n}Bu$_4$N)OH	141/8.42	1.0
2	4.33/4.70	KOH	142/9.20	2.0

[Bu$_4$N][(μ-H)$_2$Os$_3$(CO)$_8$(C(O)OMe)(μ_3,η^3-O$_3$SO) (5)

$(\mu\text{-H})_2Os_3(CO)_9(\mu_3,\eta^3\text{-}O_3SO)$ (**1**) (12.95 mg, 0.0141 mmol) was suspended in methanol (2.0 mL) and methanolic (^{n}-Bu$_4$N)OH (236 μL, 0.0597 *M*, 0.0141 mmol) added slowly with constant stirring. The reaction was followed to completion by IR. After the addition was complete, the solvent was removed at reduced pressure and the resulting residue recrystallized from diethylether/methanol to give **5** as a slightly impure pale yellow solid. Yield: 8.3 mg, 0.0071 mmol, 51%. IR bands for the neutral starting cluster **1** were observed in the isolated product, though they were considerably weaker than those for **5**. Further recrystallizations did not improve matters.

Anal. Found: C, 25.10; H, 3.04; N, 1.08. $C_{26}H_{41}NO_{14}Os_3S$ calcd.: C, 26.15; H, 3.46; N, 1.17%. ^{1}H NMR (dichloromethane-d_2): δ 3.71 (3H, C(O)OMe), 3.07 (t, ^3H(HH) = 8 Hz, 8H, ^{n}Bu$_4$N), 1.58 (m, 8H, ^{n}Bu$_4$N), 1.39 (m, 8H, ^{n}Bu$_4$N), 1.00 (t, ^3J(HH) = 7 Hz, 12H, ^{n}Bu$_4$N), −10.25 (d, ^2J(HH) = 1.5 Hz, 1H), −12.03 (d, ^2J(HH) = 1.5 Hz, 1H). MS (fast atom bombardment, negative ion, ^{192}Os): *m/z* 1079, 1079–28*x* (*x* = 1–3) (see text for assignments), 957 (M^- − Bu$_4$N), 925 (M^- − Bu$_4$N − MeOH), 925–28*x* (M^- − Bu$_4$N − MeOH − *x*CO; *x* = 1–5), and other unassigned peaks.

[PPN][(μ-H)$_2$Os$_3$(CO)$_8$(C(O)OMe)(μ_3,η^3-O$_3$PPh)] (6)

$(\mu\text{-H})_2Os_3(CO)_9(\mu_3,\eta^3\text{-}O_3PPh)$ (10.5 mg, 0.017 mmol) was dissolved in methanol (ca. 3 mL) and methanolic KOH (150 μL, 0.0657 *M*, 0.0099 mmol) added slowly with constant stirring. The reaction was followed to completion by IR. (PPN)Cl (ca. 100 mg) in methanol (ca. 1 mL) was added and the resulting solution concentrated to ca. 2 mL. Water was added, dropwise and with continuous stirring, until turbidity was evident. Storage at −15 °C gave **6** as a fine extremely pale yellow precipitate. This material was collected, washed with water/methanol (1/1), and dried in vacuo. Yield: 8.0 mg, 0.0052 mmol, 48%.

Anal. Found: C, 40.23; H, 2.52; N, 1.00. $C_{52}H_{40}NO_{13}Os_3P_3$ calcd.: C, 40.29; H, 2.60; N, 0.90%. ^1H NMR (dichloromethane-d_2): δ 7.7–7.2 (m, 30H, PPN), 3.67 (3H, C(O)OMe), −10.37 (dd, $^2J(HH) = 2.1$ Hz, $^3J(PH) = 3.0$ Hz, 1H), −12.23 (dd, $^2J(HH) = 2.1$ Hz, $^3J(PH) = 2.7$ Hz, 1H). MS (fast atom bombardment, negative ion, ^{192}Os): m/z 1139, 1111, 1003 (see text for assignments), 1017 (M^- − PPN), 989 (M^- − PPN − CO), 958 − 28x (M^- − PPN − xCO − OMe, $x = 0$–4), and other unassigned peaks.

^{13}C NMR of 6 in methanol

^{13}CO enriched (ca. 50% enrichment) $(\mu\text{-H})_2Os_3(CO)_9(\mu_3,\eta^3\text{-}O_3PPh)$ (**3**) (11.0 mg, 0.0112 mmol) was dissolved in methanol-d_4 in an NMR tube. The ^{13}C NMR spectrum was then recorded at −35 °C. Methanolic ($^nBu_4N$)OH (185 μL, 0.0597 *M*, 0.0112 mmol) was added slowly to the solution of **3**, with thorough mixing. The initially light yellow solution became essentially colorless after the addition was complete. The ^{13}C NMR spectrum of the base adduct **6**, which was thus generated, was recorded at −35 °C.

^{13}C NMR (methanol-d_4, −35 °C) before addition of base: δ 177.41 (d, $^2J(CH) =$ 7.6 Hz, 2C), 174.74 (m, $^3J(PH) = 6.9$ Hz, also unresolved CH coupling, 2C), 173.52 (2C), 165.45 (m, 2C), 165.17 (1C). ^{13}C NMR (methanol-d_4, −35 °C) after addition of base: δ 182.54 (m, $^3J(PC) =$ ca. 2 Hz, also unresolved CH coupling, 1C), 179.81 (d, $^2J(CH) = 13.3$ Hz, 1C), 179.22 (d, $^2J(CH) = 13.4$ Hz, 1C), 178.79 (m, unresolved CH coupling, 1C), 176.23 ("t", $^3J(PC) = 6.6$ Hz, $^2J(CH) =$ ca. 4.5 Hz, 1C), 175.64 (dd, $^3J(PC) = 6.7$ Hz, $^2J(CH) = 4.5$ Hz, 1C), 175.44 (d, $^2J(CH) = 2.4$ Hz, 1C), 175.28 (1C), 175.20 (1C).

^1H NMR of 8

Compound **2** (5.1 mg, 0.0056 mmol) was dissolved in methanol-d_4 (0.4 mL) in an NMR tube. The ^1H NMR spectrum was then recorded. Several portions of (Et_4N)OH (25% w/w in methanol) were added via syringe, and the ^1H NMR spectrum recorded after each addition. When a total of 2.1 equiv. of base had been added, the ^1H NMR spectrum indicated no remaining **2**.

Conclusions

Reaction of the dihydrido triosmium carbonyl clusters **1**, **3** and **4** with methoxide does not result in deprotonation, but rather the formation of stable methoxycarbonyl adducts with formula $[(\mu\text{-H})_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3ER)]^-$. The site of nucleophilic attack is an equatorial CO ligand coordinated to the unique osmium atom, which is formally an Os^{II} center. For the hydrogenphosphate cluster **2**, both adduct formation and deprotonation of the POH group occur, the final product being the cluster dianion $[(\mu\text{-H})_2Os_3(CO)_8(C(O)OMe)(\mu_3,\eta^3\text{-}O_3PO)]^{2-}$. Kaesz has found that reaction of $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-O=CMe})$ with LiMe results in deprotonation at 25 °C and in adduct formation at −30 °C [10]. This suggests that the base adducts **5–8** may be kinetic products rather than thermodynamic products; however, their stability upon heating was not examined.

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