The Interaction of $H_2Os_3(CO)_{10}$ with Alkenes. Intermediates in Hydrogenation and Carbon-Hydrogen Bond Activation[1]

Sir:

The reactivity of unsaturated species is expected to be as important for the chemistry of polynuclear organotransition metal compounds as it is for mononuclear compounds.[2] As part of our exploration of the chemistry of the unsaturated metal cluster compound $H_2Os_3(CO)_{10}$, we recently reported that it reacts with 2 equiv of ethylene to give ethane and the hydridovinyl cluster $HOs_3(CO)_{10}(CH{=}CH_2)$.[3] Further study has shown that analogous reactions obtain for a variety of 1-alkenes and that hydrogenation can be catalytic. Moreover, we have isolated and characterized a relatively stable class of hydridoalkyltriosmium clusters that are model intermediates for the hydrogen transfer process. Elimination of alkane from these compounds provides the unsaturated cluster species responsible for activation of H-H and vinylic C-H bonds.

The reactivity of an alkene toward $H_2Os_3(CO)_{10}$ is quite sensitive to steric and electronic effects. For example, ethyl acrylate and vinyl acetate react faster than ethylene, whereas propene and isobutylene react slower, and no reaction is observed for cyclooctene or norbornene. The interaction of excess 1-alkene with $H_2Os_3(CO)_{10}$ commonly provides the corresponding alkane and $HOs_3(CO)_{10}$(alkenyl) cluster,[4] with no detectable intermediates. However, treatment of $H_2Os_3(CO)_{10}$ with 1 equiv of diethyl fumarate or diethyl maleate readily forms (2 h, 25°) a hydridoalkyl intermediate, $HOs_3(CO)_{10}(CH(CH_2CO_2Et)CO_2Et)$ (**1**), which is sufficiently stable to allow purification by chromatography and isolation in a good yield as a yellow solid. A closely related compound, $HOs_3(CO)_{10}(CH(CH_2\overline{CO)COO})$ (**2**), is obtained from maleic anhydride, and ethyl acrylate provides $HOs_3(CO)_{10}(CH(CH_3)CO_2Et)$ (**3**), which is less stable than **1** or **2**. In solution these compounds decompose within 12-48 h at 25° to give the alkane and, in the absence of added substrates, numerous osmium-containing products. A primary alkyl species $HOs_3(CO)_{10}(CH_2CO_2Et)$ (**4**), prepared for comparison with compounds **1-3**, is obtained quantitatively from the combination of $H_2Os_3(CO)_{10}$ with ethyl diazoacetate at room temperature.[6]

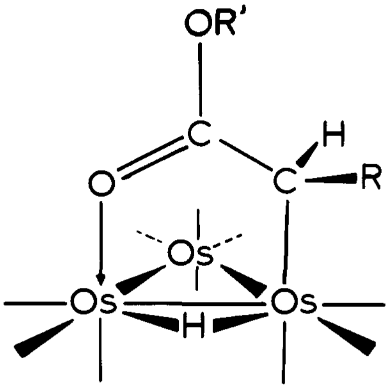
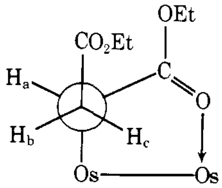


Figure 1. Proposed structure for $HOs_3(CO)_{10}$(alkyl) compounds (**1**, R = CH_2CO_2Et, R' = Et; **2**, R = CH_2CO = R'; **3**, R = CH_3, R' = Et; **4**, R = H, R' = Et).

Figure 1 depicts the general structure proposed for compounds **1-4** on the basis of spectroscopic data.[7] Coordination of the ester or anhydride carbonyl must contribute to their unusual stability, since this forms a relatively unstrained five-membered ring and the cluster as a whole is electronically saturated.[8] Compounds **1-3** exist as isomers, indicated by the two distinct hydride NMR signals observed for each, due to orientation of the α-carbon substituent (R) either syn or anti to the third osmium atom. Isomeric configurations are not possible for **4**, and only one hydride signal is found.[10] Although only one set of alkyl resonances is apparent under normal conditions, addition of a small amount of $Eu(fod)_3$ to a solution of **1** allows observation of both sets of resonances with appropriate relative intensities and essentially identical coupling constants. The vicinal coupling constants suggest predominance of one rotamer; that with the carboethoxy group on the β-carbon oriented trans to the Os-C bond is assumed.[11] Reaction of diethyl fumarate with $D_2Os_3(CO)_{10}$[13] provides **1** with H_b replaced by D, consistent with highly stereoselective cis addition. However, treatment of $D_2Os_3(CO)_{10}$ with diethyl maleate did not give the pure diastereomer, due to concurrent maleate-fumarate isomerization. Interestingly, kinetic control obtains for the insertion of maleic anhydride, in that the isomer of **2** preferentially formed early in the reaction is not the one favored at the end.



Decomposition of **1** at 25-50°, in the presence of an excess of 1-alkene, including ethylene, propene, isobutylene, styrene, and hexene, provides the corresponding $HOs_3(CO)_{10}$(alkenyl) cluster in high yield.[4] For example, $HOs_3(CO)_{10}(CH{=}CHPh)$ is formed in over 80% yield from styrene, although $H_2Os_3(CO)_{10}$ does not react directly with styrene under the same conditions. Furthermore, 2,2-disubstituted alkenyl compounds, such as $HOs_3(CO)_{10}(CH{=}CMe_2)$, which are formed rather slowly from $H_2Os_3(CO)_{10}$ and the alkene and which cannot be formed from $H_2Os_3(CO)_{10}$ and an alkyne, are readily obtained in this manner. Preliminary kinetic data indicate that the rate of decomposition of **1** is unaffected by the addition of a large excess of styrene or hexene.

When decomposition of **1** is conducted under hydrogen (50 psig, 50°), $H_2Os_3(CO)_{10}$ and diethyl succinate are the only products detected, each in high yield. This activation of molecular hydrogen closes the cycle of hydrogen transfer from $H_2Os_3(CO)_{10}$ to diethyl fumarate. Catalytic hydrogenation of diethyl fumarate or ethyl acrylate by $H_2Os_3(CO)_{10}$ is observed under similar conditions, but the number of cycles is limited by destructive side reactions. A much cleaner catalytic system is established with 1-hexene. Interaction of $H_2Os_3(CO)_{10}$ with 100 equiv of 1-hexene (50 psig H_2, 50°, octane, 35 h) results in 31 equiv of hexane and 69 equiv of internal hexenes, and essentially all of the catalyst is recovered at the end of the reaction. The high degree of isomerization indicates reversibility of the insertion and coordination steps, whereas buildup of the internal hexenes is consistent with the observed failure of $H_2Os_3(CO)_{10}$ to hydrogenate other internal alkenes, such as cyclooctene.

These observations on the interaction of $H_2Os_3(CO)_{10}$ with alkenes are accommodated compactly by the scheme of reactions shown in Figure 2. The involvement of $H_2Os_3(CO)_{10}$(alkene) intermediates (II in the scheme) is proposed by analogy with the adducts $H_2Os_3(CO)_{10}L$ (L = CO, PR_3, CNR, etc.) previously characterized,[9] and compounds **1-3** typify the hydridoalkyl species (III) formed by alkene insertion. The key presumptive intermediate in this scheme is the highly unsaturated, 44-electron species $Os_3(CO)_{10}$ (IV), which reacts with H-H or vinylic C-H bonds, if available, or decomposes by presently unknown pathways. An alternative possibility for the active species is

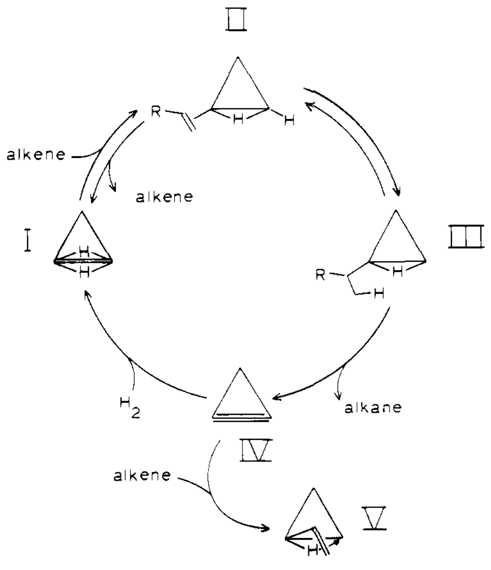


Figure 2. Reaction scheme for the interaction of $H_2Os_3(CO)_{10}$ (I) with alkenes (II, $HOs_3(CO)_{10}$(alkene); III, $HOs_3(CO)_{10}$(alkyl); IV, $Os_3(CO)_{10}$; V, $HOs_3(CO)_{10}$(alkenyl)).

$Os_3(CO)_{10}L$, where L is an adventitious donor, such as an ester or an additional alkene. This question is being examined in ongoing work, but we note at this point the recent reports on the characterization and reactivity of $[(C_5H_5)Mo(CO)_2]_2$,[14] a molecule with the same level of unsaturation as the proposed intermediate IV.

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References and Notes

(1) (a) Activation of Hydrocarbons by Unsaturated Metal Cluster Complexes. III. (b) Part II: M. Tachikawa, J. R. Shapley, and C. G. Pierpont, *J. Am. Chem. Soc.*, **97**, 7172 (1975).

(2) The possibilities for generation of unsaturated species are richer for metal–metal bonded compounds. One unique mode is via metal–metal bond scission (cf. E. L. Muetterties, B. A. Sosinsky, and K. I. Zamaraev, *J. Am. Chem. Soc.*, **97**, 5299 (1975)). However, our interest here is in the reactions of an intact metal aggregate with empty "surface" coordination sites (cf. ref 1b).

(3) J. B. Keister and J. R. Shapley, *J. Organomet. Chem.*, **85**, C29 (1975).

(4) The $HOs_3(CO)_{10}$(alkenyl) clusters have been characterized by their ir, NMR, and mass spectral data. No hydridoalkenyl species have been derived from 1,2-disubstituted alkenes. Substituents appear in the 2-positions only, a single substituent is trans to the Os–C σ bond. Thus, the compounds formed here from 1-alkenes are identical with those formed by insertion of 1-alkynes.[5]

(5) (a) A. J. Deeming, S. Hasso, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1614 (1975); (b) W. G. Jackson, B. F. G. Johnson, J. W. Kelland, J. Lewis, and K. T. Schorpp, *J. Organomet. Chem.*, **87**, C27 (1975); (c) J. R. Shapley, S. I. Richter, M. Tachikawa, and J. B. Keister, *ibid.*, **94**, C43 (1975), and unpublished data.

(6) Analogous reactions of $H_2Os_3(CO)_{10}$ with diazo and azide compounds have been observed and will be reported separately.

(7) Weak molecular ions are observed in the mass spectra of **1** and **2**, but in each case the most abundant ions are $H_xOs_3(CO)_y^+$ (x = 0–2, y = 0–10), due to decomposition and subsequent fragmentation. Solution ir spectra indicate only terminal carbon monoxide ligands. In each case an absorption band due to the coordinated acyl group is observed (**1**, 1615 cm^{-1}; **2**, 1653 cm^{-1}; **3**, 1569 cm^{-1}; **4**, 1589 cm^{-1}); for **1** and **2** a band for the free carbonyl is also found (**1**, 1688 cm^{-1}; **2**, 1855 cm^{-1}). Proton NMR data (exclusive of carboethoxy signals) ($CDCl_3$, τ): **1**, 24.47 (s, 0.3 H), 24.05 (s, 0.7 H), 7.18 (dd, 1 H_c), 6.46 (dd, 1 H_b), 6.26 (dd 1 H_a, $J_{bc} = -18.5$, $J_{ab} = 2.5$, $J_{ac} = 7.5$ Hz); **2**, 23.62 (s, 0.6 H), 22.93 (s, 0.4 H), 6.99 (m, 1 H_c), 6.71 (m, 1 H_b), 6.66 (m, 1 H_a, $J_{bc} = -18.6$, $J_{ab} = 5.2$, $J_{ac} = 10.9$ Hz); **3**, 23.51 (s, 0.2 H), 22.99 (s, 0.8 H), 8.33 (d, 3H_b), 7.32 (q, 1 H_a, $J_{ab} = 6.6$ Hz); **4**, 23.26 (d, 1 H_c), 8.09 (dd, 1 H_b), 7.87 (d, 1 H_a, $J_{ab} = -19.0$, $J_{bc} = 1.2$ Hz).

(8) The data at hand do not unambiguously eliminate a six-membered ring for **1**. However, a five-membered ring is strongly indicated for **2–4** (chelation of one osmium center with a four-membered ring is highly unlikely) and assumed for **1**. The distribution of one- and two-electron donors closely resembles that for the adducts $H_2Os_3(CO)_{10}L$.[9]

(9) J. R. Shapley, J. B. Keister, M. R. Churchill, and B. G. DeBoer, *J. Am. Chem. Soc.*, **97**, 4145 (1975).

(10) Only one isomer is obtained for the related compound $HOs_3(CO)_{10}$-$(C(=CH_2)CO_2Et)$ (formed from $H_2Os_3(CO)_{10}$ and ethyl propiolate), since isomerism at the α-carbon is not possible (M. Tachikawa and J. R. Shapley, unpublished results).

(11) Similar conformations have been assumed for $HMoCp_2(CH(CO_2Me)CH_2CO_2Me)$[12a] and for $Co(CN)_5(CH(CO_2^-)CH_2CO_2^-)^{2-}$.[12b]

(12) (a) A. Nakamura and S. Otsuka, *J. Am. Chem. Soc.*, **94**, 1886 (1972); **95**, 7262 (1973); (b) L. M. Jackman, J. A. Hamilton, and J. M. Lawlor, *ibid.*, **90**, 1914 (1968).

(13) The deuterium loss reported recently (S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 3942 (1975) in the preparation of $D_2Os_3(CO)_{10}$ is due to exchange with silica gel during chromatography and can be avoided by recrystallization from CCl_4 (J. B. Keister and J. R. Shapley, unpublished results, and H. D. Kaesz, private communication).

(14) (a) R. J. Klingler, W. Butler, and M. D. Curtis, *J. Am. Chem. Soc.*, **97**, 3535 (1975); (b) D. S. Ginley and M. S. Wrighton, *ibid.*, **97**, 3533 (1975).

Jerome B. Keister, John R. Shapley*
Department of Chemistry, University of Illinois
Urbana, Illinois 61801

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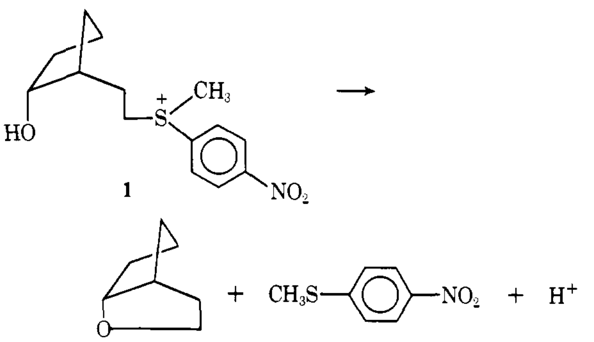
General Base Catalysis in Nucleophilic Attack at sp³ Carbon of Methylase Model Compounds

Sir:

Despite the apparent simplicity of the overall reaction, there are little data available in the literature on the mechanism of enzyme-catalyzed transmethylation reactions in which the sulfonium compound, *S*-adenosyl-L-methionine (SAM) serves as the alkyl donor.[1,2] In this communication, we report a facile intramolecular transalkylation involving general-base-catalyzed attack of an alcohol on carbon bonded to trivalent sulfur.

Over the past several years, we have studied intermolecular and intramolecular transalkylation reactions as nonenzymic models for SAM-requiring methylases.[2-4] General base catalysis of nucleophilic attack at sp^3 carbon is a rare phenomenon, the only example being the cyclization of 4-chlorobutanol.[5,6] We have synthesized **1**[7] with the expectation that proximity effects would result in a facile intramolecular transalkylation reaction, in spite of the fact that 4-chlorobutanol is ca. 10^3 more reactive than the corresponding sulfonium compound.[2] These expectations were realized, and the decomposition of **1** (eq 1) could be followed spectrophotometrically over a wide range of pH in water at 25°. The pH-rate profile shown in Figure 1 fits the general rate law, $k_o = k_{H_2O} + k_{OH}[OH^-]$, where k_o is the k_{obsd} extrapolated to zero buffer concentration. However, the following facts suggest the apparent k_{OH} term is really a term associated with the ionization of the secondary hydroxyl group. We have previously studied the reactions of several



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