the corresponding hydroxymethylcarboxylic acids.[8] We tested the ability of the enzyme system of this organism to stereoselectively oxidize one of the enantiotopic hydroxyethyl groups attached to a prochiral center in **1**.[9,10] When **1** (300 mg) was incubated with lyophylized cells (360 mg) of *F. oxydans* at pH 6.5 for 72 hr, (*S*)-mevalonolactone (46 mg) $[\alpha]^{26}D$ +21.8° (EtOH) was obtained. This result could be interpreted as indicative of the preferential oxidation of the pro-*S* hydroxyethyl grouping of **1** by *F. oxydans*. However, exposure of (3*RS*)-mevalonolactone (120 mg) to the organism afforded (*S*)-mevalonolactone (44 mg) $[\alpha]^{26}D$ +15° (EtOH) and suggested that (*R*)-mevalonolactone was selectively utilized by the enzyme system. The selective utilization of (*R*)-mevalonolactone by microorganisms has been noted before.[11] At present, the pathway of oxidation with *F. oxydans* is not clear and can be interpreted in several ways. (a) *F. oxydans* oxidized preferentially the pro-*S* hydroxyethyl group of **1**, thereby affording the (*S*)-mevalonolactone. (b) *F. oxydans* oxidizes both the pro-*R* and pro-*S* hydroxyethyl of **1** to give (±)-mevalonolactone. The organism then selectively uses up the (*R*)-mevalonolactone leaving behind the (*S*) enantiomer which is isolated.[11]

Further experimentation is required for the determination of the mechanism of oxidation by *F. oxydans*.[12]

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Synthesis and Characterization of the Fluxional Species $H_2Os_3(CO)_{10}L$. The Crystal Structure of $H_2Os_3(CO)_{11}$

Sir:

Recent work has established that the formally electron-deficient cluster compound $H_2Os_3(CO)_{10}$ is much more reactive than the saturated cluster $Os_3(CO)_{12}$ toward olefins and acetylenes.[1] In order to examine the initial state of interaction between an electron donor and $H_2Os_3(CO)_{10}$ without the complications of subsequent hydrogen transfer reactions, we have treated $H_2Os_3(CO)_{10}$ with several simpler σ-donor/π-acceptor ligands. We now report that the adducts thus formed display unique structural and dynamic features in that they each contain one bridging and one terminal hydride ligand which undergo mutual exchange.

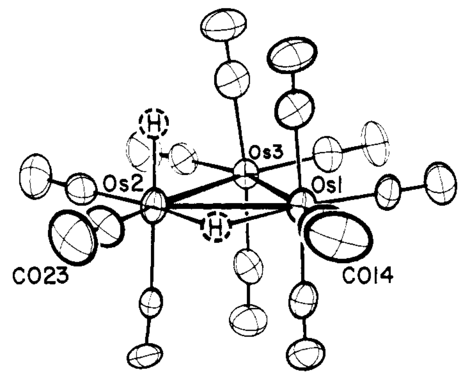


Figure 1. General view of the $H_2Os_3(CO)_{11}$ molecule, showing the probable hydrogen sites. Note that the axial H and CO on Os(2) have a 63.8%:36.2% disorder.

Addition of a two-electron donor ligand to a purple hexane solution of $H_2Os_3(CO)_{10}$ causes a rapid color change to yellow.[2] From these solutions yellow, crystalline compounds of formula $H_2Os_3(CO)_{10}L$ (L = CO (**1**), CNMe (**2**), PPh_3 (**3**), PMe_2Ph (**4**), $AsMe_2Ph$ (**5**)) have been isolated and fully characterized by elemental analysis and by ir, NMR, and mass spectra. The compounds are moderately stable to ambient conditions both as solids and in solution, although **1** in solution slowly reverts to $H_2Os_3(CO)_{10}$ in the absence of carbon monoxide. Molecular ions are observed in the mass spectra of **1**, **2**, and **5**, but the highest mass ion observed for **3** and **4** is $(M - CO)^+$. Additional features of the mass spectra together with solution ir spectra indicate that triangular structures (as determined for $H_2Os_3(CO)_{10}$[3]) terminal carbonyls only, and lack of symmetry characterize this set of compounds.

In addition to the appropriate ligand ^1H NMR resonances, at −60°, each adduct displays two equally intense signals for the hydride ligands, one near τ 20, the other near τ 30 ($J_{H-H} \sim 4$ Hz).[4] These signals are assigned to a terminal and to a bridging hydride ligand, respectively, by comparison with available chemical shift data for other saturated hydridoosmium compounds.[5] Furthermore, bands at 1930 (w, $\Delta\nu_{1/2} \sim 20$ cm^{-1}) and 1525 cm^{-1} (vw, $\Delta\nu_{1/2} \sim 50$ cm^{-1}) appearing in the ir spectrum (KBr) of solid $H_2Os_3(CO)_{11}$ shift to 1410 (vw, $\Delta\nu_{1/2} \sim 25$ cm^{-1}) and 1110 cm^{-1} (vw, $\Delta\nu_{1/2} \sim 40$ cm^{-1}) for $D_2Os_3(CO)_{11}$. The higher-frequency band may be assigned as primarily a terminal Os-H(D) stretching mode,[7] whereas the lower-frequency band must arise from vibration of a bridged Os-H(D)-Os structure.[6]

The detailed structure of $H_2Os_3(CO)_{11}$ has been determined by a single-crystal X-ray diffraction study. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with a = 8.0744 (16) Å, b = 14.7265 (29) Å, c = 14.7770 (28) Å, β = 101.36 (1)°, V = 1722.7 (6) Å^3, and ρ(calcd) = 3.396 g cm^{-3} for Z = 4 and mol wt = 880.73. X-Ray diffraction data were collected with a Picker FACS-1 diffractometer using Mo Kα radiation and a θ-2θ scan technique. The structure was solved by using the Os coordinates of $Os_3(CO)_{12}$[8] as the starting point for the usual structure-factor, least-squares refinement, difference-Fourier synthesis, iterations. All data were corrected for the effects of absorption (μ = 221.5 cm^{-1}; T = 0.166-0.307). All non-hydrogen atoms were accurately located, the final discrepancy indices being R_F = 3.68% and R_{WF} = 3.52% for the 2259 reflections with $2\theta < 45°$ (none rejected). There is a slight disorder problem with the axial ligands on

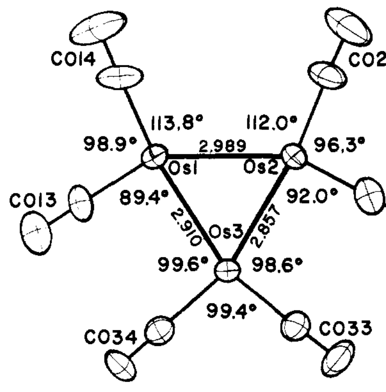
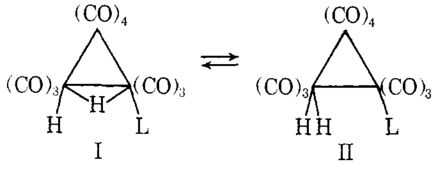


Figure 2. The equatorial plane of the $H_2Os_3(CO)_{11}$ molecule, showing angles (in deg) and Os–Os distances (in Å). The bridging hydride ligand is believed to lie between Os(1) and Os(2) near the intersection of lines extended from CO(13) → Os(1) and CO(24) → Os(2).

Os(2)—63.8 (11)% of the molecules have the geometry shown in Figure 1, whereas 36.2 (11)% have the axial CO and H ligands on Os(2) reversed.

While the hydride ligands were not located directly from the X-ray structural analysis, their positions may reliably be inferred from their effects on the geometry of the remainder of the molecule. (The virtue of this approach has already been demonstrated for $[H_2Re_3(CO)_{12}^-]$[9] and $H_2Ru_6(CO)_{18}$,[10] among others.) Thus, there are two abnormally large bond angles in the equatorial plane (see Figure 2), ∠Os(2)-Os(1)-CO(14) = 113.8 (6)° and ∠Os(1)-Os(2)-CO(23) = 112.0 (5)°; all other interligand angles lie in the range 89.4–99.6° and are more equitably distributed. Furthermore, the Os(1)-Os(2) distance of 2.9886 (9) Å is significantly longer than the bonds Os(1)-Os(3) and Os(2)-Os(3) (2.9097 (7) and 2.8574 (7) Å, respectively). Each of these observations suggests that the bridging hydride ligand lies in the equatorial plane, displaced outward from the Os(1)-Os(2) vector and near the intersection of lines extended from C(24) → Os(2) and C(13) → Os(1). The terminal hydride ligand may be assigned to an axial site on Os(2).

Mutual exchange of the bridging and terminal hydrides in $H_2Os_3(CO)_{10}L$ is evidenced by variable-temperature ^1H NMR spectra. The two limiting low-temperature hydride signals broaden as the sample temperature is raised, disappear completely into the baseline, then reappear at ca. 50° as a very broad coalesced resonance centered near the mean chemical shift. In this temperature region separate signals for coordinated and added free L are observed with **2**, **4**, and **5**, which precludes ligand dissociation as the cause of the dynamic behavior. Obtaining accurate line shapes at higher temperatures is complicated by concurrent decomposition. However, preliminary measurements of line broadening in the slow-exchange region provide an estimate of the barrier to exchange and reveal a slight dependence of the barrier upon the nature of L (**1**, $\Delta G^\ddagger_{237} = 12.4$ kcal mol^{-1}; **4**, $\Delta G^\ddagger_{219} = 10.9$ kcal mol^{-1}).[11] The probable intermediate (II) in this exchange process has both hydride ligands bound just to one osmium center.[12] This structure nicely conforms to the 18-electron rule for each osmium atom, but the fact that it is higher in energy than I indicates the extra stability associated with a bridging hydride ligand compared with a terminal one.



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(5) E.g., $H_2Os(CO)_4$, 18.73; $H_2Os_2(CO)_8$, 20.11; $HOs_3(CO)_{10}(SEt)$, 27.5 $HOs_3(CO)_{12}^+$, 29.1.[8]

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A New Type of Heteropoly Anion. Tetramolybdo Complexes of Dialkyl- and Diarylarsinates[1]

Sir:

We wish to report the synthesis and structure[2] of a nov type of heteropoly oxometalate complex that contains co alently attached organic groups. The structure exhibits number of unusual features including a localized, nontitra table proton.