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Supplementary Material Available: Tables of final positional parameters (as fractional coordinates), thermal parameters, structure factor amplitudes (observed and calculated), and NMR data for the new compounds (34 pages). Ordering information is given on any current masthead page.

Photon-Assisted CH Bond Activation in a Coordinated Methoxy. A Molecular Orbital Explanation

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Methoxy groups can be formed on unsaturated Mo^{VI} centers on edge surfaces of layered-structure MoO_3^1 and found on the surface of the $\text{Mo}_8\text{O}_{24}(\text{OCH}_3)_4^{4-}$ anion.² Thermally activated dehydrogenation occurs on warming MoO_3 to 217 °C, and at 500 °C for the anion, yielding formaldehyde and water. Exposure of the anion to UV light causes formaldehyde to form from the anion under ambient conditions, and similar behavior is seen for $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$.³ The purpose of this paper is to explain the photoactivation of methoxy CH bonds in these systems by using molecular orbital theory.

There are sufficient similarities between the anion² and bulk MoO_3 ⁴ structures (layering of distorted octahedra) to allow the use of a MoO_3 bulk-superimposable $\text{Mo}_3\text{O}_{13}^{8-}$ model with methoxy coordinated as in Figure 1. Atom superposition and electron delocalization molecular orbital (ASED-MO) theory parameters for Mo and O come from an earlier study⁵ of the electronic properties of crystalline MoO_3 . For C, the respective 2s and 2p orbital exponents and ionization potentials are 1.65 au, 18 eV, and 1.618 au, 9.26 eV; for H, the 1s parameters are 1.2 au and 11.6 eV. In the ASED-MO theory the electronic charge density of a molecule is partitioned into free-atom parts and an electron delocalization bond formation component. As the atoms bond together forming a molecule, the electrostatic forces on the nuclei are integrated to yield a repulsive energy due to rigid-atom densities and an attractive energy due to electron delocalization. The sum is the exact molecular binding energy. The atom superposition energy is easily calculated and the electron delocalization energy, though not directly calculable, is well approximated by a one-electron molecular orbital energy obtained by using a hamiltonian which shares some features with the extended Hückel hamiltonian. Our truncated model produces the electronic structure in Figure 2. All of the bands widen somewhat for larger clusters. The electronic structure of a $\text{Mo}_6\text{O}_{25}^{14-}$ cluster shown in ref 5 is more representative in this regard of the anion being modeled here and of a $\text{Mo}_6\text{O}_{19}^{3-}$ anion.⁶ By comparison of the calculated electronic structure of $\text{Mo}_6\text{O}_{25}^{14-}$ with the optical spectrum of $\text{Mo}_6\text{O}_{13}^{3-}$, it is evident that the observed⁶ transitions at 11 600 and 20 400 cm^{-1} are due to d-d transitions within the lower and between the lower and middle bands, respectively. The

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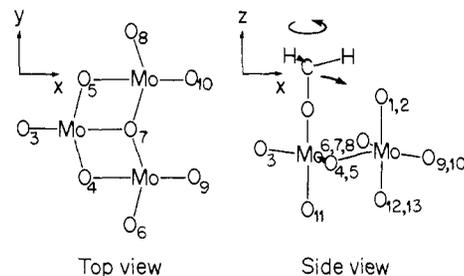


Figure 1. $\text{Mo}_3\text{O}_{13}(\text{OCH}_3)_9^{9-}$ structure.

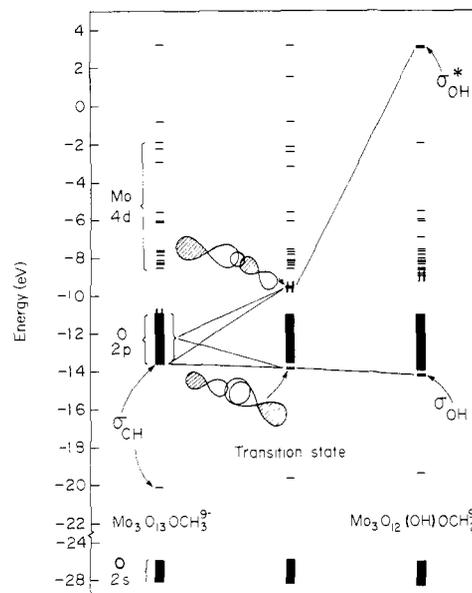


Figure 2. Orbital energy level correlations during the course of methoxy dehydrogenation to form formaldehyde and hydroxide

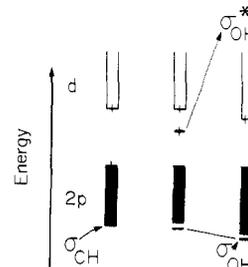


Figure 3. As in Figure 2 showing electron hole pair occupations for the reaction on the cluster with an electron-hole pair excitation.

strong transition at $\sim 31\,000\text{ cm}^{-1}$ is due to O 2p to Mo 4d charge transfer. In $\text{Mo}_8\text{O}_{24}(\text{OCH}_3)_4$ the 4d bands are empty and this charge-transfer excitation is expected to be active toward the dehydrogenation of coordinated methoxy.

When the methoxy group is rotated and tilted so that the Mo-O-C angle is 160° , the CH bond may be stretched to a transition state with CH and OH distances of 1.85 and 1.30 Å, respectively, and an H-O₁-Mo angle of 158° . The important stabilization at the transition state is a three-center C-H-O σ bond (Figure 2). The CH-O antibonding orbital is also doubly occupied, giving rise to the energy level in the O 2p-Mo 4d band gap shown in Figure 2. This orbital becomes the empty high-lying OH σ^* , and the cluster is reduced by two electrons. The calculated activation energy is 2.6 eV, which is approximate because of the nature of the theory, the structure model, and the omission of cluster geometry relaxations in the transition state.

The transition-state geometry is nearly the same when an electron is promoted from the top of the O 2p band to the bottom of the Mo 4d band. The activation energy, however, is reduced by nearly half to 1.4 eV. As may be seen in Figure 3, the photoactivation is a consequence of transferring the electron hole to

the antibonding CH-O transition-state orbital.

The general conclusion is that the CH activation process has associated with it two important bonding interactions, a CH σ donation bond to the closed-shell oxygen anion and its antibonding counterpart which correlates with the OH σ^* orbital. Photoexcitation of an electron from the latter orbital activates the hydrogen transfer process by increasing the net bond order by $1/2$ in the transition state. The products are the same with and without photoactivation, consisting in coordinated OH⁻ and H₂CO and reduced molybdenum oxide.

The three-center σ donation activation phenomenon has previously been studied theoretically on various metal and metal oxide surfaces.⁷ In the case of metals, the antibonding acetylene^{7a} and propylene^{7b} CH-M, water^{7c,d} OH-M, and ClH-M^{7e} orbitals donate their electrons into the partially filled conduction bands; this results in low dehydrogenation barriers. In the case of water OH-O^{7c,f} and ClH-O^{7e} hydrogen transfer on oxides, an electron is transferred back to OH or Cl to yield hydroxide and chloride anions, again lowering the activation barriers. Whether these and other AH bonds can be photoactivated will depend on the details of the electronic structures and the lifetimes of the electron-hole pairs. It is probable that the mechanism described here will be found to be common.

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Halide-Promoted Insertion of CO into Bridging-Methylene Ligands in Triosmium Clusters

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Halides are important promoters in various homogeneously catalyzed reactions of carbon monoxide, including methanol¹ and acetic acid² carbonylations and the reduction of CO to oxygenated products.³ One important effect of halides, and ionic promoters in general, is to facilitate carbon-carbon bond formation. In the Ru₃(CO)₁₂-catalyzed hydrogenation of CO, for example, iodide promoters dramatically shift product selectivity from methanol to ethylene glycol and ethanol,³ products that presumably arise via a CO insertion step. One possible conclusion that can be drawn from the published data is that halides promote this insertion. However, there are no reported studies of discrete well-characterized compounds that model such an accelerating effect on a

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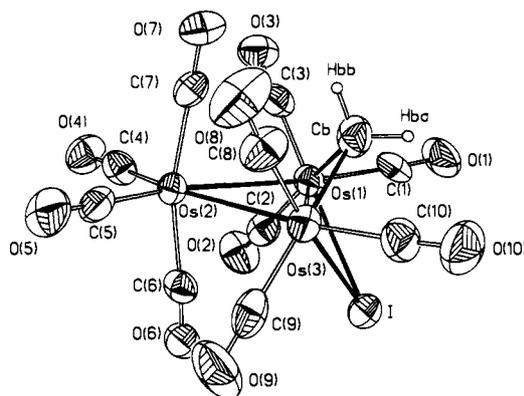


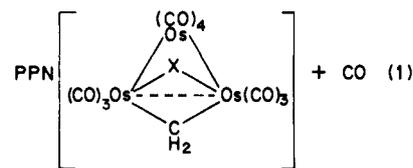
Figure 1. ORTEP drawing of **4**. Relevant bond distances (Å) and angles (deg): Os1-Os3, 3.112 (1); Os1-Os2, 2.927 (1); Os2-Os3, 2.934 (1); Os1-I, 2.863 (1); Os3-I, 2.844 (1); Os1-Cb, 2.145 (14); Os3-Cb, 2.180 (13); Os1-Cb-Os3, 92.0 (5); Os1-I-Os3, 66.1 (1).

CO insertion reaction. We describe herein such a halide effect on the insertion of CO into metal-(μ -methylene) bonds to give μ -ketene complexes.

The starting point for these studies are the [PPN][Os₃(CO)₁₀(μ -CH₂)(μ -X)] clusters **2-5** (PPN = (Ph₃P)₂N⁺). These rapidly form (1-10 min) in 89-97% yield upon reaction of Os₃(CO)₁₁(μ -CH₂) (**1**)⁴ with the appropriate PPN halide salts⁵ in CH₂Cl₂ or reaction of **1** with [PPN]N₃ in acetone/THF to give **5** (eq 1). Such reactivity is unusual for coordinatively saturated



1



2, X = Cl; **3**, X = Br; **4**, X = I; **5**, X = NCO

osmium clusters, although Lavigne and Kaesz recently reported a similar facile substitution with Ru₃(CO)₁₂ which gives [PPN][Ru₃(μ -Cl)(CO)₁₀] upon reaction with [PPN]Cl.⁶ Clusters **2-5** have been spectroscopically characterized,⁷ with the chloro, iodo, and isocyanato derivatives **2**, **4**, and **5** further defined by X-ray crystallographic studies. The three structures are similar with that of **4** shown in Figure 1.⁸ These clusters have 50 valence electrons, two more than the required 48e⁻ for a closed triangular cluster.⁹ However, all metal-metal distances are within or close to bonding values, with the dibridged Os-Os distances being somewhat longer than the nonbridged Os-Os distances, as summarized in the figure caption. Also, the Os-CH₂-Os angle of 92.0 (5)^o in **4** is the largest reported angle for this ligand bridging two

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(7) Satisfactory C and H analyses were obtained for **2-5**. **2**: IR (CH₂Cl₂) 2072 (w), 2030 (s), 2016 (m s), 1977 (s), 1949 (m), 1935 (sh); ¹H NMR (CDCl₃) δ 3.70 (d, 1 H, *J* = 8.6 Hz), 2.92 (d, 1 H). **3**: IR (CH₂Cl₂) 2070 (w), 2029 (s), 2018 (m s), 1979 (s), 1950 (m), 1933 (sh); ¹H NMR (CDCl₃) δ 3.81 (d, 1 H, *J* = 8.55 Hz), 3.19 (d, 1 H). **4**: IR (CH₂Cl₂) 2072 (w), 2027 (s), 2018 (m s), 1979 (s), 1950 (m), 1933 (sh); ¹H NMR (CDCl₃) δ 3.83 (d, 1 H, *J* = 8.01 Hz), 3.58 (d, 1 H). **5**: IR (CH₂Cl₂) 2207 (s sh), 2070 (w), 2031 (s), 2016 (m s), 1977 (s), 1948 (m s), 1930 (sh); ¹H NMR (CDCl₃) δ 3.38 (d, 1 H, *J* = 8.06 Hz), 2.79 (d, 1 H).

(8) **4** crystallizes in the space group $P\bar{1}$ with *a* = 12.978 (3) Å, *b* = 13.131 (3) Å, *c* = 14.074 (4) Å, α = 90.21 (2)^o, β = 96.40 (2)^o, γ = 90.63 (2)^o, *V* = 2383 (10) Å³, and *Z* = 2. Least-squares refinement of the 4429 reflections with *F*_o > 3 σ (*F*_o) gave convergence to *R* = 0.041 and *R*_w = 0.038.

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