

Selective Oxidations via Metal Oxides:  
The Relevance of Organometallic Oxo Complexes

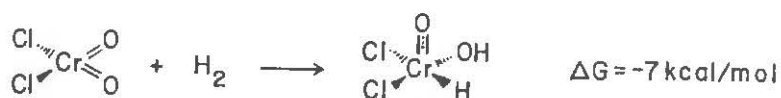
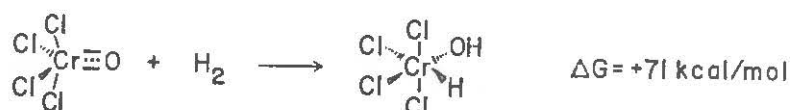
James A. Jensen

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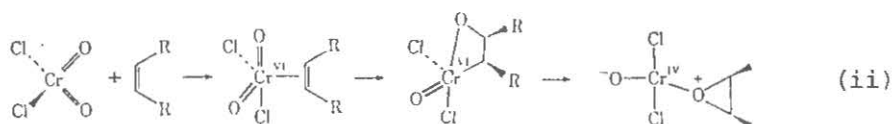
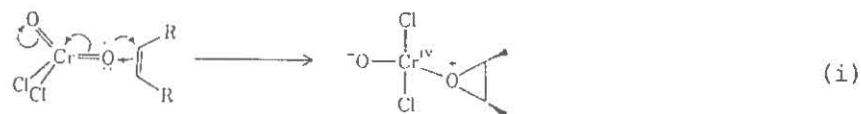
Metal oxides are known for all of the transition metals and such species are known to play a vital role in many important industrial processes, such as olefin metathesis [1], and hydrocarbon oxidations [2,3]. In most of these processes, organometallic oxo derivatives are key intermediates, however, relatively few isolated examples of complexes containing metal-oxo and metal-carbon bonds are known [4-10].

Terminal oxide ligands are strong electron donors to transition metals both in a  $\sigma$  and a  $\pi$  sense. The metal-oxygen linkages are generally considered to be double bonds, based on their relatively high infrared stretching frequencies ( $800-1000\text{ cm}^{-1}$ ) and short bond lengths ( $1.60-1.76\text{ \AA}$ ) [11]. However, the metal-oxygen bond order may be augmented in monoxo complexes of the form  $X_nMO$  (where X = halide or alkoxide and O is a terminal oxo) [12]. Two d orbitals are available to form two  $\pi$ -bonds with the single oxygen, whereas polyoxo complexes have only one d orbital available for  $\pi$ -bonding to each oxygen atom. Thus, monoxo complexes can be considered to possess metal-oxygen triple bonds. One consequence of this phenomenon is that the reactivity of metal oxo groups can be significantly enhanced by the presence of an ancillary (spectator) oxo ligand which drives the reaction by forming a strong triple bond.



This effect implies that the reactivity of surface sites of heterogeneous catalysts should be dependent on the availability of doubly bonded oxo sites. Selective oxidation of propylene and ethanol over supported molybdate catalysts has shown this experimentally [13].

The oxidation of olefins has historically been considered to occur via direct attack of the organic reductant on the oxygen end of a metal oxo moiety [2c], see (i). However, a recent proposal [14], and a theoretical study [12], suggest an alternative mechanism which involves initial nucleophilic attack of the olefin at the metal center forming a  $\pi$ -bound complex, followed by rearrangement to an oxametallacyclobutane intermediate, see (ii). The spectroscopic observation of an osmium oxametallacyclobutane lends support for this suggestion [15].

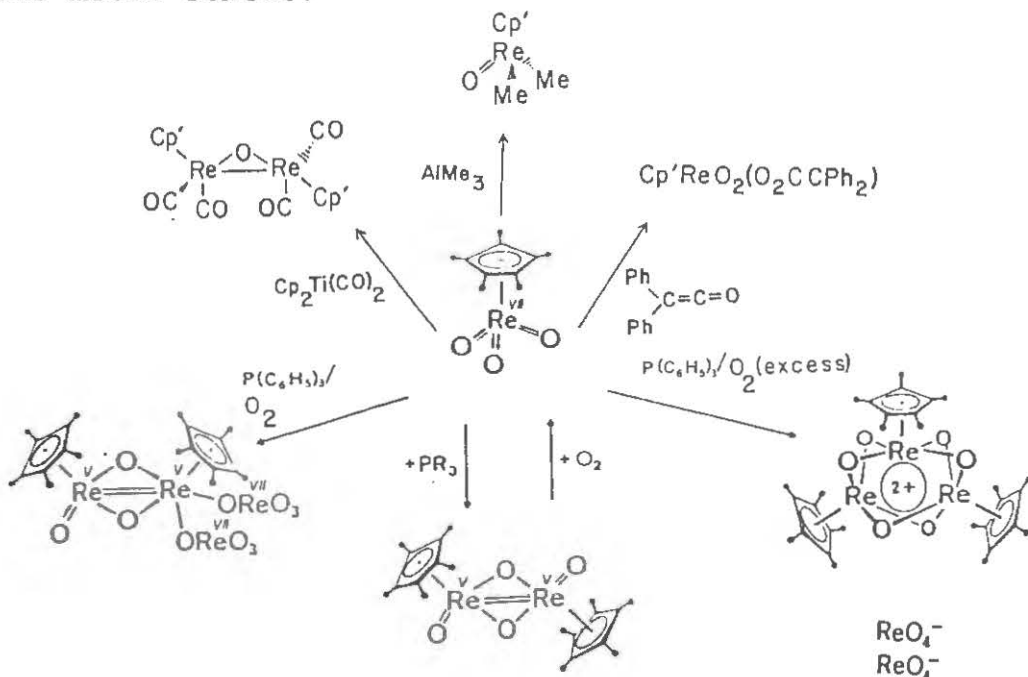


The selective oxidation of propylene to acrolein over supported bismuth molybdate catalysts is proposed to occur via a similar mechanism involving a metal  $\pi$ -allyl complex. Deuterium, carbon-13, and oxygen-18 labeling studies are consistent with this proposal [3,16].

High valent oxo-alkyl complexes are known for V [4], Mo [5], W [6], Re [7-9], and Os [10]. Reactivity studies of these species are, however, limited. The complex  $\text{ReO}_4^-$ , which is formed from the reaction of  $\text{ReOCl}_4$  with methyl lithium [7a], does not react with Lewis bases, olefins, alcohols, or mineral acids. It can be oxidized by nitric oxide and dry air to yield the polyoxo compounds  $\text{ReO}_2\text{Me}_3$  and  $\text{ReO}_3\text{Me}$ , respectively. The air stable compound,  $\text{VO}(\text{CH}_2\text{SiMe}_3)_3$ , displays a similar lack of reactivity [4a].

Polyoxo complexes with  $\pi$ -bound cyclopentadienyl ligands form another class of organometallic oxo derivatives. The dimers  $[(\text{C}_5\text{H}_5)\text{MoO}_2]_2$  and  $[(\text{C}_5\text{H}_5)\text{MoO}_2]_2\text{O}$  are unreactive toward olefins, but cleave in the presence of halogens to produce the monomeric oxo halo species  $(\text{C}_5\text{H}_5)\text{MoO}_2\text{X}$  [5a-c]. The Mo(VI) dimer oxidizes triphenyl phosphine and forms a tetramer  $[(\text{C}_5\text{H}_5)\text{MoO}_2]_4$  where each metal is bridged by two oxygens and forms a double bond to a terminal oxygen atom.

The most thoroughly studied organometallic oxo system is that of the half-sandwich Re(VII) complex  $(\text{C}_5\text{Me}_5)\text{ReO}_3$  [9]. This trioxo species is formed by oxidative decarbonylation of  $(\text{C}_5\text{Me}_5)\text{Re}(\text{CO})_3$  under UV irradiation in the presence of oxygen. Lewis acids and Lewis bases induce partial deoxygenation, with concomitant reduction of the metal center.



Although the exact role of organometallic oxo derivatives in selective oxidations is unknown, it is increasingly apparent that complexes containing metal-oxo and metal-carbon bonds are likely intermediates in hydrocarbon oxidation processes.

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