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Manmohan Krishna Upadhyay
 Department of Chemistry,
 Govt. Degree College, Dhadha
 Buzurg, Hata, Kushinagar,
 Uttar Pradesh, India

Synthetic application of cis dioxo molybdenum complex

Manmohan Krishna Upadhyay

Abstract

The isomeric form of dioxomolybdenum complexes have a variety path of application to synthesis the various valuable compounds. The geometrical form cisdioxomolybdenum takes the role in epoxidation sulfoxidation and phosphine oxidation reactions. In this course Dioxomolybdenum (VI) complexes can also be prepared with Schiff bases of amino acids. [11, 13] The general method for the preparation of such complexes follows the same procedure as shown in (scheme 1). The Schiff base which contains phenolic, carboxylic and imine groups acts as dianionic tridentate ligand which when complexes with suitable Mo-precursor give cis-dioxo Mo (VI) complexes.

Keywords: Synthetic application, dioxomolybdenum complex, dianionic tridentate ligand

Introduction

Major focus with respect to applications of *cis*-MoO₂-(ONO) type complexes have been oxo transfer reactions like epoxidation, sulfoxidation and phosphine oxidation reactions. Besides the oxidation reaction, the complexes prepared from a bisphenol ligand shown in scheme 5 along with Et₂AlCl are used as catalysts for ROMP of norbornene [34]. The molybdenum complex with Schiff base derived from 3-formyl salicylic acid and *o*-hydroxybenzylamine is supported on polymer and used as catalysts for the oxidation and oxidative bromination of organic substrates [46]. In a separate line, novel bimetallic complexes have also been reported in order to study the metal-metal interaction. Some of these applications are discussed in this section.

Oxygen atom transfer reactions it has been assumed for several years that the presence of sulfur atoms coordinated to molybdenum is a requisite for oxygen atom transfer reactions in order to mimic oxotransferases enzymes. However, certain molybdenum (VI) complexes of dibasic tridentate ONO ligands having no S center are found to oxidize a variety to tertiary phosphines, thus mimicking the active sites of oxo transfer enzymes. Although tertiary phosphines are not physiological substrates, they are the most commonly used model substrates for studying oxygen atom transfer reactions. Topich and Lyon III observed the formation of oxomolybdenum (VI) complexes during the oxo transfer process mediated by some Mo(VI) complexes [47]. Boyd and Spence have reduced Mo(VI) complexes using tertiary phosphines where upon in some cases monomeric Mo(VI) and other cases μ -oxo-dimolybdenum (V) compounds are formed [48]. Thus, whether dimer formation is an essential characteristic of the oxotransfer reaction or not is being debated. The Mo (VI) complexes i.e., *cis*-MoO₂(L) (c₂H₅OH) prepared from ligands 18a or 18b react with PPh₃ in acetonitrile under dry nitrogen, in presence or absence of bpy to give OPh₃ (scheme 12). The other products formed during the oxidation study are MoO(L) or MoO(L) (bpy) which support the formation of Mo(VI) intermediates during the oxotransfer process [41, 42]. This reaction is a good model of the oxo transfer reactions exhibited by molybdoenzymes. The Mo(VI) complexes derived from aminodiols [20] can oxidize PPh₃ catalytically in DMSO. The mechanism involve formation of Mo(VI) species as intermediate as shown in scheme 13 [44].

Catalytic epoxidation

Molybdenum complexes are considered to be very efficient catalysts for epoxidation reactions using alkyl hydroperoxide as oxidants [24]. The dioxomolybdenum (VI) complexes with Schiff base, derived from tris(hydroxymethyl) amino methane and substituted salicylaldehyde show good catalytic activity (up to 100% yield) and selectivity in the epoxidation of cyclohexene

Correspondence
 Manmohan Krishna Upadhyay
 Department of Chemistry,
 Govt. Degree College, Dhadha
 Buzurg, Hata, Kushinagar,
 Uttar Pradesh, India

with *t*-butylhydroperoxide. Introduction of electron withdrawing group to the salicylidene ring of complex strongly increases the effectiveness of a catalyst. The initial step involved in the process is the dimerization to the complex which reacts with the peroxide to give a mononuclear intermediate complex $\text{MoO}_2(\text{L})$ (TBHP) where peroxy oxygen is activated followed by epoxidation of the substrate (scheme 14). The sugar-based Schiff base Mo(VI) complexes prepared from ligand 10 show high catalytic activity for epoxidation. The enantiomeric excess up to 30% was obtained in case of *cis*- β -methyl styrene [32]. In case of epoxidation of allylic alcohol, the Schiff base Mo(VI) complexes from amino acids induce enantiomeric excess up to 15% [13].

Catalytic oxidation of sulfide

The oxidation of various organic sulfides by urea hydrogen peroxide in presence of a Mo(VI) catalyst has been reported by Sheikhshoaie *et al.* (scheme 15) [25]. The formation of sulfoxide and sulfone can be well-controlled by utilizing the suitable molar ratio of oxidant and substrate. Further, this catalyst shows excellent chemo selectivity.

A sulfide having double bond was also transformed into sulfoxide in good yield without affecting it. The sulfides having benzylic and Phenyl substituent were selectively oxidized to their corresponding sulfoxide without undergoing oxidation at benzylic carbon.

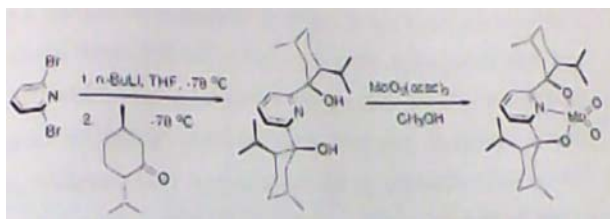


Fig 1: Dioxomolybdenum(VI) complexes with pyridine-diol ligand.

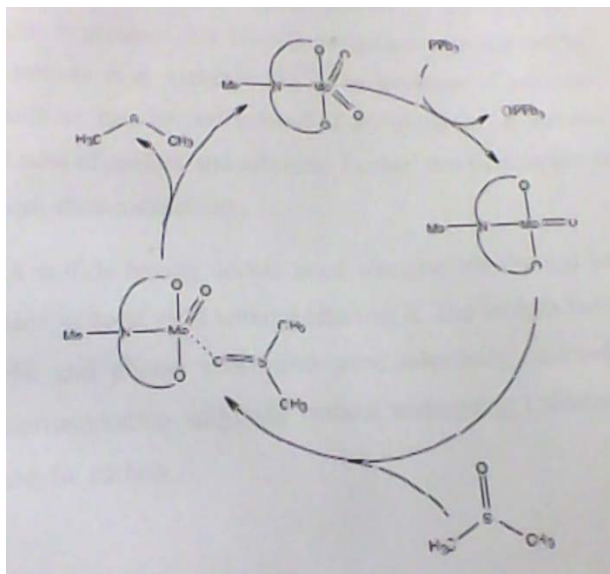


Fig 2: Proposed mechanism for the catalytic oxo transfer reaction from DMSO to PPh_3 .

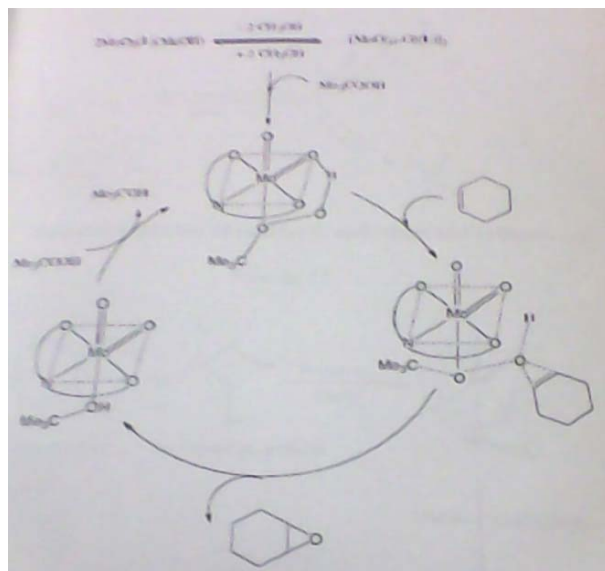


Fig 3: Proposed mechanism for catalytic epoxidation reaction.

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