



## Review

# Efficient deoxygenation methodologies catalyzed by oxo-molybdenum and oxo-rhenium complexes



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**Abbreviations:** BMIm, 1-butyl-3-methylimidazolium; MTO, methyltrioxorhenium; Dppm, bis(diphenylphosphino)methane; Hhmpbta, 2-(2-hydroxy-5-methylphenyl)benzotriazole; Hhpbt, 2-(2-hydroxyphenyl)benzothiazole; Hhpbo, 2-(2-hydroxyphenyl)benzoxazole; Hhpbi, 2-(2-hydroxyphenyl)-1H-benzimidazole; TON, turnover number; TOF, turnover frequencies; HBcat, catecholborane; HBpin, pinacolborane; DFT, density functional theory (DFT); MW, microwave; Equiv., equivalent; acac, acetylacetonate; Bipy, bipyridine; Tp', tris(3,5-dimethylpyrazolyl)hydridoborate; DODH, deoxydehydration; Cp\*, 1,2,3,4,5-pentamethylcyclopentadienyl; TEGDME, triethylene glycol dimethyl ether.

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## ABSTRACT

The deoxygenation of organic compounds is a fundamental process in both chemistry and biology and the development of new efficient methodologies for the synthesis of deoxygenated compounds is highly desired. Among the variety of catalysts used in the deoxygenation of organic compounds, high-valent oxo-molybdenum and oxo-rhenium complexes have attracted considerable interest. This review highlights the development of efficient methods for the deoxygenation of different classes of organic compounds such as sulfoxides, aromatic nitro compounds, *N*-oxides, epoxides, alcohols and polyols catalyzed by oxo-molybdenum and oxo-rhenium complexes.

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## 1. Introduction

The deoxygenation of organic compounds is an important reaction, frequently employed in natural products and pharmaceutical synthesis, which require mild conditions, selectivity, and functional group tolerance [1].

Due to the concerns about diminishing petroleum reserves, increasing fuel prices, and minimizing environmental impact, in the last few years, the development of efficient synthetic protocols for the reduced oxygen-content materials from renewable biomass resources (sugar, sugar alcohols) has been a key target in chemistry and chemical engineering.

Among the variety of metal complexes that have been used as catalysts for the deoxygenation of organic compounds, oxo-molybdenum complexes have attracted considerable attention because a monooxo- or a dioxo-molybdenum unit is found in the active sites of several molybdoenzymes such as sulfite oxidase, DMSO reductase, xanthine oxidase, and nitrate reductase (Scheme 1) [2–4]. These enzymes catalyze a variety of two electron redox reactions involving a net exchange of an oxygen atom between the Mo-enzymes and the substrate. For example, the deoxygenation of biological important sulfoxides such as DMSO, methionine sulfoxide and biotin-*S*-oxide are catalyzed by the molybdoenzymes DMSO reductase, methionine sulfoxide reductase and biotin-*S*-oxide reductase, respectively (Scheme 2).

High-valent oxo-rhenium complexes are also currently the subject of intensive research. Most rhenium complexes are easily prepared, stable in different oxidation states and air-tolerant. These remarkable properties result in the diverse applications of oxo-rhenium complexes in catalytic organic synthesis as homogeneous catalysts.

The chemistry of oxo-rhenium complexes also demonstrates particular interest due to their application in various reactions of industrial and biological importance. The Re(V/VII) redox system is isoelectronic to Mo(IV/VI) and W(IV/VI), which are observed at the active sites of molybdenum and tungsten enzymes. Although no enzymes containing rhenium ion have ever been discovered, it has been reported that the oxygen atom transfer catalytic activities of some Re complexes are superior to those of the corresponding Mo complexes.

In this perspective, the study of deoxygenation reactions using oxo-molybdenum and oxo-rhenium complexes has led to a better insight in understanding the structure and functions of various enzymes.

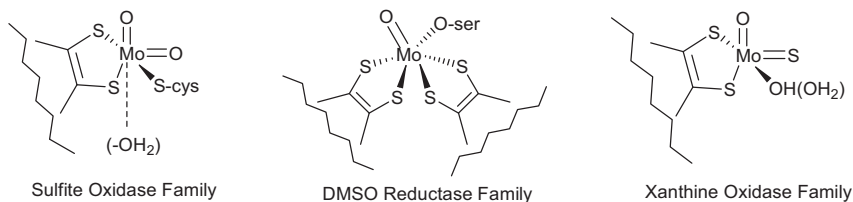
Apart from their application in deoxygenation processes, for many years, high-valent oxo-molybdenum [5–8] and oxo-rhenium [9–12] complexes were employed as excellent catalysts for oxidation reactions such as the oxidation of alkenes, sulfides, and pyridines. In recent years, several new developments into the chemistry of high-valent oxo-molybdenum and oxo-rhenium complexes were reported. Among the most interesting ones was the successful application in the activation of X–H (X = Si, B, P and H) bonds [13–18], C–X bond forming reactions [19–28], and in the reduction of a variety of functional groups such as ketones [29–33], imines [34,35], esters [36], amides [37], alkenes [38], alkynes [17], and nitriles [39].

This review will provide a summary of recent developments applying oxo-molybdenum and oxo-rhenium complexes as efficient catalysts for the deoxygenation of different classes of organic compounds. Particular attention will be given to the methods reported since the year 2000. For this purpose, this review will be divided in five parts: (1) deoxygenation of sulfoxides; (2) deoxygenation of aromatic nitro compounds; (3) deoxygenation of *N*-oxides; (4) deoxygenation of epoxides; and (5) deoxygenation of alcohols and polyols. Each part will be also exemplified the use of different reductants such as phosphorus compounds, silanes, boranes, hydrogen, sulfites and alcohols in the deoxygenation of organic compounds catalyzed by oxo-molybdenum and oxo-rhenium complexes.

## 2. Deoxygenation of sulfoxides

## 2.1. Deoxygenation of sulfoxides using phosphorus compounds as reductants

Several methods for the deoxygenation of sulfoxides catalyzed by oxo-molybdenum complexes have been developed using a phosphorus compound as reductant such as a phosphine or a phosphinite. For example, Sanz and co-workers investigated the deoxygenation of sulfoxides employing triphenylphosphite and the



Scheme 1. Active sites of molybdoenzymes [2].

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