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Molybdenum-oxo chemistry in various aspects of oxygen atom transfer processes

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Contents

Abstract

In the very important field of transition-metal chemistry, this paper describes three characteristics of the molybdenum-oxo entity, underlying its versatility: first the role it can play as an electron well, exemplified by a "proximity effect", second the basic character of the Mo=O function, shown in a "pseudo keto-enol" tautomeric transformation, and finally as an oxygen atom transfer agent, illustrated by a thiocyanatodioxo molybdenum(VI) complex.

Keywords: Metal-oxo; Oxidation; Oxygen atom transfer

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1. Introduction

The transition metal-oxo functional group is certainly very important in coordination chemistry. Nearly all elements of groups 4–8 in a high oxidation state (≥ 4)

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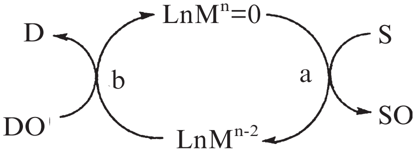
can bear one or several oxo ligands. They are found in a wide range of catalytic systems going from metalloenzymes all the way to metal-oxide surfaces. Their important role is manyfold; they can be the entity responsible for the oxidation of a substrate, either in a stoichiometric manner, simply by being reduced

$$\mathrm{LnM}^{n}{=}\mathrm{O}+\mathrm{S}\rightarrow\mathrm{LnM}^{n-2}+\mathrm{SO} \qquad (1)$$

or in a catalytic process by being the intermediate of an oxygen atom transfer from the oxidizing agent to the substrate.



(2)

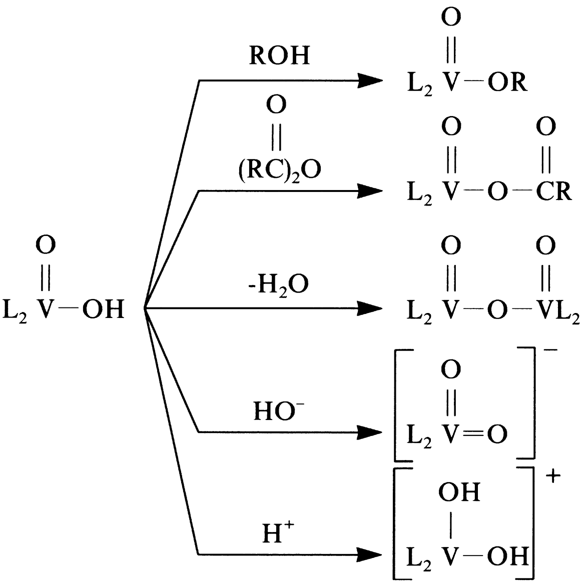
They can also play the role of an electron well, into which electronic density can be taken or given as required by the chemical transformation in the coordination sphere.

Among the numerous transition metal-oxo compounds that have been prepared, characterized and used as catalysts, molybdenum is probably the element that has been most studied as an oxygen atom transfer agent. Its presence in many isopoly and heteropolyanions, as well as its importance in several enzymatic systems, certainly contributed to these commensurate efforts.

Several comprehensive reviews concerning this field have appeared and are very valuable [1–3]. This article will emphasize a few contributions from this laboratory dealing with various aspects of molybdenum-oxo chemistry.

2. Role of the molybdenum-oxo ligand as an electron well

The metal-oxo functional group constitutes a real electronic sink and in this context quite comparable with the carbonyl group in organic chemistry. Such analogies were first drawn in the seventies, with vanadium-oxo complexes, by Floriani and coworkers [4–7], who showed how they can be esterified, acylated, dehydrated, base hydrolyzed or protonated.



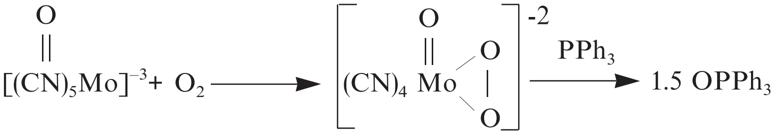
(3)

The importance of the metal-oxo function was emphasized shortly after, on a theoretical basis, by Rappé and Goddard who introduced in a pioneering work the concept of the "spectator-oxo" [8–10]. Here, in addition to the intrinsic bond polarity, $M^{\delta+}{=}O^{\delta-}$, analogous to the carbonyl group, a second metal-oxo bond present in the coordination sphere assumes an essential stabilizing role by endorsing a triple bond character via a donor–acceptor σ-bond. (Mo≡)

This possibility allows a significant stabilization of key intermediates and makes energetically feasible not only catalytic oxidation processes, but also other catalytic systems such as metathesis.

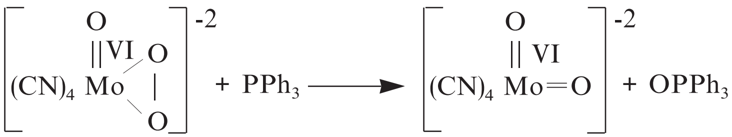
An experimental finding of this laboratory [11] in an oxygen atom transfer process mediated by a molybdenum complex was also rationalized in terms of a molybdenum-oxo moiety playing the role of an electron supplier.

It was in a study of dioxygen activation that a tetracyano-oxo-peroxo molybdate(VI) anion obtained directly from the oxo-molybdate(IV) and dioxygen, exhibited a reactivity with an unexpected stoichiometry towards triphenyl phosphine.



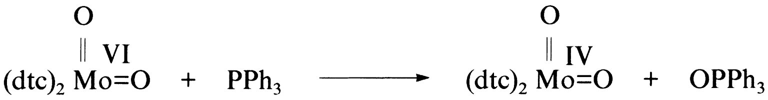
(4)

Molybdenum(VI)-peroxo complexes, just as any other metal-peroxo species, are known to oxidize phosphines to phosphine oxides, while being reduced to the corresponding molybdenum(VI)-oxo [12].



(5)

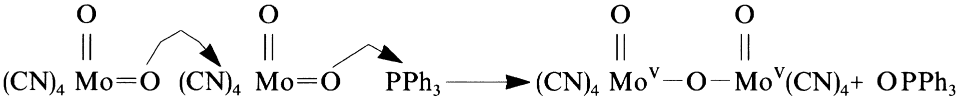
In Eq. (5), this accounted for 1 mole of phosphine oxide formed. The rest of the phosphine oxide can only be obtained by the reduction of a dioxo molybdenum(VI) to a monooxo molybdenum(IV). Such oxygen atom transfer to phosphines mediated by Mo=O are well known but have been described [13,14] only with species containing electron rich sulfur ligands such as dialkyldithiocarbamates in contrast to electron attracting ligands such as CN, as in our case.



$$(dtc)_2\,\overset{\overset{O}{\|}}{Mo}{}^{VI}{=}O + PPh_3 \longrightarrow (dtc)_2\,\overset{\overset{O}{\|}}{Mo}{}^{IV}{=}O + OPPh_3$$

dtc=dialkyldithiocarbamate

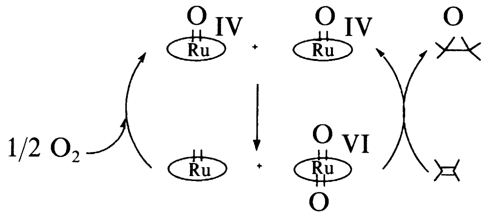
If this type of oxo transfer was nevertheless operative, the expected stoichiometry would have been two phosphines oxidized per oxo-peroxo-molybdenum complex (one from the peroxo and one from the oxo). In order to account for the observed stoichiometry, the second oxygen atom transfer must involve 2 moles of dioxomolybdenum(VI) anions in order to oxidize 1 additional mole of phosphine. This was rationalized in terms of a "proximity effect" in which a "neighboring" dioxomolybdenum unit plays the role of electron supplier for the transfer of the needed oxygen atom.



(7)

The molybdenum(V) dimer was further shown to disproportionate to the monooxo molybdenum(IV) and an unidentified polyoxo molybdenum(V1) entity. Under O_2 the Mo=O(IV) species could easily be reoxidized to the initial oxo-peroxo molybdenum(VI) complex.

This system had two interesting features: on one hand, it constitutes a good model for oxidation reactions done on molybdenum oxide surfaces, by the "proximity effect" and on the other hand it is an example of a potential dioxygen catalytic system using both atoms of O_2 analogous to Groves ruthenium porphirinic system [15], by its disproportionation ability.



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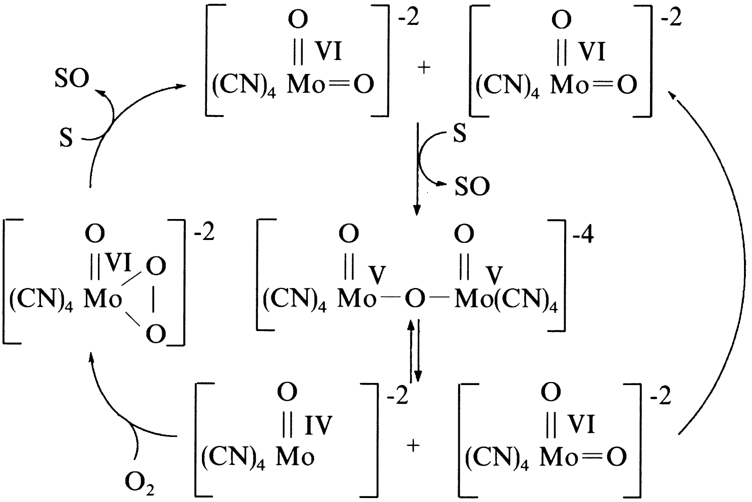
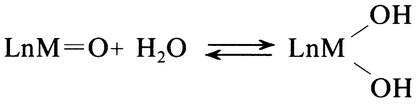


(9)

3. Role of the molybdenum-oxo ligand as a proton acceptor

Another characteristic of the M=O ligand remains, of course, the basic property of the oxygen atom if one keeps in mind that a metal-oxo is in effect an anhydride in an acid–base equilibrium.



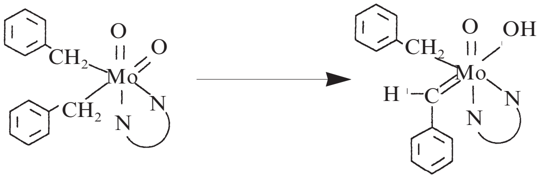
$$\mathrm{LnM{=}O + H_2O} \rightleftharpoons \mathrm{LnM}\begin{array}{l}\diagup \mathrm{OH}\\ \diagdown \mathrm{OH}\end{array} \tag{10}$$

In a metal-dioxo species, the influence of the "second" oxo group on the basic property of the "first" one must be taken into consideration. When M–L is more ionic (e.g. $L = Cl^-$, OR^-, Cp^-), the metal becomes more positive enhancing the involvment of the stabilizing spectator oxo triple bond, in a given intermediate, reducing thus the "basic" character of the other oxo group. When M–L is more covalent (e.g. L = alkyl) the situation is reversed; the oxo spectator is less involved and the intrinsic basic character of M=O is maintained [9].

We set up in this laboratory a reactivity study of alkyldioxo molybdenum(VI) compounds in an attempt to analyze the basic property of oxo-ligands and better comprehend the nature of the oxygen atom transfer process to alkyl groups [16,17].

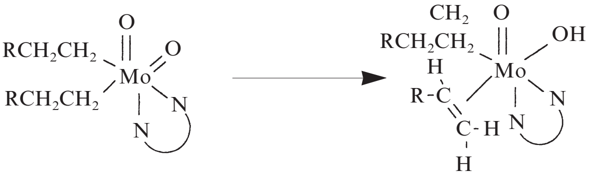
Although monoalkyl-dioxo-molybdenum(VI) complexes are scarce and not well characterized, dioxo-dialkyl-molybdenum(VI) complexes, bearing nitrogen containing ligands, such as bipyridine, are easily prepared and quite stable in the solid state [18,19]. In solution, even under mild conditions they slowly react to give rise to oxygenated products. When the alkyl aroup has only α-hydrogen atoms (e.g. benzyl, tolyl), equal amounts of the corresponding aldehyde and alcohol are formed. When α and β-hydrogen atoms are present (e.g. *n*-pentyl, iso-amyl), only the alcohol is formed, whereas when no α or β-hydrogen atoms are present (e.g. phenyl) no oxygenated products are obtained.

In the absence of any other source of oxygen atom, the transfer of oxygen must occur, in each case, from a unique intermediate, and it was proposed that it would arise for alkyl groups having only α-hydrogen atoms, from a pseudo keto-enol transformation of the dioxo complex.



(11)

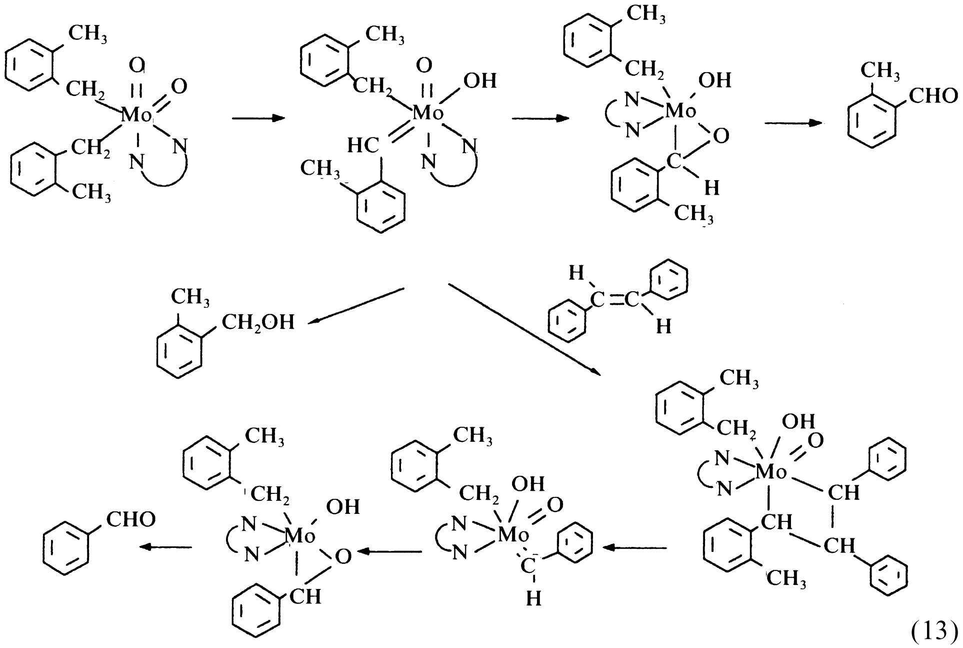
The oxo-hydroxo-alkylidene intermediate would generate the observed alcohol by an α-elimination of alkyl and hydroxo groups, whereas aldehyde formation would arise from the oxo and alkylidene moieties. When β-hydrogen atoms are present, a β-elimination pathway seems to be more favorable giving rise to an intermediate that could yield only the corresponding alcohol through α-elimination.



(12)

Finally when no α or β-hydrogen atoms are present neither of these two transformations are possible and no oxygen atom transfer occurs.

Although none of the proposed intermediate could be isolated nor thoroughly observed, supporting evidence for the oxo-hydroxo-alkyl-alkylidene formation was given by the metathetic activity of the system. Indeed, when bipyridyl-bis,(2-methylbenzyl)-dioxomolybdenum(VI) was allowed to stand in the presence of stilbene, both alcohol and aldehyde arising from the tolyl group were obtained, as expected, together with benzaldehyde which could only arise via a metathetic process. The absence of benzyl alcohol further indicated that the tautomeric transformation was not an equilibrium.



(13)

The mechanistic pathway above, although plausible, cannot be taken entirely as granted, it emphasizes, however, the basic character of the Mo=O ligand if one considers the pseudo ketoenol transformation as a proton abstraction by the oxo group. In this context, this rearrangement could be somewhat compared to the bridging hydroxy carbene intermediate suggested as being a precursor to the Etard complex for chromyl complexes [9]. It should be noted that this dioxo alkyl to oxo-hydroxo-alkyl-alkylidine rearrangement was not observed in the case of methyl trioxo rhenium [20]. This is probably the consequence of the less acidic character of the methyl group on one hand, and the intrinsic higher electropositivity of rhenium on the other.

4. Role of the molybdenum-oxo ligand as an oxo-transfer agent

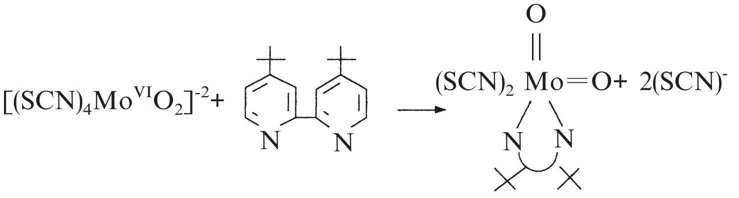
Most transition metals of groups 4–8 are known to exist as metal-oxo species and several have been characterized as key intermediate in catalytic oxidation processes either in living systems or in devised catalytic reactions [1–3]. Such oxidation — or oxygen atom transfer — is illustrated in Eq. (2), in which step a is the actual oxidation of the substrate and step b the reoxidation of the transfer catalyst by the oxygen donor (oxidizing agent) DO.

Among the early transition metals, molybdenum is certainly the elememt most studied in this oxo-transfer chemistry. Several excellent comprehensive review articles covering this field have appeared [1–3]. Here, we will only summarize a finding of this laboratory [21–23] concerning a molybdenum dioxo compound exhibiting exceptional oxo-transfer ability, illustrating with it the role of molybdenum-oxo species as oxo-transfer agents.

We had reported earlier the synthesis of a tetrathiocyanatodioxo molybdenum anion [24], which in spite of its anionic character and the lack of Mo–S bond (the thiocyanate is N-bound) exhibited oxygen atom transfer properties towards phosphines higher than the otherwise best catalyst known: diethyl dithiocarbamate dioxo molybdenum(VI) (vide infra).

$$[(SCN)_4Mo^{VI}O_2]^{-2} + PPh_3 \rightarrow [(SCN)_4Mo^{IV}O]^{-2} + OPPh_3 \qquad (14)$$

This unexpected finding prompted us to increase further the oxidizing power of anion **1** by diminishing or eliminating its ionic character. Since such a neutralization process had been shown [25] on similar anions to be most efficient by adding bipyridine, the anion **1** was reacted with various substituted bipyridines and resulted with the sterically hindered 4,4′-di-tert-butyl-2,2′bipyridine in the formation of the desired neutral dithiocyanato dioxo molybdenum complex **2** [22].



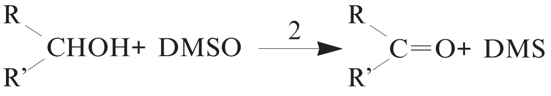
1 2 (15)

The oxygen atom transfer property of this compound was first tested towards triphenyl phosphine and found to be much higher when compared with all other Mo=O mediated oxo-transfer agents. This is illustrated on Fig. 1. As expected, in the presence of an oxidizing agent (oxo donor DO in Eq. (2)) such as DMSO, the transfer becomes catalytic.

The exceptional oxidizing strength of **2** prompted us to test it towards other substrates such as alcohols, alcanes and olefins.

4.1. Alcohols

Alcohol oxidation mediated by metal-oxo complexes is a well-known reaction especially with Cr(VI), Mn(VII), Ru(IV) and V(V) [26–32]. Molybdenum, on the other hand, considered to be too weak an oxidant, had rarely been used in this context [33–35]. When **2** was tested towards primary and secondary alcohols it was found to be a very efficient oxidant and a good catalyst in the presence of an oxygen atom donor such as DMSO [23].



$$RR'CHOH + DMSO \xrightarrow{2} RR'C{=}O + DMS$$

R'=H, Alkyl, Aryl (16)

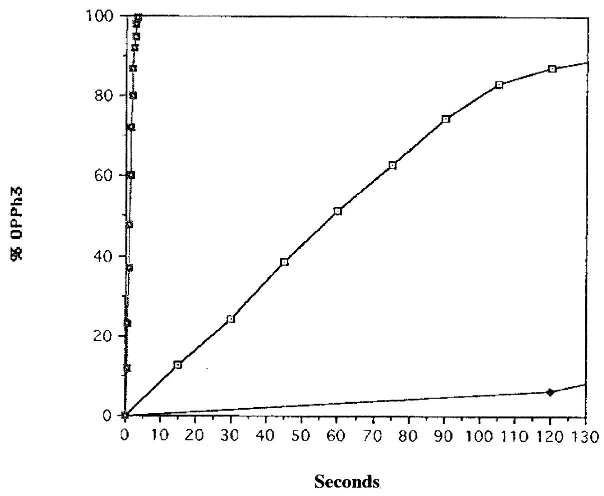


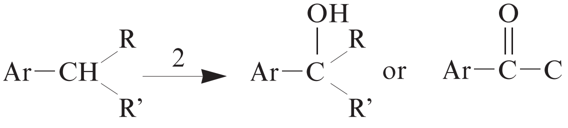
Fig. 1. Plot of percent triphenylphosphine formed against time for anion **1** (□), complex **2** (■) and $(dtc)_2MoO_2$ (◆). For clarity, only one point is shown for $(dtc)_2MoO_2$ since triphenylphosphine oxidation reaches completion only after 400 min (see Ref. [24]).

Interestingly in the case of primary alcohols, the aldehyde formed is not further oxidized to the carboxylic acid.

4.2. Alkanes and alkenes

The metal-oxo function has been established as being the key intermediate in many catalytic systems known to hydroxylate alkanes or epoxidize alkenes. These are either models of enzymatic systems (Mn, Fe) [1] or catalysts devized for synthetic purposes (Cr [1], Re [20], Ru [36–39] and W [40]). No molybdenum-oxo compound was ever reported as being able to insert an oxygen atom either in an alkane C–H, nor in an olefinic C=C. Complex **2** is able to perform both these transfers [21].

Arylalkanes are oxidized in the benzylic position either neat or in benzene, stoichiometrically or catalytically in the presence of DMSO, to yield the corresponding, alcohol or ketone for, respectively, tertiary and secondary arylalkanes. The reaction can be performed at moderate temperature (80–100 °C) but works better under UV irradiation (25 °C).

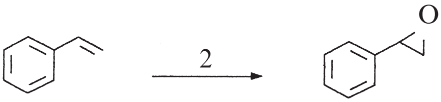


$$\mathrm{Ar{-}CH(R)(R')} \xrightarrow{2} \mathrm{Ar{-}C(OH)(R)(R')} \quad \text{or} \quad \mathrm{Ar{-}C(=O){-}C}$$

R, R'=H, Alkyl, Aryl R'=H (17)

The carbonyl products are most probably obtained via the alcohol; this is indicated by the apparent need of 2 moles of complex per mole of ketone formed, and by the fact that when the reaction is not complete both carbonyl products and alcohols are obtained.

Olefins also react with complex **2** (H. Arzoumanian and B. Lavergne, unpublished results) although more sluggishly. Styrene reacts stoichiometrically at 80 °C to give after 8 h, 30% epoxide, without any significant amount of cleavage products or other oxygenates.



(18)

Under UV irridiation and in the presence of Ph_2SO, this reaction becomes catalytic (four turnovers in 8 h), but is accompanied by the formation of cleavage products.

Less reactive cyclooctene necessitates UV irradiation to give 43% epoxide with minor amounts of allylic oxydation products, whereas terminal and sterically hindered olefins such as 3,3′-dimethyl-1-butene do not react.

Although sluggish, this reaction constitutes the first example of an epoxidation mediated by a molybdenum-oxo complex. It emphasizes the oxidation strength of **2** and confirms a forecast reported [41] in an olefin epoxidation attempt with dialkyldithiocarbamates molybdenum(VI) complexes, in which it was shown that with this type of ligands the epoxidation was a thermodynamically uphill process being endothermic by 8 kcal/mol [the reverse reaction in which epoxide is deoxygenated to olefins by the monooxo molybdenum(IV) is obtained instead]. The prediction was that an adequate ligand environment, compensating for a minimum of 8 kcal/mol should allow epoxidation. Apparently compound **2** satisfies this requirement.

Many questions remain unanswered to this day, however, concerning **2**. The mechanism by which oxygen atom transfer occurs onto substrates as different as phosphines, alcohols, olefins or alkanes is not well defined and is very likely to be different in each case. The role of the second oxo ligand, as a spectator, is certainly operative and different for each type of substrate. The electron attracting ability of the thiocyanato ligand is apparently just right for transferring an oxygen atom to the substrate but not excessive to allow reoxidation by an oxidizing agent. Finally, the sterically hindered bipyridine certainly plays an important role in avoiding the well-known tendency of molybdenum-oxo compounds to oligomerize. The combination of all these factors contribute, plausibly, to the high activity of **2**.

5. Conclusion

This review has described some contributions of this laboratory to the huge field of molybdenum-oxo chemistry. Although modest, it is hoped that it was able to underline the versatility of the Mo=O entity. Three important characteristics were exemplified. First, the role it can play as an electron well; the “proximity effect” between two neighboring dioxo molybdenum entities, a good model for metal oxide surfaces, can be considered as emanating from the oxo spectator concept, general for transition metal-oxo complexes. Second, the importance of the basic character of Mo=O in an hydrogen abstraction process, in a dialkyldioxo molybdenum compound, by a pseudo keto enol tautomeric transformation. Third the oxygen atom transfer property towards various substrates such as phosphines, alcohols, olefins and alkanes. In this last example, the adequate choice of the ligand environment is of utmost importance, it must satisfy the thermodynamics and, above all, avoid the oligomerization process so facilitated by the intrinsic high oxophilicity of molybdenum.

Acknowledgements

The research described herein and performed in this laboratory is, in great part, the fruit of a long-lasting collaboration with Venezuelian teams. Rafael Lopez initiated this work on molybdenum chemistry and was followed by Jose Sanchez and Helena Teruel who extended and developed the subject with the continuous contributions of Giuseppe Agrifoglio and Heinz Krentzien. I am deeply grateful to them, as well as to Richard Laï and Didier Nuel, in Marseille, for their participation in this exciting and continuing experience. Financial support from various international programs (PICS, PCP) as well as CONICIT is kindly acknowledged.

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