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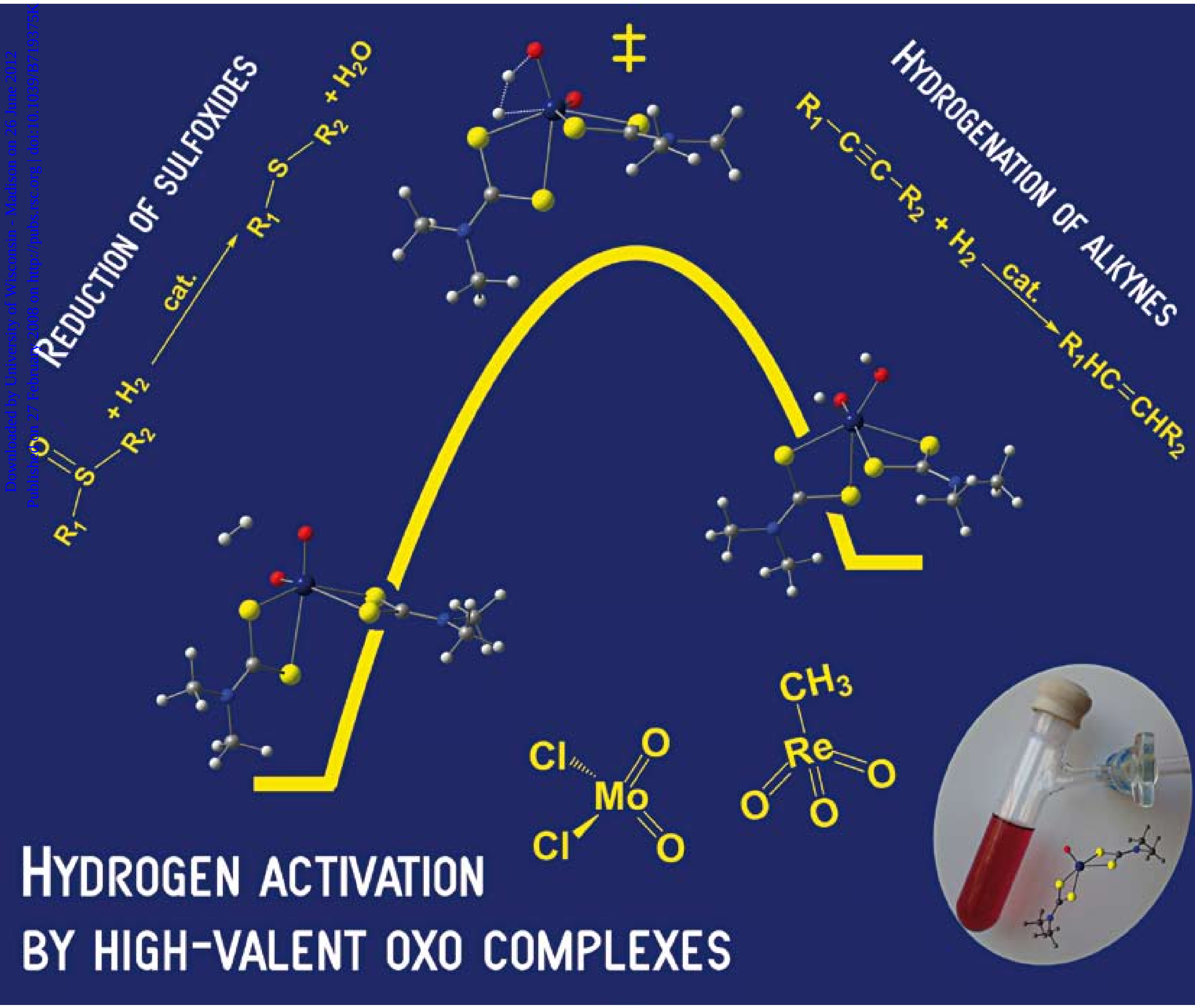

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Hydrogen activation by high-valent oxo-molybdenum(VI) and -rhenium(VII) and -(V) compounds†

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The high-valent oxo-molybdenum(VI) and -rhenium(VII) and -(V) derivatives MoO_2Cl_2, $ReCH_3O_3$ (MTO) and $ReIO_2(PPh_3)_2$ catalyze the selective hydrogenation of alkynes to alkenes at 80 °C under 40 atm of pressure. The reduction of sulfoxides to sulfides has also been performed by oxo-rhenium and -molybdenum complexes using hydrogen as a reducing agent. Activation of hydrogen by MoO_2Cl_2 and $MoO_2(S_2CNEt_2)_2$ was shown by means of DFT calculations to proceed by H–H addition to the Mo=O bond, followed by hydride migration to yield a water complex.

Introduction

Recently, high-valent transition metal complexes have been used in catalytic hydrosilylation reactions. Since the seminal report of Toste and coworkers showing the high efficiency of $ReIO_2(PPh_3)_2$ in the hydrosilylation of carbonyl groups,[1] additional related oxo-rhenium complexes were reported to catalyze the hydrosilylation of carbonyls[2–8] and imines.[9] We have recently shown the excellent efficiency of MoO_2Cl_2 in the hydrosilylation of carbonyls by means of Si–H bond activation,[10,11] and some of us have extended the scope of the use of MoO_2Cl_2 to the reduction of esters,[12] imines,[13] amides,[14] sulfoxides and pyridine *N*-oxides.[15] In a very recent re-examination of their original system, Toste and coworkers provided compelling experimental evidence for the [2 + 2] addition of a Si–H bond across a Re=O bond as the initial step of the catalytic carbonyl hydrosilylation cycle.[16] This mechanism had also been found to be the most likely one by DFT calculations.[17] In the case of MoO_2Cl_2, all attempts to observe a Mo–H intermediate failed but an initial [2 + 2] addition of Si–H to a Mo=O bond was also predicted by DFT calculations from us[18] and others.[19] Although the activation of CH_4 by MoO_2Cl_2 has been ruled out by these studies, on both thermodynamic and kinetic grounds, nothing is known about the capacity of this complex to activate H_2. Given the propensity of complexes like $ReIO_2(PPh_3)_2$ and MoO_2Cl_2 to undergo [2 + 2] type additions, we reasoned that their reaction with H_2 might produce metal hydrides exhibiting catalytic activity in hydrogenation or other reductive reactions. This would extend the role of high valent oxides as catalysts for reductive processes replacing silanes by a cheaper and more convenient reducing agent, dihydrogen.

Herein, we report the hydrogenation of alkynes to alkenes with H_2 using MoO_2Cl_2, $ReIO_2(PPh_3)_2$ and $ReCH_3O_3$ (MTO) as catalysts, and the reduction of sulfoxides to sulfides using H_2 as a reducing agent in the presence of catalytic amounts of MoO_2Cl_2, $MoO_2(S_2CNEt_2)_2$, $ReIO_2(PPh_3)_2$ and $ReOCl_3(PPh_3)_2$. This is the first report of high valent oxo-molybdenum and -rhenium complexes catalyzing the hydrogenation of alkenes. However, several imido molybdenum(IV) arene complexes are known to effect the hydrogenation of alkenes.[20] DFT calculations have shown that the activation of H_2 by MoO_2Cl_2 and $MoO_2(S_2CNEt_2)_2$ can take place in a [2 + 2]-type addition of the H–H bond to the terminal oxo–metal multiple bond, followed in the latter system by water elimination and formation of a reduced Mo(IV) species. This pathway of H_2 activation is not favored for the tetrahedral metal oxides MO_4^{z}–(M = Mn, Ru, Os) (or their adducts) which preferentially undergo [3 + 2] additions of E–H bonds (E = R_3C, R_3S, H).[21]

Experimental

General considerations

All experiments involving synthesis of metal complexes and catalysis were carried out using standard Schlenk-line techniques under a nitrogen atmosphere. Solvents were purified by conventional methods and distilled under nitrogen, prior to use. NMR spectra were recorded on a Bruker AMX 300 MHz and Bruker Avance III 400 MHz spectrometers, and IR spectra were measured on a Unicam Mattson model 7000 FTIR spectrometer. Elemental analysis were performed in our laboratories (ITQB). Commercially available reagents were used without further purification. Compounds MoO_2Cl_2,[22] $MoO_2(S_2CNEt_2)_2$,[23] $ReCH_3O_3$,[24] $ReIO_2(PPh_3)_2$,[25] and $ReOCl_3(PPh_3)_2$[26] were prepared according to the literature procedures. Catalytic reactions were assayed by gas chromatography by comparison with authentic samples. Gas chromatography was performed on a CE Instruments Trace GC-series 2000 gas chromatograph equipped with a DB-5 MS capillary column (30 m) with an injector and detector temperature of 220 °C for the system alkynes/alkenes and 280 °C for sulfoxides/sulfides. Helium was used as the carrier gas. The method used for

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separating 1-hexyne/1-hexene and 3-hexyne/*trans*- and *cis*-3-hexene was: an oven temperature of 40 °C, with a ramp rate of 5 °C/min to a final temperature of 80 °C for 1 min. For separating phenylacetylene/styrene an oven temperature of 40 °C, with a ramp rate of 5 °C/min to a final temperature of 100 °C for 1 min was used. The method for separating methyl phenyl sulfoxide/thioanisole and dibutyl sulfoxide/dibutyl sulfide was: an oven temperature of 100 °C, with a ramp rate of 10 °C/min to a final temperature of 250 °C for 1 min. The products were also identified by NMR spectroscopy. The reactions with hydrogen were performed in a 100 mL AISI 316 stainless steel autoclave.

General procedure for hydrogenation of alkynes

The hydrogenation reaction was carried out in a stainless steel autoclave, which was charged with 5 mol% of the corresponding catalyst, a magnetic stirrer and flushed with nitrogen. A solution of alkyne (3.5 mmol) in toluene (5 mL) was placed into the autoclave which was pressurized with H_2. The reaction mixture was then stirred at 80 °C. After 24 h, the autoclave was cooled to room temperature, degassed, and opened. The reaction mixture was filtered, and the filtrate was analyzed by gas chromatography.

General procedure for reduction of sulfoxides

The deoxygenation reaction was carried out in a stainless steel autoclave, which was charged with 10 mol% of the corresponding catalyst, a magnetic stirrer and flushed with nitrogen. A solution of sulfoxide (1.0 mmol) in toluene (5 mL) was placed into the autoclave which was pressurized with H_2 (50 atm). The reaction mixture was then stirred at 120 °C. After 20 h, the autoclave was cooled to room temperature, degassed, and opened. The reaction mixture was filtered and analyzed by gas chromatography.

DFT Calculations

All calculations were performed with the Gaussian03 software package,[27] using the B3LYP hybrid functional. It includes a mixture of Hartree–Fock[28] exchange with DFT[29] exchange–correlation, given by Becke's three-parameter functional[30] with the Lee, Yang and Parr correlation functional, which accounts for both local and nonlocal terms.[31,32] The standard LanL2DZ basis set with the associated ECP[33] augmented with a f-polarization function (exponent 1.043) was used for Mo,[34] and a standard 6–31G(d,p)[35] basis set for the remaining elements. The geometries were optimized without any symmetry constraints. Frequency calculations were performed in all species at this level of theory to confirm the nature of the stationary points. The transition-state structures, which yielded one imaginary frequency, were relaxed following the vibrational mode to confirm the connecting reagents. The reported zero-point corrected electronic energies (E_0) and gas-phase Gibbs free energies (G) were also obtained at this level of theory. Complex $MoO_2(S_2CNMe_2)_2$ (**6**) was taken as a model of $MoO_2(S_2CNEt_2)_2$.

Table 1 Hydrogenation of alkynes catalyzed by MoO_2Cl_2, MTO and $ReIO_2(PPh_3)_2$[a]

Entry	Substrate	Catalyst	H_2 (atm)	% Yield[b]
1	*n*-BuC≡CH	MoO_2Cl_2	8	100
2	PhC≡CH	MoO_2Cl_2	8	28
3	EtC≡CEt	MoO_2Cl_2	8	4
4	PhC≡CH	MoO_2Cl_2	40	36
5	EtC≡CEt	MoO_2Cl_2	40	45[c]
6	*n*-BuC≡CH	MTO	40	100
7	PhC≡CH	MTO	40	70
8	EtC≡CEt	MTO	40	47[d]
9	*n*-BuC≡CH	$ReIO_2(PPh_3)_2$	40	100
10	*tert*-BuC≡CH	$ReIO_2(PPh_3)_2$	8	75
11	*tert*-BuC≡CH	MTO	8	70

[a] Reaction conditions: 3.5 mmol of alkyne and 0.05 mmol of catalyst at 80 °C in toluene for 24 h. [b] Yields were determined by GC chromatography. [c] A mixture of *cis* and *trans* isomers, 16 : 29 respectively. [d] A mixture of *cis* and *trans* isomers 8 : 39, respectively.

Results and discussion

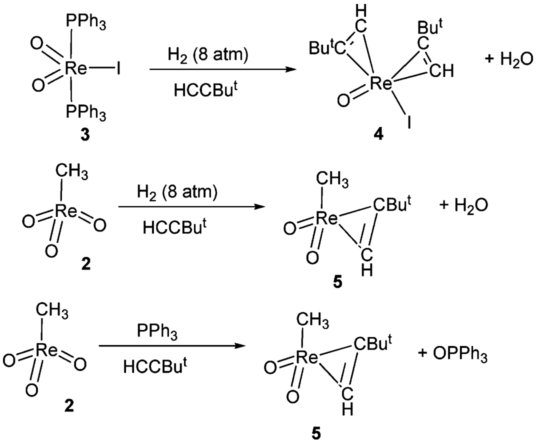
Hydrogenation of alkynes

The catalytic activity of MoO_2Cl_2 (**1**) was tested by using 5 mol% of catalyst and 3.5 mmol of 1-hexyne in toluene under 8 atm of H_2 pressure. After 24 h at 80 °C, the reaction mixture was filtered and analyzed by gas chromatography (GC), which showed 100% conversion of 1-hexyne to 1-hexene (Table 1, entry 1). Using the above catalytic conditions, low conversions were achieved for other alkynes such as phenylacetylene (28% conversion to $PhCH{=}CH_2$) and the internal alkyne 3-hexyne (4% conversion to EtCH=CHEt). Higher yields of alkenes were obtained by increasing the hydrogen pressure to 40 atm (36% conversion to $PhCH{=}CH_2$ and 45% conversion to EtCH=CHEt). Longer reaction times and higher temperatures (up to 120 °C) for the hydrogenation reactions did not increase the conversion of alkynes to alkenes.

With the optimal conditions in hand, we tested the hydrogenation reaction of alkynes with the high-valent rhenium complexes, $ReCH_3O_3$ (**2**, MTO) and $ReIO_2(PPh_3)_2$ (**3**). Both complexes are catalytically active in the hydrogenation of 1-hexyne, phenylacetylene and 3-hexyne giving conversions of 100, 70 and 47%, respectively, for MTO (Table 1 entries 6–8) and 100% yield of 1-hexene for $ReIO_2(PPh_3)_2$, after 24 h at 80 °C. Blank experiments performed for 1-hexyne in the presence of H_2, confirmed that no alkene formation was detected unless the catalyst was used.

Under catalytic conditions, we have detected the formation of reduced rhenium species along with the hydrogenation products. When catalyst **3** is used in the hydrogenation of *t*-BuC≡CH (Table 1, entry 10), we have isolated, by cooling down the toluene solution, yellow crystals which have been identified as ReIO(*t*-BuC≡CH)$_2$ (**4**). The alkyne complex **4** has been reported in the literature by Mayer and co-workers; it has been synthesized by treatment of $ReIO_2(PPh_3)_2$ with excess of the corresponding alkyne.[36] Therefore, it seems that free triphenyl phosphine (generated by replacement of PPh_3 in **3** by alkyne) could be the reducing agent responsible for the reduction of $ReIO_2(PPh_3)_2$ to ReIO(*t*-BuC≡CH)$_2$. We examined then the hydrogenation reaction catalyzed by MTO (Table 1, entry 11). For this reaction, the formation of the reduced Re(V) alkyne complex $ReCH_3O_2$(*t*-BuC≡CH)

(**5**, MDO) was also detected. In this case, we can be sure that H_2 is responsible for the reduction of MTO, since there is no other reducing agent in the reaction mixture (Scheme 1). The synthesis of $ReCH_3O_2(t\text{-}BuC{\equiv}CH)$ has been reported by Herrmann and co-workers from the reaction of MTO with an excess of alkyne using polymer-bound PPh_3 as the reducing agent (Scheme 1).[37]



Scheme 1 Reactions of $ReIO_2(PPh_3)_2$ and MTO with H_2 and PPh_3.

In order to find out if these reduced Re-(III) and -(V) complexes could be the catalytic active species in the hydrogenation reaction, complexes **4** and **5** were synthesized according to the literature procedures, and were tested in the hydrogenation reaction. A mixture of 3.5 mmol of 3,3-dimethyl-1-butyne and 0.2 mmol of compounds **4** and **5** in toluene were stirred under 40 atm of hydrogen pressure at 80 °C for 24 h. No conversion of 3,3-dimethyl-1-butyne to the corresponding alkene was observed. Therefore, species **4** and **5** are by-products of the reaction and not intermediate active species of the catalytic cycle.

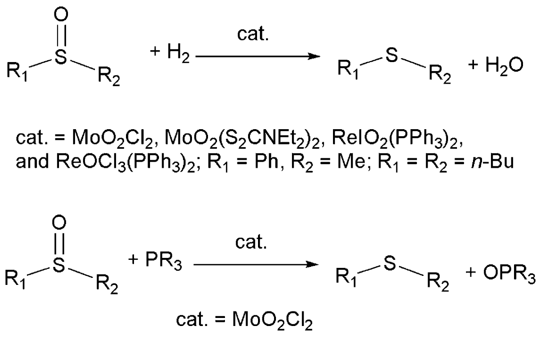
In an attempt to get additional mechanistic information, we have carried out spin trap experiments by addition of the radical scavenger DMPO (5,5-dimethyl-4,5-dihydro-3*H*-pyrrole-*N*-oxide) to the reaction mixture catalyzed by MTO (**2**). The addition of the spin trap causes an important decrease in the yield which becomes only 16% of its normal value under similar catalytic conditions. These experiments suggest that radical species are involved in the catalytic hydrogenation of alkynes.

A similar spin trap essay was carried out in the hydrogenation of 1-hexyne catalyzed by MoO_2Cl_2. In this case, the addition of radical scavengers has a drastic effect: the hydrogenation of alkyne is completely inhibited by the presence of DMPO. It seems that, also for this catalyst, radical species are participating in the hydrogenation reaction (a radical mechanism has been proposed by us in the hydrosilylation of carbonyl groups when MoO_2Cl_2 is used as catalyst).[11]

It is well known that in alkyne/alkene mixtures, the alkyne functionality can be preferentially reduced because of the better bonding capabilities of the triple bond. However, in general, when most of the alkyne has been consumed, the reduction of alkene occurs. This does not happen by using **1**, **2** and **3** as catalysts, and in fact, we do not detect formation of hexane over long reaction times (48 h). The observation of an incomplete hydrogenation selectively producing alkenes is reminiscent of the behaviour of nitrogenase and some of its crude oxo–thiol–Mo(VI) models.[38] Indeed, the selective reduction of alkynes to alkenes is a challenging task in organic synthesis, largely employed in the preparation of organic intermediates for the synthesis of several pharmaceuticals.[39] The presently available data do not shed any light upon the nature of the true catalyst. The most obvious products of the reduction under catalytic conditions are given in Scheme 1. However, none of them, per se, possesses any catalytic activity. More reduced species yet to be identified might be the actually active catalysts. The fact that radical processes are most likely involved in the reaction makes it more difficult to assign a mechanism at this stage.

Reduction of sulfoxides

In view of the ability of high-valent metal complexes to activate H_2, and knowing that H_2 is capable to reduce this type of complexes in a similar way to that achieved by PPh_3 (see Scheme 1), we decided to investigate the catalytic deoxygenation of sulfoxides by using H_2 as reducing agent. The oxygen atom of the sulfoxide is then removed as H_2O and no longer as $OPPh_3$ (see Scheme 2). Indeed, sulfoxides are readily deoxygenated by PPh_3 in a reaction catalyzed by many *cis*-Mo(VI)O_2 derivatives,[40] including MoO_2X_2 (X = Cl, Br)[41] and also by $ReOCl_3(PPh_3)_2$.[42] We were most pleased to find that MoO_2Cl_2 (**1**) catalyzes the reduction of methyl phenyl sulfoxide with H_2 (50 atm) at 120 °C affording the corresponding sulfide in quantitative yields (Scheme 2, Table 2, entry 2).



Scheme 2 Reaction of sulfoxides with H_2 and PPh_3 in the presence of catalyst.

A detrimental effect in the yield of methyl phenyl sulfoxide has been observed by decreasing the temperature (25% yield at 80 °C, no reaction at room temperature), time (60% yield in 7 h),

Table 2 Reduction of sulfoxides catalyzed by MoO_2Cl_2, $MoO_2(S_2CNEt_2)_2$, $ReIO_2(PPh_3)_2$ and $ReOCl_3(PPh_3)_2$[a]

Entry	Substrate	Catalyst	Product	%Yield[b]
1	$(n\text{-}Bu)_2SO$	MoO_2Cl_2	$(n\text{-}Bu)_2S$	100
2	PhMeSO	MoO_2Cl_2	PhMeS	100
3	PhMeSO	$MoO_2(S_2CNEt_2)_2$	PhMeS	55
4	PhMeSO	$MoO(S_2CNEt_2)_2$	PhMeS	31
5	$(n\text{-}Bu)_2SO$	$ReIO_2(PPh_3)_2$	$(n\text{-}Bu)_2S$	100
6	PhMeSO	$ReIO_2(PPh_3)_2$	PhMeS	87
7	$(n\text{-}Bu)_2SO$	$ReOCl_3(PPh_3)_2$	$(n\text{-}Bu)_2S$	100
8	PhMeSO	$ReOCl_3(PPh_3)_2$	PhMeS	83

[a] Reaction conditions: 1.0 mmol of sulfoxide, 0.1 mmol of catalyst, 50 atm of H_2 pressure at 120 °C in toluene for 20 h. [b] Yields were determined by GC chromatography.

the hydrogen pressure (67% yield with 20 atm of H_2) and the amount of catalyst (64% yield when 5 mol% of catalyst is used). Blank experiments for the reduction of sulfoxides with H_2 have been performed and no significant sulfide formation was observed under the applied conditions.

In order to know whether the active catalytic species are stable under catalytic conditions, new charges of methyl phenyl sulfoxide were added to the reactor when MoO_2Cl_2 was used as catalyst (a 100% conversion of methyl phenyl sulfoxide to methyl phenyl sulfide was obtained in the first catalytic cycle). After 24 h at 120 °C, the mixture was analyzed by GC, showing a 65% of conversion to the corresponding sulfide. A third catalytic cycle under similar reaction conditions gave 55% of conversion to the sulfide. Therefore, we can conclude that the catalyst is stable under catalytic conditions although a slight decrease in yield was observed.

When **1** is exposed to H_2 pressure under similar conditions (50 atm and 120 °C) in the absence of any substrate, no reaction takes place and the product is recovered.

The catalytic deoxygenation was also achieved by $MoO_2(S_2CNEt_2)_2$ (**6**), although less effectively (55% yield, Table 2, entry 3). We chose to study complex **6** as catalyst in this reaction because of its solubility in a variety of organic solvents and the full characterization of its reduced Mo-(IV) and -(V) species could help us identify intermediate species responsible for the reduction of the sulfoxides.

The reaction of $MoO_2(S_2CNEt_2)_2$ with H_2 (50 atm) in toluene, in the presence of molecular sieves, at 120 °C for 24 h, afforded a reddish solid which was characterized as the oxo-bis(diethyldithiocarbamato)molybdenum(IV) (Scheme 3). When molecular sieves are not employed, the reaction becomes rather irreproducible most likely due to side reactions with water at the high temperature used. Thus, the first step in the catalytic reaction is probably the reduction of **6** by H_2 (see Computational studies) affording the Mo(IV) complex $MoO(S_2CNEt_2)_2$ (**7**) and water (compound **7** was shown to be catalytically active in the reduction of sulfoxides affording a 31% yield of methyl phenyl sulfide).

We have extended our studies to the use of several oxo–rhenium complexes. We found that $ReIO_2(PPh_3)_2$ and $ReOCl_3(PPh_3)_2$ also catalyze the reduction of sulfoxides affording quantitative conversions to the corresponding sulfides (Table 2, entries 5–8).[42]

$$\underset{\mathbf{6}}{MoO_2(S_2CNEt_2)_2} \xrightarrow[\text{toluene}]{H_2\ (50\ \text{atm})} \underset{\mathbf{7}}{MoO(S_2CNEt_2)_2}$$

Scheme 3 Reaction of $MoO_2(S_2CNEt_2)_2$ with H_2.

Computational studies

DFT/B3LYP[29] calculations (Gaussian 03)[27] were performed in order to understand the mechanism of activation of H_2 by these Mo(VI) complexes (more details in the Experimental section). Since the reaction of $MoO_2(S_2CNEt_2)_2$ with dihydrogen is well defined, the reagent and the product being well characterized complexes **6** and **7**, we started by studying this reaction. As can be seen from the complete pathway shown in Fig. 1, the first step consists of the activation of the H–H bond over one of the Mo=O bonds of **6**, similar to the first step in the activation of Si–H bonds over the same type of Mo(VI) dioxo complex.[18] An intermediate (**I1**) of relatively high energy, containing a hydride and a OH ligand, is formed. The following hydrogen migration to the oxygen of the OH group gives rise to a complex with a bound water molecule (**I2**), which then leaves the coordination sphere of molybdenum.

The initial complex **6**, $MoO_2(S_2CNEt_2)_2$, has a highly distorted octahedral geometry, as can be seen in the three-dimensional representation of Fig. 2. The Mo–S and other bonds in each dithiocarbamate ligand are the same, despite the lack of symmetry constraints of the calculations. The Mo–S bond *trans* to Mo=O is much longer (2.777 Å) than the other (2.486 Å), and the S–Mo–S angle (147.5°) is narrower than the S–Mo=O (156.6°). These structural parameters reproduce very well those of the experimentally determined structure,[43] although the longer Mo–S bond is overestimated (exptl. 2.640 Å). All the others are comparable within 0.04 Å.

The H_2 molecule approaches the metal octahedral coordination sphere over one SSO face. In the transition state $\mathbf{TS_{6\text{-}I1}}$, the H–H bond is very long (1.099 Å), while the O–H and Mo–H bonds are partially formed (1.197 and 1.950 Å). The intermediate

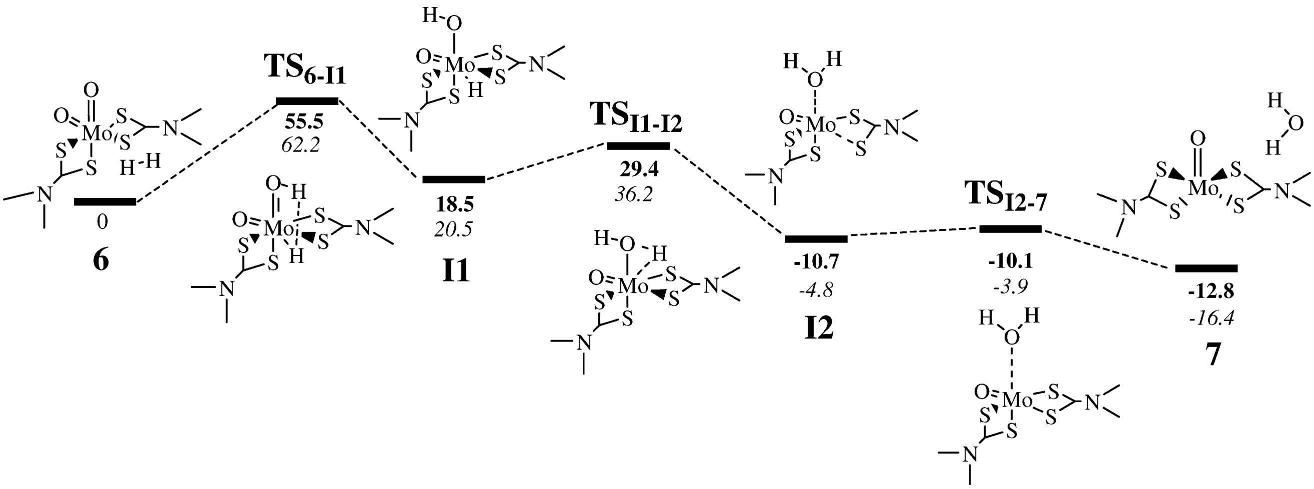


Fig. 1 Reaction pathway for the dihydrogen activation by complex **6**: ΔE_0 (bold) top and ΔG (italics) bottom, in kcal mol^{-1}.

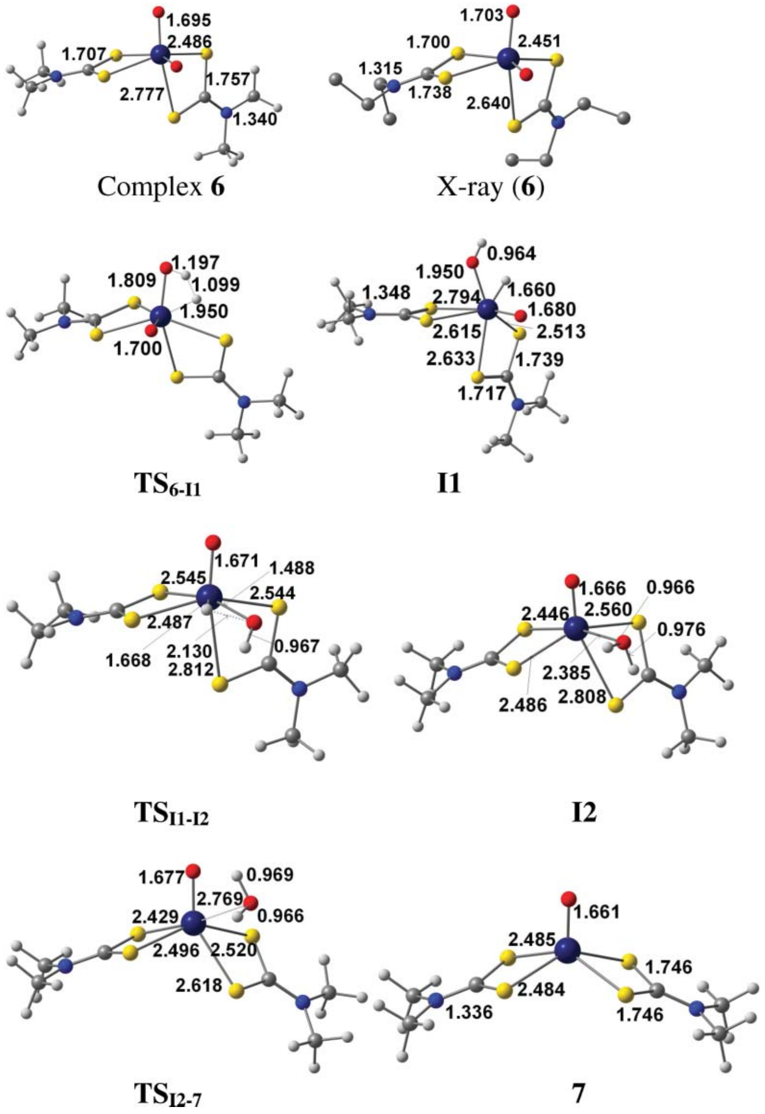


Fig. 2 Relevant distances (Å) and structures of the intermediates and transition states in the dihydrogen activation by complex **6**.

I1 is heptacoordinate, displaying a very distorted coordination environment. The coordination of another ligand, the hydride, is reflected in the four long Mo–S bonds, while the Mo=O has become slightly shorter (Fig. 2). This intermediate has a higher energy than the sum of the two isolated reagents (the zero of the energy scale), the reaction being endothermic and endergonic. The activation free energy is calculated as 62.2 kcal mol^{-1}, a value not unexpected considering the reaction conditions (Table 2).

This is the rate limiting step of the reaction. The other two steps, a migration and a dissociation, involve much lower activation free energies than the associative first step. The migration of the hydride in **I1** to the oxygen of the OH group to form intermediate **I2** has an activation barrier of 10.9 kcal mol^{-1}, or 15.7 kcal mol^{-1} in terms of free energy. There is a large reorganization of the geometry of the complex, when going from **I1** to **I2**. **I2** is again a highly distorted octahedral species, with a long Mo–O distance to the bound water molecule (2.385 Å), and two very asymmetrically coordinated dithiocarbamate ligands. One of them exhibits a 2.808 Å long Mo–S distance and is *trans* to Mo=O. It is not surprising that the complex loses the H_2O molecule very easily: the activation barrier of 0.6 kcal mol^{-1} drops when entropy effects are taken into account and free energies are considered. In the transition state $\mathbf{TS_{I2\text{-}7}}$ the Mo · · · O distance has increased significantly to 2.769 Å, while the long Mo–S bond of **I2** starts to shrink back to normal. The final stable complex **7** has a square pyramidal structure, with four short Mo–S bonds (2.484–2.485 Å) and a very low energy. It is the most stable species in the system, and this probably explains the low catalytic activity in the reduction of sulfoxides (Table 2). In the X-ray structure of the complex,[44] the Mo–S bonds are a bit shorter, though the Mo=O bond has the same length. It is very asymmetric, probably owing to crystal packing effects (there are two molecules per unit cell).

Starting from complex MoO_2Cl_2 (**1**) a similar pathway was investigated and is sketched in Fig. 3. The first step, the activation of H–H over Mo=O leading to the first intermediate **I3**, has a lower activation barrier (~5 kcal mol^{-1}) than in the pathway shown in Fig. 1. The free energy of **I3** is higher than that of **I1** relative to the reagents. In the second step, however, the migration of the hydride to the OH group, has an activation barrier of ~25 kcal mol^{-1} ($\mathbf{TS_{I3\text{-}I4}}$) almost double that for the dithiocarbamate

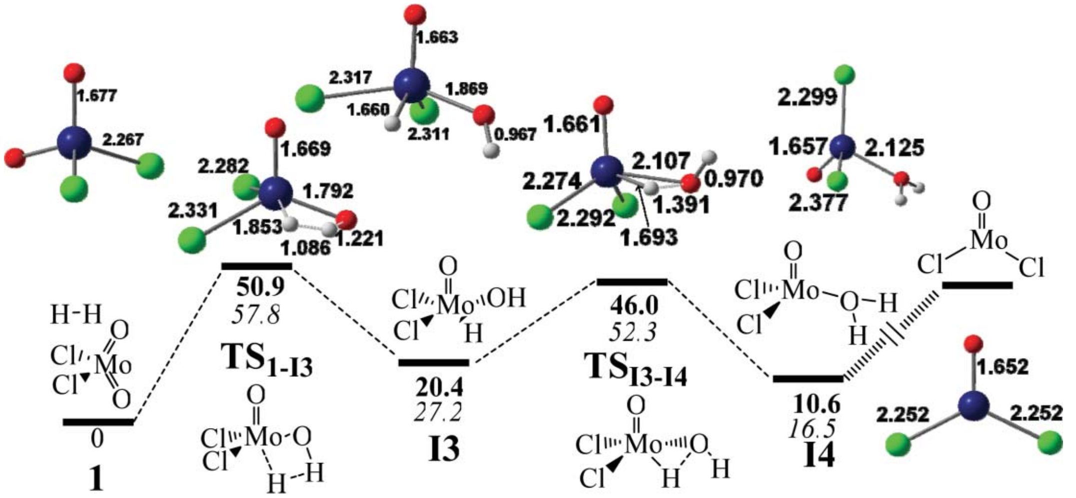


Fig. 3 Reaction pathway for the activation of H_2 by MoO_2Cl_2, showing some relevant distances: ΔE_0 (bold) top and ΔG (italics) bottom, in kcal mol^{-1}.

complex. The water complex **I4** is less stable than the reagents (another difference from the first mechanism) by 10.6 or 16.5 kcal mol^{-1}, considering electronic or free energy. The structural changes parallel those described for the first pathway. Finally, it was impossible to find a path for water elimination from complex **I4**. The triangular $MoOCl_2$ complex is not a stable species, owing to its high unsaturation. This finding is in accord with the fact that **1** does not react with H_2 in the absence of substrates. Therefore, other substrate dependent reaction pathways must be considered in order to explain the catalytic activity summarized in Tables 1 and 2. For instance, it is obvious that under the catalytic conditions of the sulfoxide deoxygenation reactions, **1** will not be present and $[MoO_2Cl_2(OSR_2)]$ will be the most likely species undergoing reduction. As shown by Arnáiz and coworkers, such a species is readily deoxygenated by PPh_3 leading to catalytic deoxygenation of sulfoxides.[41] The parallel between O abstraction by H_2 and PPh_3 (reaction conditions apart) leads us to expect that $MoO_2Cl_2(OSR_2)$ will also be readily deoxygenated by H_2 under our experimental conditions.

Conclusions

High-valent oxo–molybdenum(VI) and -rhenium(VII) and -(V) complexes are able to catalyze the hydrogenation of alkynes under 40 atm of H_2 pressure, selectively affording the corresponding alkenes. Several oxo-rhenium and -molybdenum compounds were also capable of reducing sulfoxides to sulfides by using hydrogen as a reducing agent and forming water as the only by-product. Radical scavenging experiments strongly suggest the presence of radicals in these reduction reactions. A DFT computational study showed that the mechanism for dihydrogen activation by the Mo(VI) complexes starts with a [2 + 2] addition of the H–H bond to the Mo=O bond. Depending on the ligands, this reaction may then be followed by migration of the resulting hydride to the oxygen of the new OH ligand, to afford a water complex. When the dithiocarbamate complex **6** loses water, the stable Mo(IV) complex formed, **7**, effects sulfoxide deoxygenation but is a poor catalyst under these relatively forcing reaction conditions probably due to partial decomposition. In this respect the several rhenium catalysts tested are quite effective. The fact that MoO_2Cl_2 (**1**) possesses a very high catalytic activity in this deoxygenation process in spite of having an energetically unfavored water loss pathway, means that other reaction pathways become competitive. Further work is under way in order to extend the scope of these novel reactions as well as the understanding of their mechanisms.

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