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Organorhenium(VII) and organomolybdenum(VI) oxides: synthesis and application in oxidation catalysis†

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Methyltrioxorhenium(VII) has found numerous applications in various catalytic processes. In olefin epoxidation its activity can be enhanced by the addition of aromatic Lewis base nitrogen donor ligands, e.g. pyridines and pyrazoles. Due to the comparatively weak coordination of these ligands, a significant excess has to be used. Therefore the MTO/chiral Lewis base/H_2O_2 system is not very useful for chiral epoxidations. In contrast to this, dimethyldioxomolybdenum (VI) $MoO_2(CH_3)_2$ undergoes a significantly stronger interaction with Lewis bases and seems, despite its generally somewhat lower activity, a reasonable candidate for application in chiral epoxidation reactions together with an appropriate chiral Lewis base ligand. Complexes of the type $MoO_2(CH_3)_2L$ are accessible via MoO_2X_2L (X = Cl, Br). These latter compounds are even more active in olefin epoxidation than $MoO_2(CH_3)_2L$. Unfortunately, however, all the Mo(VI) complexes mentioned above need *t*-butyl hydroperoxide as oxidizing agent and do not show activity in the presence of H_2O_2.

Keywords: catalysis; molybdenum; nitrogen ligands; olefin epoxidation; rhenium

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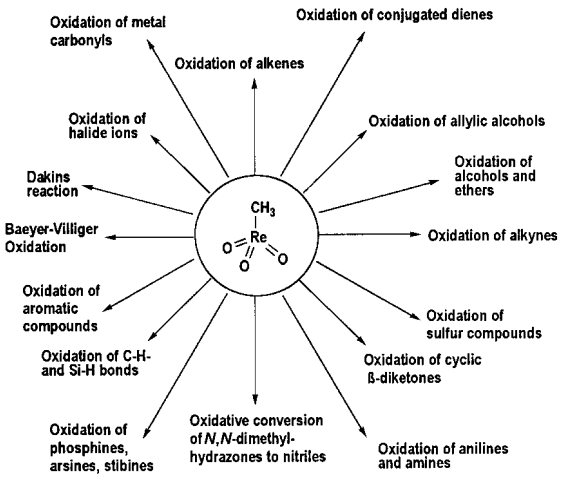
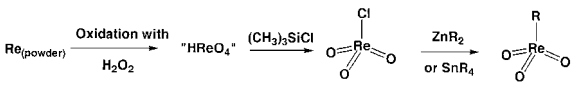
Organorhenium oxides

Since it was first synthesized in 1979 by Beattie and Jones[1] methyltrioxorhenium (MTO) has found numerous applications in oxidation catalysis.[2] Owing to its difficult and low-scale synthesis, however, MTO was first regarded as a laboratory curiosity. Only after an easy and straightforward synthetic pathway was discovered in 1988, by Herrmann *et al.*[3] could its usefulness as a catalyst be thoroughly examined. Among the numerous applications found in the following years were aldehyde olefination, the metathesis of functionalized olefins and oxidation catalysis.[4] Scheme 1 gives an overview of the numerous different oxidation processes in which MTO can be applied as a catalyst.



Scheme 1 Oxidation processes catalyzed by MTO.

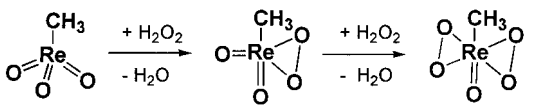
MTO is now directly available from rhenium metal in good yield and large scale by the reaction sequences shown in Scheme 2.[5]



Scheme 2 Preparation of MTO.

A similar synthetic pathway has been used to obtain other alkane derivatives, *e.g.* ethyl, *n*-pentyl, *n*-heptyl and (*S*)-2-methyl butyltrioxorhenium (VII). It was established that unbranched, noncyclic organorhenium oxides are less thermolabile than branched chain derivatives. The thermal stability also decreases with increasing chain length.[6] These facts proved to be very disadvantageous for $RReO_3$ complexes with chiral groups. Among the alkyl derivatives MTO still remains by far the most advantageous one, being soluble in all common organic solvents and in water, without decomposition. Furthermore, MTO is stable up to 300 °C and can be easily sublimed by using an oil pump vacuum at 60 °C.

In the case of olefin epoxidation, detailed studies were made concerning the nature of the catalytically active species by using H_2O_2 as oxidative agent. MTO reacts with H_2O_2 to form mono and bisperoxo complexes, depending on the amount of H_2O_2 used according to Scheme 3.



Scheme 3 Reaction of MTO with hydrogen peroxide.

The bisperoxo complex was isolated both as a water and as a hexamethylphosphoramide adduct (Fig. 1), the latter ligand often being used to stabilize peroxo complexes of molybdenum and tungsten.[7,8]

In situ experiments indicated that the reaction of MTO with one equivalent of H_2O_2 leads to a monoperoxo complex in accordance with Scheme 2, this compound also being catalytically active in certain oxidation processes.[4] Kinetic experiments conducted by Espenson[9] indicate that the rate constants for the transformation of most substrates into their oxidation products with bis- or monoperoxo complexes are of a comparable order of

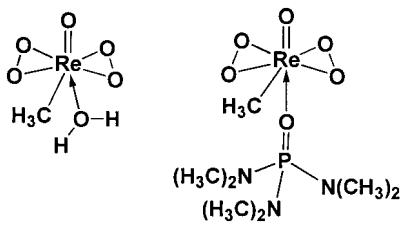


Figure 1 Isolated adducts of methyltrioxorhenium(VII) bisperoxo complexes.

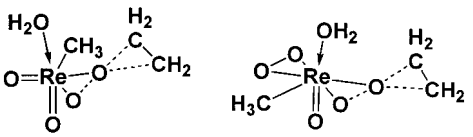


Figure 2 Low-energy states in the olefin epoxidation with MTO.

magnitude. This result is supported by density functional calculations:[10] the transition states in the olefin epoxidation process starting from the mono- or the bis-peroxo complex are not different enough in energy to exclude one of these catalysts totally from the catalytic processes. The transition states with the lowest energy are depicted in Fig. 2.

In recent years the catalytic behavior of Lewis base adducts of MTO has been studied. It was reported that pyridine and pyrazole adducts lead to very good catalytic activity, especially when the ligand is used in significant excess[11] (Fig. 3). For example, when using MTO on the epoxidation of cyclooctene, a TOF (turnover frequency) of 290 mol mol^{-1} h^{-1} was achieved, but when using MTO with pyridine in the ratio 1:10, the TOF increased to 420.

The use of pyridine and pyrazole as Lewis base ligands is particularly useful in the synthesis of sensitive epoxides (*e.g.* terminal alkenes like styrene) in which the use of Lewis acidic systems like MTO leads to the decomposition of the epoxide via diol formation. However, the Lewis bases have

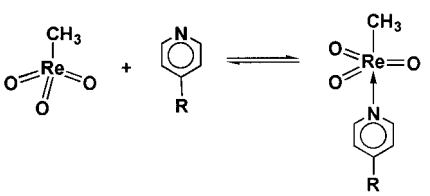
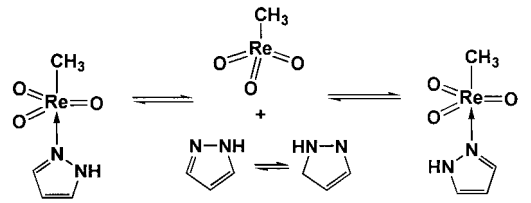


Figure 3 Synthesis of MTO Lewis base adducts.

to be used in significant excess, especially since there is always a rapid equilibrium between the coordinated and the noncoordinated species in solution[12] (Scheme 4). A series of these compounds has been isolated and fully characterized, together with the monoperoxo and the bisperoxo derivatives of the Lewis base adducts of MTO.[13]



Scheme 4 Equilibrium between coordinated and noncoordinated MTO in solution.

The trials to perform chiral epoxidation with appropriate MTO adducts or derivatives have not been successful so far. The introduction of chirality in the system by placing a branched chain instead of a methyl group was found to be a very difficult route to chiral compounds, since they are very unstable to radical decomposition (*see above*). If a chiral monodentate Lewis base is used, only racemic products are obtained.[14] On the other hand, if chiral 1,2-diols are used to synthesize chiral glyoxal complexes, enantiomeric excesses up to 40% can be achieved, but the conversions are only *ca* 5%. Use of a glyoxal complex this leads to conversions of *ca* 30%, but the enantiomeric excess then decreases to *ca* 3%.[15] Another approach was to use chiral bidentate nitrogen donor base ligands, but in this case the behavior is similar to that described for the case of the glyoxal complexes (*see* Fig. 4).

There is then the necessity of finding a system in which the R–M and M–N interactions are strong enough to make it possible in principle to introduce chirality. Several examples exist already in the literature of stable dioxo organomolybdenum(VI)

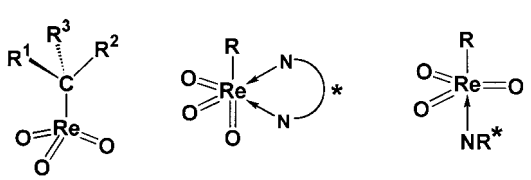


Figure 4 Possibilities of introducing chirality into the MTO system.

complexes.[16,17] In fact, in the molybdenum system the higher alkyl derivatives are as stable as the methyl derivative, which is not the case for the alkyl rhenium compounds.

Organomolybdenum oxides

In 1964 Cousins and Green synthesized $CpMoO_2Cl$, the first molybdenum dioxide organometallic complex to be prepared, together with a variety of different Cp complexes, by the oxidation of $(CpMo(CO)_3)_2$ with oxygen and UV light.[18] New developments in the cyclopentadienyl molybdenum oxide chemistry occurred much later with the synthesis of complexes with general formula $Cp'MoO_2R$ ($Cp' = Cp$, Cp^*; $R = Me$, CH_2SiMe_3) and Cp^*MoO_2Cl.[19]

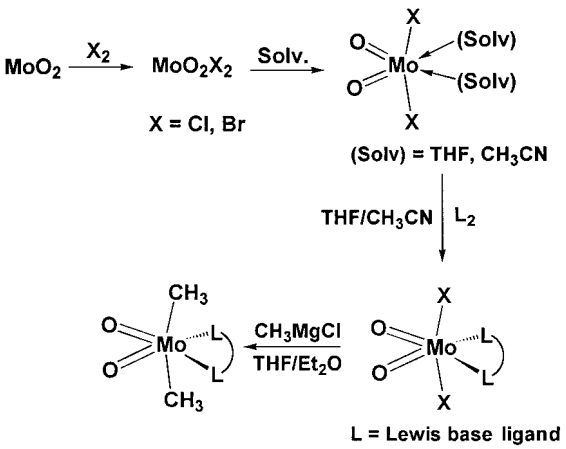
Dioxomolybdenum(VI) complexes with Mo—C σ bonds have been known since 1975, when Heyn and Hoffmann reported the preparation of $MoO_2(mes)_2$ ($Mes^- = 2,4,6$-trimethylbenzyl) complex from $MoO_2Cl_2 \cdot 2THF$ and the Grignard reagent mesitylmagnesiumbromide.[20]

In the early 1980s Schrauzer and co-workers made an important contribution to this family of complexes, with the preparation of $MoO_2R_2 \cdot bipy$. Examples such as methyl,[21] ethyl,[16] neo-pentyl,[22] benzyl,[23] or phenyl and other phenyl-substituted complexes,[17,24] are among the complexes prepared.

Some of these complexes exhibit a remarkable stability to temperature; for the $MoO_2(CH_3)_2 \cdot bipy$ (above 200 °C) or $MoO_2(CH_3C(CH_3)_2CH_2)_2 \cdot bipy$ (182 °C) derivatives, the decomposition temperatures are related to the stability of the Mo—C bond. Those most sensitive to temperature are the complexes with hydrogens in the β position, *e.g.*, the diethyl derivative.[16] The Mo—C bond shows a relative stability to hydrolysis or alkaline hydrolysis at moderate pH, decomposing slowly at room temperature, but it is very sensitive to photolysis via liberation of hydrocarbon species.

These alkyl derivatives can be obtained in a sequence of steps starting from the solvent adducts $MoO_2X_2(S)_2$ and ending with a Grignard reaction (Scheme 5). The synthesis can be carried out without isolating the intermediate compounds. However, the halogenated intermediates are also potential catalysts and were therefore isolated, characterized and tested in epoxidation reactions.

Normally, the alkyl complexes are more soluble than the halogenated precursors. This gain in solubility enabled the application of these com-



Scheme 5 Preparation of the alkyl derivatives of molybdenum(VI) oxide complexes.

plexes as useful homogeneous catalysts and also readily allowed characterization in solution through the use of ^{95}Mo NMR spectroscopy.

Solvent-stabilized complexes

The synthesis of compounds of the formula $MoO_2X_2(NCR)_2$ or $MoO_2X_2(THF)_2$ is achieved by dissolving the molybdenum dioxo dichloride or dibromide in NCR ($R = CH_3$ or C_6H_5) or THF.[25] The product complexes are nearly insoluble in nonpolar nondonor solvents (alkanes or diethyl ether), but are very soluble in most donor solvents.

The ^{17}O NMR data are very similar for all these complexes, showing signals around $\delta(^{17}O) \approx 1020$ ppm. The Mo(VI) centre is therefore comparatively electron deficient. This explains, at least partially, the stronger coordination to organic donor ligands in comparison with the Re(VII) systems, *e.g.* MTO. In the latter cases the chemical shifts range around $\delta(^{17}O) \approx 850$ ppm, despite a strong solvent dependence. The ^{95}Mo data show their signals also within a narrow range around $\delta(^{95}Mo) \approx 275$ ppm. This shift indicates a comparatively electron-poor molybdenum center.

These complexes catalyze the epoxidation of *cis*-cyclooctene with t-butylhydroperoxide.[25] A typical catalytic run is presented in Fig. 5.

The reaction quickly reaches a conversion of more than 65% but does not proceed significantly further. The reason for that observation is the pronounced water sensitivity of these complexes. In contrast to other more strongly coordinating organic ligands, the nitriles do not prevent the moisture-induced decomposition of the complexes. The $MoO_2X_2(Solv)_2$ complexes are therefore more useful as synthetic precursors for complexes with other, more strongly coordinating or chiral ligands than as catalysts themselves.

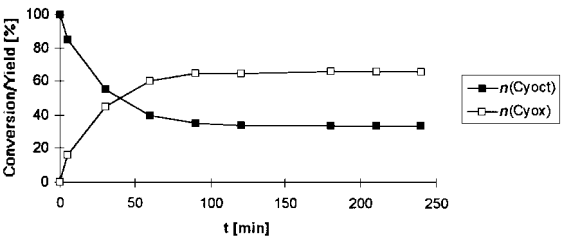


Figure 5 Catalytic performance on the epoxidation of *cis*-cyclooctene of the solvent-stabilized complex $MoO_2Br_2(NCCH_3)_2$.

N-ligand-stabilized complexes

By using systems of formula $MoO_2X_2L_2$ with chelating nitrogen ligands L_2, it is possible to vary the two different sets of ligands L and X, in order to fine tune the ligand surrounding of the Mo(VI) center.

As described before, the complexes were prepared from the solvent adducts of the halogenated Mo(VI) oxides, and a variety of substituted 1,3-diazabutadienes (R-DAB) (R-i-propyl, t-butyl, cyclohexyl, *o*-tolyl, *p*-tolyl) (Fig. 6) as ligands were used.[26]

These ligands were chosen considering their good coordinating capacities. The resulting complexes are stable and can be handled in air. The resonances in the ^{95}Mo NMR spectra appear in

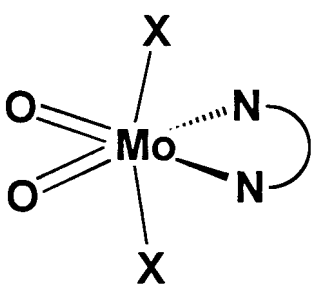


Figure 6 General formula of the N-ligand-stabilized complexes synthesized.

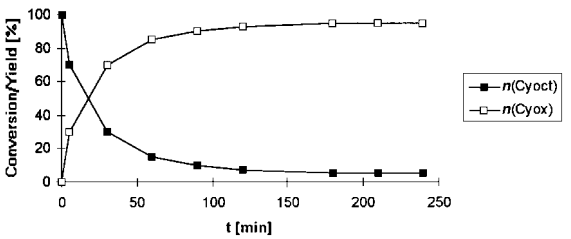


Figure 7 Catalytic performance on the epoxidation of *cis*-cyclooctene of the N-ligand-stabilized complex MoO_2Cl_2(*o*-phen—DAB).

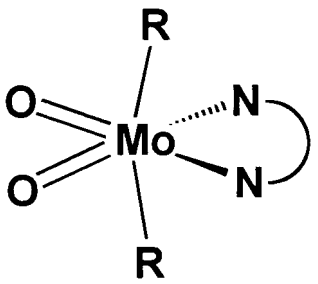


Figure 8 General formula of the synthesized alkylated molybdenum(VI) oxide complexes.

the region between *ca* 190 and 280 ppm. The shielding of the Mo(VI) core is higher than that of the solvent-coordinated starting materials $MoO_2X_2(S)_2$. The ^{95}Mo NMR signals of the chloro complexes are observed at higher field than those of the bromo derivatives. The half widths of all complexes examined are less than 100 Hz and therefore comparatively narrow, indicating an absence of special ligand exchange phenomena, contrary to what was observed in the case of the $RReO_3L$ complexes.[10]

When tested on epoxidation catalysis, these complexes gave very different performances, depending on the ligand L. A typical catalytic run for one of the most active catalysts MoO_2Cl_2(*o*-phenyl—DAB) is shown on Fig. 7. The turnover frequencies (TOFs) obtained were between *ca* 30 and 600 mol mol^{-1} h^{-1}.

In general, it can be said that the chloro complexes are more active in comparison to their bromo analogues. Complexes containing ligands with aromatic substituents are more active than those with aliphatic ligands in identical positions. The difference in yield between chlorinated and brominated complexes is in general considerably smaller than the differences caused by the changes of the Lewis base ligand. This fact suggests that the Lewis base ligands remain attached to the metal and influence the activity of the catalytic active center. Several catalytic runs were made at different temperatures, from 20 to 90 °C and it was observed that the yield increases with the temperature, without noticeable catalyst deactivation or modification.

Although some of the $MoO_2X_2L_2$ complexes show a good catalytic activity they have in many cases a low solubility which sometimes prevented a thorough spectroscopic characterization as well as investigations on the nature of the catalytically active species.

Alkylated molybdenum(VI) oxide complexes

A number of dialkyl complexes of formula $MoO_2(R)_2L_2$ (R = CH_3,C_2H_5) where L_2 represents a variety of bidentate ligands of the type 1,3-diazabutadiene(R-DAB), with different R groups, *e.g.* cyclohexyl, *p*-tolyl, bis *o*-tolyl, bipyrimidine and phenanthroline, were synthesized (Fig. 8).[27]

These complexes are much more soluble than their halogenated precursors and, therefore, are much more suitable for a detailed spectroscopic characterization. In the case of the Mo(VI) compounds described here, the stability of the ethyl derivative is comparable to that of the methyl derivative, in contrast to what was observed for the pair CH_3ReO_3/$C_2H_5ReO_3$. In the latter case, the ethyl derivative is significantly less stable than the methyl derivative.[28] The $MoO_2(R)_2L_2$ complexes can be handled in air for brief periods of time.

The ^{1}H-NMR spectra of the dialkyl complexes show only small variations between the chemical shifts of the free and bonded ligands. The proton NMR shift of the Mo-bonded CH_3 substituents varies between 0.4 and 0.9 ppm.

The $MoO_2(R)_2L_2$ complexes display their ^{95}Mo NMR resonances in the region between 420 and 520 ppm, which is at lower field relative to both their bromo and chloro analogues. This kind of inverse dependence of the $\delta(^{95}Mo)$ chemical shift with the electronegativity of the ancillary ligands has been reported before for other Mo(VI) complexes,[29] and was also observed for the bromine and chlorine derivatives (*see above*). The ^{95}Mo NMR signals of the methyl complexes with the N-heterocyclic aromatic ligands bipyrimidine and phenanthroline are shifted to higher field relative to the complexes with substituted diazabutadienes. Somewhat surprisingly, the presence of aliphatic or aromatic substituents in the R—DAB ligands does

not cause a large variation of the ^{95}Mo chemical shift.

The $MoO_2(R)_2L_2$ compounds were also tested as catalysts in olefin epoxidation. For comparative purposes, the catalytic oxidation of cyclooctene with t-butylhydroperoxide was investigated. In general, the overall yield after 4 h is relatively low (between 5 and 60%); however, over a 24 h reaction period the yield goes up and in some cases rises above 90%, showing that the stability of the catalyst under the reaction conditions is much higher than that observed for the related labile $MoO_2X_2(NCMe)_2$. The TOFs obtained for these compounds range between 200 mol mol^{-1}h^{-1} for *p*-tolyl and 40 mol mol^{-1}h^{-1} for cyclohexyl 1,3-diazabutadiene.

Catalytic runs were also performed at different temperatures, for several complexes bearing different ligands L. At a reaction temperature of 20 °C the yields are low in all cases (5–6%). Catalytic runs at higher temperatures (55 and 70 °C) lead to a significant increase of the yields. A further increase from 70 to 90 °C does not lead to further increase of the yield, and in one case the yield is even lower at this high temperature. It is therefore probable that at this temperature partial thermal decomposition of the catalysts takes place, thus reducing the amount of active catalyst species present in the reaction mixture. In fact, reacting the catalyst precursors with t-BuOOH at 90 °C produces a considerable amount of CH_4 after 4 h, whereas at 55 °C only traces of CH_4 are formed.

Further evidence for the stability of the catalyst arises from the fact that they can be used for a second catalytic run, with a new charge of substrate, leading to approximately the same yields in most cases.

In principle, it can be said that the bromo complexes are more active than their methyl analogues. This trend means that the more electronegative X substituents accelerate the epoxidation reaction. The complexes containing the phenanthroline ligand display the lowest catalytic activity independently of the nature of X. This observation suggests that the flexibility of the coordination sphere plays a very important role in the reaction. In fact, the only pronounced difference between phenanthroline and the other ligands used is the rigidity of the former ligand.

All the catalytic runs show the same time dependent curve form that is presented in Fig. 9 for the standard temperature of 55 °C for the compound $MoO_2(CH_3)_2$(*p*-phenyl—DAB).

After a quick increase of the yield within the first hour, the reaction rate slows down. The appearance of these curves gives no clear indication for the transformation of the original catalyst in another species during the reaction period, *e.g.* by loss of the ligands R or L_2. The formation of the active catalyst must, therefore, occur very quickly and take place at the very beginning of the reaction, immediately after the addition of the peroxide. If H_2O_2 or Ph_3COOH are used as oxidants, no significant product formation was observed. A similar behavior has been found for the related Cp^*MoO_2Cl in the presence of different epoxides.[30]

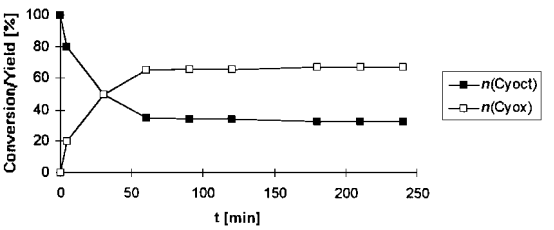


Figure 9 Catalytic performance on the epoxidation of *cis*-cyclooctene of the N-ligand-stabilized complex $MoO_2(CH_3)_2$(*p*-phen—DAB).

Conclusions

The results above show that addition of chiral ligands to MTO does not lead to active enantioselective epoxidation catalysts because ligand dissociation is occurring. In contrast, the Mo-oxide complexes $MoO_2X_2L_2$ (X = Cl, Br, CH_3; L = R—DAB, heterocyclic α-diimines) do not dissociate in solution and their catalytic activities in cyclooctene epoxidation with t-BuOOH strongly reflects the nature of the ancilliary ligands. In general, the activity decreases in the order Cl > Br > CH_3 and Aryl—DAB > t-Bubipy > alkyl—DAB. These findings suggest that enantioselectivity may be imparted to these catalysts by the introduction of chirality at the R groups or at the R—DAB ligands. These possibilities are presently being tested in our laboratories.

Experimental overview

The following notes are added in order to give a

closer insight into the synthetic aspects involved in the preparation of the catalysts mentioned in this work. More precise details are found in the Refs 13 and 25–27.

CH_3ReO_3L

MTO (0.25 g, 1.0 mmol) is dissolved in diethyl-ether to this solution 1 equiv of the corresponding Lewis base was added. The solution turned yellow immediately. The mixture was stirred for 2 h and then concentrated to half of its volume. A yellow or nearly colorless precipitate was obtained upon cooling to −78 °C, the solvent was filtered off and the precipitate was washed once with (hexane–pentane) and dried in oil pump vacuum.

$MoO_2X_2(NCR)_2$

To the powder of MoO_2X_2 [1.0 g, 5.0 mmol (X = Cl) 3.5 mmol (X = Br)] were added 20 ml of NCR and the solution turned yellow. After 10 min the solution was filtered and evaporated to dryness.

$MoO_2X_2L_2$

A solution of 1 equiv. of $MoO_2X_2(NCMe)_2$ [1.0 g, 4 mmol (X = Cl), 2.9 mmol (X = Br)[or $MoO_2X_2(THF)_2$ [1.0 g, 3.0 mmol (X = Cl), 2.3 mmol (X = Br)] is treated with 1 equiv. of the corresponding bidentate Lewis base. The reaction mixture changes its color immediately to yellow–orange and in most cases a precipitate is formed. The mixture reaction was stirred for 30 min and the suspension was then taken to dryness to yield a powder, that was washed with CH_2Cl_2 and diethyl ether.

$MoO_2(CH_3)_2L_2$

A solution of $MoO_2X_2(NCMe)_2$ [1 g, 4.0 mmol (X = Cl), 2.9 mmol (X = Br)] or $MoO_2X_2(THF)_2$ [1.0 g, 3.0 mmol (X = Cl), 2.3 mmol (X = Br)] is treated with 1 equiv. of the correspondent bidentate Lewis base. The reaction mixture changes its color immediately to yellow–orange and it is stirred for a further 30 min. To this solution/suspension at −35 °C in an isopropanol bath, 2.1 equiv. of CH_3MgBr were slowly added. The reaction was allowed to warm up to room temperature and was stirred for further 2 h. The dark red suspension was taken to dryness and distilled water was added. The product was extracted with dichloromethane and the organic phase was dried over anhydrous $MgSO_4$. The solvent was taken to dryness in a rotating evaporator and the residue was recrystallized from CH_2Cl_2–Et_2O–*n*-hexane.

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