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Mononuclear Organomolybdenum(VI) Dioxo Complexes: Synthesis, Reactivity, and Catalytic Applications

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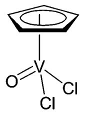
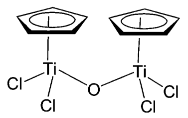
1. Introduction

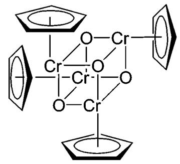
Metal oxides are important in numerous catalytic industrial processes. The desire for models of the metal oxide catalytic activity has contributed to the development of the research focused on the downsizing of metal oxides to small molecular fragments. Smaller metal oxide assemblies can be better understood in terms of structure and reactivity. The first metal oxo molecular fragment was probably the oxohalide complex MoO_2Cl_2 described by J. J. Berzelius in 1826.[1a] Interest in these inorganic molecular fragments continued in the 19th and 20th centuries. Due to their molecular character these types of complexes were good candidates for molecular models of metal oxides, but they proved to be too unstable. Addition of organic molecules to a metal center of a metal oxide with creation of a metal carbon interaction, thus generating an ***organometallic oxide***, has proven to be an interesting way to synthesize the desired models for metal oxides. Besides creating more tangible models for metal oxides, organometallic oxides can also be considered as useful models of the interaction between the metal oxides and the organic substrates of catalytic reactions[1b] and as a way of avoiding the presence of alkyl cocatalysts.[1c] The first organometallic oxides were reported by E. O. Fischer,[1d−f] P. Corradini,[1g] and M. L. H. Green.[1h] Since then, a large variety of organometallic oxides have been described in the literature.



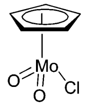
Fischer, 1958



Corradini, 1959



Fischer, 1960



Green, 1963

A large number of important chemical reactions are catalyzed by Mo^{VI} complexes. Several industrial processes such as ammoxidation of propene to acrylonitrile, olefin epoxidation, and olefin metathesis reactions are carried out over molybdenum catalysts.[1i] Furthermore, as molybdenum is highly available to biological systems, the coordination chemistry of Mo^{VI} has aroused considerable interest in view of its biochemical significance, and many Mo^{VI} complexes have been studied as models of molybdoenzymes.[1j]

Over time, stabilization of mononuclear molybdenum(VI) dioxo complexes by formation of a M−C bond has been achieved with different types of organic ligands. In this paper, the literature on mononuclear organomolybdenum dioxo complexes will be summarized. Due to recent synthetic improvements a considerable part of the mononuclear organomolybdenum(VI) dioxo complexes as well as their catalytic application are not covered in older comprehensive works.[1k,l] Recently, H. W. Roesky et al. published a review dedicated to organometallic oxides of main group and transition elements, the scope of which, however, does not include complexes with terminal $M{=}O$ bonds.[1m] A condensed personal account by some of the authors surveyed the organorhenium(VII) and organomolybdenum(VI) chemistry with respect to its applications in epoxidation catalysis.[1n] Beyond the scope of the present review are the mononuclear organomolybdenum dioxo complexes grafted or supported on materials.[1o]

This review includes three sections: synthesis and reactivity, structural and spectroscopic characterization, and catalytic applications. Due to historical synthetic developments the section regarding synthesis and reactivity is divided into two subsections. The first focuses on mononuclear organomolybdenum(VI) dioxo complexes with Mo−C σ bonds and

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Fritz E. Kühn studied chemistry at the Technische Universität München (TUM), Germany, where he received his Ph.D. under the direction of W. A. Herrmann in 1994. After a postdoctorate in the group of F. A. Cotton (Texas A&M University) during 1995–1996, he performed his Habilitation in Munich to become Privatdozent in 2000. From June 2005 to March 2006 he replaced W. A. Herrmann on the Chair of Inorganic Chemistry of the TUM. He has been appointed Principal Researcher at the Instituto Técnológico e Nuclear (ITN) in Sacavém, Portugal, effective April 2006. Dr. Kühn is author or coauthor of more than 160 scientific papers and has received several awards.

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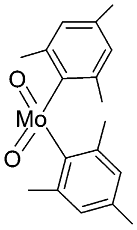
the second on mononuclear organomolybdenum(VI) dioxo complexes with cyclopentadienyl ligands, a class of ligands, which can form Mo−C π or σ bonds, that has been extensively studied for metal oxides[1k] and is estimated to be present in more than 80% of all known transition metal organometallic complexes.[1p]

2. Synthesis and Reactivity

2.1. Dioxomolybdenum(VI) Complexes Bearing Mo–C σ Bonds

The first example of a dioxomolybdenum(VI) complex with a Mo−C σ bond, MoO$_2$(mes)$_2$ (**1**) (mes = 2,4,6-trimethylbenzyl), was published in 1976 by Heyn and Hoffmann.[2a] This compound was obtained by reacting MoO$_2$Cl$_2$ with mesitylmagnesium bromide at 0 °C.[2a] The yield obtained by this method was moderate, but attempts to improve the product yield by reacting MoO$_2$Cl$_2$ with dimesitylmagnesium did not afford better results or avoid the formation of byproducts.[2b] Complex **1** was isolated as a bright yellow solid, relatively stable to air and humidity.[2a] The compound was reported to be thermally stable up to 170 °C. Later it was found to be insoluble and unstable in both liquid and supercritical (42 °C, 130 bar) CO$_2$.[2c] The X-ray crystal structure of **1** could also be determined.[2d]

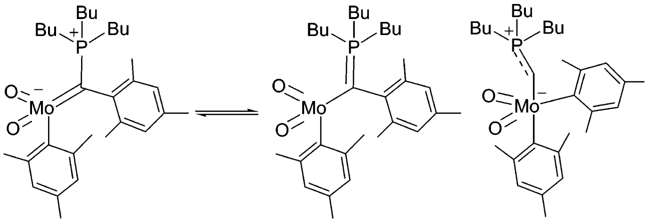


1

Compound **1** does not form Lewis base adducts, even when recrystallized in pyridine due to the steric bulk of the mesityl groups.[2a] It was reported that **1** reacts with MeLi in ether solution under formation of LiOMe and a thermally instable compound with an analytical composition corresponding to the formula Mo(mes)$_2$·(OEt$_2$)$_2$.[2a] Later, the product of the reaction of MeLi and MoO$_2$(mes)$_2$ was found to be of the composition LiMoO$_2$Me$_2$(mes)$_2$(OEt$_2$)$_2$ (**2**).[3a,b] The X-ray crystal structure of this compound was determined.[3b]

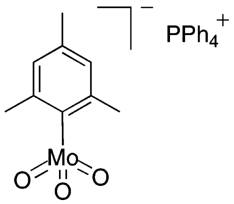
Insertion reactions of **1** with carbon monoxide,[3c,d] isocyanides,[3e] and isocyanates[3f] were also studied. **1** reacts with CO in pyridine to give dimesityl ketone and a dihydropyridine dimer, which represented the first example of N-acylation of a pyridine by CO mediated by a transition metal complex.[3d] Isocyanides react with **1**, affording dimesityl imine (mes$_2$C=NR), mesitylamide (mesCONHR), and dinuclear μ-oxo-η^2-iminoacyl complexes [mesMo(C(mes)=NR)O]$_2$(μ-O) (R = ^{t}Bu, C$_6$H$_{11}$, CH$_2$C$_6$H$_5$).[3e] A terminal isocyanide complex, MoO$_2$mes$_2$(CN)^{t}Bu (**3**), was also isolated and considered to be a possible intermediate in the previous reaction.[3e] Compound **1** was also reported to react with phenyl isocyanate via an insertion into the Mo−mes bond, leading to an oxazamolybdenacycle, which hydrolyzed to phenyl mesityl amide.[3f]

The reactivity of **1** toward phosphonium ylides has also been investigated.[3g,h] The fact that the metal-oxo group M═O can sometimes show ketone-like behavior prompted a check of whether a Wittig reaction was possible between a metal-oxo complex and a phosphonium ylide ($R_3P{=}CH_2$). Laï et al. treated **1** with 2 and 1 equiv, respectively, of phosphonium ylide $Bu_3P{=}CH_2$, yielding MoO_2(mes)[C(mes)-PBu_3] (**4**)[3g] and $MoO_2(mes)_2CH_2PBu_3$ (**5**),[3h] respectively. The expected complex $MoO_2(mes)_2CH_2$ could not be obtained with both stoichiometries applied. The structures of both product compounds were determined by X-ray diffraction.



4a **4b** **5**

The reaction of **1** with ethylidenetriethylphosphorane in THF at low temperature yields tetraethylphosphonium mesityltrioxomolybdate(VI) (see formula below) in moderate yields.[4a]

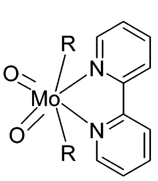


The reaction of **1** with $Pt(O_2)(PPh_3)_2$ at −35 °C in pyridine results in the transfer of the dioxygen ligand from platinum to molybdenum giving, in the presence of PPh_4Cl, a molybdenum peroxo complex of the formula $[Mo_2(O)_6(O_2)]$-$[PPh_4]_2$, having lost all of the organic moieties.[4b]

In the late 1970s and 1980s, interest in stable organometallic complexes arose during the development of models for reactive intermediates for the enzyme nitrogenase.[5] For this reason, the reactions of MoO_2X_2(2,2′-bipyridyl) (X = Cl, Br) (bpy = 2,2′-bipyridyl) precursors with different Grignard reagents were thoroughly explored by Schrauzer and co-workers. The first compounds obtained were of the type MoO_2BrR(bpy) and were synthesized by the reaction of MoO_2Br_2(bpy) with different organomagnesium halides in THF. Some of the MoO_2BrR(bpy) complexes were isolated [R = Me (**6**),[5a] Et (**7**),[5a] CH═CH_2 (**8**)[5b]], and the others were only generated in solution [R = Pr (**9**), ^{i}Pr (**10**), ^{t}Bu (**11**), $CH_2C(CH_3)_3$ (**12**)].[5c] Complexes **6** and **7** react with Br_2 to yield CH_3Br, C_2H_5Br, and MoO_2Br_2(bpy). To demonstrate the carbanionic reactivity of the molybdenum-bound alkyl groups, these complexes were also reacted with hydroxycobalamine and yielded methyl and ethylcobalamine and the correspondent cobaloxime. Compound **6** was also found to methylate Hg^{2+} and As^{3+}.

A modification of the synthetic method used for MoO_2-BrR(bpy) afforded the preparation of complexes of composition MoO_2R_2(bpy) (Chart 1). The first compound of this type obtained, MoO_2Me_2(bpy) (**13**),[6] was synthesized by reacting MoO_2Br_2(bpy) with methylmagnesium chloride in THF. This compound exhibits a high thermal stability (melting point = 230 °C) and is stable under air. The decomposition temperatures were found to be related to the stability of the Mo−C bond. Decomposition was observed to occur on prolonged heating in basic or acidic solutions. Several other complexes, namely, ethyl (**14**),[7c] propyl (**15**, **16**),[7c] butyl (**17**, **18**),[7c] neopentyl (**19**),[7a] cyclopentyl (**20**),[7c] cyclohexyl (**21**),[7c] benzyl (**22**),[7b] several aryl (**22**−**30**),[7d,e,8] and organosilicium (**31**)[7f] derivatives, were synthesized in the following years using different Grignard reagents.

Chart 1



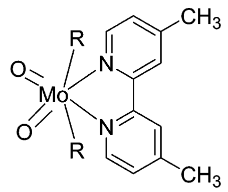
R = CH_3 (**13**),
C_2H_5 (**14**),
n-C_3H_7 (**15**),
i-C_3H_7 (**16**),
n-C_4H_9 (**17**),
i-C_4H_9 (**18**),
CH_2-$C(CH_3)_3$ (**19**),
c-C_5H_9 (**20**),
c-C_6H_{11} (**21**),
C_6H_5 (**22**),
o-$CH_3C_6H_4$ (**23**),
p-$CH_3C_6H_4$ (**24**),
p-ClC_6H_4 (**25**),
p-$CH_3OC_6H_4$ (**26**),
$CH_2C_6H_5$ (**27**),
o-$CH_3C_6H_4$ CH_2 (**28**),
p-$CH_3C_6H_4CH_2$ (**29**),
$CH_2CH_2C_6H_5$ (**30**)
CH_2SiMe_3 (**31**).

Most of the obtained Mo complexes have also been structurally characterized by X-ray single-crystal analysis. The most temperature sensitive among them are those complexes with hydrogens in *β*-position like the diethyl derivative (**14**) or those where the steric effects cause an additional Mo−C bond labilization, for example, the *c*-C_6H_{11} derivative (**21**).

The derivatives $MoO_2(CH_2CH_2Ph)_2$(bpy) (**30**), MoO_2(*p*-$MeC_6H_4CH_2)_2$(bpy) (**29**), and MoO_2(*o*-$MeC_6H_4CH_2)_2$(bpy) (**28**) were synthesized as microcrystalline solids that require no special handling precautions.[8] The latter compound could be synthesized with higher yields using an organolithium instead of a Grignard reagent. Stirring complexes **28** and **29** for 5 days in acetonitrile leads to a color change and to the detection of oxygenated organic products such as *p*-methylbenzaldehyde and *p*-methylbenzyl alcohol in the solution. An intramolecular rather than an intermolecular oxygen atom transfer throughout a pseudo "keto−enol" tautomerism has been proposed to explain these results. Solutions of complex **30** show no visual changes during prolonged stirring in acetonitrile, and no organic products are formed at any time. The authors assume that in this case *β*-elimination is not possible and/or the tautomeric equilibrium is not favored. In all cases, in the presence of a moderate excess of triphenylphosphine, no phosphine oxide was detected in solution even after prolonged reaction times.

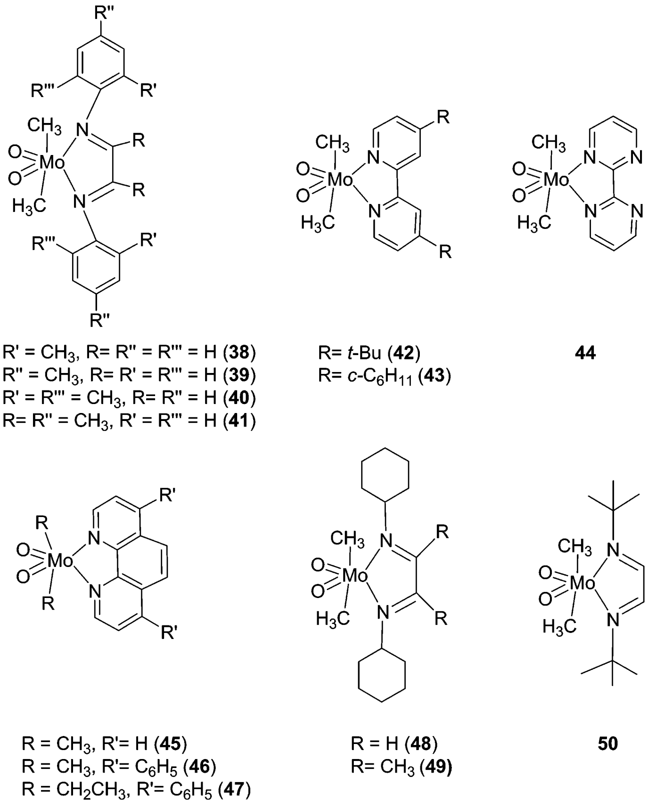
In 1991 the first examples of $MoO_2R_2L_2$ complexes were reported, where L_2 was not bpy but 4,4′-dimethyl-2,2′-dipyridyl (Me-bpy), conferring a higher solubility to the synthesized compounds.[9] The molybdenum(VI) compounds $MoO_2R_2L_2$ [L_2 = 4,4′-dimethyl-2,2′-dipyridyl, R = CH_2-$CHMe_2$ (**32**), CH_2CMe_3 (**33**), $(CH_2)_4CH{=}CH_2$ (**34**), CH_2Ph (**35**), $CH_2C_6H_4Me$-*p* (**36**), and CH_2CMe_2Ph (**37**) (Chart 2)] were prepared by reaction of the corresponding Grignard reagents with $MoO_2Br_2L_2$, followed by aerobic oxidation of the resulting reaction mixture. The authors, Vetter and Sen, executed a very detailed study of the decomposition reactions of these compounds. The complexes were found to decompose in solution under an inert gas atmosphere at varying rates, the course or rates of the reaction being not influenced by the nature of the solvent in use. As the decomposition progresses, insoluble molybdenum oxides are formed and

Chart 2



R = $CH_2CH(CH_3)_2$ (**32**)
$CH_2C(CH_3)_3$ (**33**)
$(CH_2)_4CH=CH_2$ (**34**)
$CH_2C_6H_5$ (**35**)
p-$CH_3C_6H_4CH_2$ (**36**)
$CH_2C(CH_3)_2C_6H_5$ (**35**)

Chart 3



R' = CH_3, R= R" = R''' = H (**38**)
R" = CH_3, R= R' = R''' = H (**39**)
R' = R''' = CH_3, R= R" = H (**40**)
R= R" = CH_3, R' = R''' = H (**41**)

R= t-Bu (**42**)
R= c-C_6H_{11} (**43**)

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R = CH_3, R'= H (**45**)
R = CH_3, R'= C_6H_5 (**46**)
R = CH_2CH_3, R'= C_6H_5 (**47**)

R = H (**48**)
R= CH_3 (**49**)

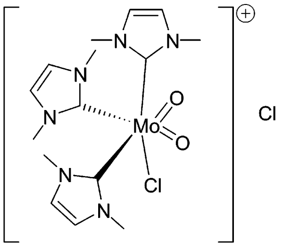
50

in solution quantitative amounts of hydrocarbons can be detected. The anaerobic decomposition mode associated with a given complex is a sensitive function of the hydrocarbyl group R. If β-hydrogens are present on R, equal amounts of alkane and alkene are formed through a β-hydrogen abstraction pathway. When β-hydrogens are absent from R, the free radical $R^{\bullet}$ formed by Mo−R homolysis is the predominant product.

Other complexes of the type $MoO_2R_2L_2$ (R = CH_3, C_2H_5; L = bidentate Lewis base ligand) were reported by the research groups of Gonçalves, Kühn, and Romão during the past decade.[10a−e] A wide range of compounds was synthesized, bearing a variety of bidentate ligands of the type 1,4-diazobutadiene (R-DAB), with different R groups, phenanthroline, and substituted bypiridines (Chart 3).

Besides providing access to more soluble complexes, which are better amenable to reactivity and spectroscopic characterization than the modestly soluble MoO_2R_2(bpy) derivatives, the different stereochemical and electronic characteristics of these ligands impart distinct reactivities to the MoO_2R_2 core. The complexes were obtained by alkylation of $MoO_2X_2L_2$ (X = Cl, Br) with the appropriate Grignard reagent.[10a,c−e]

The first report of a dioxo molybdenum N-heterocyclic carbene complex (**51**) was provided by the research group of Herrmann.[10f] The cationic carbene complex was obtained by the reaction of $MoO_2Cl_2(THF)_2$ with an N-heterocyclic carbene, namely, 1,3-dimethylimidazoline-2-ylidene, in THF at −20 °C. On the basis of spectroscopic evidence the authors suggested that the complex should exhibit two equivalent carbene ligands in the plane of the *cis*-dioxygen molybdenum core and the third carbene ligand in a position *trans* to the chloro ligand. In solution ($CDCl_3$, DMSO-d_6) the complex is prone to hydrolysis. First, $MoO_2Cl_2L_2$ (L = carbene ligand) and then, later, the imidazolium salt were detected as hydrolysis products by ^{13}C NMR.



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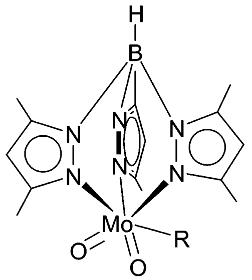
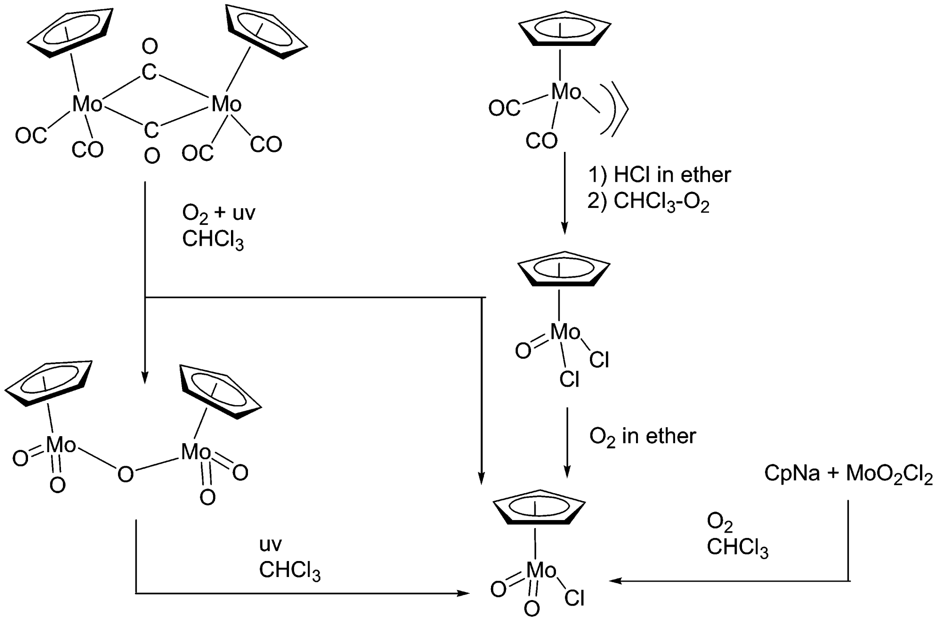
Early attempts to synthesize compounds of the type Tp^*MoO_2R [Tp* = hydridotris(3,5-dimethyl-1-pyrazolyl)-borate] using Grignard reagents led to the formation of a mixture of up to six components (likely to possess di- or polynuclear structures), in which the main product was a mixed-valence dinuclear complex of the formula $Tp^*Mo^{V}OCl(\mu\text{-}O)Mo^{VI}O_2Tp^*$.[11a] A few years later they were reported almost simultaneously and independently by Sundermeyer et al. and Onishi et al. using different synthetic routes.[11b,c] The group of Onishi reported the synthesis and characterization of Tp^*MoO_2R [R = CH_3 (**52**), $(CH_3)_3SiCH_2$) (**53**)], obtained by reaction of excess CH_3MgI and $(CH_3)_3SiCH_2MgCl$ with Tp^*MoO_2Cl at −10 °C. The latter authors reported that the same reaction conducted at room temperature did not lead to the formation of the alkylated derivatives in a detectable extent, which once more points to the extreme sensitivity of these type of reactions to the conditions used experimentally. Sundermeyer et al. obtained compound **52** in higher yields than Onishi by reacting Tp^*MoO_2Cl with $AlMe_3$ in toluene.



R = CH_3 (**52**), $CH_2Si(CH_3)_3$ (**53**)

The reaction is inhibited in THF, and therefore Sundermeyer et al. were led to believe that the first step of the reaction consists of an electrophilic attack of the free $AlMe_3$ (not blocked by a coordinating solvent) to the chloro or oxo functionality of the molybdenum complex, followed by a chloro−methyl exchange leading to a Lewis acid adduct

Scheme 1



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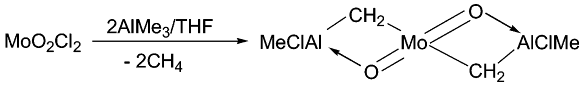
intermediate from which the desired compound can be obtained by hydrolytic workup.

The reaction of MoO_2Cl_2 with 2 equiv of $AlMe_3$[12] leads, via cleavage of 2 equiv of methane, to a bismethylene complex (**54**), the hypothetical structure of which shows similarities to the Tebbe reagent (eq 1).



(**1**)

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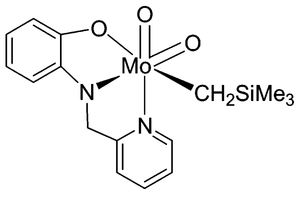
Although its structure could not be established beyond any doubt due to decomposition problems, this species was found to transfer in the course of carbonyl olefination about 1.5 CH_2 units per Mo atom to benzaldehyde, the latter being present in excess. The hypothetical compound is thermolabile. Consequently, the products of carbonyl olefination are only isolable in good yields when, before addition of the substrate, the molybdenum halide is first allowed to react with $AlMe_3$ at −70 °C and the reaction mixture is heated to 20 °C until evolution of CH_4 ceases.

The first example of a dioxomolybdenum(VI) alkyl complex supported by a N_2O-type ancillary ligand (**55**) was obtained by reacting $MoO_2(L)Cl$ with the Grignard reagent Me_3SiCH_2MgCl.[13] The precursor complex $MoO_2(L)Cl$ can be obtained from $MoO_2Cl_2(DME)$ (DME = 1,2-dimethoxyethane) and HL [2-*N*-(2-pyridylmethyl)aminophenol]. Attempts to prepare other dioxomolybdenum(VI) alkyl complexes by treating the chloro precursor with the Grignard reagents RMgX (R = CH_3, C_2H_5, $C_6H_4{}^tBu$-4) were reported to have failed. The complex obtained, $MoO_2(L)(CH_2SiMe_3)$ (**55**), is virtually insoluble in hydrocarbons and diethyl ether, but readily soluble in dipolar aprotic solvents. This compound could be alternatively obtained from $[MoO_2L]_2O$ with the appropriate Grignard reagent.



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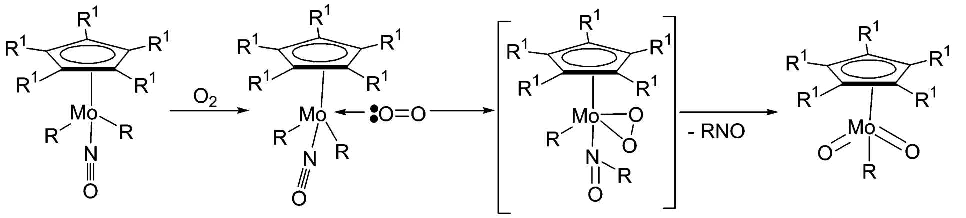
2.2. Dioxomolybdenum(VI) Complexes with a Cyclopentadienyl Ligand (Mo–C π Bond)

In 1963 Cousins and Green reported the first example of an organometallic molybdenum(VI) dioxo complex, $CpMoO_2Cl$ (**56**),[1h] being one of the first monomeric high oxidation state organometallic oxides ever obtained. This complex, however, was synthesized in very low yields and adventitiously as the only isolable product from air oxidation of $CpMo(CO)_2(\pi\text{-}C_3H_5)$ in the presence of HCl. Green and co-workers continued to develop this chemistry and rationalized several synthetic methods of obtaining $CpMoO_2Cl$ (**56**)[14] and the corresponding bromo derivative $CpMoO_2Br$ (**57**)[14b] (obtained by UV irradiation of the pentoxide $[CpMoO_2]_2O$ in bromoform). Both **56** and **57** are yellow solids, stable under nitrogen atmosphere, decomposing slowly under air and rapidly in solution. Compound **56** was found to be soluble in both liquid and supercritical (45 °C, 125 bar) CO_2, showing no signs of reaction with CO_2.[2c] The different synthetic pathways developed by Green and co-workers are shown in Scheme 1.

As mentioned before, the yields obtained via these synthetic procedures are generally low and the synthetic pathways are quite unspecific for obtaining $CpMoO_2Cl$, because several other species (not depicted in the scheme) such as mono oxo and dimeric complexes are also formed. These difficulties are probably the cause for a gap between these early works and the next work published dealing with Cp dioxo molybdenum complexes.

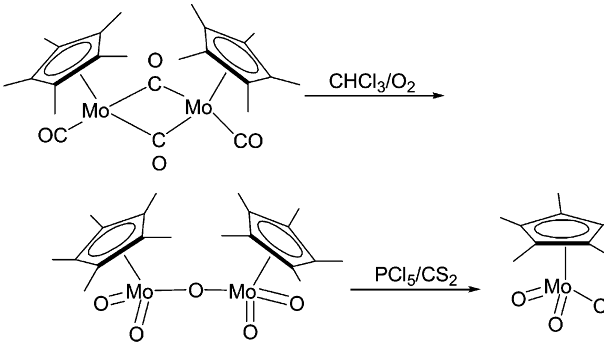
In 1988, possibly inspired by the recent developments in the preparation and characterization of diverse organometallic oxo complexes, particularly of Cp^*ReO_3, synthesized independently nearly at the same time by Herrmann et al. and

Scheme 2



R= CH_3, R^1 = H (**59**)
R = CH_3, R^1 = CH_2SiCH_3 (**60**)
R= H, R^1 = H (**61**)
R = H, R^1 = CH_2SiCH_3 (**62**)

Sutton et al.,[15] Faller and Ma reported the synthesis of Cp^*MoO_2Cl (**58**) (Cp^* = pentamethyl cyclopentadienyl).[16] Complex **58** was obtained by oxidation of the carbonyl complex $[Cp^*Mo(CO)_2]_2$ with O_2 in chloroform to a μ-oxo bridged dimer and subsequent treatment of this dimer with PCl_5 (eq 2). A substantial improvement in the stability (the compound is thermally stable and can be handled easily in dry air), ease of preparation, and ease of separation from other reaction products was observed in comparison to its Cp counterpart. X-ray crystallography showed that **58** presents the expected mononuclear piano stool structure, but disorder between an oxygen and the chloride prevented the authors from obtaining accurate structural data.



(**2**)

58

The reactivity of **58** was additionally studied in some detail, for example, regarding its behavior in the presence of peroxides, acids, and alkylating agents. The alkylation of the chloro derivative with a methylmagnesium chloride gave as main product $Cp^*MoO(CH_3)_3$ and $Cp^*MoO_2CH_3$ (**59**) in residual amounts, but reaction of **58** with Me_3SiCH_2MgCl resulted in only $Cp^*MoO_2CH_2SiMe_3$ (**60**).

Still in 1988, Legzdins et al.[17a,b] reported a more general synthetic route to prepare complexes of the type $Cp'MoO_2R$ (**59**−**62**) (Cp' = Cp, Cp^*; R = CH_3, CH_2SiMe_3) (Scheme 2). The synthetic procedure consists of the exposure of 16-electron dialkyl nitrosyl complexes $Cp'Mo(NO)R_2$ to water and molecular oxygen, converting them into the corresponding dioxo alkyl compounds in high yields (>80%). Curiously, the yields obtained in the absence of water were ~15% lower, and no clear explanation could be given for this observation. The spectroscopic properties of the compounds reported by the research group of Legzdins are consistent with the familiar three-legged piano stool molecular structures having mirror symmetry at the central metal atom. The mechanism of the preparation of $Cp'MO_2R$ type compounds was studied in detail for the equivalent tungsten complex $Cp^*W(NO)(CH_2SiMe_3)_2$, and the molybdenum complexes were assumed to follow a similar formation pathway. The authors suggested the mechanism to proceed first via coordination of molecular oxygen to the 16-electron metal center in the dialkyl nitrosyl reactant (a Lewis acid), forming a simple 1:1 adduct, followed by migratory insertion of the bound nitrosyl group into one of the Mo−C σ bonds. The resulting peroxo alkylnitroso complex could then expel the nitrosalkane from the metal's coordination sphere in the final step and rearrange concomitantly to the final dioxo alkyl product. Treatment of the complexes **59**−**62** with 30% H_2O_2 (aq) in Et_2O results in their clean conversion to $Cp'MoO(\eta^2\text{-}O_2)R$ (Cp' = Cp, Cp^*; R = Me, $SiMe_3$).

While studying the reactivity of Cp-metal-nitrosyl complexes toward oxygen, Hubbard et al. found that $CpMo(NO)_2Cl$ and $Cp^*Mo(NO)_2Cl$ are transformed in the presence of oxygen into **56** and **58**, respectively.[17c] Experimental evidence led the authors to suggest that the reaction pathway involves formation of the highly oxidative NO_2, which is formed from O_2 and NO, easily liberated from the $Cp'Mo(NO)_2Cl$ complexes. The work also showed that treatment of $Cp'Mo(NO)_2CH_2X$ complexes with O_2 led to the initial formation of CH_2O together with the generation of $Cp'Mo(NO)_2Cl$. This shows that the Mo−CH_2 moiety is more sensitive to oxidation than the Mo−NO moiety. In contrast to the $Cp'Mo(NO)_2CH_2X$ derivatives, alkyl complexes $CpMo(NO)_2R$ (R = Me, Et) and $Cp^*Mo(NO)_2R$ react with O_2 to originate $CpMoO_2R$ [R = Me (**61**), Et (**63**)] and Cp^*MoO_2Me (**59**), showing that in this case the Mo−C bond is surprisingly resistant to oxidative attack, probably due to the absence of a labile α substituent.

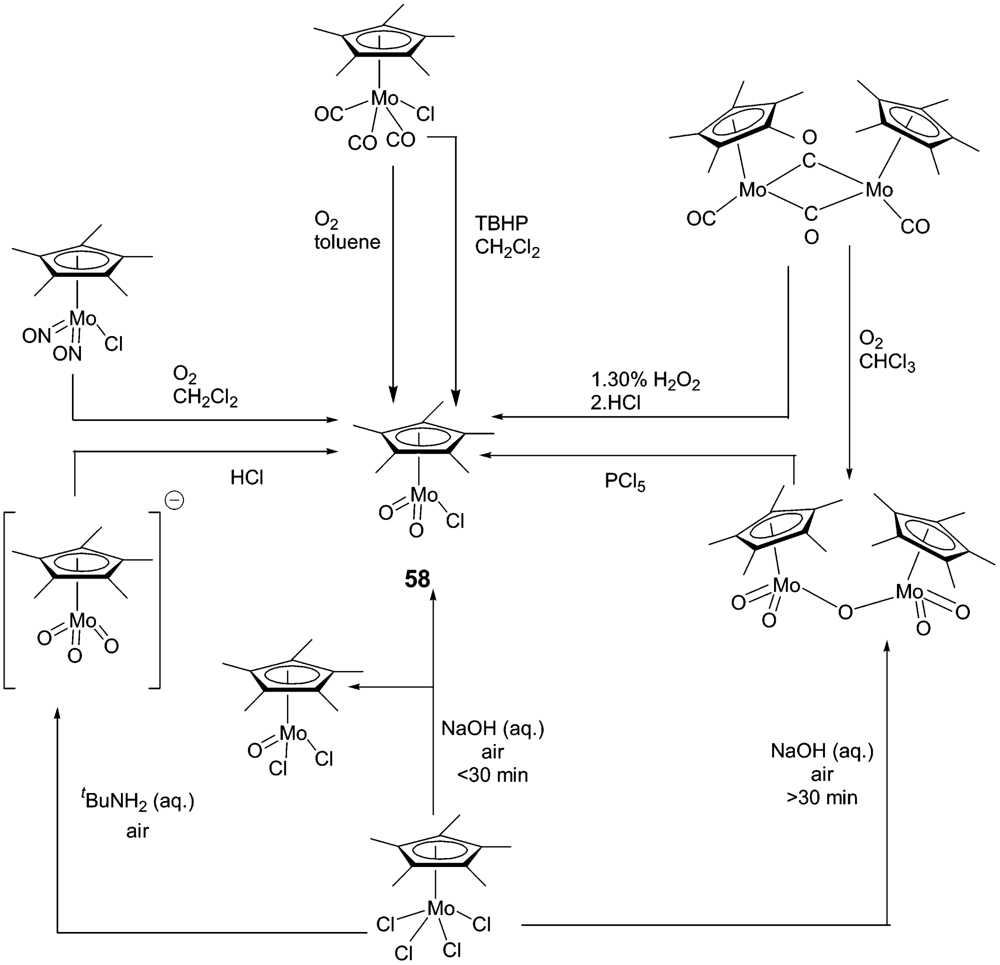
While trying to synthesize oxosulfido complexes, Faller and Ma reported the reactivity of Cp^*MoO_2R [R = CH_3 (**59**), CH_2SiMe_3 (**60**)] complexes in the presence of H_2S. **60** reacts with H_2S to afford $Cp^*MoOS(CH_2SiMe_3)$, but **59** afforded a complex believed to be $Cp^*MoO(\eta^2\text{-}S_2)Me$. Differences in reactivity were attributed by the authors to the smaller steric effect of the methyl group.[17d]

On the basis of the synthetic methodology of Legzdins et al., the research group of Royo obtained Cp^*MoO_2Br (**64**) and its hydrolysis product $[Cp^*MoO_2]_2\mu$-O by exposing the complex $[Cp^*Mo(NO)MeBr]_2$ to air and light for a week.[17e]

Several methods were reported in the following years for the synthesis of $Cp'MoO_2Cl$ [Cp' = Cp (**56**), Cp^* (**58**)] and will be briefly outlined in the next paragraphs. The several synthetic pathways developed for Cp^*MoO_2Cl (**58**) are summarized in Scheme 3.

Irradiation of $Cp^*Mo(CO)_3Cl$ in toluene under an oxygen purge for 2 h resulted in the formation of **58** in ~60% yield.[18] The use of the chloride carbonyl compound as precursor eliminated the need to conduct the reaction in chlorinated solvents. The reaction also generates some blue insoluble materials, from which the desired complex could be separated

Scheme 3



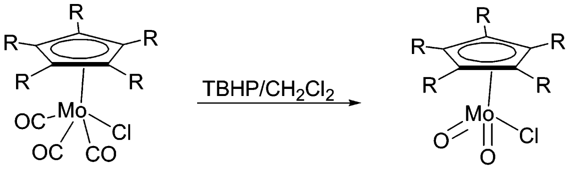
by extraction with toluene. Cp*MoCl$_4$ was found to yield **58** by reaction with aqueous NaOH in the presence of air.[19] Reaction times of <30 min led to the formation of a mixture of **58** and Cp*MoOCl$_2$ (the logical intermediate to the dioxo complex); on the other hand, the use of excess base and longer reaction times led to the formation of the already mentioned μ-bridged oxo dimer [Cp*MoO$_2$]$_2$O. This dimer is likely formed by hydrolysis of **58** to generate Cp*MoO$_2$-OH (**65**), which then undergoes condensation via loss of H$_2$O. The base used in these reactions also has a strong influence on the products obtained. In fact, when Cp*MoCl$_4$ is reacted with ^{t}BuNH$_2$ in the presence of water and air, an anionic trioxo complex [Cp*MoO$_3$]$^-$ is formed that can be isolated as its ^{t}BuNH$_3^+$ salt. The treatment of this complex with gaseous HCl gives a clean formation of **58**.

In 1994 Bottomley et al.[20a] reported the essentially quantitative (86% yield) synthesis of **58** by oxidation of [Cp*Mo(CO)$_2$]$_2$ with 30% aqueous H$_2$O$_2$ followed by immediate addition of HCl. The decomposition of **58** was found to be thermal, but accelerated by light and inhibited by dry oxygen. The authors assumed a radical reaction involving loss of the Cp* and/or Cl resulted in the formation of an intractable “molybdenum blue” [mixed oxides of Mo(VI) and Mo(V)[20b]].

Cp*MoO$_2$CH$_3$ (**59**) could also be obtained by hydrolysis of Cp*Mo(N^{t}Bu)$_2$CH$_3$ with excess aqueous HCl in THF.[21]

More than 20 years after the last synthesis presented by Green et al. for CpMoO$_2$Cl (**56**),[14c] the readily available (NH$_4$)$_2$Mo$_2$O$_7$ was used as a starting material and reacted with Me$_3$SiCl in 1,2-dimethoxyethane (DME), yielding MoO$_2$Cl$_2$(DME), which reacts with TlCp to originate **56**. However, the obtained yields were comparable to the ones previously reported.[22a] Cp(SiMe$_3$)MoO$_2$Cl (**66**) and Cp(SiMe$_3$)$_2$-MoO$_2$Cl (**67**) could also be obtained by reacting MoO$_2$Cl$_2$-(DME) with NaCp(SiMe$_3$) and NaCp(SiMe$_3$)$_2$.[22a] Product yields are also moderate even if the reaction is carried out at low temperature. The presence of the tri-methylsilane group in the cyclopentadienyl ring is responsible for an enhancement of the complex solubility in supercritical CO$_2$ (*sc*-CO$_2$) without significant modifications of the chemical properties of the metal.[22b]

A general and straightforward one-step synthesis of (η^5-C$_5$R$_5$)MoO$_2$Cl [R = H (**56**), CH$_3$ (**58**), CH$_2$Ph(Bz) (**68**)] complexes from their corresponding and readily available (η^5-C$_5$R$_5$)Mo(CO)$_3$Cl precursors was reported by Romão, Kühn et al.[23a] The desired complexes could be obtained in yields up to 75% by stirring a solution of the carbonyl precursors in CH$_2$Cl$_2$ with excess of *tert*-butyl hydroperoxide (TBHP) for ~2 h (eq 3). Dimethyldioxirane is unable to oxidatively decarbonylate the (η^5-C$_5$R$_5$)Mo(CO)$_3$Cl to (η^5-



(**3**)

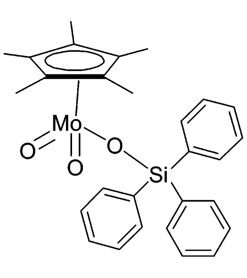
R = H (**56**), CH$_3$ (**58**), CH$_2$Ph (**68**)

$C_5R_5)MoO_2Cl$ in contrast to the examples of Cp^*ReO_3 and $[TpMo(CO)_3]^-$ [23b] (Tp = hydridotris(1-pyrazolyl)borate).

In comparison to the synthetic routes described previously, the oxidative decarbonylation of $(\eta^5\text{-}C_5R_5)Mo(CO)_3Cl$ provides a more general route comprising different substituents on the Cp ring. All three compounds originally described in the paper of Romão, Kühn et al.[23a] can be handled in air for brief periods of time, but are somewhat moisture sensitive in solution. $(\eta^5\text{-}C_5Bz_5)MoO_2Cl$ (**68**) is significantly more stable than its Cp and Cp* counterparts, probably due to the steric bulk of the Cp ligand. A noteworthy increase in stability, even in comparison to Cp^*MoO_2Cl (**58**), had been previously observed with the compound $[\eta^5\text{-}C_5Ph_4(2,5\text{-dimethoxyphenyl})]MoO_2Br$ (**69**).[24] Detailed spectroscopic examinations have shown that the carbonyl precursors show a stronger $Mo-(\eta^5\text{-}C_5R_5)$ interaction than their dioxo congeners.[23a] Among the oxo complexes, **68** displays the lowest force constant (297 Nm^{-1}) compared to 343 Nm^{-1} (for complex **56**) and 389 Nm^{-1} (for complex **58**), and therefore its higher stability cannot originate from electronic, but from steric reasons.

Recently, another synthetic method for $(\eta^5\text{-}C_5Bz_5)MoO_2Cl$ (**68**) was presented by Martins, Romão, Poli et al.[25] Treatment of the η^2-acyl complex $(\eta^5\text{-}C_5Bz_5)MoCl_3(COCH_3)$ with excess TBHP in CH_2Cl_2 afforded **68**. The obtained yield is much higher than the yields previously reported for other cyclopentadienyl complexes. An X-ray structure of **68** has been obtained. Attempts to alkylate complex **68** with allylmagnesium bromide and $ZnMe_2$ were not successful.

In attempts to obtain model compounds for transition metal complexes anchored on silica surfaces, complexes of the type Cp^*MoO_2OR [R = $Si(CH_2Ph)_3$ (**70**), $[(2,6\text{-}^iPr_2C_6H_3)N(SiMe_3)]$ (**71**)] were obtained.[26] $Cp^*MoO_2OSi(CH_2Ph)_3$ (**70**) was received by the reaction of $[CpMoO_3]^-$ with $(PhCH_2)_3SiCl$.[26b] This reaction also afforded as byproduct Cp^*MoO_2Cl (**58**). Reaction of Cp^*MoCl_4 and $[(2,6\text{-}^iPr_2C_6H_3)N(SiMe_3)]SiOH$ in the presence of triethylamine led to the isolation of $Cp^*MoORSi_2O_3(OH)_2$ [R = $[(2,6\text{-}^iPr_2C_6H_3)N(SiMe_3)]$], which on exposure to the atmosphere is oxidized to Cp^*MoO_2OR [R = $[(2,6\text{-}^iPr_2C_6H_3)N(SiMe_3)]$] (**71**).[26a]



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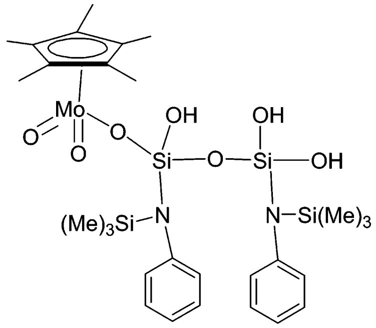
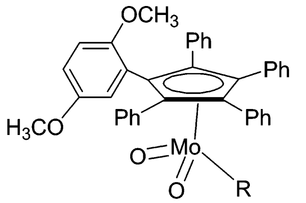


71

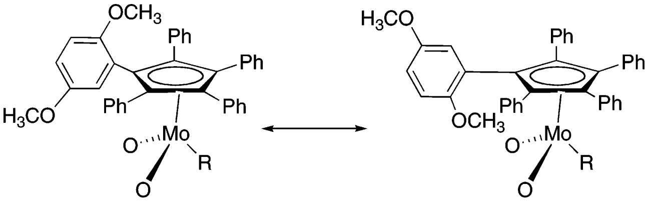
Tatsumi et al. explored the reactivity of molybdenum sulfur complexes and found that $Cp^*Mo(S\text{-}^tBu)_3$ reacts readily with O_2 to originate $Cp^*MoO_2(S\text{-}^tBu)$ (**72**). Interestingly, in this reaction, one of the three ^{t}BuS ligands remains intact during the reaction.[27]

The previously mentioned $[\eta^5\text{-}C_5Ph_4(2,5\text{-dimethoxyphenyl})]MoO_2Br$[24] (**69**) complex was obtained by heating a toluene solution of $[\eta^5\text{-}C_5Ph_4(2,5\text{-dimethoxyphenyl})]Mo(CO)_3Br$ at reflux temperature under a dioxygen atmosphere until the carbonyl bands disappear completely from the infrared spectrum (yield > 80%). **69** reacts cleanly with aliphatic alcohols (with phenols, no reaction takes place) to give nearly quantitative yields of the corresponding alkoxide complexes $[\eta^5\text{-}C_5Ph_4(2,5\text{-dimethoxyphenyl})]MoO_2OR$ [R = Me (**73**), Et (**74**), ^{i}Pr (**75**), ^{t}Bu (**76**)] (Chart 4). The alkoxide complexes are pale yellow microcrystalline solids, which are thermally and air stable but decompose easily in solution by hydrolysis, probably under formation of a μ-oxo dimer $[\{Mo(C_5Ph_4(2,5\text{-dimethoxyphenyl}))O_2\}_2(\mu\text{-}O)]$, but the reaction products could not be isolated. Detailed ^1H NMR spectroscopy studies were performed to investigate the fluctional behavior of these complexes. In fact, they show double the number of peaks expected. This is particularly evident for the phenyl methoxy groups at low temperatures. Changes in the spectra with temperature were completely reversible, suggesting that exchange between two conformers for the complexes takes place. The authors suggest that the underlying dynamic process is the exchange between distal and proximal rotamers arising from the hindered rotation of the dimethoxy phenyl group, because the rotation of the bulky cyclopentadienyl ligand with respect to the metal–ligand tripod is associated with high $\Delta G^\ddagger$ values.

Chart 4



R= Br (**69**), OMe (**73**), OEt (**74**), O^{i}Pr (**75**), O^{t}Bu (**76**)



Other examples of complexes in which the cyclopentadienyl ring shows a high degree of substitution are, for instance, $C_5H(^iPr)_4)MoO_2Cl$ (**77**) reported recently by Poli et al.[28a] The authors have followed the same synthetic approach as Geoffrey et al.[19] for Cp^*MoO_2Cl (**58**) and reported also the X-ray crystal structure of **77**. Following this work, Poli et al. also reported speciation studies of Cp*Mo complexes over the entire pH range in an essentially pure aqueous environment by stopped-flow kinetic analysis, on-line electrochemical flow cell, and electrospray mass spectroscopy,[28b–d] revealing the existence and stability among others of the complexes Cp^*MoO_2OH (**65**) (15% relative amount at a pH 4) and $[Cp^*MoO_2]^+$ (predominant species at pH <2.5). The authors also concluded that the inertness of the Cp*–Mo bond, which resists hydrolysis down to pH 0, has as consequence the blocking of three coordination positions, rendering the Cp^*Mo^{VI} species unable to form extended oligonuclear aggregates.

3. Structural and Spectroscopic Characterization

3.1. Structural Studies

The mononuclear organomolybdenum(VI) dioxo complexes, which have been characterized by means of X-ray

Table 1. Selected Bond Lengths and Bond Angles of $MoO_2R_2L_2$ Compounds

			distance/Å			angle/deg			
compd no.	R =	L_2 =	Mo═O	M─C	M─N	O─Mo─O	C─Mo─C	N─Mo─N	ref
13	CH_3	bpy	1.707(2) 1.708(2)	2.189(3) 2.194(2)	2.314(2) 2.346(2)	110.20(9)	149.03(10)		6
44	CH_3	bipyrimidine	1.699(2) 1.717(2)	2.187(3) 2.190(2)	2.364(2) 2.336(2)	110.26(9)	140.0(2)	67.41(7)	10c
14	C_2H_5	bpy	1.695(6) 1.709(5)	2.21(2) 2.193(8)	2.338(6) 2.313(6)	110.4(3)	151.9(3)	69.0(2)	7c
19	*neo*-C_5H_{11}	bpy	1.709(3) 1.706(3)	2.237(5) 2.235(5)	2.348(4) 2.317(4)	110.0(2)	145.8(2)	68.6(1)	7a
31	CH_2SiMe_3	bpy	1.71(2) 1.74(2)	2.20(2) 2.20(2)	2.36(2) 2.34(2)	114.4(5)	149.5(6)	68.8(4)	7f
22	Ph (C_6H_5)	bpy	1.701(3) 1.713(4)	2.204(5) 2.193(5)	2.327(5) 2.342(5)	110.5(2)	151.4(2)		7d
27	C_6H_5─CH_2-	bpy	1.68(1) 1.71(1)	2.24(2) 2.26(2)	2.27(1) 2.30(1)	110.2(6)	155.5(8)	69.9(5)	7b
26	*p*-MeO─C_6H_4-	bpy	1.700(2) 1.712(2)	2.199(3) 2.205(3)	2.291(2) 2.343(2)	109.7(1)	153.6(1)	68.92(9)	7d
28	*o*-Me─C_6H_4─CH_2─	bpy	1.712(2)	2.235(4)	2.344(3)	113.1(1)	152.4(1)		8b

Table 2. Selected Bond Lengths and Bond Angles of Other MoO_2 Compounds

		distance/Å		angle/deg		
compd no.	compd	Mo═O	M─C	O─Mo─O	C─Mo─C	ref
1	$MoO_2(mes)_2$	1.699(3)	2.101(3)	109.5(1)	112.5(2)	2d
4	$MoO_2(mes)$═C(mes)PBu_3	1.69(2) 1.68(2)	1.95(1) (Mo═C) 2.15(5) (Mo-mes)	114(1)	105.5(5)	3g
5	$MoO_2(mes)_2CH_2PBu_3$	1.688(5) 1.706(5)	2.249(7) (Mo─CH_2P) 2.224(6) (Mo-mes) 2.227(7) (Mo-mes)	113.5(3)	151.0(2) 75.3(2) (mes-Mo-mes)	3h
2	$LiMoO_2(Me)_2(mes)(OEt_2)_2$	1.731(2) 1.730(2)	2.175(2) 2.165(2) 2.214(2) (Mo-mes)	119.53(8)	144.62(9) (Me-Mo-Me) 72.67(9) (Me-Mo-mes)	3b

Table 3. Selected Bond Lengths and Bond Angles of L_3MoO_2X Compounds

			distance/Å			angle/deg			
compd no.	L_3 =	X =	Mo═O	M─Cp	M─X	O─Mo─O	Cp─Mo─O	X─Mo─O	ref
71	Cp*	R[a]	1.708(3) 1.711(3)		1.915(2)	105.72(14)		104.36 105.78	26a
77	$C_5H(i\text{-}Pr)_4$	Cl	1.720(2) 1.700(2)	2.113(3)	2.3251(7)	106.83(11)	118.1(2) 117.2(3)	102.15(8) 101.54(8)	28a
73	$C_5Ph_4(2,5\text{-}(MeO)_2C_6H_3)$	OMe	1.708(2) 1.677(3)	2.546(3) 2.599(3) 2.497(3) 2.433(3) 2.398(3)	1.881(2)	107.1(2)		101.1(2) 103.1(1)	24
68	$C_5(CH_2Ph_5)$	Cl	1.891(4)[b] 1.748(5)	2.0894(10)	2.282(2)[b]	109.0(2)	116.04(13) 115.69(18)	100.32(14) 102.1(2)	25
			Mo═O	M─Tp	M─X	O─Me─O	Tp─Mo─O	X─Mo─O	
52	Tp*	Me	1.736(5) 1.713(5)	2.169(6) 2.344(6) 2.336(6)	2.168(8)	103.8(2)	152.6(2) 168.8(2) 167.7(2)		11b

[a] R = $[(2,6\text{-}iPr_2C_6H_3)N(SiMe_3)]_2SiO_2(OH)_3$. [b] Possibility of positional disorder between O and Cl positions.

studies, are listed in Tables 1−3. The dioxo complexes exhibit four different types of geometries according to the type of ligands present. $MoO_2(mes)_2$ (**1**) and $MoO_2(mes)$═C(mes)PBu_3 (**4**) present a tetrahedral geometry.[2d,3g] In the case of **4** bond lengths and angles indicate the sp^2 character of the Mo═C(mes) bond, which is almost coplanar to Mo, P, and C of the same mesityl group.[3g] $MoO_2(mes)_2CH_2PBu_3$ (**5**) and $LiMoO_2Me_2mes(OEt)_2$ (**2**) present a distorted trigonal bipyramidal geometry.[3b,h] Complexes of the type $MoO_2R_2L_2$[6,7a−d,8b,10c] and Tp*MoO_2Me[11b] (**52**) present a distorted octahedral geometry, and complexes of the type Cp′MoO_2X present a piano stool geometry.[24,26a,28a]

The mean value of the Mo═O bond distances in mononuclear organomolybdenum(VI) dioxo complexes is 1.713 Å. Averages of Mo═O bond distances for each geometry type are listed in Table 4. Tetrahedral complexes have the shortest average Mo═O bonds. In the case of the complexes with distorted octahedral geometry, the average Mo═O bond

Table 4. Average Mo═O Bond Lengths and O─Mo─O Bond Angles According to Complex Geometry

geometry	distance/Å Mo═O	angle/deg O─Mo─O
all (average)	**1.713**	**110**
tetrahedral	1.690	112
distorted trigonal bipyramidal	1.714	116
distorted octahedral	1.716	107
piano stool	1.733	107

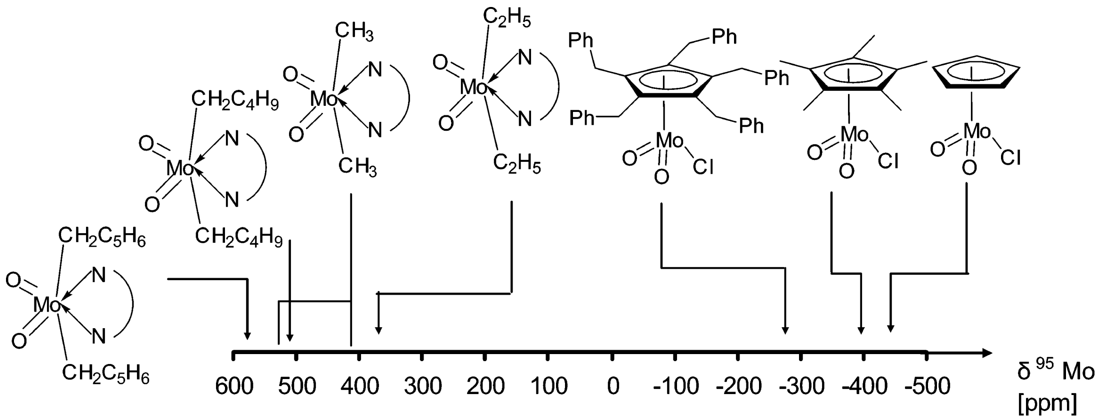


Figure 1. Graphical representation of ^{95}Mo NMR chemical shifts. Arrows indicate values, and merged lines indicate an interval of values. The reference standard, considered as 0 ppm, was a 2 M solution of Na_2MoO_4 in D_2O at an apparent pH of 11.

Table 5. ^{95}Mo NMR Chemical Shifts of $MoO_2R_2L_2$ Compounds

compd no.	R =	L_2 =	^{95}Mo δ^{a}	$\Delta v_{1/2}^{b}$/Hz	solvent	ref
13	CH_3	bpy	425		CH_3CN	10c
19	$CH_2C_4H_9$	bpy	500		not stated	29
27	$CH_2C_6H_5$	bpy	576		not stated	29
42	CH_3	^{t}Bu-bpy	432	170	$CDCl_3$	10a
44	CH_3	bipyrimidine	425	210	CD_2Cl_2	10a
			422		CH_2Cl_2	10c
38	CH_3	*o*-tolyl-DAB	526	200	CD_2Cl_2	10a
39	CH_3	*p*-tolyl-DAB	471	170	$CDCl_3$	10a
45	CH_3	phen	447	150	CD_2Cl_2	10a
46	CH_3	4,7-diphenyl-1,10-phen	436	210	CD_2Cl_2	10a
48	CH_3	CYDAB	469	130	$CDCl_3$	10a
50	CH_3	^{t}Bu-DAB	520	320	$CDCl_3$	10a
43	CH_3	*n*-hexyl-bpy	424	740	$CDCl_3$	10e
47	C_2H_5	4,7-diphenyl-1,10-phen	370	200	CD_2Cl_2	10a

[a] The reference standard, considered as 0 ppm, was a 2 M solution of Na_2MoO_4 in D_2O at an apparent pH of 11. [b] $\Delta v_{1/2}$ = line width at the half-height of the peak.

Table 6. ^{95}Mo NMR Chemical Shifts of L_3MoO_2X Compounds

compd no.	L_3 =	X =	^{95}Mo δ^{a}	solvent	ref
56	Cp	Cl	−448	$CDCl_3$	23a
58	Cp*	Cl	−399	$CDCl_3$	23a
68	$C_5(CH_2Ph)_5$	Cl	−282	$CDCl_3$	23a

[a] The reference standard, considered as 0 ppm, was a 2 M solution of Na_2MoO_4 in D_2O at an apparent pH of 11.

is 1.716 Å, but it is important to mention that for complexes of the type $MoO_2R_2L_2$ the average Mo═O bond length is 1.708 Å and that for complex Tp^*MoO_2Me (**52**) the Mo═O bond length is 1.725 Å. The average O—Mo—O bond angle is 110°. Mo—C bond distances vary between 1.95 and 2.599 Å with an average of 2.23 Å. This large interval includes several types of bonds present in the different complexes. The average of Mo—*C*H_3 bond length in distorted octahedral complexes is 2.210 Å. For Mo—mes the average bond length is 2.183 Å, and for Mo—Cp the average bond length determined for two complexes is 2.382 Å. For complex **4** the Mo═C bond length is 1.95 Å.

3.2. Spectroscopic Studies

^{95}Mo NMR studies are a good spectroscopic tool to differentiate between octahedral complexes of the type $MoO_2R_2L_2$ and piano stool complexes of the type $Cp'MoO_2Cl$ (see Tables 5 and 6 and Figure 1) because ^{95}Mo NMR signals of the later are shifted to negative values (refer to Tables 5 and 6 for reference standards). The main difference between these two ligand groups regarding their electronic properties is the higher π-acceptor capability of the diazobutadiene ligands. Complexes of the type $Cp'MoO_2X$ display ^{95}Mo NMR signals between −448 and −282 ppm. Given the structural similarities of the three complex types, it would be tempting to draw conclusions about the electronic richness of the metal center in this case. However, much caution must be taken in interpreting ^{95}Mo NMR chemical shifts.[23a] Teruel et al. have reported a study that correlates ^{95}Mo NMR chemical shifts, p and d orbital population estimated by a semiempirical molecular orbital method (CNDO), and oxygen transfers for several dioxo molybdenum complexes.[29] Two mononuclear organomolybdenum(VI) dioxo complexes, $MoO_2(CH_2C_4H_9)_2(bpy)$ (**19**) and $MoO_2(CH_2C_6H_5)_2(bpy)$ (**27**), have been included in this study. The authors concluded that the studied complexes exhibiting more negative chemical shifts tolerate an oxygen donor nucleophilic attack with concomitant intermolecular oxygen transfer. In contrast, among the studied compounds, the ones exhibiting more positive chemical shifts, such as **19** and **27**, will not be as reactive to oxygenation but to electrophilic attack instead.[29]

Table 7. ^{17}O NMR Chemical Shifts of ^{17}O Labeled Compounds

compd no.	complex	^{17}O δ	$\Delta v_{1/2}^{b}$/Hz	solvent	ref
44	$MoO_2(CH_3)_2$(bipyrimidine)	843		CH_2Cl_2	10c
43	$MoO_2(CH_3)_2$(*n*-hexyl-bpy)	845	720	$CDCl_3$	10e
70	$Cp^*MoO_2OSi(CH_2Ph)_3$	843 (MoO_2) 128.9 (Mo−O−Si)		CD_2Cl_2	26b

[a] The reference standard, considered as 0 ppm, was H_2O.[17] [b] $\Delta v_{1/2}$: line width at the half-height of the peak.

^{17}O NMR data of mononuclear organomolybdenum(VI) dioxo complexes are scarce (Table 7) and have not yet been utilized in probing ligand effects on the MoO_2 fragment. The ^{17}O NMR chemical shifts attributed to Mo═O bond in complexes examined to date are found at ~845 ppm (reference standard, considered as 0 ppm, was H_2O[17]).

^{1}H NMR data are listed in Tables 8−11. In the case of $MoO_2R_2L_2$ complexes (Table 8) the ^{1}H NMR chemical shifts of Mo−C*H* protons are mainly determined by the type of alkyl substituent present in the complex. In the specific case of $MoO_2Me_2L_2$ complexes, ^{1}H NMR chemical shifts of Mo−C*H*$_3$ protons appear between 0.43 and 0.87 ppm (Figure 2) and can be related to the type of base present. Bipyridyl- and bipyrimidine-derived complexes present chemical shifts in the range of 0.55−0.59 ppm, phenanthroline presents a chemical shift at 0.43 ppm, cyclohexyl diazobutadiene

Table 8. Selected ^{1}H NMR Chemical Shifts of $MoO_2R_2L_2$ Compounds

compd no.	R =	L_2 =	^{1}H δ (Mo−C*H*)	solvent	ref
13	CH_3	bpy	0.58 (s)	CD_3OD	6
50	CH_3	^{t}Bu-bpy	0.55 (s)	CD_2Cl_2	10a
44	CH_3	bipyrimidine	0.56 (s)	CD_2Cl_2	10a
38	CH_3	*o*-tolyl-DAB	0.86 (s)	CD_2Cl_2	10a
39	CH_3	*p*-tolyl-DAB	0.87 (s)	$CDCl_3$	10a
40	CH_3	2,6-Me-phenyl-DAB	0.87 (s)	CD_2Cl_2	10a
45	CH_3	phen	0.43 (s)	CD_2Cl_2	10a
46	CH_3	4,7-diphenyl-1,10-phen	0.43 (s)	CD_2Cl_2	10a
48	CH_3	CYDAB	0.50 (s)	$CDCl_3$	10a
49	CH_3	Me-CYDAB	0.50 (s)	$CDCl_3$	10a
50	CH_3	^{t}Bu-DAB	0.85 (s)	$CDCl_3$	10a
41	CH_3	*p*-tolyl-2,3-dimethyl-DAB	0.82 (s)	CD_2Cl_2	10d
43	CH_3	*n*-hexyl-bpy	0.59 (s)	$CDCl_3$	10e
14	C_2H_5	bpy	1.34 (C_2H_5)	$CDCl_3$	7c
47	C_2H_5	4,7-diphenyl-1,10-phen	1.15 (t, C*H*$_3$) 3.42 (m, C*H*$_2$)	CD_2Cl_2	10a
32	*i*-C_4H_9	Me-bpy	1.33 (d, C*H*$_3$) 1.43 (d, C*H*$_2$) 2.78 (7plet,C*H*)	C_6D_6	9
19	*neo*-C_5H_{11}	bpy	0.95 (s, C*H*$_3$) 1.15 (s, C*H*$_2$)	$CDCl_3$	7a
33	*neo*-C_5H_{11}	Me-bpy	1.48 (s, C*H*$_3$) 1.67 (s, C*H*$_2$)	C_6D_6	9
31	CH_2SiMe_3	bpy	0.05 (s, C*H*$_3$) 0.10 (s, C*H*$_2$)	$CDCl_3$	7f
34	$CH_2{=}CH(CH_2)_4-$	Me-bpy	1.41−1.56 (br)	C_6D_6	9
22	Ph (C_6H_5)	bpy	7.43 (m, ring) 7.20 (m, ring)	CD_2Cl_2	7d
27	$C_6H_5-CH_2-$	bpy	3.10 (s, C*H*$_2$) 5.95 (dd, ring) 6.50 (m, ring)	$CDCl_3$	7b
35	$C_6H_5-CH_2-$	Me-bpy	3.10 (s, C*H*$_2$)	C_6D_6	9
24	*p*-Me-C_6H_4-	bpy	2.06 (s, C*H*$_3$) 6.68 (d, ring) 7.07 (d, ring)	CD_2Cl_2	7d
23	*p*-Me−C_6H_4-	bpy	2.53 (s, C*H*$_3$) 6.45 (m, ring) 6.86 (m, ring) 7.11 (m, ring)	CD_2Cl_2	7d
25	*p*-Cl−C_6H_4-	bpy	7.43 (m, ring) 7.52 (m, ring)	CD_2Cl_2	7d
26	*p*-MeO−C_6H_4-	bpy	3.57 (s, C*H*$_3$) 6.41 (m, ring) 7.09 (d, ring)	CD_2Cl_2	7d
28	*o*-Me−$C_6H_4-CH_2-$	bpy	2.20 (s, C*H*$_3$) 2.46 (s, C*H*$_2$)	CD_2Cl_2	8a
29	*p*-Me−$C_6H_4-CH_2-$	bpy	2.04 (s, C*H*$_3$) 2.77 (s, C*H*$_2$)	CD_2Cl_2	8b
36	*p*-Me−$C_6H_4-CH_2-$	Me-bpy	3.30 (s, C*H*$_2$)	C_6D_6	9
30	$C_6H_4-CH_2-CH_2-$	bpy	1.44 (m, C*H*$_3$) 3.16 (m, C*H*$_2$)		8b
37	$C_6H_4-C(Me)_2-CH_2-$	Me-bpy	1.66 (s, C*H*$_2$) 1.90 (s, C*H*$_3$)		9

Table 9. Selected ^{1}H NMR Chemical Shifts of MoO_2RXL_2 Compounds

compd no.	R =	X =	L_2 =	^{1}H δ (Mo−C*H*)	solvent	ref
6	CH_3	Br	bpy	0.62 (s)	$CDCl_3$	5a
7	C_2H_5	Br	bpy	1.1 (t, C*H*$_3$) 3.3 (m, C*H*$_2$)	$CDCl_3$	5a

Table 10. Selected ^{1}H NMR Chemical Shifts of Other MoO_2 Compounds

compd no.	compd	^{1}H δ (Mo−C*H*)	matrix	ref
1	$MoO_2(mes)_2$	2.22 (s, *p*-Me) 2.65 (s, *o*-Me) 6.88 (s, *m*-C*H*)	C_4D_8O	3b
2	$LiMoO_2Me_2mes(OEt_2)_2$	0.77 (s)	C_4D_8O	3b
51	[MoO_2(1,3-dimethyl-imidazoline-2-ylidene)$_3$Cl]Cl	4.03 (C═C*H*N) 4.23 (C═C*H*N) 6.96 (N−C*H*$_3$) 7.42 (N−C*H*$_3$)	$CDCl_3$	10f

presents a chemical shift at 0.5 ppm, and all of the other diazabutadiene complexes present chemical shifts in the range of 0.82−0.87 ppm. Complexes $RMoO_2CH_3$ (R = Cp, Cp*, Tp*) present ^{1}H NMR chemical shifts of Mo−C*H*$_3$ protons between 0.90 and 1.81 ppm (Figure 2). In the case of complexes of the type Cp′MoO_2X (Table 9) ^{1}H NMR chemical shifts of protons directly attached to the cyclopentadienyl ring vary between 5.42 and 6.85 ppm. These chemical shifts seem to depend on the type of X ligand present and on the type of substituents present in the cyclopentadienyl ring. However, comparison between the different shifts is hampered due to the large variety of solvents used in the analysis.

Table 11. Selected ^{1}H NMR Chemical Shifts of L_3MoO_2X Compounds

compd no.	L_3 =	X =	^{1}H δ (Mo−C*H*)	solvent	ref
56	Cp	Cl	6.60 (s)	CS_2	1h
			6.60 (s)	$CDCl_3$	14a
			6.61 (s)	$CDCl_3$	14b
			6.67 (s)	$CDCl_3$	23a
57	Cp	Br	6.85 (s)	$(CD_3)_2CO$	14b
61	Cp	Me	1.19 (s, CH_3)	C_6D_6	17b
			5.42 (s, C*H* from Cp ring)		
63	Cp	Et	1.77 (d, CH_3)	$CDCl_3$	17c
			2.56 (q, CH_2−CH_3)		
			6.29 (s, C*H* from Cp ring)		
60	Cp	CH_2SiMe_3	0.32 (s, CH_3)	C_6D_6	17b
			1.20 (s, CH_2)		
			5.61 (s, C*H* from Cp ring)		
58	Cp*	Cl	2.09 (s, CH_3 from Cp ring)	$CDCl_3$	16a
			2.08 (s, CH_3 from Cp ring)	$CDCl_3$	23a
			1.63 (s, CH_3 from Cp ring)	C_6D_6	18a
64	Cp*	Br	1.55 (s, CH_3 from Cp ring)	C_6D_6	17e
59	Cp*	Me	0.98 (s, CH_3)	$CDCl_3$	16b
			1.98 (s, CH_3 from Cp ring)		
			0.95 (s, CH_3)	$CDCl_3$	21
			1.96 (s, CH_3 from Cp ring)		
			0.90 (s, CH_3)	C_6D_6	17b
			1.57 (s, CH_3 from Cp ring)		
60	Cp*	CH_2SiMe_3	0.05 (s, CH_3)	$CDCl_3$	16b
			0.66 (s, CH_2)		
			1.93 (s, CH_3 from Cp ring)		
			0.37 (s, CH_3)	C_6D_6	17b
			0.63 (s, CH_2)		
			1.59 (s, CH_3 from Cp ring)		
70	Cp*	$OSi(CH_2Ph)_3$	1.89 (s, CH_3 from Cp ring)	CD_2Cl_2	26b
			2.18 (s, CH_2Ph)		
			7.00−7.25 (m, Ph)		
71	Cp*	[(2,6-*i*Pr$_2$C$_6$H$_3$)N(SiMe$_3$)]$_2$- -SiO$_2$(OH)$_3$	−0.11 (s, SiMe$_3$)	$CDCl_3$	26a
			−0.07 (s, SiMe$_3$)		
			0.90 (m, C(CH_3)$_2$		
			1.80 (s, CH_3 from Cp ring)		
			2.37 (s, SiO*H*)		
			2.5 (s, SiO*H*)		
			2.9 (s, SiO*H*)		
			3.32 (m, C*H*)		
			6.87 (m, aromatic CH)		
72	Cp*	S*t*Bu	1.62 (s, SCMe$_3$)	C_6D_6	27
			1.72 (s, CH_3 from Cp ring)		
66	$C_5H_4(SiMe_3)$	Cl	0.10 (s, CH_3)	C_6D_6	22a
			5.93 (C*H* from Cp ring)		
67	$C_5H_3(SiMe_3)_2$	Cl	0.19 (s, CH_3)	C_6D_6	22a
			6.26 (C*H* from Cp ring)		
			6.66 (C*H* from Cp ring)		
77	C$_5$H(i-Pr)$_4$	Cl	1.25 (d, CH_3)	$CDCl_3$	28a
			1.31 (d, CH_3)		
			1.35 (d, CH_3)		
			1.40 (d, CH_3)		
			3.14 (m, C*H*)		
			6.06 (s, C*H* from Cp ring)		
68	$C_5(CH_2Ph)_5$	Cl	3.81 (s, CH_2)	CD_2Cl_2	23a
			6.54−6.97 (m, Ph)		
69	C$_5$Ph$_4$[2,5-(MeO)$_2$C$_6$H$_3$]	Br	2.98 [s, C$_6$H$_3$(O*Me*)$_2$]	$CDCl_3$	24
			3.12 [s, C$_6$H$_3$(O*Me*)$_2$]		
			3.31 [s, C$_6$H$_3$(O*Me*)$_2$]		
			3.55 [s, C$_6$H$_3$(O*Me*)$_2$[		
			6.22 (d, C$_6$$H_3$)		
			6.45 (dd, C$_6$$H_3$)		
			6.78−7.25 (m, Ph)		
73	C$_5$Ph$_4$[2,5-(MeO)$_2$C$_6$H$_3$]	OMe	2.97 [s, C$_6$H$_3$(O*Me*)$_2$]	$CDCl_3$	24
			3.12 [s, C$_6$H$_3$(O*Me*)$_2$]		
			3.33 [s, C$_6$H$_3$(O*Me*)$_2$]		
			3.52 [s, C$_6$H$_3$(O*Me*)$_2$]		
			4.36 (s, OMe*)		
			4.38 (s, OMe*)		
			6.06 (d, C$_6$$H_3$)		
			6.29 (d, C$_6$$H_3$)		
			6.58−7.21 (m, Ph and C$_6$$H_3$)		
74	C$_5$Ph$_4$[2,5-(MeO)$_2$C$_6$H$_3$]	OEt	2.97 [s, C$_6$H$_3$(O*Me*)$_2$]	$CDCl_3$	24
			3.11 [s, C$_6$H$_3$(O*Me*)$_2$]		
			3.32 [s, C$_6$H$_3$(O*Me*)$_2$]		
			3.51 [s, C$_6$H$_3$(O*Me*)$_2$]		
			4.36 (s, OMe*)		
			4.52 (2q, OE*t**)		
			6.29 (d, C$_6$$H_3$)		
			6.23−7.20 (m, Ph and C$_6$$H_3$)		

Table 11. (Continued)

compd no.	$L_3 =$	X =	$^1H\ \delta$ (Mo−C*H*)	solvent	ref
75	$C_5Ph_4[2,5\text{-}(MeO)_2C_6H_3]$	O-*i*Pr	1.24 (d, O*i*Pr*) 1.25 (d, O*i*Pr*) 2.96 [s, $C_6H_3(OMe)_2$] 3.08 [s, $C_6H_3(OMe)_2$] 3.36 [s, $C_6H_3(OMe)_2$] 3.52 [s, $C_6H_3(OMe)_2$] 4.65 (m, O*i*Pr*) 6.25 (2s, C_6H_3) 6,58−7,21 (m, Ph and C_6H_3)	$CDCl_3$	24
76	$C_5Ph_4[2,5\text{-}(MeO)_2C_6H_3]$	O*t*Bu	1.30 (s, O*i*Pr*) 1.32 (s, O*i*Pr*) 2.96 [s, $C_6H_3(OMe)_2$] 3.07 [s, $C_6H_3(OMe)_2$] 3.29 [s, $C_6H_3(OMe)_2$] 3.52 [s, $C_6H_3(OMe)_2$] 6.15−7.19 (m, Ph and C_6H_3)	$CDCl_3$	24
52	Tp*	Me	1.81 (s)	C_6D_6	11b
			1.47 (s)	$CDCl_3$	11c
53	Tp*	CH_2SiMe_3	0.54 (s, CH_3) 2.13 (s, CH_2)	C_6D_6	11c
			0.20 (s, CH_3) 1.93 (s, CH_2)	$CDCl_3$	11c
55	PAP	CH_2SiMe_3	0.02 (s, CH_3) 0.34 (d, CH_2) 1.77 (d, CH_2)	DMSO-d_6	13

Table 12. Selected ^{13}C NMR Chemical Shifts of $MoO_2R_2L_2$ Compounds

compd no.	R =	$L_2 =$	$^{13}C-\{^1H\}\ \delta$	solvent	ref
28	*o*-Me−C_6H_4−CH_2−	bpy	19.69 (CH_3) 45.51 (CH_2)	CD_2Cl_2	8a
29	*p*-Me−C_6H_4−CH_2−	bpy	19.69 (CH_3) 45.53 (CH_2)	CD_2Cl_2	8b
36	*p*-Me−C_6H_4−CH_2−	Me-bpy	20.65 21.21 46.24 121.61 125.90 127.40 127.55 131.60 144.47 148.82 149.64 150.58	C_6D_6	9

^{13}C NMR data are listed in Tables 12−14. For complexes of the type $MoO_2R_2L_2$, ^{13}C NMR data are scarce and limited to three similar complexes (Table 12). Chemical shifts for the carbon atom connected to the metal (Mo−CH_3) vary between 45.51 and 46.24 ppm. In the case of complexes of the type $Cp'MoO_2X$ (Table 14), ^{13}C NMR data of cyclopentadienyl carbons are good indicators of the substitution of the cyclopentadienyl ring with electron-donating groups. More substituted cyclopentadienyl rings present higher values for the ^{13}C NMR chemical shifts of the cyclopentadienyl ring. For the specific case of $Cp'MoO_2Cl$ complexes the ^{13}C NMR chemical shifts range from 114.10 to 128.9 ppm.

IR spectroscopy is a useful tool for establishing the electronic properties of the MoO_2 fragment. Tables 15−18 display values for υ(Mo=O) for the studied complexes, which are characteristic *cis*-Mo=O stretching frequencies. In the case of the $MoO_2R_2L_2$ complexes (Table 15), these Mo=O stretching frequencies are relatively insensitive to the alkyl group present.[8b] Nevertheless, it is possible to detect that in the case of aryl substituents the presence of electron-donating substituents causes a lowering of one or both of the Mo=O stretching frequencies.[7d] Furthermore, the presence of a benzyl group as an alkyl substituent is also held responsible for the shift of the Mo=O stretching frequencies to lower energies. Both shifts can be explained by the

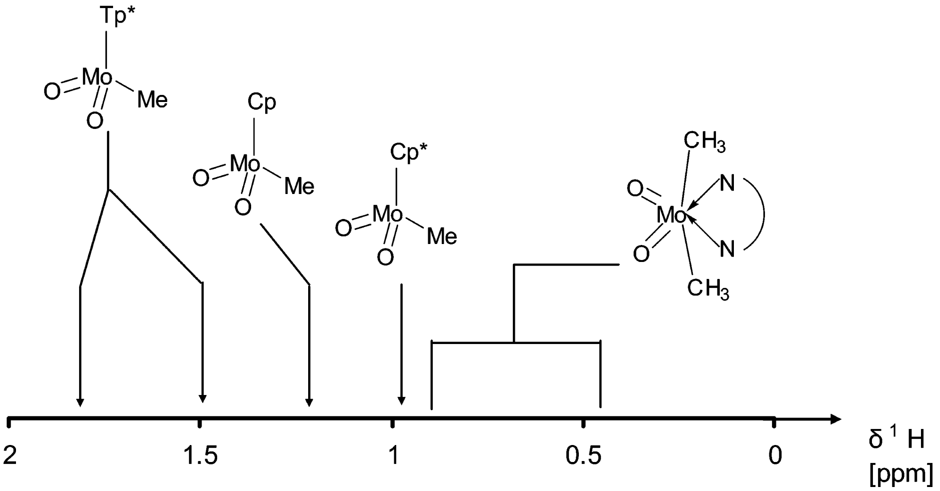


Figure 2. Graphical representation of selected ^1H NMR chemical shifts. Arrows indicate values, and merged lines indicate an interval of values. In the case of Tp^*MoO_2Me the two merged arrows represent two different values for different solvents (1.81 ppm with C_6D_6 and 1.47 ppm with $CDCl_3$).

Table 13. Selected ^{13}C NMR Chemical Shifts of Other MoO_2 Compounds

compd no.	R =	$^{13}C-\{^1H\}$ δ	solvent	ref
1	$MoO_2(mes)_2$	21.7 (*p*-Me) 23.53 (*o*-Me) 128.39 (C_{meta}) 142.95 (C_{para}) 145.01 (C_{ortho}) 189.00 (C_{ipso})	C_4D_8O	3b
2	$LiMoO_2Me_2(mes)(OEt_2)_2$	15.56 (OCH_2CH_3) 20.89 (Mo-CH_3) 21.49 (*p*-Me) 27.46 (*o*-Me) 66.20 (OCH_2CH_3) 127.21 (C_{meta}) 129.96 (C_{para}) 132.55 (C_{ortho}) 191.11 (Mo$-C_{mes}$)	C_4D_8O	3b
4	$MoO_2(mes)=C(mes)$-PBu_3	174 (quaternary C) (NMR DEPT sequence)	C_6D_6	3g
51	[MoO_2 (1,3-dimethylimidazoline- 2-ylidene)$_3$Cl]Cl	36.5 (NCH_3) 39.9 (NCH_3) 123.0 ($C=CHN$) 123.2 ($C=CHN$) 177.2 (carbene$-$C) 177.7 (carbene$-$C)	$CDCl_3$	10f

increase of electron density around the molybdenum atom. In the first case, this electron density is provided by the electron-donating groups of the aryl group. In the case of the benzyl group, the phenyl planes of the benzyl group are nearly parallel to the bipyridyl plane (X-ray evidence), thus increasing the electron density on the bipyridyl ligand, which is transferred to the molybdenum atom through increased back-bonding. In both cases, the increased charge density is in part shifted onto the oxygen atom and the Mo=O bond is weakened.[7b,9] The Mo=O stretching frequencies for $MoO_2R_2L_2$ complexes are also influenced by the base strength of the bidentate ligand present. Weaker bases donate less electron density to the molybdenum center. Accordingly, more electron density is shifted from the other ligands, thereby strengthening the Mo=O bond. For two of the studied complexes, $MoO_2(Me)_2$bpy (**13**) and $MoO_2(Me)_2$bipm (bipm = bipyrimidine) (**44**), this trend is also reflected in the calculated force constants for the Mo=O bond.[10c] In the case of complexes of the type L_3MoO_2X (Table 18) the Mo=O frequencies are influenced in a similar fashion by the donor abilities of the ligands (X or L_3). Stronger electron-donating ligands, such as the Cp* ligand, are responsible for the shifting of Mo=O stretching frequencies to lower energies, when compared to less electron donating ligands, such as Cp or Tp*.[30] The presence of electron-attracting groups in the X position, such as halogens, has the same effect on the M=O stretching frequencies. On the basis of IR and Raman data, force constants have been calculated for the Mo−Cp

Table 14. Selected ^{13}C NMR Chemical Shifts of L_3MoO_2X Compounds

compd no.	L_3 =	X =	$^{13}C-\{^1H\}$ δ	solvent	ref
56	Cp	Cl	114.11	$CDCl_3$	23a
63	Cp	Et	22.3 (CH_2CH_3) 34.6 (CH_2CH_3) 119.8 (C_5H_4)	$CDCl_3$	17c
58	Cp*	Cl	11.09 [$C_5(CH_3)_5$] 126.17 [$C_5(CH_3)_5$]	$CDCl_3$	23a
59	Cp*	Me	11.6 ($C_5(CH_3)_5$) 17.5 (Mo-CH_3) 118.5 [$C_5(CH_3)_5$]	$CDCl_3$	23a
70	Cp*	$OSi(CH_2Ph)_3$	11.8 [$C_5(CH_3)_5$] 24.4 (CH_2Ph) 121.6 [$C_5(CH_3)_5$] 124.7−138.7 (Ph)	CD_2Cl_2	26b
66	$C_5H_4(SiMe_3)$	Cl	−1.6 [$Si(CH_3)_3$] 118.5 (C_5H_4) 119.5 (C_5H_4, ipso) 120.2 (C_5H_4)	C_6D_6	22a
67	$C_5H_3(SiMe_3)_2$	Cl	−1.24 ($Si(CH_3)_3$) 123.8 (C_5H_3) 126.2 (C_5H_3) 128.9 (C_5H_3)	C_6D_6	22a
68	$C_5(CH_2Ph)_5$	Cl	32.90 ($-CH_2$) 126.81 (C_{para}, Ph) 128.35 $C_5(CH_2Ph)_5$ 128.34 (C_{meta}, Ph) 129.08 (C_{ortho}, Ph) 137.37 (C_α, Ph)	$CDCl_3$	23a
69	$C_5Ph_4[2,5\text{-}(MeO)_2C_6H_3]$	OMe	50.82−55.53 70.26−70.89 111.83−116.71 124.58−132.15 149.60−153.28	CH_3OH	24
52	Tp*	Me	12.42 (5-CH_3, pyr ring) 12.61 (5-CH_3, pyr ring) 14.45 (3-CH_3, pyr ring) 15.20 (3-CH_3, pyr ring) 28.71 (Mo$-CH_3$) 116.96 (4-*C*, pyr ring) 117.11 (4-*C*, pyr ring) 143.58 (3-*C*, pyr ring) 146.74 (3-*C*, pyr ring) 152.24 (5-*C*, pyr ring) 152.70 (5-*C*, pyr ring)	$CDCl_3$	11b
			27.74 (Mo$-CH_3$)	C_6D_6	11c
53	Tp*	CH_2SiMe_3	1.43 (Si$-CH_3$) 50.94 (CH_2)	C_6D_6	11c

Table 15. Selected IR Vibrations of $MoO_2R_2L_2$ Compounds

compd no.	R =	L_2 =	ν_{sym}(Mo=O) (1/cm)	ν_{asym}(Mo=O) (1/cm)	matrix	ref
13	CH_3	bpy	934	905	KBr	6
42	CH_3	^{t}Bu-bpy	928	903	KBr	10a
44	CH_3	bipyrimidine	936	901	KBr	10a
38	CH_3	*o*-tolyl-DAB	939	907	KBr	10a
39	CH_3	*p*-tolyl-DAB	936	905	KBr	10a
40	CH_3	2,6-Me-phenyl-DAB	945	912	KBr	10a
45	CH_3	phen	930	914	KBr	10a
46	CH_3	4,7-diphenyl-1,10-phen	932	912	KBr	10a
48	CH_3	CYDAB	926	899	KBr	10a
49	CH_3	Me-CYDAB	934	907	KBr	10a
50	CH_3	^{t}Bu-DAB	936	908	KBr	10a
41	CH_3	*p*-tolyl-2,3-dimethyl-DAB	934	907	KBr	10d
43	CH_3	*n*-hexyl-bpy	930	906	KBr	10e
14	C_2H_5	bpy	934	905	KBr	7c
47	C_2H_5	4,7-diphenyl-1,10-phen	930	885	KBr	10a
15	*n*-C_3H_7	bpy	926	889	KBr	7c
17	*n*-C_4H_9	bpy	933	901	KBr	7c
16	*i*-C_3H_7	bpy	914	882	KBr	7c
18	*i*-C_4H_9	bpy	932	898	KBr	7c
33	*i*-C_4H_9	Me-bpy	898	871	KBr	9
20	*cyc*-C_5H_9	bpy	914	882	KBr	7c
19	*neo*-C_5H_{11}	bpy	922	890	KBr	7a
31	CH_2SiMe_3	bpy	927	895	KBr	7f
33	*neo*-C_5H_{11}	Me-bpy	921	896	KBr	9
21	*cyc*-C_6H_{11}	bpy	919	890	KBr	7c
34	$CH_2{=}CH(CH_2)_4-$	Me-bpy	894	872	KBr	9
22	Ph (C_6H_5)	bpy	929	898	KBr	7d
27	$C_6H_5-CH_2-$	bpy	915	885	KBr	7b
35	$C_6H_5-CH_2-$	Me-bpy	892	873	KBr	9
24	*p*-Me$-C_6H_4-$	bpy	930	892	KBr	7d
23	*p*-Me$-C_6H_4-$	bpy	931	893	KBr	7d
25	*p*-Cl$-C_6H_4-$	bpy	933	898	KBr	7d
26	*p*-MeO$-C_6H_4-$	bpy	924	889	KBr	7d
28	*o*-Me$-C_6H_4-CH_2-$	bpy	920	889	KBr	8a
29	*p*-Me$-C_6H_4-CH_2-$	bpy	931	893	KBr	8b
36	*p*-Me$-C_6H_4-CH_2-$	Me-bpy	913	899	KBr	9
30	$C_6H_4-CH_2-CH_2-$	bpy	922	897	KBr	8b
37	$C_6H_4-C(Me)_2-CH_2-$	Me-bpy	920	900	KBr	9

Table 16. Selected IR Vibrations of MoO_2RXL_2 Compounds

compd no.	R =	X =	L_2 =	ν_{sym}(Mo=O) (1/cm)	ν_{asym}(Mo=O) (1/cm)	matrix	ref
6	CH_3	Br	bpy	927	908	Nujol	5a
7	C_2H_5	Br	bpy	931	900	Nujol	5a

Table 17. Selected IR Vibrations of Other MoO_2 Compounds

compd no.	compd	ν_{sym}(Mo=O) (1/cm)	ν_{asym}(Mo=O) (1/cm)	matrix	ref
4	$MoO_2(mes){=}C(mes)PBu_3$	940	920	Nujol	3g
3	$MoO_2(mes)_2CN$*t*Bu	924	910	KBr	3e
51	$[MoO_2$(1,3-dimethylimidazoline-2-ylidene)$_3$Cl]Cl	916	912	KBr	10f

interaction for complexes $CpMoO_2Cl$ (**56**) (343 Nm^{-1}), Cp^*MoO_2Cl (**58**) (389 Nm^{-1}) and $C_5Bz_5MoO_2Cl$ (**68**) (297 Nm^{-1}), thus indicating that the metal ligand interaction is strongest for Cp* derivative and weakest for the C_5Bz_5 derivative.[23a]

3.3. Thermochemical Studies

Thermal stability data of mononuclear organomolybdenum(VI) dioxo complexes are listed in Tables 19−21. Among the complexes with octahedral geometry (Tables 19 and 20), MoO_2Me_2bpy (**13**) is the most stable compound, decomposing above 230 °C. In the case of complexes of the type MoO_2RXL an increase in the alkyl chain length from one to two carbon atoms does not influence the thermal stability of the complexes significantly. In the case of complexes of the type MoO_2R_2bpy, however, changing the alkyl substituent has a pronounced effect on the stability of complexes. The thermal stability appears to be primarily dependent on the number of hydrogen atoms in a β position relative to molybdenum and on the size of R, which together with electronic factors determine Mo−C bond strength.[7c] In the case of phenyl groups electron-donating groups (such as Me or O−Me) increase the thermal stability and electron-abstracting groups (such as Cl) decrease thermal stability.

With regard to complexes with piano stool geometry (Table 21), complexes bearing a Cp* ligand decompose at higher temperatures than complexes with a Cp ligand, due to the electron-donating effects of the methyl groups of the Cp* ring, which helps to stabilize the Cp*−Mo bond (see force constants in previous section). In the case of the Cl derivatives, it has been shown that the force constant of the Mo−Cp bond is higher in the case of the Cp* ligand.[23a] The

Table 18. Selected IR Vibrations of L_3MoO_2X Compounds

compd no.	L_3 =	X =	ν_{sym}(Mo=O) (1/cm)	ν_{asym}(Mo=O) (1/cm)	matrix	ref
56	Cp	Cl	920	887	(CCl4/CS_2)	1h
			920	887	CCl4/CS_2	14a
			925	895	KBr	17c
			935	905	CS_2	17c
57	Cp	Br	920	885	Nujol/HCBD	14b
61	Cp	Me	926	902	Nujol	17b
63	Cp	Et	920	891	KBr	17c
62	Cp	CH_2SiMe_3	924	895	Nujol	17b
58	Cp*	Cl	912	882	CS_2	16a
			913	879	KBr	23a
			920	890	C_6D_6	18
64	Cp*	Br	915	883	Nujol	17e
59	Cp*	Me	920	888	Nujol	21
			918	887	Nujol	17b
			920	894	CS_2	16b
60	Cp*	CH_2SiMe_3	919	890	CS_2	16b
			912	893	Nujol	17b
71	Cp*	$[(2,6\text{-}i\text{Pr}_2C_6H_3)N(SiMe_3)]_2\text{-}SiO_2(OH)_3$	908	882	KBr/Nujol	26a
70	Cp*	$OSi(CH_2Ph)_3$	923	871	KBr	26b
72	Cp*	S*t*Bu	901	875	Nujol	27
66	$C_5H_4(SiMe_3)$	Cl	924	894	Nujol	22a
67	$C_5H_3(SiMe_3)_2$	Cl	922	893	Nujol	22a
77	$C_5H(i\text{-}Pr)_4$	Cl	920	890	Nujol	28a
68	$C_5(CH_2Ph)_5$	Cl	921	889	KBr	23a
69	$C_5Ph_4[2,5\text{-}(MeO)_2C_6H_3]$	Br	926	895	Nujol	24
73	$C_5Ph_4[2,5\text{-}(MeO)_2C_6H_3]$	OMe	910	883	Nujol	24
74	$C_5Ph_4[2,5\text{-}(MeO)_2C_6H_3]$	OEt	910	883	Nujol	24
75	$C_5Ph_4[2,5\text{-}(MeO)_2C_6H_3]$	O-*i*Pr	914	893	Nujol	24
76	$C_5Ph_4[2,5\text{-}(MeO)_2C_6H_3]$	O*t*Bu	922	890	Nujol	24
52	Tp*	Me	936	904	Nujol	11b
			940	905	KBr	11c
53	Tp*	CH_2SiMe_3	942	902	KBr	11c
55	PAP	CH_2SiMe_3	934	900	KBr	13

Table 19. Melting Points of $MoO_2R_2L_2$ Compounds

compd no.	R =	L_2 =	temp/°C	ref
13	CH_3	bpy	230^a	6
14	C_2H_5	bpy	138^a	7c
15	*n*-C_3H_7	bpy	120^a	7c
17	*n*-C_4H_9	bpy	156^a	7c
18	*i*-C_4H_9	bpy	141^a	7c
20	*cyc*-C_5H_9	bpy	117^a	7c
19	*neo*-C_5H_{11}	bpy	182^a	7a
21	*cyc*-C_6H_{11}	bpy	105^a	7c
22	Ph (C_6H_5)	bpy	175^a	7d
27	$C_6H_5-CH_2-$	bpy	155^a	7b
24	*p*-Me$-C_6H_4-$	bpy	182^a	7d
23	*p*-Me$-C_6H_4-$	bpy	180^a	7d
25	*p*-Cl$-C_6H_4-$	bpy	154^a	7d
26	*p*-MeO$-C_6H_4-$	bpy	182^a	7d
1	mes		170^a	8a

^{a} Decomposes.

Table 20. Melting Points of MoO_2RXL_2 Compounds

compd no.	R =	X =	L_2 =	temp/°C	ref
6	CH_3	Br	bpy	200^a	5a
7	C_2H_5	Br	bpy	200^a	5a

^{a} Decomposes.

Table 21. Melting Points of L_3MoO_2X Compounds

compd no.	L_3 =	X =	temp/°C	ref
56	Cp	Cl	140^a	1h
61	Cp	Me	95^a	17b
62	Cp	CH_2SiMe_3	95−98^a	17b
58	Cp*	Cl	151−157^a	18
59	Cp*	Me	91^a	21
			104−106	17b
60	Cp*	CH_2SiMe_3	104−106	17b
52	Tp*	Me	238^a	11b
			240−280^a	11c
53	Tp*	CH_2SiMe_3	210−212^a	11c
55	PAP	CH_2SiMe_3	216−218^a	13

^{a} Decomposes.

Tp* ligand has even a more pronounced effect on increasing the stability of the complexes toward temperature, although it has been described as a weaker electron donor than the Cp* ligand in a spectroscopic study performed by Kiefer et al. for complexes Tp*MO_2Me and Cp*MO_2Me (M = Mo, W).[30]

3.4. Theoretical Studies

Blaine et al. applied molecular mechanics to the prediction of geometries MoO_2(mes)$_2$ (**1**) and several other dioxo- or diimido-tetrahedral transition metal complexes, which exhibit strong valence angle deformations around the metal and for which crystal structures were already known.[31] In this study, missing parameters were designed according to the electron configuration of the metal, thus enabling the prediction of satisfactory geometries.

As previously mentioned (see section 3.2), Teruel et al. have reported a study that correlates ^{95}Mo NMR chemical shift, semiempirical molecular orbital method (CNDO) estimated p and d orbital population, and oxygen atom transfer capacity for several dioxo molybdenum complexes, including $MoO_2(CH_2C_4H_9)_2$bpy (**19**) and $MoO_2(CH_2C_6H_5)_2$bpy (**27**).[29]

3.5. Electrochemical Studies

Although the redox behavior of molybdenum complexes is relevant for the understanding of oxygen transfer reactions catalyzed by the organometallic complexes, few electrochemical studies have been performed for organometallic molybdenum(VI) dioxo complexes.

The cyclic voltammogram of MoO_2(*p*-$MeC_6H_4CH_2)_2$(bpy) (**24**) exhibits a completely irreversible reduction at −1.38

V. The redox behavior of $MoO_2(CH_2CH_2Ph)_2(bpy)$ (**30**) contrasts sharply with that observed for **24** (because the process for the first compound is electrochemically quasi reversible at scan rates of 100 mV s^{-1}).[8b] According to the authors, this is an usual feature; similar *cis*-dioxoalkylmolybdenum species display irreversible voltammetric patterns.

Cyclic voltammograms of complexes of formulas (η^5-C_5Ph_4(2,5-dimethoxyphenyl))MoO_2R [R = Br (**69**), OMe (**73**), Et (**74**), O^{i}Pr (**75**), O^{t}Bu (**76**)] show a reduction attributed to the Mo(VI)/Mo(V) redox couple.[24] The couples are almost, but not completely, chemically reversible. The couple for **69** at −0.55 V is ≈1.0 V more positive than those for the alkoxide complexes, being consistent with the donor abilities of the ligands.

In the case of (η^5-C_5Bz_5)MoO_2Cl (**68**), the cyclic voltammogram shows an irreversible one-electron reduction peak at −1.378 V attributed to the Mo(VI)/Mo(V) redox couple, followed by a second irreversible reduction peak at 1.670 V, assigned to the Mo(V)/Mo(IV) process.[25] Increasing the scan rate causes a shift of the peaks to cathodic potential, and the current function is approximately independent of the scan rates used.

3.6. Photochemical Studies

Several photolysis studies were reported for complexes of the type $MoO_2BrR(bpy)$ and $MoO_2R_2(bpy)$. The complexes are light sensitive and originate as decomposition products alkanes and alkenes. The photochemical Mo−C bond cleavage is assumed to take place via homolysis and under formation of radical species[5a] or by formation of hydridoalkylmolybdenum species, which dissociate to anionic species and thus suffer a reductive elimination.[7c] Mo−C bond strengths were estimated from λ_{max} of UV−vis absorption spectra for several complexes of this type.[7a,b]

Faller and Ma reported on the absorption spectra of Cp^*MoO_2Cl (**58**), which shows a relatively strong charge-transfer band at 379 nm.[16b] According to the authors this band is typical for Mo=O complexes and is responsible for the yellow color of the compound.

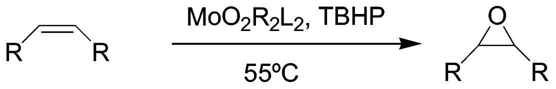
4. Catalytic Applications of Organometallic Molybdenum(VI) Dioxo Complexes

4.1. Polymerization

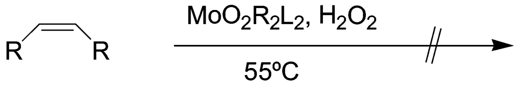
The complexes $MoO_2(CH_3)_2(bpy)$ (**13**) and $MoO_2(C_2H_5)_2(bpy)$ (**14**) were found to catalyze the ring-opening metathesis polymerization (ROMP) of norbornene in combination with the Grignard reagent MeMgBr as cocatalyst.[32] **13** was the most effective catalyst of these two, giving an overall yield of 88% of polynorbornene of which 24% was soluble in chloroform. Surprisingly, when similar polymerization reactions were attempted with the commonly used metathesis cocatalyst $EtAlCl_2$, the molybdenum compounds produced only a small amount of insoluble polymer. The authors assume that the strong Lewis acid $EtAlCl_2$ decomposes the catalysts before the polymerization begins. The methyl and ethyl complexes were also used without cocatalysts; however, when the reaction mixture was warmed, decomposition of the molybdenum compounds occurred and no polymerization was observed.

4.2. Oxidation Reactions

The catalytic properties of $MoO_2R_2L_2$ [R = CH_3, C_2H_5; L = 1,4-diazobutadiene (R-DAB), with different R groups, phenanthroline, or substituted bypiridines] have been recently studied in detail by the research groups of Gonçalves, Kühn, and Romão, partially in cooperation, partially independently.[10a−e] The compounds were found to be active for the epoxidation of olefins using *tert*-butylhydroperoxide as oxidant and at moderate temperatures (55 °C) (eq 4). However, when H_2O_2 was employed as the oxidant, no epoxidation products could be obtained (eq 5).



(**4**)

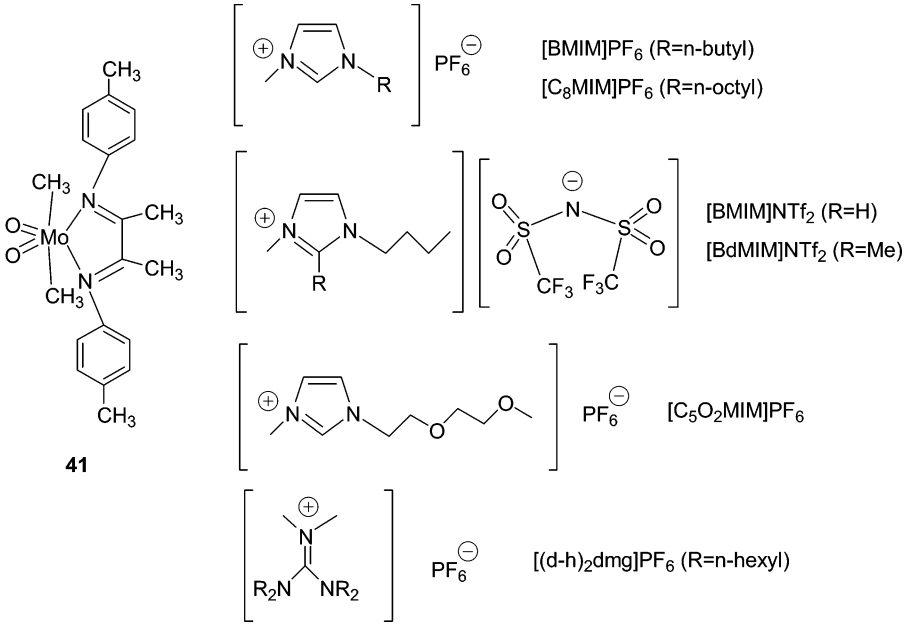


(**5**)

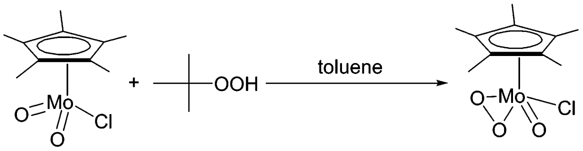
In general, the overall yield obtained after 4 h is relatively low (between 5 and 60%). Over a 24 h period the yields proved to be strongly dependent on the types of ligands L and R used. Electron-attracting ligands L lead to more active compounds, rendering the molybdenum center electron deficient. Steric effects of the ligands also seem to play an important role on the catalytic activity. Ligands, which create more steric hindrance near the metal center, usually decrease the catalytic performance of complexes. Increases of both reaction time and temperature lead to a significant increase in the product yield in all examined cases. However, at ∼90 °C catalyst decomposition hampers a further increase in the product yield. It is also noteworthy that during the catalytic runs the loss of the methyl group as methane, ethane, or methanol by a potential breaking of the $Mo-CH_3$ bond does not play an important role. Integrated in this line of work, Valente et al. studied the catalytic properties of the complex MoO_2Me_2(Me−*p*-tolylDAB)$_2$ (**41**) (Me−*p*-tolyl-DAB = 1,4-*p*-tolyl-1,4-diaza-2,3-dimethyl-1,3-butadiene) for the epoxidation under the previously applied conditions (TBHP as oxidant, 55 °C) but also using as alternative solvent several room temperature ionic liquids (RTILs) (Chart 5).[33] The authors reported that this complex presents excellent selectivity toward the formation of epoxide and observed relatively high activity without additional solvent, with chlorinated solvent, or with an adequate RTIL. The application of the RTILs also enabled the recycling of the catalyst. Among the several RTILs tested for recycling complex **41** the best results were observed for the system with $[BMIM]NTf_2$.

The catalytic activity of dioxomolybdenum complexes containing cyclopentadienyl ligands was—until recently—solely examined for Cp^*MoO_2Cl (**58**) by Bergman and Trost.[18] **58** was shown to act as a catalyst for the epoxidation of several olefins (such as cyclooctene, geraniol, and 1,2,4,5-tetramethylcyclohexa-1,4-diene), as long as they do not include any electron-withdrawing groups. Apart from TBHP, other alkyl hydroperoxides such as cumene hydroperoxide and *n*-hexylhydroperoxide could be used as oxidants. However, with both H_2O_2 and Ph_3COOH no catalytic reaction occurred and $Cp^*Mo(O_2)OCl$ was formed. The authors found

Chart 5



TBHP to react with Cp^*MoO_2Cl (in the absence of olefins), originating a complex of the type $Cp^*Mo(O_2)OCl$ (eq 6).



58

(**6**)

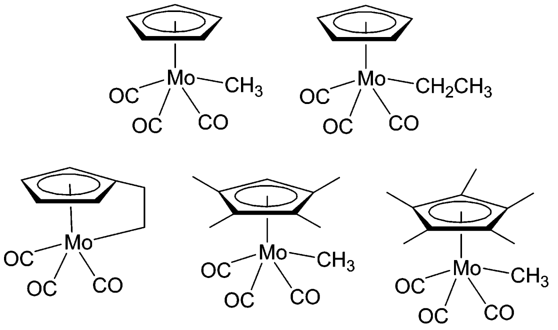
Curiously, catalytic reactions performed with the isolated $Cp^*Mo(O_2)OCl$ led to no epoxidation products; therefore, this complex was considered to be an unwanted side product, and it was concluded that the active species cannot be a η^2-coordinated peroxo complex. These results were later supported by Roesky et al., who received an X-ray crystal structure of $Cp^*Mo(O_2)OCl$. They also described this compound as being not active as olefin epoxidation catalyst in the presence of excess TBHP.[34]

Except for the formation of the peroxo complex, the catalyst precursor seems to maintain its integrity during the catalytic reaction, showing no observable oxidation of the Cp* ligand (the catalytic reaction was performed in a deuterated solvent and monitored by ^{1}H NMR).[18] The effect of the alkyl peroxide used on the relative rate of the epoxidation reaction was investigated, and the obtained rates were consistent with the formation of an intermediate species in which the alkyl group of the peroxide moiety is intact. That is, the relative rates depend on the structure of the alkyl group of the alkyl peroxide. Catalyst loads of 2−5% were used depending on the substrate, and the reaction temperatures spanned from room temperature to 60 °C.

Kühn, Romão et al.[23a] have extended the study of the catalytic properties of $Cp'MoO_2Cl$ compounds. The complexes $(\eta^5\text{-}C_5R_5)MoO_2Cl$ [R = H (**56**), CH_3 (**58**), CH_2Ph-(Bz) (**68**)] were used as catalysts for the epoxidation of cyclooctene, styrene, and 1-octene. The reactions were conducted using catalyst loadings of 1 mol %, with TBHP as oxidant and at 55 °C. The influence of the ring substituents on the catalyst activity was studied in detail for cyclooctene. Both of the complexes **56** and **68** show good activity, reaching a 100% conversion after 4 h of reaction time; however, in a second and third catalytic run (by addition of new substrate) most of the activity of the complex **68** is maintained, whereas that of the Cp derivative strongly declines due to catalyst decomposition. **58** reaches only ~60% of the activity of the other derivatives in the first run and shares the same decomposition problems observed for **56** under catalytic conditions. Due to its high stability and activity, catalytic runs were performed using a lower catalyst load of **68**. Using a 0.1% catalyst load under the same reaction conditions, turnover frequencies (TOF) of 4000 h^{-1} were obtained, and lowering the load to 0.01% led to values of 20000 h^{-1}. However, at these low catalyst loadings the residual amount of water present in the system gains increasing influence on the catalytic performance after some time and, therefore, the catalytic activities trail off considerably after 1 h of reaction time for the lowest catalyst amounts applied. The high activity of **68**, despite its higher steric bulk, was ascribed both to its higher stability toward moisture and to the lower electronic density at the Mo center in comparison to the derivatives **56** and **58**, due to a weaker Mo-ring bond, as reflected in the ^{95}Mo NMR and vibrational spectroscopy (see above). Styrene and 1-octene could also be transformed to their respective epoxides with **56**, **58**, and **68**, the best results being again obtained with **68**. Ring opening of the styrene epoxide to the diol is not significant under the conditions applied; 1-octene, being an unactivated, unfunctionalized olefin, reacts significantly more slowly than the other substrates.

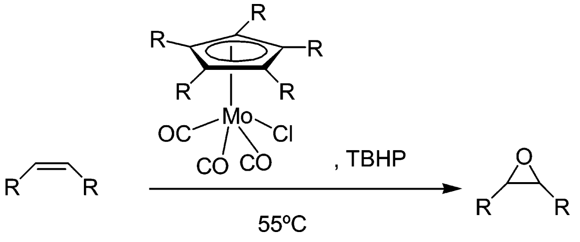
Recently, the groups of Martins, Romão, and Poli extended the study of the catalytic performance of the dioxomolybdenum complexes containing cyclopentadienyl ligands to the complex $C_5H(^iPr)_4MoO_2Cl$ (**77**) and to several dinuclear complexes.[25] One of the aims of this study was to assess the activity dependence of $Cp'MoO_2Cl$ complexes by the nature of the ring substituents using TBHP as oxidant. The authors concluded that the nature of the substituents strongly influences the overall performance of the catalysts, both in terms of initial activity rates but, more importantly, in terms of their long-term performance at 24 h of reaction. The steric bulk was not considered to be the decisive parameter to

Chart 6



control this dependence, but the authors state that the reactivity of the complexes can be explained in terms of the ability of the Cp′MoO_2Cl complexes to undergo ring slippage or distortion that might alleviate the steric pressure of the intermediates. The same study also showed that Cp′MoO_2Cl complexes are catalytically active in aqueous solutions provided TBHP is used instead of H_2O_2. These results came not unexpectedly, because the authors had previously reported on the Cp*MoO_2(VI) fragment surviving a wide range of pH conditions in aqueous solutions.[28c] The mechanism of the reaction of Cp′MoO_2Cl-type complexes with TBHP, however, remains to be clarified.[25]

The precursor carbonyl compounds of the Cp′MoO_2Cl complexes were also found to be active catalysts for the epoxidation reactions (eq 7).[23a,25] This follows directly from



(7)

the chemistry involved in the synthesis of the dioxo complexes, because in the catalysis TBHP is present in large excess and oxidizes readily the carbonyl compounds. Because the carbonyl complexes are more stable than the dioxo complexes, they can be used directly as easily storable forms of catalyst precursors. In fact, the carbonyl compounds reach (within the measurement error) the same TOFs as do the oxides when used as epoxidation catalysts in the presence of TBHP.[23a] However, in the case of $(C_5Bz_5)Mo(CO)_3Me$ conversion to the epoxide was also reported to stagnate after 30 min of reaction.[25]

On the basis of the finding that precursor carbonyl compounds of the Cp′MoO_2Cl complexes were also found to be active catalysts for the epoxidation reactions, several carbonyl compounds of the formula Cp′$Mo(CO)_3R$ (R = alkyl) were synthesized and applied directly as epoxidation catalysts in the presence of excess TBHP (Chart 6).[35]

The formation of the respective dioxo complexes was confirmed by in situ IR spectroscopy. The authors showed that the carbonyl complexes can be applied as active (TOFs up to ~6000 h^{-1}; TON > 500) and selective epoxidation catalysts. The study also showed that increasing the alkyl substitution of the Cp ligand lowers the catalytic activity and that ansa-bridged derivatives, being more difficult to synthesize than their nonbridged congeners, seem to show no significant advantage when applied in catalysis. The original idea behind the synthesis of ansa-bridged compounds was to hinder Cp loss after possible intermediate ring slippage.

The catalytic performance of complexes of the type $(\eta^5\text{-}C_5R_5)Mo(CO)_3X$ (R = H, Me; X = Me, Cl) has also been examined in systems containing different RTILs.[36] The authors concluded that the catalytic performance for cyclooctene epoxidation (with TBHP at 55 °C) depended on several factors, such as the water content of the ionic liquid, the catalyst solubility in the RTIL, and the reaction behavior of the RTIL under the applied conditions. The catalysts can be recycled without significant loss of activity when a reaction system containing $[BMIM]NTf_2$ and $[BMIM]PF_6$ in a 4:1 ratio is used. High proportions of $[BMIM]PF_6$ lead to a ring-opening reaction (diol formation), due to the formation of HF (from $[BMIM]PF_6$ and residual water).

The catalytic activity of $Cp(SiMe_3)MoO_2Cl$[22a,b] (**66**) and $Cp(SiMe_3)_2MoO_2Cl$[22b] (**67**) in oxidation reactions was also reported. $Cp(SiMe_3)MoO_2Cl$ acts as a good catalyst for the oxo-transfer model reaction from dimethyl sulfoxide to PPh_3. At 25 °C and after 24 h of reaction, the complex converts 38% of PPh_3 into $OPPh_3$. Although no detailed kinetic experiments were carried out, the rate constant observed for the oxidation of PPh_3 in the presence of **67** is 1−2 orders of magnitude higher than that observed for **66**.[22a] While studying the effect of trimethylsilyl-substituted ligands as solubilizers of metal complexes in *sc*-CO_2, Montilla et al. have studied the catalytic properties of **66** in the oxidation of PPh_3 by molecular oxygen and the epoxidation of cyclohexene by TBHP in different media.[22b] The complex is active in PPh_3 oxidation by molecular oxygen in *sc*-CO_2. Conversion of PPh_3 into $OPPh_3$ was reported to increase with the increase of oxygen partial pressure, and experiments performed with other solvents (hexane, toluene, and chloroform) show that for this reaction the conversions obtained with *sc*-CO_2 were surpassed only by chloroform. Epoxidation of cyclohexene was first attempted with O_2 and H_2O_2 as oxidant but failed under various conditions. On the contrary (and also not unexpectedly), **66** was shown to catalyze the epoxidation of cyclohexene with TBHP in *sc*-CO_2, under a variety of temperatures (from 40 to 70 °C) and with 1.4 mol % of catalyst.[22b] Less satisfactory values than those obtained by using Cp′MoO_2Cl in conventional solvents[18] were attributed to technical problems during the depressurization process.

5. Conclusions

Mononuclear organomolybdenum(VI) dioxo complexes can be divided into two categories: complexes with Mo−C *σ* bonds and complexes with cyclopentadienyl ligands. The synthetic developments for each category have run almost independently and have determined their application in catalysis. Although $CpMoO_2Cl$ was among the first examples of organometallic oxides, the application in catalysis of cyclopentadienyl mononuclear organomolybdenum(VI) dioxo complexes started comparatively late. This was probably due to the lack of an efficient and accessible method for the synthesis of this type of compound, which was actively pursued by several research groups, as proved by the multiple synthetic pathways developed during the years. As a consequence of all the years of synthetic efforts, the recent synthetic developments have enabled the easier synthesis of several complexes of the type Cp′MoO_2Cl and their application in catalysis. Catalytic results are promising and should lead to further investigations regarding, for example, mechanistic aspects or, in particular, application in chiral epoxidation catalysis. Introduction of chirality in these Mo(VI) catalysts should be easier than in the related Re(VII) compounds of the formula $R{-}ReO_3$, which still overshadow the compounds described here with respect to popularity (but not necessarily in availability, applicability, and catalytic activity).

The study of mononuclear organomolybdenum(VI) dioxo complexes with $Mo{-}C$ σ bonds included the extensive examination of dioxo molybdenum complexes with mesityl ligands and the development of models for reactive intermediates of the enzyme nitrogenase, which has led to the development of the chemistry of complexes of the type $MoO_2R_2L_2$ (R = alkyl; L_2 = bidentate ligand) or MoO_2RL_3 (R = alkyl; L_3 = tridentate ligand). Catalytic applications of $MoO_2R_2L_2$ complexes have been extensively performed, and successful results have prompted these complexes to be used in nonconventional solvents (e.g., RTILs). Catalytic application of some $MoO_2R_2L_2$ complexes continues beyond the scope of this review, with the successful immobilization of the complexes into several mesoporous materials.

6. Abbreviations

[BMIM]NTf_2	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[BMIM]PF_6	1-butyl-3-methylimidazolium hexafluorophosphate
2,6-Me-phenyl-DAB	1,4-di(2,6-dimethylphenyl)-1,4-diaza-1,3-butadiene
bpy	2,2′-bipyridyl
Bu	butyl
Bz	benzyl
Cp	C_5H_5
Cp*	C_5Me_5
Cp′	general abbreviation for a substituted cyclopentadienyl ring
CYDAB	1,4-cyclohexyl-1,4-diaza-1,3-butadiene
DME	1,2-dimethoxyethane
DMSO	dimethyl sulfoxide
Et	ethyl
^{i}Pr	*iso*-propyl
Me	methyl
Me-*p*-tolylDAB	1,4-*p*-tolyl-1,4-diaza-2,3-dimethyl-1,3-butadiene
Me-bpy	4,4′-dimethyl-2,2′-bipyridyl
Me-CYDAB	1,4-cyclohexyl-1,4-diaza-2,3-dimethyl-1,3-butadiene
mes	mesityl (2,4,6-trimethylbenzene)
n-hexylbpy	4,4′-di-*n*-hexyl-2,2′-bipyridyl
o-tolylDAB	1,4-di-*o*-tolyl-1,4-diaza-1,3-butadiene
PAP	2-*N*-(2 pyridylmethyl)aminophenolate
Ph	phenyl
phen	phenanthroline
Pr	propyl
p-tolylDAB	1,4-di-*p*-tolyl-1,4-diaza-1,3-butadiene
R-DAB	substituted 1,4-diazobutadiene ligand
RTIL	room temperature ionic liquid
sc-CO_2	supercritical CO_2
TBHP	*tert*-butylhydroperoxide
^{t}Bu	*tert*-butyl
^{t}Bu-bpy	4,4′-di-*tert*-butyl-2,2′-bipyridyl
^{t}Bu-DAB	1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene
THF	tetrahydrofuran
Tp	hydridotris(1-pyrazolyl)borate
Tp*	tris[(3,5-dimethyl)-1-pyrazolyl]hydroborate

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8. References

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