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A Simple Entry to (η^5-C_5R_5)chlorodioxomolybdenum(VI) Complexes (R = H, CH_3, CH_2Ph) and Their Use as Olefin Epoxidation Catalysts

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The complexes (η^5-C_5R_5)MoO_2Cl (R = H, CH_3 (Me), CH_2Ph (Bz)) are readily prepared from the parent carbonyls (η^5-C_5R_5)$Mo(CO)_3Cl$ upon reaction with *t*-BuOOH (TBHP) in *n*-decane. The compounds are characterized by vibrational spectroscopy, ^1H, ^{13}C, and ^{95}Mo NMR spectroscopy, and elementary analysis and are compared to their (η^5-C_5R_5)ReO_3 homologues. The Mo−C_5R_5 force constants have been determined. (η^5-C_5Bz_5)MoO_2Cl can be stored and handled at room temperature without decomposition, in contrast to the more temperature sensitive Cp (R = H) and Cp* (R = Me) analogues. The (η^5-C_5R_5)MoO_2Cl complexes catalyze the epoxidation of cyclooctene, styrene, and 1-octene with TBHP as oxidizing agent. The highest activity is found for (η^5-C_5Bz_5)MoO_2Cl: TOF 21000 mol/(mol × h) for cyclooctene in CH_2Cl_2 at 55 °C with a ratio catalyst:substrate:TBHP = 0.0001:1:2.5. This activity even surpasses that of the well-known $MeReO_3$/H_2O_2 system. The stable parent carbonyls (η^5-C_5R_5)$Mo(CO)_3Cl$ can be used as catalyst precursors since they are transformed into (η^5-C_5R_5)MoO_2Cl under the operating catalytic conditions.

Introduction

High oxidation state organometallic chemistry has provided a number of highly efficient catalytic processes. One important step in this development was the synthesis and study of (Cp^*ReO_3)[1] ($Cp^* = \eta^5$-C_5Me_5), which was soon followed by a new generation of highly active organometallic oxidation catalysts where methyltrioxorhenium(VII) (MTO) plays a prominent role.[2]

Although $CpMoO_2Cl$ and related compounds are among the earliest examples of organometallic oxides,[3] their application in oxidation catalysis is rather limited. Nevertheless, the well-known and widespread catalytic activity of the *cis*-MoO_2 fragment in oxidation and oxygen transfer reactions suggested that the study of organometallic derivatives of this fragment would be rewarding. Indeed, in contrast to Cp^*ReO_3, usually regarded as a “model complex”, the Mo(VI) compound Cp^*MoO_2Cl has been shown to be an active catalyst for olefin epoxidation,[4] like the isoelectronic derivatives of general formula $MO_2X_2L_2$ (M = Mo, W; X = Cl, Br, Me, Et; L = Lewis base ligands) that we and others have studied.[5] Despite the several methods that have been presented throughout the years in the literature for the synthesis of (η^5-C_5R_5)MoO_2X derivatives,[3,6] none of them is as easy and efficient as the synthesis of Cp^*ReO_3[7] and its catalytically active congeners MTO[8] and $CpReO_3$.[9] In this work, we present a general and straightforward one-step synthesis of (η^5-C_5R_5)MoO_2Cl complexes from their corresponding and readily available (η^5-C_5R_5)$Mo(CO)_3Cl$ precursors. This easy synthesis enables the study of the (η^5-C_5R_5)MoO_2Cl complexes in olefin ep-

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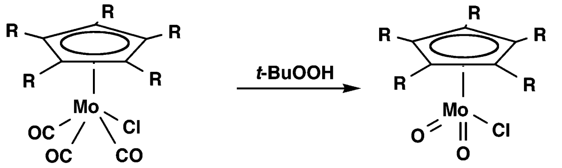
oxidation and the comparison of the properties and catalytic behavior of these compounds with $MoR'_2O_2L_2$,[5] $R'ReO_3$,[2,10] and $R'ReO_3L_2$[11] (R' = alkyl, L = Lewis base ligands) complexes.

Results and Discussion

1. Synthesis and Characterization. Our approach to the synthesis of the $Cp'MoO_2Cl$ complexes (Cp' = Cp, Cp*, η^5-C_5Bz_5) follows the concept of oxidative decarbonylation of $Cp'Mo(CO)_3Cl$ that was so successfully used for the synthesis of Cp^*ReO_3 from $Cp^*Re(CO)_3$[12] and had been also previously used for the synthesis of $[TpMoO_3]^-$ from $[TpMo(CO)_3]^-$ (Tp = hydridotris(1-pyrazolyl)borate).[12b] This methodology also required a practical and reliable synthesis of the $Cp'Mo(CO)_3Cl$ precursors. Among the several methods available in the literature[13] we found that the reaction of $Mo(CO)_3(EtCN)_3$ (readily obtained from $Mo(CO)_6$ and proprionitrile) with the corresponding C_5R_5H produces the hydride $(C_5R_5)Mo(CO)_3H$. This can be reacted with CCl_4 without isolation and purification to form (η^5-C_5R_5)$Mo(CO)_3Cl$ (R = H (**1**), Me (**2**), Bz (**3**)). The yields (based on $Mo(CO)_6$) are 44 and 65%, for the Cp and Cp* derivatives, respectively, and 30% for the C_5Bz_5 complex. In the latter case this doubles the value reported in the literature.[13g]

In an initial attempt, we found that dimethyldioxirane is unable to oxidatively decarbonylate $CpMo(CO)_3Cl$ to produce $CpMoO_2Cl$ in contrast to the above-mentioned examples with $Cp^*Re(CO)_3$ and $[TpMo(CO)_3]^-$, and we then abandoned this route. On the contrary, oxidative decarbonylation of **1**−**3** takes place smoothly with *tert*-butylhydroperoxide (TBHP) as in the case of $Cp^*Re(CO)_3$ and other complexes.[12]

The complexes **1**−**3** are dissolved in CH_2Cl_2 and treated in a dropwise manner with 10 equiv of a 5−6 M (TBHP) solution in *n*-decane (eq 1). Upon stirring at room temperature, the mixture turns from red to yellow within 2−3 h. The remaining TBHP is then destroyed by addition of MnO_2. The mixture is filtered and the yellow-orange products (η^5-C_5R_5)MoO_2Cl (R = H (**4**), Me (**5**), Bz (**6**)) are isolated after evaporation of the solvent and washing with cold *n*-hexane. Yields up to ca. 75% have been obtained by this method. Although it may not be absolutely general, this route is far superior for these particular complexes than any of the other ones already reported.[3,4,6]



(1)

R= H (1), CH_3 (2), Bz (3)

R= H (4), CH_3 (5), Bz (6)

All three $Cp'MoO_2Cl$ complexes **4**−**6** can be handled in air for brief periods of time but are quite moisture sensitive in solution. They are soluble in polar solvents such as $CHCl_3$, CH_2Cl_2, but insoluble in nonpolar solvents, e.g., *n*-hexane. Compound **6** is significantly more stable than both **4** and **5** and does not decompose at room temperature, in the solid state, even after weeks. A comparable increase in stability in comparison to compound **5** has also been stated for $[Mo(\eta^5$-$C_5Ph_4(2,5$-dimethoxyphenyl$))O_2Br]$[6f] and was ascribed to the steric bulk of the ligand.[6f,14] For prolonged storage complexes **4** and **5** should be kept below room temperature (refrigerator); otherwise they decompose under formation of intractable blue solids.[6e] The decomposition of compounds **4** and **5** has been already described in the literature, and it has been stated that light accelerates its decomposition.[6e] In this respect it is worth noting that the stability of these complexes increases upon dilution in water-free solvents, a fact that has already been noted for most of the $RReO_3$ complexes although never properly understood.[15] It should be noted in this context that $CpReO_3$ is also light sensitive and has to be kept in the darkness at low temperatures for prolonged storage.[11,16] The decomposition of $CpReO_3$ proceeds via a radical pathway,[16a] as it has also been assumed for compound **5**.[6e] Cp^*ReO_3, however, is stable in the presence of light and room temperature for unlimited periods of time.[16]

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Table 1. Selected FT-IR and Raman Frequencies (cm^{-1}) of Compounds 1 and 4−6 (force constants (10^2 N m^{-1}) calculated according to ref 17)[a]

1		4		5		6		
IR	Raman	IR	Raman	IR	Raman	IR	Raman	assignment
281 vvs	280 m	398 s,m	394 w	398 s, sh	[b]	382 vs	381 m	ν (MoCl)
361 s	355 w,sh	355 m	351 w	393 s		335 m	335 m	ν_a (MoCp)
337 vw	339 vvs	331 m	328 vs	373 s		305 m	305 m	ν_s (MoCp)
		265 m	261 vs	349 vs		(279) m	250 m	w (MoO_2)[c]
		238 m	238 m	273 m		226 w	227 s	t (MoO_2)[c]
		375 s	376 s	243 w		372 sh	(380) s	δ (MoO_2)[c]
3.67		3.43		3.89		2.97		K (MoCp)

[a] Effective G matrix element: 0.018465, see ref 17, Table 13. [b] Not determined. [c] w, wagging; t, twisting; δ scissoring mode.

The symmetric and asymmetric Mo═O stretching frequencies are located at (ν_{sym}/ν_{asym}) 922/893 cm^{-1} for compound **4**, at 910/879 cm^{-1} for compound **5**, and at 921/889 cm^{-1} for compound **6**. This is quite similar to the Re═O vibrations in $CpReO_3$ (914/885) and Cp^*ReO_3 (910/886),[17] indicating a similar M═O bond order. The other metal ligand vibrations were observed below 600 cm^{-1}. The strong IR bands around 355 cm^{-1} have been assigned to the ring tilt mode and the very strong Raman features at ca. 330 cm^{-1} to the symmetric Mo−Cp stretching vibration. The Mo−C asymmetric stretching is generally stronger in the IR spectrum; therefore bands for complex **1** at 430 cm^{-1} were selected for this vibration and the strong Raman band at 463 cm^{-1} has been assigned to the symmetric Mo−C stretching mode. Usually the metal−chlorine stretches show intense IR bands and their position depends strongly on the oxidation state of the metal. Due to this fact the strong IR band at 398 cm^{-1} for compound **4** should refer to the Mo−Cl stretching vibration, while in the case of complex **1** the very strong band at 281 cm^{-1} can be assigned as the Mo−Cl stretching vibration.

The carbonyl complexes **1**−**3** always display a stronger Mo−(C_5R_5) interaction than their oxo congeners **4**−**6**. This general observation is exemplified in Table 1 for complexes **1** and **4**. The same metal−(C_5R_5) bond strength relationship has been established for the related Re compounds ($CpRe(CO)_3/CpReO_3$ and $Cp^*Re(CO)_3/Cp^*ReO_3$).[17] On the other hand, on the basis of the force constants for the Mo−(C_5R_5) interaction, the metal−ligand interaction is strongest for the Cp* derivative and weakest for the C_5Bz_5 derivative (see Table 1). Therefore, the stabilization against decomposition of compound **6** in comparison to compounds **4** and **5** (see above) must mainly originate from steric and not from electronic reasons. Otherwise the $(\eta^5\text{-}C_5R_5)$−Mo interaction in compound **6** would have to be the strongest, not the weakest. The long Mo−C(ring) bonds observed in the crystal structure of the complex $(\eta^5\text{-}C_5Bz_5)Mo(CO)_3I$ can be interpreted in the same way.[13f] The weak donor ability of the C_5Bz_5 ligand seems to be responsible for the higher Lewis acidity of the metal center of complex **6**, resulting in a higher catalytic activity in olefin epoxidation (see below) when compared to derivatives **4** and **5**. The similarities between the $(C_5R_5)MoO_2Cl$ and $(C_5R_5)ReO_3$ compounds are also reflected in the M═O bond lengths obtained by X-ray diffraction. The average Re═O bond distances in $CpReO_3$ and $(C_5(Me_4)(Et))ReO_3$ are equivalent within the measurement error (170 pm); in $(C_5H_4(CH_3))ReO_3$ the average Re═O bond length is 172 pm.[2b] For the only known X-ray structure of a $Cp'MoO_2Cl$ derivative, $(C_5H(i\text{-}Pr)_4)MoO_2Cl$,[6g] the Mo═O bond distances are 170.0(2) and 172.0(2) pm. Considering the results mentioned for the Re complexes,[2b] a detectable influence of the Cp-ring ligands on the Mo═O bond length is not to be expected. The almost invariant Mo═O bond distance has also been shown in a large series of structures of Re and Mo oxo complexes with varying ancillary ligands.[5c,18]

The ^{95}Mo NMR spectra of the complexes **4**−**6** display the ^{95}Mo signal at −448 (**4**), −399 (**5**), and −282 (**6**) ppm, respectively. Given the structural similarity of the three complexes it is tempting to conclude that the electronic richness around the metal decreases in the order **4** (C_5H_5) > **5** (C_5Me_5) > **6** (C_5Bz_5), but much caution must be taken in interpreting ^{95}Mo NMR shifts.[19] It is interesting to note in this context that the ^{95}Mo shift of compounds of formula $MoX_2O_2L_2$ (X = Me, Cl, Br) is very different from compounds **4**−**6**. It is located in the region of 420−520 ppm (Me derivatives), 170−300 ppm (Br derivatives), 160−220 (Cl derivatives) and has an inverse halogen dependence.[5b,20] Nevertheless, despite the quite different ^{95}Mo shifts, the chemical similarities between these complex classes should be quite pronounced. In the case of the Re(VII) congeners, namely, Cp^*ReO_3 and $(CH_3)ReO_2(t\text{-bubipy})$, the similarity with respect to the chemical behavior has also been closely examined and proven.[2b,21]

Compound **4** displays its ^{13}C NMR ring-carbon signal at 114.1 ppm (compare $CpReO_3$: $\delta(^{13}C) = 114.0$ ppm[9]), and compound **5** has its ^{13}C NMR signals at 126.2 (ring-carbons) and 11.1 (Me-carbons) ppm (compare Cp^*ReO_3: $\delta(^{13}C) = 120.4$ and 10.2 ppm[1a]). In the case of the Cp complexes the similarity of the chemical shift of the ring carbons of the Re(VII) and the Mo(VI) species is particularly striking and indicative of a very similar electronic situation in the Cp ring. In the case of complex **6** the ring carbons are observed at 128.4 ppm. Six ^{13}C signals are observed in total, proving the free rotation of the Cp ring and its benzyl ligands, which has also been observed for other C_5Bz_5-ligated transition metal complexes.[22] Unfortunately, the measurement of ^{17}O NMR spectra at natural abundance was precluded due to the accelerated decomposition observed at the

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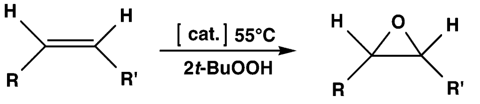
high concentrations and long measurement times necessary for these experiments. Such data could have been very helpful in order to probe the electronic situation of the terminal Mo=O bonds.

2. Catalysis. Dioxomolybdenum(VI) complexes are important catalysts or catalyst precursors for oxygen atom transfer reactions in chemical and biological systems.[23] The wealth of chemistry that started in the late 1960s spurred by the ARCO and Halcon patents on the olefin epoxidation catalyzed by Mo(VI) compounds in homogeneous phase [24a,b] has been reviewed.[24c,d] Among the large variety of complexes bearing the *cis*-MoO_2 fragment we and others have explored the catalytic properties of a series of distorted octahedral $MoO_2X_2L_2$ complexes in olefin epoxidation.[5] Such complexes are isoelectronic and arguably isostructural with the (η^5-C_5R_5)MoO_2Cl complexes where the (η^5-C_5R_5) ring formally occupies three coordination positions taken up by the two L and one Cl ligand in the former species. The work of Bergman and Trost, who found that Cp^*MoO_2Cl is an olefin epoxidation catalyst, further underlines this comparison.[4] In this system a peroxo complex of formula $Cp^*MoO(O_2)Cl$, later characterized by X-ray crystallography,[25] is formed as a catalyst deactivation product. This result clearly rules out a peroxo complex as the catalytically active species and points to an intermediate with an intact alkylperoxo group. However, to the best of our knowledge, no further report about the catalytic performance of $Cp'MoO_2Cl$ derivatives has appeared.

Compounds **4**−**6** were tested as catalysts for the epoxidation of cyclooctene, styrene, and 1-octene with TBHP (eq 2) in order to compare the effect of the substituent on the catalytic activity. In the present study the catalyst:substrate ratio is substantially smaller than in the original study reported for compound **5**.[4]



(2)

R = R' = $(CH_2)_3$
R = H, R' = $(CH_2)_6CH_3$
R = Ph, R' = H

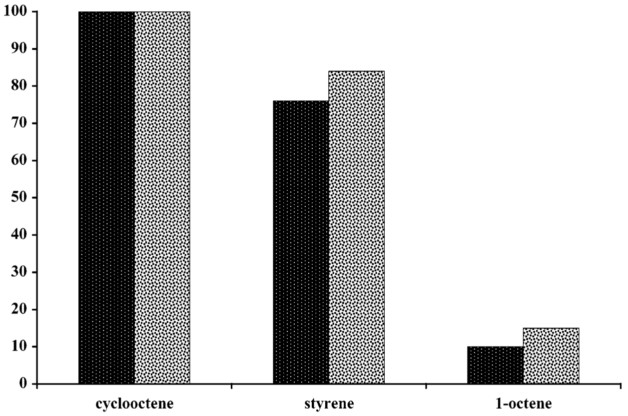


Figure 1. Conversion after 4 and 24 h reaction time of selected olefins with compound **6** as catalyst and TBHP as oxidizing agent at 55 °C (catalyst:substrate:oxidizing agent = 0.01:1:2).

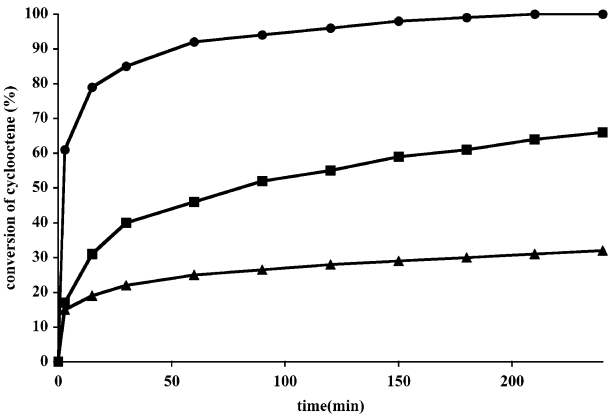


Figure 2. Time-dependent and catalyst concentration-dependent conversion of cyclooctene in the presence of compound **6** as catalyst at 55 °C. The curves represent a catalyst to cyclooctene to TBHP relationship of 0.01:1:2 (top curve, measured values are given as dots), 0.001:1:2 (medium curve, squares symbolize measurement results), 0.0001:1:2 (bottom curve, triangles represent measured values).

The details concerning the catalytic reaction are given in the Experimental Section. Blank reactions showed that no significant amount of epoxide was formed in the absence of catalyst. For all three olefins no significant formation of products (e.g., diol) other than epoxide was observed. All catalytic reactions show the same time-dependent curve (Figure 2), having a quick increase of the yield during the first reaction hour and then slowing down (first-order kinetics). These curves do not show an observable induction period or a clear indication that the original catalyst is transformed into another species as also noted by NMR monitoring of the reaction of **5**.[4]

The influence of the ring substituents on the catalytic activity is rather interesting and was studied for the epoxidation of cyclooctene in a ratio cat:cyclooctene:TBHP = 0.01:1:2 relationship. Under these conditions both the Cp (**4**) and C_5Bz_5 (**6**) derivatives have the same activity, within the error range of the measurements. Both reach the 100% yield within 4 h (see Figure 1). The main difference between both is that in a second or third run, made by addition of new charges of substrate to the reaction mixture after 4 h, the C_5Bz_5 derivative maintains most of its activity, while that of

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the Cp derivative strongly declines due to catalyst decomposition. This decomposition is already visible in a color change of the reaction solution to green or greenish blue during the first run with catalyst **4**. The Cp* (**5**) derivative reaches only about 50−60% of the activity of the other derivatives in the first run and shares the decomposition problems of compound **4**, again observable in a color change. However, all three derivatives seem to be more stable under catalytic conditions (at 55 °C) than in isolated (pure) form or in concentrated solution. Compound **1** behaves essentially like **4** under catalytic conditions. The TOFs at a ratio cat:cyclooctene:TBHP = 0.01:1:2 are ca. 1300:1200:1200: 800 mol/(mol × h) for compounds **1**, **4**, **6**, and **5**, respectively. Interestingly enough, for catalyst **6**, higher activities can be reached using a lower concentration of the catalyst. When cat:cyclooctene:TBHP = 0.001:1: 2, compound **6** reaches TOFs higher than 4000, and under cat:cyclooctene:TBHP = 0.0001:1:2 TOFs higher than 20 000 can be reproducibly obtained. In all cases the yield increases from 4 h reaction time to 24 h reaction time. In the case of complex **6** at cat:cyclooctene:TBHP = 0.001:1:2 the yield increases from ca. 66 to ca. 80%; in the case of 0.0001:1:2, from 32 to 48%. In the other cases, where we do not reach 100% after 4 h (e.g., with compound **5** under 0.01:1:2 conditions), there is only a small increase in yield from 4 h to 24 h, again emphasizing the fact that the catalyst must be already partially decomposed.

The activities mentioned for catalyst **6** are even higher than the highest turnover frequencies reported to date for the MTO/H_2O_2 system (ca. 14000 mol/mol × h),[24d,26a] which, however, can only be reached in fluorinated alcohols as solvents. The usual turnovers reported for the cyclooctene/MTO/H_2O_2 system are commonly not above ca. 2000 mol/(mol × h).[12a] Since there is only a residual amount of water present in the system, the slow decomposition of the catalyst **6** by water plays usually no important role. However, when the amount of catalyst is reduced, the tiny amount of residual water gains increasing influence on the catalytic performance after some time. As can be observed in Figure 2, the catalytic activity trails off significantly after 1 h reaction time in the case of the lowest catalyst amount used (0.0001:1 catalyst:substrate), but is not completely quenched. Control experiments in CH_2Cl_2 solution show that a 2-fold excess of H_2O leads to visible decomposition of **6** after 1 h noted by the appearance of a bluish color. Such decompostion is faster for both **4** and **5**. The highest TOFs for cyclooctene/$MoO_2X_2L_2$/TBHP observed to date are around 8000 mol/(mol × h) under the same reaction conditions described here for compound **6**.[27] The observation that complex **6** is more active than the compounds **4** and **5**, despite its significantly greater steric bulk, might be ascribable to its pronounced stability in comparison to the congeners **4** and **5**. Another possible contribution to the higher activity of compound **6** might come from its lower electron density at the Mo center in comparison to the derivatives **4** and **5**, due to a weaker Mo-ring bond as reflected in the ^{95}Mo NMR and vibrational spectroscopic data (see above).

Styrene and 1-octene are also transformed to their respective epoxides with compounds **4**−**6** and TBHP. Ring opening of the styrene epoxide to the diol[24,26] is not significant under the conditions applied. 1-Octene, an unfunctionalized and unactivated olefin,[24,26b] reacts significantly slower than both cyclooctene and styrene. The catalytic results are summarized in Figures 1 and 2.

The compounds **1**−**3** also act as catalysts for the olefin epoxidation. This is in accord with the well-known results of Sheldon et al., who used $Mo(CO)_6$ as oxidation catalysts,[28a−c] and follows directly from the chemistry involved in the synthesis of the complexes **4**−**6** reported in this work. The carbonyl complexes **1**−**3** are oxidized by TBHP to **4**−**6**, respectively. The latter immediately catalyze olefin epoxidation provided sufficient excess of TBHP is available. Oxidations of the C_5R_5 ring systems are not observed. Since the carbonyl complexes are more stable than the dioxo complexes, they can be used directly as easily storable forms of catalyst precursors, but require—in principle—higher amounts of TBHP present. Since the compounds described here are used in very small concentrations with respect to the substrate, the amount of excess TBHP for the oxidation of the carbonyls is negligible under the reaction conditions for the oxidation catalysis. Accordingly, the carbonyl complexes **1**−**3** reach—within the measurement error—the same TOFs as the (freshly synthesized) oxides **4**−**6** when used as epoxidation catalyts in the presence of excess TBHP.

On the basis of the studies with the related complexes, e.g., $MoO_2X_2L_2$ (X = Cl, Br, CH_3; L = bidentate Lewis base ligand)[5d,29] as well as in the study reported for **5**,[4] it can be assumed that the active species is a η^1-*tert*-butylperoxo complex, which is in equilibrium with the original compounds **4**−**6** (the catalyst precursors). The formation of the active species is fast and completely reversible. Attempts to isolate the active species led to the catalyst precursors, as it has been observed in the case of the $MoO_2X_2L_2$ compounds and their tungsten derivatives. We did not pursue the isolation of peroxo complexes similar to the Cp*MoO(O_2)Cl already mentioned above. Drawing an analogy to the isoelectronic $MO_2X_2L_2$ (M = Mo, W) complexes,[5d,30] it seems reasonable to assume that the active species has the composition (η-C_5R_5)MoO(OH)(OO-*t*-Bu)Cl. The fact that we do not assign a specific hapticity to such an intermediate arises from the suspicion that ring-slippage may play a role in facilitating the formation of such a crowded species when compared to the similar $MO_2X_2L_2$ complexes. Indeed, the effect of oxygen and oxo ligands (and other π-donors) on the slippage of C_5R_5 rings and the elongation of the ring−M bonds has been recognized and structurally documented for Re(V) oxo complexes Cp*Re(V)O_nX_m.[18] The steric protection of the benzyl substituents in complex **6** may be responsible for a stabilization

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of a distorted or elongated ring−Mo coordination, thus preventing complex decomposition. However reasonable and tempting these arguments may be, they must remain as a speculation in the absence of other data, namely, a crystallographic study of complexes **4**−**6** and kinetic data on the interaction of these with TBHP.

Conclusions

(η^5-C_5R_5)MoO_2Cl derivatives (exemplified with R = H, CH_3, CH_2Ph) are easily synthesized from (η^5-C_5R_5)Mo(CO)$_3$Cl precursors and TBHP. The latter complexes are available effortlessly from $Mo(CO)_6$. With this methodology an easy and general access to (η^5-C_5R_5)MoO_2Cl derivatives is available, paving the way to the catalytic application of this class of compounds. As a first step in this direction we examined the use of (η^5-C_5R_5)MoO_2Cl derivatives in olefin epoxidation catalysis. The compounds proved to be surprisingly active, revealing a dependence on the stability of the ring−Mo interaction. To avoid storage problems of the sensitive dioxo complexes, the carbonyl precursors of formula (η^5-C_5R_5)$Mo(CO)_3Cl$ can be directly used as catalyst precursors in the olefin epoxidation, without isolation of the dioxo complexes prior to application. Work aimed at investigating further catalytic applications of this kind of complexes in other oxidation reactions and reaction systems is currently under way in our laboratories. Particular attention is being given to the possibility of building enantioselective oxidation catalysts in either homogeneous or heterogeneous (supported) conditions.

Experimental Section

General Considerations. All preparations and manipulations were done using standard Schlenk techniques under an atmosphere of nitrogen. Solvents were dried by standard procedures (toluene and *n*-hexane over Na/benzophenone ketyl; CH_2Cl_2, NCEt, and $CHCl_3$ over CaH_2), distilled under nitrogen, and kept over 4 Å molecular sieves.

Microanalyses were performed by M. Conceição Almeida at the Elemental Analysis Service of ITQB. Mid-IR spectra were measured on a Mattson 7000 FT-IR spectrometer using KBr pellets. Far-IR measurements were performed in a Bio-Rad FTS 525 system as Nujol mulls or polyethylene pellets using a 6 μm Mylar beam splitter. Raman spectra were recorded with a Bio-Rad FT-Raman accessory attached to the same FTS-525 interferometer, using the near-infrared 1064 nm excitation from a Nd:YAG laser. Raman spectra of solids were measured as powders positioned on a horizontal sample stage using 200−500 mW laser power. ^{1}H NMR spectra were recorded at 300 MHz on a Bruker CXP 300, and ^{95}Mo and ^{13}C NMR were obtained using a 400 MHz Bruker Avance DPX-400 spectrometer. Gas chromatographic studies were performed with a Thermo Quest Trace GC gas chromatograph.

(C_5R_5)Mo(CO)$_3$Cl (R = H (**1**), CH_3 (**2**))[13a,h,31] and (C_5R_5)Mo(CO)$_3$H derivatives were synthesized according to literature procedures (R = CH_3)[31] or adaptations of these procedures (R = H) using CCl_4 instead of $CHCl_3$. The obtained elemental analyses for compounds **1** and **2** were correct. The IR data for compound **1** are given in Table 1. Selected IR data for compound **2** are as follows: IR (KBr/cm^{-1}): ν 2962 (m), 2918 (m), 2031 (s), 1955 (s), 1915 (s), 1382 (m), 1257 (vs), 1009 (vs), 917 (vs), 522 (w). CpH was obtained by cracking of $C_{10}H_{10}$, which is commercially available. Cp*H[32] and C_5Bz_5H[22] were synthesized according to previously described methods.

Preparation of (C_5Bz_5)Mo(CO)$_3$Cl (3). A 0.5 g (1.9 mmol) sample of $Mo(CO)_6$ and 5 mL of proprionitrile were refluxed overnight to give $Mo(CO)_3(EtCN)_3$. Solvent was removed, and C_5Bz_5H (0.98 g, 1.9 mmol) in 15 mL of toluene was added to the residue. The obtained brown suspension was stirred for 2 h and then warmed to 50−60 °C for 15 min. After that, the suspension was filtered. The filtrate was evaporated, and brown oil was obtained. This oil was redissolved in CH_2Cl_2. Addition of 3 mL of CCl_4 changed the color of the solution to dark red. After evaporating the solvent, the residue was washed with cold hexane. The obtained solid was subjected to column chromatography (silica gel) under inert gas conditions. First CH_2Cl_2/hexane (1:3) was used to elute a yellow band of impurities. After this band was eluted, the eluent ratio was changed to CH_2Cl_2/hexane (3:1) and the desired product was eluted as an orange band. After evaporation of the solvents, a crystalline orange product was obtained. Yield (based on Mo(CO)$_6$): 30%. IR (KBr/cm^{-1}): ν 3083 (m), 3060 (m), 3027 (m), 2923 (m), 2036 (vs), 1979 (vs), 1961 (vs), 1874 (m), 1600 (w), 1495 (ms), 1452 (ms), 1417 (w), 1384 (w), 1076 (w), 1030 (w), 735 (s), 698 (s), 561 (w), 524 (m), 485 (ms). ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 6.97−6.70 (m, 25H, 5 C_6H_5); 3.60 (s, 10H, 10 CH_2).

General Method for the Preparation of (C_5R_5)MoO_2Cl (R = H (4), CH_3 (5), CH_2-Ph (6)). One equivalent of (C_5R_5)Mo(CO)$_3$Cl is dissolved in CH_2Cl_2. Under continuous magnetic stirring, 10 equiv of a *tert*-butylhydroperoxide solution (5.0−6.0 M in *n*-decane) was added in a dropwise manner to the (C_5R_5)Mo(CO)$_3$Cl solution. The mixture was stirred at room temperature until the solution turned yellow (ca. 2−3 h). The reaction was stopped by the addition of manganese dioxide. The obtained suspension was filtered. Evaporation of the filtrate gave a yellow-orange powder that was thoroughly washed with cold hexane.

(C_5H_5)MoO_2Cl (4). Yield: 55%. IR (KBr/cm^{-1}): see Table 1. ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 6.67 (s). ^{13}C NMR ($CDCl_3$, 400 MHz, rt): δ 114.10. ^{95}Mo NMR ($CDCl_3$, 400 MHz, rt): δ −448.

($C_5(CH_3)_5$)MoO_2Cl (5). Yield: 56%. IR (KBr/cm^{-1}): ν 2960 (m), 2922 (ms), 2856 (m), 1523 (w), 1448 (ms), 1373 (m), 1356 (w), 1255 (ms), 1161 (w), 1072 (w), 1022 (ms), 960 (w), 930 (vs), 910 (vs), 879 (vs), 802 (w), 669 (w) 567 (w), 442 (w). ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 2.08 (s). ^{13}C NMR ($CDCl_3$, 400 MHz, rt): δ 126.17 ($C_5(CH_3)_5$), 11.09 ($C_5(CH_3)_5$). ^{95}Mo NMR ($CDCl_3$, 400 MHz, rt): δ −399.

($C_5(CH_2C_6H_5)_5$)MoO_2Cl (6). Yield: 75%. IR (KBr/cm^{-1}): ν 3063 (m), 3028 (m), 2920 (w), 1600 (w), 1495 (ms), 1454 (ms), 1439 (ms), 921 (s), 889 (s), 729 (vs), 696 (vs), 669 (w), 478 (w). ^{1}H NMR (CD_2Cl_2, 300 MHz, rt): δ 6.97−6.54 (m, 25H, 5 C_6H_5); 3.81 (s, 10H, 10 CH_2). ^{13}C NMR ($CDCl_3$, 400 MHz, rt): δ 137.37 (Cα, benzyl), 129.08 (*C*-ortho, benzyl), 128.64 (*C*-meta, benzyl), 128.35 (Bz_5C_5), 126.81 (*C*-para, benzyl), 32.90 (−CH_2−). ^{95}Mo NMR ($CDCl_3$, 400 MHz, rt): δ −282.

Catalytic Reactions with Compounds 4−6 as Catalysts. Method A. *cis*-Cyclooctene (800 mg, 7.3 mmol), 800 mg of *n*-dibutyl ether (internal standard), 1 mol % (73 μmol) of compounds **4**−**6** as catalyst.

Method B. Styrene (250 mg, 2.39 mmol), 100 mg of mesethylene (internal standard), 1 mol % (24 μmol) of compounds **4**−**6** as catalyst.

Method C. 1-Octene (800 mg, 7.12 mmol), 800 mg of *n*-dibutyl ether (internal standard), 1 mol % (71 μmol) of compounds **4**−**6** as catalyst.

For all methods A, B, and C TBHP (5.5 M in *n*-decane), 2.64, 0.869, and 2.58 mL, was added to a thermostated reaction vessel and stirred for 24 h at 55 °C. The course of the reaction was monitored by quantitative GC analysis. Samples were taken every 30 min, diluted with chloroform, and chilled in an ice bath. For the destruction of hydroperoxide and removal of water a catalytic amount of manganese dioxide and magnesium sulfate were added. After the gas evolution ceased the

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resulting slurry was filtered over a filter-equipped Pasteur pipet and the filtrate injected in the GC column.

The conversion of cyclooctene, styrene, and 1-octene as well as the formation of cyclooctene oxide were calculated from calibration curves ($r^2 = 0.999$) recorded prior to the reaction course.

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