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Mononuclear and Binuclear Cyclopentadienyl Oxo Molybdenum and Tungsten Complexes: Syntheses and Applications in Olefin Epoxidation Catalysis

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New half-sandwich molybdenum complexes [Mo(CpBz)Cl$_2$(O)] (**1**), [{Mo(CpBz)(O)$_2$}$_2$(μ-O)] (**5**), and [Mo(CpBz)Cl$_2$]$_2$ (**6**) (CpBz = C$_5$(CH$_2$Ph)$_5$), the tungsten derivative [W(CpBz)Cl(O)$_2$] (**3**), and a high yield synthesis of [Mo(CpBz)Cl(O)$_2$] (**2**) are described. The molecular structures and cyclic voltammetry measurements of **1** and **2** and a comparative study of various molybdenum dioxo complexes as olefin epoxidation catalyst precursors are also presented. The performance of [Mo(CpPr$^i_4$)Cl(O)$_2$] (**9**) as cyclooctene epoxidation catalyst using TBHP as oxidant was determined and compared with other [MoCp′Cl(O)$_2$] complexes (Cp′ = C$_5$H$_5$ (**7**), C$_5$Me$_5$ (**8**), CpBz (**2**)) to assess the activity dependence on the ring substituents. Under the same experimental conditions, bimetallic compounds [{MoCp′(O)$_2$}$_2$(μ-O)] (Cp′ = CpBz (**5**), Cp* (**10**), CpBu$^t_3$ (**11**), CpPr$^i_4$ (**12**)) have been tested and [CpMoO$_2$]$_2$O was checked in aqueous solution, with H$_2$O$_2$ and TBHP as oxidant. Finally, [Mo(CpBz)(CO)$_3$CH$_3$] (**4**) was used as a catalyst precursor for cyclooctene epoxidation in the presence of TBHP. The analogy between the behaviors displayed by this complex and complex **2** is discussed.

Introduction

Metal oxo and dioxo complexes are important catalysts of oxygen transfer reactions. Molybdenum and tungsten complexes, in particular, have been studied as models of oxotransferase active sites[1] and played an important role in homogeneous industrial catalysis through the olefin epoxidation ARCO and Halcon processes in the late 1960s. Recently, some of us have been exploring several aspects of Mo and W dioxide chemistry including (i) a range of inorganic and organometallic catalysts for olefin and sulfide oxidation with ^{t}BuOOH (TBHP)[2−4] and, in one case, with H$_2$O$_2$;[5] (ii) new synthetic pathways to the organometallic Cp′Mo(O)$_2$X derivatives;[2,6] and (iii) the aqueous chemistry of Cp′Mo(O)$_2$X and [Cp′Mo(O)$_2$]$_2$ complexes.[7] The later topics are particularly interesting since they offer the possibility of extending the usually versatile catalytic potential of organometallic complexes to aqueous media, a central concern of "green chemistry".

Since the pioneering studies on CpMo(O)$_2$X and related complexes led by Malcolm Green,[8,9] the synthesis of organometallic oxides has improved substantially.[10,11] Recently, very mild synthetic routes led to high yields of a number of Cp′Mo(O)$_2$X and [Cp′Mo(O)$_2$]$_2$ complexes where the substituents on Cp′ vary from H to very bulky groups, e.g., ^{i}Pr, ^{t}Bu, CH$_2$Ph.[2,6] [Cp′Mo(O)$_2$-Cl] (Cp′ = C$_5$H$_5$, C$_5$Me$_5$, and C$_5$(CH$_2$Ph)$_5$) have been tested as olefin epoxidation catalysts with TBHP.[2,12] The catalyst performance has been shown to depend on the cyclopentadienyl ligand, and [Mo(CpBz)O$_2$Cl] (CpBz = C$_5$(CH$_2$Ph)$_5$) led simultaneously to the most active and most stable catalytic system, when activated by ^{t}BuOOH.

In this work we present yet another synthetic method of high oxidation state pentabenzylcyclopentadienyl molybdenum and tungsten complexes, their structures,

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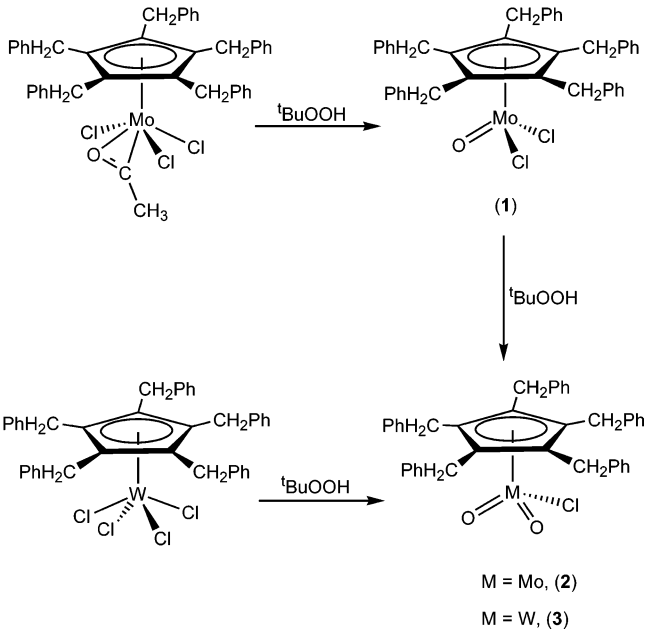
Scheme 1



and the results obtained on the catalytic epoxidation of olefins with several differently substituted Cp′Mo(O)$_2$X and [Cp′Mo(O)$_2$]$_2$ complexes with both TBHP and H$_2$O$_2$.

Results and Discussion

Synthetic and Structural Studies. As represented in Scheme 1, the readily accessible η^2-acyl complex [Mo(CpBz)Cl$_3$(COCH$_3$)][13] proved to be a convenient starting material for the high-yield synthesis of molybdenum oxo complexes. Treatment of [Mo(CpBz)Cl$_3$(COCH$_3$)] with 1 equiv of ^{t}BuOOH ([Mo]:ROOH = 1:0.5) in CH$_2$Cl$_2$ led to [Mo(CpBz)Cl$_2$(O)] (**1**) in 86% yield, whereas the same reaction carried out in the presence of an excess of ^{t}BuOOH gave [Mo(CpBz)Cl(O)$_2$] (**2**) in 73% yield. The analogous tungsten complex, [W(CpBz)Cl(O)$_2$] (**3**), was prepared in 43% yield by treatment of [W(CpBz)Cl$_4$][13] with an excess of ^{t}BuOOH (Scheme 1). Taking as reference [Mo(CO)$_6$], which is the starting material for the preparation of [Mo(CpBz)Cl$_3$(COCH$_3$)], the global yields of **1** and **2** are respectively 66% and 56%, which are much higher than the yields reported in the literature for other cyclopentadienyl molybdenum oxo complexes.[2,8,11,12] The yield obtained for **3**, although less significant than that of **2**, also corresponds to a major increase when compared to [WCp*(O)$_2$Cl].[10]

The ^{1}H NMR spectra of complexes **2** and **3** show singlets for the methylenic benzyl protons and the usual 2:2:1 patterns for the benzyl aromatic protons of the pentabenzylcyclopentadienyl ligand, indicating that there are no constraints to the free rotation of the benzyl groups. The M=O moieties are readily identified by the IR spectra that show characteristic bands at 941 cm^{-1} for **1**, at 918 and 889 cm^{-1} for **2**, and at 944 and 903 cm^{-1} for **3**.

Treatment of [Mo(CpBz)(CO)$_3$CH$_3$] (**4**)[13] with an excess of ^{t}BuOOH led to [{Mo(CpBz)(O)$_2$}$_2$(μ-O)] (**5**) in 35% yield. The IR spectrum of **5** shows terminal Mo=O stretching peaks at 914 and 886 cm^{-1} and a bridging Mo−O−Mo band at 775 cm^{-1}. These values are identical to those reported for [{MoCp′(O)$_2$}$_2$(μ-O)] (Cp′ = C$_5$H$_5$, C$_5$Me$_5$)[8,10] and are consistent with a linear Mo−O−Mo arrangement, as characterized by X-ray diffraction for [{MoCp*(O)$_2$}$_2$(μ-O)]. The proton and carbon NMR spectra of **5** display only one set of resonances for the pentabenzylcyclopentadienyl ligands, consistent with average C_s symmetry.

Alkylation reactions of **1** and **2** were attempted using AllylMgBr and ZnMe$_2$, respectively. Treatment of **1** with 2 equiv of AllylMgBr led to a diamagnetic microcrystalline yellow solid. ^{1}H and ^{13}C NMR spectra of this complex show one set of CpBz resonances, and elemental analysis is consistent with the formulation [Mo(CpBz)Cl$_2$]$_2$ (**6**). The formation of **6** excludes the occurrence of chloride metathesis and suggests that the attack of the Grignard reagent takes place through electrophilic abstraction of the oxo ligand by magnesium, resulting in metal reduction. Three different types of molecular structures have been determined by X-ray diffraction for related [MCp′Cl$_2$]$_2$ (M = Mo, W).[14] In all cases, the existence of metal−metal bonds accounts for the diamagnetism of those M(III) derivatives. Attempts to ascertain the molecular structure of **6** failed due to the small size of the crystals.

Reactions of **2** with ZnMe$_2$ did not give the foreseen methyl derivative and also did not allow the characterization of any reaction product.

Attempts to prepare cationic complexes were carried out by reacting **2** with chloride abstractors such as TlPF$_6$ and AgPF$_6$ in CH$_2$Cl$_2$, in the presence or absence of xylyl isocyanide. Precipitation of a blue material, which was not identified, was observed regardless of the conditions used.

The molecular structures of [Mo(CpBz)(O)Cl$_2$], **1**, and [Mo(CpBz)(O)$_2$Cl], **2**, have been determined by X-ray diffraction. Relevant bond lengths and angles are presented in Table 1, and Figures 1 and 2 depict ORTEP representations of the complexes with the corresponding atomic labeling scheme.

In complexes [M(CpBz)(O)Cl$_2$], **1**, and [M(CpBz)(O)$_2$Cl], **2**, the metal adopts a three-legged piano-stool geometry with the basal angles X−Mo(1)−Y (X, Y = O(1), Cl(1), Cl(2), and O(2)) ranging from 92.12(7)° to 108.94(14)° for **1** and 100.41(14)° to 109.0(2)° for **2**, smaller than the angles defined with the CpBz centroid, which range from 114.29(5)° to 116.85(14)° in compound **1** and 111.80(7)° to 116.014(13)° in complex **2** (see Table 1). In both compounds the phenyl rings of four benzyl fragments are directed opposite to the metal and one is bent down toward the metal although sufficiently far apart to prevent any bonding interaction. Also in both complexes the Cp ring is practically parallel to the planes defined by the three basal atoms, the dihedral angle being 6.4(3)° for **1** and 4.7(4)° for complex **2**. The Mo atom is closer to the basal plane than to the Cp (0.892(2)/2.058(2) and 0.805(2)/2.085(3) Å respectively for **1** and **2**). To better characterize the relative conformation of the phenyl rings, we present in Table 1 the torsion angles of the pendant benzyl arms (defined as M−C(CpBz ring)−C(CH$_2$ bridge)−C(first C atom of the Ph ring)). In both compounds the longest Mo−C bonds

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Table 1. Relevant Bond Distances and Angles for Compounds 1 and 2

	[Mo(CpBz)(O)Cl$_2$], **1**	[Mo(CpBz)(O)$_2$Cl], **2**
M−Cl(1)	2.3078(18) 2.306(3)	2.282(2)
M−Cl(2)	2.3349(18) 1.999(3)	
M−O(1)	1.735(4) 1.150(3)	1.891(4)
M−O(2)		1.748(5)
M−CT^a	2.0600(7) 2.022(5)	2.0894(10)
Cl(1)−M−Cl(2)	92.12(7) 74.67(12)	
Cl(1)−M−O(1)	108.94(14) 130.00(11)	100.32(14)
Cl(2)−M−O(1)	105.71(15) 71.57(12)	
Cl(1)−M−O(2)		102.1(2)
O(1)−M−O(2)		109.0(2)
CT−M−Cl(1)	115.89(5) 112.5(8)	111.80(7)
CT−M−Cl(2)	114.29(5) 131.2(7)	
CT−M−O(1)	116.85(14) 117.3(7)	116.04(13)
CT−M−O(2)		115.69(18)
M−C(1)−C(10)−C(11)	−40.7(8) 10.0(3)	50.3(9)
M−C(2)−C(20)−C(21)	161.8(4) −157.1(2)	−155.7(5)
M−C(3)−C(30)−C(31)	153.5(4) −169.3(2)	177.6(5)
M−C(4)−C(40)−C(41)	156.1(4) −171.8(3)	161.1(6)
M−C(5)−C(50)−C(51)	167.5(4) 173.4(3)	155.9(5)

[a] CT = CpBz centroid.

reflect the trans effect due to the oxo ligands, and therefore the Mo−C distances in the dioxo complex **2** are, on average, longer than in **1**. In compound **1** the Mo−Cl distances are on average longer than the Mo−Cl distance in compound **2**, whereas the Mo−O distance is relatively shorter in **1**. The Mo−Cl distances in compound **1** are, on average, slightly longer than those of CpMoOCl$_2$ [2.297(3) and 2.306(3) Å],[15] but slightly shorter than those of Cp*MoOCl$_2$ [2.3260(8) and 2.3420(7) Å].[11] This phenomenon seems more consistent with an electronic effect than with a steric one, since Cp* is less sterically encumbering but more electron releasing than CpBz. The Mo−O distance of **1** is, on the other hand, longer than that observed for the Cp* analogue [1.683(2) Å] and closer to that reported for the Cp analogue [1.740(6) Å]. These distances should be treated with great caution, because of the possible presence of O in the Cl site, and vice versa. Given that the cocrystallization of small amounts of **2** into the crystals of **1** (and vice versa) has been absolutely excluded on the basis of the spectroscopic analyses, there exists always the possibility of positional disorder between the O and Cl positions. Partial O occupancy in the Cl site would render the Mo−Cl distance artificially shorter, whereas partial Cl occupancy in the O site renders the Mo−O

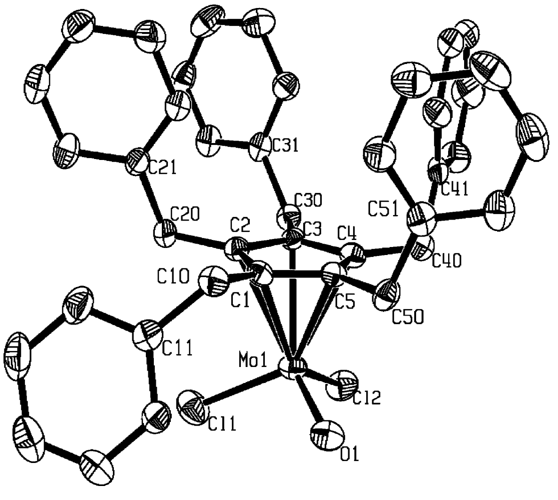

Figure 1. Molecular structure of **1**. H atoms were excluded for clarity. Thermal ellipsoids at 30% probability level.

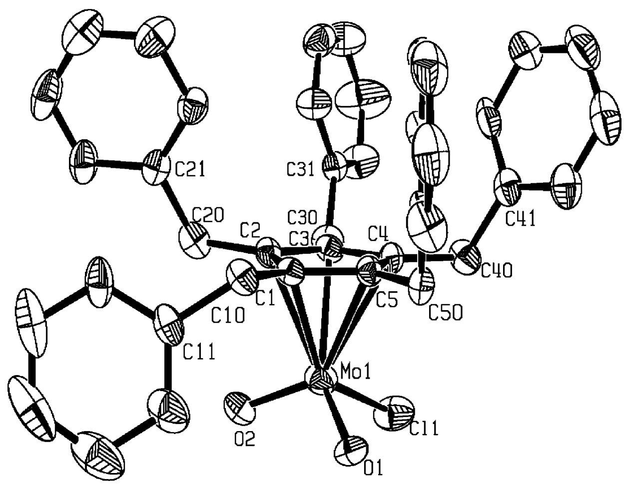

Figure 2. Molecular structure of **2**. H atoms were excluded for clarity. Thermal ellipsoids at 30% probability level.

Table 2. Electrochemical Data for Complexes 1 and 2[a]

compound	$E_{1/2}^{\mathrm{red}}$ (V)	$E_{\mathrm{p}}^{\mathrm{red}}$ (V)	$E_{\mathrm{p}}^{\mathrm{ox}}$ (V)
$Mo(CpBz)(O)Cl_2$	−1.012		0.995 (irr)
$Mo(CpBz)(O)_2Cl$		−1.378 (irr) −1.670 (irr)	

[a] Cyclic voltammetry in THF at 25 °C: (3.6–4.8) × 10^{-3} M complex;10^{-1} M Bu_4NBF_4 supporting electrolyte; 10^{-3} M ferrocene as internal standard. All potentials were evaluated at 200 mV/s.

distance artificially longer. This argument suggests that the Cp*$MoCl_2O$ structure, with shorter Mo−O and longer Mo−Cl distances, is probably less affected by potential disorder problems, although it does not represent positive proof of disorder for the other structures. For compound **2**, the Mo−Cl distance is much shorter than in compound $(C_5HPr^i_4)MoO_2Cl$ [2.3251(7) Å], which appears to be the only other well-determined structure for a Cp′MoO_2Cl compound.[6] Compound Cp*MoO_2Cl was also crystallographically characterized, but an orientational disorder prevented the accurate determination of the bonding parameters.[10] On the other hand, the Mo−O distances of **2** are relatively long compared to $(C_5HPr^i_4)MoO_2Cl$ [1.700(2) and 1.720(2) Å]. The latter are even slightly shorter than that measured for **1**, as would be expected given the smaller radius associated with the higher oxidation state. This argument, once again, tends to suggest the potential presence of positional disorder in the O and Cl positions for the determined crystal structure of **2**. Short intramolecular hydrogen interactions are observed in complex **1** between the oxo ligand and the hydrogen atom H(16), that is in the phenyl ortho position of the benzyl group that bends toward the metal, and the hydrogen atoms H(501) and H(502) that are the methylenic protons of a benzyl substituent (O(1)···H(16), 2.781(7) Å; O(1)···H(501)/(502), 2.893(7)/2.990(7) Å). Complex **2** displays close contacts involving the same atoms [O(1)···H(16), 2.664(7) Å, O(1)···H(502), 2.630(7) Å]. Moreover, O(2) also interacts with one of the hydrogen atoms of another methylenic benzyl group, O(2)···H(201), 2.616(7) Å. Although these interactions are too week to be observed by NMR in solution, it is relevant to mention that related intramolecular bonds have been characterized by Thiel and co-workers[16] and also that an intermolecular interaction between an oxo ligand and the ^{t}BuOOH proton is proposed as a key step in the activation of *tert*-butylhydroperoxide by molybdenum epoxidation catalysts.[3,17]

The redox behavior of molybdenum oxo complexes has attracted much attention owing to its relevance to the oxygen atom transfer catalyzed by molybdenum enzymes. [1] In general, complexes with the $[Mo^V{=}O]$ core exhibit a reversible reduction that has been assigned to the Mo(V)/Mo(IV) pair. This behavior is also displayed in the CV of $[Mo(CpBz)(O)Cl_2]$, which shows a reversible reduction at $E_{1/2}^{\mathrm{red}} = -1.012$ V in THF (vs Fc^+/Fc). The anodic process is irreversible with a half-wave potential of 0.995 V (Table 2). The lack of electrochemical data for half-sandwich complexes of general type $[MCp'(O)X_2]$ (Cp′ = Cp-type ligand; X = anionic ligand) compels us to compare our result with hexacoordinated complexes $[Mo(L)OCl_2]$ where L represents tripodal scorpionate-type monoanionic ligands such as $(pz)_3BH$ or $(pz)_2CHX$ (X fragment containing O or S donors), in which $E_{1/2}^{\mathrm{red}}$ values range between 0.54 and 1.38 V.[18,19] The value encountered for **1** compares well with those of *cis*- (−0.934 V) and *trans*-$LMoOCl_2$ (−1.15 V) where L is the anion of $(pz)_2CH\{(5\text{-Me})(3\text{-}^tBu)(2\text{-OH})Ph\}$.[20] However, contrary to those compounds, but like most Mo(V) oxo complexes, the anodic process is irreversible, a result that accounts for the instability of mono-oxo Mo(VI) species that readily convert into $[MoO_2]^+$ through reaction with traces of water present in the medium.

The CV of $[Mo(CpBz)(O)_2Cl]$ shows an irreversible one-electron reduction peak at $E_{\mathrm{p}}^{\mathrm{ox}} = -1.378$ V vs Fc^+/Fc attributed to the Mo(VI)/Mo(V) redox couple, followed by a second reduction irreversible peak at −1670 V assigned to the Mo(V)/Mo(IV) process. These results are in conformity with CV results reported for dioxomolybdenum complexes, and, accordingly with the irreversible character of these processes, increasing the scan rate causes a shift of the peaks to cathodic potentials and the current function is approximately independent of the scan rates used.[21,22]

Catalysis Studies on Cyclooctene Epoxidation. Previous studies on the epoxidation of olefins carried out with Cp′MoO_2X complexes as catalysts were only effective with TBHP as the terminal oxidant. A dependence on the bulk of the Cp′ ring was also noted, and the loss of activity of the $CpMoO_2Cl$ complex was attributed to the presence of water in the reaction medium, on the basis of circumstantial proof. [2] Later on some of us have established the stability of Cp*Mo-oxo species, derived from bimetallic compounds such as $[Cp^*MoO_2]_2O$, in aqueous solution within a wide range of pH values. These studies started to unveil an extensive aqueous chemistry of cyclopentadienyl oxo complexes, namely, that of the $[Cp^*MoO_2]_2O$.[6,7,23] This kind of binuclear complex might be considered a special case of Cp′MoO_2X (X = $Cp'MoO_3]^-$) and has never been studied in epoxidation catalysis. This situation prompted the following prospective studies with a threefold aim: (i) assess the activity dependence of Cp′MoO_2Cl on the nature of the ring substituents using TBHP as oxidant; (ii) screen the catalytic activity of the bimetallic species $[Cp'MoO_2]_2O$ using TBHP as oxidant; (iii) check for catalytic activity of $[Cp'MoO_2]_2O$ in aqueous solution with both H_2O_2 and TBHP as oxidant.

Questions (i) and (ii) were addressed only by carrying out experiments in nonaqueous solutions ($CHCl_3$ as solvent), at 55 °C with 1% catalyst, cyclooctene as olefin and TBHP as terminal oxidant (see Experimental Section for details). These conditions have been systematically used in our previous studies to allow for a better comparison of the catalytic performance of different molecular systems all operating through activation of

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Table 3. Conversion (%) of Cyclooctene to Its Epoxide in $CHCl_3$ Solution at 55 °C with TBHP Catalyzed by $Cp'MoO_2X$ and Related Complexes

	time (h)												
	0.083	0.1	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	5.0	6.0	24
Cp′ ring in $Cp'MoO_2Cl$													
C_5Bz_5 (**2**)	60.8		79.3	84.5	93.1	94.8	96.6	98.3	100.0	100.0			100.0
C_5H_5 (**7**)	75.6		82.2	86.7	91.1	97.8	98.0	98.5	100.0	100.0			100.0
C_5Me_5 (**8**)	38.0		46.0	55.0	59.0	60.0	61.0	62.0	63.0	64.0			64.0
$C_5H^iPr_4$ (**9**)	6.2		55.7	65.1	49.0	59.1				67.0		75.0	85.0
$(C_5Bz_5)Mo(CO)_3Me$ (**4**)			82.2										
Cp′ ring in $[Cp'MoO_2]_2$													
C_5Bz_5 (**5**)		0.7	21.4	45.1	36.3	50.2		43.8			67.6	44.6	70.2
C_5Me_5 (**10**)		2.7	43.3		46.3			51.4		55.5	59.1	59.7	86.7
(**10a**)													90.0
$C_5H_2{}^tBu_3$ (**11**)		3.5	69.3	67.0	74.3			75.0		72.3	78.2	70.9	78.9
(**11a**)													76.4
$C_5H^iPr_4$ (**12**)		17.9	67.8	62.6	73.7	70.4				74.5	82.7	85.1	99.9
(**12a**)													100.0

TBHP by the $Mo(VI)O_2$ fragment. Blank reactions showed that no significant amount of epoxide was formed in the absence of catalyst. The values measured for cyclooctene conversion to its epoxide as a function of time are given in Table 3 for mononuclear $Cp'MoO_2Cl$ and binuclear $[Cp'MoO_2]_2O$ catalysts. No significant formation of byproducts (e.g., diol from epoxide ring opening) other than epoxide was observed. As can be seen, from these results, the mononuclear complexes $Cp'MoO_2Cl$ are clearly faster in the early stages of the reaction. In particular, $(CpBz)MoO_2Cl$ (**2**) and $CpMoO_2Cl$ (**7**) attain rather high conversions already at ca. 5 min reaction time: 60.8% and 75.6%, respectively. After 3.5 h both catalysts achieved 100% conversion. $Cp(^iPr)_4MoO_2Cl$ (**9**) has a comparatively slow start but rapidly overtakes the performance of Cp^*MoO_2Cl (**8**), which becomes almost inactive after 1.5 h. After 24 h the conversion achieved with **9** largely exceeds that of **8**. The tricarbonyl **4** was used as plausible catalyst precursor for $CpBzMoO_2Me$ in a similar way to the formation of $Cp'MoO_2Cl$ from $Cp'Mo(CO)_3Cl$.[2,24] A conversion of 82.2% was obtained within the first 30 min. However, in contrast to **7**, this value did not further increase. It seems evident that the catalyst decomposed under the reaction conditions.

Under the same operating conditions the bimetallic compounds achieve conversions in the same range as the monomers **8** and **9**. In contrast to the corresponding monomer, the C_5Bz_5 derivative, $[(CpBz)MoO_2]_2O$ (**5**), is the least performing of all the compounds tested. Conversely, at 24 h reaction time, $[Cp^iPr_4MoO_2]_2O$ (**12**) outperforms all other complexes tested, except **2** and **7**. Both **12** and $[Cp^*MoO_2]_2O$ (**10**) achieve higher conversions at 24 h than their mononuclear congeners.

Figure 3 shows the time dependence curve of this reaction for the monometallic catalysts, which is typical for all other $MoO_2X_2L_2$-type catalysts tested so far. There is no observable induction period or a clear indication that the original catalyst is transformed into another species, in agreement with previous NMR observations by Bergman and Trost for epoxidation with **8**.[12] Kinetic and spectroscopic studies on $MO_2X_2L_2$ (M = Mo, W) complexes indicate that the catalyst initially activates TBHP to form an intermediate that transfers one O atom to the olefin.[3] The kinetic model for these reactions explains the slowing down of the reaction as the result of the increasing amount of ^tBuOH formed, which competes with TBHP for coordination positions at the metal, thereby blocking the TBHP activation step. Given the coordination and electronic similarity between $MO_2X_2L_2$ and $Cp'MoO_2X$ complexes, we believe that the latter follow a similar reaction pathway in their olefin epoxidation catalysis.

The corresponding profile for the binuclear compounds, Figure 4, shows a slower start and a slow progression of the reaction after ca. 2 h. This retardation of the reaction is noted at the same time that an off-white precipitate starts to separate slowly from the initially homogeneous solution. These precipitates, named **10a**, **11a**, and **12a** from the reactions of **10**, **11**, and **12**, respectively, are not formed in the reactions of mononuclear $Cp'MoO_2Cl$. The reaction profiles in Figure 4 clearly show this pronounced inhibition of the reaction velocity. However, the reaction does not stop and can lead to high conversions at 24 h, as noted above. The precipitates **10a**, **11a**, and **12a** isolated and washed at the end of the reaction were reused as heterogeneous catalysts on a second run, under similar initial condi-

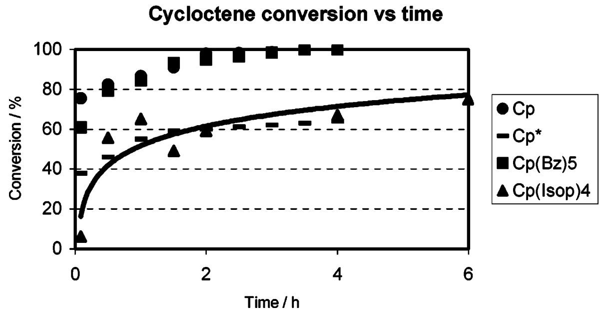

Figure 3. Reaction conditions: olefin: cyclooctene; temp: 55 °C; oxide: TBHP; cat.: 1% $Cp'MoO_2Cl$; solvent: $CHCl_3$.

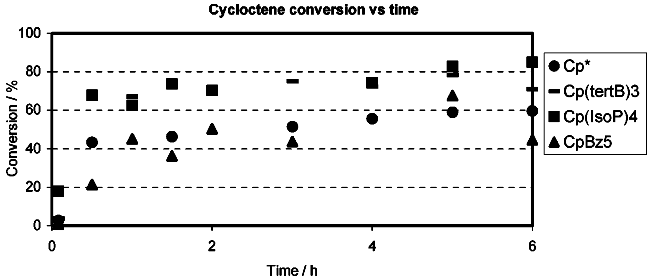

Figure 4. Reaction conditions: olefin: cyclooctene; temp: 55 °C; oxide: TBHP; cat.: 1% $[Cp'MoO_2]_2O$; solvent: $CHCl_3$.

tions. In all cases the conversion after 24 h was essentially the same as the first run, started with the respective homogeneous solution of the bimetallic complexes **10**, **11**, and **12**. This means that these insoluble species are also an active, slow, yet resistant catalyst for COE epoxidation. It should also be noted that the supernatant solutions obtained after separation of **10a**, **11a**, and **12a** are still active for COE epoxidation upon addition of another charge of both COE and TBHP. Since the quantification of the results was problematic, they are not shown on a quantitative basis.

The identification of the molecular nature of the precipitates was attempted only with **10a**. Its IR spectrum shows the presence of Cp* (2963.5 cm^{-1}). However, it does not reveal any terminal M=O stretch, and a band at 804 cm^{-1} seems to be too low for a typical O−O bond in a Mo peroxo complex. The insolubility of the compound in organic solvents prevented NMR studies. Therefore, full characterization of this product and its analogues is still under way, namely, via solid state spectroscopic and analytical methods.

To study the activity of these systems in aqueous solution, H_2O_2 and TBHP were used as oxidants in COE epoxidation. Complex **10** was tested with 30% H_2O_2 both at the natural pH of its solution and at pH 1.5. After 4 h, the conversions were around 2% in both cases. On the contrary, both **8** and **10** catalyzed COE epoxidation in aqueous 70% TBHP. After 4 h the conversion was around 27% for **10** and 37% for the monomer **8**. No attempts have been made to optimize these reaction conditions because our first aim in these exploratory studies was to establish whether water was deleterious for the catalytic system and whether H_2O_2 is capable of being used as terminal oxidant. The results confirm that the catalysts are still active in water solution but only when TBHP is used as oxidant. In agreement with previous observations, H_2O_2 is unable to be activated to olefin epoxidation by octahedral or pseudo-octahedral $MoO_2X_2L_2$ or $Cp'MoO_2X$ complexes.

Discussion

As already stated, the catalytic reaction profile of $Cp'MoO_2X$ complexes (Figure 3) fits entirely to the one already described at length for other (isoelectronic) $MoO_2X_2L_2$. This mechanism invokes a *tert*-butylperoxide intermediate that is the catalytically active species for oxygen transfer to the olefin. This picture was first proposed by Chong and Sharpless for the catalyst precursor $MoO_2(acac)_2$[25] as well as by Trost and Bergman for Cp^*MoO_2Cl.[12] Both authors ruled out peroxo complexes as catalytic intermediates in their systems with the TBHP oxidant. Moreover, isolated $Cp^*MoO(O_2)Cl$ was shown to be inactive. This *tert*-butylperoxide intermediate leads to a rather sterically crowded coordination sphere. Such crowding creates a difficulty in explaining the order of activity that can be qualitatively extracted from the early reaction times in Figure 3, Cp $\sim C_5Bz_5 \gg C_5Me_5 \sim C_5H^iPr_4$. An alternative electronic explanation for this order could be based either on the ability of the Cp′ ligands to undergo ring-slippage (or distortion) that might alleviate the steric pressure of the intermediate or on the electronic richness of the terminal oxo ligands. The former argument is in line with a recent report where enhanced catalytic action is achieved by loss of one ancillary ligand.[26] Presently we have no kinetic or spectroscopic data (^{17}O NMR) that might confirm any of these hypotheses. However, DFT modulation of the interaction of $Cp'MoO_2X$ complexes with TBHP is presently under study and might shed some light on this question.

Nevertheless, the steric argument is in accord with the fact that the mononuclear species are more active than the binuclear ones. In the latter X is formally replaced by the very bulky $[Cp'MoO_3]^-$. This effect has its higher instance in the case of $Cp' = C_5Bz_5$, which is the least active of the bimetallic compounds. In other words, sterics makes it difficult to have both metal centers operating simultaneously. However, this may not be decisive in their catalytic performance since they transform into an insoluble, catalytically active species. The understanding of the nature of such species is necessary to clarify the mode of action of the bimetallic compounds and is in progress.

The present studies also meet our expectation that $Cp'MoO_2X$ complexes are catalytically active in aqueous solution provided TBHP is used instead of H_2O_2. Indeed, the Cp^*MoO_2 (VI) fragment survives a wide range of pH conditions in aqueous solution, where species such as $[Cp^*MoO_2(H_2O)]^+$, $[Cp^*MoO_2(OH)]$, and $[Cp^*MoO_3]^-$ have been identified.[23] Their *cis*-MoO_2 moiety is expected to form a peroxo complex with H_2O_2. Whichever such peroxo complex may be, it is now clear that it is incapable of epoxidizing olefins, even in acidic medium, as has been shown for many other Mo-oxo-peroxo complexes.[12,25,27]

On the other hand, this *cis*-MoO_2 moiety is capable of activating TBHP to produce a catalytically active species. We believe that such activation results from the direct interaction of TBHP with the $Cp'MoO_2X$ complex. However, TBHP is also capable of originating peroxo complexes from *cis*-MoO_2 fragments. Some studies have shown that these peroxo complexes may become active in the presence of excess TBHP,[26,27] although this does not seem to be the case in the $Cp'MoO_2X$ system.[12] Nevertheless, both versions of this mechanism of TBHP activation remain to be clarified and warrant further study.

Conclusions

The synthesis of $Cp'MO_2Cl$ (M = Mo, W) derivatives can be performed from several $Cp'MX_n$ precursors upon direct reaction with ^tBuOOH under very mild conditions and with high yields. These compounds, together with bimetallic complexes of the type $[Cp'MoO_2]_2O$, were tested as catalysts for olefin epoxidation with both ^tBuOOH and H_2O_2 as terminal oxidants. Although it is obvious that the nature of the substitutents on the Cp′ ring strongly influences the overall performance of the catalysts, both in terms of initial activity rates but, more

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importantly, in terms of their long-term performance at 24 h reaction, steric bulk is not the decisive parameter to control this dependence. The bimetallic complexes $[Cp'MoO_2]_2O$ produce higher yields at long reaction times than their monomeric $Cp'MoO_2Cl$ counterparts. However, they decompose during the reaction to form an insoluble catalytically active species still unidentified. $[Cp'MoO_2]_2O$ and $Cp'MoO_2Cl$ are active in aqueous solution with TBHP but not with H_2O_2 as an oxidant. Theoretical and experimental studies aiming at clarifying the mechanistic issues raised are in progress.

Experimental Section

General Procedures. All manipulations were carried out under a dry nitrogen atmosphere with standard Schlenk techniques except those where O_2 from air was used as an oxidant. Solvents were predried and distilled from the following drying agents: hexane and dichloromethane (CaH_2), d_6-benzene, and diethyl ether (Na). Literature methods were used to prepare HCpBz,[28] $[Mo(CpBz)Cl_3(\eta^2\text{-}COCH_3)]$, $[W(CpBz)Cl_4]$, $[Mo(CpBz)(CO)_3CH_3]$,[13] and $Cp^*{}_2Mo_2O_5$, $(C_5HPr^i{}_4)_2Mo_2O_5$, $(C_5H_2\text{-}Bu^t{}_3)_2Mo_2O_5$, and $(C_5HPr^i{}_4)MoO_2Cl$.[6] NMR spectra were recorded on a Varian Unity 300 instrument at room temperature and were referred to the residual ^1H and ^{13}C NMR solvent resonances. Infrared spectra were recorded using KBr pellets on a Jasco FT/IR 430. Mass spectra were recorded on a Finnegan MAT System 8200 spectrometer, except that of complex **5**, which was obtained by a Fourier transform ion cyclotron resonance mass spectrometer (Finnegan FT/MS 2001-DT spectrometer), equipped with a 3 T superconducting magnet. Elemental analyses were obtained from the Laboratório de Análises do IST (Fisons Instrument 1108). Cyclic voltammetry measurements were carried out using a Radiometer DEA 101 digital electrochemical analyzer interfaced with an IMT 102 electrochemical interface. $[Bu_4N][BF_4]$ (Fluka, electrochemical grade) was used as supporting electrolyte in THF with ca. 10^{-1} M concentration. All experiments were performed with concentrations of complexes in the range $(4.2-4.8) \times 10^{-3}$ M. All potentials were referenced to the ferrocene/ferrocenium couple as internal standard with $E_{1/2} = 0.50$ V versus SCE. A Pt disk (with $\phi = 1$ mm) was used as working electrode. All experiments were carried out at 25 °C in the absence of oxygen.

$[Mo(CpBz)(O)Cl_2]$ (1). A solution of $[Mo(CpBz)Cl_3(\eta^2\text{-}COCH_3)]$ (0.66 g, 0.86 mmol) in dichloromethane was treated with a 5.5 M solution of *tert*-butylhydroperoxide in *n*-decane (0.08 mL, 0.44 mmol). After 1.5 h at room temperature, the reaction mixture was evaporated to dryness, and the oily product formed was extracted in diethyl ether. The filtered solution was concentrated and cooled overnight at −20 °C, leading to the formation of yellow crystals that were separated by filtration. Yield: 0.52 g (0.74 mmol, 86%). IR (KBr): ν(Mo=O), cm^{-1} 941(s). Anal. Calcd for $C_{40}H_{35}Cl_2OMo$: C 68.78; H 5.05. Found: C 68.74; H 5.15.

$[Mo(CpBz)(O)_2Cl]$ (2). A 5.5 M *tert*-butylhydroperoxide solution in *n*-decane (0.78 mL, 4.26 mmol) was added dropwise to a solution of $[Mo(CpBz)Cl_3(\eta^2\text{-}COCH_3)]$ (1.08 g, 1.42 mmol) in dichloromethane. The mixture was stirred at room temperature during 12 h until the solution turned yellow. The reaction was stopped by the addition of manganese dioxide. The solution was filtered off and the solvent removed under vacuum to dryness. The solid obtained was washed with cold hexane and extracted in diethyl ether. Cooling at −20 °C gave **2** as a yellow crystalline solid. Yield: 0.70 g, 1.03 mmol, 73%. ^1H NMR (C_6D_6): δ 6.76 (m, 15H, *m*-C_6H_5, *p*-C_6H_5), 6.46 (d, 10H, *o*-C_6H_5), 3.86 (s, 10H, CH_2Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 137.8 (*i*-C_6H_5), 129.3 ($C_5(CH_2Ph)_5$), 129.2 (*o*-C_6H_5), 128.5 (*m*-C_6H_5), 126.6 (*p*-C_6H_5), 33.0 (CH_2Ph). IR (KBr), cm^{-1}: 918(vs), 889(vs), ν(Mo=O); 586(s), ν(O=Mo=O). Anal. Calcd for $C_{40}H_{35}ClO_2Mo$: C 70.57; H 5.19. Found: C 70.12; H 5.22.

$[W(CpBz)(O)_2Cl]$ (3). A solution of $[W(CpBz)Cl_4]$ (0.50 g, 0.60 mmol) in dichloromethane was treated with an excess of a 5.5 M solution of *tert*-butylhydroperoxide in *n*-decane at room temperature. The excess of *tert*-butylhydroperoxide was destroyed after stirring for 12 h by addition of manganese dioxide. The solution was filtered off and the solvent was removed to dryness under vacuum. The residue was washed with cold hexane (2 × 3 mL) and extracted in diethyl ether. Green crystals of **3** formed at −20 °C from the Et_2O solution. Yield: 0.20 g, 43%. ^1H NMR (C_6D_6): δ 6.76 (m, 15H, *m*-C_6H_5, *p*-C_6H_5), 6.46 (d, 10H, *o*-C_6H_5), 3.95 (s, 10H, CH_2Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 137.9 (*i*-C_6H_5), 129.5 ($C_5(CH_2Ph)_5$), 129.2 (*o*-C_6H_5), 128.5 (*m*-C_6H_5), 126.6 (*p*-C_6H_5), 32.9 (CH_2Ph). IR (KBr): ν(W=O), cm^{-1} 944(vs), 903(vs). Anal. Calcd for $C_{40}H_{35}ClO_2W$: C 62.64; H 4.60. Found: C 62.55; H 4.74.

$[Mo(CpBz)(O)_2]_2(\mu\text{-}O)$ (5). An excess of a 5.5 M solution of *tert*-butylhydroperoxide solution in *n*-decane was added dropwise to a solution of $[Mo(CpBz)(CO)_3CH_3]$ (3.55 g, 5.0 mmol) in dichloromethane. The mixture was stirred at room temperature during 5 h, and manganese dioxide was added to destroy the excess of *tert*-butylhydroperoxide. The solids were removed by filtration, and the solvent was evaporated to dryness under vacuum. The residue was washed with cold hexane (2 × 3 mL), extracted in diethyl ether, and filtered. Cooling at −20 °C led to the separation of yellow crystals of **5** in 35% yield (2.28 g). ^1H NMR (C_6D_6): δ 6.83 (m, 15H, *m*-C_6H_5, *p*-C_6H_5), 6.68 (m, 10H, *o*-C_6H_5), 4.27 (s, 10H, CH_2Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 138.6 (*i*-C_6H_5), 129.5 (*o*-C_6H_5), 128.6 (*m*-C_6H_5), 126.5 (*p*-C_6H_5), 125.6 ($C_5(CH_2Ph)_5$), 32.8 (CH_2Ph). IR (KBr): ν(Mo=O), cm^{-1} 914(vs), 886(s); ν(Mo−O−Mo), cm^{-1} 775(vs). MS: 791, $[\{(CpBz)Mo_2O_5\}^-]$; 661, $[\{(CpBz)MoO_3\}^-]$; 644, $[\{(CpBz)MoO_2\}^-]$; 515, CpBz. Anal. Calcd for $C_{80}H_{70}O_5Mo$: C 73.73; H, 5.41. Found: C 74.00; H 5.46.

X-ray Diffraction Experimental Determination. Crystal structures were obtained using a MACH3 Nonius diffractometer equipped with Mo radiation ($\lambda = 0.71069$ Å) for the two compounds. Experimental details of the crystal structure determination and refinement are given in Table 3.

All data were corrected for Lorentz, polarization, and long-term intensity fluctuations. Absorption effects in compound **1** were corrected using semiempirical psi-scans;[29] no absorption correction was performed in compound **2**. Structures were solved by direct methods using SIR99[30] and refined by full-matrix least squares against F^2 using SHELXTL[31] all included in the suit of programs WinGX v1.64.05 for windows.[32]

In both structures all non-hydrogen atoms were refined anisotropically and the hydrogen atoms were inserted in idealized positions riding on the parent C atom.

More experimental details are given in the Supporting Information. Illustrations of the molecular structures were made with ORTEP3.[33] Data were deposited in the CCDC under the deposit numbers CCDC 256118 and 256119 for compounds **1** and **2**, respectively.

Catalytic Experiments. Catalytic epoxidation of cyclooctene was performed under nitrogen atmosphere in a reaction vessel equipped with a magnetic stirrer and immersed

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Table 4. Experimental Details on X-ray Data Collection and Structure Refinement

	1	**2**
empirical formula	$C_{40}H_{35}Cl_2MoO$	$C_{40}H_{35}ClMoO_2$
fw	698.52	679.07
temperature	293(2) K	293(2) K
wavelength	0.71069 Å	0.71069 Å
cryst syst	monoclinic	monoclinic
space group	$P21/n$	$P21/n$
unit cell dimensions	$a = 13.335(4)$ Å	$a = 11.681(4)$ Å
	$b = 16.863(2)$ Å	$b = 14.790(4)$ Å
	$c = 15.241(2)$ Å	$c = 19.840(6)$ Å
	$\beta = 100.456(16)°$	$\beta = 104.59(3)°$
volume	3370(2) Å^3	3316.9(18) Å^3
Z	4	4
calcd density	1.377 Mg/ m^3	1.360 Mg/m^3
absorption coeff	0.578 mm^{-1}	0.509 mm^{-1}
F(000)	1436	1400
cryst size	0.4 × 0.25 × 0.1 mm	0.3 × 0.1 × 0.08 mm
cryst morphology	parallelepiped	parallelepiped
color	dark red	yellow
θ range for data collection	1.82 to 25.00°	2.12 to 24.98°
limiting indices	$-15 \le h \le 0$	$-13 \le h \le 0$
	$0 \le k \le 19$	$0 \le k \le 17$
	$-17 \le l \le 18$	$-22 \le l \le 23$
reflns collected/unique	6129/5863 [R(int) = 0.0699]	6105/5807 [R(int) = 0.0505]
completeness to θ	99.0% (θ =25.00)	99.4% (θ = 24.98)
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	5863/0/430	5807/0/397
goodness-of-fit on F^2	0.999	0.912
final R indices [$I > 2\sigma(I)$]	R1 = 0.0580, wR2 = 0.1335	R1 = 0.0782, wR2 = 0.1269
R indices (all data)	R1 = 0.1098, wR2 = 0.1544	R1 = 0.2045, wR2 = 0.1536
extinction coeff	0.0020(5)	none
largest diff peak and hole	0.913 and −0.582 e Å^{-3}	0.433 and −0.335 e Å^{-3}

in a thermostated oil bath. A 1% molar ratio of catalyst/substrate (73 μmol of complex and 0.8 g, 7.3 mmol of cyclooctene) and a substrate/oxidant (2.64 mL, *tert*-butyl hydroperoxide (TBHP), 5.5 M in decane) ratio of 0.5 were used, with 0.8 g of *n*-dibutyl ether (internal standard) and 3 mL of dried chloroform as solvent. The solution was stirred for 24 h at 55 °C, and the course of the reaction was monitored by quantitative GC analysis. Samples were taken every 30 min and diluted with dichloromethane. For the destruction of the peroxide a small amount of manganese dioxide was added, the resulting slurry was filtered over a Pasteur pipet with cotton and silica, and the filtrate was injected on a gas chromatograph (Thermofinnigan Trace 2000 GC) equipped with a J&W capillary column (Cyclosilb, 30 m × 0.25 mm × 0.25 μm) and a flame ionization detector. To recycle the catalyst, the reaction medium was filtered and washed with dichloromethane and *n*-hexane, and the precipitate was recharged with *n*-dibutyl ether, cyclooctene, *tert*-butyl hydroperoxide, and chloroform as solvent in the original quantities and submitted to the catalytic process under the conditions performed in the first run. A single sample was taken after 24 h of reaction.

The catalytic epoxidation of cyclooctene with hydrogen peroxide was performed by adding 1.5 mL of a 30 wt % solution of hydrogen peroxide in water to the substrate, internal standard, and catalyst. The 0.5 ratio of substrate/oxidant was maintained. After 4 h of stirring at 55 °C the reaction was stopped by the addition of manganese dioxide and magnesium sulfate for the destruction of hydrogen peroxide and removal of water. After the gas evolution ceased, the slurry was filtered over a Pasteur pipet with cotton and silica, and the filtrate was extracted with 4 × 25 mL of dichloromethane and injected in the GC column. Similarly, the catalytic epoxidation of cyclooctene with TBHP/water as oxidant was performed adding 2.1 mL of a 70 wt % solution of *tert*-butyl hydroperoxide in water to the catalyst, substrate, and internal standard solution. After 4 h of stirring at 55 °C, the reaction was stopped with the addition of manganese dioxide for the destruction of peroxides. After the gas evolution ceased, the slurry was filtered and extracted with 4 × 25 mL of dichloromethane and injected in the GC column.

The catalytic experiments performed in acidic media were done by adding 1.5 mL of a 30 wt % solution of hydrogen peroxide in 3 mL water and adding a concentrated solution of sulfuric acid until the pH reached 1.5. This solution was then added to the reaction vessel containing the substrate, internal standard, and catalyst and stirred for 4 h at 55 °C. The reaction was stopped by the addition of manganese dioxide and magnesium sulfate for the destruction of hydrogen peroxide and removal of water. After the gas evolution ceased, the slurry was filtered over a Pasteur pipet with cotton and silica, and the filtrate was extracted with 4 × 25 mL of dichloromethane and injected in the GC column.

The conversion of cyclooctene oxide in all the experiments was calculated from a calibration curve recorded prior to the reaction course.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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