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Chiral Cationic $[Cp'Mo(CO)_2(NCMe)]^+$ Species – Catalyst Precursors for Olefin Epoxidation with H_2O_2 and *tert*-Butyl Hydroperoxide

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A novel cyclopentadienyl ligand bearing a chiral oxazoline pendant group (Cp^{ox}) has been prepared. Its coordination to molybdenum and tungsten afforded optically pure (*R*)-$Cp^{ox}M(\eta^3\text{-}C_3H_5)(CO)_2$ (M = Mo, W) in which the pendant oxazoline fragment is not coordinated to the metal center. Reaction of (*R*)-$Cp^{ox}Mo(\eta^3\text{-}C_3H_5)(CO)_2$ with tetrafluoroboric acid gives the bidentate η^5-cyclopentadienyloxazoline complex $[Cp^{ox}Mo(CO)_2(NCMe)]BF_4$ in which the oxazoline is coordinated through the N-atom to the molybdenum center. Their catalytic performance in the epoxidation of *cis*-cyclooctene, (*R*)-limonene, and *trans*-β-methylstyrene with H_2O_2 and *tert*-butyl hydroperoxide (TBHP) as oxidants has been studied. (*R*)-$Cp^{ox}W(\eta^3\text{-}C_3H_5)(CO)_2$ displayed high catalytic activity achieving quantitative conversion of cyclooctene epoxide in 2 h with H_2O_2. $[Cp^{ox}Mo(CO)_2(NCMe)]^+$ has been shown to be an efficient catalyst with TBHP and H_2O_2, reaching quantitative conversions of the corresponding epoxide in 30 min and 11 h, respectively. ESI-MS studies of the reaction of $[Cp^{ox}Mo(CO)_2(NCMe)]^+$ with H_2O_2 and TBHP revealed the in situ formation of the corresponding peroxido $[Cp^{ox}Mo(O_2)O]^+$ and dioxido $[Cp^{ox}MoO_2]^+$ species, respectively. Further oxidation of these complexes resulted in the loss of the cyclopentadienyloxazoline ligand. Based on spin trap experiments, the involvement of both carbon- and oxygen-centred radicals in the olefin epoxidation catalyzed by $[Cp^{ox}Mo(CO)_2(NCMe)]^+$ has been proved.

Introduction

The excellent catalytic performance of $CpMoO_2X$ (Cp = $\eta^5\text{-}C_5R_5$; X = Cl, Br, CH_3) derivatives and their carbonyl precursors $CpMo(CO)_3X$ in the epoxidation of olefins with TBHP is well established.[1] The catalytic activity of $CpMoO_2Cl$ derivatives, first reported by Trost and Bergman in 1991,[2] has recently been the subject of intensive studies. Olefin epoxidation with a variety of cyclopentadienylmolybdenum complexes of the general formula $CpMoO_2X$ containing differently substituted cyclopentadienyl rings has been reported.[3,4] Attempts to introduce chirality into these systems through cyclopentadienyl groups containing linked chiral ligands suffers from a major drawback that free rotation of the cyclopentadienyl ring yields negligible asymmetric induction when applied as catalysts.[5] To avoid this problem, Kühn and coworkers have developed a series of catalytically active *ansa*-bridged cyclopentadienyl compounds of molybdenum.[6] However, some of these complexes show low stability under oxidative conditions leading to a significant decomposition of the catalyst during the catalytic cycle. With the aim of stabilizing cyclopentadienyl *ansa*-bridged complexes, we recently prepared a series of *ansa*-(Cp-NHC)$Mo(CO)_2I$ (Cp = $\eta^5\text{-}C_5H_4$, $\eta^5\text{-}C_5Me_4$, $\eta^5\text{-}C_5(CH_2Ph)_4$, NHC = N-heterocyclic carbene) derivatives containing a cyclopentadienyl group functionalized with a NHC, which were applied as olefin epoxidation catalysts.[7] We envisioned that the strong M–NHC bond would help to stabilize this type of complex. However, poor catalytic activity and stability under oxidative conditions were displayed by (Cp–NHC)$Mo(CO)_2I$ compounds.[7,8] Based on these results, we decided to develop a novel chelate cyclopentadienyl ligand capable of both stabilizing molybdenum complexes under oxidative conditions and introducing chirality into the system. Herein, we report the preparation of a cyclopentadienyl ring bearing a pendant oxazoline group. Oxazolines have been used as stabilizing agents for many transition metals based on their robustness under a variety of reaction conditions.[9] Upon coordination of the oxazoline ring through the N atom, the stereo directing substituent is situated in close proximity to the metal center controlling the space available for the substrate. Several chiral dioxidomolybdenum(VI) complexes containing oxazoline ligands have been applied as epoxid-

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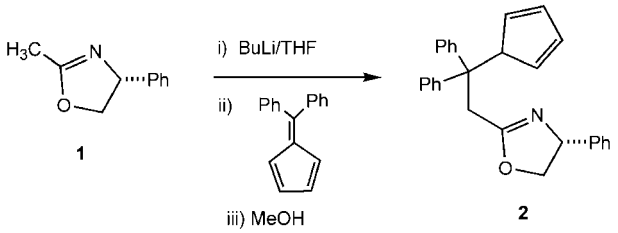
ation catalysts.[10] However, little success has been achieved until now in asymmetric epoxidation, probably due to labile behavior of the oxazoline moiety bound to dioxido-molybdenum(VI) fragments.[10b] We envisaged that functionalization of the oxazoline ligand with a cyclopentadienyl ring might provide a bidentate ligand capable of stabilizing chelate molybdenum complexes and preventing oxazoline decoordination. It is well known that the excellent spectator ligand qualities of cyclopentadienyl rings, which usually bind very strongly to transition metal centers, give high thermal stabibilty.[11] To the best of our knowledge, chelate oxazoline-derived cyclopentadienyl systems are not known.

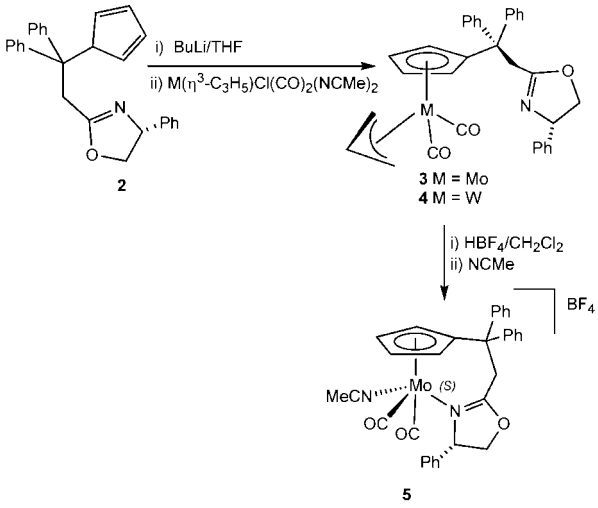
Here we report the synthesis of the new cyclopentadienyloxazoline hybrid ligand **2** (Cp^{ox}) and its coordination to molybdenum and tungsten. The chiral η^3-allyl complexes (*R*)-Cp^{ox}M(η^3-C_3H_5)(CO)$_2$ (M = Mo, W) and ionic [Cp^{ox}Mo(CO)$_2$(NCMe)]BF_4 have been fully characterized and applied as catalysts in olefin epoxidation with TBHP and H_2O_2.

Results and Discussion

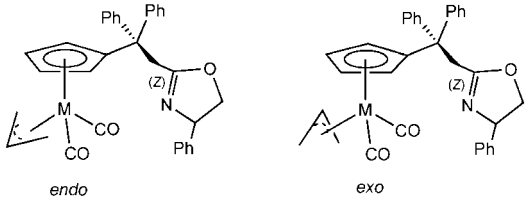
The cyclopentadienyl group bearing an oxazoline pendant ligand **2** (Cp^{ox}) was obtained as shown in Scheme 1 by deprotonation at the methylene group of 2-methyl-(4*R*)-phenyl-4,5-dihydrooxazole (**1**)[12] with *n*BuLi, followed by reaction with 6,6-diphenylfulvene and treatment with methanol. The product was isolated as an orange oil in high yield (88%) and characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. Reaction of **2** with *n*BuLi and subsequent treatment with Mo(η^3-C_3H_5)Cl(CO)$_2$-(NCMe)$_2$ afforded the η^3-allyl dicarbonyl complex (*R*)-Cp^{ox}Mo(η^3-C_3H_5)(CO)$_2$ (**3**) as a crystalline yellow solid in quantitative yield (Scheme 2). Compound **3** was characterized by means of IR and NMR spectroscopy (^{1}H, ^{13}C, ^{95}Mo), elemental analysis, and an X-ray single-crystal diffraction study. Details on the NMR characterization of this complex are giving in the Supporting Information [including complete assignments of ^{13}C NMR resonances based on heteronuclear multiple quantum coherence (HMQC) data]. On the basis of NMR spectroscopic data the two isomers, *endo* and *exo*, were shown to be present in solution (Scheme 3). The ^{1}H NMR spectrum of **3** displayed a single set of broadened resonances for the allyl protons at room temperature due to *exo–endo* fluxional interconversion; two broad signals at δ = 0.73 and 2.48 ppm were assigned to the allyl *anti* (H_a) and *syn* (H_s) protons, respectively. The signal of H_c (corresponding to the central proton of the allyl group) overlaps with the signal of the CH_2 protons of the linker between the cyclopentadienyl and oxazoline fragments. At low temperature (263 K), each of the broad signals splits into two signals of the same intensity at δ = 0.67 and δ = 0.71 ppm for H_a and two resonances at δ = 2.38 and δ = 2.45 ppm for H_s, indicating that the two isomers coexist in solution in a 1:1 ratio. This situation is common in molybdenum complexes of general type CpMo(η^3-C_3H_5)(CO)$_2$, which exist in solution as an approximate 1:1 mixture of *endo* and *exo* isomers.[13] Nevertheless, the *exo* configuration predominates in the solid state as shown by X-ray crystallographic studies.[14] This contrasts with that seen for **3** as both isomers crystallize from dichloromethane, which has been established by X-ray crystallography (Figure 1, see below for discussion).



Scheme 1. Synthesis of compound **2**.



Scheme 2. Synthesis of molybdenum and tungsten complexes **3**–**5**.



Scheme 3. *endo* and *exo* isomers.

The analogous reaction of W(η^3-C_3H_5)Cl(CO)$_2$-(NCMe)$_2$ with **2**, previously deprotonated with *n*BuLi, gave (*R*)-Cp^{ox}W(η^3-C_3H_5)(CO)$_2$ (**4**), which was isolated as a crystalline yellow solid in high yield. Its ^{1}H NMR spectrum recorded at room temperature showed broad resonances for the allyl *anti* and *syn* protons at δ = 0.87 and δ = 2.43 ppm, respectively, suggesting the presence of *exo* and *endo* conformers of **4** in solution. Lowering the temperature of the NMR probe to 263 K, causes splitting of the broad resonance at δ = 2.43 ppm into two multiplets at δ = 2.42 and 2.25 ppm (in 1:1 ratio); however, the signal corresponding to the allyl *anti* protons remained as a broad multiplet. Fur-

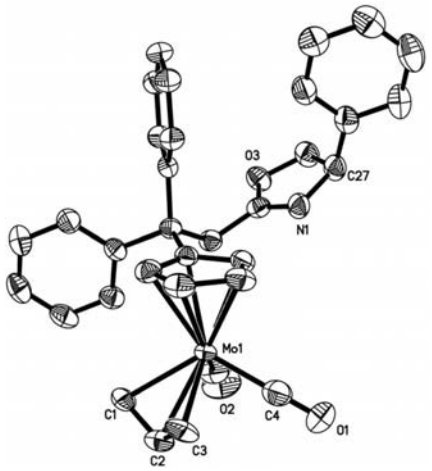


Figure 1. ORTEP diagram of compound **3** with 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths distances [Å] and angles [°]: Mo(1)–C(4) 1.935(4), Mo(1)–C(5) 1.946(3), Mo(1)–C(1) 2.282(19), Mo(1)–C(2) 2.319(6), Mo(1)–C(3) 2.331(18), Mo(1)–Cp*centroid 2.026, C(4)–Mo(1)–C(5) 75.60(15), C(5)–Mo(1)–C(1) 79.2(5), C(4)–Mo(1)–C(3) 81.1(14).

ther temperature decrease leads to the precipitation of **4** from the solution.

Both *exo* and *endo* isomers for **3** and **4** were not distinguished by their IR spectra recorded from KBr pellets. Two characteristic carbonyl absorption bands at ν(CO) 1941 and 1855 cm^{-1} with a shoulder at 1846 cm^{-1} for **3** and 1932 and 1842 cm^{-1} with a shoulder at 1833 cm^{-1} for **4** were observed. As expected, the CO absorption bands for the tungsten complex were found at lower frequencies than those of related molybdenum complex **3**, due to the electron-rich nature of W compared to Mo. These data correlate with those of corresponding $CpM(\eta^3\text{-}C_3H_5)(CO)_2$ complexes (M = Mo, W).[13d,15]

Reaction of **3** with HBF_4 in dichloromethane at room temperature followed by addition of acetonitrile, yielded the ionic complex $[Cp^{ox}Mo(CO)_2(NCMe)]BF_4$ (**5**) which was isolated as a brown solid in high yield (Scheme 2). Compound **5** has been identified by NMR and IR spectroscopy and HRMS spectrometry. Its ^1H NMR spectrum indicates intramolecular coordination of the oxazoline ring to the metal center through the N atom. The methylene protons of the group adjacent to the oxazoline ligand are nonequivalent (AB system), displaying two doublets at δ = 3.90 and 3.75 ppm with J_{H-H} = 16 Hz, suggesting the coordination of the oxazoline group, whereas in complex **3**, these CH_2 protons displayed a single resonance at δ = 3.78 ppm. The singlet at δ = 1.95 ppm proved the coordination of acetonitrile. Additional evidence for coordination of the oxazoline ligand was provided by the ^{13}C NMR spectrum, which displayed two resonances for the carbonyl ligands at δ = 248.7 and 248.5 ppm, indicating that they are *cis*-oriented. The IR spectrum of **5** in the solid state exhibited two carbonyl stretching bands at ν_{sym}(CO) at 1996 cm^{-1} and ν_{asym}(CO) 1904 cm^{-1}. The band due to the symmetric CO stretching vibration was found to be more intense than the asymmetric one, corroborating the *cis* orientation of the CO ligands. The shift to higher frequency of the CO stretching band in **5** (compared with that of **3**) is in agreement with the cationic nature of compound **5**. These values are in agreement with other carbonyl stretching bands reported in the literature for related complexes of general type $[CpMo(CO)_2(NCMe)_2]BF_4$.[16] The high resolution ESI mass spectrum of **5** gave the molecular peak corresponding to $[M - NCMe]^+$ at *m*/*z* = 544.0883. The BF_4 anion was detected in the negative mode of the ESI mass spectrum at *m*/*z* = 87 with the characteristic isotopic pattern of boron. Attempts to synthesise the analogous tungsten cationic complex $[Cp^{ox}W(CO)_2(NCMe)]BF_4$ were made following a similar synthetic method to that used for **5**. The reaction of **4** with HBF_4 yielded a red oil which contained the ionic complex $[Cp^{ox}W(CO)_2(NCMe)]BF_4$ [ESI-MS analysis displayed a molecular peak at *m*/*z* = 630 assigned to $[Cp^{ox}W(CO)_2]^+$; but its NMR spectrum revealed that this compound was contaminated with unidentified products. Therefore, the tungsten complex $[Cp^{ox}W(CO)_2(NCMe)]BF_4$ was not used in catalysis.

Complex **3** crystallized from concentrated ether/hexane solutions affording single crystals suitable for X-ray diffraction studies. The structure and selected bond lengths and angles are shown in Figure 1. The structure shows a pseudotetrahedral coordination around the Mo^{II} center with η^3-allyl, η^5-substituted cyclopentadienyl, and two carbonyl ligands. The crystal contains both the *exo* and *endo* isomers in a ratio of ca. 1:1. The average bond distance of molybdenum to the five-membered cyclopentadienyl ring is 2.026 Å, and the Mo–CO bond lengths are 1.946 and 1.935 Å. These bond lengths are in close accordance to those observed for dicarbonyl(η^3-allyl)(η^5-cyclopentadienyl)molybdenum(II) complexes.[14] The pendant oxazoline arm is situated away from the metal center; the stereocenter (C27) shows *R* absolute configuration.

Compounds 3 and 5 as Pre-Catalysts in Olefin Epoxidation with TBHP

We first investigated the catalytic activity of **3** and **5** with cyclooctene at 55 °C in chloroform using a catalyst:substrate:oxidant ratio of 1:100:200. Catalytic data are summarized in Table 1. Compounds **3** and **5** were found to be highly efficient catalysts for the epoxidation of cyclooctene. They showed similar activities, achieving quantitative substrate conversion towards 1,2-epoxycyclooctane in 30 min for the ionic complex **5**, and in 45 min for the η^3-allyl compound **3** (Figure 2, entries 4 and 1 in Table 1). Reduction of the amount of **5** to 0.2 mol-% did not affect the yield (90%); a turnover frequency (TOF) of 5421 mol mol_{cat}^{-1} h^{-1} was obtained (TOF calculated at 5 min). Four consecutive catalytic runs were carried out without noticeable loss of activity of **5**. The catalytic activity of **3** and **5** is comparable to that observed for complexes of the general formula $CpMo(CO)_3X$ (X = Cl, Br, CH_3) reported in the literature.[1–3] While we were preparing the submission of this manuscript, Gonçalves and coworkers reported the

catalytic activity of $Cp'Mo(\eta^3\text{-}C_3H_5)(CO)_2$ (Cp' = $\eta^5\text{-}C_5H_5$; $\eta^5\text{-}C_5H_4Me$; $\eta^5\text{-}C_5Me_5$) in olefin epoxidation with TBHP.[17]

Table 1. Olefin epoxidation catalyzed by **3** and **5** with TBHP.[a]

Entry	Catalyst	Olefin	Time	Yield [%][b]
1	**3**	cyclooctene	45 min	96
2	**3**	(*R*)-limonene	1 h	100
3	**3**	*trans*-β-methylstyrene	16 h	58[c]
4	**5**	cyclooctene	30 min	98
5	**5**	(*R*)-limonene	1 h	100
6	**5**	*trans*-β-methylstyrene	16 h	14[c]

[a] All reactions were carried out using a catalyst:substrate:oxidant ratio 1:100:200 in $CHCl_3$ at 55 °C. [b] Yield determined by GC. [c] Reactions carried out at room temperature.

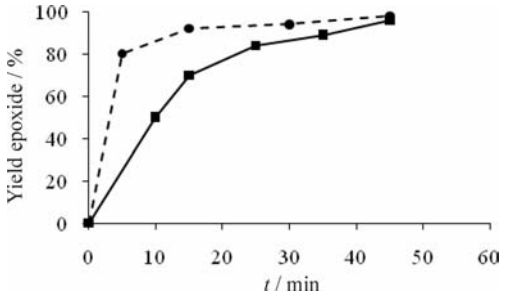
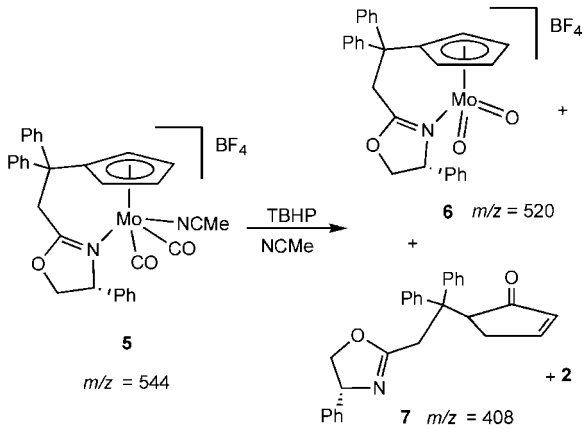


Figure 2. Kinetic profiles for the epoxidation of cyclooctene with TBHP at 55 °C in the presence of complexes **3** (■) and **5** (●) (catalyst load 1 mol-%).

The high catalytic performance of **3** and **5** extends to the oxidation of (*R*)-(+)-limonene with TBHP achieving 100% conversion to limonene oxide in 1 h. The reaction was fully selective to the oxide giving a mixture of the corresponding *cis*/*trans* epoxide in a ratio of 50:50 for **3** and 60:40 for **5**. Next, we investigated the epoxidation of *trans*-(β)-methylstyrene, a model substrate for *trans*-olefins, in order to explore the capability of these catalytic precursors to promote asymmetric induction. In a typical catalytic run, one equivalent of substrate was mixed with 1 mol-% catalyst and two equivalents of TBHP. The reaction was carried out at room temperature in order to optimize conditions for asymmetric epoxidation, since higher temperatures are usually regarded as detrimental for catalyst enantioselectivity. Poor conversion of *trans*-β-methylstyrene was obtained after 16 h (38% conversion) in the presence of a catalytic amount of **5**, and the reaction was not selective to the epoxide (14% yield, entry 6 in Table 1) giving nearly racemic methylstyrene oxide (≤ 5% *ee*). Using **3**, the reaction was fully selective to methylstyrene epoxide (58% yield in 16 h, entry 3 in Table 1) without asymmetric induction (*ee* ≤ 5%).

An intramolecular coordination of the oxazoline moiety during the catalytic process was expected to effect an asymmetric induction. However, negligible enantiomeric excess was observed, even at low temperature. This behavior could be due to the decoordination of the oxazoline moiety during the catalytic reaction.

Despite intensive studies on molybdenum cyclopentadienyl compounds as catalysts for olefin epoxidation, the stability of Cp-oxido-molybdenum catalysts during epoxidation catalysis remains uncertain.[4] In order to gain an insight into the nature of the species formed during the course of the reaction, the catalytic precursor **5** was treated with a 10-fold excess of TBHP in acetonitrile at room temperature, and the reaction was followed by ESI-MS. After addition of TBHP, three new peaks at *m*/*z* = 520, 408, and 392 immediately appeared in the mass spectrum along with the peak at *m*/*z* = 544, which corresponds to **5**. The intensity of the three new peaks increased in the first minute, while the intensity of the peak corresponding to **5** decreased. After approximately 2 min of reaction, the peaks at *m*/*z* = 520 and 544 completely disappeared from the spectrum, while the peaks at *m*/*z* = 408 and 392 remained. The peak at *m*/*z* = 520 displayed the characteristic pattern arising from the natural abundance of molybdenum isotopes and it was assigned to the dioxido-molybdenum species $[Cp^{ox}MoO_2]^+$ (**6**). Similar ionic dioxido-molybdenum species have been isolated from the reaction of $[CpMo(CO)_2(NHC)(NCMe)]^+$ with TBHP.[8] The peaks at *m*/*z* = 408 and 392 correspond to a species that does not contain molybdenum, and on the basis of the *m*/*z* values they have been assigned to the cyclopentenone (**7**) and cyclopentadienyloxazoline ligand (**2**) (Scheme 4, mass spectra can be found in the Supporting Information). At the end of the reaction of **5** with TBHP, a pale yellow solid precipitated from the acetonitrile solution. Attempts to characterize this yellow solid were unsuccessful.



Scheme 4. Reaction of compound **5** with TBHP monitored by ESI-MS analysis.

Similar ESI-MS analyses were carried out in the presence of cyclooctene in a **5**:TBHP:olefin ratio of 1:10:10 in order to explore if the presence of the olefin would prevent the decomposition of the dioxido species **6**. We found that a similar reaction took place in the presence of the olefin. The addition of TBHP to a mixture of **5** and cyclooctene in acetonitrile rapidly produced **6**, **7**, and **2** (Scheme 4). In view of these results, two main conclusions can be made: i) the first step in the epoxidation reaction is the in situ formation of the dioxido-molybdenum compound **6**, which is generated by complete oxidative decarbonylation of the carb-

onyl metallic precursor; and ii) complex **6** reacts further losing the cyclopentadienyl fragment (Cp^{ox}).

The loss of the cyclopentadienyl ligand from $CpMoO_2Cl$ compounds leading to the in situ generation of a much more efficient molybdenum (per)oxido species has been already detected in the epoxidation of *cis*-cyclooctene with THBP in the presence of $Cp^{Ar}MoO_2Cl$ (Cp^{Ar} = η^5-C_5Ph_5).[4] Based on NMR and kinetic data, Colbran and coworkers demonstrated that at the end of the catalytic reaction the only molybdenum-containing species present were formed by loss of the cyclopentadienyl ligand. Loss of the cyclopentadienyl-bearing oxazoline ligand would explain the lack of asymmetric induction found in our experiments. It should be noted that in a recent mechanistic study reported by Kühn and coworkers on epoxidation catalyzed by $CpMoO_2Me$,[18] the decomposition of the catalyst to a more active catalyst not containing the cyclopentadienyl group has not been reported. Based on our findings, we believe the warning given by Colbran et al.[4] that the loss of the cyclopentadienyl ring must be taken into account when these systems are applied as catalysts in epoxidation reactions.

Despite the fact that a radical mechanism has not been proposed in previous studies on epoxidation catalyzed by cyclopentadienylmolybdenum complexes,[18,19] we performed radical trapping experiments in order to confirm the nonexistence of radicals in the epoxidation catalyzed by our $[Cp^{ox}Mo(CO)_2(NCMe)]^+$/TBHP system. Under a nitrogen atmosphere, addition of 20 equiv. per catalyst of Ph_2NH, an efficient scavenger of alkylperoxyl radicals,[20] inhibited cyclooctene oxidation. A 10% yield of the corresponding epoxide was obtained after 24 h of reaction, while 96% yield in 45 min was obtained in the absence of radical scavenger. Other radical scavengers such as 2,2,6,6-tetramethypiperidine-1-oxyl (TEMPO) also slowed down the reaction to a great extent (Figure 3). In addition, 2,6-di-*tert*-butyl-4-methylphenol (BHT) and $CBrCl_3$ diminished the reaction rate in the first 40 min, reaching quantitative conversion of the corresponding epoxide in 90 min (Figure 3). These results indicate that free radical species are involved in the epoxidation reaction catalyzed by **5**.

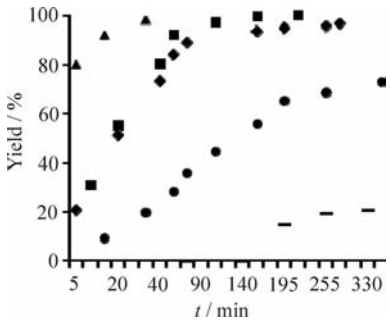


Figure 3. Kinetic profiles for the epoxidation of cyclooctene with TBHP at 55 °C using **5** as catalyst in the presence of several spin traps: without spin trap (▲), $CBrCl_3$ (■), BHT (♦), TEMPO (●), and Ph_2NH (—).

Compounds 3–5 and $CpM(CO)_3Cl$ (M = Mo, W) as Pre-Catalysts in Olefin Epoxidation with H_2O_2

Based on our recent findings on the capability of $CpMo(CO)_3Cl$ complexes to catalyze the oxidation of sulfides with H_2O_2[21] and the ability of molybdenum η^3-allyl carbonyl complexes to perform olefin epoxidation with H_2O_2,[22] we decided to explore the catalytic performance of **5** in the epoxidation of *cis*-cyclooctene with H_2O_2 (30% in H_2O) at 70 °C. The use of hydrogen peroxide is an attractive option on environmental and economic grounds. The by-product generated is water and the aqueous solution is inexpensive and easy to handle. The catalytic reaction was performed using acetonitrile as a co-solvent to give a homogeneous mixture in which complex **5**, substrate, and oxidant were completely dissolved. Blank runs performed in the absence of catalyst showed no epoxide formation under the conditions applied. Compound **5** exhibited moderate catalytic activity, reaching quantitative conversion in 11 h (92% conversion). The catalytic reaction was entirely selective for epoxidation with 1,2-epoxycyclooctane the only product obtained (Table 2, entry 2). Complex **3** also catalyzed the epoxidation of *cis*-cyclooctene with H_2O_2. Despite the slower reaction, the epoxide selectivity was 100% achieving 77% of epoxide yield in 20 h (Table 2, entry 1). This is remarkable, since cyclopentadienyl compounds of molybdenum have been reported as inactive catalysts for olefin epoxidation using H_2O_2 as oxidant.[2,3b,5b,23] Nevertheless, the catalytic tests described in the literature were performed at 55 °C, without evaluation of the effect of temperature. For comparative purposes, we studied the performance of $CpMo(CO)_3Cl$ in the epoxidation of *cis*-cyclooctene with H_2O_2 at 70 °C in acetonitrile. The catalytic epoxidation reaction yielded 1,2-epoxycyclooctane as the only product in a 92% yield after 10 h (Table 2, entry 5). Similar experiments carried out at 55 °C gave negligible epoxide yields using different catalytic precursors, 8% yield of 1,2-epoxycyclooctane for $CpMo(CO)_3Cl$ and 9% for **5** (Table 2, entries 6 and 3, respectively), indicating that the effect of the temperature is crucial in the epoxidation of olefins with H_2O_2. In view of these results, we decided to explore the catalytic performance of **4** under similar conditions, as according to some literature reports, tungsten complexes afford better results with H_2O_2 compared to molybdenum species.[24] Complex **4** showed excellent catalytic ac-

Table 2. Catalytic epoxidation catalysed by **3**–**5**, $CpMo(\eta^3$-$C_3H_5)(CO)_2$, and $CpW(\eta^3$-$C_3H_5)(CO)_2$ with H_2O_2.[a]

Entry	Catalyst	*T* [°C]	*t* [h]	Yield [%][b]
1	**3**	70	20	77
2	**5**	70	11	92
3	**5**	55	20	9
4	**4**	70	2	88
5	$CpMo(CO)_3Cl$	70	10	92
6	$CpMo(CO)_3Cl$	55	20	8
7	$CpW(\eta^3$-$C_3H_5)(CO)_2$	70	5	92

[a] All reactions were carried out with a catalyt:substrate:oxidant ratio 1:100:200 in acetonitrile. [b] Yield determined by GC.

tivity in the epoxidation of cyclooctene with H_2O_2 affording quantitative conversion to 1,2-epoxycyclooctane (88% yield) in 2 h (Table 2, entry 4). The unsubstituted cyclopentadienyl derivative CpW(η^3-C_3H_5)(CO)$_2$ displayed similar catalytic activity when applied as catalyst for *cis*-cyclooctene epoxidation with H_2O_2 achieving quantitative conversion to the corresponding epoxide in 5 h (Table 2, entry 7). The course of the epoxidation reactions with H_2O_2 and catalysts **3**–**5** and CpW(η^3-C_3H_5)(CO)$_2$ is shown in Figure 4 and additional data are summarized in Table 2. The catalytic activity of [Cp*$_2$M$_2$O$_5$] (M = Mo, W) in the epoxidation of cyclooctene using aqueous H_2O_2 as oxidant has recently been reported by Poli and coworkers.[19]

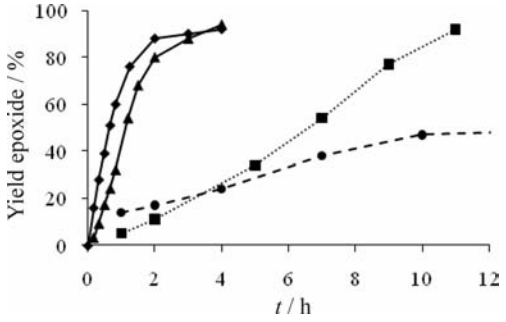
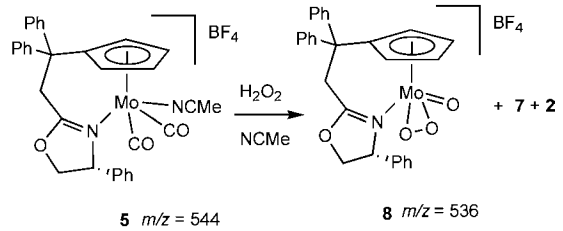


Figure 4. Kinetic profiles for the epoxidation of cyclooctene with H_2O_2 at 70 °C in the presence of complexes **3** (●), **4** (▲), **5** (■), and CpW(η^3-C_3H_5)(CO)$_2$ (♦).

The reaction of **5** with a 10-fold excess of H_2O_2 was monitored by ESI-MS analysis. After addition of 10 equiv. of H_2O_2 to an acetonitrile solution of **5**, three new peaks at *m*/*z* = 536, 408, and 392 immediately appeared in the spectrum. The peak at *m*/*z* = 536 has been assigned to the oxido(peroxido)molybdenum complex [Cp^{ox}Mo(O$_2$)O]$^+$ (**8**) (assigned on the basis of the *m*/*z* value and its isotopic distribution), the peak at *m*/*z* = 408 corresponds to **7** (already detected in the reaction of **5** with TBHP, see above), and the peak at *m*/*z* = 392 corresponds to **2** (Scheme 5). After some minutes of reaction, the peak at *m*/*z* = 536 completely disappeared from the spectrum and the only peaks that remained were those at *m*/*z* = 408 and 392. Despite the fact that Cp*Mo(O$_2$)OCl has been shown to be totally inactive in olefin epoxidation,[2] subsequent studies by Kühn have shown that related complexes with different ligands such as CpMoO(O$_2$)(CH$_3$) are catalytically active.[18]



Scheme 5. Reaction of **5** with H_2O_2 monitored by ESI-MS analysis.

A further insight into the mechanism of the catalytic reaction with H_2O_2 came from radical trapping experiments, suggesting the involvement of both C- and O-centred radicals in the catalytic epoxidation of olefins, as the addition of C- and O-centred radical traps such as $CBrCl_3$, Ph_2NH, BHT, and TEMPO to the catalytic reaction mixture suppress the formation of the corresponding epoxide (Figure 5). These findings provide strong evidence for a radical mechanism involved in the epoxidation of olefins catalyzed by this system.

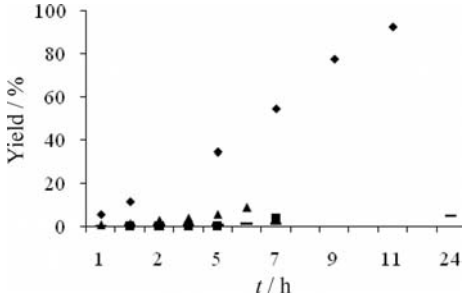


Figure 5. Kinetic profiles for the epoxidation of cyclooctene with H_2O_2 at 70 °C using **5** as catalyst in the presence of several spin traps: without spin trap (♦), TEMPO (■), $CBrCl_3$ (▲), and BHT (—).

Conclusions

In this work, we have prepared the novel cyclopentadienyl ligand **2** (Cp^{ox}) functionalized with an oxazoline ring, which has been coordinated to molybdenum and tungsten affording the corresponding metal complexes (*R*)-Cp^{ox}M(η^3-C_3H_5)(CO)$_2$ [M = Mo (**3**), W (**4**)]. The pure chiral cationic complex of molybdenum [Cp^{ox}Mo(CO)$_2$(NCMe)]BF$_4$ (**5**) has been isolated and fully characterized. Compound **5** is a highly active catalyst in olefin epoxidation with TBHP and a moderate catalyst with H_2O_2. Our findings based on ESI-MS analysis corroborate the instability of cyclopentadienyl-oxido-molybdenum(VI) catalysts during the epoxidation reaction already observed by Colbran and coworkers, and suggest that different reaction pathways can compete in the epoxidation of olefins catalyzed by [Cp^{ox}Mo(CO)$_2$(NCMe)]$^+$ systems. We have disclosed the involvement of both C- and O-centred radicals in the epoxidation reaction catalyzed by the [Cp^{ox}Mo(CO)$_2$(NCMe)]BF$_4$ as shown by experiments with radical traps. As far as we know, this is the first time that experimental results prove the involvement of radicals in the epoxidation reaction catalyzed by cyclopentadienyl molybdenum complexes. These findings might explain the lack of asymmetric induction displayed by these systems.

Experimental Section

General Procedures: Mo(η^3-C_3H_5)Cl(CO)$_2$(NCMe)$_2$,[13d] W(η^3-C_3H_5)Cl(CO)$_2$(NCMe)$_2$,[15] and 6,6-diphenylfulvene[25] were prepared following literature procedures. (4*R*)-2-Methyl-4-phenyl-4,5-dihydrooxazole (**1**) was prepared following the method described by Meyers,[12] starting from (*R*)-(–)-2-phenylglycinol and triethyl orthoacetate. All other reagents were used as received from commercial suppliers and used without further purification. ^{1}H and

^{13}C NMR spectra were recorded with Bruker Avance III 400 MHz. Infrared spectra were recorded from samples as KBr pellets using a Mattson 7000 FTIR spectrometer. Electrospray mass spectra were recorded with a Micromass Quatro LC instrument, nitrogen was employed as the drying and nebulizing gas. Optical rotations were determined with a Perkin–Elmer 241 polarimeter. Elemental analyses were performed in our laboratories at ITQB. Complex **5** did not give reproducible elemental analysis do to the retention of fractional amounts of solvent. In lieu of acceptable elemental analysis for compound **5** HRMS (ESI-TOF) were recorded.

X-ray Diffraction Studies: X-ray data for crystal **3** were collected at low temperature (193 K) using an oil-coated shock-cooled crystal with a Bruker-AXS APEXII diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct phase determination (SHELXS-97)[26] and refined for all non-hydrogen atoms by full-matrix least-square methods on F^2 and subject to anisotropic refinement.[27]

Crystal data for 3: $C_{33}H_{29}MoNO_3$, M = 583.51, orthorhombic, space group $P212121$, a = 10.0441(2) Å, b = 11.4927(2) Å, c = 23.2420(2) Å, V = 2682.91(8) Å3, Z = 4, crystal size 0.38 × 0.28 × 0.06 mm^3, 50594 reflections collected (6615 independent, R_{int} = 0.0609), 371 parameters, $R1$ [$I > 2\sigma(I)$] = 0.0314, $wR2$ [all data] = 0.0717, largest diff. peak and hole: 0.532 and –0.354 e Å^{-3}.

CCDC-793815 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 2: A hexane solution of *n*BuLi (1.9 mL of 1.6 M in hexane, 3.04 mmol) was added dropwise to a solution of **1** (473 mg, 2.93 mmol) in dried THF (20 mL) at –60 °C. The mixture was stirred for 30 min, 6,6-diphenylfulvene (675 mg, 2.93 mmol) was added and the reaction mixture was allowed to reach room temperature with stirring for 3 h. Methanol (2 mL) was added, and the volatiles were evaporated. The crude oil was purified by flash chromatography (hexane/ethyl acetate, 4:1) affording **2** as an orange oil (101 mg, 88%). $[\alpha]_D^{20}$ = +21.2 (c = 0.9, diethyl ether). ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.37–6.85 (m, 15 H, C*H*$_{Ph}$), 6.47–6.28 (m, 4 H, C*H*$_{Cp}$), 4.89 (m, 1 H, NC*H*Ph), 4.30 (m, 1 H, OCH_2), 3.66 (m, 1 H, OCH_2), 3.56 (s, 2 H, C$H_{2\ linker}$), 3.04 (s, 1 H, CH_{Cp}) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 166.1 (O*C*N), 145.6 (C_{Ph}), 134.6 (C_{Cp}), 132.9 (C_{Cp}), 129.7 (C_{Ph}), 129.14 (C_{Ph}), 127.7 (C_{Ph}), 126.7 (C_{Ph}), 126.3 (C_{Ph}), 74.3 (O*C*H$_2$), 69.5 (N*C*HPh), 42.46 (C_{Cp}), 40.98 (*C*H$_{2\ linker}$), 39.0 (*C*Ph$_{2\ linker}$) ppm. MS (EI): m/z (%) = 392 [M + H$^+$].

Synthesis of 3: A solution of **2** (256 mg, 0.65 mmol) in THF (30 mL) was treated with *n*BuLi (0.41 mL of 1.6 M in hexane, 0.68 mmol) at –60 °C. The mixture was stirred for 15 min followed by warming to room temperature and further stirred for 1 h. To the resulting mixture, a solution of Mo(η^3-C_3H_5)Cl(CO)$_2$(NCMe)$_2$ (203 mg, 0.65 mmol) in THF (5 mL) was added at –30 °C, and the reaction mixture was warmed to room temperature and stirred overnight. All volatiles were removed under vacuum and the remaining solid was extracted into diethyl ether yielding **3** as a yellow solid (426 mg, 89%). $[\alpha]_D^{20}$ = +18.1 (c = 0.2, CH_2Cl_2). $C_{33}H_{29}MoNO_3(OC_4H_8)$ (657): calcd. C 67.56, H 5.67, N 2.13; found C 67.70, H 5.65, N 2.01. The NMR assignments below were determined with the help of ^1H-^{13}C-HMQC (400 MHz, CD_2Cl_2): δ = 0.73 (broad m, 2 H, H$_a$ *allyl*), 2.48 (broad m, 2 H, H$_s$ *allyl*), 3.55 (m, 1 H, O–CH_AH$_B$–CHPhN), 3.67 (m, 3 H, H$_m$ *allyl*, C$H_{2\ linker}$), 4.28 (m, 1 H, O–CH$_A$*H*$_B$–CHPhN), 4.89 (m, 1 H, O–CH$_2$–C*H*PhN), 5.17 (m, 2 H, *Cp*), 5.29 (s, 1 H, *Cp*), 5.62 (s, 1 H, *Cp*), 6.80 (m, 2 H, *Ph*), 7.12–7.28 (m, 13 H, *Ph*) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 237.7 (CO), 166.5 (N*C*O), 147.3 (C_{ipso} Ph), 142.2 (C_{ipso} Ph), 129.1(C_{Ph}), 128.7 (C_{Ph}), 128.5 (C_{Ph}), 128.1 (C_{Ph}), 127.8 (C_{Ph}), 124.5 [C_5(Cp)-C], 93.5 (Cp), 93.2 (Cp), 92.8 (Cp), 92.6 (Cp), 74.5 (O–*C*H$_2$–CHPh), 69.6 (O–CH$_2$–*C*HPh), 67.9 ($C_{central}$ *allyl*), 51.6 (*C*Ph$_{2\ linker}$), 41.3 ($C_{anti/syn}$ *allyl*), 40.7 (*C*H$_{2\ linker}$) ppm. ^{95}Mo NMR (26 MHz, CD_2Cl_2): δ = 92.3 ppm. IR (KBr): $\tilde{\nu}$ = 1941 (vs), 1855 (vs), 1846 (sh) [ν(CO)] cm^{-1}.

Synthesis of 4: A solution of **2** (145 mg, 0.37 mmol) in THF (30 mL) was treated with *n*BuLi (0.24 mL of 1.6 M in hexane, 0.38 mmol) at –60 °C. The mixture was stirred for 15 min followed by warming to room temperature and further stirred for 1 h. To the resulting mixture, a solution of W(η^3-C_3H_5)Cl(CO)$_2$(NCMe)$_2$ (147 mg, 0.37 mmol) in THF (5 mL) was added at –10 °C, and the reaction mixture was warmed to room temperature and stirred overnight. All volatiles were removed under vacuum and the remaining solid was extracted into diethyl ether yielding **4** as a yellow solid (149 mg, 54%). $C_{33}H_{29}NO_3W(OC_4H_8)$ (743): calcd. C 59.73, H 5.02, N 1.88; found C 59.40, H 5.20, N 1.64. $[\alpha]_D^{20}$ = –6.0 (c = 0.2, CH_2Cl_2). The NMR assignments below were determined with the help of ^1H-^{13}C-HMQC. ^1H NMR (400 MHz, CD_2Cl_2): δ = 0.87 (broad m, 2 H, H$_a$ *allyl*), 2.43 (broad m, 2 H, H$_s$ *allyl*), 3.40 (m, 1 H, H$_m$ *allyl*), 3.54 (m, 1 H, O–CH_AH$_B$–CHPhN), 3.77 (s, 2 H, C$H_{2\ linker}$), 4.29 (m, 1 H, O–CH$_A$*H*$_B$–CHPhN), 4.93 (m, 1 H, O–CH$_2$–C*H*PhN), 5.38 (s, 2 H, *Cp*), 5.78 (s, 2 H, *Cp*), 6.78 (m, 2 H, *Ph*), 7.13–7.33 (m, 13 H, *Ph*) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 226.3 (CO), 166.2 (N*C*O), 147.0 (C_{ipso} Ph), 142.3 (C_{ipso} Ph), 129.1 (C_{Ph}), 128.9 (C_{Ph}), 128.7 (C_{Ph}), 128.4 (C_{Ph}), 127.9 (C_{Ph}), 122.5 [C_5(Cp)–C], 92.4 (Cp), 92.3 (Cp), 91.7 (Cp), 74.3 (O–*C*H$_2$–CHPh), 69.6 (O–CH$_2$–*C*HPh), 61.1 ($C_{central}$ *allyl*), 51.8 (*C*Ph$_{2\ linker}$), 40.9 (*C*H$_{2\ linker}$), 32.9 ($C_{anti/syn}$ *allyl*) ppm. IR (KBr): $\tilde{\nu}$ = 1932 (vs), 1842 (vs), 1833 (sh) [ν(CO)] cm^{-1}.

Synthesis of 5: A solution of **3** (474 mg, 0.72 mmol) in CH_2Cl_2 (20 mL) was treated with HBF_4 (0.44 mL, 54% in diethyl ether, 1.74 mmol) at room temperature. The mixture was stirred for 15 min followed by addition of acetonitrile (10 mL), and the reaction mixture was stirred for further 2 h. All volatiles were removed under vacuum and the remaining solid was washed with toluene and extracted into dichloromethane yielding **5** as a brown solid (290 mg, 60%). The NMR assignments below were determined with the help of ^1H-^{13}C-HMQC. ^1H NMR (400 MHz, CD_3CN): δ = 1.95 (s, 3 H, NCMe), 3.75 (d, $J_{H\text{-}H}$ = 16 Hz, 1 H, CH_AH$_B$ linker), 3.90 (d, $J_{H\text{-}H}$ = 16 Hz, 1 H, CH$_A$*H*$_B$ linker), 4.47 (m, 1 H, O–CH_AH$_B$–CHPhN), 5.14 (m, 1 H, O–CH$_A$*H*$_B$–CHPhN), 5.26 (m, 1 H, O–CH$_2$–C*H*PhN), 5.81 (m, 1 H, *Cp*), 5.85 (m, 2 H, *Cp*), 5.90 (m, 1 H, *Cp*), 6.82 (m, 2 H, *Ph*), 7.21–7.46 (m, 13 H, *Ph*) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 248.7 (CO), 248.5 (CO), 178.8 (N*C*O), 145.8 (C_{ipso} Ph), 144.8 (C_{ipso} Ph), 135.5–130.2 (C_{Ph}), 123.7 [C_5(Cp)–C], 102.3 (Cp), 99.0 (Cp), 96.9 (Cp), 95.3 (Cp), 81.8 (O–*C*H$_2$–CHPh), 61.4 (O–CH$_2$–*C*HPh), 52.8 (*C*Ph$_{2\ linker}$), 39.3 (*C*H$_{2\ linker}$) ppm. ^{95}Mo NMR (26 MHz, CD_2Cl_2): δ = 40.1 ppm. HRMS (EI): m/z = 544.0883 [M – NCMe]$^+$. IR (KBr): $\tilde{\nu}$ = 1996 (vs), 1904 (vs) [ν(CO)] cm^{-1}.

Olefin Epoxidation Experiments with TBHP: The catalytic reactions were performed in a reaction vessel equipped with a magnetic stirrer immersed in an oil bath at the appropriate temperature. A catalyst:olefin:TBHP ratio of 1:100:200 was used, with 2 mL of $CHCl_3$. Olefin, chloroform, mesitylene (as internal standard), and the catalyst were placed into the reaction vessel, and TBHP was added to the mixture. The course of the reaction was monitored by quantitative GC analysis. Samples taken were diluted with CH_2Cl_2 and treated with $MgSO_4$ and MnO_2 to remove water and destroy

the excess peroxide. The resulting slurry was filtered, and the filtrate was injected into a GC column. The conversion of the olefin and the formation of the corresponding epoxide were calculated from calibration curves (r^2 = 0.999) recorded prior to the reaction.

Olefin Epoxidation Experiments with H_2O_2: The catalytic reactions were performed in a reaction vessel equipped with a magnetic stirrer and immersed in an oil bath at the appropriate temperature. A catalyst:olefin:H_2O_2 ratio of 1:100:200 was used, with 2 mL of NCMe. Olefin, acetonitrile, mesitylene (as internal standard), and the catalyst were placed into the reaction vessel, and H_2O_2 was added to the mixture. The course of the reaction was monitored by quantitative GC analysis as described above.

Radical Trap Experiments: The catalytic reactions were performed in a reaction vessel equipped with a magnetic stirrer immersed in an oil bath at the appropriate temperature. A **5**:olefin:oxidant ratio of 1:100:200 was used with 2 mL of $CHCl_3$ (for TBHP) and NCMe (for H_2O_2). Olefin, chloroform, mesitylene (as internal standard), and spin trap in a ratio 1.3:1 relative to substrate, and the catalyst were placed into the reaction vessel, and the oxidant was added to the mixture. The course of the reaction was monitored by quantitative GC analysis as described above.

Supporting Information (see footnote on the first page of this article): Mass spectra, NMR spectra, details on the crystal structure determination.

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[1] For recent reviews, see: a) F. E. Kühn, A. M. Santos, M. Abrantes, *Chem. Rev.* **2006**, *106*, 2455; b) C. Freud, M. Abrantes, F. E. Kühn, C. C. Romão, *J. Organomet. Chem.* **2006**, *691*, 3718.
[2] M. K. Trost, R. G. Bergman, *Organometallics* **1991**, *10*, 1172.
[3] a) M. Abrantes, A. M. Santos, J. Mink, F. E. Kühn, C. C. Romão, *Organometallics* **2003**, *22*, 2112; b) A. M. Martins, C. C. Romão, M. Abrantes, M. C. Azevedo, J. Cui, A. R. Dias, T. Duarte, M. A. Lemos, T. Lourenço, R. Poli, *Organometallics* **2005**, *24*, 2582; c) J. Zhao, A. M. Santos, E. Herdtweck, F. E. Kühn, *J. Mol. Catal. A* **2004**, *222*, 265; d) A. A. Valente, J. D. Seixas, I. S. Goncalves, M. Abrantes, M. Pillinger, C. C. Romão, *Catal. Lett.* **2005**, *101*, 127.
[4] M. Pratt, J. B. Harper, S. B. Colbran, *Dalton Trans.* **2007**, 2746.
[5] a) M. Abrantes, A. Sakthivel, C. C. Romão, F. E. Kühn, *J. Organomet. Chem.* **2006**, *691*, 3137; b) M. Abrantes, F. A. Almeida Paz, A. A. Valente, C. C. L. Pereira, S. Gago, A. R. Rodrigues, J. Klinowski, M. Pillinger, I. S. Gonçalves, *J. Organomet. Chem.* **2009**, *694*, 1826.
[6] a) J. Zhao, E. Herdtweck, F. E. Kühn, *J. Organomet. Chem.* **2006**, *691*, 2199; b) J. Zhao, K. R. Jain, E. Herdtweck, F. E. Kühn, *Dalton Trans.* **2007**, 5567; c) A. Capapé, A. Raith, F. E. Kühn, *Adv. Synth. Catal.* **2009**, *351*, 66.
[7] V. V. K. M. Kandepi, A. P. da Costa, E. Peris, B. Royo, *Organometallics* **2009**, *28*, 4544.
[8] During the preparation of this manuscript, stability studies of CpMo(NHC)(CO)$_2$X complexes under oxidative conditions have been described: S. Li, C. W. Kee, K.-W. Huang, T. S. A. Hor, J. Zhao, *Organometallics* **2010**, *29*, 1924.
[9] M. Gómez, G. Muller, M. Rocamora, *Coord. Chem. Rev.* **1999**, *193–195*, 769.
[10] a) M. Gómez, S. Jansat, G. Muller, G. Noguera, H. Teruel, V. Moliner, E. Cerrada, M. Hursthouse, *Eur. J. Inorg. Chem.* **2001**, 1071; b) J. A. Brito, M. Gómez, G. Muller, M. Teruel, J.-C. Clinet, E. Duñach, M. A. Maestro, *Eur. J. Inorg. Chem.* **2004**, 4278; c) J. A. Brito, H. Teruel, G. Muller, S. Massou, M. Gómez, *Inorg. Chim. Acta* **2008**, *361*, 2740; d) F. E. Kühn, A. M. Santos, A. D. Lopes, I. S. Gonçalves, J. E. Rodríguez-Borges, M. Pillinger, C. C. Romão, *J. Organomet. Chem.* **2001**, *621*, 201; e) P. Neves, S. Gago, C. C. L. Pereira, S. Figuereido, A. Lemos, A. D. Lopes, I. S. Gonçalves, M. Pillinger, C. M. Silva, A. A. Valente, *Catal. Lett.* **2009**, *132*, 94.
[11] Selected reviews on cyclopentadienyl rings bearing functional groups: a) U. Siemeling, *Chem. Rev.* **2000**, *100*, 1495; b) H. Butenschön, *Chem. Rev.* **2000**, *100*, 1527.
[12] A. I. Meyers, G. Knaus, K. Kamata, M. E. Ford, *J. Am. Chem. Soc.* **1976**, *98*, 567.
[13] a) R. B. King, *Inorg. Chem.* **1966**, *5*, 2242; b) J. W. Faller, M. J. Incorvia, *Inorg. Chem.* **1968**, *7*, 840; c) J. W. Faller, A. Jakubowski, *J. Organomet. Chem.* **1971**, *31*, C75; d) J. W. Faller, C.-C. Chen, M. J. Mattina, A. Jakubowski, *J. Organomet. Chem.* **1973**, *52*, 361; e) J. W. Faller, B. C. Whitmore, *Organometallics* **1986**, *5*, 752.
[14] a) W. E. Vanarsdale, J. K. Kochi, *J. Organomet. Chem.* **1986**, *317*, 215; b) J. W. Faller, D. F. Chodosh, D. Katahira, *J. Organomet. Chem.* **1980**, *187*, 227; c) S. Was, M. J. Begley, P. Mountford, *J. Organomet. Chem.* **1995**, *489*, C28; d) M. J. Begley, P. Mountford, P. J. Stewart, D. Swallow, S. Wan, *J. Chem. Soc., Dalton Trans.* **1996**, 1323; e) M. Green, T. D. McGrath, R. L. Thomas, A. P. Walker, *J. Organomet. Chem.* **1997**, *532*, 61; f) H. G. Alt, H. E. Engelhardt, B. Wrackmeyer, R. D. Rogers, *J. Organomet. Chem.* **1989**, *379*, 289.
[15] I. S. Gonçalves, C. C. Romão, *J. Organomet. Chem.* **1995**, *486*, 155.
[16] a) S. A. Benyunes, A. Binelli, M. Green, M. J. Grimshire, *J. Chem. Soc., Dalton Trans.* **1991**, 895; b) I. J. S. Fairlamb, J. M. Lynam, I. E. Taylor, A. C. Whitwood, *Organometallics* **2004**, *23*, 4964.
[17] P. Neves, C. C. L. Pereira, F. A. A. Paz, S. Gago, M. Pillinger, C. M. Silva, A. A. Valente, C. C. Romão, I. S. Gonçalves, *J. Organomet. Chem.* **2010**, *695*, 2311.
[18] A. M. Al.-Ajulouni, D. Veljanosvki, A. Capapé, J. Zhao, E. Herdtweck, M. J. Calhorda, F. E. Kühn, *Organometallics* **2009**, *28*, 639.
[19] Ch. Dinoi, M. Ciclosi, E. Manoury, L. Maron, L. Perrin, R. Poli, *Chem. Eur. J.* **2010**, *16*, 9572.
[20] P. A. MacFaul, D. D. M. Wayner, K. U. Ingold, *Acc. Chem. Res.* **1998**, *31*, 159.
[21] C. A. Gamelas, T. Lourenço, A. P. da Costa, A. L. Simplício, B. Royo, C. C. Romão, *Tetrahedron Lett.* **2008**, *49*, 4708.
[22] V. V. K. M. Kandepi, J. M. S. Cardoso, B. Royo, *Catal. Lett.* **2010**, *136*, 222.
[23] A. A. Valente, J. D. Seixas, I. S. Goncalves, M. Abrantes, M. Pillinger, C. C. Romão, *Catal. Lett.* **2005**, *101*, 127.
[24] A. V. Biradar, M. K. Dongare, S. B. Umbakar, *Tetrahedron Lett.* **2009**, *50*, 2885.
[25] J. L. Kice, F. M. Parham, *J. Am. Chem. Soc.* **1958**, *80*, 3792.
[26] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, **1997**.
[27] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

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