

N-Heterocyclic Carbene-Based Molybdenum and Tungsten Complexes as Efficient Epoxidation Catalysts with H₂O₂ and *tert*-Butyl Hydroperoxide

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Abstract The molybdenum and tungsten η^3 -allyl dicarbonyl complexes bearing *N*-heterocyclic carbene (NHC) ligands [M(η^3 -C₃H₅)Cl(CO)₂(bis-NHC^{Bz})] (M = Mo, W; bis-NHC^{Bz} = 1,1'-dibenzyl-3,3'-methylenediimidazoline-2,2'-diylidene) have been prepared from the corresponding acetonitrile precursors [M(η^3 -C₃H₅)Cl(CO)₂(NCMe)₂] by treatment with free carbene. Their catalytic performance in epoxidation of *cis*-cyclooctene using H₂O₂ as oxidant has been studied. All complexes can be applied as catalysts precursors in olefin epoxidation displaying 100% selectivity for the formation of cyclooctene oxide. The tungsten acetonitrile precursor [W(η^3 -C₃H₅)Cl(CO)₂(NCMe)₂] displayed the highest catalytic activity achieving quantitative conversion of epoxide in 30 min. The molybdenum NHC-based compound [Mo(η^3 -C₃H₅)Cl(CO)₂(bis-NHC^{Bz})] displayed higher activity when the epoxidation reaction was performed using H₂O₂ as oxidant compared to *tert*-butyl hydroperoxide.

Keywords *N*-heterocyclic carbenes · Molybdenum · Tungsten · Epoxidation · Hydrogen peroxide

1 Introduction

In the last decade the use of *N*-heterocyclic carbenes (NHCs) as ancillary ligands for transition metal catalysts and as organic catalysts on their own has proved very fruitful [1]. Not only have NHCs yielded improved transition metal

catalysts, but they have also lead to the isolation of unusual low-coordinate metal complexes, which often play a key role in catalytic processes [2]. In particular, NHCs emerge as effective ligands in late transition metal chemistry, in which they have found successful applications in homogeneous catalysis such as in olefin metathesis and C–C coupling reactions [2, 3]. Recently, also in the field of oxidation catalysis significant progress has been achieved. A variety of oxidation reactions have been studied using NHC catalysts, being the oxidation of alcohols and olefins the most explored. However, most of the work in the area of oxidation catalysis with NHCs has been performed with late transition metals [4]. With strong sigma-donor properties, NHCs are well suited to stabilize high-oxidation-state metal complexes. Nevertheless, the number of complexes that have been prepared to date is quite small and very little has been described concerning the oxidizing properties of these complexes [5]. In particular, the chemistry of high-valent molybdenum and tungsten-NHCs is almost unexplored [6]. The only examples of NHC-Mo(VI) and -W(VI) complexes were described by Herrmann and co-workers in 1996 [7]. Low-valent NHC-based molybdenum carbonyls are known, although their oxidative decarbonylation reaction has never been investigated [8–11]. Recently, we became interested in developing the chemistry of molybdenum-NHCs and exploring their potential in olefin epoxidation [12, 13]. Preliminary studies performed in our group showed the capability of NHC-based molybdenum carbonyl species to catalyze the epoxidation of *cis*-cyclooctene with *tert*-butyl hydroperoxo (TBHP) [13]. Based on these results and knowing that molybdenum η^3 -allyl dicarbonyl complexes of general formula [Mo(η^3 -allyl)X(CO)₂(L)_{*n*}] (X = Cl, Br; L = NCMe, *n* = 2; 1,4-diaza-1,3-butadienes, *n* = 1) are efficient catalysts for olefin epoxidation with TBHP [14], we decided to explore the performance of molybdenum and

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tungsten η^3 -allyl complexes bearing bis-*N*-heterocyclic carbene ligands in epoxidation of *cis*-cyclooctene using *tert*-butyl hydroperoxide and H_2O_2 as oxidant.

The employment of H_2O_2 is an attractive option both on environmental and economic grounds. It is cheap, readily available and gives water as the only by-product [15]. Molybdenum and tungsten complexes have been widely investigated because of their demonstrated high activity for selective oxidation with TBHP [16–20] and H_2O_2 [21–28]. However, to the best of our knowledge, the catalytic performance of Mo(II) and W(II) carbonyl compounds in olefin epoxidation using H_2O_2 has never been reported. Recently, tetracarbonyl complexes of the type $[\text{M}(\text{CO})_4(\text{L})]$ (L = bipyridyl) showed to exhibit good activity for epoxidation with TBHP, but they were inactive with H_2O_2 (only a 6% conversion of *cis*-cyclooctene was obtained when aqueous H_2O_2 was used as oxidant) [29]. In the present work, we demonstrate that molybdenum and tungsten η^3 -allyl dicarbonyl complexes of general formula $[\text{M}(\eta^3\text{-allyl})\text{Cl}(\text{CO})_2(\text{L})]$ (L = NCMe, bis-NHC) can be used as precatalysts for the selective epoxidation of *cis*-cyclooctene with H_2O_2 . Under the reaction conditions, the *N*-heterocyclic carbenes complexes of the family $[\text{M}(\eta^3\text{-allyl})\text{X}(\text{CO})_2(\text{L})]$ (M = Mo, W; X = halogen; L = Lewis base) are readily transformed to active catalytic species.

2 Results and Discussion

2.1 Synthesis of Complexes **3-Mo** and **4-W**

Molybdenum and tungsten complexes studied in this work are presented in Chart 1. The complexes $[\text{M}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{NCMe})_2]$ [M = Mo (**1**), W (**2**)] were obtained according the literature methods [30, 31]. The new complexes $[\text{M}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{bis-NHC}^{\text{Bz}})]$ (M = Mo (**3**), W (**4**); bis-NHC^{Bz} = 1,1'-dibenzyl-3,3'-methylenediimidazoline-2,2'-diylidene) were prepared by treatment of the corresponding acetonitrile complexes **1-Mo** and **2-W** with one equivalent of bis-NHC^{Bz}, previously prepared by deprotonation of the corresponding imidazolium diiodide salt with KO^tBu (Scheme 1). All complexes were characterized by elemental analyses, IR, ^1H NMR and ^{13}C NMR spectra.

Complexes of the general type $[\text{M}(\eta^3\text{-C}_3\text{H}_5)\text{X}(\text{CO})_2(\text{L-L})]$ (M = Mo, W; X = halogen; L-L = bidentate Lewis base) show pseudo-octahedral geometry around the metal centre in which the favourable orientation of the allyl ligand is its open face directed toward two carbonyl ligands [32, 33]. Two stable isomers, axial and equatorial, are known for this family of complexes (Scheme 2). The preferences between them are not clear and often they interconvert in solution [14]. Nevertheless, the formation of the axial isomer predominates in many structurally

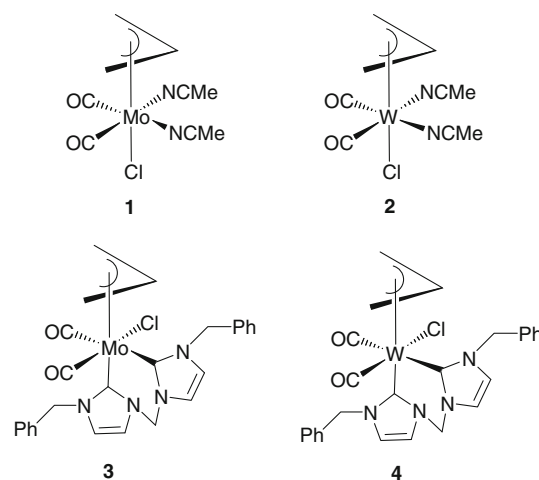


Chart 1 Carbonyl complexes $[\text{M}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{L})_n]$ [M = Mo, W; L = NCMe, $n = 2$; L = bis-NHC^{Bz}, $n = 1$]

characterized species. Based on these findings and in our spectroscopic data, which shows that only one isomer was observed for **3-Mo** and **4-W**, we propose an axial conformation for complexes **3-Mo** and **4-W** in which the η^3 -allyl group is positioned *trans* to one NHC ligand.

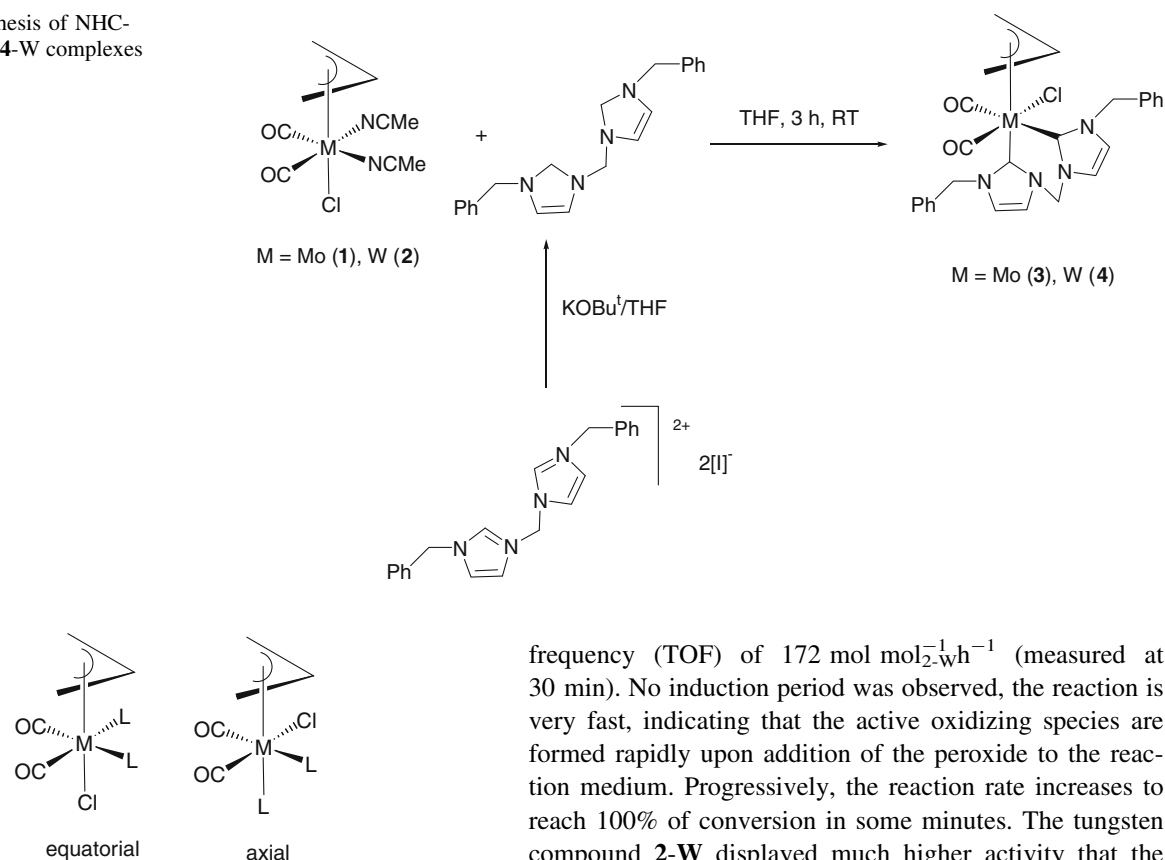
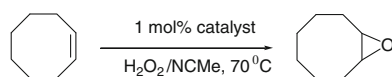
The ^{13}C NMR spectrum of **3-Mo** and **4-W** shows the signal due to the $\text{M-C}_{\text{carbene}}$ at δ 203 and 161, respectively, confirming the coordination of the NHC fragment to the metal centre. These values are in agreement with other $\text{M-C}_{\text{carbene}}$ reported in the literature [8–11]. Two carbonyl resonances at δ 230 and 228 (for **3-Mo**) and δ 219 and 221 (for **4-W**) were observed in the ^{13}C NMR spectra for the non-equivalent CO ligands.

The IR spectra of **3-Mo** and **4-W** displayed two terminal carbonyl stretching bands at 1919 and 1815 cm^{-1} (for **3-Mo**) and 1915 and 1806 cm^{-1} (for **4-W**). The two carbonyl bands were found in equal intensity indicating that the two carbonyls are mutually *cis* [31]. The shift to lower frequency of the CO stretching band in **3-Mo** and **4-Mo** compared to those of **1-Mo** (1947, 1852 cm^{-1}) and **2-W** (1933, 1839 cm^{-1}) indicates the stronger electron-donating properties of the NHC fragments.

2.2 Catalytic Studies

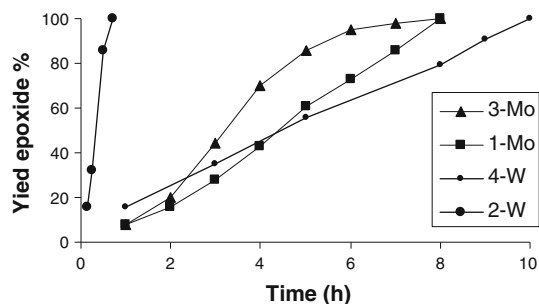
The catalytic performance of **1–4** (Chart 1) was investigated using *cis*-cyclooctene as a model substrate, at 70 °C with H_2O_2 (30% in H_2O) in the presence of 1 mol% of catalyst (molar ratio of substrate:oxidant = 100:300) (Scheme 3). Control experiments confirmed that no reaction takes place in the absence of catalyst.

Complexes **1–4** exhibited good catalytic activity in the epoxidation of *cis*-cyclooctene with H_2O_2 . For all the catalysts, the catalytic reactions were entirely selective for epoxidation, being 1,2-epoxycyclooctane the only product

Scheme 1 Synthesis of NHC-based **3-Mo** and **4-W** complexes**Scheme 2** Axial and equatorial isomers of $[M(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{L})_2]$ complexes**Scheme 3** Epoxidation of *cis*-cyclooctene with H_2O_2

obtained. The courses of epoxidation reactions, employing compounds **1–4** as catalysts, are shown in Fig. 1, and additional data are summarized in Table 1.

The highest reaction rate was observed for the tungsten complex **2-W**. The selective conversion to the epoxide was completed in 50 min corresponding to a turnover

**Fig. 1** Kinetic profiles of *cis*-cyclooctene epoxidation with H_2O_2 in the presence of complexes **1–4**

frequency (TOF) of $172 \text{ mol mol}^{-1}_{\text{W}}\text{h}^{-1}$ (measured at 30 min). No induction period was observed, the reaction is very fast, indicating that the active oxidizing species are formed rapidly upon addition of the peroxide to the reaction medium. Progressively, the reaction rate increases to reach 100% of conversion in some minutes. The tungsten compound **2-W** displayed much higher activity than the molybdenum analogue **1-Mo** (8 h were necessary to achieve 100% of conversion (Table 1, entry 5)). The corresponding NHC-based tungsten compound **4-W** exhibited lower activity than **2-W**, achieving 100% of conversion in 10 h (Table 1, entry 3). In contrast, different trend was observed for the molybdenum compounds, with the molybdenum NHC-based catalyst **3-Mo** displaying slightly more activity than the corresponding molybdenum compound **1-Mo**; TOFs of 18 (for **3-Mo**) and 11 (for **1-Mo**) $\text{mol mol}^{-1}_{\text{catal}}\text{h}^{-1}$ were calculated at 4 h. Both catalysts displayed similar kinetic profiles with induction periods of ~ 1 h and quantitative conversions in 8 h, indicating that similar catalytic active species are formed. In addition, both molybdenum catalysts showed higher activity compared to the NHC-W adduct **4-W** (Fig. 1).

Second runs were performed for complexes **1–4** by recharging the reaction mixture with the same amount of oxidant and substrate used initially in the first run. For each complex, the reaction is faster in the second run compared with the first one indicating that the first step of the catalytic reaction involves the oxidative decarbonylation of complexes **1–4** with formation of oxo-peroxo species that are the active species in the epoxidation reaction. A similar effect has been observed in the epoxidation of *cis*-cyclooctene with TBHP using $[\text{Mo}(\text{CO})_4\text{L}_n]$ complexes as catalysts [29]. The kinetic curves for the two runs are practically coincident for complexes **1–4**, giving quantitative conversions at

Table 1 Epoxidation of *cis*-cyclooctene with H₂O₂

Entry	Catalyst	Solvent	Yield of epoxide (%)	Time
1	MoCl(η^3 -C ₃ H ₅)(CO) ₂ (bis-NHC ^{Bz}) (3-Mo)	NCMe	100	8 h
2	MoCl(η^3 -C ₃ H ₅)(CO) ₂ (bis-NHC ^{Bz}) (3-Mo)	EtOH	85	8 h
3	WCl(η^3 -C ₃ H ₅)(CO) ₂ (bis-NHC ^{Bz}) (4-W)	NCMe	100	10 h
4	WCl(η^3 -C ₃ H ₅)(CO) ₂ (bis-NHC ^{Bz}) (4-W)	EtOH	63	10 h
5	MoCl(η^3 -C ₃ H ₅)(CO) ₂ (NCMe) ₂ (1-Mo)	NCMe	100	8 h
6	MoCl(η^3 -C ₃ H ₅)(CO) ₂ (NCMe) ₂ (1-Mo)	EtOH	45	10 h
7	WCl(η^3 -C ₃ H ₅)(CO) ₂ (NCMe) ₂ (2-W)	NCMe	100	50 min
8	WCl(η^3 -C ₃ H ₅)(CO) ₂ (NCMe) ₂ (2-W)	EtOH	100	1 h

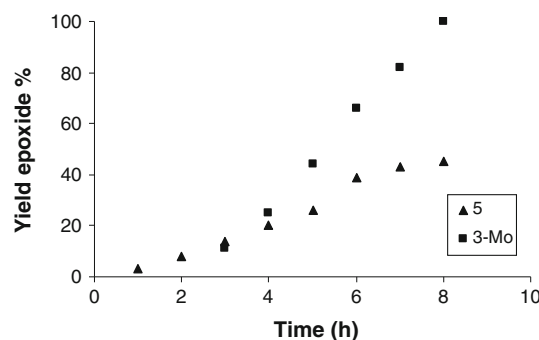
similar reaction times. Thus, it seems that the catalytic systems formed by **1–4**/H₂O₂/NCMe are fairly stable under the reaction conditions used.

The catalytic reactions were also studied in ethanol since according with some literature reports, ethanol is a suitable solvent for H₂O₂ affording in some cases better results compared to acetonitrile [27]. The results of the epoxidation of *cis*-cyclooctene with the ethanol/H₂O₂ system and complexes **1–4** are summarized in Table 1. It is clear from these data that the use of ethanol does not improve the catalytic performance of complex **2-W** (Table 1, entries 7 and 8) and decreases the performance of catalysts **1-**, **3-Mo** and **4-W**.

In an attempt to characterise the nature of the species formed during the course of the reaction with H₂O₂, complex **3-Mo** was treated with a 100-fold excess of H₂O₂ in acetonitrile for 2 h at room temperature. The solvent was then reduced to 5 mL under vacuum, and the reaction mixture was cooled to –20 °C yielding a yellow crystalline solid, which was isolated by filtration, washed with hexane and dried under vacuum to give a sample designated as **5**. The infrared spectrum of compound **5** is very different from that for complex **3-Mo**. The new bands at 950, 859, 713 and 583 cm^{–1} indicated the formation of an oxoperoxo complex. Its ¹H NMR spectrum showed a resonance at δ 9.56 indicating that the protonation of the NHC has occurred, affording the corresponding imidazolium cation [bis-NHC^{Bz}H₂]²⁺. No signals of the allyl group were observed in its ¹H NMR spectrum. A catalytic run carried out with compound **5** under conditions equivalent to those used for the fresh catalyst precursor **3-Mo** revealed different performance for the oxidation of *cis*-cyclooctene. Thus, after 8 h, a conversion of 43% was reached, which is rather lower than that obtained with **3-Mo** in the first run (Fig. 2). Therefore, we can conclude that the isolated species **5** were not the active species of the catalytic reaction, but collateral species. These results indicate that the Mo(II)–NHC complex suffers decomposition when treated with H₂O₂ affording the imidazolium cation [bis-NHC^{Bz}H₂]²⁺ as a result of protonation of the NHC ligand. Similar reaction of the molybdenum compound **1-Mo** with

100-fold excess of H₂O₂ in acetonitrile produced instantaneously the well known molybdenum-blue color (due to an intervalence charge transfer transition between Mo^V and Mo^{VI}) [34].

In order to establish the stability and activity of the NHC-based catalysts with different oxidants, we have investigated the catalytic activity of complexes **3-Mo** and **4-W** in epoxidation of *cis*-cyclooctene using *tert*-butylhydroperoxide (TBHP) as oxidant in chloroform at 55 °C. Their kinetic profiles are different from that of H₂O₂. In the presence of complex **3-Mo** and using TBHP as oxidant, the conversion of *cis*-cyclooctene is relatively fast during the first 4 h (no induction periods are observed), and then slows down significantly as the reaction progresses reaching a 100% yield of epoxide after 10 h of reaction (Fig. 3). Complexes of the general type CpMoX(CO)₃ also exhibited this kind of behaviour when used as epoxidation catalysts with TBHP, suggesting that a similar reaction mechanism may be involved. The slowdown in the reaction rate for these compounds has been attributed to an auto-retardation effect where *tert*-butyl alcohol, a by-product of the epoxidation, is a competitive inhibitor of TBHP for coordination to the Mo(VI) centre [14]. In contrast, when the catalytic reaction was performed using H₂O₂ as oxidant, complex **3-Mo** was initially less active in the epoxidation of *cis*-cyclooctene than when TBHP was used as oxidant, but after 5 h the yield of epoxide was higher with

**Fig. 2** Kinetic profiles of *cis*-cyclooctene epoxidation with H₂O₂ in the presence of complexes **5** and **3-Mo**

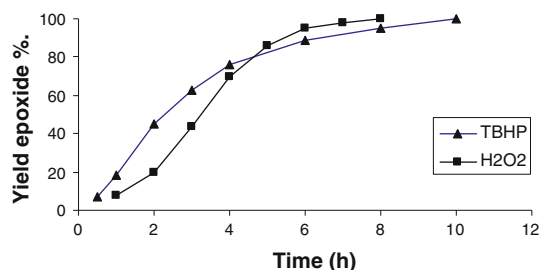


Fig. 3 Kinetic profiles of *cis*-cyclooctene epoxidation with H_2O_2 and TBHP in the presence of complex **3-Mo**

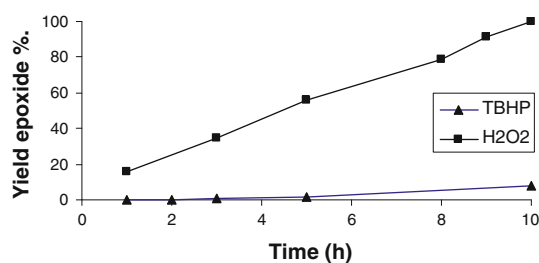


Fig. 4 Kinetic profiles of *cis*-cyclooctene epoxidation with H_2O_2 and TBHP in the presence of complex **4-W**

H_2O_2 reaching a 100% of conversion in 8 h while 10 h were necessary to complete the reaction with TBHP (Fig. 3). This is remarkable since molybdenum compounds are commonly more active with TBHP than with H_2O_2 .

The NHC–tungsten complex **4-W** was almost inactive in the epoxidation of *cis*-cyclooctene when TBHP is used as oxidant, yielding only 8% of the corresponding epoxide after 10 h of reaction. In contrast, 100% of epoxide was formed by using H_2O_2 as oxidant in the presence of **4-W** (Fig. 4).

3 Conclusions

We have reported the synthesis and characterization of new complexes of molybdenum and tungsten containing the $\text{M}(\eta^3\text{-allyl})\text{Cl}(\text{CO})_2$ fragment and *N*-heterocyclic carbene ligands. We have demonstrated the catalytic efficiency of these novel carbonyl complexes as precatalysts in the epoxidation of *cis*-cyclooctene using H_2O_2 as oxidant. The W-acetonitrile precursor $[\text{W}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{NCMe})_2]$ displayed high catalytic activity yielding quantitative conversions of the corresponding epoxide in 30 min of reaction. Decomposition of the NHC-based catalysts produces the imidazolium cation $[\text{bis-NHC}^{\text{Bz}}\text{H}_2]^{2+}$, resulting from protonation of the NHC ligand, indicating the vulnerability of the NHC ligand under the reaction conditions used in the catalytic experiments.

4 Experimental

4.1 Materials and Methods

All experiments were carried out under dry nitrogen using standard Schlenk or dry-box techniques. Solvents were dried by standard methods and distilled under nitrogen. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer at room temperature and referenced to the residual ^1H and ^{13}C signals of the solvents. Catalytic runs were monitored by GC (Trace 2000 Series) equipped with a capillary column (cyclosilb, 30 m $\times$ 0.25 mm $\times$ 0.25 mm) and a flame ionization detector. Elemental analyses were carried out in our laboratories at ITQB. Infrared (IR) spectra were recorded on samples as KBr pellets using a Mattson 7000 FT-IR spectrometer. KOBU^t , $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ were purchased from Aldrich and used as received. The imidazolium salt 1,1'-dibenzyl-3,3'-methylenediimidazolium diiodide was prepared according the literature procedure [35]. Complexes $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{NCMe})_2]$ and $[\text{W}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{NCMe})_2]$ were prepared following the synthetic procedure reported in the literature [30, 31].

4.2 Syntheses

4.2.1 $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{bis-NHC}^{\text{Bz}})$ (**3**)

A solution of **1** (0.32 g, 1.05 mmol) in THF (10 mL) was added at room temperature to a THF solution of 1,1'-dibenzyl-3,3'-methylenediimidazoline-2,2'-diylidene (0.61 g, 1.05 mmol), prepared in situ by deprotonation of the corresponding imidazolium salt with KOBU^t . The reaction mixture was stirred for 3 h, after which the solvent was evaporated in vacuum, and the product was recrystallized from a dichloromethane/hexane mixture. The title compound **3** was isolated as a red crystalline solid. Yield: 0.3 g, 50%. Anal. Calcd for $\text{C}_{26}\text{H}_{25}\text{N}_4\text{O}_2\text{MoCl}$ (556.9)1/2 THF: C, 56.55; H, 4.92; N, 9.43. Found: C, 56.40; H, 4.67; N, 9.75. Selected IR data (KBr, cm^{-1}): $\nu(\text{CO})$ 1919, 1815. ^1H NMR (400 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$): δ = 0.88 (d, 2H, $J_{\text{H-H}} = 9$ Hz, H_{anti}), 3.39 (d, 2H, $J_{\text{H-H}} = 9$ Hz, H_{syn}), 3.73 (m, 1H, H_{meso}), 5.02 (s, 4H, CH_2Ph), 6.8 (s, 2H, $\text{NCH} = \text{CHN}$), 7.07 (s, 2H, NCH_2N), 7.32–7.59 (10 H, Ph), 7.97 (s, 2H, $\text{NCH} = \text{CHN}$). ^{13}C NMR (CD_2Cl_2): δ = 230.4 (CO), 228.4 (CO), 203.1 (Mo- $\text{C}_{\text{carbene}}$), 142–127 ($\text{CH}_{\text{Ph}} + \text{NCH}_2\text{N}$), 121.6 ($\text{CH}_{\text{imidazole}}$), 121.4 ($\text{CH}_{\text{imidazole}}$), 75.7 (C_{meso}), 62.2 ($\text{C}_{\text{anti/syn}}$), 53.3 (N- CH_2 -Ph).

4.2.2 $\text{W}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{bis-NHC}^{\text{Bz}})$ (**4**)

A solution of **2** (0.33 g, 0.85 mmol) in THF (10 mL) was added at room temperature to a THF solution of

1,1'-dibenzyl-3,3'-methylenediimidazoline-2,2'-diylidene (0.49 g, 0.85 mmol), prepared in situ by deprotonation of the corresponding imidazolium salt with KOBu^t. The reaction mixture was stirred for 6 h, after which the solvent was evaporated in vacuum, and the product was recrystallized from a dichloromethane/hexane mixture. The title compound **4** was isolated as a red crystalline solid. Yield: 0.26 g, 47%. Anal. Calcd for C₂₆H₂₅N₄O₂WCl (644): C, 48.43; H, 3.91; N, 8.69. Found: C, 48.20; H, 4.14; N, 8.35. Selected IR data (KBr, cm⁻¹): ν(CO) 1915, 1806. ¹H NMR (400 MHz, CD₂Cl₂, 25 °C): δ = 0.85 (d, 2H, J_{H-H} = 8.5 Hz, H_{anti}), 1.46 (d, 2H, J_{H-H} = 8.5 Hz, H_{syn}), 2.87 (m, 1H, H_{meso}), 5.04 (s, 4H, CH₂Ph), 6.73 (s, 2H, NCH = CHN), 7.08 (s, 2H, NCH₂N), 7.30–7.40, 10 H, Ph), 8.10 (s, 2H, NCH = CHN). ¹³C NMR (CD₂Cl₂): δ = 221 (CO), 219.2 (CO), 161.4 (W-C_{carbene}), 142–126 (CH_{Ph} + NCH₂N), 120.4 (CH_{imidazole}), 119.9 (CH_{imidazole}), 65.8 (C_{meso}), 53.1 (C_{anti/syn}), 52.1 (N-CH₂-Ph).

4.3 Catalytic Reactions

4.3.1 Epoxidation of *cis*-Cyclooctene with H₂O₂

The catalytic reactions were carried out under an open atmosphere in a flask equipped with a magnetic stirrer. In a typical experiment, 0.14 mL (1.109 mmol) of olefin, 1 mol% catalyst (0.011 mmol) in 2 mL of acetonitrile, 0.37 mL of 30% H₂O₂ (3.32 mmol, 3 equiv) and 0.2 mL mesitylene as internal standard were added to initiate the reaction. The reaction was heated then to 70 °C for a specific time. Samples were taken periodically and analyzed by a GC. The conversion of olefin and the selectivity to the corresponding epoxide were calculated using calibration curves recorded prior to the reaction.

4.3.2 Epoxidation of *cis*-Cyclooctene with TBHP

The catalytic reactions were carried out under an open atmosphere in a flask equipped with a magnetic stirrer. In a typical experiment, 0.14 mL (1.109 mmol) of olefin, 1 mol% catalyst (0.011 mmol) in 2 mL of chloroform, 0.66 mL of TBHP (6 M solution in decane, 3.32 mmol, 3 equiv) and 0.2 mL mesitylene as internal standard were added to initiate the reaction. The reaction was heated then to 55 °C for a specific time. Samples were taken periodically and analyzed by a GC. The conversion of olefin and the selectivity to the corresponding epoxide were calculated using calibration curves recorded prior to the reaction.

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