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Synthesis and characterization of novel cyclopentadienyl molybdenum imidazo[1,5-a]pyridine-3-ylidene complexes and their application in olefin epoxidation catalysis



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ABSTRACT

Two novel cyclopentadienyl molybdenum complexes [CpMo(CO)₂(ImPyMes)CI] (1) (ImPyMes = 2-mesitylimidazo[1,5-a]pyridine-3-ylidene) and [CpMo(CO)₂(ImPyMes)(NCCH₃)]BF₄ (2) were employed as pre-catalysts in olefin epoxidation catalysis using *tert*-butylhydroperoxide (TBHP) as oxidant. Turnover frequencies (TOFs) of 40,900 h⁻¹ (0.005 mol% 1) and 53,100 h⁻¹ (0.01 mol% 2) were achieved in *cis*-cyclooctene epoxidation in CHCl₃ at 55 °C, outperforming most previously reported Mo epoxidation catalysts. The synthesis of 1 proceeds *via* the silver carbene transmetallation route in 90% yield, and further treatment of 1 with AgBF₄ in CH₃CN leads to the ionic complex 2 in 87% yield. Even at very low pre-catalyst concentrations, quantitative *cis*-cyclooctene conversion with high selectivity is achieved. Furthermore, epoxidation of more challenging substrates results in good conversions and recycling experiments in room temperature ionic liquid (RTIL) [C₈mim]NTf₂ (C₈mim = 1-methyl-3-octylimidazolium, NTf₂ = bis(trifluoromethanesulfonyl)imide) shows reusability of 1 in catalytic epoxidation for several runs without loss of activity.

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1. Introduction

Transition metal-catalyzed epoxidation reactions are of considerable interest due to the industrial demand for epoxides as intermediates for the synthesis of pharmaceuticals, agrochemicals, and many other compounds [1,2]. Over the past two decades, η^5 -cyclopentadienyl molybdenum complexes have been extensively studied as olefin epoxidation catalysts. Bergman and Trost were the first to report on olefin epoxidation with a η^5 -pentamethylcyclopentadienyl Mo catalyst [Cp*MoO₂Cl] in the presence of hydroperoxides [3]. The pre-catalysts [CpMo(CO)₃Cl] [4,5] and [Cp Mo(CO)₃CH₃] [6], which can be easily oxidized to their catalytically active species using alkyl hydroperoxides, show good catalytic activities with turnover frequencies (TOFs) of up to 6000 h⁻¹ at a pre-catalyst loading of 0.1 mol% and with *cis*-cyclooctene as substrate. Cyclopentadienyl molybdenum(II) tricarbonyl complexes [Cp*Mo(CO)₃R] (R = alkyl, halide) are known to undergo oxidative

decarbonylation to give catalytically active dioxo [CpMoO₂R] and oxo-peroxo [CpMo(O)(O₂)R] complexes (Scheme 1) [3,5,7,8].

To date, a number of η^5 -cyclopentadienyl tricarbonyl molybdenum complexes with different ligand spheres have been investigated as pre-catalysts in olefin epoxidation [2,9–15]. Of these, the *ansa*-bridged cyclopentadienyl Mo complex [{ η^5 -C₅H₄ [CH(CH₂)₃]- η^1 -CH}Mo(CO)₃] [16] shows the highest TOF in *cis*cyclooctene epoxidation, namely 11,800 h⁻¹ in organic solvents [17] and TOFs up to 44,000 h⁻¹ in room temperature ionic liquids (RTILs) [18].

The use of *N*-heterocyclic carbene (NHC) ligands has extended the scope of cyclopentadienyl molybdenum complexes in olefin epoxidation catalysis. As spectator ligands, they often lead to higher complex stability due to their strong σ -donating and poor π -accepting character [19]. Royo et al. synthesized the first *ansa*-bridged cyclopentadienyl-imidazolylidene molybdenum complexes with the general formula [η^5 -C₅R₄{CR₂CRPh- η^1 -NHC^{Me}}Mo(CO)₂I] (R = H, alkyl) [20]. All of these complexes are catalytically active in olefin epoxidation; however, the catalytic reactions exhibit long induction periods and proceed rather slowly in comparison with tricarbonyl molybdenum complexes. On the other hand, longer

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Scheme 1. Oxidation of $[CpMo(CO)_3R]$ precatalysts with TBHP. Adapted from Kühn et al. [8].

catalyst lifetimes are observed due to their increased stability under oxidative conditions, and thus, higher conversions are obtained. In 2010, Hor, Zhao et al. reported the synthesis of a series of cyclopentadienyl imidazolylidene molybdenum complexes [21]. The neutral complexes [CpMo(C O)₂(NHC)X] (X = halide) show comparatively poor catalytic activities in epoxidation reactions, whereas the ionic complex [CpMo(CO)₂(IMes)(NCCH₃)]BF₄ (IMes = 1,3-bis(2,4,6-trimethy lphenyl)imidazol-2-ylidene) is quite active with a TOF of >34 00 h⁻¹. Another type of NHC molybdenum complexes of the formula [CpMo(CO)₂(NHC)CI] (NHC = 1-methyl-2-phenyl-4-tolyl-1,2,3-triazol-5-ylidenyl) has been recently reported by our group [22]. This triazolylidene-based Mo catalyst was applied as precatalyst in epoxidation catalysis and features moderate catalytic activity in ionic liquids.

Imidazo[1,5-a]pyridine-3-ylidenes (ImPy) are among the strongest heteroaromatic σ -donors and are sterically more demanding than 1,3-disubstituted imidazolylidenes. Consequently, the stereoelectronic environment at the metal center may be manipulated easily by varying substituents on the NHC ligand [23–25]. Several imidazo[1,5-a]pyridine-3-ylidene transition metal complexes based on Rh [26-28], Ir [23,26] and Pd [23,27] have been reported previously and applied as catalysts in allylic substitution [27], Suzuki-Miyaura cross-coupling [23] and other cross-coupling reactions [24]. To the best of our knowledge, no reports of their application in olefin epoxidation are known. The bicyclic structure of ImPy ligands facilitates a unique stereoelectronic environment. Therefore, interest in the effect of this type of ligand for molybdenum complexes and their activities in olefin epoxidation appears to be justified. This report discusses the synthesis and characterization of two novel NHC molybdenum complexes [CpMo(CO)₂(ImPy-Mes)Cl1 (1) (ImPyMes = 2-mesitylimidazo[1,5-a]pyridine-3ylidene) and [CpMo(CO)₂(ImPyMes)(NCCH₃)]BF₄ (2) and their application as pre-catalysts in olefin epoxidation.

2. Experimental section

2.1. General remarks

All preparations and manipulations were performed using standard Schlenk techniques under an argon atmosphere. All reagents were purchased from commercial sources and used without further purification. All solvents were dried with a MBraun MB SPS 800 purification system and stored under argon over molecular sieves. Chromatographic separations were performed using silica gel (40–63 μ m). All catalytic reactions were carried out under laboratory atmosphere. NMR spectra were recorded with a Bruker Avance DPX 400 or a Bruker Avance III 400 spectrometer at a temperature of 298 K. The spectra were referenced to the residual ¹H and ¹³C{¹H} signals of the solvents in parts per million (ppm) [29]. Abbreviations for NMR multiplicities are as follows: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). Coupling constants J are given in Hz. The IR spectra were recorded on a Varian ATR-FTIR instrument. Elemental analyses were carried out by the microanalytical laboratory of Technische Universität München. FAB mass spectra were obtained with a Finnigan MAT 90 spectrometer. Catalytic runs were monitored by GC methods on a Varian CP-3800 gas chromatograph. 2-Mesitylimidazo[1,5a]pyridinium chloride was prepared according to the known procedure [25].

2.2. Single-crystal XRD structure determination

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-985095 (1), and CCDC-985096 (2). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. Fax: +44 1223 336 033; e-mail, deposit@ccdc.cam.ac.uk (see also Table 1).

2.3. Computational details

All calculations were performed with Gaussian09 [30]. The hybrid functional B3LYP [31-33] and the nonhybrid functional BPW91 [34,35] were used with the split valence double- ζ (DZ) 6-31G** basis set [36,37] for all atoms except Mo, which was treated with the Stuttgart97-ECP with a DZ description of the valence electrons [38]. This level of theory was used for geometry optimization and frequency calculation. Carbonyl absorption bands and partial atomic charges (Mulliken [39] and NBO [40-46]) were taken from the Gaussian-09 outputs of the frequency calculations and Natural Bond Orbital Analysis, respectively. No symmetry or coordinate constraints were applied during optimizations. All reported optimized geometries were verified as being true minima by the absence of eigenvalues in the vibrational frequency analysis. Calculation of ⁹⁵Mo NMR shifts was carried out using the GIAO method [47-51] and the B3LYP and BPW91 functionals with the IGLOII basis set [52] instead of 6-31G** [53]. For ⁹⁵Mo NMR shift calculation, the BPW91 functional was found to be superior to the popular B3LYP in previous studies, justifying its supplementary use in the present study [53,54]. The polarizable continuum model (PCM) [55–74] was applied for all calculations in solvent media.

2.4. Synthesis of [CpMo(CO)₂(ImPyMes)Cl] (1)

2-Mesitylimidazo[1,5-a]pyridinium chloride (0.400 g, 1.5 mmol, 1.0 equiv.) and silver(I)-oxide (0.170 g, 0.7 mmol, 0.5 equiv.) were suspended in dry dichloromethane (20 mL). The reaction mixture was stirred at room temperature under exclusion of light for 16 h.

Table 1Crystallographic data for complexes 1 and 2.

	1	2
Formula	$C_{24}H_{22}C_{14}MoN_2O_2$	$C_{25}H_{24}BF_4MoN_3O_2$
Formula wt.	608.18	581.22
Space group	Р	P 21/n
a (Å)	8.8892(2)	13.5880(3)
b (Å)	10.8399(2)	12.2260(3)
<i>c</i> (Å)	13.5088(3)	15.0385(4)
α(°)	102.602(1)	90
β (°)	93.068(1)	95.550(1)
γ(°)	101.799(1)	90
$V(Å^3)$	1236.90(5)	2496.59(11)
Ζ	2	4
$D_{\rm calc}~({\rm g~cm^{-3}})$	1.633	1.553
N _{ref}	4509	4567
N _{par}	301	409
$R1$ ($I > 2\sigma(I)$)	0.0236	0.0257
wR2 (all data)	0.0532	0.0585
Goodness of fit	1.059	1.020

The suspension was filtered through Celite and dried under reduced pressure to give a pale yellow solid. The solid was dissolved in dry toluene (25 mL) and [CpMo(CO)₃Cl] (0.253 g, 0.9 mmol, 0.6 equiv.) was added. The solution was heated to reflux under exclusion of light for 1 h. The dark red solution was concentrated under reduced pressure and the residue was purified by column chromatography (gradient elution with hexane:ethyl acetate = 2:1). The eluting pink band was collected and concentrated under reduced pressure to give the product as a pink solid (0.395 g, 90%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.21 (d, ${}^{3}J_{H,H}$ = 7.5 Hz, 1H, H₅), 7.32 (d, ${}^{3}J_{H,H}$ = 9.2 Hz, 1H, H₈), 7.25 (s, 1H, H₁), 7.11 (s, 1H, m-H_{Mes}), 7.07 (s, 1H, m-H_{Mes}), 6.92 (dd, ${}^{3}J_{H,H}$ = 9.1, 6.5 Hz, 1H, H7), 6.65 (t, ${}^{3}J_{H,H}$ = 7.0 Hz, 1H, H₆), 4.94 (s, 5H, H_{Cp}), 2.43 (s, 3H, p-CH₃), 1.98 (s, 6H, o-CH₃). ¹³C NMR (101 MHz, $CDCl_3$): δ (ppm) = 257.4 (CO), 252.2 (CO), 179.6 (C_{Carbene}), 140.4 (C_{ar}), 138.0 (C_{ar}), 137.2 (C_{ar}), 135.5 (C_{ar}), 133.4 (C_{ar}), 130.7 (C_{ar}), 129.3 (C_{ar}), 129.1 (C_{ar}), 123.4 (C_{ar}), 11 7.0 (C_{ar}), 113.4 (C_{ar}), 113.2 (C_{ar}), 95.2 (CH_{Cp}), 21.3 (*p*-CH₃), 18.2 (*o*-CH₃), 17.8 (*o*-CH₃). ⁹⁵Mo NMR (26 MHz, CDCl₃): δ (ppm) = -513. IR (solid): v (cm⁻¹) = 1943 (CO), 1834 (CO). MS (FAB): m/z(%) = 455.1 ([M-Cl]⁺). EA: Anal. Calcd for C₂₃H₂₁ClMoN₂O₂ (%): C 56.51, H 4.33, N 5.73. Found: C 56.49, H 4.41, N 5.71.

2.5. Synthesis of $[CpMo(CO)_2(ImPyMes)(NCCH_3)]BF_4$ (2)

Complex 1 (0.488 g, 1.0 mmol, 1.0 equiv.) was dissolved in dry acetonitrile (25 mL), and AgBF₄ (0.389 g, 2.0 mmol, 2.0 equiv.) was added to the pink solution. The mixture was stirred at room temperature for 1 h to create a red suspension, which was filtered through celite. Volatiles were removed under reduced pressure. The red residue was purified by recrystallization from acetonitrile and diethyl ether to obtain the product as red crystals (0.504 g, 87%). ¹H NMR (400 MHz, CD₃CN): δ (ppm) = 8.07 (d, ³J_{H,H} = 7.6 Hz, 1H, H₅), 7.72 (s, 1H, H₁), 7.61 (d, ${}^{3}J_{H,H}$ = 9.3 Hz, 1H, H₈), 7.20 (s, 1H, *m*-H_{Mes}), 7.18 (s, 1H, *m*-H_{Mes}), 7.11 (dd, ${}^{3}J_{H,H}$ = 9.2, 6.5 Hz, 1H, H₇), 6.91 (t, ${}^{3}J_{H,H}$ = 6.9 Hz, 1H, H₆), 5.12 (s, 5H, H_{Cp}), 2.42 (s, 3H, p-CH₃), 2.10 (s, 3H, o-CH₃), 1.96 (s, 3H, NCCH₃), 1.81 (s, 3H, o-CH₃). ¹³C NMR (101 MHz, CD₃CN): δ (ppm) = 250.8 (CO), 248.7 (CO), 171.7 (C_{Carbene}), 141.8 (C_{ar}), 138.1 (C_{ar}), 136.9 (C_{ar}), 136.5 (C_{ar}), 134.9 (C_{ar}), 130.3 (C_{ar}), 130.1 (C_{ar}), 129.1 (C_{ar}), 12 4.3 (Car), 119.4 (Car), 117.6 (Car), 116.0 (Car), 95.7 (CH_{Cp}), 21.2 (*p*-CH₃), 17.7 (*o*-CH₃), 17.5 (*o*-CH₃). ⁹⁵Mo NMR (26 MHz, CD₃CN): δ (ppm) = -643. ¹¹B NMR (128 MHz, CD₃CN): δ (ppm) = -1.18. ¹⁹F NMR (377 MHz, CD₃CN): δ (ppm) = -151.68 (¹⁰BF₄), -15 $1.73 (^{11}BF_4^-)$. IR (solid): $v (cm^{-1}) = 1969 (CO)$, 1860 (CO), 10 47 (BF₄). MS (FAB): m/z (%) = 455.1 [M–NCCH₃]⁺. EA: Anal. Calcd for C₂₅H₂₄BF₄MoN₃O₂ (%): C 51.66, H 4.16, N 7.23. Found: C 51.41, H 4.18, N 7.06.

2.6. Epoxidation catalysis reactions

For *cis*-cyclooctene: Substrate (1.10 g, 10 mmol) and pre-catalyst [0.1 mol%, 10 µmol (or: 1 mol%, 0.05 mol%, 0.01 mol%, 0.005 mol%)] were added to the reaction vessel. The catalyses were carried out neat, in an organic solvent, *e.g.* CHCl₃ (5 mL) or in RTIL [C₈mim]NTf₂ (0.5 mL) at 55 °C or at room temperature. The reaction was initiated by adding the oxidant TBHP (3.64 mL, 5.5 M in *n*-decane). For other substrates: Olefin [1-octene (112 mg), *cis*-stilbene (180 mg) or *trans-β*-methylstyrene (118 mg); 1 mmol], 1,2-dichloroethane (99 mg, 1 mmol, internal standard) and pre-catalyst (0.1 mol%, 1 µmol) were dissolved in CDCl₃ (0.5 mL). The reaction was carried out in an NMR tube at 55 °C and initiated by adding TBHP (364 µL, 5.5 M in *n*-decane).

The course of the epoxidation reaction of *cis*-cyclooctene was monitored by quantitative GC analysis. Samples (0.2 mL) were taken at specific time intervals, treated with activated MnO₂ to decompose excess alkyl hydroperoxide and MgSO₄ to remove water and diluted with iso-propanol (0.3 mL). After filtration, a mixture of indane and p-xylene (4 mg/mL each) in iso-propanol was added as external standard, and the solution was injected into a GC column. The conversion of *cis*-cyclooctene and the formation of cyclooctene epoxide were calculated from calibration curves $(r^2 = 0.999)$ recorded prior to the reaction course. For the recycling experiments in RTIL [C₈mim]NTf₂, a sample was taken after 24 h and treated as described above. For subsequent runs, the upper phase was removed by means of cannulation from the reaction vessel. Tert-butanol was removed from the remaining ionic liquid phase under reduced pressure. After drying, the next batch of *cis*cyclooctene (1.10 g, 10 mmol) and TBHP (3.64 mL, 5.5 M in *n*-decane) was added to the RTIL phase at 55 °C. The procedure was repeated 10 times. The course of the reaction in case of the other substrates (1-octene, *cis*-stilbene and *trans-B*-methylstyrene) was monitored by ¹H NMR analysis at specific time intervals. The conversion of the olefins and the vields of epoxides were calculated according to the internal standard.

3. Results and discussion

3.1. Synthesis and characterization of 1

The ligand precursor 2-mesitylimidazo[1,5-a]pyridinium chloride was prepared according to a literature procedure *via* a threecomponent coupling reaction between picolinaldehyde, formalin and 2,4,6-trimethylaniline [25]. 2-Mesitylimidazo[1,5-a]pyridine-3-ylidene Mo complex **1** was synthesized by the transmetalation route *via* silver carbene of 2-mesitylimidazo[1,5-a]pyridinium chloride according to a modified synthesis of similar compounds [21]. The silver carbene was formed *in situ* by treating the imidazo[1,5-a]pyridinium salt with silver(1)-oxide. **1** was obtained as a pink solid in 90% yield by reacting the silver carbene with [CpMo(CO)₃CI] (Scheme 2).

Complex 1 is stable towards air and moisture and can be stored and handled in laboratory atmosphere: it is highly soluble in polar and non-polar solvents such as methanol, acetonitrile, chloroform. THF, toluene and benzene but poorly soluble in *n*-hexane and *n*-pentane. TG–MS analysis confirms the stability of **1** at ambient temperature, as decomposition starts at 241.5 °C by loss of a carbonyl ligand relating to a MS signal with 28 m/z (CO). Complex **1** has been characterized by IR, NMR (¹H, ¹³C, ⁹⁵Mo), FAB-MS and elemental analysis. The successful metallation is confirmed by the appearance of the characteristic carbene signal at 179.6 ppm in ¹³C NMR and by the shift of the Cp signal from 5.66 ppm in [CpMo(CO)₃Cl] upfield to 4.94 ppm in ¹H NMR of **1**. The formation of the new complex [CpMo(CO)₂(ImPyMes)Cl] is further verified by two carbonyl signals at 252.2 and 257.4 ppm in ¹³C NMR, indicating a cis-configuration of the carbonyls [75,76]. The IR spectra show a strong shift from v_{CO} = 1931, 2043 cm⁻¹ of [CpMo(CO)₃Cl] to v_{CO} = 1834, 1943 cm⁻¹ of **1**, illustrating the strong σ -donating character of the NHC ligand. In comparison with similar literature known complexes (Fig. 1) [20-22], the imidazo[1,5-a]pyridine-3ylidene in **1** exhibits slightly stronger σ -donor characteristics than the triazolylidene (A: 1848, 1944 cm⁻¹) [22] and the ansa-NHC ligands first reported by Royo et al. (**B**: 1851, 1945 cm⁻¹) [20] and significantly stronger σ -donor properties than the imidazolylidenes originally described by Hor, Zhao et al. (C: 1860, 1956 cm⁻¹) [21].

The IR spectrum of **1** provides further indication of a *cis*-configuration of CO ligands with the relative intensities I_{asym} and I_{sym} of $v_{asym(CO)}$ and $v_{sym(CO)}$ using the ratio $I_{asym}/I_{sym} = \tan 2\theta$ ($2\theta = OC-Mo-CO$ bond angle) [75,76]. The ⁹⁵Mo NMR signal is shifted from -836 ppm in [CpMo(CO)₃Cl] [77] downfield to -513 ppm in **1** and provides insight into the electronic situation of the metal.



Scheme 2. Synthesis of complex 1.



Fig. 1. Previously reported cyclopentadienyl NHC molybdenum complexes A [22], B [20], C [21], and D [21] with similar structural motifs.

Compared to the signal of the *ansa*-NHC Mo complex **B** at -810 ppm [20], the ⁹⁵Mo NMR signal of **1** is shifted downfield, indicating lower electron density at the Mo center and thus higher Lewis acidity of molybdenum. This is supported by NBO and Mulliken charges at Mo obtained from DFT calculations on the B3LYP/6-31G** level of theory (see Table S2). Even though ⁹⁵Mo NMR shifts are susceptible to small changes within the ligands sphere, they can be used as indicators of the electronic situation at the metal center due to similar structural motifs of **B** and **1** [78]. This effect is counterintuitive when the σ -donor properties of the NHC-ligands in **1** and **B** are considered, but may be attributed to the simultaneous variation of NHC and halide ligand.

3.2. Synthesis and characterization of 2

The synthesis of the ionic imidazo[1,5-a]pyridine-3-ylidene molybdenum complex **2** was conducted according to a modified literature procedure by treating **1** with $AgBF_4$ in acetonitrile (Scheme 3) [21].

After recrystallization, **2** was isolated as red crystals in 87% yield; it is less stable towards air and moisture than **1** but can be handled in a laboratory atmosphere for a few hours. Compound **2** is highly soluble in polar solvents such as methanol and acetonitrile, but poorly soluble in chloroform. The ionic complex **2** has been characterized by IR, NMR (¹H, ¹³C, ⁹⁵Mo, ¹¹B, ¹⁹F), FAB-MS and elemental analysis. The successful substitution of chloride is indicated by ¹H NMR spectroscopy. A downfield shift of the Cp signal from 4.94 ppm (**1** in CDCl₃) to 5.12 ppm (**2** in CD₃CN) is observed. ¹³C NMR shows the upfield shift of the carbene signal



Scheme 3. Synthesis of complex 2.

to 171.7 ppm and of the carbonyl signals to 248.7 and 250.8 ppm. ¹¹B NMR and ¹⁹F NMR confirm the presence of BF₄ as a counterion. The appearance of a signal in ¹H NMR at 1.96 ppm from acetonitrile, the elemental analysis and the MS spectrum indicate that one solvent molecule coordinates to molybdenum, as observed for **D** (Fig. 1) [21]. The ⁹⁵Mo NMR signal appears upfield at -643 ppm compared to 1 (-513 ppm). However, this should not be taken to indicate lower Lewis acidity in 2, since ⁹⁵Mo NMR shifts are comparable only for closely related compounds. The substitution of chloride for acetonitrile and the subsequent formation of an ionic complex render the direct comparison of ⁹⁵Mo NMR shifts of **1** and **2** impossible. CO absorption bands in IR spectra, however, appear to give a better indication of the electronic situation at the metal center. The CO bands of 2 are shifted to higher frequencies (1860 and 1969 cm⁻¹), indicating less π -backbonding of molybdenum compared to **1** and thus higher Lewis acidity. This assumption is supported by DFT investigations of Mulliken and NBO charges on the B3LYP 6-31G** level of theory, which point to a higher Lewis acidity of 2 compared to 1. The tendencies observed for CO absorption bands in IR and signals in ⁹⁵Mo NMR correspond well to the results of the theoretical study of the complexes, supporting the validity of the theoretical model. Further details on DFT studies can be found in the Supporting Information. As in 1, ¹³C NMR and IR spectra of 2 indicate a *cis*-arrangement of the carbonyl ligands.

3.3. Single-crystal XRD structure determination of 1 and 2

The molecular structures of **1** and **2** were determined by singlecrystal XRD. Suitable crystals of **1** were obtained by diffusion of *n*-hexane into a solution of **1** in ethyl acetate. Single crystals of **2** were obtained by diffusion of diethyl ether into a solution of **2** in acetonitrile. The molecular structures of both complexes as well as selected bond lengths and angles are depicted in Figs. 2 and 3. Both structures can be described as four-legged piano stool halfsandwich Mo(II) complexes. The L-Mo-L (L = ligand) bond angles vary from 74.36(8)° to 82.43(6)° for **1** and from 75.55(9)° to 84.72(8)° for **2** and thus fall within the range of related compounds [20,21]. The OC-Mo-CO bond angles of 74.67(9)° in **1** and 75.55(9)° in **2** confirm the *cis*-arrangement of the carbonyl ligands in both complexes. A comparison of some selected bond distances of **1**, **2**, **A**, **C**, and **D** is given in Table 2.

The σ -donating character of different NHC ligands is reflected in the Mo–C_{Carbene} bond distance. Complexes **1** and **2** feature bond lengths (2.227(2) and 2.222(2) Å) comparable to the triazolylidene complex **A** (2.221(4) Å) and shorter Mo–C_{Carbene} distances than **C** (2.244(3) Å) and **D** (2.249(3) Å). The Mo–CO distances of **1** (1.961(2) and 1.956(2) Å) are on average longer than in **A** (1.965(4) and 1.945(4) Å) and **C** (1.939(5) and 1.932(4) Å), indicating that oxidative decarbonylation might be facilitated in **1** compared to known molybdenum NHC complexes. The Mo–CO bond lengths are even longer in the ionic complex **2** (1.985(3) and 1.941(3) Å), illustrating even weaker bonding of the carbonyl ligands to molybdenum. Because of the proposed increased Lewis acidity of **2** compared to **1** and the resulting stronger π -acceptor character, the Mo–Cp_{Centroid} distance of **2** (2.002 Å) is slightly shorter than



Fig. 2. ORTEP style plot of **1**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1-C22 1.956(2), Mo1-C23 1.961(2), Mo1-C1 2.227(2), Mo1-Cl1 2.5389(5); C22-Mo1-C23 74.67(9), C23-Mo1-C1 74.36(8), C1-Mo1-Cl1 78.58(5), C22-Mo1-Cl1 82.43(6).



Fig. 3. ORTEP style plot of **2**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms and BF_4^- anions are omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1-C23 1.941(3), Mo1-C22 1.985(3), Mo1-C1 2.222(2), Mo1-N3 2.177(2); C23-Mo1-C22 75.55(9), C22-Mo1-C1 76.43(9), N3-Mo1-C1 79.05(7), C23-Mo1-N3 84.72(8).

of **1** (2.015 Å). Overall, the data obtained from the crystal structures of **1** and **2** support the structural indications and conclusions of NMR and IR measurements.

3.4. Application in olefin epoxidation catalysis

The catalytic performance of complexes **1** and **2** as catalyst precursors in olefin epoxidation catalysis was investigated to deter-

Table 2

Selected bond lengths [Å] of complexes 1 and 2 as well as of compounds A [22], C [21], and D [21].

Bond	1	2	Α	С	D
Mo-CO	1.961(2)	1.985(3)	1.965(4)	1.939(5) 1.932(4)	1.996(3)
Mo-Cp _{Centroid}	2.015	2.002	_ ^c	1.932(4) _ ^c	_ ^c
Mo-X	2.5389(5) ^a	2.177(2) ^b	$2.519(1)^{a}$	_c	$2.172(2)^{b}$
Mo-C _{Carbene}	2.227(2)	2.222(2)	2.221(4)	2.244(3)	2.249(3)

a X = Cl.

^b $X = CH_3CN$.

^c Not available.

mine the effect of the ImPyMes ligand on the catalytic activity of these Mo NHC complexes. *Cis*-cyclooctene, 1-octene, *cis*-stilbene, and *trans*- β -methylstyrene were employed as olefins under various reaction conditions, varying temperature, substrate:oxidant ratio, solvent, and pre-catalyst loading. In all catalytic experiments, TBHP (5.5 M in *n*-decane) was used as an oxidant for the sake of comparison with known Mo(II) catalytic systems. Control experiments without catalyst yielded no epoxide. In all catalytic reactions, no significant formation of byproducts was observed; thus conversion of substrate equals yield of epoxide. Every catalysis was performed three times. The single data points are averaged values of these three independent measurements.

To determine the optimum reaction conditions regarding temperature, substrate:oxidant ratio, solvent, and pre-catalyst concentration, several experiments were conducted using *cis*-cyclooctene as a model substrate. The kinetic profiles were monitored by GC and plotted in time-conversion graphs; activities and turnover frequencies (TOFs) were determined at the steepest slope after 5 min and/or 15 (30) min. The applied pre-catalysts **1** and **2** were oxidized to their catalytically active species using TBHP. Since the exact catalyst concentration cannot be determined due to the *in situ* formation, all TOFs are referenced to the pre-catalyst concentration.

Epoxidation at room temperature with 0.1 mol% pre-catalyst loading gave an induction period (Fig. 4). Oxidative decarbonylation of the pre-catalyst is indicated by gas evolution and a rapid color change of the catalyst mixture from pink (1) or red (2) to colorless. At room temperature, oxidative decarbonylation occurs after 25 min for 1 and after 12 min for 2. At 55 °C, oxidative decarbonylation was observed within the first 5 min, after 4 min for 1 and after 1 min for 2. In general, complex 2 was found to be more active than 1 in epoxidation catalysis of *cis*-cyclooctene both at room temperature and at 55 °C. This is in line with its faster activation *via* oxidative decarbonylation as illustrated by the



Fig. 4. Kinetic profile of *cis*-cyclooctene epoxidation with pre-catalysts **1** and **2** (0.1 mol%) in CHCl₃ at room temperature and 55 °C using TBHP (pre-catalyst:substrate:oxidant = 1:1000:2000).

exceptionally long Mo–CO bond lengths in **2** and may be attributed to its higher Lewis acidity as indicated by IR vibrational frequencies of CO absorption bands and DFT investigation (see above).

In addition, epoxidation of cis-cyclooctene with 0.1 mol% of precatalyst 1 was conducted in chloroform at 55 °C using different substrate:oxidant ratios (see Supporting Info Fig. S1). In agreement with previously published results, catalysis using a cis-cyclooctene:TBHP ratio 1:2 outperforms catalysis using a ratio of 1:1. To circumvent the induction period observed at room temperature and for sake of comparison with other epoxidation catalysts in literature, all subsequent experiments were conducted at 55 °C and with a substrate:TBHP ratio of 1:2. In order to identify the best solvent for olefin epoxidation with catalysts of this type, a variety of solvents were screened at 55 °C with 1 (0.1 mol%) (Table 3). Due to their coordinating character, epoxidation in polar solvents such as methanol. THF. and acetonitrile results in lower catalytic activities compared to chlorinated and non-polar solvents. A coordinating solvent can compete with the oxidant TBHP for coordination to molybdenum, thus lowering catalytic activity [14]. Benzotrifluoride (BTF) is in some cases a useful alternative for chlorinated solvents (e.g. CHCl₃), because it is a non-coordinating and environmentally benign solvent [79-82]. However, *cis*-cyclooctene conversion achieved in BTF here is guite low and compares to the conversions in coordinating solvents. Epoxidation of cis-cyclooctene with **1** in RTIL $[C_8 mim]NTf_2$ ($C_8 mim = 1$ -methyl-3-octylimidazolium, $NTf_2 = bis(trifluoromethanesulfonyl)-imide)$ is substantially slower compared to homogeneous one-phase catalysis; this may be attributed to mass transfer limitations of the biphasic system [83]. The best catalyst performance is observed in toluene, dodecane, chloroform, and without solvent (neat). Thus, further experiments were conducted in chloroform or neat for comparison purposes with previously published results.

Complex **1** is a prototype for studying the effect of imidazo[1,5-a]pyridine-3-ylidene type ligands on the catalytic activities of NHC molybdenum(II) systems toward olefin epoxidation. It is reasonable to assume that optimum reaction conditions for **1** will be appropriate for a catalytic application of **2**.

To determine the pre-catalyst concentration yielding the highest conversion and TOF, catalysis was carried out using different pre-catalyst concentrations at 55 °C both in chloroform and neat. The kinetic profiles for **1** are shown in Figs. 5 and S2 (Supporting Information), and the resulting TOFs and conversions after 24 h are given in Table 4. Even at low catalyst loadings (0.005 mol%), pre-catalyst **1** exhibits remarkably high TOFs and high conversion rates of 97% in chloroform and 87% neat. The fact that the induction period is prolonged at lower pre-catalyst loadings is noteworthy (Fig. 5: 5 min at 0.01 mol% and 15 min at 0.005 mol%, both in CHCl₃). Since the same amount of solvent (5 mL) was used for all pre-catalyst concentrations, this might be ascribed to an increased dilution resulting in a decreased reaction rate of the activation

Table 3Conversions of *cis*-cyclooctene with 1 (0.1 mol%) using TBHP (5.5 M in *n*-decane) asoxidant at 55 °C in different solvents (pre-catalyst:substrate:oxidant = 1:1000:2000).

Solvent	Conversion (%) after	
	4 h	24 h
MeOH	45	75
CH₃CN	21	45
Benzotrifluoride	29	50
THF	31	78
CHCl ₃	100	100
Toluene	100	100
Dodecane	100	100
[C ₈ mim]NTf ₂	75	97
Neat/n-decane	100	100



Fig. 5. Kinetic profile of *cis*-cyclooctene epoxidation with different concentrations of pre-catalyst **1** in CHCl₃ and neat at 55 °C using TBHP (substrate:oxidant = 1:2).

reaction. This corresponds well to the observation in neat reaction mixtures, where the induction period is still present, but diminishes significantly. A higher catalyst concentration, i.e. higher number of catalyst molecules per unit volume, will increase the rate of the induction reaction, since more reactive encounters can take place [84]. The same concept applies to the increased TBHP concentration when the reaction is performed neat. Another noteworthy aspect is that the reactions with a pre-catalyst concentration of 0.1 and 0.05 mol% perform with higher reaction rates in the absence of solvent (neat), and full conversion was obtained after 5 min. In contrast, the reactions with 0.01 and 0.005 mol% pre-catalyst loads are slower without solvent. This may be reasoned by a slower formation of the catalytic active species and by catalyst inhibition due to competitive coordination of the byproduct tertbutanol [85]. In neat reaction mixtures, the continuous formation of *tert*-butanol results in a polar reaction medium. This is analogous to solvent coordination to the metal center as described above [14].

In further experiments, a pre-catalyst concentration of 0.1 mol% **1** in chloroform was chosen, since these conditions yield the highest TOF $(11,100 h^{-1})$ after 5 min with quantitative conversion after 30 min. However, pre-catalyst loadings of 0.01 and 0.005 mol% perform extraordinarily well, yielding almost 100% conversion after 24 h and TOFs up to 40,900 h⁻¹.

In a separate series of experiments, the optimum pre-catalyst concentration of **2** was determined by several catalytic runs in chloroform at 55 °C. The kinetic profile of epoxidation reactions is depicted in Fig. 6 and the obtained data are given in Table 5. All four reactions, performed with different pre-catalyst loadings, surpass the activities observed for **1**. TOFs between 11,800 and 53,100 h⁻¹ and conversions of 100% after 30 min (0.1 mol% and 0.05 mol%) or 24 h (0.01 mol% and 0.005 mol%), respectively, were obtained. No induction periods were observed for epoxidation catalysis with **2**.

Complex **1** provides TOFs up to 40,900 h⁻¹ at a pre-catalyst concentration of 0.005 mol%, which is the highest reported TOF of Mo NHC complexes so far; it exhibits TOFs even higher than the structurally related complexes of the type $[CpMo(CO)_3X]$ (X = alkyl, halide) [5,6,15]. As far as we are aware, only *ansa*-cyclopentadienyl molybdenum complexes in RTIL [18] exceed the activity of the reported pre-catalyst **1** in terms of TOF. Catalytic investigations of **2** show even higher activities with TOFs up to 53,100 h⁻¹ at a pre-catalyst loading of 0.01 mol%. These constitute the highest TOF of cyclopentadienyl molybdenum pre-catalysts reported to date.

In order to determine the limitations of the catalytic system, we employed additional substrates such as 1-octene, *cis*-stilbene, and *trans-\beta*-methylstyrene in olefin epoxidation catalysis using

Table 4

Catalytic activities in terms of TOFs and conversions of *cis*-cyclooctene with different concentrations of **1** using TBHP (5.5 M in *n*-decane) as oxidant at 55 °C in CHCl₃ or neat (substrate:oxidant = 1:2). Time-conversion plots for conditions not displayed in Fig. 5 are assembled in Fig. S2 (Supporting Information).

Solvent	Pre-catalyst loading (mol%)	TOF_{5min} (h^{-1})	$TOF_{max}(h^{-1})$	Conv. ^a (%)
CHCl ₃	1	1200	1200	100
	0.1	11,100	11,100	100
	0.05	6900	6900	100
	0.01	2000	18,500	99
	0.005	1900	40,900	97
Neat/n-decane	0.1	12,000	12,000	100
	0.05	23,800	23,800	100
	0.01	4700	25,800	93
	0.005	2300	30,000	87

^a Conversion after 24 h.



Fig. 6. Kinetic profile of *cis*-cyclooctene epoxidation with different concentrations of pre-catalyst **2** in CHCl₃ at 55 °C using TBHP (substrate:oxidant = 1:2).

Table 5

Catalytic activities in terms of TOFs and conversions of *cis*-cyclooctene epoxidation after 24 h with different concentrations of **2** using TBHP as oxidant at 55 °C in CHCl₃ (substrate:oxidant = 1:2).

Pre-catalyst loading (mol%)	$TOF_{5min}(h^{-1})$	Conversion after 24 h (%)
0.1	11,800	100
0.05	22,300	100
0.01	53,100	99
0.005	45,800	99
	,	

Table 6

Conversions of different substrates after epoxidation with **1** (0.1 mol%) using TBHP as oxidant at 55 °C in $CDCl_3$ (pre-catalyst:substrate:oxidant = 1:1000:2000).

Substrate	Conversion (%) after		Selectivity (%)
	4 h	24 h	
1-Octene	66	75	100
<i>cis</i> -Stilbene	82	100	100
trans-β-Methylstyrene	99	100	100

pre-catalyst **1** under optimized reaction conditions (see above). Quite remarkable conversions of the aforementioned olefins were obtained with a pre-catalyst loading of 0.1 mol% **1** in CDCl₃ at 55 °C (Table 6). Conversions were determined by ¹H NMR spectroscopy, using 1,2-dichloroethane as the internal standard. Identical results for *cis*-cyclooctene conversions were obtained by monitoring either by GC or by ¹H NMR; thus ¹H NMR is considered a viable method for monitoring conversion. All catalytic reactions proceeded without significant formation of byproducts. Since 1-octene is electronically disfavored as substrate for olefin epoxidation with cyclopentadienyl molybdenum carbonyl catalysts using TBHP as

oxidant due to the terminal position of the double bond [2,3], lower conversion was observed.

The catalytic epoxidation of *cis*-cyclooctene was also carried out in a RTIL. For comparison with known NHC molybdenum systems [22], $[C_8mim]NTf_2$ was chosen as RTIL. Using 0.1 mol% **1** at 55 °C, epoxidation proceeds with 97% conversion after 24 h in the biphasic catalytic system. The kinetic profile of *cis*-cyclooctene epoxidation with pre-catalyst **1** in RTIL is shown in Fig. S3 (Supporting Information). However, the reaction is substantially slowed down with a TOF of 2400 h⁻¹, probably due to phase transfer limitations. The upper phase consists of substrate and *n*-decane, while the lower phase contains RTIL plus catalyst; TBHP is partially soluble in both phases. Taking into account the advantages of RTILs such as low volatility, thermal stability, high polarity, simple catalyst recycling, and product separation [18,86], the prolonged reaction times are acceptable for potential applications, especially considering the obtained high conversion.

To investigate the stability and reusability of pre-catalyst **1** and accordingly of the active species, recycling experiments were performed with pre-catalyst loading of 0.1 mol% in $[C_8mim]NTf_2$ at 55 °C. The catalyst was recycled for ten catalytic runs; quantitative conversion was observed for each run after 24 h (see Supporting Info Table S1). Deviations lie within the experimental error.

In contrast to triazolylidene-based molybdenum complex **A** [22], complex **1** shows excellent performance in recycling experiments. Therefore, the catalysis in $[C_8mim]NTf_2$ indicates higher stability of **1** compared to molybdenum NHC pre-catalysts as known in literature. Further catalytic experiments and stability studies of these complexes under catalytic conditions are currently the subject of investigation in our laboratories.

4. Conclusion

The synthesis of two novel cyclopentadienyl 2-mesitylimidazo[1,5-a]pyridine-3-ylidene molybdenum complexes is reported. Synthesis proceeds in excellent yields via the silver carbene transmetallation route for 1 and subsequent substitution reaction for 2. Compounds 1 and 2 were characterized by NMR, IR, elemental analysis, FAB-MS, and by single-crystal XRD. 1 and 2 were applied as pre-catalysts in catalytic epoxidation of aliphatic and aromatic olefins under various reaction conditions and with TBHP as oxidant. Both compounds surpass previously reported molvbdenum epoxidation pre-catalysts in catalytic activity. Even at low pre-catalyst concentrations (0.005 mol%), full conversion of cis-cyclooctene was obtained after 24 h, and high TOFs up to 40,900 h^{-1} (**1**) and up to 53,100 h^{-1} (**2**) are observed. In addition, more challenging substrates such as 1-octene, cis-stilbene, and *trans*- β -methylstyrene were applied in olefin epoxidation with **1**, resulting in good yields and high selectivity. Pre-catalyst 1 was successfully applied in recycling experiments in RTIL [C₈mim]NTf₂ and can be reused for at least 10 subsequent runs without loss of

activity, indicating high stability of the catalyst. The outstanding catalytic activities of pre-catalysts 1 and 2 compared to closelyrelated catalytic systems have been attributed to steric and electronic effects such as the strong σ -donating character of imidazo[1,5-a]pyridine-3-ylidenes and the high Lewis acidity of the metal center. The higher Lewis acidity of 2 compared to 1 may account for the improved catalytic performance of **2**. The sterically demanding imidazo-[1,5-a]pyridine-3-ylidenes feature properties that appear to be beneficial in epoxidation catalysis. Further studies examining the stability and active species of these systems are currently the subject of investigation in our laboratories.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2014.08.013. These data include MOL files and InChiKeys of the most important compounds described in this article.

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