EurJIC
European Journal of Inorganic Chemistry

Chemistry Europe
European Chemical Societies Publishing

Accepted Article

Title: Molybdenum (VI) Complexes Containing Pyridylimine Ligands: Effect of the Imine Nitrogen Substituent in the Epoxidation Reaction

Authors: Daniel Martínez-Martínez, Mayra León Santiago, Rubén A. Toscano, and Manuel Jose Amezquita Valencia

To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.202000790

Link to VoR: https://doi.org/10.1002/ejic.202000790

WILEY-VCH

WILEY-VCH

FULL PAPER

Molybdenum (VI) Complexes Containing Pyridylimine Ligands: Effect of the Imine Nitrogen Substituent in the Epoxidation Reaction

Daniel Martínez-Martínez,[a] M. León Santiago,[a] Rubén A. Toscano,[a] and Manuel Amézquita-Valencia*[a]

[a] Daniel Martínez Martínez, M. Sc. Mayra León Santiago, Dr. Rubén A. Toscano, Dr. Manuel Amézquita Valencia
Department of inorganic Chemistry
Universidad Nacional Autónoma de México, Instituto de Química
Ciudad Universitaria, Ciudad de México, 04510, México
E-mail: manuel.amezquita@iquimica.unam.mx
https://iquimica.unam.mx/dr-manuel-jose-amezquita-valencia

Supporting information for this article is given via a link at the end of the document.

Abstract: A series of pyridylimine ligands with variations of the substituent at the imine nitrogen were synthesized and coordinated to the [$MoCl_2O_2$] core. The novel molecular structures of the complexes were fully characterized by ^1H and ^{13}C NMR, FT-IR, ESI, EA, and X-ray crystallography, and their catalytic activity was studied for the epoxidation of alkenes using *tert*-butyl hydroperoxide (TBHP) as the oxidant. The new complexes showed excellent catalytic activity and fine selectivity in the epoxidation reaction compared with similar homogeneous molybdenum complexes. The results demonstrated that there is a significant change in the catalytic performance, depending on the alkyl arm on the structure of the pyridilimine ligand. The catalytic results indicated that complex [$MoCl_2O_2$(**L**)] (**L:** N-(2-Pyridinylmethylene)-1-*tert*-butylimine) **C_5** is the best catalytic precursor in the epoxidation of cyclohexene (TON: 92920 and TOF: 30974 h^{-1}).

Introduction

Epoxides are important compounds that participate in useful organic syntheses and their reactivity permits the preparation of a diverse array of intermediates that play a crucial role in fine chemistry.[1,2] In general, different heterogeneous and homogeneous catalysts have been used in the epoxidation reaction, but homogeneous systems are the most widely applied industrial process for oxidation of olefins.[2,3] As expected, various metal complexes have been employed in oxygen atom transfer reactions,[4-9] however, the molybdenum complexes have always been an alternative for epoxidation of olefins, on account of their high activity.[10] It is well known that the use of nitrogen-containing ligands leads to an increase in both catalytic activity and the selectivity in these types of processes. [11,12] These improvements are attributed to the possibility of modifying the steric and electronic properties on the ligand.

Considerable efforts have been devoted to developing catalysts with high catalytic performance containing bidentate nitrogen donor ligands. In this context, Kühn´s group synthesized a series of molybdenum complexes of the type [MoX_2O_2(N-N)] (X: Cl, Br) using various bidentate N-ligands, where 1,4-diaza-1,3-butadiene-bearing aryl groups on the nitrogen atoms showed good activity in the epoxidation of *cis*-cyclooctene with *tert*-butyl hydroperoxide (TBHP) as the oxidant.[13] Gonçalves et al. reported an interesting modification replacing X from Cl to Me, with the new complex presenting similar results in comparison to its predecessor [turnover frequency (TOF), 174 h^{-1}].[14-15] In the same way, the analogous $MoCl_2O_2$ complexes using bipyridine ligands were synthesized, giving promising results in the epoxidation of olefins (TOF around 1150 h^{-1}).[16] The authors found that catalytic activity was influenced by the donor capability of the substituent on the bipyridine ring. The solubility of the [$MoCl_2O_2$(N-N)] complexes in an organic solvent is an important factor to consider, which may be responsible in some cases of poor catalytic activity. Hence, replacing the solvent could increase the reactivity. For example, a Mo complex with 5,5´-bis-methoxycarbonyl-2-2´-bipyridine ligand showed a high activity in the epoxidation of *cis*-cyclooctene (TOF 8000 h^{-1}) in ionic liquids; this excellent result was attributed to the Mo complex's high solubility.[17]

Pyrazolylpyridines are another class of diimine ligands that have been used to generated coordination compounds of Mo(VI). The catalytic behaviors of these complexes resulted in the production of the desired epoxide in excellent selectivity with moderate TOF (347 h^{-1}).[18-19] In seeking to broaden the utility of this class of catalysts, the use of pyrazole monohydrate as the monodentate ligand in the Mo-catalyzed epoxidation of cyclic olefins led to a yield of 90% with a good TOF of 1800 h^{-1} after 5 min.[20] An alternative class of ligand that can be used in the epoxidation reaction are the pyridylimines, which have presented similar properties to bipyridines (N-N donor set), yet are much easier to prepare and modify. Despite these advantages, there are only a handful of reports describing the Mo-catalyzed epoxidation employing pyridylimine ligands. In this regard, Gomes et al. reported the synthesis of a complex [$Mo(CO)_4$(pyim)] (pyim: *N*-(*n*-propyl)-2-pyridylmethanimine) and its subsequent immobilization on MCM-41.[21] Later, the same group demonstrated the utility of the ligand previously synthesized in the preparation of [$MoCl_2O_2$(pyim)]. The new complex showed a relevant catalytic activity (TOF of 1855 h^{-1}) in the epoxidation of various olefins.[22] Recently, a series of allyl molybdenum complexes supported by these kinds of ligands were studied. However, the presence of different substituents (H, Me, Ph) at the imine-carbon did not significantly change the activity.[23] Despite the outcome, we consider that the selection of the appropriate substituent present at the nitrogen of the imine moiety could change the catalytic activity.

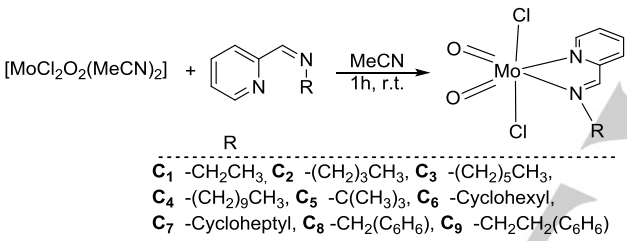
Herein, we aimed to expand the range of molybdenum complexes of the type [$MoCl_2O_2$(pyridylimine)] used in the epoxidation of olefins. For purposes of comparison, we studied

the influence of the substituent on the imine nitrogen, considering both their size and electron-donating properties.

Results and Discussion

Synthesis and Characterizations of Molybdenum Complexes

Pyridylimine ligands (**L_1-L_9**) were obtained in quantitative yields by the condensation reaction between 2-pyridinecarboxadehyde and the corresponding amine and the products obtained were used without purification. Coordination tests were performed using $MoCl_2O_2(MeCN)_2$ in acetonitrile solution at room temperature, affording the expected monomeric coordination entity of formula [$MoCl_2O_2$(**L**)] (Scheme 1). The different complexes were obtained in good yields and purified by washes with diethyl ether, and finally by co-precipitation using methylene chloride and hexane. The new complexes **C_1-C_9** showed good solubility in methylene chloride, acetone, and dimethyl sulfoxide. These complexes were partially soluble in acetonitrile and methanol, but poor solubility in chloroform and insoluble in diethyl ether and hexanes.



Scheme 1. Molybdenum complexes synthesized (**C_1-C_9**)

The complexes were characterized by FTIR, elemental analysis, ESI, ^{1}H, ^{13}C NMR, and X-ray crystallography. The FTIR spectra of all nine complexes (See experimental section, Table S1) are in agreement with the coordination of the pyridylimine ligand to the $MoCl_2O_2$ core through the nitrogen atoms.[21-23] The $\nu_{C=N}$ stretching frequencies are observed around 1647 cm^{-1} and 1597 cm^{-1}. The strong band at 903 cm^{-1} (average) and medium band at 937 (average) were assigned to the asymmetric and symmetric stretching vibrations, respectively, of the *cis*-[MoO_2] unit.[22]

The ^{1}H and ^{13}C NMR spectra of the different complexes (**C_1-C_9**) revealed a variation between the chemical shifts of the free ligand and the bound ligand, with the proton signal of all complexes being shifted to lower field after complexation. In all cases, there was a notable rearrangement of hydrogens near the imine and pyridine nitrogens. Furthermore, one set of resonances for the iminopyridine ligand was observed, which corresponded to a mononuclear complex.[21-22] Elemental analyses of newly made complexes were consistent with the proposed structures shown in Scheme 1.

The structures of some molybdenum compounds were unambiguously determined with X-ray crystallographic analysis. Crystals of complexes **C_1**, **C_6**, **C_8**, and **C_9** suitable for X-ray diffraction were obtained by slow diffusion of hexane or diethyl ether into their concentrated CH_2Cl_2 solution. Molecular structures are shown in Figures 1 and 2, with data collection and general parameters summarized in Table 1.[24]

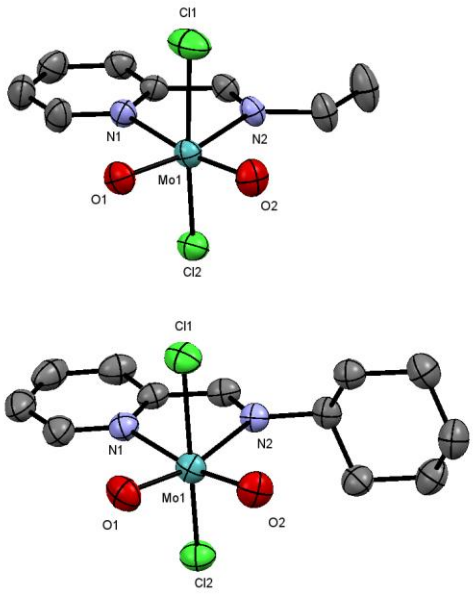


Figure 1. Crystal structures of complexes **C_1** and **C_6**, with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

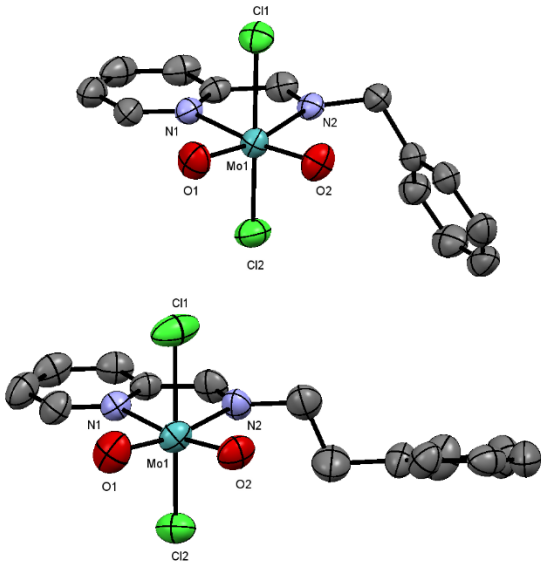


Figure 2. Crystal structures of complexes **C_8** and **C_9**, with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

The complexes (**C_1**, **C_6**, **C_8** and **C_9**) are isostructural and crystallized with a distorted octahedral coordination environment,[25] which can be explained mainly by *cis*-oxo-*trans*-Cl-*cis*-N-N rearrangement.[26] Thus, the metal center is bonded to two terminal *cis*-oxo groups [Mo=O, 1.6865(19)-1.6940(17) **C_1**,

1.6830(2)-16910(2) **C_6**, 1.6831(2)-1.686(2), **C_8** and 1.6830(6)-1.6880(6), **C_9**, Å]. The N-N-chelated moiety is positioned *trans*- to the oxygen atom [2.3483-2.3256 (Average), Å] and two axially coordinated Cl atoms [2.3870(7)-2.3369(7) **C_1**, 2.3646-2.3673 **C_6**, 2.3603-2.3714(9) **C_8**, 2.3680(2)-2.3380(2) **C_9**, Å].

Table 1. Crystallographic data for compounds **C_1**, **C_6**, **C_8** and **C_9**.

	C_1	**C_6**	**C_8**	**C_9**
Empirical formula	$C_8H_{10}Cl_2MoN_2O_2$	$C_{12}H_{16}Cl_2MoN_2O_2$	$C_{13}H_{12}Cl_2MoN_2O_2$	$C_{14}H_{14}Cl_2MoN_2O_2$
Formula weight	333.02	387.11	395.09	409.11
Temperature	298	303(2)	304(2)	298
λ (Å)	0.71073	0.71073	0.71073	0.7173
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	P-1	$P2_1/c$	P b c a	P 21
a (Å)	8.0504(6)	13.350(4)	11.2803(4)	8.4616 (14)
b (Å)	8.7834(7)	6.8217(13)	12.8812(4)	8.7904(13)
c (Å)	8.9280(7)	17.265(4)	20.6749(6)	11.629(2)
α (°)	83.953(1)	90	90	90
β (°)	84.288(1)	108.048(6)	90	110.789(5)
γ (°)	74.143(1)	90	90	90
V ($Å^3$)	602.24(8)	1495.0(6)	3004.14(17)	808.7(2)
Z	2	4	8	2
D_{cal} (mg/cm3)	1.837	1.720	1.747	1.680
μ (mm^{-1})	1.514	1.233	1.230	1.145
Reflections collected	11362	32913	56057	4683
Independent reflections	3484	4188	4213	4683
R_{int}	0.0369	0.0571	0.0550	0.0421
R1 [I>2σ(I)]	0.0312	0.0408	0.0380	0.0646
wR_2[all data]	0.0661	0.0709	0.0840	0.0796
Goodness-of-fit	1.026	1.054	1.094	1.203

For the complexes **C_1**, **C_8** and **C_9**, the Mo-$N_{pyridine}$ bond lengths were longer than those of Mo-N_{imine} due to the different basicity for the pyridine with respect to the imine. In the **C_6** complex, Mo-N_{imine} bond length was larger, which is associated with a steric effect. The N-Mo-N angle in the complexes were approximately 69.9° (Average). The molecular structure of complex **C_1** had both the pyridine fragment and the alkyl moiety in the same plane while in the case of **C_6** these groups were parallel (89.87°). In contrast, the alkyl moiety from the **C_8** and **C_9** complexes were hinged and the angles between the planes were 66.1° and 18.9°, respectively. These different angles relate to the flexibility of the substituent on the imine-nitrogen.

Catalytic Activities of Molybdenum Complexes (C_1-C_9) in Epoxidation of Olefins

To optimize the reaction conditions, we started our catalytic study using the **C_4**, **C_6** and **C_8** complexes in combination with cyclohexene as a model substrate and an oxidant. Initially, different oxygen sources were tested. For this purpose, the reactions were performed using 3.0 mol% of catalyst, 1.5 equivalent of oxidant [H_2O_2 (30% in water), *t*-BuOOH (80% in water) and *t*-BuOOH (5.5 M in decane)] in methylene chloride as a solvent, at reflux temperature for 15 h.

Although the epoxidation reactions in all cases were effective, our results showed that *t*-BuOOH in decane was the best option, giving 100% of conversion and 96% of selectivity for the epoxide using the **C_8** complex (See supporting information, Table S2). In the case of the oxidants in an aqueous medium, the selectivity toward the epoxide was affected severely. We observed that the formations of 2-cyclohexenol and 2-cyclohexenone were favored. Continuing with the optimization of the reaction, the combinations of different solvents, oxidants, and temperatures were evaluated by using the **C8** complex and cyclohexene as a substrate; the results are displayed in Table 2.

First, we optimized the solvent and the temperature of the reaction. The results showed that the highest conversions were obtained at 40 °C in dichloromethane, with excellent selectivities (Tabla 2, entry 1). In contrast, Employing other solvents such as acetonitrile, tetrahydrofuran, chloroform, or ethanol led to poor conversions (entries 2-4). Similar results were observed in the cyclooctene epoxidation reaction, where the complexes containing the *cis*-[MoO_2] core were inactive under these conditions.[27-30] These conversions could be associated with the tendencies of the solvents to coordinate strongly with Mo (VI) ion, competing directly with the oxidant. In contrast, noncoordinating solvents such as dichloromethane and dichloroethane facilitated the epoxidation reaction (Entries 1 and 5).[31] The increase in the temperature to 80 °C did not improve substantially the catalytic activity (Entries 6-7). The use of a chlorinated solvent afforded excellent conversion with good selectivity to the corresponding epoxide (Entry 8). Similar results have been reported in the literature, where chlorinated solvents presented an excellent performance in the epoxidation of olefins.[32-33]

Table 2. Screening of reaction conditions.[a]

Entry	Oxidant	Solvent	Conversion (%)[b]	Selectivity (%)[b]
1	TBHP	DCM	100	96
2	TBHP	ACN	20	100
3	TBHP	THF	45	99
4	TBHP	EtOH	18	99
5	TBHP	DCE	83	98
6[c]	TBHP	ACN	28	99
7[c]	TBHP	THF	78	97
8[c]	TBHP	DCE	96	96
9	$H_2O_{2(aq)}$	ACN	97	17
10	$H_2O_{2(aq)}$	EtOH	100	18
11	$H_2O_{2(aq)}$	DCM	100	16
12	$TBHP_{(aq)}$	ACN	98	24
13	$TBHP_{(aq)}$	EtOH	96	15
14	$TBHP_{(aq)}$	DCM	100	14
15[c]	$TBHP_{(aq)}$	ACN	100	10
16[c]	$H_2O_{2(aq)}$	EtOH	98	11
17[c]	$TBHP_{(aq)}$	DCM	99	14
18[c]	$H_2O_{2(aq)}$	DCM	100	10
19[d]	TBHP	DCM	97	90
20[e]	TBHP	DCM	100	94

[a] Reaction conditions: Cyclohexene (2.0 mmol), TBHP (1.5 equivalent, 5.5 M, decane), 40 °C, 15 h, 5 mL of solvent. [b] Determined by GC-MS. [c] Temperature of reaction 80 °C. [d] 1.0 equivalent of TBHP (5.5 M, decane) was used. [e] 2.0 equivalent of TBHP (5.5 M, decane) was used.

The effect of different oxidants was evaluated in the epoxidation of cyclohexene at 40 °C (Entries 9-14). These results indicate that the presence of water in the oxidant had a negative effect on the reaction. The high conversion and low selectivity toward epoxide can be explained by the formation of 1,2-diol, through the epoxide ring-opening process in the presence of water. Also, we found that elevating the temperature of the reaction caused an increase in the ring-opening reaction and the over oxidation of the substrate. (Entries 15-18).[34] Finally, the influence of the amounts of oxidant was evaluated. Using 1.0 equivalent of TBHP the conversion was slightly affected (Entry 19). With 2.0 equivalent of TBHP, no change in the catalytic behavior was observed (Entry 20). For subsequent epoxidation reactions, we chose 1.5 equivalent of TBHP, 40 °C in dichloromethane as a solvent.

Next, the reaction time was optimized (Figure 3), as exemplified by the kinetic curve obtained for the complex **C_8**. First, 3.0 mol % of catalyst was used and the results indicated 34% of conversion in the first hour; after 3 hours the conversion tended to converge to 100%, with 1,2-epoxycyclohexane being the only reaction product observed.

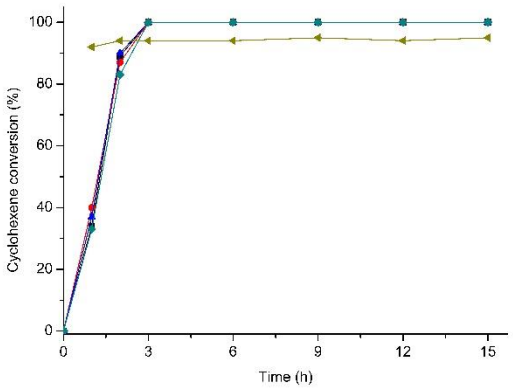


Figure 3. Time-dependent conversion of cyclohexene epoxidation at 40 °C using TBHP and different concentrations of complex **C_8** in 5 mL of CH_2Cl_2. 3.0 mol% (■, black), 1.0 mol% (●, red), 0.1 mol% (▲, blue) and 0.01 mol% (♦, light green), average of selectivity (◄, green). Conversion and selectivity determined by GC-MS.

Continuing with the optimization of the reaction, the catalyst loading was changed over the range of 1.0% to 0.01%. The variation of the amount of catalyst did not have a remarkable effect on the performance of the reaction (Figure 3, 1.0 mol% (●, red), 0.1 mol% (▲, blue) and 0.01 mol% (♦, light green). Even when the reaction was carried out at 0.01 mol% of catalyst, high conversion (98%) and excellent selectivity (95%) was obtained. In general, epoxidation of cyclohexene was almost the same in the different catalyst loadings, showing an overall conversion between 36% to 42% after the first hour of reaction. Then, the conversion increased significantly, being almost quantitative in approximately 3 h. This indicates that the catalyst has a notable catalytic activity and a high selectivity at low concentration.

With the optimal reaction conditions in hand, we compared the catalytic activity of the other complexes synthesized. In

general, the efficiency of complexes **C_1-C_9** for the epoxidation of cyclohexene and *n*-hexene was satisfactory, affording the corresponding epoxides in good conversion with excellent selectivity (72%-100%) within 3 hours of reaction (Table 3).

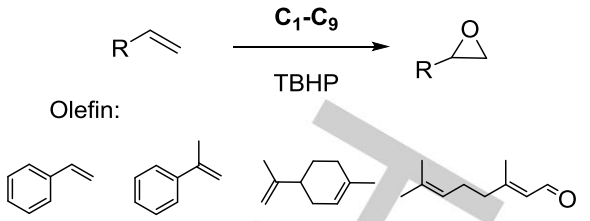
All examined complexes displayed quite high catalytic activity (turnover number (TON) up to 9752 and turnover frequency (TOF) up to 3208 h^{-1}, **C_3**). It is worth noting that all catalysts led epoxidation of the alkene irrespective of the substituent on the imine-nitrogen, although there were subtle differences between catalysts. Using the complex **C_5** for both alkenes, the desired product was obtained in excellent conversion (Entry 5, TON over 9000 and TOF over 3000 for both alkenes). Similar results employing the **C_6**, **C_7**, and **C_9** complexes were found (Entries 6 and 7). Interestingly, when using the complexes **C_1-C_4** and **C_8-C_9** with an extended methylene chain on the imine, the epoxidation performance of the linear olefin was affected by chain length (Entries 1-4, 8 and 9). Hence, it is possible that the degree of the selectivity in the reaction is dependent on the bulkiness of the ligand used. The general tendency showed better activity with *tert*-butyl, cyclohexyl, and cycloheptyl groups present on the imine-nitrogen. This behavior could be associated with the ability of the ligand to donate electrons, affording the formation of more reactive Mo species.[35]

Table 3. Epoxidation of cyclohexene and *n*-hexene using **C_1-C_9**.[a]

Entry	Complex	Substrate	Conv./Sel.(%)[b]	TON[c]	TOF (h^{-1})[d]
1	**C_1**	cyclohexene	100/96	9625	3208
		1-hexene	78/99	7814	2605
2	**C_2**	cyclohexene	100/92	9244	3081
		1-hexene	81/72	5846	1949
3	**C_3**	cyclohexene	100/98	9752	3251
		1-hexene	84/100	8440	2813
4	**C_4**	cyclohexene	100/83	8291	2764
		1-hexene	77/81	6216	2072
5	**C_5**	cyclohexene	100/93	9280	3093
		1-hexene	92/100	9148	3049
6	**C_6**	cyclohexene	98/89	8751	2917
		1-hexene	88/100	8800	2933
7	**C_7**	cyclohexene	99/93	9225	3075
		1-hexene	89/100	8900	2967
8	**C_8**	cyclohexene	98/95	8520	2840
		1-hexene	51/100	5051	1684
9	**C_9**	cyclohexene	100/96	9568	3189
		1-hexene	82/100	8161	2720

[a] Conditions: Substrate (2.0 mmol), TBHP (1.5 equivalent, 5.5 M, decane), catalyst (0.01 mol%, **C_1-C_9**), 40 °C, CH_2Cl_2 (5 mL), 3 h. [b] Conversion and selectivity were determined by GC-MS. [c] TON calculated per molecules of catalyst. [d] TOF after of 3 hours.

The catalytic activity of the different molybdenum complexes was next investigated in the epoxidation of representative olefins such as styrene, α-methylstyrene (Me-styrene), *S*-limonene, and citral (Scheme 2).



Scheme 2. Epoxidation of different olefins using **C_1-C_9**.

As shown in the Table 4, the epoxidation of styrene and α-methyl styrene occurred to a lesser degree with respect to aliphatic olefins, and the selectivity was affected by the exclusive formation of benzaldehyde, acetophenone, and α-methylphenylacetaldehyde, respectively. As reported in the literature,[18,36] the complexes with the structure $MoCl_2O_2$(N-N) have presented low reactivity and selectivity with these kinds of alkenes. It is important to note that the complexes **C_1**, **C_5**, and **C_9** were more active, confirming the influence of the substituent. Interestingly, in the case of more sterically hindered olefins, our results point once again to the strong influence of the substituent at the imine nitrogen on the catalytic activity. The family of complexes **C_1** to **C_4** showed a low conversion, but a good selectivity toward the desired epoxide. The complex **C_5** which contains the *tert*-butyl group at the nitrogen of the imine moiety was the best catalyst of the series, affording 62% of conversion and 88% of selectivity in the epoxidation of limonene, with *p*-mentha-2,8-dien-1-ol as a byproduct. However, the performance in the epoxidation of citral was a critical result. Complexes containing ligands with substituents that were sterically more-demanding such as **C_6** and **C_7** showed a minor catalytic activity with respect to **C_5**. Meanwhile, the complex **C_8** was more active than **C_9** in the epoxidation of limonene, but **C_9** was better in the transformation of citral.

Table 4. Epoxidation of aromatic and aliphatic olefins using **C_1-C_9**.[a]

Complex	Substrate	Conv./Sel.(%)[b]	TON[c]	TOF (h^{-1})[d]
	styrene	11/76	803	268
C_1	Me-styrene	32/85	2700	900
	limonene	53/89	4703	1568
	citral	21/90	1884	628
	styrene	2/35	64	22
C_2	Me-styrene	8/70	558	186
	limonene	40/90	3625	1208
	citral	19/99	1868	623
	styrene	8/94	748	249
C_3	Me-styrene	14/90	1234	411
	limonene	39/90	3510	1170
	citral	19/99	1885	628
	styrene	8/81	613	204
C_4	Me-styrene	5/54	279	93
	limonene	8/93	721	241
	citral	24/99	2423	808
	Styrene	14/77	1080	360
C_5	Me-styrene	26/83	2193	731
	Limonene	62/88	5495	1832
	citral	26/99	2568	856
	styrene	9/83	774	258
	Me-styrene	29/91	2625	875

C_6	limonene	49/92	4475	1492
	citral	16/99	1586	529
	styrene	8/78	648	216
C_7	Me-styrene	8/69	538	179
	limonene	46/94	4369	1456
	citral	8/99	804	268
	styrene	2/66	155	52
C_8	Me-styrene	5/62	288	96
	limonene	34/99	3392	1131
	citral	6/99	592	197
	styrene	6/70	451	150
C_9	Me-styrene	22/78	1713	571
	limonene	23/86	1965	655
	citral	24/92	2257	752

[a] Same conditions as in table 3 were used. [b] Conversion and selectivity were determined by GC-MS. [c] TON calculated per molecules of catalyst. [d] TOF after of 3 hours.

To demonstrate the importance of the ligand bearing the *tert*-butyl substituent, we examined the complexes **C_5**, **C_6**, and **C_9**, which had similar backbones and presented comparable activity. To improve the reaction, the effect of the catalytic loading was evaluated (Table 5). Our test commenced with cyclohexene under previously optimized conditions using the **C_5** complex (See Table 3). Notably, by decreasing the catalyst loading to 0.001 mol%, we obtained the corresponding epoxide in >99% of conversion and excellent selectivity 93% (TON: 92920 and TOF: 30974 h^{-1}). Applying **C_6** and **C_9** gave the desired product in moderate selectivities of 63% and 58%, respectively. In comparison to previously reported Mo(VI) complexes bearing a nitrogen-chelating ligand, the current system **C_5** exhibited a notable catalytic activity in the reaction of epoxidation under similar conditions.[22,29,37]

Table 5. Effect of the catalyst amount on the epoxidation of cyclohexene using **C_5**, **C_6** and **C_9**.

Complex[a]	Conv./Sel. (%)[b]	TON[c]	TOF[d]
C_5	100/93	92920	30974
C_6	100/63	63472	21157
C_9	100/58	58262	19421

[a] 0.001 mol% of catalyst was used. [b] Conversion and selectivity were determined by GC-MS. [c] TON calculated per molecules of catalyst. [d] TOF after of 3 hours.

It was necessary to increase the catalyst loading and the reaction time to obtain the best outcome with styrene and α-methyl styrene. Using 0.1 mol% of **C_5** with styrene, the best results were obtained at 12 hours of reaction, achieving 60% of yield and 92% of selectivity to obtain the specific epoxide. In the presence of **C_6** and **C_9**, less than 20% of styrene oxide product was obtained. For epoxidation of α-methyl styrene, **C_6** gave the best performance with 61% of conversion and 90% of selectivity. Various attempts to increase the conversion using **C_5** and **C_9** were fruitless. Finally, the epoxidation of limonene was carried out with the three complexes. Notably, the **C_5** complex displayed the best activity. In the presence of this complex, the conversion and selectivity could be improved to 86% and 90% (1,2-epoxylinonen), respectively. For citral, the **C_5** complex displayed the best results once again, but the performance was poor (33% of conversion and 100% of selectivity at 12 hours). The results achieved above demonstrated the superiority of the ligand containing the *tert*-butyl group compared to previously used ligands.

Conclusion

Nine new mononuclear molybdenum complexes containing pyridylimine ligands have been synthesized and structurally characterized. The ligand adopt a bidentate coordination mode to give distorted octahedral molybdenum complexes. The catalytic activities of the Mo (VI) complexes were tested in the epoxidation of aliphatic and aromatic olefins by using *tert*-butyl hydroperoxide as the oxidant. The results demonstrated that the nature of the substituents on the imine-nitrogen have an important influence on the catalytic activity. A long carbon chain on the ligand generated low stability on the complex, impairing the oxidation of the double bond, resulting in lower activity. Epoxidation was favored when bulky substituents such as *tert*-butyl, cyclohexyl, and cycloheptyl were present on the nitrogen of the imine, as was the case for complexes **C_5-C_7**. It is interesting to note that complex **C_5** exhibits the best catalytic activity in the epoxidation reaction. Therefore, the design of new ligands based on these classes of substituents is relevant to insights into the chemistry of these systems.

Experimental Section

Material and reagents

All solvents were dried and distilled under nitrogen prior to use. Molybdenum precursor and other reagents were obtained from Strem Chemical or Aldrich Chemical Co. Column chromatography was undertaken with silica gel (60, 230-400 mesh). 1H NMR and 13C {1H} NMR spectra were measured in $CDCl_3$ on a BRUKER Advance 300 MHz spectrometer. Chemical shifts are reported in ppm with the solvent signal as a reference, and coupling constants (J) are given in Hertz (Hz). Melting points were determined on a Fischer-Johns apparatus and are uncorrected. The infrared spectra were recorded on an Alpha ATR spectrometer from Bruker Optics and analysed with OPUS soft-ware. Elemental analyses were carried out with an Exeter Analytical. X-ray determination was collected on a Bruker SMART APEX CCD area diffractometer by the ω-scan method. The reaction was monitored using a GC-MS Agitent technologies 7890B-5977A-MSD and a HP-5-MS column. The product identifications were performance on the base of commercial mass spectroscopy database (NIST14). Mass spectra were obtained using a JEOL the ACCUTOF JMS-T100LC (DART method) and Bruker Esquire 6000 for ESI.

Synthesis of ligand, L_1[38]

2-Pyridinecarboxaldehyde (0.10 mol) was added in a solution of 10 mL of a 40% aqueous ethylamine solution (0.1 mol) at 0 °C. The reaction was stirred for 1 h, after that time, the mixture was extracted four times with 30 mL of methylene chloride each. Finally, organic layers were combined, dried (Na_2SO_4) and the solvent was removed under reduced pressure, affording the desired product in excellent yield.

Synthesis of ligands, L_2-L_9

A 50 mL bottom flask was loaded with 2-Pyridinecarboxaldehyde (2.1 mmol), corresponding amine (2.1 mmol), and Na_2SO_4, the mixture was dissolved in dry THF (10 mL). The reaction was stirred at room

temperature overnight, then the solution was filtered and the solvent was removed. The oil residue was used without prior purification (Quantitative yield).

N-(2-Pyridinylmethylene)-1-ethanamine (L_1): Yellow oil (98%), $C_8H_{10}N_2$. ^{1}H NMR (300 MHz, $CDCl_3$-d, δ ppm): 8.62–8.52 (d, 1H, H1), 8.33 (s, 1H, H_6), 7.91 (d, J = 7.9 Hz, 1H, H_4), 7.74–7.61 (t, 1H, H_3), 7.30–7.17 (t, 1H, H_2), 3.65 (q, J = 7.2, 1.7 Hz, 2H, H_7), 1.26 (t, J = 7.2 Hz, 3H, H_8). 13C {1H} RMN (75 MHz, CDCl3-d, δ ppm): 161.2 (C_6), 154.5 (C_5), 149.3 (C_1), 136.4 (C_3), 124.5 (C_2), 121.1 (C_4), 55.5 (C_7), 16.0 (C_8). IR (ATR-FTIR, cm-1), 1648 C=N (Imine) y 1585-1566 C=N (Py). MS (DART, m/z): [M+1]+ 135.

N-(2-Pyridinylmethylene)-1-butanamine (L_2): Brown oil (93%), $C_{10}H_{14}N_2$. ^{1}H NMR (300 MHz, $CDCl_3$-d, δ ppm): 8.56 (d, J = 4.8 Hz, 1H, H_1), 8.30 (s, 1H, H_6), 7.91 (d, J = 7.9 Hz,1H, H_4), 7.66 (t, J = 7.7 Hz, 1H, H_3), 7.22 (t, J = 7.5, 4.9 Hz, 1H, H_2), 3.60 (t, J = 7.0 Hz, 2H, H_7), 1.64 (p, J = 7.1 Hz, 2H, H_8), 1.41–1.23 (m, 2H, H_9), 0.87 (t, J = 7.3 Hz, 3H, H_{10}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$-d, δ ppm): 161.65 (C_6), 154.65 (C_5), 149.37 (C_1), 136.50 (C_3), 124.56 (C_2), 121.15 (C_4), 61.24 (C_7), 32.75 (C_8), 20.41 (C_9), 13.85 (C_{10}). IR (ATR-FTIR, cm^{-1}): 1648 C=N (Imine) y 1586-1566 C=N (Py). MS (DART, m/z): $[M+1]^+$ 163.

N-(2-Pyridinylmethylene)-1-hexanamine (L_3): Brown oil (99%), $C_{12}H_{18}N_2$. ^{1}H NMR (300 MHz, $CDCl_3$-d, δ ppm): 8.64 (d, J = 4.5 Hz, 1H, H_1), 8.37 (s, 1H, H_6), 7.98 (d, J = 7.9 Hz, 1H, H_4), 7.73 (td, J = 7.7, 1.5 Hz, 1H, H_3), 7.33–7.25 (m, 1H, H_2), 3.67 (t, J = 7.0 Hz, 2H, H_7), 1.72 (p, J = 7.1 Hz, 2H, H_8), 1.44–1.23 (m, 6H, $H_{9\text{-}11}$), 0.91–0.85 (m, 3H, H_{12}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$-d, δ ppm): 161.66 (C_6), 154.67 (C_5), 149.39 (C_1), 136.53 (C_3), 124.58 (C_2), 121.18 (C_4), 61.61 (C_7), 31.64 (C_8), 30.67 (C_{10}), 27.02 (C_9), 22.61 (C_{11}), 14.07 (C_{12}). IR (ATR-FTIR, cm^{-1}): 1648 C=N (Imine) y 1586-1566 C=N (Py). MS (DART m/z): $[M+1]^+$ 191.

N-(2-Pyridinylmethylene)-1-decanamine (L_4): Dark yellow oil (90%), $C_{16}H_{26}N_2$. ^{1}H NMR (300 MHz, $CDCl_3$-d, δ ppm): 8.56 (dt, J = 4.9, 1.3 Hz, 1H, H_1), 8.30 (d, J = 1.4 Hz, 1H, H_6), 7.91 (d, J = 7.9 Hz, 1H, H_1), 7.66 (td, J = 7.7, 1.8 Hz, 1H, H_3), 7.23 (ddd, J = 7.3, 4.8, 1.2 Hz, 1H, H_2), 3.59 (td, J = 7.0, 1.4 Hz, 2H, H_7), 1.65 (p, J = 7.1 Hz, 2H, H_8), 1.31–1.12 (m, 18H, $H_{9\text{-}15}$), 0.83–0.76 (m, 4H, H_{16}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$-d, δ ppm): 161.65 (C_5), 154.67 (C_6), 149.38 (C_1), 136.51 (C_3), 124.57 (C_2), 121.17 (C_4), 61.61 (C_7), 31.89 (C_8), 30.70 (C_{14}), 29.58 ($C_{10\text{-}11}$), 29.43 (C_{12}), 29.32 (C_{13}), 27.34 (C_9), 22.68 (C_{15}), 14.11 (C_{16}). IR (ATR-FTIR, cm^{-1}): 1649 C=N (Imine) y 1586-1567 C=N (pyr). MS (DART, m/z): $[M+1]^+$ 247.

N-(2-Pyridinylmethylene)-1-*tert*-butylimine (L_5): Dark yellow oil (92%), $C_{10}H_{14}N_2$. ^{1}H NMR (300 MHz, $CDCl_3$-d, δ ppm): 8.56 (ddd, J = 5.0, 1.8, 0.9 Hz, 1H, H_1), 8.30 (s, 1H, H_6), 7.95 (dt, J = 8.0, 1.1 Hz, 1H, H_4), 7.65 (td, J = 7.6, 1.5 Hz, 1H, H_3), 7.33–7.06 (m, 1H, H_2), 1.25 (s, 9H, H_8). ^{13}C {^{1}H} NMR (76 MHz, $CDCl_3$-d, δ ppm): 156.41 (C_6), 155.50 (C_5), 149.24 (C_1), 136.52 (C_3), 124.40 (C_2), 120.97 (C_4), 57.83 (C_7), 29.58 (C_8). IR (ATR-FTIR, cm^{-1}): 1644 C=N (Imine) y 1587-1567 C=N (Py). MS (DART, m/z): $[M+1]^+$ 163.

N-(2-Pyridinylmethylene)-1-Cyclohexanamine (L_6): Dark yellow oil (93%), $C_{12}H_{16}N_2$. ^{1}H NMR (300 MHz, $CDCl_3$-d, δ ppm): 8.65–8.50 (m, 1H, H_1), 8.33 (s, 1H H_6)), 7.92 (d, J = 7.9 Hz, 1H, H_4), 7.65 (td, J = 7.7, 1.6 Hz, 1H, H_3), 7.22 (ddd, J = 7.4, 4.9, 1.2 Hz, 1H, H_2), 3.37–3.08 (m, 1H, H_7), 1.92–1.45 (m, 8H, $H_{8\text{-}9}$), 1.38–1.24 (m, 2H, H_{10}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$-d, δ ppm): 159.49 (C_6), 154.93 (C_5), 149.37 (C_1), 136.48 (C_3), 124.48 (C_2), 121.38 (C_4), 69.64 (C_7), 34.17 (C_8), 25.62 (C_{10}), 24.71 (C_9). IR (ATR-FTIR, cm^{-1}): 1646 C=N (Imine) y 1587-1566 C=N (Py). MS (DART, m/z): $[M+1]^+$ 189.

N-(2-Pyridinylmethylene)-1-Cycloheptanamine (L_7): Dark yellow oil (93%), $C_{13}H_{18}N_2$. ^{1}H NMR (300 MHz, $CDCl_3$-d, δ ppm): 8.63 (dt, J = 4.9, 1.3 Hz, 1H, H_1), 8.34 (s, 1H, H_6), 7.99 (d, J = 8.0 Hz, 1H, H_4), 7.72 (td, J = 7.7, 1.7 Hz, 1H, H_3), 7.28 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H, H_2), 3.46 (m, J = 6.4 Hz, 1H, H_7), 1.83–1.74 (m, 6H, H_9), 1.65–1.52 (m, 6H, H_{10}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$-d, δ ppm): 158.72 (C_6), 155.05 (C_5), 149.38 (C_1), 136.49 (C_3), 124.44 (C_2), 121.37 (C_4), 72.25 (C_7), 36.17 (C_8), 28.49 (C_{10}), 24.66 (C_9). IR (ATR-FTIR, cm^{-1}): 1644 C=N (Imine) y 1586-1566 C=N (Py). MS (DART, m/z): $[M+1]^+$ 203.

N-(2-Pyridinylmethylene)-1-Benzylamine (L_8): Dark yellow oil (84%), $C_{13}H_{12}N_2$. ^{1}H NMR (300 MHz, $CDCl_3$-d, δ ppm): 8.68 (dd, J = 4.8, 0.9 Hz, 1H, H_1), 8.52 (s, 1H, H_6), 8.09 (d, J = 7.9 Hz, 1H, H_4), 7.76 (td, J = 7.8, 1.7 Hz, 1H, H_3), 7.42–7.25 (m, 6H, $H_{2,\ 9\text{-}11}$), 4.90 (s, 2H, H_7). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$-d, δ ppm): 162.84 (C_6), 154.52 (C_5), 149.41 (C_1), 138.68 (C_8), 136.58 (C_3), 128.58 (C_{10}), 128.19 (C_9), 127.18 (C_{11}), 124.86 (C_2), 121.37 (C_4), 64.95 (C_7). IR (ATR-FTIR, cm^{-1}): 1645 C=N (Imine) y 1585-1566 C=N (Py). MS (DART, m/z): $[M+1]^+$ 197.

N-(2-Pyridinylmethylene)-1-benzeneethanamina (L_9): Dark yellow oil (99%), $C_{14}H_{14}N_2$. ^{1}H NMR (300 MHz, $CDCl_3$-d, δ ppm): 8.53 (d, J = 4.8 Hz, 1H, H_1), 8.21 (s, 1H, H_6), 7.89 (d, J = 7.9 Hz, 1H, H_4), 7.63 (td, J = 7.7, 1.7 Hz, 1H, H_3), 7.24–7.07 (m, 6H, $H_{2,\ 10\text{-}12}$), 3.84 (td, J = 7.6, 1.3 Hz, 2H, H_8), 2.95 (t, J = 7.5 Hz, 2H, H_7). ^{13}C {1H} NMR (75 MHz, $CDCl_3$-d, δ ppm): 162.33 (C_6), 154.48 (C_5), 149.44 (C_1), 139.69 (C_9), 136.56 (C_3), 128.95 (C_{11}), 128.40 (C_{10}), 126.21 (C_{12}), 124.71 (C_2), 121.27 (C_4), 62.92 (C_7), 37.33 (C_8). IR (ATR-FTIR, cm^{-1}): 1647 C=N (Imine) y 1585-1566 C=N (Py). MS (DART, m/z): $[M+1]^+$ 211.

Synthesis of $[MoCl_2O_2(L_1\text{-}L_9)]$ complexes, C_1-C_9

In a Schlenk tube under nitrogen atmosphere, a solution of $[MoCl_2O_2(CH_3CN)_2]$ (0.5 mmol) in acetonitrile (10 mL) was added 1.0 equivalent of the pyridylimine ligand corresponding (**L_1-L_9**) and stirred for 1 hour under nitrogen at room temperature. The solvent was removed under vacuum and the crude obtained was washed with diethyl ether and hexane, then solid was dissolved in methylene chloride and precipitated used hexane, affording the desired complex (**C_1-C_9**).

Epoxidation

The analytic activity of all complexes toward different olefins epoxidation was examined by treating a solution of the corresponding complex in methylene chloride by using *tert*-butyl hydroperoxide in decane (5.5 M) as an oxidant. The catalytic reaction was carried out at 40 °C. The oxygenated product was identified by an Agilent technologies GC-MS instrument equipped with the 7890B GC system and 5977A MSD using the HP-5MS capillary column. **Catalytic epoxidation:** The epoxidation reaction of olefins was carried out at 40 °C for 3h, in a flask with magnetic stirred. The flask was loaded with olefin (2.0 mmol), complex $[MoCl_2O_2(\mathbf{L})]$ (0.01% relation catalyst/substrate), *tert*-butyl hydroperoxide (1.5 equivalent) and methylene chloride (5 mL) as a solvent.

$[MoCl_2O_2(L_1)]$ (C_1): Gray solid (92%), m.p. 125-127 °C, $C_8H_{10}Cl_2MoN_2O_2$. ^{1}H NMR [300 MHz, $CDCl_3$-d, δ ppm]: 9.39 (d, J = 4.7 Hz, 1H, H_1), 8.38 (s, 1H, H_6), 8.13 (t, J = 6.4 Hz, 1H, H_3), 7.84 (d, J = 6.7 Hz, 1H, H_4), 7.77–7.69 (m, 1H, H_2), 4.34 (q, J = 7.0 Hz, 2H, H_7), 1.64 (t, J = 7.1 Hz, 3H, H_8). ^{13}C {^{1}H} NMR [75 MHz, $CDCl_3$-d, δ ppm]: 158.63 (C_6), 152.53 (C_1), 147.97 (C_5), 140.83 (C_3), 128.42 (C_2), 128.12 (C_4), 56.47 (C_7), 14.79 (C_8). IR [ATR-FTIR, cm^{-1}]: 1647 C=N (Imine), 1597-1569 C=N (Py), 904 (Mo=O). MS (ESI, m/z): $[M\text{-}Cl]^+$ 298. Anal. Calcd. for $C_8H_{10}Cl_2MoN_2O_2$: C, 28.85; N, 8.41; H, 3.03. Found: C, 27.28; N, 7.65; H, 3.12.

$[MoCl_2O_2(L_2)]$ (C_2): Gray solid (82%), m.p. 94-96 °C, $C_{10}H_{14}Cl_2MoN_2O_2$. ^{1}H NMR [300 MHz, $CDCl_3$-d, δ ppm]: 9.38 (d, J = 4.9 Hz, 1H, H_1), 8.33 (s, 1H, H_6), 8.13 (t, J = 7.4 Hz, 1H, H_3), 7.83 (d, J = 7.5 Hz, 1H, H_4), 7.73 (dd, J = 7.6, 5.0 Hz, 1H, H_2), 4.25 (t, J = 7.2 Hz, 2H, H_7), 2.17–2.00 (m, 2H, H_8), 1.48–1.33 (m, 2H, H_9), 0.93 (t, J = 7.3 Hz, 3H, H_{10}). ^{13}C {^{1}H} NMR [75 MHz, $CDCl_3$-d, δ ppm]: 159.21 (C_6), 152.54 (C_1), 147.90 (C_5), 140.83 (C_3), 128.44 (C_2), 128.13 (C_4), 62.12 (C_7), 30.81 (C_8), 20.22 (C_9), 13.70 (C_{10}). IR [ATR-FTIR, cm^{-1}]: 1597 C=N (Py), 904 (Mo=O). MS [ESI, m/z]: $[M+4Na]^+$ 453. Anal. Calcd. for $C_{10}H_{14}Cl_2MoN_2O_2$: C, 33.26; N, 7.76; H, 3.91. Found: C, 33.98; N, 7.31; H, 3.99.

[$MoCl_2O_2(L_3)$] (C_3): Gray solid (76%), m.p. 122-123 °C, $C_{12}H_{18}Cl_2MoN_2O_2$. ^{1}H NMR [300 MHz, $CDCl_3$-d, δ ppm]: 9.39 (d, J = 5.0 Hz, 1H, H_1), 8.32 (s, 1H, H_6), 8.12 (td, J = 7.7, 1.6 Hz, 1H, H_3), 7.82 (d, J = 7.6 Hz, 1H, H_4), 7.72 (dd, J = 7.7, 5.2 Hz, 1H, H_2), 4.24 (t, J = 7.3 Hz, 2H, H_7), 2.10 (p, J = 7.3 Hz, 2H, H_8), 1.37–1.24 (m, 6H, $H_{9\text{-}11}$), 0.82 (t, J = 6.9 Hz, 3H, H_{12}). ^{13}C {^{1}H} NMR [75 MHz, $CDCl_3$-d, δ ppm]: 159.0 (C_6), 152.52 (C_1), 147.89 (C_5), 140.73 (C_3), 128.35 (C_2), 127.98 (C_4), 62.39 (C_7), 31.35 (C_8), 28.78 (C_{10}), 26.67 (C_9), 22.53 (C_{11}), 14.03 (C_{12}). IR [ATR-FTIR, cm^{-1}]: 1647 C=N (Imine), 1597-1568 C=N (Py), 901 (Mo=O). MS (ESI, m/z): $[M+K+2Na]^+$ 492. Anal. Calcd. for $C_{12}H_{18}Cl_2MoN_2O_2$: C, 37.04; N, 7.20; H, 4.66. Found: C, 37.39; N, 7.42; H, 4.97.

[$MoCl_2O_2(L_4)$] (C_4): Gray solid (76%), m.p. 122-123 °C, $C_{16}H_{26}Cl_2MoN_2O_2$. ^{1}H NMR [300 MHz, $CDCl_3$-d, δ ppm]: 9.49 (dd, *J* = 5.1, 1.5 Hz, 1H, H_1), 8.41 (s, 1H, H_6), 8.21 (td, *J* = 7.7, 1.6 Hz, 1H, H_3), 7.90 (d, *J* = 7.6 Hz, 1H, H_4), 7.82 (dd, *J* = 7.7, 5.2 Hz, 1H, H_2), 4.33 (t, *J* = 7.3 Hz, 2H, H_7), 2.19 (m, 2H, H_8), 1.55–1.15 (m, 14H, $H_{9\text{-}15}$), 1.00–0.73 (m, 3H, H_{16}). ^{13}C {^{1}H} NMR [75 MHz, $CDCl_3$-d, δ ppm]: 159.1 (C_6), 152.5 (C_1), 147.9 (C_5), 140.8 (C_3), 128.4 (C_2), 128.1 (C_4), 62.4 (C_7), 31.8 (C_8), 29.5 (C_{14}), 29.5 (C_{10}), 29.2 (C_{11}), 29.20 (C_{12}), 28.8 (C_{13}), 27.0 (C_9), 22.6 (C_{15}), 14.1 (C_{16}). IR [ATR-FTIR, cm^{-1}]: 1597-1568 (C=N), 901 (Mo=O). MS [ESI, m/z]: $[M+4K]^+$ 604. Anal. Calcd. for $C_{12}H_{26}Cl_2MoN_2O_2$: C, 43.16; N, 6.26; H, 5.89. Found: C, 42.81; N, 6.67; H, 6.06.

[$MoCl_2O_2(L_5)$] (C_5): Gray solid (86%), m.p. 137 °C (Desc.). $C_{10}H_{14}Cl_2MoN_2O_2$. ^{1}H NMR [300 MHz, $CDCl_3$-d, δ ppm]: 9.42 (d, *J* = 4.7 Hz, 1H, H_1), 8.37 (s, 1H, H_6), 8.12 (t, *J* = 7.7 Hz, 1H, H_3), 7.82 (d, *J* = 7.6 Hz, 1H, H_4), 7.72 (dd, *J* = 7.6, 5.3 Hz, 1H, H_2), 1.94 (s, 2H, H_8), 1.70 (s, 7H, H_8). ^{13}C {^{1}H} NMR [75 MHz, $CDCl_3$-d, δ ppm]: 155.87 (C_6), 152.40 (C_1), 148.55 (C_5), 140.62 (C_3), 128.49 (C_2), 128.20 (C_4), 65.03 (C_7), 29.43 (C_8). IR [ATR-FTIR, cm^{-1}]: 1634 C=N (Imine), 1597 C=N (Py), 908 (Mo=O). MS [ESI, m/z]: $[M+2K]^+$ 436. Anal. Calcd. for $C_{10}H_{14}Cl_2MoN_2O_2$: C, 33.26; N, 7.76; H, 3.91. Found: C, 33.86; N, 8.09; H, 6.01.

[$MoCl_2O_2(L_6)$] (C_6): Gray solid (74%), m.p. 160 °C (Desc.). $C_{12}H_{16}Cl_2MoN_2O_2$. ^{1}H NMR [300 MHz, $CDCl_3$-d, δ ppm]: 9.49 (d, J = 4.8 Hz, 1H, H_1), 8.39 (s, 1H, H_6), 8.11 (t, J = 7.4 Hz, 1H, H_3), 7.79 (d, J = 7.5 Hz, 1H, H_4), 7.71 (dd, J = 7.7, 5.1 Hz, 1H, H_2), 4.26–4.18 (m, 1H, H_7), 2.28-1.19 (m, 10H, $H_{8\text{-}10}$). ^{13}C {^{1}H} NMR [75 MHz, $CDCl_3$-d, δ ppm]: 157.5 (C_6), 152.4 (C_1), 148.3 (C_5), 140.6 (C_3), 128.2 (C_2), 128.0 (C_4), 71.5 (C_7), 33.0 (C_8), 25.4 (C_{10}), 25.2 (C_9). IR [ATR-FTIR, cm^{-1}]: 1637 C=N (Imine), 1524 C=N (Py), 905 (Mo=O). MS [ESI, m/z]: $[M+2K+Na]^+$ 488. Anal. Calcd. for $C_{12}H_{16}Cl_2MoN_2O_2$: C, 37.22; N, 7.24; H, 4.17. Found: C, 36.96; N, 6.80; H, 4.44.

[$MoCl_2O_2(L_7)$] (C_7): Gray solid (91%), m.p. 170 °C (Desc.), $C_{13}H_{18}Cl_2MoN_2O_2$. ^{1}H NMR [300 MHz, $CDCl_3$-d, δ ppm]: 9.38 (d, J = 4.9 Hz, 1H, H_1), 8.42 (s, 1H, H_6), 8.11 (t, J = 7.7 Hz, 1H, H_3), 7.81 (d, J = 7.6 Hz, 1H, H_4), 7.74–7.67 (m, 1H, H_2), 4.35 (td, J = 10.4, 3.8 Hz, 1H, H_7), 2.36–1.50 (m, 12H, $H_{8\text{-}10}$). ^{13}C {^{1}H} NMR [75 MHz, $CDCl_3$-d, δ ppm]: 157.58 (C_6), 152.32 (C_1), 148.42 (C_5), 140.70 (C_3), 128.24 (C_2), 128.11 (C_4), 74.56 (C_7), 35.09 (C_8), 27.16 (C_{10}), 25.05 (C_9). IR [ATR-FTIR, cm^{-1}]: 1639 C=N (Imine), 1595 C=N (Py), 910 (Mo=O). MS [ESI, m/z]: $[M+3K]^+$ 518. Anal. Calcd. for $C_{13}H_{18}Cl_2MoN_2O_2$: C, 38.92; N, 6.98; H, 4.52. Found: C, 38.26; N, 6.81; H, 4.86.

[$MoCl_2O_2(L_8)$] (C8): Brown solid (80%), m.p. 128 °C (Desc.). $C_{13}H_{12}Cl_2MoN_2O_2$. ^{1}H NMR [300 MHz, $CDCl_3$-d, δ ppm]: 9.42 (d, *J* = 4.6 Hz, 1H, H_1), 8.05 (td, *J* = 7.7, 1.5 Hz, 1H, H_3), 7.88 (t, *J* = 2.0 Hz, 1H, H_6), 7.73–7.67 (m, 1H, H_4), 7.64 (d, *J* = 7.6 Hz, 1H, H_2), 7.44–7.35 (m, 5H, $H_{9\text{-}11}$), 5.56 (d, *J* = 2.0 Hz, 2H, H_7). ^{13}C {^{1}H} NMR [75 MHz, $CDCl_3$-d, δ ppm]: 158.68 (C_6), 152.62 (C_1), 148.04 (C_5), 140.63 (C_3), 133.08 (C_8), 130.64 (C_{10}), 129.50 (C_9), 129.29 (C_{11}), 128.28 (C_2), 128.24 (C_4), 63.07 (C_7). IR [ATR-FTIR, cm^{-1}]: 1642 C=N (Imine), 1598 C=N (Py), 910 (Mo=O). MS [ESI, m/z]: $[M+K]^+$ 434. Anal. Calcd. for $C_{13}H_{12}Cl_2MoN_2O_2$: C, 39.52; N, 7.09; H, 3.06. Found: C, 40.18; N, 7.13; H, 3.29.

[$MoCl_2O_2(L9)$] (C9): Brown solid (79%), m.p. 121-124 °C, $C_{14}H_{14}Cl_2MoN_2O_2$. ^{1}H NMR (300 MHz, $CDCl_3$-d, δ ppm): 9.52–9.42 (d, 1H, H_1), 8.15 (td, J = 7.7, 1.6 Hz, 1H, H_3), 7.97 (s, 1H, H_6), 7.83–7.74 (m, 1H, H_4), 7.71 (d, J = 7.6 Hz, 1H, H_2), 7.40–7.23 (m, 5H, $H_{10\text{-}12}$), 4.57 (t, J = 7.0 Hz, 2H, H_8), 3.46 (t, J = 7.1 Hz, 2H, H_7). ^{13}C {^{1}H} NMR [75 MHz, $CDCl_3$-d, δ ppm]: 159.67 (C_6), 152.54 (C_1), 147.68 (C_5), 140.75 (C_3), 137.83 (C_9), 129.28 (C_{11}), 128.76 (C_{10}), 128.49 (C_{12}), 128.02 (C_2), 126.94 (C_4), 63.28 (C_7), 35.09 (C_8). IR [ATR-FTIR, cm^{-1}]: 1645 C=N (Imine), 1598-1567 C=N (Py), 901 (Mo=O). MS [ESI, m/z]: $[M+3K+Na]^+$ 548. Anal. Calcd. for $C_{14}H_{14}Cl_2MoN_2O_2$: C, 41.10; N, 6.85; H, 3.45. Found: C, 40.48; N, 6.27; H, 3.54.

Acknowledgments

We gratefully acknowledge the financial support from DGAPA-UNAM (PAPIIT IA-203820) and CONACyT (626716 grant to D. M-M). We also thank M. Paz Orta, R. Patiño, S. Hernández-Ortega, J. Pérez, M. C. García, C. Márquez, L. Rios, E. García, G. Cortés (UCTIC), H. Rios, E. Huerta, M. A. Peña, M. Reyes Lezama, E. Tapia Mendoza (LANCIC-IQ-UNAM), B. Quiroz and N. Esturau (LURMN-IQ-UNAM) for the excellent technical support.

Keywords: Molybdenum • Epoxidation • 2-Pyridylimino • Turnover frequency • Homogeneous catalysis

[1] J. E. Bäckvall, *Modern Oxidation Methods*, Wiley-VCH, **2011**, pp 1–79.
[2] S. T. Oyama, *Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis*, Elsevier, Amsterdam, **2008**, pp. 4–57.
[3] K. A. Joergensen, *Chem. Rev.* **1989**, *89* 431–458.
[4] T. Punniyamurthy, S. Velusamy, J. Iqbal, *Chem. Rev.* **2005**, *105,* 2329–2364.
[5] F. G. Gelalcha, *Adv. Synth & Catal.* **2014**, *356,* 261–299.
[6] P. Liu, E. L.-M. Wong, A.W.-H. Yuen, C.-M. Che, *Org. Lett.* **2008**, *10*, 3275–3278.
[7] I. Garcia-Bosch, X. Ribas, M. Costas, *Adv. Synth. & Catal.* **2009**, *351,* 348–352.
[8] E. M. McGarrigle, D. G. Gilheany, *Chem. Rev.* **2005**, *105*, 1563–1602.
[9] P. Saisaha, J. W. de Boer, W. R. Browne, *Chem. Soc. Rev.* **2013**, *42*, 2059–2074.
[10] Q. H. Xia, H. Q. Ge, C. P. Ye, Z. M. Li, K. X. Su. *Chem. Rev.* **2005**, *105*, 1603–1662.
[11] A. Syamal, M. R. Maurya. *Coord. Chem. Rev.* **1989**, *95*, 183-238.
[12] F. Fache, E. Schulz, M. L. Tommasino, M. Lemaire. *Chem. Rev.* **2000**, *100*, 2159–2232.
[13] F. E. Kühn, A. D. Lopes, A. M. Santos, E. Herdtweck, J. J. Haider, C. C. Romão, A. Gil Santos, *J. Mol. Catal. A: Chem.* **2000**, *151*, 147–160.
[14] A. Valente, J. Moreira, A. D. Lopes, M. Pillinger, C. D. Nunes, C. C. Romão, F. E. Kühn, I. S. Gonçalves. *New J. Chem.* **2004**, *28*, 308–313.
[15] F. E. Kühn, A. M. Santos, I. S. Gonçalves, C. C. Romão, A. D. Lopes. *Appl. Organometal. Chem.,* **2001**, 15, 43–50.
[16] A. Günyar, M.-D. Zhou, M. Drees, P. N. W. Baxter, G. Bassioni, E. Herdtweck, F. E. Kühn. *Dalton Trans.* **2009**, 8746–8754.
[17] A. Gunyara, D. Betzb, M. Dreesb, E. Herdtweckb, F. Ebruno. *J. Mol. Catal. A: Chem.* **2010**, *331*, 117–124.
[18] S. M. Bruno, C. C. L. Pereira, M. S. Balula, M. Nolasco, A. A. Valente, A. Hazell, M. Pillinger, P. Ribeiro-Claro, I. S. Gonçalves. *J. Mol. Catal. A: Chem.* **2007**, *261*, 79–87.
[19] A. C. Coelho, M. Nolasco, S. S. Balula, M. M. Antunes, C. C. L. Pereira, F. A. Almeida Paz, A. A. Valente, M. Pillinger, P. Ribeiro-Claro, J. Klinowski, I. S. Gonçalves. *Inorg. Chem.* **2011**, *50*, 525–538.
[20] C. C. L. Pereira, S. S. Balula, F. A. A. Paz, A. A. Valente, M. Pillinger, J. Klinowski, I. S. Gonçalves. *Inorg. Chem.* **2007**, *46*, 8508–8510.
[21] A. C. Gomes, S. M. Bruno, S. Gago, R. P. Lopes, D. A. Machado, A. P. Carminatti, A. A. Valente, M. Pillinger, I. S. Gonçalves. *J. Organomet. Chem.* **2011**, *696*, 3543–3550.

[22] S. S. Balula, S. M. Bruno, A. C. Gomes, A. A. Valente, M. Pillinger, I. S. Gonçalves, D. J. Macquarrie, J. H. Clark. *Inorg. Chim. Acta*, **2012**, *387*, 234–239.

[23] M. Vasconcellos-Dias, J. Marreiros, R. Sales, V. Félix, P. Brandão, C. D. Nunes, M. J. Calhorda. *Molecules*, **2019**, *24*, 578.

[24] CCDC 2022764 (**C_1**), 2022765 (**C_6**), 2022763 (**C_8**), 2022762 (**C_9**); these data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[25] S. R. Gilani, Z. Mahmood. *J. Chem. Soc. Pak.* **2003**, *25*, 41–43.

[26] G. Barea, A. Lledos, F. Maseras, Y. Jean. *Inorg. Chem.* **1998**, *37*, 3321–3325.

[27] R. Bikas, V. Lippolis, N. Noshiranzadeh, H. Farzaneh-Bonab, A. J. Blake, M. Siczek, H. Hosseini-Monfared, T. Lis. *Eur. J. Inorg. Chem.* **2017**, 999–1006.

[28] M. Mirzaee, B. Bahramian, A. Amoli, *Appl. Organometal. Chem.* **2015**, *29*, 593–600.

[29] M. Bagherzadeh, S. Ataie, H. Mahmoudi, J. Janczak, *Inorg. Chem. Commun*. **2017**, *84*, 63–67.

[30] R. Bikas, V. Lippolis, N. Noshiranzadeh, H. Farzaneh-Bonab, A. J. Blake, M. Siczek, H. Hosseini-Monfared, H. T. Lis. *Eur. J. Inorg. Chem.* **2017**, 999–1006.

[31] M. Ghorbanloo, A. Mohamadi, M. Amini, J. Tao. *Transition Met. Chem.* **2015**, *40*, 321–331.

[32] M. Bagherzadeh, R. Latifi, L. Tahsini, V. AMani, A. Ellern, L. K. Woo. *Polyhedron* **2009**, *28*, 2517–2521.

[33] A. Rezaeifard, I. Sheikhshoaie, N. Monadi, H. Stoeckli-Evans. *Eur. J. Inorg. Chem.* **2010**, *2010*, 799–806.

[34] T-U. Yoon, S. Ahn, A-R. Kim, J. M. Notestein, O. Farha, Y-S. Bae. *Catal. Sci. Technol*, **2020**, *10*, 4580–4585.

[35] A. Al-Ajlouni, A. A. Valente, C. D. Nunes, M. Pillinger, A. M. Santos, J. Zhao, C. C. Romao, I. S. Gonçalves, F.E. Kuhn. *Eur. J. Inorg. Chem.* **2005**, 1716–1723.

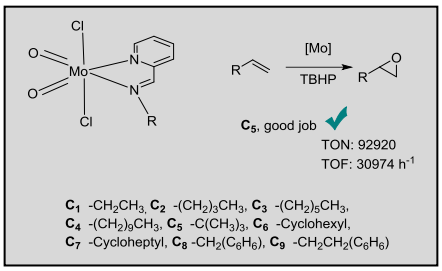
[36] F. E. Kühn, A. M. Santos, A. D. Lopes, I. S. Gonçalves, E. Herdtweck, C. C. Romão, *J. Mol. Catal A: Chem.* **2000**, *164*, 25–38.

[37] L. M. Peschel, F. Belaj, J. A. Schachner, N. C. Mösch-Zanetti, *Eur. J. Inorg. Chem.*, **2017**, 2808-2817.

[38] M. Schulz, M. Klopfleisch, H. Görls, M. Kahnes, M. Westerhausen, *Inorg. Chim. Acta*, **2009**, *362*, 4706–4712.

10.1002/ejic.202000790

Entry for the Table of Contents



Dioxomolybdenum (VI) complexes with the general formula [$MoCl_2O_2$(pyridilimine)] were applied as homogeneous catalysts for the epoxidation of olefins. The new compounds showed high catalytic activity. The performance of the complexes in the reaction can be attributed to the substituent at the imine fragment.