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Catalytic Activity of Chloro and Triflate Manganese(II) Complexes in Epoxidation Reactions: Reusable Catalytic Systems for Alkene Epoxidation

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The catalytic oxidation of a series of alkenes by three Mn^{II} complexes, $MnCl_2[(-)-L]_2$ (1), ($\{MnCl[(-)-L]\}_2(\mu-Cl)_2$) (2), and $Mn(CF_3SO_3)_2[(-)-L]_2$ (3), having the bidentate N-ligand (-)-pinene[5,6]bipyridine, (-)-L, and using peracetic acid as oxidant in acetonitrile is described. The performance of catalysts 1 and 2 is enhanced by the use of additives (NaHCO₃ and imidazole) and also using a [bmim]/acetonitrile mixture as reaction media. The latter conditions allow recyclability of

Introduction

Metal-catalysed oxidation is one of the most important transfer reactions in chemistry and biology.^[1] In particular. olefin epoxidation has received considerable interest from both academics and industry; clearly, enantiomerically pure epoxides play an eminent role as intermediates and buildings blocks in organic synthesis and materials science.^[2] Chiral manganese complexes have been studied as catalysts for enantioselective oxidation reactions in combination with H_2O_2 . The most thoroughly investigated systems are those based on Mn porphyrins and Mn salen complexes,^[3] which afford excellent enantioselectivities. Manganese complexes bearing non-heme ligands have been described as versatile catalysts in oxidation reactions.^[4] Although numerous procedures have been developed,^[5] the need to understand the mechanisms of metal-mediated oxygenation processes demands the synthesis of new, stable and readily available catalysts. These reactions are known to proceed via oxo- or

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the catalytic system, keeping good selectivity and conversion values in some cases. The nature of the species formed in acetonitrile after the addition of peracetic acid has been investigated through EPR and UV/Vis spectroscopy. The results point to the formation of high-valent manganese species, among which a di- μ -oxo-bridged Mn₂(III,IV) binuclear species was unambiguously identified for complex **3** through a typical 16-line EPR signature.

peroxo-metal intermediates. The exact nature of the oxygenating species and the mechanism of oxygen transfer to the substrate remain unclear, although the participation of multiple active oxidants has been proposed in most cases.^[6] The efficiency of the oxygen transfer step is influenced by the coordination environment on the metal centre; the ligands can, through steric bulk and chirality, affect the approach of molecules toward the metal centre and, hence, induce selectivity.

The use of additives is an important aspect of metalcatalysed epoxidation, and their use can often lead to an increase in activity.^[7] In the specific case of Mn^{III} complexes, the epoxidation activity is, in some cases, directly dependent on the basicity of the additives used.^[7b,7c] Certain additives such as carboxylic acids, carboxylate or carbonate salts have been reported to cause increased chemoselectivity and diastereoselectivity in the catalytic epoxidation of chiral allylic alcohols by binuclear Mn^{IV} complexes.^[8]

Heterogeneisation and reuse of catalysts are fields of unquestionable importance, especially in large-scale processes.^[9] In this context, room temperature ionic liquids (RTILs) have received a good deal of attention in recent years as potential alternative solvents or co-solvents in catalysis^[10] because of their potential benefits including the simplicity of product separation and the ease with which catalyst recycling can be achieved.^[11] Numerous possible combinations of cations and anions offer convenient ways to fine-tune the physicochemical properties of ILs, such as polarity, viscosity, and miscibility with others reagents. Most metal catalysts are soluble in ILs without modifica-

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tion of the ligands, and usually the noncoordinating anions of ILs leave the active sites of catalysts available for interaction with the substrates.

Catalytic epoxidation processes have been tested in ionic liquids with Mn^{III} complexes containing porphyrin and Schiff base ligands,^[12] but, to the best of our knowledge, the only Mn^{II} compound evaluated to date as an epoxidation catalyst in such media is manganese(II) acetate, which has been tested in the epoxidation of aliphatic terminal alkenes.^[13]

Our group has recently described new Mn^{II} complexes with the (–)-pinene[5,6]bipyridine ligand, (–)-L,^[5d] which have displayed good efficiency in the epoxidation of aromatic olefins and complete stereoselectivity in the epoxidation of *cis*- β -methystyrene as substrate, using peracetic acid as oxidant. In the mentioned work, we pointed out that, although triflate Mn complexes have been extensively tested as epoxidation catalysts (sometimes invoking the lability of the monodentate triflate ligands), our chloro complexes proved to be better catalysts for styrene epoxidation than the triflate analogues. This led us to undertake a more in-depth study on these catalytic systems by varying the experimental conditions, to improve further their catalytic performances.

In this paper, we report the performance of the Mnchloro catalysts $MnCl_2[(-)-L]_2$, **1**, and $[{MnCl((-)-L)}_2(\mu-Cl)_2]$, **2**, in the epoxidation of aromatic olefins and 1-octene with peracetic acid, in the presence of additives such as imidazole or NaHCO₃ (Figure 1). We have also investigated their epoxidation activity in ionic liquid/solvent media, a system that constitutes the first example of polypyridyl Mn^{II} complexes tested under such conditions. Furthermore, we have tested the activity of $Mn(CF_3SO_3)_2[(-)-L]_2$, **3**, with respect to the epoxidation of some alkenes as a comparison with the behaviour of chloro complexes **1** and **2** in the homogeneous phase.



Figure 1. Structure of the complexes studied.

Finally, the nature of the manganese species generated in solution in the course of the catalysis has been investigated through EPR and UV/Vis spectroscopy.

Results and Discussion

Catalytic Olefin Epoxidation in CH₃CN

The catalytic activity of the manganese chloro complexes 1 and 2 was investigated in the epoxidation of a selection of alkenes in CH₃CN using commercial peracetic acid

(32%) as oxidant both in the absence and in the presence of two different additives, imidazole and NaHCO₃. No epoxidation occurred in the absence of catalyst^[5d] or in the presence of Mn^{II} salts [MnCl₂ or Mn(CF₃SO₃)₂] used instead of the catalysts. Hydrogen peroxide was also tested as oxidant but no catalytic activity was detected.

Table 1 summarises the conversion and selectivity values obtained for the corresponding epoxide products. In general, low enantioselectivity values (up to 20%) were achieved (see Table S1 in the Supporting Information).

Table 1. Epoxidation tests performed with catalysts 1 and 2 in the absence and the presence of additives. Conversion (conv) and selectivity (sel) values are given in %.^[a]

	Additive \rightarrow			-	Imida	ızole	NaH	CO ₃
	Substrate	Cat.	conv	sel ^[b]	conv	sel	conv	sel
1	$\bigcirc \frown$	1	70 ^[c]	74	>99.9 ^[c]	98	>99.9 ^[c]	96
2		2	>99.9 ^[d]	65	>99.9 ^[d]	72	>99.9 ^[d]	79
3		1	37	95 c/t: ^[e] 100	82	88 c/t: 83	>99.9	89 c/t: 72
4		2	35	93 c/t: 99	>99.9	80 c/t: 76	92	73 c/t: 76
5	\sim	1	56	96	60	>99.9	>99.9	>99.9
6	\bigcup	2	47	>99.9	97	>99.9	92	94
7	Ô	1	22	27	36	61	85	84
8	Ŭ	2	20	18	62	64	91	67
9		1	21	64	47	67	94	70
10	(-/5 🔍	2	12	52	80	61	93	71

[a] Reaction conditions: catalyst (2.5 μ mol), substrate (250 μ mol), additive (25 μ mol), CH₃CN (1 mL). Peracetic acid 32% (500 μ mol) added in 3 min at 0 °C, then 3 h of reaction at room temp. After addition of an internal standard, an aliquot was taken for GC analysis. [b] Selectivity for epoxide (sel) given as [yield/conversion] × 100. [c] Time: 2 h. [d] Time: 1 h. [e] c/t represents the percent of *cis* isomer obtained.

As can be seen in Table 1, high conversions and selectivities for the epoxide product were obtained in most cases. An overall comparison between the activities displayed by catalysts **1** and **2** indicates that both chloro complexes present comparable performance in the absence of additives, as well as an increase of the conversion values in the presence of either imidazole or NaHCO₃, which is particularly noticeable for the latter. The selectivity for the epoxide also increases with the use of additives, except in the case of *cis*- β -methylstyrene substrate (entries 3 and 4), for which a slight decrease was observed.

It is remarkable that the epoxidation of cis- β -methylstyrene is stereospecific when using complex **1** as catalyst because previous reports on Mn(salen) catalysts bearing chloro as counterion/axial ligand display a much higher degree of $cis \rightarrow trans$ isomerisation than other catalysts with www.eurjic.org

noncoordinating species as counterions.^[14] Complex **2** is also outstanding, with only 1% of *trans* epoxide formed when the process is conducted in the absence of additives. However, the presence of imidazole or NaHCO₃ in the epoxidation of this substrate not only decreases the selectivity for the epoxide product as mentioned above, but also leads to the formation of a certain degree of the *trans* isomer, thus indicating the involvement of either a radical mechanism that operates through one-electron oxidation of the substrate, or an ionic mechanism, under these conditions for both catalysts.

In the case of styrene (Table 1, entries 1 and 2), total consumption of substrate is obtained with high epoxide yields, particularly in the case of complex 1 in the presence of NaHCO₃ or imidazole, constituting one of the most selective catalytic systems described to date for the epoxidation of this substrate.^[7b-7e] Moreover, aliphatic alkenes such as 1-octene, which tend to be the least reactive olefins in metal-catalysed epoxidation,^[6a] are readily epoxidised with both catalysts 1 and 2, again with the use of sodium hydrogen carbonate providing the best catalytic conditions with respect to conversion and selectivity.

Different requirements for the additives have been reported for catalytic systems using H_2O_2 as oxidant: (i) a minimum basicity of the additive is necessary to achieve some enhanced catalytic activity,^[7b] and (ii) additives such as monocarboxylate ions, which allow the oxidation of Mn^{II} to higher oxidation states without considerably disturbing the first coordination sphere of the Mn ion, also improve the catalytic activity.^[15] In our case, the additives used may influence the catalyst in a similar way, although we used peracetic acid as oxidant. Some authors such as Stack et al.^[16] have observed that, in the presence of peracetic acid as oxidant, a decrease of the acidity in the catalytic media prevents decomposition of complexes into the protonated ligand and free Mn²⁺, consequently leading to an increase in the catalytic activity. However, in our case, the molar amount of additives used would exert an almost negligible influence on the overall pH of the reaction media, so the improvement of the catalytic performance is probably related to the presence of the additives in the close surroundings of the metal in the catalyst.

Finally, with the aim of comparing the activities of two structurally analogous mononuclear complexes, 1 and 3, which only differ in the nature of their monodentate (chloro or triflate) anionic ligands, we also investigated the activity of $[Mn(CF_3SO_3)_2((-)-L)_2]$, 3, in the epoxidation of alkenes in acetonitrile without additives using peracetic acid as the oxidant. Table 2 summarises the conversion and selectivity values for the corresponding epoxide products formed (compound 1 is also included for comparison). As expected,^[5d] we observed that, in general, the conversion and selectivity values for the chloro complex 1 were higher than those presented by the triflate complex 3 within the same reaction time. This indicates that the intermediate species involved in the catalytic cycle for both catalysts could be distinct, in spite of their structural similarity (see below).

Table 2. Epoxidation tests performed with complexes 1 and 3 in the absence of additives. Conversion (conv) and selectivity (sel) values are given in %.^[a]

Substrate	MnC conv	$l_{2((-)-L)_{2}, 1}$ sel ^[b]	Mn(CF conv	³ SO ₃) ₂ ((-)-L) ₂ , 3 sel
$\overline{\bigcirc}$	70 ^[c]	74	24 ^[c]	33
	37	95 c/t: ^[d] 100%	30	62 c/t: 100%
\bigcirc	56	96	50	70
Ms	21	64	4	30

[a] Reaction conditions: catalyst (2.5 μ mol), substrate (250 μ mol), CH₃CN (1 mL). Peracetic acid 32% (500 μ mol) added in 3 min at 0 °C, then 3 h of reaction at room temp. After addition of an internal standard, an aliquot was taken for GC analysis. [b] Selectivity for epoxide (sel) given as [yield/conversion] × 100. [c] Time: 2 h. [d] c/t represents the percent of *cis* isomer obtained.

Catalytic Olefin Epoxidation in Ionic Liquid/CH₃CN Media and Reusability of Catalysts

The performance and reusability of the most efficient catalysts, i.e., chloro complexes 1 and 2, have been tested in ionic liquid/solvent media. The ionic liquid used was the commercially available [bmim]PF₆ and the reaction conditions were initially optimised ([bmim]PF₆/solvent ratios from 1:0 to 1:1 were tested, with acetonitrile and dichloromethane as solvent). Optimal performance was obtained by using [bmim]PF₆/CH₃CN (1:1) as solvent, and these conditions were used for the epoxidation of a range of alkenes (Table 3). In general, remarkably better performances were observed in the presence of the ionic liquid/acetonitrile mixture than with acetonitrile (data previously discussed in Table 1), although a slight decrease in the selectivity was observed in some cases in the presence of ionic liquid. It is significant that an enhancement in the performance for 1octene was observed when using ionic liquid media because, as previously reported,^[13] the epoxidation of aliphatic terminal alkenes in ILs is challenging due to the poor miscibility of alkenes among the reaction components, which often leads to slow reaction rates and low conversion yields. The [bmim]PF₆/CH₃CN (1:1) system leads to threefold

Table 3. Epoxidation tests performed with complexes 1 and 2 in [bmim]PF₆/CH₃CN media. Conversion (conv) and selectivity (sel) values are given in %.^[a]

Entry	Entry Substrate		MnCl ₂ ((-)-L) ₂ , 1		$[{MnCl((-)-L)}_2(\mu-Cl)_2], 2$	
		conv	sel ^[b]	conv	sel	
1		95	71	86	66	
2	Č	64	63 c/t ^[c] : 97%	60	81 c/t: 95%	
3	$\bigcirc \frown$	91	81	75	77	
4	Ms	61	57	58	56	

[a] Reaction conditions: catalyst (2.5 μ mol), substrate (250 μ mol), CH₃CN/[bmim]PF₆ 1:1 (2 mL). Peracetic acid 32% (500 μ mol) added in 3 min at 0 °C, then 3 h of reaction at room temp. [b] Calculated as [epoxide yield/substrate conversion] × 100. [c] c/t represents the percent of *cis* isomer obtained.

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higher conversion values when using either catalyst 1 or 2 with respect to the use of acetonitrile as sole solvent, while maintaining good selectivity values.

We tested the effect of the addition of NaHCO₃ as additive to the [bmim]PF₆/CH₃CN (1:1) medium but no further improvement of the catalytic performance was observed.

The recyclability of the catalytic systems in $[bmim]PF_6/$ CH₃CN media was also investigated. The results obtained by using catalyst 1 for a number of consecutive runs are displayed in Figure 2 and Figure S1 for the four substrates evaluated. The catalyst maintains a remarkable performance in up to 7–9 runs in all cases. The selectivity for the epoxide is relatively well maintained along the consecutive runs for trans-β-methylstyrene, 1-octene and cis-β-methylstyrene, whereas it clearly decreases for styrene. The overall turnover numbers for the respective epoxides are 304 for styrene, 283 for cis-β-methylstyrene, 617 for trans-β-methylstyrene and 169 for 1-octene and, in the case of *cis*-β-methylstyrene, the stereoselectivity for the *cis* epoxide is maintained throughout all runs. The reusability of catalyst 2 was tested by following an analogous procedure using styrene as substrate; the results obtained are shown in the Supporting Information (Figure S2). The overall turnover number of 261 is slightly lower for this complex than for 1 when performing the same number of runs, but both catalysts attain similar selectivity values.



Figure 2. Conversion (black bars) and selectivity (grey bars) values obtained throughout a number of consecutive reuses of complex 1 in the epoxidation of *trans*- β -methylstyrene in [bmim]PF₆/CH₃CN (see text for experimental conditions).

It is important to note that only the ionic liquid exerts a significant stabilising effect on the catalyst, which allows its reuse without loss of activity. Indeed, when a similar recycling procedure was performed using CH_3CN as single solvent, no conversion was obtained in the second run. On the other hand, the presence of NaHCO₃ in CH₃CN allows the reuse of the catalyst until a third run in the case of styrene, although a significant decrease in the level of conversion was observed after each run (conversion values: 99.9, 26, 5% for first, second, and third run, respectively).

Formation of High-Valent Manganese Species in Peracetic Acid/CH₃CN Based Systems

To obtain further information on the nature of the species formed in CH₃CN after addition of peracetic acid, UV/ Vis and EPR spectroscopy were carried out with complexes 1–3. The evolution of the UV/Vis and EPR spectra of a solution of these complexes was monitored upon addition of oxidant at -30 or -40 °C and subsequent addition of styrene after allowing the mixture to warm to 15 °C. The behaviour of the chloro complexes 1 and 2 was shown to be similar throughout the whole set of experiments, so we limit the discussion below to complexes 1 and 3, which, in contrast, display significantly different activity in catalysis.

The UV/Vis spectra of solutions of 1 and 3 are featureless, as expected for Mn^{II} species [Figure 3, spectra (a)]. Addition of 2 equiv. peracetic acid causes a solution colour change from colourless to brown [Figure 3, spectra (b–d)], which attests the formation of high-valent manganese species. In the case of 1, two bands appear in the visible region at 670 and 550 nm (shoulder) and a strong increase of the absorbance below 500 nm can also be observed. For complex 3, whereas a similar increase in absorbance is observed



Figure 3. Evolution of the UV/Vis spectra of solutions of complexes 1 and 3 in CH₃CN upon addition of 2 equiv. peracetic acid at -40 °C, warming to 15 °C and addition of 10 equiv. styrene substrate: (A) complex 1 (2.5 mM): (a) initial solution; (b-d) after addition of peracetic acid [time: 30 s (b), 36 s (c), 15 min (d)]; (e-f) after addition of styrene [time: 20 min (e), 21 h (f)]. (B) Complex 3 (2.5 mM): (a) initial solution; (b-d) after addition of styrene [time: 10 min (b), 13 min (c), 15 (d)]; (e-f) after addition of styrene [time: 30 min (e), 24 h (f)]. Path length: 1 cm.

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below 500 nm, only a shoulder around 640 nm is detected. Similar visible features (shape and wavelength values) have previously been observed for oxo-bridged binuclear manganese complexes with polypyridyl ligands:^[17] di-µ-oxo $Mn_2(IV,IV)$ in the case of $1^{[18,19]}$ and mixed-valent Mn₂(III,IV) species in the case of 3.^[20] These assignments are consistent with EPR experiments (Figure 4). Indeed, initial 100 K EPR spectra of complexes 1 and 3, which are typical of high-spin mononuclear Mn^{II} species (S = 5/2),^[21] clearly changed 15 min after addition of peracetic acid at -40 °C [Figure 4, spectra (a-b)]. In the case of complex 3, the formation of an oxo-bridged mixed-valent Mn₂(III,IV) binuclear complex^[17] is unambiguously confirmed by the appearance of a new 16-line signal that is highly characteristic of such species [Figure 4, B(b)]. In such complexes, the two Mn ions are strongly antiferromagnetically coupled, leading to an S = 1/2 species. The spectral width of 125 mT (from the first peak to the last peak of the 16-line feature) is also in accordance with a $[Mn^{III}(\mu-O)_2Mn^{IV}]$ core.^[20a] In the case of 1, the occurrence of a 6-line signal centred at



Figure 4. Evolution of the 100 K X-band EPR spectra of complexes 1 and 3 upon addition of 2 equiv. peracetic acid at low temperature, warming to 15 °C and addition of 10 equiv. styrene substrate: (A) Complex 1 in CH₃CN at -40 °C (2 mM): (a) initial solution; (b) 15 min after addition of peracetic acid; (c-d) after subsequent addition of styrene [time: 15 min (c), 3 h (d)]. (B) Complex 3 in CH₃CN at -30 °C (2.5 mM): (a) initial solution; (b) 15 min after addition of peracetic acid; (c-d) after subsequent addition of styrene [time: 3 h (c), 21 h (d)].

g = 2.00 after addition of peracetic acid [Figure 4, A(b)], presumably indicates the presence in a low amount of a Mn^{II} mononuclear species. The absence of other significant signals is consistent with the generation of diamagnetic EPR-silent oxo-bridged Mn₂(IV,IV) binuclear complexes (two strongly antiferromagnetically coupled Mn ions, leading to an S = 0 species), but cannot be considered as real evidence for the formation of such species.^[17]

It should be noted that high-valent oxo-bridged or mononuclear oxo or peroxo manganese species have previously been reported as intermediates in some epoxidation reactions with peracids.^[6a,22] Evidence for the formation of di- μ -oxo binuclear complexes has also been reported at the mixed-valence (III,IV) oxidation state in most cases in other catalytic oxidations mediated by Mn complexes using oxidants such as *t*Bu-OOH, H₂O₂ or hypochlorite.^[23]

On the other hand, for the brown, oxidised solutions of both complexes, no additional paramagnetic oxidised species such as mononuclear Mn^{IV} species were detected. Indeed, these species could be observed at lower temperature and no new features appear by recording EPR spectra of the oxidised brown solutions at 12 K (not shown).^[21c] Otherwise, the concomitant formation of Mn^{III} mononuclear and oxo-bridged Mn₂(III,III) binuclear species cannot be excluded because these species cannot be detected by conventional X-band EPR spectroscopy.^[24] Oxo-bridged Mn₂(III,III) binuclear species exhibit less intense visible bands than their (III,IV) or (IV,IV) analogues and are more difficult to detect by UV/Vis spectroscopy, especially when these species are present in low concentration.^[17a,25] If some of these species are present, they can also contribute to the visible absorption features, especially below 600 nm.

The absorption spectra of the brown, oxidised species of complexes 1 and 3 are unchanged after 15 min at -40 °C and are maintained after allowing the temperature to rise to 15 °C (or also to room temperature) attesting to the good stability of these oxidised species at high temperature. At this stage, for both complexes, the addition of styrene induces a decrease in the intensity of the visible bands, leading to new featureless spectra (Figure 3, dashed lines). Moreover, the initial EPR spectrum of complex 1 is fully restored in 3 h after addition of styrene, whereas for complex 3, the 16-line EPR signal vanishes after 15 min and the initial EPR spectrum of complex 3 is partially restored after 21 h [Figure 4, spectra (c-d)]. From these results, we can assert that the high-valent manganese species formed after addition of peracid are involved in the catalytic oxidation of styrene because these species are reduced again to lowvalent Mn^{II} forms after addition of the substrate, as attested by the results of UV/Vis and EPR spectroscopy. Clearly, in addition to the different possible oxidised species mentioned above, other transiently formed species (and thus not spectroscopically observable), can also be involved as catalytic active species.

Finally, analogous UV/Vis measurements performed with complex 1 in the presence of NaHCO₃ led to similar results, except that the amount of the brown, oxidised spe-

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cies increased by approximately 20% (see Figure S4 in the Supporting Information).

Based on the spectroscopy results gathered for the oxidation of complexes 1 and 3 we can certainly conclude that di- μ -oxo-bridged binuclear species are formed in solution from the mononuclear complex 3. The formation of such di- μ -oxo-bridged species most certainly involves the release of one of the two bipyridyl ligands coordinated to each Mn ion, as a consequence of steric hindrance of the pinene substituents. This is consistent with the structure found for binuclear complex 2, for which only one (–)-L ligand is bound to each metallic centre.

In addition, the different oxidised species arising from complexes 1 and 3 could be related to differences observed in the catalytic performance for both categories of catalysts, chloro vs. triflate, and also highlight the crucial importance that monodentate ligands seem to have in the fine tuning of the intermediate species formed during Mn oxidative catalysis. Indeed, due to the stronger coordinating ability of the chloride vs. triflate anions, we can infer that chloro ligands remain (at least partially) coordinated to the Mn centre in the high-valent intermediate species (see below). The role of anions as ligands during the catalytic process has been discussed in several studies carried out with Mn(salen) type of complexes bearing different counterions,^[7a,14,26] on the basis of the coordinating/noncoordinating nature of the counterions present.

Electrochemical Study

We have also investigated the electrochemical behaviour of complexes 1 and 3 in acetonitrile solution (Figure S4). The cyclic voltammogram [CV, Figure S4(a)] exhibits a oneelectron quasi-reversible redox wave at $E_{1/2} = +0.83$ V vs. SCE ($\Delta E_{\rm p}$ = 110 mV, scan rate 100 mV s⁻¹) corresponding to the $\dot{Mn}^{\rm III}/Mn^{\rm II}$ system, and a second irreversible oxidation wave at E_{pa} = +1.1 V vs. SCE with a very small intensity that possibly corresponds to the oxidation of some chloride ions (generally $E_{pa} = 1.1-1.4$ vs. SCE) that are in equilibrium.^[20a] This conclusion was supported by the addition of Bu₄NCl to a solution of complex 1, which resulted in an increase in the oxidation peak at 1.1 V (see Figure S5). The monoelectronic nature of the wave was confirmed by a bulk electrolysis of the solution at $E_{app} = +1$ V, which transfers 0.9 electron per molecule of complex and leads to the quantitative generation of $\{Mn^{III}Cl_2[(-)-L]_2\}^+$ as attested by the CV obtained [Figure S4(b)]. The redox wave $E_{1/2}$ = +0.83 V appears to be more reversible, indicating that coordination of the Cl- ligands to the Mn^{III} oxidation state is stronger. The EPR signal of the initial solution at 100 K almost completely disappears, in accordance with the formation of the X-band EPR silent high-spin Mn^{III} species (S = 2) (Figure S6).^[27]

The UV/Vis spectrum of the resulting green-olive solution (Figure S7), which is quite different to that obtained upon peracetic acid mediated oxidation (Figure 3), shows two bands at $\lambda_{\text{max}} = 388$ and 577 nm, that can be respectively be a statement of the second second

tively assigned to a Cl⁻ \rightarrow Mn^{III} ligand to metal charge transfer (LMCT) transitions on the basis of reported values for other Mn^{III} complexes with nitrogen and chloro based ligands,^[20a,28] and also to d–d Mn^{III} transitions.^[29] From this spectrum, we can infer that if {Mn^{III}Cl₂[(–)-L]₂}⁺ is present after the chemical oxidation by peracetic acid, the amount is very low. Back electrolysis of the oxidised solution at +0.5 V quantitatively restores the initial solution, demonstrating the perfect reversibility of the oxidation process.

Triflate complex **3** is oxidised at a very high potential compared with the structurally similar chloro complex **1**. Indeed, the CV of **3** in CH₃CN evidences two successive irreversible oxidation peaks at $E_{pa} = +1.3$ and +1.75 V vs. SCE (Figure S4), a difference that can be explained in terms of the stronger electron-donating capacity of chloride compared with triflate anions (or to CH₃CN if substitution of the triflate ligands by the solvent occurred). It is consequently easier to oxidise complex **1** than **3**.

Conclusions

New catalytic systems for the epoxidation of alkenes have been developed by using manganese chloro complexes as catalysts and peracetic acid as the oxidant in the presence of additives, which have been shown to increase the conversion and selectivity values remarkably, especially with NaHCO₃. We have also studied the catalytic activity of the corresponding Mn^{II} triflate compound in epoxidation of alkenes. In general, both the conversion and selectivity values of the chloro complexes have been found to be higher than those presented by the triflate complex, within the same reaction time. The Mn^{II} chloro complexes have also been investigated in epoxidation catalysis carried out in ionic liquid/solvent media and both catalysts display a remarkable effectiveness and selectivity for the epoxide product as well as a good degree of reusability.

A study of the species involved in olefin epoxidation with peracetic acid mediated by Mn chloro and triflate complexes has also been undertaken. The results reveal the crucial role of the monodentate ligands attached to the metal centre in the nature of the oxidised species found and, consequently, in the catalytic performance observed. Based on the UV/Vis and EPR spectroscopy, evidence for di-µ-oxobridged Mn₂(III,IV) binuclear species formed in situ have been unambiguously found for the triflate compound. Future studies will focus on elucidating the exact mechanism of oxygen transfer to the substrate, which remains unclear.

Experimental Section

Instrumentation and Measurements: UV/Vis spectroscopy was performed with a Cary 50 Scan (Varian) UV/Vis spectrophotometer with 1 cm quartz cells. Low-temperature control was performed with a cryostat from Unisoku Scientific Instruments, Japan. Cyclic voltammetry (CV) experiments were performed with a PAR 263A EG&G potentiostat or an IJ-Cambria IH-660 using a three-elec-

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trode cell. Pt and Glassy carbon disk electrodes (3 mm diameter) from BAS were used as working electrode, platinum wire as auxiliary and SCE as the reference electrode. All $E_{1/2}$ values reported in this work were estimated from cyclic voltammetry as the average of the oxidative and reductive peak potentials $(E_{p,a}+E_{p,c})/2$ at a scan rate of 100 mV/s. X-band EPR spectra were recorded with a Bruker EMX, equipped with the ER 4116DM and ER-4192 ST Bruker cavity for the 12 and 100 K experiments, respectively.

Materials: All reagents were obtained from Aldrich Chemical Co and were used without further purification. Reagent grade organic solvents were obtained from SDS and high purity deionised water was obtained by passing distilled water through a nano-pure Mili-Q water purification system.

Preparations: The (-)-pinene[5,6]bipyridine ligand, (-)-L,^[30] and the complexes $Mn(CF_3SO_3)_2$,^[31] $MnCl_2[(-)-L]_2$, **1**, ({ $MnCl[(-)-L]_2$, **2**, and $Mn(CF_3SO_3)_2[(-)-L]_2$, **3**,^[5d] were prepared according to literature procedures. All synthetic manipulations were routinely performed under ambient conditions.

Catalytic Epoxidation: A CH₃CN (1 mL) solution of alkene (250 μ mol), catalyst (2.5 μ mol), additive (25 μ mol) and biphenyl (250 μ mol, internal standard) was prepared in a 10 mL flask and cooled in an ice bath. Peracetic acid (32 wt.-% in dilute acetic acid with <6.0% hydrogen peroxide, 500 μ mol) was slowly added by using syringe whilst stirring. The reaction vessel was then taken out of the ice bath and allowed to progressively warm to room temp. Aliquots of the reaction were taken for analysis, filtered through a basic alumina plug, and analysed with a Shimadzu GC-2010 gas chromatography apparatus equipped with an Astec CHIRALDEX G-TA column and a FID detector, and quantification was achieved from calibration curves.

Catalytic Epoxidation in Ionic Liquid/Solvent Media: Catalyst (2.5 µmol) and substrate (250 µmol) were dissolved in [bmim]PF₆/ CH₃CN (1:1) (bmim = 1-butyl-3-methylimidazolium; 2 mL). Peracetic acid (32%, 500 µmol) was added by using a syringe over 3 min at 0 °C, then the solution was stirred at room temperature for 3 h. Upon completion, CH₃CN was removed under vacuum and the resulting suspension was washed with diethyl ether (3×5 mL) to extract the epoxide (which was then analysed by GC after addition of 250 µmol biphenyl) and the oxidant byproducts. The remaining mixture was washed with NaOH aqueous solution and dried in vacuo. A new load of substrate and oxidant dissolved in acetonitrile was then added and the mixture was stirred for an additional 3 h run. This procedure was repeated up to seven times.

Supporting Information (see footnote on the first page of this article): Enantiomeric excess values. Conversion and selectivity values obtained throughout a number of consecutive reuses of complexes 1 and 2 in the epoxidation of different substrates. Evolution of UV/ Vis spectra of complex 1 upon the addition of peracetic acid and styrene in the presence of NaHCO₃ as additive. CV of complexes 1 and 3. EPR and UV/Vis spectra of 1 before and after electrolysis.

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Ionic Liquids and Epoxidation

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Catalytic Activity of Chloro and Triflate Manganese(II) Complexes in Epoxidation Reactions: Reusable Catalytic Systems for Alkene Epoxidation

Keywords: Manganese / Epoxidation / Oxidation / Recycling / Ionic liquids



The epoxidation activity of mononuclear Mn complexes with peracetic acid has been tested in CH₃CN and in ionic liquid/ CH₃CN media. The latter conditions allow recyclability of the catalytic systems for several substrates keeping good selectivity and conversion values for up to 7–9 runs.