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Alkane hydroxylation reactions catalysed by binuclear manganese and iron complexes

David Tetard, Jean-Baptiste Verlhac *

Laboratoire de Chimie Organique et Organométallique, URA 35 CNRS, Université Bordeaux I, 351 cours de la Libération, 33405 Talence cedex, France

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Abstract

Binuclear manganese(III/IV) or iron(III/III) complexes efficiently functionalize cyclohexane using hydroperoxides or peracids as oxidants. A mechanistic study clearly demonstrate the role of dioxygen gas in these hydroxylation reactions. Moreover, it was demonstrated that the cleavage of the peroxy bond occurred mainly by homolysis.

Keywords: Alkane hydroxylation; Manganese complex; Iron complex; Hydroperoxyde; Peracid

The functionalization of saturated hydrocarbons under mild conditions has received great interest because of their inertness towards chemical conversion [1]. Among biological catalysts, cytochrome P450, which uses oxygen to hydroxylate or epoxidize various substrates, has been extensively studied [2]. More recently, non-heme iron and manganese enzymes have received a great deal of attention because they are just beginning to be characterised [3]. The interest in non-porphyrin complexes as C–H functionalization catalysts coincides with the emergence of these discoveries.

A number of oxidative catalysts, such as divalent transition metal salts [4], binuclear complexes [5], polyoxometalates [6] and Gif and other related systems [7] are known to catalyse hydroxylation of alkanes or epoxidation of alkenes with oxidants such as iodosylbenzene, *t*-butylhydroperoxide, hydrogen peroxide or oxygen. Although iron clusters and to a lesser extent manganese complexes are widely proposed as catalysts for alkane hydroxylation, the mechanism of such reactions is still controversial especially concerning the hydrogen abstracting species. Recent papers from Minisci and Arends clearly suggest that the abstraction of hydrogen occurred via oxyl or peroxyl radicals rather than via a high-valent metal-oxo species [8]. Herein we describe the synthesis of some di-μ-oxo mixed valence manganese(III/IV) dimers as well as μ-acetato, μ-oxo diiron(III/III) complexes coordinated by imidazole or pyridine containing ligands (Scheme 1). These complexes proved to be efficient catalysts for alkane hydroxylation by various oxidants (TBHP, MCPBA, etc.) under mild conditions.

* Corresponding author.

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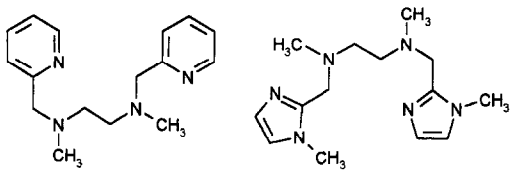

L1 L2

Scheme 1. Structures of L1 and L2.

We also report some mechanistic studies in order to try to elucidate the mechanism and particularly the role of dioxygen and the nature of the hydrogen abstracting species.

1. Experimental section

1.1. Preparation of the complexes

The preparation of L1 has been already described but involves a rather tedious procedure [9]. We obtained the free base by direct alkylation of *N,N'*-dimethylethane-1,2-diamine with 2-chloromethylpyridine. The corresponding di-μ-oxo dimanganese(III/IV) complex (**1**) was prepared as described [10]. $[Mn_2(TPA)_2O_2](ClO_4)_3$ (TPA: tris(2-pyridylmethyl)amine) (**3**) was synthesised as described previously [11]. The various $[Fe_2(L)_2O(OAc)](ClO_4)_3$ complexes are all prepared according to the procedure described by L. Que and co-workers [12]. Complex **4** is identical as the μ-acetato complex recently described by Toftlund [13].

1.2. Synthesis of N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)-1,2-ethanediamine (Mebispicen)(L1)

To a solution of *N,N'*-dimethylethane-1,2-diamine (10 mmol) and 2-picolylchloride hydrochloride (20 mmol) in water (5 ml), sodium hydroxide (5 M, 8 ml) was added at such a rate that the pH never exceeded 9.5 (total reaction time 24 h). Dichloromethane extraction of the alkaline reaction mixture and bulb-to-bulb distillation (120–130°C/0.05 mmHg) of the residue after evaporation of the dichloromethane afforded the ligand as a pale yellow oil in 62% yield. NMR spectra were recorded on a Brucker AC250 spectrometer. EPR spectra for dinuclear manganese complexes were recorded at 4 K in 0.1 M TEAP acetonitrile solutions on a Brucker ER200 D spectrometer. The mixed valence III/IV complexes displayed a 16-line spectrum centered at $g = 2.009$ for **1** and 2.017 for **2**.

1.3. Synthesis of N,N-dimethyl-N,N' bis((1-methyl imidazol-2-yl)methyl)-1,2-ethanediamine Mebisim (L2)

1-Methyl-2-chloromethylimidazole [14] was added portion-wise (40 mmol) to a solution of *N,N'*-dimethyl-1,2-ethanediamine (20 mmol) and triethylamine (80 mmol) in acetonitrile (30 ml). The suspension was refluxed for 2 h and evaporated to dryness. Inorganic salts were precipitated by diluting the residue in a chloroform/ethanol mixture. The ligand was isolated as the free base after crystallisation from cyclohexane: Yield 47%, m.p. 102–104°C. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 6.88 (*d*, 2H), 6.82 (*d*, 2H), 3.65 (*s*, 4H), 3.55 (*s*, 4H), 2.5 (*s*, 6H), 2.16 (s, 6H). Anal. Calcd. for $C_{14}H_{24}N_6$: C, 60.84; H, 8.75; N, 30.41. Found: C, 60.56; H, 8.74; N, 30.16.

1.4. $[Mn_2(L2)_2O_2](ClO_4)_3$ (2)

Using the general procedure described by Toftlund, we obtained crude complex **2** as the perchlorate salt [10]. It was recrystallized from an acetonitrile/dichloromethane mixture to afford green black crystals in 32% yield. Anal. calcd. for $[Mn_2C_{28}H_{48}N_{12}O_2](ClO_4)_3 \cdot H_2O$: C, 33.26; H, 4.95; N, 16.62; Cl 10.88; Mn, 10.52. Found C, 34.15; H, 4.98; N, 16.72; Cl 10.73; Mn, 10.50. UV/VIS (H_2O, 25°C) λ (nm): 595, 408 (sh).

1.5. $[Fe_2(L1)_2O(OAc)](ClO_4)_3$ (4)

A solution $Fe(ClO_4)_3 \cdot 10H_2O$ (0.537 g, 1.0 mmol) in MeOH (2 ml) was slowly added to a mixture of the ligand (0.270 mg, 1.0 mmol) and Et_3N (0.150 g, 1.5 mmol) dissolved in MeOH (30 ml). To this red-brown solution $NaOAc \cdot 3H_2O$ (68 mg, 0.5 mmol) was added. The resulting red-brown powder was collected by filtration (0.282 g, yield 55%). Anal. calcd. for $[Fe_2C_{34}H_{47}N_8O_3](ClO_4)_3$: C, 39.8; H, 4.6; N, 10.9. Found C, 39.76; H, 4.72; N, 10.64. UV/VIS (CH_3CN, 25°C) λ (nm), $\epsilon \times 10^{-3}$ ($M^{-1} \cdot cm^{-1}$): 464, 1.18; 512, 0.77; 678, 0.15

1.6. $[Fe_2(L2)_2O(OAc)](ClO_4)_3$ (5)

The same procedure as for complex **4** allowed us to obtain complex **5** in 43% yield as an olive-green powder. Anal. calcd. for $[Fe_2C_{30}H_{51}N_{12}O_3](ClO_4)_3 \cdot CH_3OH$: C, 34.8; H, 5.2; N, 15.7. Found C, 34.7; H, 5.3; N, 15.3. UV/VIS (CH_3CN, 25°C) λ (nm), $\epsilon \times 10^{-3}$ ($M^{-1} \cdot cm^{-1}$): 440, 1.2; 500, 0.55; 638, 0.2

1.7. General procedure for alkane hydroxylation

In a typical reaction, alkane (3.75 mmol) was allowed to react with TBHP (660 μmol) in acetonitrile (5 ml) in the presence of the manganese catalyst (3.75 μmol; cyclohexane/TBHP/catalyst ratio: 1000:175:1) at 25°C in air atmosphere. The reaction was monitored by GC analysis, and the amounts of both alcohol and ketone were estimated with the aid of an internal standard (anisole). The reaction was completed after ca. 8 h for most of the complexes. In some experiments, TBHP was replaced by CHP (cumyl hydroperoxyde), MPPH (2-methyl-1-phenyl-2-propyl hydroperoxide), MCPBA (3-chloroperbenzoic acid), PPAA (phenylperacetic acid) or PDA (perdodecanoic acid).

2. Results and discussion

In this study, complexes **1**, **2** and $Mn_2O_2TPA_2(ClO_4)_3$ (TPA: tris(2-pyridylmethyl)amine) (**3**) were tested as catalysts. The formation of cyclohexanol (CyOH) and cyclohexanone (CyONE) was followed as a function of time. The shape of the curves obtained for complex **1** displayed a rather long induction period (ca. 4 h) followed by a rapid oxidation reaction (Fig. 1). The same shape was obtained when small amounts of TBHP were added every 2 h for 8 h (the total TBHP volume being equal to the volume in the typical procedure). More interesting was the fact that the catalyst **1** was not altered during the catalytic cycle, as a second addition of TBHP after 20 h doubled the amount of cyclohexanol and cyclohexanone (Fig. 2A), without the presence of a lag period (Fig. 2B). Thus, the activity of the catalyst appeared not to be modified by oxidative conditions. This stability was not observed for complex **2**, but the reaction is more rapid as completion occurred in 2 h (Fig. 3). Moreover, the oxidative ability and the stability of complex **1** was not affected by the presence of 7.5 mmol of water (water/catalyst ratio: 2000) as a second addition of TBHP produced the same amount of hydroxylation products. The only detectable effect of water was a diminution of the initial rate of the reaction. We also discovered that, like for most iron catalysts used in

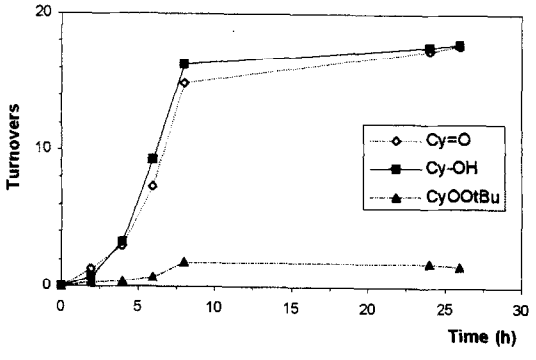

Fig. 1. Time course of oxidation of cyclohexane in the presence of TBHP and complex **1** (Cy=O: cyclohexanone; Cy–OH: cyclohexanol; CyOOtBu: *t*-butylcyclohexyl peroxide).

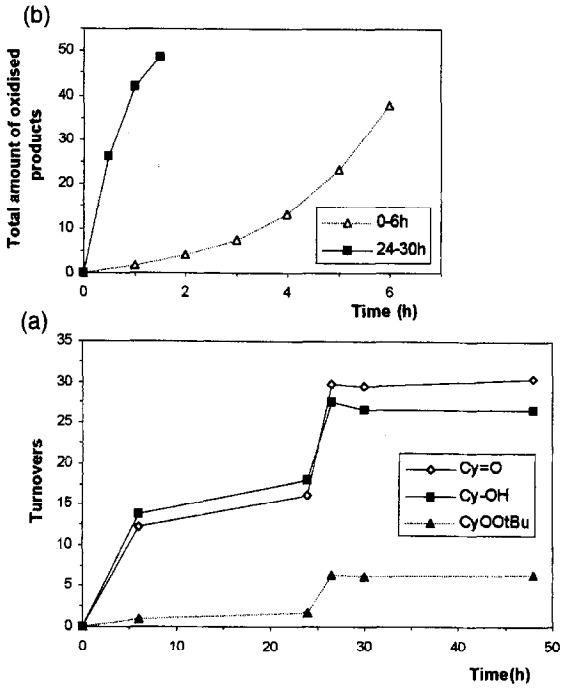

Fig. 2. (a) Time course of oxidation of cyclohexane in the presence of TBHP and complex **1** (a second addition of TBHP is performed after 24 h). (b) Comparison between the initial rate before (0–6 h) and after the addition of a second amount of TBHP (24–30 h) in the presence of complex **1** (the amount of oxidized products are referred to CyOH + CyONE + CyOOtBu).

alkane hydroxylation reactions, complexes **4** and **5** give a very rapid reaction (completion in a few minutes). But they are also less stable as a

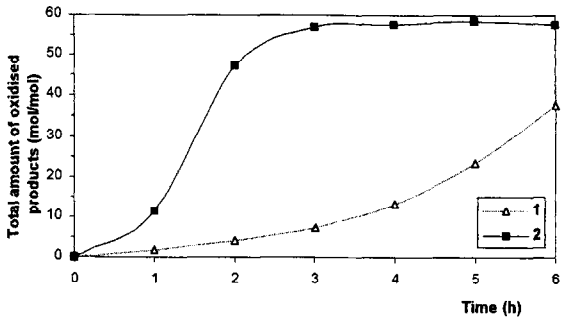

Fig. 3. Comparison between the catalytic activity of complexes **1** and **2** towards oxidation of cyclohexane.

second addition of TBHP results in a loss of about 40% of the activity. Addition of dimethylsulfide (Me_2S) inhibited the formation of CyOH and CyONE (Table 1). Addition of acetic acid (AcOH) or sodium acetate to complex **1** greatly accelerated the formation of the oxidation products (completion of the reaction in about 2 h) without modifying the CyONE/CyOH ratio (Fig. 4), whereas 1-methylimidazole (1-MeIm) accelerated the reaction with concomitant modification of the CyONE/CyOH ratio (3 : 1). In the presence of a large excess of CH_2Br_2, cyclohexylbromide (CyBr) could be detected, indicating the involvement of cyclohexyl radicals in this reaction. Small amounts of *t*-butylcyclohexyl peroxide (CyOOtBu) could also be

Table 1
Product distributions for the manganese catalysed TBHP oxidation of cyclohexane

Catalyst [a]	Total reaction time,(h)	Products [b]				Yield [c]
		CyOH	CyONE	CyOOtBu	Other	
1	12	16	16	2	–	28
1 [d]	24	19	17	3	–	32
1(+AcOH)	2	17	17	2	–	30
1(+Me_2S)	12	9	3	0.5	27(Me_2SO)	8
1(+1-MeIm)	6	7	20	10	–	32
1(+CH_2Br_2)	24	14	13	1	3(CyBr)	23
2	12	14	18	1	–	29
3	12	2	2	–	–	3
4	1	17	19			33 [e]
5	1	4.5	5.5			11

[a] When specified, various compounds were added (μmol): AcOH (2.6), Me_2S (476), 1-MeIm (2.2), CH_2Br_2 (7000).
[b] Moles of product per mole of catalyst (abbreviations appeared in the text).
[c] Yield based on TBHP consumed.
[d] Gradual addition of TBHP throughout reaction.
[e] Reaction completed in 30 min.

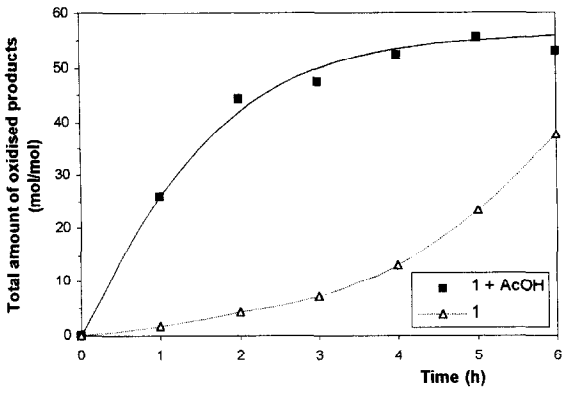

Fig. 4. Effect of the addition of acetic acid to complex **1**.

detected in the reaction mixture. This product was not detected by R. Fish in the TBHP mediated oxidation of cyclohexane catalysed by the dimeric manganese complex $Mn_2O(AcO)(tmima)(ClO_4)_3$ (tmima: tris[(1-methylimidazol-2-yl)methyl]amine) [5], but was systematically present in the anaerobic iron complex catalysed oxidation of cyclohexane reported by L. Que Jr. [5]. The catalytic efficiency of the manganese as well as the iron complexes described herein is comparable to previously reported catalysts, the differences between stability of iron vs. manganese complexes have been also previously observed [5]. The major difference is that manganese complexes, except complex **2**, displayed rather low initial rate.

The role of acetic acid or acetate is to catalyse the formation of the active catalyst as the yield and the product distribution are not modified. The acetate presumably acts as a bridging ligand for the dimanganese complex. The entity thus obtained has a more labile coordination position on the metal.

The effect of 1-methylimidazole is quite different, because the distribution of the product was dramatically modified, particularly concerning the amount of CyOOtBu.

Substitution of the pyridine moieties of the ligand by 1-methyl imidazole heterocycle greatly enhanced the reaction which was completed in about 2 h, without affecting the yield of the oxidation products. On the other hand, modification of the geometry of the ligand by using the tripodal TPA unit (**3**) dramatically inhibited the oxidation of cyclohexane.

Other experiments were performed in order to confirm the role of dioxygen in the trapping of alkyl radicals formed by hydrogen abstraction. As it is difficult to purge completely the reaction vessel by a vigorous bubbling of argon gas without evaporation of the substrate (cyclohexane), we used adamantane as a less volatile alkane. In the presence of **1** and TBHP under an air atmosphere, we observe the formation of adamantan-1-ol (12 turn overs), adamantan-2-ol (2 t.o.) and adamantanone (2 t.o.). Normalized C_3/C_2 selectivity values (10) were comparable with other metallo-porphyrin and non-porphyrin oxidation systems [15]. It was not possible to purge continuously the reaction mixture with argon without complete evaporation of the solvent because of the large reaction time required. Thus, we performed this experiment with the more active complex **4**. This

Table 2
Influence of the oxidant on the oxidation of cyclohexane catalysed by complex **1**

Oxidant(reaction time)	CyONE	CyOH	$C_6H_5CH_2OH$	C_6H_5CHO	$C_6H_5(CH_2)_2C_6H_5$
TBHP (24 h)	16	18	–	–	–
CHP (24 h)	8	12	–	–	–
MPPH (6 h)	0	0	6	29	
MPPH (6 h) [a]	0	0	15	21	1
MCPBA (6 h)	0	8	–	–	–
PPAA (24 h)	0	1.6	1.5	16	0
PDA (6 h)	2.1	5.4	–	–	–

[a] This reaction was performed under nitrogen.

reaction was completely inhibited when performed under argon (under air, the adamantan-1-ol, adamantan-2-ol, adamantanone ratio was 5.4 : 0.6 : 1.2).

We also performed reactions with various oxidants. The results are reported in Table 2. The use of cumylhydroperoxide (CHP) results in a decrease of the yield of oxidation products. This diminution was even more dramatic when we used MPPH as oxidant. This hydroperoxide has been suggested by Arends to check for participation of alkoxy radicals as with MPPH extremely rapid β-scission led to stable benzyl radical. The only detectable products were benzaldehyde, benzyl alcohol and traces of 1,2-diphenylethane. In the presence of MCPBA we obtained only cyclohexanol in relatively low yield (no cyclohexanol was formed if the metal catalyst is omitted). When replaced by phenyl peracetic acid, the amount of cyclohexanol was even lower, and we obtained mostly benzaldehyde (Table 2).

The primary kinetic isotope effect (KIE) was measured for the hydroxylation of cyclohexane (C_6H_{12}/C_6D_{12}) with complex **1** and complex **4** in the presence of TBHP. We determined k_H/k_D values of 4.6 and 3.7 for CyOH formation respectively with **1** and **4**. These values are within the range of those found in other non-porphyrin systems [16].

Due to the crucial role of dioxygen and to the high primary kinetic isotope effect, it is clear that the first step of these hydroxylation reactions is the hydrogen abstraction from the alkane. In the case of cyclohexane, the cyclohexyl radical reacts further with oxygen out of the solvent cage, as postulated by R. Fish, to produce cyclohexylperoxyl radical (CyOO·). As suggested previously by Arends the roughly equal yields of CyOH and CyONE could be explained by a Russel-type termination of these secondary peroxyl radicals [17]. CyOOH could also be a valuable intermediate in these reactions as its well-known transition metal catalysed decomposition gives a mixture of CyOH and CyONE. Detection of CyOOH is tedious because this hydroperoxide is very rapidly decomposed in the injector of the GC apparatus. But even if the reaction mixture is treated with a NaI solution at the end of the reaction (selective reduction of CyOOH to CyOH) before analysis, we could not detect a modification of the CyOH/CyONE ratio. Formation of dialkylperoxide (CyOOtBu) has been proposed to occur via an Haber-Weiss mechanism leading to tBuO · radicals. It has been previously suggested that this product is not a precursor for the formation of CyONE, but rather a competitive oxidation product. Effectively, TBHP oxidation of CyOOtBu catalyzed by **1** produces 30 mmol CyONE (without CyOH) and 90 mmol of cyclohexene oxide per mmole of **1** (this reaction did not proceed if TBHP was omitted). The formation of this epoxide could be explained by β-hydrogen abstraction and rearrangement of the peroxide. When cyclohexane is in excess, this process is not favoured due to steric hindrance; as we never detected any trace of this epoxide during the oxidation of cyclohexane, this dialkyl peroxide can hardly be a precursor for the formation of cyclohexanone.

The active catalytic species is not the di-μ-oxo manganese complex because the induction period disappears when a second dose of TBHP is added. The active complex is formed during the reaction and persists after all TBHP has been consumed. When the reaction mixture is trapped at low temperature (4 K) and analysed by EPR spectroscopy, we observe the rapid apparition of a $g = 2$ centered singlet and a concomitant slow diminution of the 16-line signal. At the end of the reaction (24 h) we only observed a residual 6-line signal probably due to manganese(II) species. During the reaction there is an overall diminution of the visible absorption. These observations are consistent with the accumulation of reduced manganese species during catalysis. A single electron reduction of the manganese(III/IV) cluster by TBHP could explain the diminution of the visible absorption, the decrease of the 16-line signal as manganese(III/III) complexes are EPR silent

and the apparition of an organic radical signal centered at $g = 2$ (probably tBuOO·). This hypothesis is also consistent with the fact that when the pyridine ring of the bispicen ligand is substituted by an electron releasing group (ethoxy) at the 4 position we observe a low catalytic activity although this activity is enhanced by electron withdrawing groups (nitro). As previous cyclic voltametry results displayed a higher redox potential for the III/III ↔ III/IV quasi-reversible process with the latter complex [18], the one-electron reduction process would be favoured for the nitro-substituted complex. This influence of the redox potential of the ligand on the initial step of the Haber-Weiss mechanism (reduction of the metal complex) has been previously postulated by Que to rationalize the formation of dialkyl peroxide (CyOOtBu) [5].

In the case of iron complexes, no significant changes were observed by UV-visible spectroscopy during the reaction.

We performed trapping experiments with Me_2S in order to check for the participation of high-valent metal oxo species resulting from peroxide heterolysis as suggested by Labeque [19]. Formation of dimethyl sulfoxide could also arise from nucleophilic substitution on a metal bound hydroperoxide, the metal acting as a Lewis acid catalyst [20].

The major controversial point in these TBHP mediated oxidation reactions is the nature of the oxidising species. As a high valent metal complex as well as peroxyl or oxyl radicals could abstract a hydrogen from alkane, many mechanisms have been postulated. Due to the absence of oxidation products from cyclohexane when MPPH or PPAA are used as oxidants, it is clear that the cleavage of the peroxy bond occurred mainly by homolysis [8,21]. The hydroperoxide (MPPH) or peracid (PPAA), when cleaved homolytically, decomposed very rapidly by β-scission or by decarboxylation, respectively, to produce a stabilised benzyl radical. This radical is unable to abstract a hydrogen atom from cyclohexane. One major difference observed from previously reported results from Arends is the very low yield of 1,2-diphenylethane even in the absence of O_2. This result could be explained either by the slow behaviour of the reaction of hydroperoxide with **1** leading to a very low steady-state concentration of benzyl radicals or, by monoelectronic oxidation of this radical by a high-valent metal complex arising from homolysis of the peroxy bond. This reaction could occur within the solvent cage and the resulting benzyl cation could further react with water or with the hydroxo ligand present on the metal (this ligand resulted from homolysis of the hydroperoxide) to give benzyl alcohol and benzaldehyde. In this electron transfer process, the metal is reduced and thus unable to abstract a hydrogen from cyclohexane. Formation of carbocationic intermediates has been previously suggested during oxidation of 1,1-dimethylcyclopropane catalysed by methane monooxygenase [22].

There are significant differences between manganese and iron complexes. Omitting the higher stability of manganese complexes, the iron derivatives are generally more reactive but this reactivity is inverted when pyridine ligands are replaced by imidazole. The mechanisms involved are probably different for manganese and iron complexes. One hypothesis could be the different behaviour towards reduction of the native complex. One electron reduction potentials are generally shifted to more positive values for dimanganese(III/IV) complexes compared to diiron(III/III) complexes. For instance values ranging from -0.65 to -0.75 V vs. SCE for the reduction of various bispicen type diiron(III/III) complexes [23] have to be compared with the reversible one-electron potential for reduction of **1** which occurred at 0.22 V vs. SCE [18].

Further experiments will be reported in order to study the influence of the electron density on the metal relative to the oxidising power towards alkanes. Our interest will be to try to modulate the ratio of heterolytic versus homolytic cleavage of the peroxy bond, as it has

been previously reported that minor changes in the structure or the oxidation state of the metal allowed a control of this ratio [21].

Acknowledgements

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