

DOI:10.1002/ejic.201500576

# Catalytic Oxidation of Alkanes and Alkenes by $H_2O_2$ with a $\mu$ -Oxido Diiron(III) Complex as Catalyst/Catalyst Precursor



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Keywords: Monooxygenases / Iron / Lithium / Oxidation / Homogeneous catalysis

A new  $\mu$ -oxo diiron(III) complex of the lithium salt of the pyridine-based unsymmetrical ligand 3-[(3-{[bis(pyridin-2-ylmethyl)amino]methyl}-2-hydroxy-5-methylbenzyl)(pyridin-2-ylmethyl)amino]propanoate (LiDPCPMPP), [Fe<sub>2</sub>( $\mu$ -O)-(LiDPCPMPP)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, has been synthesized and characterized. The ability of the complex to catalyze oxidation of several alkanes and alkenes has been investigated by using CH<sub>3</sub>COOH/H<sub>2</sub>O<sub>2</sub> (1:1) as an oxidative system. Moderate activity in cyclohexane oxidation (TOF = 33 h<sup>-1</sup>) and good activity in cyclohexene oxidation (TOF = 72 h<sup>-1</sup>) were detected. Partial retention of configuration (RC = 53 %) in *cis*- and

### Introduction

Oxidation of saturated, unsaturated, and aromatic hydrocarbons to oxygen-containing compounds are industrial processes of considerable importance, generating much chemical feedstock as well as fine chemicals. In nature, similar biological C–H bond oxidation reactions are effected by heme and non-heme iron metalloenzymes that are capable of activating dioxygen. Mononuclear oxygenases such as the heme-based cytochrome P-450 monooxygenases and non-heme 2His,1carboxylate-dioxygenases (Rieske and others, Figure 1b) have been extensively studied, and the mechanisms of these enzymes are relatively well under-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201500576.

trans-1,2-dimethylcyclohexane oxidation, moderate  $3^{\circ}/2^{\circ}$  selectivity (4.1) in adamantane oxidation, and the observation of a relatively high kinetic isotope effect for cyclohexane oxidation (KIE = 3.27) suggest partial metal-based oxidation, probably in tandem with free-radical oxidation. Low-temperature UV/Vis spectroscopy and mass spectrometric studies in the rapid positive detection mode indicate the formation of a transient peroxido species,  $[Fe_2(O)(O_2)-(LiDPCPMPP)_2]^{2+}$ , which might be an intermediate in the metal-based component of the oxidation process.

stood.<sup>[1]</sup> In contrast, the mechanisms of dinuclear nonheme iron oxygenases, for example soluble methane monooxygenase (sMMO),<sup>[2–5]</sup> which contains a dinuclear active site (Figure 1a), are not known to the same detail. A high-valent diamond-core  $\text{Fe}^{IV}_2(\mu\text{-O})_2$  intermediate (intermediate Q) has been identified for sMMO, and this is the active species involved in oxidizing substrates.<sup>[6–11]</sup> It is believed that carboxylate groups (glutamate) in the first coordination sphere and the non-coordinating groups in the second coordination sphere play important roles in this arduous task.<sup>[5a–5c]</sup>



Figure 1. Schematic depiction of the active sites of (a) the hydroxylase subunit (MMOHox) of soluble methane monooxygenase (inactive diferric form); (b) taurine: $\alpha$ -ketoglutarate dioxygenase (TauD), containing the characteristic His<sub>2</sub>Asp triad found in many non-heme iron oxygenases.<sup>[10b]</sup>



Considering the importance of oxidation reactions, the development of catalysts for such processes that are based on cheap and readily available metals and oxidants is a very active research area.<sup>[12]</sup> Drawing inspiration from the iron oxygenases, much attention has been paid to iron-based catalysts. Several bio-inspired heme and non-heme catalysts for oxidation processes have been developed. Reactive intermediates such as Fe<sup>IV</sup>=O and Fe<sup>V</sup>=O species have been captured and characterized in bio-inspired chemical oxidation systems and have been postulated as key active intermediates in the oxidation processes.<sup>[13]</sup>

There are many well-characterized bio-inspired mononuclear iron complexes that have been used as effective catalysts for oxidation of different hydrocarbons with hydrogen peroxide, peracids, or O2.<sup>[14a]</sup> The mechanisms of some of these reactions are relatively well understood.<sup>[14a-14c]</sup> Dinuclear iron complexes have been studied mainly as structural or spectroscopic models of the active center of sMMO or its transient intermediates P (a peroxide Fe<sup>III</sup>-O-O-Fe<sup>III</sup> species) and Q (vide supra).<sup>[15,16]</sup> Catalytic hydrocarbon oxidation by dinuclear iron complexes is much less well studied, and there are relatively few such systems where hydrogen peroxide is used as the ultimate oxidant. An early study on the catalytic system [Fe<sup>III</sup><sub>2</sub>O(Phen)<sub>2</sub>- $(H_2O)_2]^{4+}/H_2O_2$  was the first to demonstrate involvement of a metal-based mechanism for a non-heme catalyst.<sup>[17]</sup> This dinuclear complex was found to catalyze alkane oxidation with partial retention of configuration (RC = 30-70%) in the oxidation of *trans*-dimethylcyclohexane and also partial retention of the cyclopropane ring in the oxidation of the radical-clock substrate trans-1-methyl-2-phenylcyclopropane. Although better selectivity is usually achieved when *m*-CPBA is used as oxidant,  $H_2O_2$  is preferable as a green, cheap, and biomimetic oxidant. However, freeradical reactions often complicate the selectivity in systems where hydrogen peroxide is used as oxidant, and the catalase-like decomposition/disproportionation of  $H_2O_2$  (2 $H_2O_2 \rightarrow O_2 + 2H_2O$ ) in the presence of iron diminishes its efficiency.<sup>[18]</sup> Thus, the establishment of the oxidation mechanism is a difficult task in systems based on hydrogen peroxide, and reliable proof of metal-based mechanisms in such systems have been presented only in a few cases.[19]

In the most interesting synthetic systems using  $H_2O_2$  as oxidant, turnover numbers (TON) are about 30–50, while the turnover frequencies (TOF) evaluated by TON/time are only moderate (TOF = 2–20 h<sup>-1</sup>).<sup>[20,21]</sup> Mechanistic data on hydrocarbon oxidations catalyzed by Fe<sub>2</sub>O complexes using  $H_2O_2$  as oxidant are scarce and indirect. In some systems the active species is a mononuclear complex formed through cleavage of the dinuclear complex,<sup>[22,23]</sup> while it is likely that a dinuclear µ-oxo complex of iron with 1-carboxymethyl-4,7-dimethyl-1,4,7-triazocyclononane catalyzes methane oxidation to MeOH with participation of HO' radicals.<sup>[24,25]</sup> More reliable evidence for metal-based mechanisms have been obtained using *m*-CPBA as oxidant, for example in studies with efficient diiron complexes having polydentate N-donor ligands.<sup>[26–28]</sup> To improve the selectivity of the oxidation reaction, in most studies a large surplus of hydrocarbon has been used in comparison to oxidant. This leads, unavoidably, to very low hydrocarbon conversions and makes such systems impractical. Better conversion has been achieved in systems where the concentrations of hydrocarbons and  $H_2O_2$  are comparable. For example, Wang reported stereospecific epoxidation of alkenes with up to 500 turnovers using an Fe<sup>III</sup>–O–Fe<sup>III</sup> catalyst and 1:1 substrate/H<sub>2</sub>O<sub>2</sub> ratio,<sup>[22]</sup> and Stack suggested [{(Phen)<sub>2</sub>(H<sub>2</sub>O)Fe<sup>III</sup>}<sub>2</sub>(µ-O)]/MeCOOOH as an efficient catalytic epoxidation system at high substrate concentration.<sup>[23]</sup>

Recent studies have shown that phenolate donors may be very useful for the design of bio-inspired ligands that support oxidation catalysis by dinuclear iron complexes.<sup>[26,29,30]</sup> The (non-innocent) phenolate ligands are capable of stabilizing the high-valent metal intermediates, forming coordinated phenoxyl radical moieties and can survive hydrocarbon oxidation.<sup>[26,31]</sup> The integrity of diiron complexes in dilute catalytic solutions may be ensured by design of a rigid polydentate dinucleating ligand that provides a scaffold for the dinuclear entity.<sup>[32]</sup> We have previously investigated the ability of the µ-oxo diiron(III) complex [{Fe(H-IPCPMP) $_{2}(\mu-O)(Piv)$ ]ClO<sub>4</sub> (H<sub>2</sub>IPCPMP = 2-{*N*-isopropyl-N-[(2-pyridyl)methyl]aminomethyl}-6-{N-(carboxymethyl)-N-[(2-pyridyl)methyl]aminomethyl}-4-methylphenol; Piv = Pivalate) to effect alkane oxidation.<sup>[33]</sup> This catalyst showed moderate activity in cyclohexane oxidation, using  $H_2O_2$  as the oxidant, and evidence suggests that both metal-based and radical mechanisms were involved in the oxidation reaction.

Here we report the synthesis and characterization of a new carboxylate-containing unsymmetric ligand, lithium 3-[(3-{[bis(pyridin-2-ylmethyl)amino]methyl}-2-hydroxy-5-methylbenzyl)(pyridin-2-ylmethyl)amino]propanoate (LiDPCPMPP), and the tetranuclear Fe<sub>2</sub>Li<sub>2</sub> complex [Fe<sup>III</sup><sub>2</sub>O(LiDPCPMPP)<sub>2</sub>] (1) containing a  $\mu$ -oxo diiron(III) moiety. Complex 1 is capable of functioning as a catalyst/ catalyst precursor that promotes efficient oxidation of al-kanes and alkenes, using H<sub>2</sub>O<sub>2</sub> as terminal oxidant.

### **Results and Discussion**

### Synthesis and Characterization of Ligand and Complex

The new ligand lithium 3-[(3-{[bis(pyridin-2-ylmethyl)amino]methyl}-2-hydroxy-5-methylbenzyl)(pyridin-2-ylmethyl)amino]propanoate (LiDPCPMPP) with an  $N_5O_2$ donor set was synthesized from 2-hydroxy-3-(hydroxymethyl)-5-methylbenzaldehyde (**a**) in an overall 54% yield (Scheme 1). Condensation of dipicolylamine [bis(pyridin-2ylmethyl)amine] with **a**, followed by reduction with NaBH(OAc)<sub>3</sub>, led to the formation of 2-{[bis(pyridin-2-ylmethyl)amino]methyl}-6-(hydroxymethyl)-4-methylphenol (**b**). The latter product was treated with an excess of thionyl chloride to convert the primary alcohol moiety to a chloride, which could be substituted by ethyl 3-[(pyridin-2-ylmethyl)amino]propanoate (**c**) to form the corresponding



Scheme 1. Synthetic route to LiDPCPMPP.

ethyl ester of the DPCPMPP ligand, ethyl 3-[(3-{[bis-(pyridin-2-ylmethyl)amino]methyl}-2-hydroxy-5-methylbenzyl)(pyridin-2-ylmethyl)amino]propanoate (**d**), in the presence of triethylamine, using ethanol as solvent. The ligand LiDPCPMPP was isolated after the hydrolysis of the DPCPMPP ester **d** by LiOH in methanol.

Addition of one equivalent of iron(III) perchlorate to a methanol solution of LiDPCPMPP, followed by continuous stirring for one hour led to the formation of the dark purple complex 1, which was characterized by IR and UV/Vis spectroscopy, as well as X-ray crystallography (Scheme 2). An acetonitrile solution of complex 1 exhibits three absorption maxima at around  $\lambda_{\text{max}} = 504 \text{ nm}$  ( $\varepsilon = 1325 \text{ m}^{-1} \text{ cm}^{-1}$ ), 345 nm ( $\varepsilon = 3885 \text{ m}^{-1} \text{ cm}^{-1}$ ), and 296 nm ( $\varepsilon = 5760 \text{ m}^{-1} \text{ cm}^{-1}$ ) (Figure S3). The 504 nm peak may be assigned to the phenolate-to-Fe<sup>III</sup> p $\pi$ -to-d $\pi$ \* LMCT band.<sup>[34]</sup> The peak at 345 nm is in the so-called "oxo dimer region" and is characteristic of the Fe-O-Fe moiety, as has been observed for similar (µ-oxo)diiron(III) complexes.<sup>[35,36]</sup> Moreover, the absorption maximum at 296 nm can be attributed to the highest energy band arising from the oxo  $p_z$  to Fe  $d_{z^2}$  charge transfer of  $\sigma$  symmetry, as has been discussed by Kurtz, Reem et al.<sup>[35]</sup>

The IR spectrum of 1 shows characteristic resonances for a bridging carboxylate and a Fe–O–Fe unit.<sup>[36]</sup> The difference between the asymmetric and symmetric stretching frequencies ( $\Delta v = v_{asym} - v_{sym}$ ) of the carboxylate moieties in the IR spectrum has been used extensively to understand the ligation mode.<sup>[36]</sup> Empirical correlation indicates that a value of  $\Delta v$  relates to unidentate coordination of a carboxylate moiety when  $\Delta v > 200 \text{ cm}^{-1}$ , or bridging when it is  $100 < \Delta v < 200 \text{ cm}^{-1}$ . The separation between the two sharp peaks at 1474 and 1168 cm<sup>-1</sup> ( $306 > \Delta v > 200 \text{ cm}^{-1}$ ) thus suggests a unidentate mode for the carboxylate moiety.



Scheme 2. Synthetic route to  $[Fe_2(\mu-O)(LiDPCPMPP)_2]^{2+}$ .

Moreover, the sharp bands at 845 and 800 cm<sup>-1</sup> in the IR spectrum can be assigned to asymmetric and symmetric Fe– O stretching frequencies of the Fe–O–Fe unit, respectively.<sup>[35]</sup>

The mass spectrum of **1** was found to exhibit two major peaks at m/z = 580.2 and 1195.4 (Figure 4, vide infra). Investigation of the isotope patterns reveals that the peak at 580.2 originates from a doubly charged species consistent with the formulation [{Fe<sup>III</sup><sub>2</sub>( $\mu$ -O)(LiDPCPMPP)\_2}]<sup>2+</sup> and that at 1195.4 corresponds to a singly charged species with the formulation [{Fe<sup>III</sup><sub>2</sub>( $\mu$ -O)(LiDPCPMPP)\_2Cl}]<sup>+</sup> (Figure 5, vide infra).

The zero-field <sup>57</sup>Fe Mössbauer spectrum of the dark purple microcrystalline powder of **1** (Figure S1) has one quadrupole doublet with  $\delta = 0.48$  mm/s and  $\Delta E_Q = 1.40$  mm/s, consistent with the presence of high-spin Fe<sup>III[37]</sup> and in close agreement with observed Mössbauer spectra of similar dinuclear Fe<sup>III</sup> complexes.<sup>[36,38]</sup> A magnetic susceptibility measurement (SQUID) in the temperature range from 295 to 2 K revealed very strong antiferromagnetic coupling between the Fe<sup>III</sup> centers with an exchange coupling constant J = -427 cm<sup>-1</sup> [using the Hamiltonian  $\hat{H} =$ 

3592



 $-2J\hat{S}_1\hat{S} + g\mu_B \vec{B}(\vec{S}_1 + \vec{S}_2)$ ; see Supporting Information for details].

### Crystal and Molecular Structure of 1

Slow vapor diffusion of diethyl ether into an acetonitrile solution of 1 led to the formation of dark purple crystals suitable for X-ray diffraction. The selected distances and angles as well as the crystallographic data are collated in Tables 1 and 3, respectively. The crystal structure (Figure 2) confirms that complex 1 is a tetranuclear  $Fe_2Li_2$  complex consisting of a central ( $\mu$ -oxo)diiron(III) unit with two equivalents of the unsymmetric ligand LiDPCPMPP in each molecule.

Each dinucleating DPCPMPP- ligand coordinates a heterodimetallic Fe<sup>III</sup>Li<sup>I</sup> entity that is bridged by the central phenolate group of the ligand, and the terminal carboxylate entity of each ligand is triply coordinated so that one carboxylate oxygen atom coordinates in *syn* fashion to the iron ion of the "opposite" FeLi entity, while the second carboxylate oxygen bridges the two lithium ions. The immediate coordination environments of the two iron and the two lithium ions in complex 1 thus constitute a tetranuclear heterometallic Fe-O-Li-OCO core that is, to the best of our knowledge, unprecedented (Figure 2b). The observed pentadentate coordination mode of Li in this structure is typical for lithium ions;<sup>[39]</sup> the lithium ions are approximately trigonal bipyramidal, with  $\tau$  values of 1.01 (Li1) and 0.76 (Li2).<sup>[40]</sup> The nearest precedents for similar heterometallic core structures are Mn/Ca clusters such  $[Mn_{13}Ca_2O_{10}(OH)_2(OMe)_2(O_2CPh)_{18}(H_2O)_4]$ , which are bio-inspired models of the oxygen-evolving complex of photosystem II.<sup>[40]</sup>

The Fe<sup>III</sup> centers are in N<sub>3</sub>O<sub>3</sub> coordination environments with distorted octahedral geometries. The central phenoxide moiety of each DPCPMPP<sup>-</sup> ligand is coordinated to one corresponding Fe<sup>III</sup> center in complex **1**, with slightly different Fe–O(phenoxide) bond lengths [1.996(3) Å for Fe1–O1(phenoxide) but 1.985(3) Å for Fe2–O5(phenoxide)]. A shorter Fe<sup>III</sup>–O(phenoxide) bond length [1.933(2) Å] was observed by Jarenmark et al. for the complex [{Fe(H–IPCPMP)}<sub>2</sub>( $\mu$ -O)(Piv)]ClO<sub>4</sub>.<sup>[33]</sup> The phenoxide moieties ligated to Fe<sup>III</sup> can be useful in stabilizing higher oxidation states (IV or even V) of the metal, but may, in principle, also act as non-innocent ligands to form coordinated phenoxyl radical moieties (vide supra).<sup>[7,42,43]</sup>

The distance between the Fe<sup>III</sup> centers, 3.58(1) Å, and the Fe–O–Fe angle of 166.9(4)° are due to the absence of a bridging carboxylate in **1**, but they match well with those observed for complexes [Fe<sub>2</sub>O(H<sub>2</sub>O)<sub>2</sub>(BPG<sub>2</sub>E)]X<sub>2</sub> (3.57/170.4) {H<sub>2</sub>BPG<sub>2</sub>E = 1,2-bis[2-(*N*-2-pyridylmethyl-*N*-glycin-ylmethyl)-6-pyridyl]ethane},<sup>[44]</sup> [Fe<sub>2</sub>O(H<sub>2</sub>O)<sub>2</sub>(6HPA)]-(ClO<sub>4</sub>)<sub>2</sub> (3.61/179.2) {6-HPA = 1,2-bis[2-{bis(2-pyr-idylmethyl)aminomethyl}-6-pyridyl]ethane},<sup>[28]</sup> and [(tpenaH)Fe( $\mu$ -O)Fe(tpenaH)]<sup>4+</sup> [tpena<sup>-</sup> = *N*,*N*,*N'*-tris(2-pyridylmethyl)ethylendiamine-*N'*-acetate],<sup>[45]</sup> none of which are bridged by carboxylates. The relatively short Fe···Fe dis-

Table 1. Selected bond lengths (Å) and angles (°) for 1.

Fe1–O2	1.807(3)
Fe1–O1	1.996(3)
Fe1–O7	2.041(3)
Fe1–N3	2.158(4)
Fe1–N1	2.253(4)
Fe1–N2	2.233(1) 2.274(4)
$Fe^2-\Omega^2$	1 798(3)
Fe2-05	1.985(3)
Fe2-O4	2 045(3)
Fe2-N8	2.015(3) 2.178(4)
Fe2-N6	2.170(1) 2 214(4)
Fe2-N7	2.211(1) 2.278(4)
O1-Li2	1.968(8)
$O_3 - L_1 2$	2 007(8)
03_Li1	2.007(0)
05-Li1	1.948(8)
$O_{6}$ Li2	1.948(8)
06-Li1	2 008(8)
	2.000(0)
En-Enz Fel Fel	2.510(10) 3 570(3)[a]
$Fe^2 - \Omega^2 - Fe^1$	166 85(17)
$\Omega^2 - Fe^1 - \Omega^1$	100.03(17) 107.92(12)
$O_2$ -Fe1-O7	98 51(11)
01 - Fe1 - 07	94 76(11)
$O_2$ Fel N3	05.82(12)
$02 - Fe^2 - 05$	105.27(11)
$O_2 = 102 = 0.5$	105.27(11) 00 12(12)
$05 - Fe^2 - 04$	94.74(10)
$O_{2} = F_{e2} = N_{8}$	08 11(12)
$O_{2} = Fe_{2} = N_{3}$	84 30(11)
$O_{4}F_{e2}N_{8}$	162 35(12)
$O_2$ -Fe $2$ -N6	94 88(12)
$O_{2} - Fe_{2} - N_{6}$	159 66(12)
O4-Fe2-N6	84 60(11)
$N8 - Fe^2 - N6$	90 13(12)
$\Omega^2$ -Fe <sup>2</sup> -N <sup>7</sup>	165 36(11)
$L_1^2 = 01 = Ee1$	115 4(3)
Li2 = 01 - 101 Li2 = 03 - Li1	92 9(3)
$Li_{2}$ $C_{3}$ $E_{11}$ $Li_{1}$ $C_{5}$ $E_{6}$	116 4(2)
Li2_06_Li1	93 2(3)
05-Li1-06	1204(4)
05-Li1-03	94 3(3)
06-Li1-03	85.8(3)
05-Li1-Li2	120 3(3)
O6-Li1-Li2	43 3(2)
$O_3$ -Li1-Li2	43 5(2)
N10-Li1-Li2	103.1(3)
N9–Li1–Li2	132.9(4)
O1-Li2-O6	94.7(3)
01 - Li2 = 03	118.7(4)
06-Li2-O3	86.1(3)

[a] Determined using Diamond v. 3.1.

tance may be an effect of interligand connections through the COOLi moieties.

Each Fe<sup>III</sup> center (Fe1 and Fe2) in **1** is coordinated by two pyridyl N atoms with average Fe–N(pyridine) distances of 2.205 and 2.196 Å, respectively. Kodera et al. found a shorter average Fe–N(pyridine) bond length (2.153 Å) in case of a similar  $\mu$ -oxo bridged diiron(III) complex, [Fe<sub>2</sub>(6-HPA)(O)(OH<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub>, in which every Fe<sup>III</sup> center is coordinated with three pyridine N atoms.<sup>[28]</sup>





Figure 2. (a) A Mercury plot of the molecular structure of  $[Fe_2(\mu-O)(LiDPCPMPP)_2]^{2+}$  (1) with thermal ellipsoids at the 50% probability level. All hydrogen atoms have been omitted for the sake of clarity. (b) Corresponding Mercury plot emphasizing the central, unprecedented,  $Fe_2Li_2O_7N_{10}$  core of 1.

### **Electrochemical Studies**

The cyclic voltammogram of  $[Fe_2(\mu-O)(LiDPCPMPP)_2]$ (1) in acetonitrile solution (1 mM) shows one irreversible and two quasi-reversible redox couples (Figure S2). The irreversible peaks at -0.27 V and the quasi-reversible peak at -0.67 V can be attributed to the Fe<sup>III</sup>Fe<sup>III</sup>/Fe<sup>III</sup>Fe<sup>II</sup> and Fe<sup>III</sup>Fe<sup>II</sup>/Fe<sup>II</sup>Fe<sup>II</sup> couples, respectively. A similar kind of redox behavior has been observed by Neves and co-workers for the complex  $[Fe^{III}_2(BPCINOL)_2(H_2O)_2]^{2+}$  (BPCINOL =  $\{N-(2-hydroxybenzyl)-N-(2-pyridylmethyl)]((3-chloro)(2$  $hydroxy)]propylamine\}).<sup>[38]</sup> The irreversibility appears to be$ due to chemical irreversibility caused by changes in the coordination environment of the iron ions upon reduction.<sup>[38]</sup>

### **Reactivity Studies**

Keeping in mind the parameters that can affect the oxidation pathway, as well as the key oxidizing species, the catalytic ability of 1 in oxidation of alkanes and alkenes with  $H_2O_2$  as an oxidant has been investigated. Depending on the conditions, the alcohol/ketone (A/K) ratio for the benchmark substrate cyclohexane changes from 0.6 up to 2. Oxidation of cyclohexane by  $H_2O_2$ , in the presence of 1 as catalyst under standard conditions ([1] = 0.2 mM and 1/ $H_2O_2/RH = 1:200:100$ ), produces cyclohexanol and cyclohexanone with A/K = 1.1, and the turnover number is 30 within 1 h (TOF =  $30 \text{ h}^{-1}$ ) based on the combined yield of products (Table 2). The efficiency of the catalyst and the A/ K ratio changed during the reaction (for example, TOF =90 h<sup>-1</sup> for the first 10 min but only 20 h<sup>-1</sup> for 2 h). This catalyst also demonstrated moderate activity in the oxidation of cyclooctane and other alkanes (Table 2, entries 2, 3, 9-11,

TOF =  $20-43 \text{ h}^{-1}$ ), good activity in alkene oxidation (entries 6–8, TOF =  $24-46 \text{ h}^{-1}$ ) and also in alcohol oxidation (entry 13).

The system is efficient in oxidizing both linear and cyclic alkanes with no primary C-H bond oxidation products being observed. Oxidation of secondary C-H bonds leads to the formation of both the corresponding alcohols and ketones. Adamantane has previously been used to probe the nature of oxidation of hydrocarbons that have both secondary and tertiary C-H bonds. Indiscriminate hydroxyl radicals typically afford selectivity ratios for 3°/2° oxidation of around 2, whereas more selective oxidants give substantially higher values.<sup>[46]</sup> In this context, the present catalyst system with a 3°/2° value around 4 (after statistical correction) and TON of 38 is indicative of a more selective metal-based oxidant rather than unselective OH radicals (Table 2, entries 4 and 5). Interestingly, the catalyst is capable of oxidizing linear alkanes, such as *n*-octane in the secondary C-H bond position with a higher preference for C4. It is interesting that in the case of *n*-octane, the attack is directed mainly to C4. Terminal alkenes were found to undergo epoxidation together with formation of carbonyl compounds, while no dihydroxylation was observed. More importantly, this catalyst allows the preparative synthesis of valuable difunctional substances such as 2-hydroxyhexanal (30% yield). The hydrocarbon conversion and product yield is 20-87% in the present system, which, together with some selectivity, suggests its potential use in preparative chemistry.

A complete elucidation of the reaction mechanism lies outside the scope of the present study. Nevertheless, some observations may be noted and some conclusions may be reached. At first glance, the reaction patterns in Table 2 suggest free-radical processes, but the presence of hydroxyl



Entry	Substrate	Products (% yield) <sup>[b]</sup>	Total % yield	Remarks
1	cyclohexane	cyclohexanol (18)	33	TON = 51
	2	cyclohexanone (15)		A/K = 1.2
2	cyclooctane	cyclooctanol (9)	29	TON = 57
	2	cyclooctanone (20)		A/K = 0.45
3	octane	4-octanol (17)	44 <sup>[c]</sup>	TON = 74
		4-octanone (17)		A/K = 1.0
		3-octanone (10)		
4	adamantane	1-adamantanol (11)	19	TON = 38
		2-adamantanol (4)		$3^{\circ}/2^{\circ} = 4.1$
		2-adamantanone (4)		
5	adamantane <sup>[d]</sup>	1-adamantanol (13)	21	TON = 42
		2-adamantanol (3)		$3^{\circ}/2^{\circ} = 4.8$
		2-adamantanone (5)		
6	cvclohexene	epoxycyclohexane (13)	36	TON = 72
		cvclohexenol (15)		
		2-hydroxy cyclohexanone (8)		
7	2-hexene	2-epoxyhexane (23)	87	TON = 158
		2.3-hexanol (8)		
		2-ol-3-hexanone (56)		
8	1-hexene	epoxyhexane (15)	45	TON = 90
-		2-ol-hexanal (30)		
9	cis-1.2-dimethylcyclohexane	<i>cis</i> -1.2-dimethylcyclohexanol (13)	54	TON = 100
-		<i>trans</i> -1.2-dimethylcyclohexanol (4)		$3^{\circ}/2^{\circ} = 0.46$
		1.2-dimethylcyclohexanol (12)		cis/trans = 53%
		1.2-dimethylcyclohexanone (25)		
10	trans-1.2-dimethylcyclohexane	<i>trans</i> -1.2-dimethylcyclohexanol (36)	65	TON = 130
10		<i>cis</i> -1.2-dimethylcyclohexanol (2)		$3^{\circ}/2^{\circ} = 1.1$
		1.2-dimethylcyclohexanone (30)		trans/cis = 90%
11	1.3-dimethylcyclohexane	1.3-dimethylcyclohexanol (10)	25	TON = 50
	-,	1.3-dimethylcyclohexanone (15)		A/K = 0.7
12	ethylbenzene	1-phenylethanol (6)	20 <sup>[c]</sup>	TON = 37
	ethyleenleite	acetophenone (10)	20	$CH_{ather}/CH_{ather} = 12$
		2-ethylphenol (4)		errenyr errpnenyl 12
13	benzyl alcohol	benzaldehyde (26)	56	TON = 112
		benzoic acid (30)		

Table 2. Catalytic oxidation results.<sup>[a]</sup>

[a] Reaction conditions (see Experimental Section and Supporting Information): substrate (2.0 mmol, 0.16 M in CH<sub>3</sub>CN), 1 (1.0 mol-%), CH<sub>3</sub>CO<sub>2</sub>H (1 equiv. relative to 1), H<sub>2</sub>O<sub>2</sub> (aqueous 30 wt.-%, 10 mmol, in CH<sub>3</sub>CN, added dropwise over 2 min), 30 °C, 180 min. [b] GC yields were determined by using dichlorobenzene as an internal standard. [c] Isolated yields based on an average of three runs. [d] Reaction with acetone as solvent instead of CH<sub>3</sub>CN.

radicals may be ruled out (vide infra). While the A/K ratio of **1** formally indicates the involvement of freely diffusing carbon-centered radicals, the low value of this ratio may also be due to overoxidation of the initially formed alcohols to the corresponding ketones in our system as a result of the relatively large concentration of oxidant and the prolonged reaction times. It should be noted that all catalytic oxidation reactions were conducted in the presence of an equimolar amount of acetic acid relative to the catalyst (complex **1**). It is generally believed that the combination of hydrogen peroxide and acetic acid with mononuclear and dinuclear non-heme iron and Fe<sub>2</sub>O complexes (catalysts) leads to the in situ formation of peracetic acid, which is a relatively strong oxidant/oxygen atom donor (vide in-fra).<sup>[47]</sup>

To shed further light on the nature of the oxidizing species, the kinetic isotope effect (KIE) for cyclohexanol formation (based on a competition experiment between  $H_{12}$ and  $D_{12}$ -cyclohexane) was determined (Figures S4, S5). For a Fenton-type radical auto-oxidation mechanism, the KIE value is expected to be close to 1, whereas for metal-based oxidation, a higher value is expected. The relatively high KIE value of 3.27 and the moderate regioselectivity (3°/2° ratio) in adamantane oxidation (vide supra) suggest that significant participation of hydroxyl radicals may be excluded. This is further supported by the minor effect on the yield of the reaction of using acetone (a hydroxyl radical scavenger) as a solvent and the predominance of the alkyl over aryl (a hydroxyl radical scavenger) oxidation (Figure S6).<sup>[46]</sup> On the other hand, the oxidations of *cis*- and trans-1,2-dimethylcyclohexane with TONs of 100 and 130, respectively, occur with retention of configuration at the tertiary C-H bonds (RC = 53 and 90%, respectively), and this observation definitely indicates the involvement of a metal-based oxidant.<sup>[17,24,48-52]</sup> Such a conclusion is further supported by the isolation of 2,3-epoxyhexane and 1,2-epoxyhexane amongst the major products of 2-hexene and 1hexene oxidation, respectively (with TONs of 158 and 90, respectively). It thus seems that in this system, we observe the same situation that has been found in other diiron complex/hydrogen peroxide catalytic systems,<sup>[17,24,33,52]</sup> that is, there is a combination of a metal-based mechanism with a



radical process, but it is unlikely that the radical process is initiated by hydroxyl radicals.

## Low-Temperature UV/Vis Spectroscopy and Mass Spectrometry

In a UV/Vis spectroscopic experiment performed at 228 K, the reddish purple starting complex 1 ( $\lambda_{max} = 285$ , 325, and 498 nm) was found to transform into a greenish blue species with a maximum absorption at 614 nm ( $\varepsilon$  = 2825 M<sup>-1</sup> cm<sup>-1</sup>) upon addition of acetic acid and hydrogen peroxide in a solvent mixture of acetonitrile and dichloromethane (1:1 v/v), with an overall 3:1:1 ratio of solvent/ CH<sub>3</sub>COOH/H<sub>2</sub>O<sub>2</sub>. No isosbestic point was found, probably due to the involvement of a multi-step process. Changing the solvent to pure dichloromethane, again with an overall 3:1:1 ratio of solvent/CH<sub>3</sub>COOH/H<sub>2</sub>O<sub>2</sub>, made it possible to observe isosbestic points at 435 and 535 nm with a maximum absorbance at 602 nm ( $\varepsilon = 2860 \text{ M}^{-1} \text{ cm}^{-1}$ ; Figure 3) (greenish blue solution) at 228 K, indicating a single-step conversion leading to the formation of a new species. The new absorbance occurs at a wavelength that is similar to what has been observed for peroxo species in related diiron systems. Aukauloo and co-workers have observed the development of a band at 620 nm ( $\varepsilon = 2900 \text{ M}^{-1} \text{ cm}^{-1}$ ), proposed to arise from a peroxo-bridged diiron species, on addition of 1.5 equiv. of  $H_2O_2$  to the complex  $[Fe^{III}_2(N-$ EtHPTB)(H<sub>2</sub>O)<sub>2</sub>(CH<sub>3</sub>O)(CH<sub>3</sub>OH)](ClO<sub>4</sub>)<sub>4</sub> [NEtHPTB = N,N,N',N'-tetrakis(N-ethyl-2-benzimidazolylmethyl)-2hydroxy-1,3-diaminopropane] at 233 K.[53]

Similar observations have been made by Dong et al., who reported an absorption maximum at 600 nm as characteristic for a  $\mu$ -1,2-peroxo species and by Do et al. for the complex [Fe<sup>III</sup><sub>2</sub>( $\mu$ -O<sub>2</sub>)(*N*-EtHPTB)( $\mu$ -PhCO<sub>2</sub>)]<sup>2+</sup>, which is formed on exposure of [Fe<sup>II</sup><sub>2</sub>(*N*-EtHPTB)( $\mu$ -PhCO<sub>2</sub>)]<sup>2+</sup> to O<sub>2</sub> at 243 K.<sup>[54,55]</sup> When H<sub>2</sub>O<sub>2</sub> only was added to a solution of **1**, no absorbance around 600 nm could be detected, suggesting that only a stronger oxidant (the combination of



Figure 3. Spectral changes observed in the reaction of  $[Fe^{III}_2 (\mu - oxo)(LiDPCPMPP)_2]$ , CH<sub>3</sub>COOH, and H<sub>2</sub>O<sub>2</sub> (overall 3:1:1). The inset indicates isosbestic points at 435 and 535 nm.

 $H_2O_2$  and  $CH_3COOH$ ) is capable of producing the new species. It has been suggested that the active oxidant formed through reaction of mononuclear iron complexes with peracetic acid is an (acetate)Fe<sup>V</sup>=O complex<sup>[56]</sup> or, as indicated in a computational study, a (carboxylate)Fe<sup>IV</sup>=O valence tautomer (analogous to Cytochrome P-450 compound I) formed from an initial cyclic Fe<sup>III</sup>–peracetate complex.<sup>[57]</sup> On slow heating to room temperature, the greenish blue solution slowly changes its color to pale yellow with concomitant evolution of oxygen gas, as confirmed by the pyrogallate test {a colorless ethanol solution of potassium pyrogallate [C<sub>6</sub>H<sub>3</sub>(OK)<sub>3</sub>] turns brownish purple (3-hydroxy-1,3-benzoquinone) immediately on exposure to the gas}; the mechanism leading to O<sub>2</sub> evolution is not known.

Measurements of ESI mass spectra in the rapid positive detection mode were made on the greenish blue solution prepared at 228 K. The mass spectrum reveals a prominent doubly charged positive ion cluster of the starting complex  $[Fe_2O(LiDPCPMPP)_2]^{2+}$  (obsd. 580.2; calcd. 580.2) and a corresponding singly charged positive ion cluster  $[Fe_2O(LiDPCPMPP)_2]^{2+}$ 



Figure 4. ESI mass spectra of complex 1 (left) and of the intermediate (right) at the rapid positive detection mode.

Eur. J. Inorg. Chem. 2015, 3590-3601



Figure 5. Isotopic distribution pattern of the major peaks (ESI-MS) in  $CH_2Cl_2 + CH_3CN$  (1:20) solutions of complex 1 [experimental (a) and simulated (b)] and the newly developed peak at 228 K after the addition of  $CH_3COOH$  and  $H_2O_2$ ; overall solvent/  $CH_3COOH/H_2O_2 = 3:1:1$  [experimental (c) and simulated (d)].

(LiDPCPMPP)<sub>2</sub>Cl]<sup>+</sup> at 1195.4 (calcd. 1195.4) (Figures 4 and 5). On the basis of the cumulative results from the lowtemperature UV/Vis spectroscopic and the ESI-MS measurements, we tentatively propose that the new species with a doubly charged cluster [Fe<sub>2</sub>O<sub>3</sub>(LiDPCPMPP)<sub>2</sub>]<sup>2+</sup> (obsd. 596.2; calcd. 596.2) and a singly charged cluster [Fe<sub>2</sub>O<sub>3</sub>-(LiDPCPMPP)<sub>2</sub>Cl]<sup>+</sup> (obsd. 1227.4; calcd. 1227.3) is from the transient intermediate [Fe<sup>IV</sup><sub>2</sub>( $\mu$ -O)( $\mu$ -O<sub>2</sub>)(LiL)<sub>2</sub>]<sup>2+</sup>, which may be involved in the substrate oxidations catalyzed by complex 1; an alternative valence tautomer would be a diperferryl species, [(O=Fe<sup>V</sup>)<sub>2</sub>( $\mu$ -O)(LiL)<sub>2</sub>]<sup>2+</sup>.

Such a structure may be considered feasible, because a similar but mononuclear very active alkylperoxo–iron(IV) complex has been observed earlier.<sup>[58]</sup> As phenolate moieties are potentially non-innocent, the real electronic structure of our intermediate may involve an iron(III)–phenoxyl radical state.<sup>[59]</sup> Such a proposed  $\mu$ -oxo- $\mu$ -peroxodiiron(III)/phenoxyl intermediate can, in principle, serve as active oxidant in our system in similarity to the peroxido intermediate of toluene monooxygenase<sup>[60]</sup> or undergo O–O bond scission to form Fe<sup>IV</sup>=O,<sup>[19]</sup> which, if coupled with a coordinated phenoxyl radical, is effectively an Fe<sup>V</sup>=O species.

The presence of Li in **1** and the proposed  $\mu$ -oxo- $\mu$ -peroxo-diiron(IV) intermediate may in principle facilitate an achievement of a high-valent iron oxidation state and increase the electrophilicity of a ferryl oxygen atom by coordination of Li to that oxygen, in a manner similar to the activation and stabilization of a Co<sup>IV</sup>=O complex stabilized and activated by binding a redox-inactive metal,<sup>[61,62]</sup> and the way that the coordination of Sc<sup>3+</sup> to the ferryl oxygen increases the reactivity of a ferryl moiety.<sup>[63]</sup> The participation of such an active transient species may explain some of the peculiarities of our catalytic system.

### **Summary and Conclusions**

The new ligand LiDPCPMPP and the µ-oxo-bridged diiron complex  $[Fe_2(\mu-O)(LiDPCPMPP)_2](ClO_4)_2$   $[1(ClO_4)_2]$ have been synthesized and characterized. Complex 1 acts as a catalyst/catalyst precursor for the catalytic oxidation of a number of alkanes and alkenes, with H<sub>2</sub>O<sub>2</sub>/CH<sub>3</sub>COOH as the oxidant. The measured kinetic isotope effect for cyclohexane oxidation and the excellent retention of configuration in the oxidation of *cis*- or *trans*-1,2-dimethylcyclohexane suggest that the reactions proceed by the formation of a high-valent iron-oxo intermediate. The low-temperature reaction of 1 with H<sub>2</sub>O<sub>2</sub>/CH<sub>3</sub>COOH in the absence of substrate permits the detection of an unstable intermediate, which is tentatively formulated as the diiron(IV) µ-oxido- $\mu$ -peroxido complex [Fe<sup>IV</sup><sub>2</sub>( $\mu$ -O)( $\mu$ -O<sub>2</sub>)(DPCPMPP)<sub>2</sub>]<sup>2+</sup>, on the basis of UV/Vis absorption spectroscopy and mass spectrometry measurements. The latter species may be an active oxidant, or an immediate precursor to a high-valent ironoxo oxidant that is the catalytically active species in the oxidation reactions effected by 1. Further studies are needed to properly identify the intermediate and investigate its reactivity.

### **Experimental Section**

Materials and Methods: The starting materials 2-hydroxy-3-(hydroxymethyl)-5-methylbenzaldehyde (a), 2-{[bis(pyridin-2ylmethyl) amino]methyl}-6-(hydroxymethyl)-4-methylphenol (b), and ethyl 3-[(2-pyridylmethyl)amino]propanoate (c) were synthesized by previously described methods.<sup>[64,65]</sup> All other chemicals and solvents were of analytical or spectroscopic grade and were purchased from Sigma Aldrich, Fischer Chemicals, or VWR, and they were used without further purification. Infrared spectra were recorded in the 4000-400 cm<sup>-1</sup> range with a Nicolet Avatar 360 FTIR spectrometer, by using KBr pellets. UV/Vis spectra were recorded with a Cary 300 UV/Vis spectrometer. Mass spectrometry was performed with a Bruker HCT Ultra mass spectrometer in the ESI mode. The low-temperature UV/Vis spectra were measured with a quartz transmission probe (1 mm, Hellma Analytics). The Mössbauer spectrum was recorded at 80 K with a <sup>57</sup>Co source in a Rh matrix, using an alternating constant-acceleration Wissel Mössbauer spectrometer operated in the transmission mode and equipped with a Janis closed-cycle helium cryostat. The isomer shift  $\delta$  is given relative to elemental iron at ambient temperature. Temperature-dependent magnetic susceptibility measurements were carried out with a Quantum-Design MPMS-XL-5 SQUID magne-



tometer equipped with a 5 T magnet in the range from 295 to 2.0 K at a magnetic field of 0.5 T. Analytical GC was performed with an Agilent 6850 GC instrument having a FID detector by using an Agilent DB-WAX (30.0 m  $\times$  0.25 mm) column. Chiral GC was performed with an Agilent 6850 GC instrument having a FID detector. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Varian Gemini 200 MHz, a Varian Mercury 300 MHz, or a Varian Unit 500 MHz spectrometer.

### **General Experimental Details**

All chemicals were obtained from commercial suppliers and used without further purification. Cyclohexene ( $\geq$  99.0%) contained about 0.01% 2,6-di-*tert*-butyl-4-methylphenol as stabilizer and was used as received.

Caution! Even though no problems were encountered in this work, caution should be taken while using high concentrations of hydrogen peroxide  $(H_2O_2)$ .

Substrate conversions were determined by a GC–MS method. The GC–MS analyses were performed with an Agilent 6890N Network GC system equipped with a DB-1MS column (30 m  $\times$  0.250 mm) and an Agilent 5973 Network MS detector (1,2-dichlorobenzene was used as an internal standard). Calibration curves were obtained by using commercial products purchased from Aldrich or TCI, when available, or pure isolated products obtained from a catalytic reaction; A FID GC instrument with an HP-INOWAX column (30 m  $\times$  0.25 mm) was used. The concentrations of each organic product were calibrated relative to that of an internal standard (1,2-dichlorobenzene) with a known concentration.

**Ligand Synthesis:** The ligand lithium {3-[(3-{[bis(pyridin-2-ylmethyl)amino]methyl}-2-hydroxy-5-methylbenzyl)(pyridin-2-ylmethyl)amino]}propanoate (LiDPCPMPP) was prepared in an overall 28% yield using the synthetic procedure depicted in Scheme 1.

Caution! Transition metal perchlorates should be handled with great care and be prepared in small quantities, because they are hazardous and may explode upon heating.

3-[(3-{[Bis(pyridin-2-ylmethyl]amino]methyl}-2-hydroxy-5-Ethyl methylbenzyl) (pyridin-2-ylmethyl)amino|propanoate (d): 2-{[bis(pyridin-2-ylmethyl)amino]methyl}-6-(hydroxymethyl)-4-methylphenol (b) (1.2 g, 3.43 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 mL), and SOCl<sub>2</sub> (15 mL) was added dropwise with continuous stirring. The yellow color changed to green immediately and became brown after 30 min. The mixture was stirred at room temperature for 12 h and dried under high vacuum overnight to remove excess HCl and SOCl<sub>2</sub>, giving 2-{[bis(pyridin-2-ylmethyl)amino]methyl}-6-(chloromethyl)-4-methylphenol (1.13 g, 3.08 mmol) as a pale brown solid. Triethylamine (2 mL, 14.3 mmol) was added dropwise to an ethanol solution of ethyl 3-[(2-pyridylmethyl)amino]propanoate (c) (0.61 g; 2.9 mmol) at -40 °C. Then the ethanol solution of 2-{[bis(pyridin-2-ylmethyl)amino]methyl}-6-(chloromethyl)-4methylphenol (1.06 g, 2.9 mmol) was added dropwise, while maintaining the temperature at -40 °C, and after 30 min of stirring at the same temperature the solution was warmed to room temperature and was heated at reflux for 3 h. The solvent was subsequently removed under reduced pressure (rotary evaporator). The remaining solid was dissolved in aqueous phosphate buffer (0.1 M, pH 7) and extracted with dichloromethane (150 mL;  $3 \times 50$  mL) and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography on silica gel (eluent: CHCl3/heptane/triethylamine 3:2:1) to obtain d (1.22 g, 2.26 mmol). Yield 78%. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD):  $\delta$  = 8.34 (m, 3 H), 7.43 (m, 3 H), 7.24 (m, 3 H), 7.02 (s, 1 H), 6.96 (m, 3 H), 6.84 (s, 1 H), 4.09 (s, 1 H), 3.93 (q, 1 H), 3.86 (s, 1 H), 3.83 (s, 1 H), 3.67 (m, 4 H), 2.85 (t, 1 H), 2.71 (q, 3 H), 2.03 (s, 3 H), 0.941 (t, 3 H) ppm. <sup>13</sup>C NMR (500 MHz, CD<sub>3</sub>OD):  $\delta$  = 170.9, 158.12, 152.48, 149.11, 137.46, 130.31, 127.66, 123.32, 122.60, 60.86, 58.37, 56.92, 51.31, 49.5, 48.12, 47.61, 46.55, 43.21, 32.27, 30.82, 19.46, 14.57 ppm.

Lithium 3-[(3-{[Bis(pyridin-2-ylmethyl]amino]methyl}-2-hydroxy-5methylbenzyl)(pyridin-2-ylmethyl)amino]propanoate (LiDPCPMPP): LiOH (0.089 g, 3.7 mmol) was added to a methanol solution of **d** (1.0 g, 1.85 mmol). After 48 h of continuous stirring, the reaction mixture was filtered and the filtrate was dried under reduced pressure. The residue was washed with cold water (3 × 20 mL) and dried under vacuum to give LiDPCPMPP (0.774 g, 1.52 mmol). Yield 82%. C<sub>30</sub>H<sub>35</sub>ClLiN<sub>5</sub>O<sub>4</sub> [DPCPMPP·H<sub>2</sub>O·LiCl]: C 62.99, H 6.17, N 12.24; found C 62.52, H 5.90, N 11.97. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD): δ = 8.62 (m, 2 H), 8.5 (m, 1 H), 7.65 (m, 3 H), 7.34 (m, 3 H), 7.22 (m, 3 H), 6.78 (m, 1 H), 6.73 (s, 1 H), 3.75 (b, 5 H), 3.6 (m, 4 H), 3.30 (m, 1 H), 2.82 (b, 2 H), 2.47 (b, 2 H), 2.2 (s, 3 H) ppm. <sup>13</sup>C NMR (500 MHz, CD<sub>3</sub>OD): δ = 179.8, 158.76, 148.32, 137.28, 123.87, 123.7, 123.33, 122.17, 59.10, 58.66, 51.64, 48.46, 47.96, 46.55, 43.21, 22.92, 19.07 ppm.

[Fe<sub>2</sub>O(LiDPCPMPP)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> ([1](ClO<sub>4</sub>)<sub>2</sub>): A methanol solution of Fe(ClO<sub>4</sub>)<sub>3</sub> (0.56 g, 1.57 mmol, 10 mL) was added to a methanol solution of LiDPCPMPP (0.8 g, 1.57 mmol, 20 mL), and the solution was stirred for 2 h at room temperature and pressure. The yellow color of the ligand solution turned purple immediately after addition of Fe(ClO<sub>4</sub>)<sub>3</sub>, and the color kept on intensifying during the next half hour, after which no further change in the color was observed. The resulting solution was filtered through a Celite pad to remove Fe-hydroxide impurities. The filtrate was taken in a 50 mL round-bottomed flask and was dried under vacuum. A total of 15 mL of ice cold water was added to remove the unreacted perchlorate salt. After decanting the water, the flask was kept under high vacuum overnight, which gave  $[Fe_2O(LiDPCPMPP)_2]$  (1) (1.22 g, 67.8%) as a dark purple powder. This powder was redissolved in dry acetonitrile, and slow vapor diffusion of diethyl ether into the acetonitrile solution gave rise to dark purple crystals suitable for X-ray diffraction. The crystals were fairly stable in the mother liquor but decomposed upon exposure to air; they were therefore stored under vacuum. UV/Vis (CH<sub>3</sub>CN):  $\lambda_{max}$  ( $\varepsilon$  $[M^{-1}cm^{-1}]$  = 504 (1325), 345 (3885), 296 (5760) nm. <sup>57</sup>Fe Mössbauer (80 K):  $\delta = 0.48$  mm/s;  $\Delta E_0 = 1.40$  mm/s. ESI-MS in CH<sub>2</sub>Cl<sub>2</sub>/ CH<sub>3</sub>CN (1:20 v/v): calcd. for  $C_{60}H_{62}Fe_2Li_2N_{10}O_7^{2+}$  [{Fe<sup>III</sup><sub>2</sub>(µ-O)-(LiDPCPMPP)<sub>2</sub>}<sup>2+</sup>] 580.3, found 580.2; calcd. for  $C_{60}H_{62}Fe_2Li_2N_{10}O_7Cl^+$  [{Fe<sup>III</sup><sub>2</sub>(µ-O)(LiDPCPMPP)<sub>2</sub>Cl}<sup>+</sup>] 1195.3, found 1195.4. C<sub>60</sub>H<sub>70</sub>Cl<sub>5</sub>Fe<sub>3</sub>Li<sub>2</sub>N<sub>10</sub>O<sub>27</sub> [Fe<sub>2</sub>O(LiDPCPMPP)<sub>2</sub>-(ClO<sub>4</sub>)<sub>2</sub>Fe(ClO<sub>4</sub>)<sub>3</sub>]: C 42.00, H 3.76, N, 8.12; found C 41.65, H 4.33, N 7.50. IR (KBr):  $\tilde{v}$  = 3432 (b, s), 2974(s), 2937(s), 2753(s), 2733(s), 2761(s), 2631(sh), 2598(sh), 1474(s), 1425(s), 1397(s), 1168(s), 1033(s), 845(s) 800(s) cm<sup>-1</sup>.

### X-ray Crystallography

A crystal of 1 was immersed in cryo-oil, mounted in a MiTeGen loop, and measured at a temperature of 170 K. The X-ray diffraction data was collected with an Agilent Technologies Supernova diffractometer using Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å). The Crys-AlisPro program package was used for cell refinements and data reductions.<sup>[66]</sup> The structure was solved by the charge flipping method with the SUPERFLIP program.<sup>[67]</sup> A multi-scan absorption correction based on equivalent reflections (CrysAlisPro) was applied to the data.<sup>[69]</sup> Structural refinement was carried out by using SHELXL-2014 with the Olex2 and SHELXLE graphical user interfaces.<sup>[68–70]</sup> Hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms with C–H = 0.95–0.99 Å



and  $U_{iso} = 1.2-1.5U_{eq}$  (parent atom). The crystallographic details are summarized in Table 3.

Table 3. Crystal data and structure refinement for 1.

Empirical formula	C <sub>64</sub> H <sub>68</sub> Cl <sub>4</sub> Fe <sub>3</sub> Li <sub>2</sub> N <sub>12</sub> O <sub>7</sub>
Fw	1440.53
Temperature (K)	170(2)
$\lambda$ (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_{1}/c$
a (Å)	15.6160(7)
b (Å)	15.9767(8)
c (Å)	26.0954(13)
β (°)	95.033(4)
$V(Å^3)$	6485.5(5)
Ζ	4
$\rho_{\text{calc}}$ (Mg/m <sup>3</sup> )	1.475
$\mu$ (Mo- $K_a$ ) (mm <sup>-1</sup> )	0.890
No. of reflections	26621
Unique reflections	14791
GOOF $(F^2)$	0.994
R <sub>int</sub>	0.0462
$R1^{[a]} (I \ge 2\sigma)$	0.0598
$wR2^{[b]} (I \ge 2\sigma)$	0.1378

[a]  $R1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$ . [b]  $wR2 = \{\Sigma [w(F_0^2 - F_c^2)^2] / \Sigma [w(F_0^2)^2] \}^{1/2}$ .

CCDC 1403038 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

### **General Oxidation Procedures**

**Oxidation of Cyclooctane (as an example):** Cyclooctane (228 mg, 268 mL, 2 mmol) was added to a solution of 1 (0.02 mmol) in MeCN/acetic acid (1.0:0.03 mL). After the addition of  $H_2O_2$  (30% in  $H_2O_2$ ; 258  $\mu$ L, 10 mmol), the reaction mixture was heated at 30 °C for 3 h. The mixture was then cooled to room temperature. The organic phase was extracted with Et<sub>2</sub>O (3 × 1 mL), washed with brine, and dried (MgSO<sub>4</sub>). After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; diethyl ether/pentane = 1:9 as eluent), and the product was analyzed by GC–MS with 1,2-dichlorobenzene as an internal standard.

### GC Analysis

Substrate conversions and product yields were calculated relative to the internal standard integration. Calibration curves with dichlorobenzene as internal standard were obtained by using commercial products when available or pure isolated products obtained from a catalytic reaction. The products were identified by GC-MS by comparing their retention times with authentic samples of possible oxidized products. The product yields should not be confused with the given product distributions; all experiments were repeated at least three times, and the data in Table 2 are averages of all experiments for a given entry. Note: alkyl hydroperoxides decompose during GC measurements to mixtures of products, and, if accumulated, will disturb analysis of oxidation results. According to wellknown methods, we used Ph<sub>3</sub>P treatment of the reaction samples as a test to reveal whether ROOH had accumulated. Our results indicated that the product distribution was unchanged after the treatment with Ph<sub>3</sub>P prior to GC analysis.<sup>[71]</sup>

The 3°/2° ratio in adamantane oxidation was calculated by the expression 3[1-adamantanol]/([2-adamantanol] + [2-adamantanone]).

The percentage of retention of configuration in the oxidation of the tertiary H bonds of *cis*-1,2-dimethylcyclohexane (DMCH) was calculated by the expression  $(cis - trans)/(cis + trans) \times 100$ .

*trans*-Dimethylcyclohexane (*trans*-DMCH) was purified by flash chromatography over silica (eluent: hexane 100%) and analyzed by NMR spectroscopy and GC–MS. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.69–1.63 (m, 2 H), 1.54–1.48 (m, 2 H) 1.46–1.20 (m,5 H), 1.18 (s, 3 H), 0.90 (d, *J* = 6.5 Hz, 3 H) ppm. GC–MS: *m*/*z* = 128.1 (ketone C<sub>2</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.42–2.36 (m, 1 H), 2.29 (ddt, *J*<sub>1</sub> = 1.2, *J*<sub>2</sub> = 5.9, *J*<sub>3</sub> = 13.2 Hz; 1 H), 2.08–1.99 (m, 2 H), 1.86–1.81 (m, 1 H), 1.71–1.59 (m, 1 H), 1.53–1.40 (m, 2 H), 1.06 (d, *J* = 6.1 Hz, 3 H), 1.03 (d, *J* = 6.6 Hz, 3 H) ppm. GC–MS: *m*/*z* = 126.1 (ketone C<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.36–2.31 (m, 3 H), 2.09–1.96 (m, 2 H) 1.54–1.35 (m,3 H), 1.01 (d, *J* = 5.8 Hz, 3 H), 1.00 (d, *J* = 6.1 Hz, 3 H) ppm. GC–MS: *m*/*z* = 126.1.

**Supporting Information** (see footnote on the first page of this article): Mössbauer spectrum, cyclic voltammogram, and UV/Vis spectrum of complex 1, plots of time dependence of yields (kinetic isotope effect) for the catalytic oxidation of c-C<sub>6</sub>H<sub>12</sub> and c-C<sub>6</sub>D<sub>12</sub>, substrate concentration dependence on rate of oxidation, cyclohexane oxidation using acetone and [D<sub>6</sub>]acetone as solvent, details of the magnetic susceptibility measurement, and GC-FID traces.

### Acknowledgments

This research has been carried out within the framework of the International Research Training Group *Metal Sites in Biomolecules: Structures, Regulation and Mechanisms* (www.biometals.eu) and has been supported by the COST Action CM1003. We thank the European Comission for an Erasmus Mundus fellowship to B. D., and Dr. Ivan Castillo Pérez for useful discussions. A. A-H. is grateful for the financial support from the Inorganic Materials Graduate Program and Tekes - the Finnish Funding Agency for Technology and Innovation (project 40099/10).

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Received: May 28, 2015 Published Online: July 17, 2015