First example of a rigid (μ-oxo-di-μ-acetato)diiron(III) complex with 1,2-bis[2-di(2-pyridyl)methyl-6-pyridyl]ethane; its efficient catalysis for functionalization of alkanes

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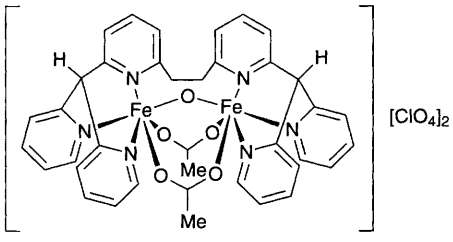
The μ-oxo-di-μ-acetatodiiron(III) complex $[Fe_2(hexpy)(O)(OCOMe)_2][ClO_4]_2$ {hexpy = 1,2-bis[2-di(2-pyridyl)-methyl-6-pyridyl]ethane} efficiently catalyses the oxygenation of cyclohexane, methylcyclohexane and adamantane in the presence of *m*-chloroperbenzoic acid.

Efficient functionalization of alkanes catalysed by metal complexes is one of the most exciting research areas in chemistry.[1] In biological systems, soluble methane monooxygenase (sMMO) is known to catalyse conversion of methane to methanol quantitatively[2] and the μ-hydroxodiiron(III) centre of sMMO had been revealed by X-ray crystallography.[3] Although many artificial sMMO systems have been developed using μ-oxodiiron(III) complexes and oxidants such as ROOH,[4,5] H_2O_2[5,6] and O_2 (+ electron source),[7] the catalytic activity of these systems is still lower than that of sMMO. Recently, most substrate oxygenations in the artificial systems have been demonstrated to proceed *via* a radical-chain mechanism[8] which differs from that of sMMO.

We have synthesised a μ-oxo-di-μ-acetatodiiron(III) complex of a dinucleating hexapyridine ligand, $[Fe_2O(O_2CMe)_2(hexpy)][ClO_4]_2$ **1** {hexpy = 1,2-bis[2-di(2-pyridyl)methyl-6-pyridyl]ethane} aiming to construct a more efficient artificial sMMO system. The dinuclear structure of **1** is highly stabilised by hexpy.[9] Herein, we report a rapid and efficient functionalization of alkanes catalysed by **1** with *m*-chloroperbenzoic acid (*m*-CPBA).



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In a typical reaction, to a CH_2Cl_2 (1.5 ml) solution of 1.6 ml of cyclohexane and 690 mg of *m*-CPBA was added a MeCN–CH_2Cl_2 (0.3 ml–1.5 ml) solution of 9.7 mg of **1** under Ar with vigorious stirring at 25 °C. The reaction was complete within 5 min and the reaction mixture was analysed by GLC; results are summarized in Table 1.

This system shows both a large turnover frequency of 70 [mol product (mol catalyst)$^{-1}$ min^{-1}] and a turnover number of 164 [mol product (mol catalyst)$^{-1}$] for the formation of cyclohexanol. The turnover frequency in the present system is the largest amongst reported values for oxygenations of alkanes catalysed by diiron complexes.[4–7,10] The turnover frequency and the turnover number of the present system were unaffected by the presence of O_2, indicating that oxidation does not proceed *via* a radical-chain mechanism.

Catalyst **1** was extremely stable during oxygenation and ^{1}H NMR spectroscopy showed that 80% of **1** remained at the end of the reaction. In order to examine the durability of **1** as a catalyst, an experiment with repeated addition of *m*-CPBA was performed under similar conditions. After the fourth addition, the turnover number of **1** was 658 (*cf.* 164 × 4 = 656) for the formation of cyclohexanol (Fig. 1) indicating no loss in activity.

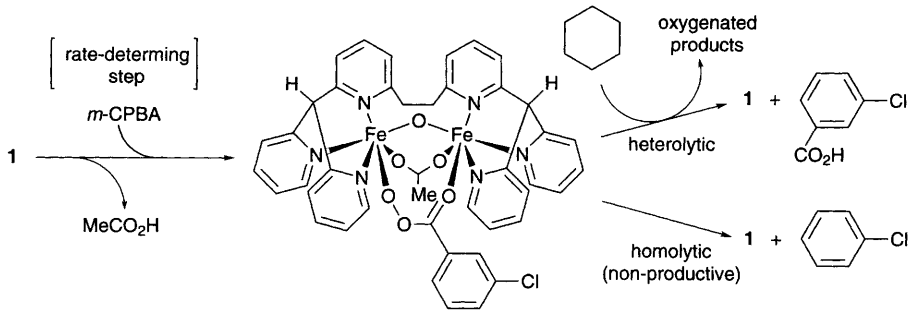
When (5,10,15,20-tetraphenylporphinato)iron(III) chloride **2**, which is known as a catalyst for substrate oxygenation,[11] was used in place of **1**, the turnover number was only *ca.* 100 after the fourth addition of *m*-CPBA. The much higher turnover number shown by **1** is ascribed to both its higher stability toward oxidation and its higher catalytic efficiency.

In order to detect the active species, we monitored the reaction of **1** with *m*-CPBA by electronic absorption spectroscopy. However, no prominent spectral changes were observed

Table 1 Oxygenation[a] of alkanes catalysed by **1**

Alkane	Reaction time/min	Products	Yields[b]/%	Turnover number
Cyclohexane	5	Cyclohexanol	41	164
		Cyclohexanone	17	68
		ε-Caprolactone	12	48
		Chlorocyclohexane	3	12
Adamantane[c]	20	1-Adamantanol	41	163
		2-Adamantanol	10	39
		Adamantanone	6	24
Methylcyclohexane	15	1-Methylcyclohexanol	26	104
		2-, 3- and 4-Methycyclohexanols	25	100
		Cyclohexylmethanol	0.5	2
		Methylcyclohexanones	12	48

[a] *Reaction conditions*: [**1**] = 2.0 mmol dm^{-3}, [alkane]$_0$ = 3.0 mol dm^{-3}, [*m*-CPBA]$_0$ = 0.8 mol dm^{-3} in a mixture of CH_2Cl_2 (3 ml) and MeCN (0.3 ml). [b] Yields are based on *m*-CPBA used. [c] Diluted conditions were used; [**1**] = 1.67 mmol dm^{-3}, [adamantane]$_0$ = 1.0 mol dm^{-3}, [*m*-CPBA]$_0$ = 0.67 mol dm^{-3} in the same solvent system.



Scheme 1

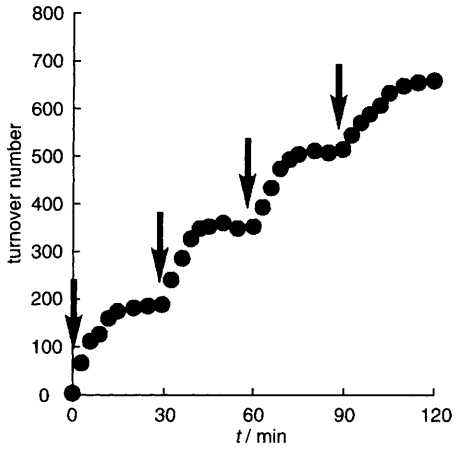


Fig. 1 Catalytic activity of **1** for the formation of cyclohexanol in the reaction of cyclohexane (3.0 mol dm^{-3}) with *m*-CPBA in CH_2Cl_2–MeCN (10 : 1, *v*/*v*) containing catalyst (0.20 mmol dm^{-3}) under Ar at 25 °C. 0.4 mmol of *m*-CPBA was added in each step as indicated by arrows

even at low temperature. This suggests that the ligand exchange of **1** between acetate and *m*-CPBA is the rate-determining step in the catalytic cycle. The slow ligand exchange and the fast subsequent oxidation results in very low concentration of the active species. *m*-CPBA was converted to *m*-chlorobenzoic acid (72%) and chlorobenzene (24%) during the reaction. The formation of chlorobenzene is rationalized by a homolytic scission of an O–O bond of *m*-CPBA followed by a subsequent decarboxylation of the generated benzoyloxyl radical. This suggests that *m*-CPBA is consumed *via* two parallel reaction pathways, *i.e.* homolytic and heterolytic scission of the O–O bond promoted by **1**. Heterolytic scission may provide an active species [$Fe^{IV}(O)_2Fe^{IV}$] capable of oxygenating alkane substrates while homolytic scission does not lead to oxygenated products (Scheme 1).

The reactivity ratios of tertiary : secondary : primary C–H for methylcyclohexane and of tertiary : secondary C–H for adamantane are 150 : 15 : 1 and 12 : 1, respectively, suggesting a radical-rebound mechanism similar to that for sMMO systems.[2] This mechanism is further supported by other findings. When chloroform was used as a solvent, the yield of chlorocyclohexane increased from 3 to 6%. When dibromomethane was used, bromocyclohexane was formed in 6% yield. These results suggest the formation of the cyclohexyl radical as an intermediate. 2,6-Di-*tert*-butyl-4-methylphenol blocked alkane oxygenation completely, also supporting the radical mechanism.

Further information about the active species was obtained from kinetic isotope effect experiments. 1,3-Dideuterioadamantane having two tertiary C–D bonds and two tertiary C–H bonds was used as a substrate. The mass spectral analyses of resultant adamantanol revealed an intramolecular kinetic isotope effect k_H/k_D of 3.5. A similar intermolecular kinetic isotope effect k_H/k_D of 3.2 was obtained using an equimolar mixture of cyclohexane and perdeuteriated cyclohexane. These values are slightly lower (less selective) than those reported for the sMMO systems (k_H/k_D = 4.2–5.1),[12] is reasonable because the coordination of pyridine groups in **1** instead of carboxylate groups as in sMMO destabilises a high valent state of the active species generated from **1**.

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