H_2O_2

$ROOH$

$PhIO$

O_2

Cobalt
27

Iron
26

Fe

55.845

Nickel
28

Manganese

Cr

51.996

Mn

54.938

Molybdenum
42

Technetium
43

Ruthenium
44

Rhodium

Co
Ni
693

53 33

Palladium
46

Pd

106.

Mo

95.94

Tc

[98]

Ru

101.07

2.91

Osmium
76

Iridium
77

Plat

Tungsten
74

Rhenium
75

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Molecular iron complexes as catalysts for selective C–H bond oxygenation reactions

Inspired by naturally occurring enzymes, molecular iron heme and nonheme complexes have proven their potential as catalysts for the selective oxygenation of aliphatic and aromatic C–H bonds.

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Molecular iron complexes as catalysts for selective C−H bond oxygenation reactions

A. C. Lindhorst, S. Haslinger and Fritz E. Kühn*

The selective oxygenation of C−H bonds is a promising and interesting task for both academia and chemical industry. Inspired by the efficiency and selectivity of naturally occurring enzymes, iron heme and nonheme complexes have proven to be valuable candidates for the development of environmentally friendly catalysts as alternative to traditional systems. This feature article summarises developments of the last decade regarding oxygenation reactions of aliphatic and aromatic substrates with various oxidants catalysed by molecular iron complexes. With a special focus on the catalytic performance of the systems, both the potential and the limitations as well as mechanistic aspects are discussed in some detail.

1. Introduction

The selective oxidative functionalization of hydrocarbons is a fundamental process in nature and holds high significance for the chemical industry.[1–3] Raw materials obtained from crude oil and natural gas are converted to bulk chemicals and substrates for fine chemical synthesis. Technical processes often involve harsh reaction conditions and require reagents and oxidants in stoichiometric amounts.[4] Moreover, difficulties posed by the inherent chemical inertness of the starting materials

can result in the accumulation of mostly unwanted by-products. To render these processes more environmentally friendly and atom efficient, mild reaction conditions and the use of non-toxic oxidants such as dioxygen (preferably directly from air) are desirable.[5]

In nature, the oxidation of alkanes and arenes is mediated by both heme and nonheme metalloenzymes.[6–9] They exhibit excellent selectivity and operate under mild reaction conditions. Many of them are based on active iron sites with the most extensively studied examples belonging to the Cytochrome P450 (Cyt P450) superfamily, which enable the hydroxylation of a plethora of substrates employing dioxygen as the terminal oxidant.[10,11] Their active site contains an Fe^{III} porphyrin cofactor, which is coordinated axially by a cysteinate residue of the protein backbone, leaving a *trans* coordination site for the

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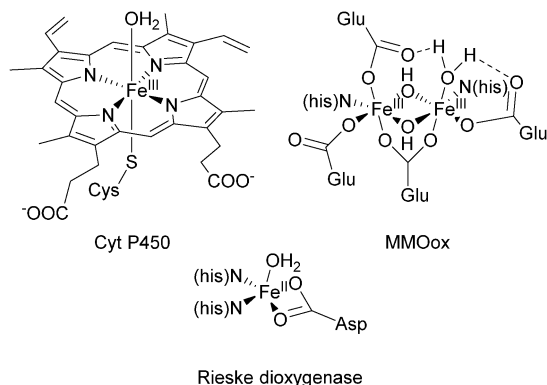
S. Haslinger

Fig. 1 Structural environment of the active sites of Cyt P450, Rieske dioxygenase, and the oxidised form of methane monooxygenase.[10,12,13]

binding of O_2 (Fig. 1).[11] In nonheme enzymes the iron centre is coordinated by amino acid functionalities to form the active site. Prominent examples, capable of mediating the oxidation of C–H bonds are the methane monooxygenase (MMO), the Rieske dioxygenases, and the aromatic amino acid hydroxylases (Fig. 1). A common mechanistic feature of these enzymes is the formation of an iron(III)–peroxo intermediate, which directly reacts to form a high-valent iron–oxo species.[6,10]

Inspired by the high catalytic efficiency of the enzymatic model systems, indicated by high conversions and selectivity, numerous biomimetic heme and nonheme complexes have been developed and applied in C–H bond oxygenation reactions.[14,15] Due to its biological relevance, commonness in nature and unique properties iron is often the metal of choice. Forming a plethora of non-toxic and environmentally benign compounds, its use in catalytic processes helps to increase their sustainability.[16,17] In this context the choice of oxidant also plays an important role. Depending on the application molecular oxygen, hydrogen peroxide (H_2O_2) or air are most desirable, with the latter two involving less safety risks.[18,19] The use of *tert*-butyl hydroperoxide (*t*BHP) results in the formation of *tert*-butanol as

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by-product, which can be recycled and is therefore preferable to several other (*e.g.* heavy metal containing) oxidants.[20]

On the one hand, artificial catalyst systems aim at mimicking the structure and reactivity of natural enzymes, on the other hand they help to increase mechanistic understanding of the natural systems.[15,21,22] For instance, active intermediates may be more stable in synthetic metal complexes and can be characterised spectroscopically or crystallographically. In terms of efficiency and selectivity biomimetic catalysts usually cannot compete with metalloenzymes as they tend to suffer from (oxidative) degradation outside of the protective protein surroundings. However, they allow higher flexibility regarding reaction conditions, substrates and tuning of selectivity.[6] In the past decades many systems have been reported that catalyse the oxidation of hydrocarbons with varying oxidants. This article summarises key developments achieved in the field of homogeneous C–H bond oxygenation catalysed by molecular iron complexes in the last decade. The primary focus will be laid on the performance of the catalytic systems, however some mechanistic aspects will be discussed when necessary.

2. Oxygenation of aliphatic C−H bonds

The selective functionalization of saturated hydrocarbons plays an important role in the production of many commodity chemicals and in classical organic synthesis. For example, within the DuPont process cyclohexane is oxidised to a mixture of cyclohexanol and cyclohexanone, which constitute raw materials for the production of Nylon 6 and Nylon 6,6′ in a scale of mega tons per year.[23–25] Dioxygen is used as the oxidant in combination with cobalt or manganese catalysts. Temperatures between 150 and 175 °C are required and the alkane conversion is kept at 3–8% to compensate for the low selectivity of the radical reaction. This demonstrates the need for catalytic systems with increased activity and selectivity, which is and has been a main goal of academic and industrial research through the last decades.

Molecular heme and nonheme iron complexes have often been used to achieve such improvements.[13,15,26,27] Main challenges regarding selectivity are caused by the inertness of the substrates. Nature and topology of the ligand supporting the iron centre are important features, which can be altered to tune catalytic activity and selectivity. The oxygenation of a hydrocarbon generally requires two individual steps, namely C–H bond cleavage and C–O bond formation.[12,23] The first step is generally assumed to proceed *via* homolytic bond fission. The lifetime of the intermediate alkyl radical is decisive for the product distribution. A long lifetime is usually associated with a radical-based mechanism, where free radicals are formed directly from the oxidant, *e.g.* H_2O_2, by Fenton-type reactions. The selectivity of this reaction type is generally low as long-lived alkyl radicals are prone to unselective interaction with O_2 for instance.[12,23] A short lifetime relates to a more selective metal-centred oxidation mechanism. In many cases this includes the interaction of the iron catalyst with the oxidant to form an iron–peroxo species. This can either
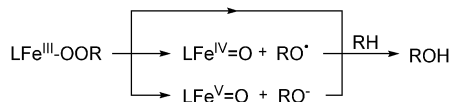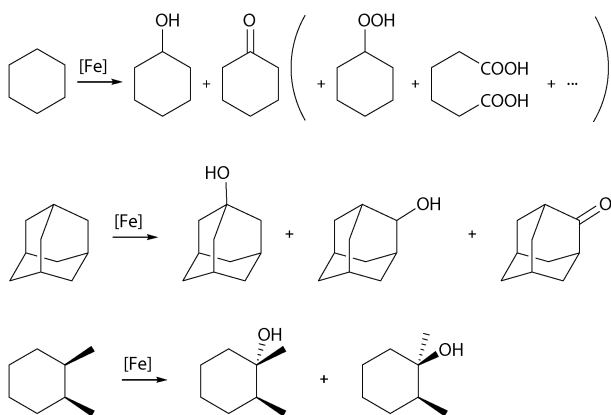
Scheme 1 Oxidation of alkanes by a reactive iron–peroxo intermediate.

interact directly with the substrate or decompose to form the active oxidant (Scheme 1).[12,23] High-valent iron–oxo species have often been proposed to be the active oxidant and their spectroscopic, structural, and electronic properties were investigated.[13,28,29] However, often they cannot be tracked by experimental techniques under catalytic conditions and therefore model reactions have been established, which help to elucidate the prevalent oxidation mechanism.

The product distribution resulting from catalytic cyclohexane oxidation (Scheme 2), the so-called alcohol-to-ketone or A/K ratio, provides important information about alkyl radical lifetime. Long-lived cyclohexyl radicals can be trapped by O_2 to form cyclohexyl peroxide, which may decompose in a Russell-type termination step to yield equal amounts of alcohol and ketone.[23] Therefore, an A/K ratio close to one indicates a radical mechanism, whereas higher values support the involvement of a metal-centred oxidation mechanism. The regioselectivity can be evaluated by the oxidation of adamantane (Scheme 2) and is commonly expressed as the ratio of oxidised tertiary and secondary C–H bonds (3°/2°). Furthermore, the degree by which stereoinformation is retained during the oxidation of substituted cyclohexanes (cis-1,2-dimethylcyclohexane, cis-DMCH, Scheme 2), reflects the balance between epimerisation and C–O bond formation.[12] A high amount of configuration retention (% RC) implies a short alkyl radical lifetime. The same accounts for the observation of kinetic isotope effects (KIE). In the competitive oxidation of cyclohexane and d_{12}-cyclohexane with H_2O_2 a low KIE of 1–2 (4–5 for tBHP) points towards a radical-based mechanism, the presence of a metal-centred oxidation mechanism is indicated by a higher KIE of ∼7.[12,23] Labelling experiments with ^{18}O enriched reactants additionally provide information about the origin of the oxygen atoms incorporated in the product.

2.1 Iron heme complexes and related derivatives

Iron complexes bearing porphyrin or closely related ligands such as phthalocyanines or corroles have been applied frequently in the oxidation of alkanes since the late 1970s.[23,27,30] They resemble the active sites of naturally occurring hemoproteins such as Cyt P450, which are able to catalyse the oxidation of hydrocarbons under ambient conditions and therefore provide attractive inspiration for the design of biomimetic oxidation catalysts.

Groves and co-workers reported the first example of the catalytic hydroxylation of non-activated alkanes by a mononuclear Fe^{III} complex of 5,10,15,20-tetrakis(phenyl)porphyrin (**1a**, Fig. 2) with iodosylbenzene (PhIO) in 1979.[31] Cyclohexane and adamantane were selectively oxidised to the corresponding alcohols in yields of 8 and 13% respectively (Table 1). These early investigations showed that both the nature of the ligand and the oxidant significantly influence catalytic performance. The introduction of bulky, substituted arene units in the meso
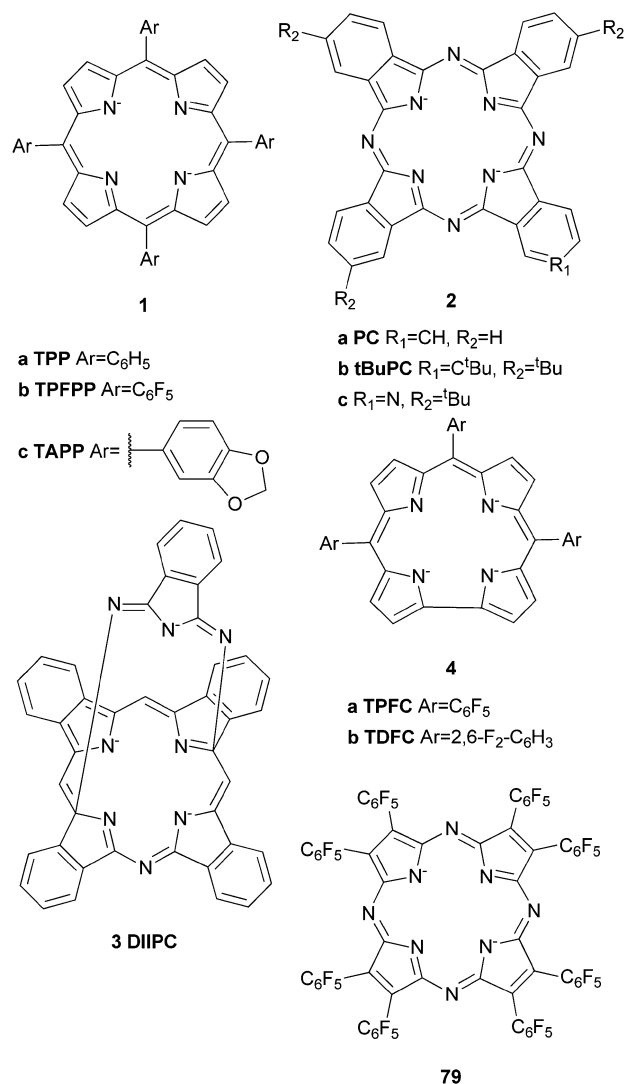

Fig. 2 Examples of porphyrin, phthalocyanine, corrole and porphyrazine ligands used in iron-based oxidation catalysis.

Scheme 2 Benchmark substrates for iron-catalysed alkane oxidation reactions.

Table 1 Selected catalytic data for alkane oxidation reactions catalysed by molecular iron complexes

Catalyst	Oxidant	% yield[a]	A/K[b]	TO[c]	% RC[d]	3°/2° [e]	Ref.
$[Fe^{III}(1a)Cl]$	PhIO	8	—[f]	0.5		48	31
$[Fe^{III}(3)S]^{g}$	H_2O_2		6.7	116			37
$[Fe^{IV}(4a)Cl]$	tBHP	27	0.58	23		10.2	40
$[Fe^{II}(5a)(CH_3CN)_2](ClO_4)_2$	H_2O_2	32	5	3.2	100	17	48 and 49
$[Fe^{II}(5a)(OTf)_2]^{h}$	H_2O_2	18	3.5	1.8	93		55
$[Fe^{II}(10)(OTf)_2]$	H_2O_2	65	9.5	6.5		13	60
$[Fe^{II}(14c)(CH_3CN)_2](ClO_4)_2$	H_2O_2	7.2	1.8	2.2			52
$[Fe^{II}(15c)(OTf)_2]$	H_2O_2	0.0078	2.25	3.9			53
$[Fe^{II}(16a)(CH_3CN)_2](ClO_4)_2$	H_2O_2	19.2	4.6	9.6	85	10.3	56
$[Fe^{II}(16a)(CH_3CN)_2](ClO_4)_2^{h}$	H_2O_2	21.6	4.4	10.8	82	24.9	56
$[Fe^{II}(17)(CH_3CN)_2](ClO_4)_2$	H_2O_2	25.5	9.2	2.5	74		59
$[Fe^{II}(19h)(CH_3CN)_2](SbF_6)_2$	H_2O_2	40	7.3	4.0	40		75
$[Fe^{II}(20c)(CH_3CN)_2](SbF_6)_2$	H_2O_2	24.4	5.0	122			156
$[Fe^{II}(22b)(OTf)_2]$	H_2O_2	42	0.15	42	99		72
$[Fe^{II}(23)(CH_3CN)](ClO_4)_2$	H_2O_2	12	7	50	96	6	78
$[Fe^{II}(24c)(OTf)_2]$	H_2O_2	65	12	6.5	93	30	82
$[Fe^{II}(24d)(OTf)_2]^{i}$	H_2O_2	20	8	20			88
$[Fe^{II}(26)_3](OTf)_2$	tBHP	27.3	0.6	27.3	27	19.9	90
$[Fe^{II}(28b)_2][Fe^{II}(28b)Cl(H_2O)_2]_2Cl_4$	H_2O_2	1.6	6.6	317.3			93
$[Fe^{II}(29a)(CH_3CN)_2]$	H_2O_2	34	1.5	34		17.0	95
$[Fe^{III}(31a)(H_2O)](ClO_4)_2$	H_2O_2	78	11.3	15.6		18.8	99
$[Fe^{II}(32)(CH_3CN)_2](ClO_4)_2$	H_2O_2	23	1.2	2.3			101
$[Fe^{II}(33)(CH_3CN)](ClO_4)_2$	H_2O_2	25	1.3	25			102
$[Fe^{II}(35a)](PF_6)_2$	H_2O_2	37	1.2	7.4			105
$[Fe^{II}(37a)(OTf)_2]$	H_2O_2	5.2	1.0	0.52			107
$\{[Fe^{II}(37d)(CH_3CN)]_2O\}(BF_4)_4$	H_2O_2	41	7.2	4.1		9.4	109
$[Fe^{II}(39)Cl_2]$	H_2O_2	17.5	74.5	16.7			111
$[Fe^{III}(41)Cl]$	tBHP	10.2	0.7	112.2			114
$[Fe^{III}(42h)Cl]$	H_2O_2	45.8	3.4	45.1			111
$[(Fe^{III})_2(46)(O)(OBz)]ClO_4$	mCPBA	37	6.5	270		17.1	122
$[Fe^{III}(50b)_3]$	H_2O_2	16	1.1	32			125
$[(Fe^{III})_2(51)(O)(H_2O)_2]_2(ClO_4)_6$	H_2O_2	52	3.7	4.3	94		126
$[Fe^{II}(Fe^{III})_2(54)_6Cl_2](C_5H_{12})$	O_2	14	7				129
$[(Fe^{II})_4(55a)(O_2)](PF_6)_4$	H_2O_2	9.3	6	43	61.5		130
$[Fe^{II}(64)(Ph_2C(OH)COO)]$	O_2	55	10		100	11.7	141
$\{[Fe^{II}(65)Cl]_2O\}(ClO_4)_2$	H_2O_2	53	3.5	5.3			142
$Fe^{II}(H_2O)_6(BF_4)_2/67$	H_2O_2	98.7	1	98.7			144
$[Fe^{II}(71a)(CH_3CN)](PF_6)_2$	H_2O_2	8	19	32			154
$[Fe^{III}(75)](PBu_3)$	H_2O_2	15	6.1	75			155

[a] % yield of cyclohexanol and cyclohexanone from cyclohexane oxidation based on the minor component. [b] Ratio of cyclohexanol to cyclohexanone in cyclohexane oxidation. [c] Catalytic turnovers, moles of products from cyclohexane oxidation per mole of catalyst. [d] Retention of configuration of the tertiary bonds of cis-1,2-dimethylcyclohexane. [e] 3°/2° = 3 × (1-adamantol)/((2-adamantol) + (2-adamantone)). [f] Only alcohol detected. [g] S = solvent (MeOH or H_2O). [h] Reaction carried out in acetone as solvent. [i] Ionic liquid used as solvent.

positions and electron withdrawing substituents to the pyrrole β-position increased catalyst stability under oxidising conditions.[30] Additional optimisation of the reaction conditions led to the development of catalyst systems exhibiting high reactivity towards hydroxylation of alkanes. For instance Wang et al.[32] established the use of chloramine-T (N-chloro-para-toluenesulfonylamide) in combination with dioxygen as oxidant. Remarkably, cyclohexanol is formed exclusively from cyclohexane in 13% yield with [Fe^III(1a)]Cl as the catalyst (2.6 turnovers). Similarly Bandyopadhyay et al.[33] reported on the selective conversion of cyclohexane to cyclohexanol with tBHP in 47% yield based on the oxidant (19 catalytic turnovers) using a pentafluorophenyl substituted porphyrin (1b, Fig. 2) as ligand for an iron(III) complex. Investigations of the solvent influence revealed that the addition of water to the system significantly improves yields. Nakagaki and co-workers applied an acetalphenyl-substituted iron porphyrin (1c, Fig. 2) complex to the oxidation of cyclohexane with PhIO, which also could be successfully immobilized on silica while remaining catalytically active.[34]

Similarly to the hydroxylation reactions mediated by Cyt P450 enzymes, a high-valent iron(IV)–oxo porphyrin π-radical cation is understood as the active species in biomimetic iron heme model systems, although its exact nature strongly depends both on the reaction conditions and oxidant used.[10]

In 2011 a μ-nitrido mixed-valent iron phthalocyanine complex of ligand 2b was reported to be an active catalyst in the oxidation of methane to formic acid with H_2O_2 as oxidant.[35] Phthalocyanines are structurally closely related to porphyrin ligands (Fig. 2). A detailed review of their use in oxidation catalysis was given by Sorokin.[36] It is remarkable that although porphyrin iron μ-oxo and μ-nitrido dimers are considered as inactive, their phthalocyanine analogues have proven to be highly active catalysts in C–H bond activation. Similar to the porphyrin ligands, functionalization of the macrocycle enhances their stability against oxidative degradation.[36] McGaff et al.[37] for example described a "helmet" phthalocyaninato (3, Fig. 2) iron(III) complex, which was used as a cyclohexane oxidation catalyst with up to 116 catalytic turnovers using H_2O_2 as the oxygen source (Table 1).

Seldomly corrole-based iron complexes (**4**, Fig. 2) find application in the catalytic oxygenation of C–H bonds. The first example of an iron(IV) corrole compound, which was used to oxygenate benzylic C–H bonds was published in 1999; however, the respective activation of cyclohexane has been reported only in 2010.[38] Since then various oxidants (*e.g. m*CPBA and *t*BHP) have been examined and it was found that the use of *m*CPBA as the terminal oxidant in the presence of 1.25 mol% *meso–tris*(pentafluorophenyl)-corrolatoiron(IV)chloride leads to the exclusive formation of cyclohexanol from cyclohexane in yields of 50%.[39–41]

2.2 Iron nonheme complexes bearing pure N-donor ligands

Iron complexes bearing multidentate N-donor ligands have been studied extensively as catalysts for the oxidation of alkane C–H bonds in the last 25 years and have proven great potential (Fig. 3). A broad variety of substrates can be covered nowadays ranging from model substrates such as cyclohexane or adamantane to complex biorelevant molecules and polymers. This allows their use in organic synthesis and environmental applications such as waste water treatment or degradation of pollutants.[42,43]

In the early 1990s Que and co-workers reported iron complexes [Fe^{III}(**5a**)Cl$_2$](ClO$_4$) and [Fe^{III}(**5a**)Br$_2$](ClO$_4$) to act as catalysts for the oxidation of cyclohexane with *t*BHP (Fig. 3).[44,45] A series of ligands derived from the tris(2-pyridylmethyl)amine (TPA) scaffold (**6–8**, Fig. 4) was examined in the following years and their μ-oxo bridged diiron complexes exhibit more than 20 turnovers in cyclohexane oxidation with *t*BHP.[46,47]

An important breakthrough was achieved by the same group in 1997 when they reported on the stereospecific oxidation of alkanes using a ferrous TPA complex and H$_2$O$_2$ as the terminal oxidant.[48] High A/K ratios and nearly 100% retention of configuration in the oxidation of *cis*-1,2-dimethylcyclohexane revealed the presence of a metal-centred mechanism rather than involvement of long lived alkyl radicals (Table 1). In this context the authors stressed the importance of *cis* labile coordination sites and a *cis*-α coordination of the ligand regarding catalyst stability and catalytic efficiency. These findings were supported by a range of iron(II) complexes carrying various TPA derived tetradentate and a pentadentate pyridine ligands (**5b**, **5c**, **9–13**, Fig. 4), which were tested in the oxidation of cyclohexane.[49,50] The use of diluted H$_2$O$_2$ allowed minimisation of side reactions initiated by hydroxyl radical formation. The authors proposed the high-valent iron–oxo species Fe^V(O)(OH) as catalytically active species, which was formed *via* a ferric hydroperoxo intermediate. While at this stage evidence was found through mechanistic probe

reactions and spectroscopic methods, it was confirmed later by density functional theory (DFT) calculations.[51] The proposed mechanism for water-assisted oxidations catalysed by nonheme iron complexes bearing tetradentate N-donor ligands is depicted in Scheme 3. Inspired by the promising results obtained with this ligand system many studies dealing with derivatives thereof were published. For example, the introduction of up to three nitro groups to the pyridyl units of the TPA ligand (**14**, Fig. 4) was reported by Hitomi *et al.*[52] However, with increasing number of nitro groups they observed a decrease in yield and selectivity for catalytic cyclohexane oxidation, presumably due to enhanced formation of hydroxyl radicals (Table 1). Similar results were obtained for chloro-substituted ligands **15a–c**.[53] TPA derived ligands **15d–g** were designed to mimic enzymatic binding pockets by introduction of hydrophobic moieties (**15d–f**) and allow hydrogen bonding (**15f** and **15g**).[54] Unfortunately this did not lead to higher selectivity compared to the parent TPA complexes.

Moreover, not only the ligands themselves but also the solvent has a decisive impact on the reaction mechanism and outcome as emphasised independently by Que *et al.* and by Feringa *et al.*[55,56] For both TPA and N$_3$Py (**16**) based complexes, the observed selectivity in the oxidation of cyclohexane and *cis*-1,2-dimethylcyclohexane is lower in acetone than in acetonitrile (Table 1). These results suggest that in acetone a competing reaction pathway becomes available, reducing the selectivity.[56]

Also in 1997 a μ-oxo bridged diiron(III) complex bearing a *N,N′*-dimethyl-*N,N′*-bis(2-pyridylmethyl)ethane-1,2-diamine (BPMEN) ligand **10** (Fig. 3) was reported to be more catalytically active than the TPA analogue in the oxidation of cyclohexane with H$_2$O$_2$.[57] This structural motif was further employed by Ménage and co-workers who synthesised iron complexes incorporating a tetradentate *N*-(trimethoxybenzyl)ethane substituted BPMEN ligand (**17**).[58,59] It became clear that beside the structure of the tetradentate N-donor ligand the nature of the additional monodentate ligands filling the coordination sphere of the metal cation strongly influences the balance between metal- and radical-based reaction pathways. Thus, with [Fe^{II}(**17**)(CH$_3$CN)$_2$](ClO$_4$)$_2$ as catalyst cyclohexane is oxidised yielding 25.5% cyclohexanol and cyclohexanone with an A/K ratio of 9.2 (Table 1). A series of ferrous iron complexes containing BPMEN derived ligands (**18** and **19a–d**, Fig. 5) was investigated by Britovsek *et al.*[60,61] with respect to stability under oxidising conditions and catalytic efficiency. Complexes with a *cis*-α opposed to a *cis*-β or *trans* coordination geometry exhibit a significantly higher catalytic efficiency (Fig. 6).[61] Oxidative ligand degradation was identified to be the main deactivation pathway and the authors underlined the importance of the presence of pyridine donors, which induce a strong ligand field and thereby stabilise reactive intermediates.[62]

These findings were supported by further topological variations of the BPMEN ligand system.[64–66] It was found that catalyst stability under oxidising conditions and can be altered by ligand tuning. Despite these efforts the best catalytic results in cyclohexane oxidation remained those achieved with the parent BPMEN ligand. Using [Fe^{II}(**10**)(OTf)$_2$] as the catalyst 65% yield and an A/K ratio of 9.5 are reached in the oxidation of cyclohexane with H$_2$O$_2$ (Table 1).[60] When the ethyl bridge connecting the two amine units
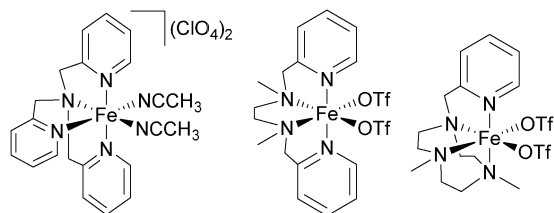

Fig. 3 Prominent examples of iron-based alkane oxidation catalysts bearing tetradentate N-donor ligands.[44,57,82]
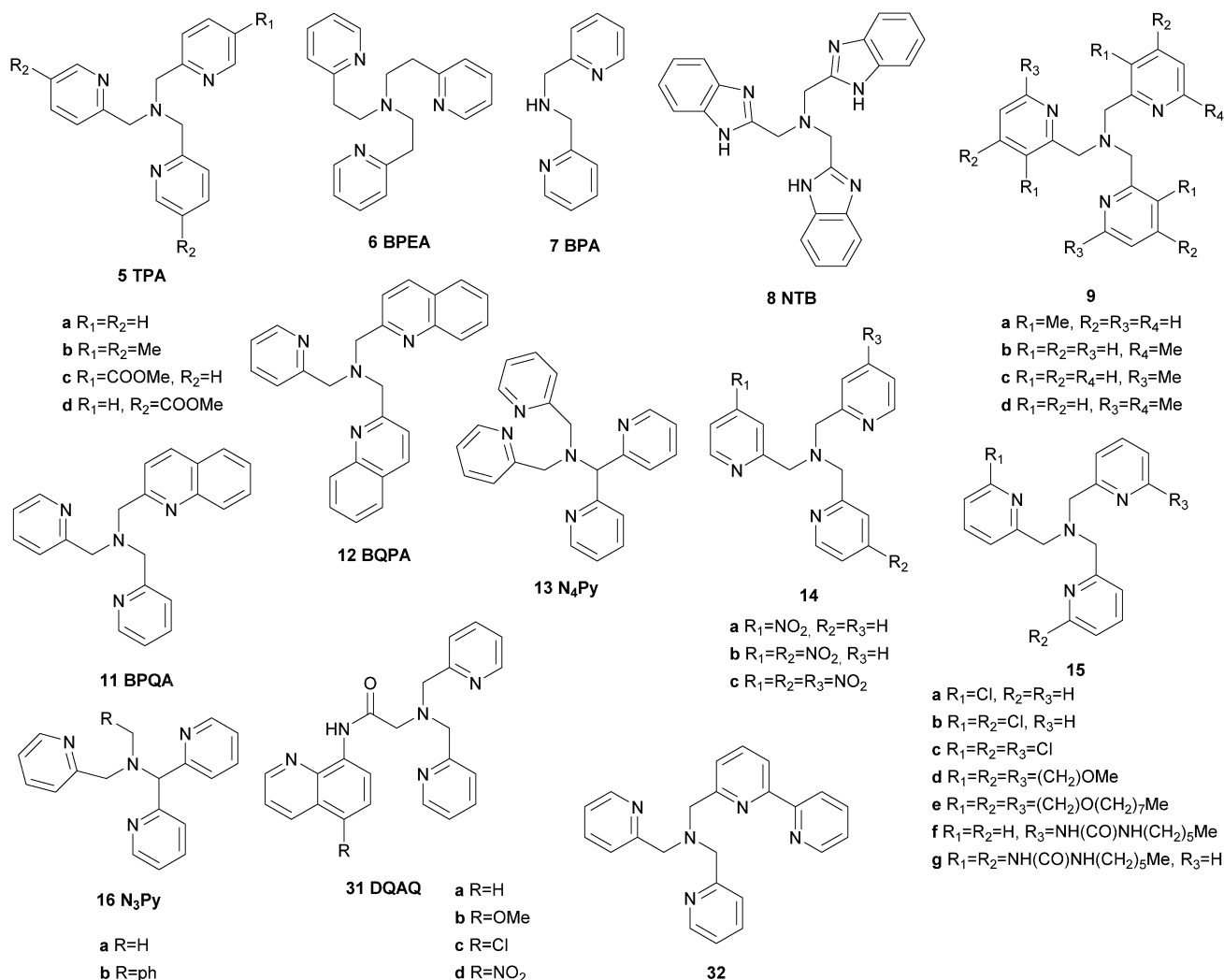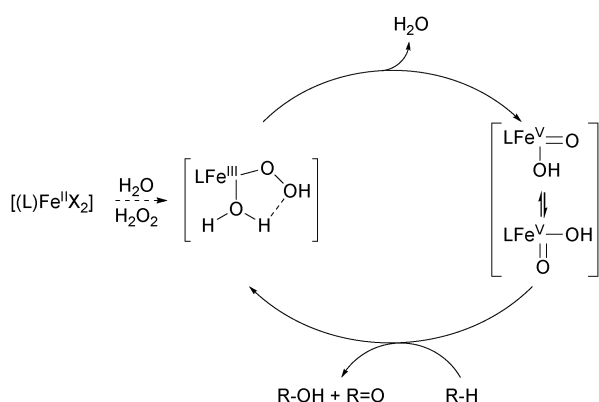
Fig. 4 Pure N-donor ligands derived from the TPA structural motif used in iron-based oxygenation catalysis.

Scheme 3 Mechanism of water-assisted oxidation of alkanes with H_2O_2 catalysed by iron(II) complexes bearing tetradentate N-donor ligands.[6,13]

of the BPMEN ligand is replaced by a biphenyl (**19e**) or biphenyl-ether bridge (**19f**), the *trans* coordination of the remaining triflate ligands leads to a significant decrease in catalytic performance with A/K ratios of ∼1.[63] Substitution of the bridging nitrogen donors by

oxygen or sulphur atoms (**20a–d**, Fig. 11) results in a complete lack of catalytic activity.[65] In this context Britovsek *et al.*[60,65] proposed that a strong ligand field inducing primarily low spin iron complexes positively influences catalytic activity and selectivity.

A milestone was reached by Chen and White in 2007.[67,68] For the first time an iron-based molecular catalyst was used to selectively oxidise functionalised organic molecules with H_2O_2 under synthetically applicable conditions. A large substrate excess is no longer required and a high tolerance towards functional groups is given with the chiral BPMEN derived complex [$Fe^{II}((S,S)$-**21a**)](SbF_6)$_2$ as catalyst. The presence of acetic acid alters both yields and stereoselectivity of the reactions. The selectivity is mainly guided by the electronic properties of the substrate C–H bonds rather than their steric demand. Thus electronically rich, tertiary bonds turned out to be more reactive than secondary or primary bonds despite their better sterical accessibility. However, suitable stereoelectronic modification of tertiary and secondary bonds within the substrate allowed the selective oxidation of the latter.[68] By slow addition of the oxidant even natural products such as (−)-ambroxide and (+)-sclareolide are oxidised with higher

Fig. 5 Pure N-donor ligands derived from the BPMEN structural motif used in iron-based oxygenation catalysis.

Fig. 6 Coordination modes of linear tetradentate N-donor ligands.[63]

Scheme 4 Selective oxidation of secondary C–H bonds in complex substrates using [Fe^{II}(**21a**)](SbF$_6$)$_2$ and H$_2$O$_2$.[68]

yields and orthogonal site selectivity compared to the analogous enzyme-catalysed reactions.[69] In Scheme 4 examples of the diastereoselective oxidation of complex substrates are shown to underline the synthetic utility of this system. By adding sterically demanding substituents to the ligand pyridyl units (**21b**, Fig. 5), control of the site-selectivity could be shifted from the substrate to the ligand as shown by Gormisky and White in 2013.[70] Through the development of a structure-based reactivity model the observed selectivities could be reliably predicted for many substrates. In 2014 Gebbink and co-workers further demonstrated that the

Feature Article

presence of the *R,S*-isomer of the PDP iron(II) catalyst does not have a negative impact on the catalytic efficiency of the system, but merely acts as a spectator.[71] This implies a considerable simplification in catalyst synthesis and allows its preparation in multi-gram scale.

In 2009 Ribas, Costas and co-workers reported the efficient use of another series of BPMEN derived complexes bearing bulky pinene groups at remote positions of the ligand (**22**, Fig. 5).[72] The isolation of the iron centre limits bimolecular degradation pathways and oxidation of various alkane substrates with H_2O_2 in acidic media was achieved with excellent stereoretention and high catalytic efficiency (Table 1). Furthermore, the oxidation of complex organic molecules under mild conditions was achieved with good yields using chiral iron complexes of ligands **19b**, **22b** and **22c**.[73,74] (−)-Ambroxide for example was oxidised with H_2O_2

under similar conditions applied by Chen and White[68] but with lower catalyst loadings (Scheme 5). The selectivity of the reactions turned out to be guided by the special structure of the iron active site as well as the structural and electronic properties of the substrates.

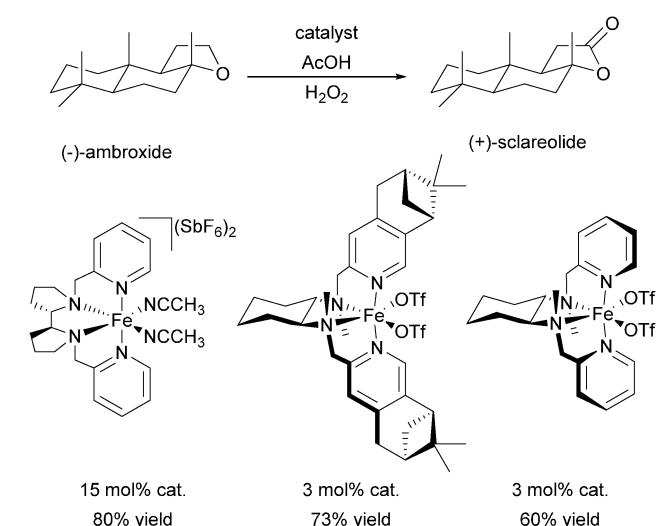A similar methodology was applied by Goldsmith et al.[75,76] who employed sterically demanding BPMEN derived ligands (**19g** and **19h**, Fig. 5) to direct the selectivity of the corresponding iron complexes towards secondary instead of tertiary C–H bonds. This approach proved to be viable as the bulky ligand structure appeared to inhibit the oxidation of sterically congested C–H bonds, although in case of ligand **19g** comparatively low catalytic turnovers were observed. Both iron complexes are also capable of promoting the oxidation of benzylic and allylic C–H bonds by using molecular oxygen as the terminal oxidant.[77] In comparison to the H_2O_2-driven reaction, oxidation of alkanes with these systems proceeds much slower and substrates containing exclusively aliphatic primary and secondary C–H bonds cannot be activated.

Shteinman et al.[78–81] introduced the tetradentate ligand TPCAH bearing an amide functionality (**23**, Fig. 7), which was also successfully applied in iron-based catalytic oxygenation of alkane substrates with H_2O_2. The mononuclear complex $[Fe^{II}(\mathbf{23})(CH_3CN)_2](ClO_4)_2$ exhibits remarkably high stereospecificity (Table 1).

Another ligand family, which affords *cis*-α coordinated iron(II) complexes, has been described by Que, Costas and co-workers.[82,83] The ligands they used are based on a methylpyridine derivatised triazacyclononane (PyTACN) scaffold (**24**, Fig. 7) and the corresponding iron complexes (Fig. 3) produced unprecedented catalytic efficiency in biomimetic oxidation reactions including cyclohexane oxidation (Table 1). Their reactivity can be tuned by modification of the ligand structure resulting in TONs of up to 64 in cyclohexane oxidation and a high degree of stereospecificity in the oxidation of *cis*-DMCH. These results implicate a metal-centred reaction

Scheme 5 Oxidation of (−)-ambroxide with H_2O_2 by chiral iron(II) complexes bearing tetradentate BPMEN derived ligands.[68,73,74]
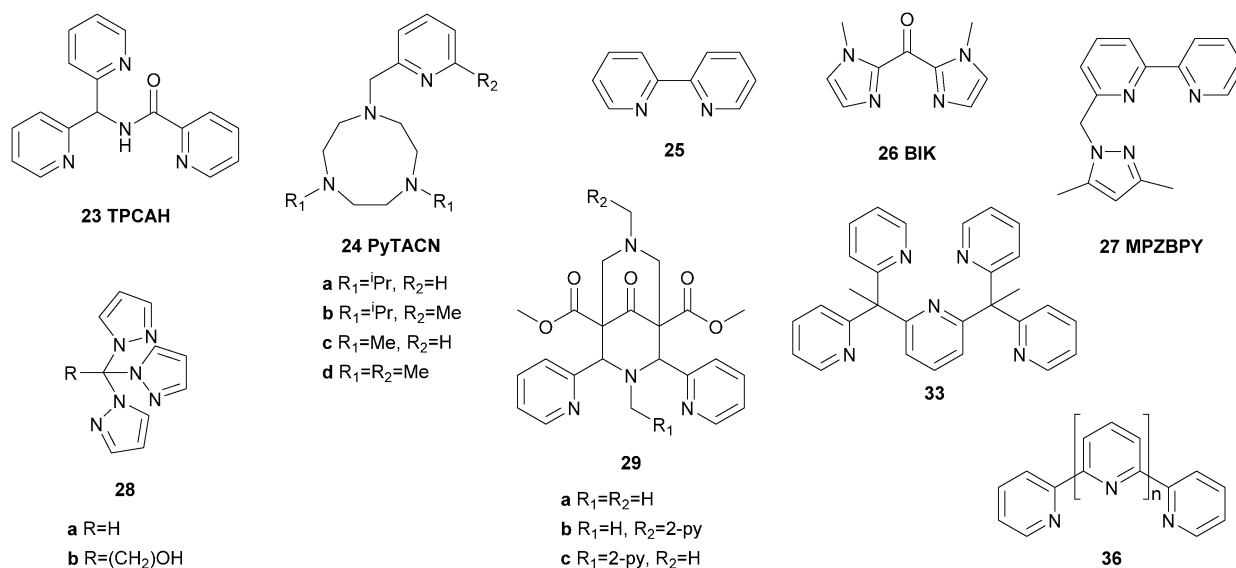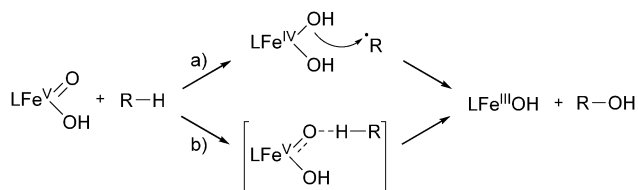

Fig. 7 Pure N-donor ligands used in iron-based oxygenation catalysis.

Scheme 6 Oxidation of an alkane C–H bond by a $Fe^V(O)(OH)$ species *via* a rebound (a) or concerted (b) mechanism.[86]

pathway, which was proposed to occur *via* an alkyl radical rebound mechanism (Scheme 6).[82] Support for the existence of the proposed reactive $Fe^V(O)(OH)$ species could be provided by variable-temperature mass spectrometry.[84] The oxidation of more complex organic molecules, such as biologically relevant terpenoids, has also been investigated. It could be shown, that the catalyst $[Fe^{II}(24d)(OTf)_2]$ displays enhanced selectivity towards the oxidation of methylene sites in acidic media.[85] Further studies on the mechanism of iron complexes bearing PyTACN family ligands with different substitution patterns of the pyridyl unit have been published in 2013.[86,87] The formerly proposed rebound mechanism could be ruled out by DFT calculations and it was shown that hydrogen abstraction and C–O bond formation occur in a concerted process (Scheme 6). Recently, ionic liquids were considered as valuable alternatives to traditionally used solvents such as acetonitrile.[88] The oxidation of cyclohexane with H_2O_2 and $[Fe^{II}(24d)(OTf)_2]$ as the catalyst yields 20% oxygenated products with an A/K ratio of 8, indicating that the use of ionic liquids promotes a metal-centred reaction pathway (Table 1).

In addition to tetradentate N-donor ligands a few examples for ligands with lower and higher denticity have been reported in the context of iron-based catalytic C–H bond oxygenation. Shul'pin *et al.*[89] described the *in situ* formation of an Fe^{III} complex bearing bidentate 2,2′-bipyridine ligands (**25**, Fig. 7), which catalyses C–H bond oxidation. However, the selectivity of the catalytic system with H_2O_2 as the oxidant was rather low and free hydroxyl radicals were found to dominate alkane oxidation reactions. This also applies to catalytic alkane oxidation reactions with *t*BHP employing $[Fe^{II}(26)_3](OTf)_2$ as the catalyst, where **26** is a bidentate bis(imidazolyl)ketone (Table 1).[90] Reedijk *et al.*[91] observed the *in situ* formation of an iron complex bearing a tridentate ligand with a pyrazole unit (**27**). However, the catalytic efficiency of the complex in the oxidation of cyclohexane with H_2O_2 is comparatively low. The scorpionato type ligands **28a** and **28b** were used by Pombeiro and co-workers to afford half-sandwich and sandwich iron(II) complexes, which were tested as catalysts in cyclohexane oxidation.[92,93] Despite coordinative saturation of the sandwich complexes they display high reactivity, exhibiting 385 turnovers in acidic media (Table 1). The closely related half-sandwich complexes reached even more turnovers but a radical mechanism is assumed to dominate the reaction as suggested by low A/K ratios. These results indicate that tridentate N-donor ligands are not as suitable as tetradentate N-donor ligands to support iron-based alkane oxidation catalysts, as they cover either 3 or 6 coordination sites of the iron centre. For pure

N-donor ligands the presence of two *cis*-oriented labile coordination sites has proven to be an important feature, enabling the selective oxidation of aliphatic C–H bonds *via* a metal-centred, water assisted mechanism (Scheme 3).

A comparison of the catalytic efficiency of iron(II) complexes with tetra- and pentadentate N-donor ligands was drawn by Comba *et al.*[94,95] Experimental and theoretical investigations indicate that the oxidation of alkanes with H_2O_2 catalysed by iron bispidine complexes bearing ligands **29a–29c** (Fig. 7) proceeds along different pathways depending on the denticity of the ligand. The complex with tetradentate ligand **29a** is more efficient than those with pentadentate ligands **29b** or **29c** (Table 1).[95] However, both types of bispidine complexes are capable of promoting the oxidation of *cis*-1,2-dimethylcyclo-hexane with O_2 as the terminal oxidant.[96] Moreover, complexes of pentadentate ligands **13** and **30** as well as a number of tetradentate ligands (**24c**, **24d** and **22c**) were described to catalyse the oxidation of aliphatic C–H bonds with H_2O as oxygen atom donor and Ce(IV) salts as single-electron oxidants.[97,98] Despite a low A/K value of only 0.2 tertiary C–H bonds can be oxidised with a high degree of stereoretention using $[Fe^{II}(24d)(OTf)_2]$ as the catalyst, which rules out the formation of long-lived alkyl radicals.[98]

The first example of a mononuclear nonheme iron(III) complex, which catalyses selective C–H bond hydroxylation, was reported by Hitomi *et al.*[99] in 2012. Containing a pentadentate amide ligand (**31a**, Fig. 4) the iron(III) complex efficiently catalyses the oxidation of cyclohexane (78% yield with respect to oxidant) with an A/K ratio of 11.3 (Table 1). The proposed reaction pathway includes the formation of an iron(V)–oxo active species generated from a ferric hydroperoxo intermediate. No prior oxidation of the metal atom, as it is often assumed for iron(II) complexes with *cis*-labile coordination sites, is required. Derivatisation of the quinoline unit of the ligand led to a series of complexes with tuneable electronic properties.[100] With adamantane as a test substrate an increase in catalytic turnovers and selectivity for the oxidation of tertiary bonds was observed with rising electron deficiency of the catalyst.

Another pentadentate TPA derived ligand (**32**, Fig. 4) was described by Britovsek *et al.*[101] in 2013. The corresponding ferrous complex exhibits moderate catalytic activity towards the oxidation of cyclohexane with H_2O_2 (Table 1). This was attributed to a short lifetime of the tentative iron(IV)–oxo species, which dimerises to form a μ-oxo bridged iron(III) complex. Xiang and co-workers reported the synthesis of an iron complex bearing the rigid pentadentate N-donor ligand **33**.[102] Cyclohexane is oxidised with 25% yield with respect to H_2O_2 and an A/K ratio of 1.3, pointing to the presence of free radicals during the reaction (Table 1).

Unusual iron complexes bearing hexadentate ligands (**34a** and **34b**, Fig. 5) have been prepared by Banse and co-workers and reacted readily with peracids to form high-valent iron(IV)–oxo species that could be isolated and characterized spectroscopically.[103,104] The selectivity of the complexes in alkane oxidation, however, is rather low and it was concluded that ligand oxidation proceeds through a bimolecular autoxidation mechanism. Lifetime of the catalysts under oxidising conditions

could be improved by adding ethyl groups to the pyridyl moieties (**34b**), which rendered them more sterically demanding.[104] When one of the pyridine units was replaced by a methoxyphenyltriazole moiety (**35**, Fig. 5), hexa-coordinated complexes were formed, with one donor coordinating only weakly.[105] The triazole unit can be replaced by electrophilic anions and does not bind to the iron centre in the reaction intermediates, which is of possible interest for surface grafting.

Mono- and dinuclear iron(II) complexes of penta- to heptadentate oligopyridine ligands (**36**, n = 3–5) were prepared by Che et al.[106] and applied in a large variety of oxidation reactions including alkene epoxidation as well as alkane, arene, and amine oxidation with oxone as the terminal oxidant. Unfortunately, the observed selectivities in alkane hydroxylation were low (A/K: 0.3).

There are few examples reported in the last decade dealing with the application of iron complexes with pure N-donor imine ligands in alkane oxidation catalysis. Imine ligands are good sigma donors and allow a high degree of π-backbonding. In 2005 Britovsek et al.[107] reported a series of tridentate imine ligands bearing bulky substituents at the wingtips (**37a** and **37b**, Fig. 8). They were used for the synthesis of coordination compounds of various transition metals, amongst them iron. The ferrous complexes exhibited an unusual trigonal bipyramidal geometry and moderate reactivity in the oxidation of cyclohexane (Table 1). The A/K ratios close to 1 indicate that the reaction mechanism is mainly guided by Fenton type chemistry.[107] Similar observations were made by Reedijk and co-workers who used ligand **37c** for the in situ formation of catalysts with different iron(II) and iron(III) salts.[108] Surprisingly, in the absence of the ligand higher conversions of cyclohexane with H_2O_2 were observed while showing only slightly lower selectivity.

On the contrary a metal-centred mechanism was assumed in alkane oxidation reactions using complexes of ligand **37d** as catalysts.[109] The monomeric complex $[Fe^{II}(\textbf{37d})(CH_3CN)](BF_4)_2$

is highly air sensitive and reacts readily with O_2 to form a μ-oxo dimer, which yields 41% cyclohexanol and cyclohexanone with respect to H_2O_2 with an A/K ratio of 7.2 (Table 1).

Bauer et al.[110] described the syntheses and application of iron complexes of the general formula $[Fe^{II}(\textbf{38})_2(OTf)_2]$ bearing bidentate iminopyridine ligands. Although selectivity in cyclohexane oxidation with H_2O_2 is low, activated methylene groups can be oxidised with tBHP and 3 mol% catalyst in yields of up to 91% (fluorene to fluorenone). Silva et al.[111] reported an extraordinarily high selectivity towards the formation of cyclohexanol using $[Fe^{II}(\textbf{39})Cl_2]$ and H_2O_2 in the presence of nitric acid (Table 1). 17.5% of cyclohexane is converted to the respective oxidation products with an A/K ratio of 74.5. An iron(II) complex containing two tridentate ligands of type **40** was described by Di Stefano and co-workers.[112] The authors highlighted its easy preparation and applicability in alkane oxidation reactions with H_2O_2 in the presence of acetic acid as additive. However, the nature of the active species derived from the coordinatively saturated complex could not be revealed so far.

2.3 Iron nonheme complexes bearing C-, O- and S-donor ligands

There are many examples of iron-based oxidation catalysts bearing ligands with carbene, oxygen, or sulphur donors instead of or in addition to nitrogen donor atoms. Prominent examples are salen or carboxylate complexes.

In contrast to many pure N-donor ligands, salen ligands mainly form pentacoordinate iron(III) complexes with one additional anionic ligand in the axial position.[113] Complexes of this ligand class thereby closely resemble the active site of Cyt P450 enzymes. In 2006 Antunes and co-workers reported the capability of an iron(III) salen (**41**, Fig. 9) complex to catalyse the oxidation of cyclohexane with tBHP in the presence of acetic acid (Table 1).[114] Yields of 10.2% cyclohexanol and cyclohexanone are reached after 24 hours reaction time. Higher yields of up to 23% can be achieved using PhIO as the oxidant and catalysts bearing chiral salen ligands of type **42a–42d** (Fig. 9).[115] Similarly to iron porphyrin complexes this increase in reactivity was attributed to the introduction of electron withdrawing substituents. However, both examples exhibit a lack of selectivity regarding the formation of alcohols and ketones as indicated by low A/K ratios. The exclusive formation of alcohols from adamantane with mCPBA as the oxidant and a high A/K ratio of 12.2 in cyclohexane oxidation was observed by Palaniandavar et al.[116] who used a μ-oxo diiron(III) complex of ligand **42e** as the catalyst. Assuming a reactivity distinct from Fenton chemistry, the authors proposed a high-valent iron salen π–cation radical as the active species. The use of H_2O_2 as the oxidant in the catalytic oxidation of alkanes with an iron complex of salen-type ligand **43** was described by Louloudi and co-workers.[117,118] In homogeneous phase the reaction with cyclohexane affords oxygenated products in 12.2% yield (2.4 turnovers) with A/K of 1.8. Furthermore, Silva et al.[111] reported iron(III)salen complexes of ligands (**42f–42h**, Fig. 9) to be capable of C–H bond oxidation with H_2O_2 in acidic media. The catalysts feature high catalytic efficiency and good selectivity towards the formation of alcohols (Table 1).

a R₁=…=R₅=H
b R₁=F, R₂=…=R₅=H
c R₁=R₅=Et, R₂=…=R₄=H
d R₁=R₅=ᶦPr, R₂=…=R₄=H
e R₁=R₅=H, R₂=…=R₄=OMe
f R₁=R₃=R₅=Me, R₂=R₄=H
g R₁=tBu, R₂=…=R₅=H

37

a n=0, R=2,6-ᶦPr₂C₆H₃
b n=0, R=2,6-Me₂C₆H₃
c n=1, R=C₆H₅
d n=1, R=2-py
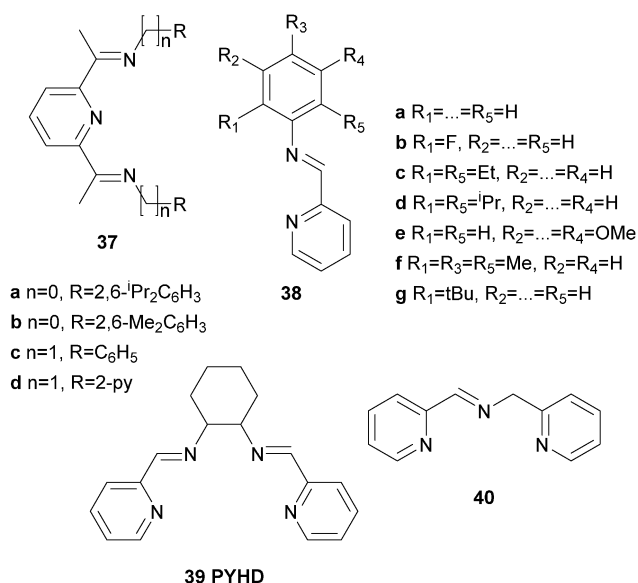
38

39 PYHD

40

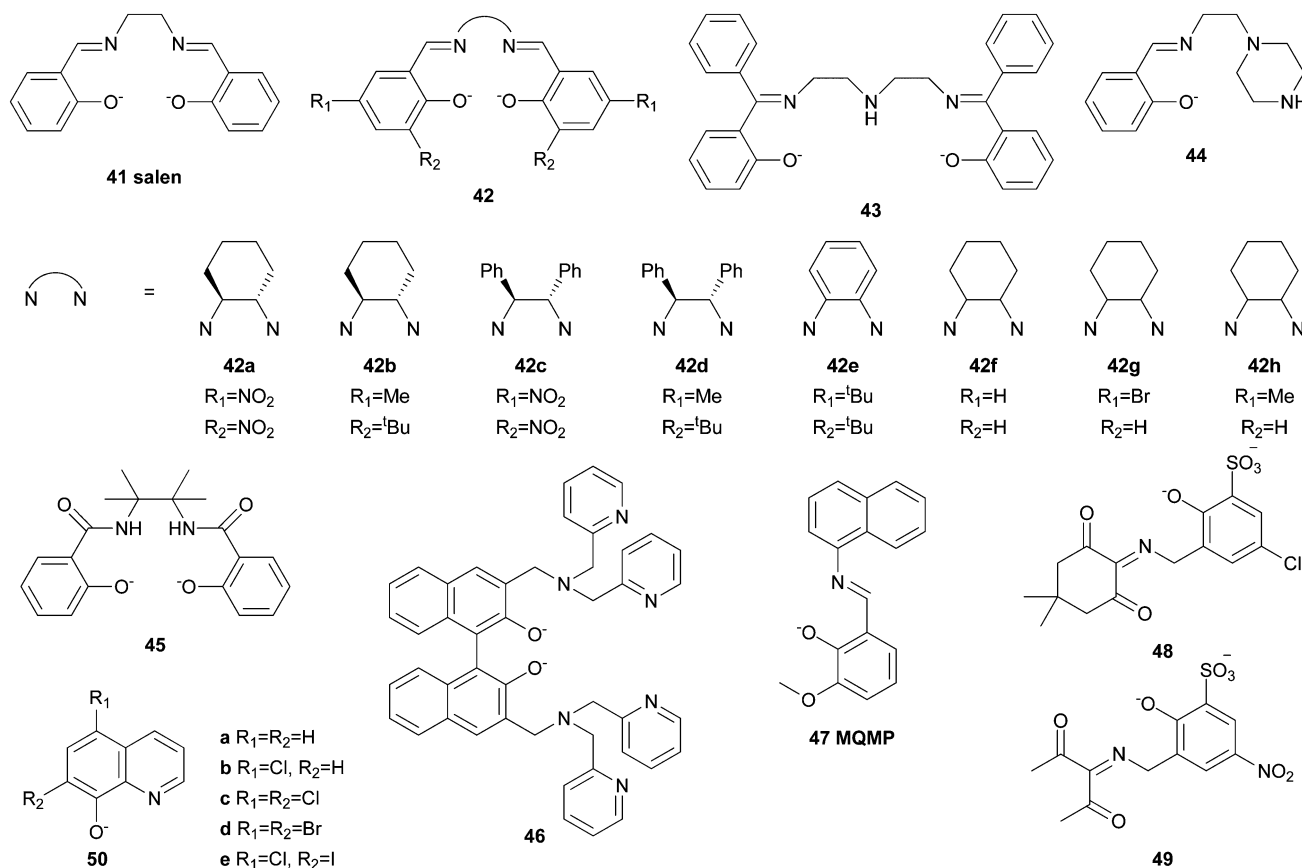**Fig. 8** Imine ligands used in iron-based oxygenation catalysis.

Fig. 9   Salen and phenolate O-donor ligands used in iron complexes for catalytic C−H bond oxidation.

In contrast to that alkane oxidation reactions catalysed by a Schiff base iron(III) complex bearing salicylidene derived ligand **44** are dominated by a hydroxyl radical-based mechanism.[119]

Caradonna *et al.*[120,121] reported the application of a diiron(II) complex bearing tetracoordinate phenolate ligand **45** (Fig. 9) in cyclohexane oxidation catalysis using 2-methyl-1-phenylprop-2-yl hydroperoxide (MPPH) as oxygen atom donor. The complex shows high catalytic efficiency (230 turnovers) and selectivity for alcohol formation. An observed decrease of the product formation rate prior to full consumption of oxidant and/or substrate was attributed to product inhibition rather than decomposition of the catalyst.[121] Rational ligand design was exerted in the case of bisphenolate ligand **46**, which forms a doubly bridged diiron(III) complex, thus resembling the active site of MMO type enzymes.[122] The oxidation of aliphatic substrates with this catalyst was achieved using *m*CPBA with high turnovers and good selectivity (Table 1). However, when H_2O_2 or *t*BHP are used as oxidants the catalytic efficiency is significantly reduced, which implies that differing reaction pathways must be present depending on the oxidant. On the other hand Reedijk *et al.*[123] described the iron(III) complex bearing phenolate ligand **47** to be capable of catalysing the oxidation of alkanes with H_2O_2 as the oxidant. This also holds for the water-soluble iron(III) complexes of hydrazone ligands **48** and **49**, which provide a coordination environment inspired by nonheme metalloenzymes.[124] An alteration of the catalytic

performance of a series of symmetrically coordinated 8-quinolinolato (**50**, Fig. 9) complexes could be observed by visible light irradiation during catalytic oxidation reactions with H_2O_2 (Table 1).[125] This effect was particularly pronounced when dihalogenated ligands **50c**–**50e** were used and it applies not only to aliphatic but also aromatic substrates.

Ligand systems incorporating carboxylate groups often act as bridging agents between two iron centres. This renders them particularly useful when mimicking dinuclear active sites of enzymes such as MMO. Nordlander, Shteinman *et al.*[126] reported the syntheses and characterisation of a series of tetranuclear iron(III) complexes bearing octadentate ligand **51**, which contains a benzoic acid group (Fig. 10). Those complexes, where the carboxylate unit of the ligand bridges two iron centres, catalyse the oxidation of *cis*-DMCH with H_2O_2 displaying a consistently high degree of configuration retention (Table 1). Moreover, cyclohexane oxidation is achieved in high yields and selectivity (A/K: 3.7). The same group later described a similarly bridged diiron complex containing ligand **52**, which exhibits slightly lower catalytic efficiency.[127] Equal amounts of alcohol and ketone are formed in the catalytic oxidation of cyclohexane with H_2O_2 using a hexanuclear iron(III) complex carrying nitrobenzoate ligands (**53**, Fig. 10).[128] A mixed-valent trinuclear iron complex bearing tetramethylreductic acid ligands (H_2TMRA, **54**) was used for the oxidation of cyclohexane with O_2 as the terminal oxidant (Table 1).[129] Under addition of excess H_2TMRA the reaction yields

14% products with an A/K ratio of 7. Shul'pin *et al.*[130] explored the application of di- and tetranuclear iron complexes containing ligand **55a**, which is structurally closely related to the successful PyTACN motif. The tetrameric complex proves to be more robust than the dimeric and even methane can be oxidised under moderate reaction conditions (50 °C, 60 bar). On the other hand, the mononuclear iron complexes carrying two tridentate oxazoline ligands of type **56a** or the structurally closely related, phosphine containing ligands **56b–56d**, exhibit only modest reactivity in the oxidation of benzylic C–H bonds with H_2O_2 or *t*BHP respectively.[131,132] Antunes and co-workers reported a series of tri- and tetradentate ligands of type **57a–57d** (Fig. 10).[133–135] The corresponding iron complexes catalyse the oxidation of cyclohexane with H_2O_2 and mainly produce cyclohexanol and cyclohexanone. For example with 0.1 mol% [Fe^{III}(**57a**)Cl$_3$] as the catalyst 11.4% alcohol and 8.1% ketone with respect to the substrate are obtained.[133] Nevertheless, significant amounts of side products such as cyclohexyl hydroperoxide (12.1%) and adipic acid (2.3%) are formed, which cannot be prevented by neither optimisation of reaction conditions nor microwave irradiation.

High sensitivity of catalytic hydrocarbon oxidation reactions towards the catalyst structure as well as the experimental conditions was also emphasised by Reedijk *et al.*[136] who investigated the catalytic efficiency of mono- and dimeric iron complexes bearing pyrazine-2-carboxylic acid ligands (PCA, **58**, Fig. 10). The latter was used as additive for the *in situ* formation of highly active hydrocarbon oxidation catalysts from hexa- and undecanuclear iron(III)-2,4,5-trimethoxybenzoate (**59**) complexes.[137] Cyclohexane is oxidised with H_2O_2 in the presence of the pre-catalysts and pyrazine-2-carboxylic acid with exceptionally high

turnovers of up to 2210 but low selectivity for alcohol formation. A surprisingly high selectivity for the oxidation of secondary compared to tertiary C–H bonds of methylcyclohexanes with H_2O_2 was observed for iron compounds containing carboxylate ligands of type **60**.[138] Moreover, visible light irradiation significantly accelerates cyclohexane oxidation. L-proline derived ligands **61**, **62a**, and **62b** were designed to mimic the coordination environment of nonheme iron enzymes, but instead of achieving a metal-centred oxidation mechanism, cyclohexene is oxidised via a radical mechanism in allylic position.[139]

A high-valent iron–oxo species could be observed spectroscopically and by mass spectrometry during hydrocarbon oxidation by iron complexes bearing the independent ligands **55b** and Racac (**63**, Fig. 10) with oxone.[140] The combination of a neutral, robust N-donor and the redox active acetylacetonate (acac) derivative allows even the oxidation of challenging substrates such as ethane and propane. Recently Chatterjee and Paine observed the formation of an electrophilic Fe^{IV} oxidant, which evolved from the reaction of a ferrous benzilate complex containing scorpionato ligand **64** with molecular oxygen in the presence of a Lewis acid.[141] It catalytically oxidises cyclohexane and other alkanes in high yields and exhibited excellent selectivity for cyclohexanol formation (Table 1).

Furthermore, iron coordination compounds carrying neutral N_xO_y ligands and their potential application as catalysts in C–H bond oxidation have been described (Fig. 11). In the presence of H_2O_2 the μ-oxo bridged diiron complex [[Fe^{III}(**65**)Cl]$_2$O](ClO$_4$)$_2$ catalyses the oxidation of cyclohexane with a conversion of 53% with respect to the oxidant and an A/K ratio of 3.5 (Table 1).[142] A similar iron complex reported by Sun and co-workers bearing only one additional nitrogen donor unit (N$_4$O, **66**) shows lower catalytic

Fig. 10 Carboxylate ligands used in iron complexes for catalytic C–H bond oxidation.

efficiency with H_2O_2 and requires the use of mCPBA as oxidant.[143] Further exploiting the above mentioned imine ligand qualities, Reedijk et $al.$[144] used an iron complex bearing ligand **67** and observed full conversion of cyclohexane with H_2O_2 (Table 1). Equal amounts of cyclohexanol and cyclohexanone are formed, which was explained by the presence of free radicals. Gebbink and co-workers came to the same conclusion when they described an iron(III) complex with N_3O_2 ligand **62c**, which adopts an unusual heptacoordinate coordination geometry.[145] The catalytic performance of iron(II) complexes bearing N_xO ligands of varying denticity (x = 2–4, **68a–68c**, **69**, Fig. 11) was compared by Bauer and co-workers.[146] At low catalyst loadings the complexes with tetra- and pentadentate ligands perform better than those with tridentate ligands. However, low A/K ratios indicating a radical-based mechanism were observed throughout all catalytic experiments. This also applies to reactions catalysed by the ferrous complex of ligand **70**, which displays a rare heptacoordinate geometry.[147]

Our group has reported the synthesis and characterisation of a series of iron complexes supported by cyclic and acyclic

tetradentate N-heterocyclic carbene ligands **71–74** (Fig. 12).[148–151] The octahedral coordination geometry of iron is completed by coordination of labile acetonitrile solvent molecules. For ligands **71a**, **71b**, **73**, and **74** the iron complexes exhibit $trans$-labile sites, for **71c** and **72b** cis-labile sites as a consequence of the coordination mode of the respective tetradentate ligand. In case of ligand **72a** a fluctuation between equatorial and sawhorse-type coordination is observed. It has been shown that the electronic structure of the Fe(II) complexes can be influenced by target-oriented variation of different coordinating additives in the labile sites.[152]

The ferrous complex $[Fe^{II}(\mathbf{71a})(CH_3CN)_2](PF_6)_2$ was the first organometallic iron compound to be used as olefin epoxidation catalyst and also exhibits high efficiency in the oxygenation of alkanes with H_2O_2 as the oxidant.[153,154] Under ambient conditions and at low catalyst loadings cyclohexane is oxidised with up to 32 turnovers and high selectivity towards the formation of cyclohexanol and cyclohexyl hydroperoxide ((A + H)/K = 19). Substitution of one of the axial acetonitrile units by a phosphine or isonitrile ligand stabilises the catalyst under oxidising conditions without altering the selectivity, which translates to increased turnovers.[154]

Fig. 11 O- and S-donor ligands used in iron complexes for catalytic C–H bond oxidation.

Fig. 12 N-heterocyclic carbene ligands and a corresponding iron complex used for catalytic oxidation reactions.

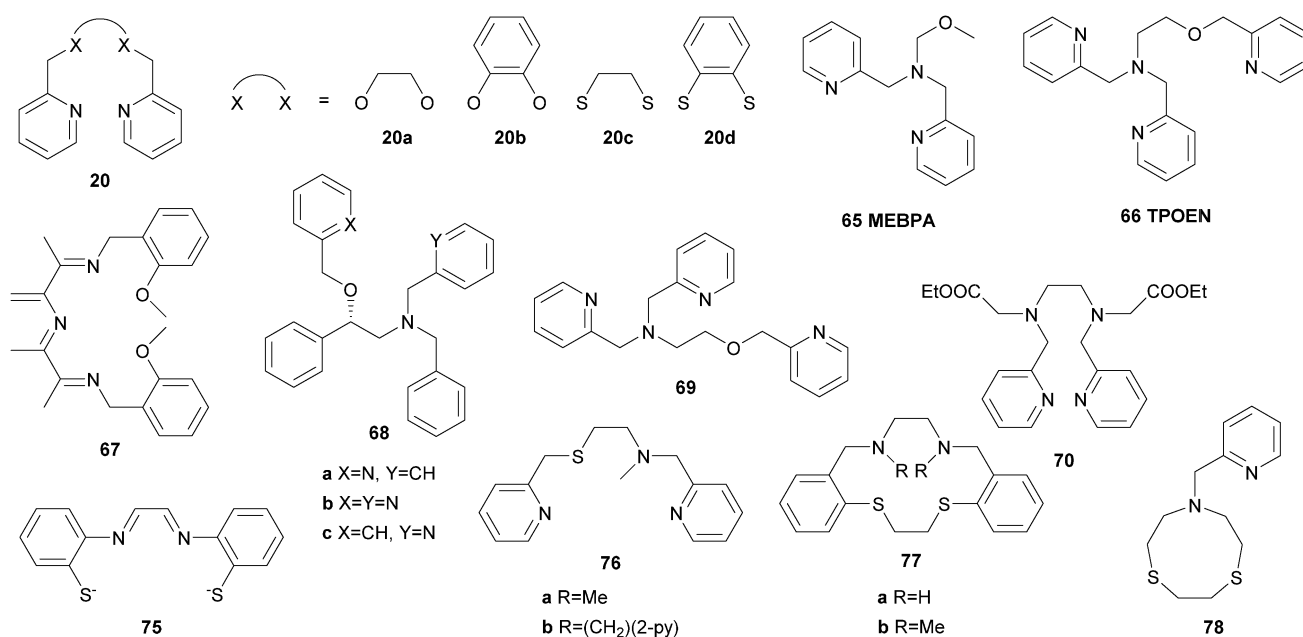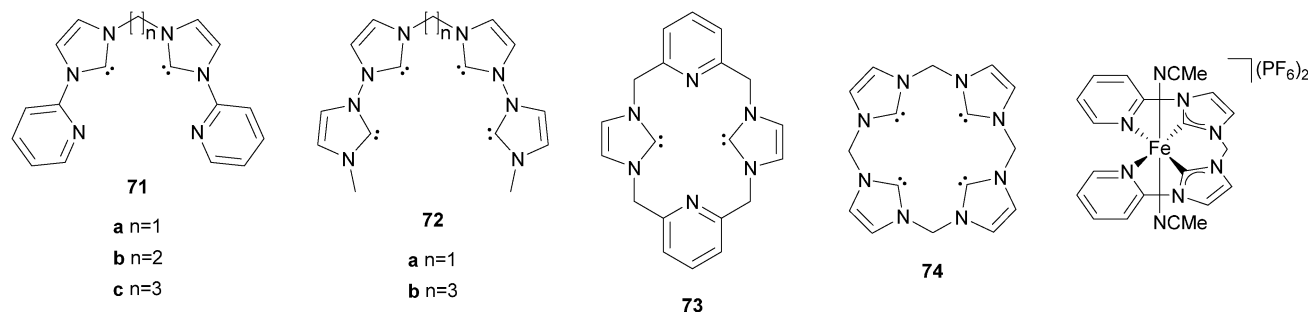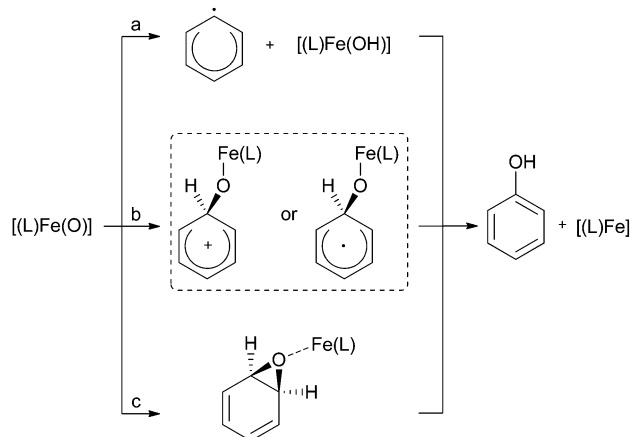As the active site of Cyt P450 enzymes exhibits a coordinating thiolate in addition to the porphyrin moiety, ligands bearing sulphur donor atoms have been applied to mimic catalytic and structural features of those enzymes. Pombeiro *et al.*[155] reported the use of a ferric complex containing the tetradentate N_2S_2 ligand **75** as catalyst for the oxidation of cycloalkanes with H_2O_2 as the terminal oxidant. In the presence of PCA as co-catalyst cyclohexanol and cyclohexanone are produced from cyclohexane in yields up to 16.3% based on the substrate while the selectivity varies significantly depending on the reaction time and temperature (Table 1). Although Britovsek *et al.*[65] reported [Fe^{II}(**20c**)(OTf)$_2$] to be catalytically inactive, Pombeiro and co-workers demonstrated the opposite for the analogous complexes bearing chloride and acetonitrile instead of triflate ligands (Table 1).[156] High selectivity towards alcohol formation and up to 1450 turnovers can be achieved by use of acid additives, in particular trifluoroacetic acid (TFA) and triflic acid (HOTf). Under similar reaction conditions iron(II) complexes containing BPMEN derived or macrocyclic ligands (**76–78**, Fig. 11), and also a dinuclear iron(I) thiophenolate carbonyl complex has been found to catalyse hydrocarbon oxidation reactions with H_2O_2.[157–159] In general, these reports demonstrate the importance of suitable reaction conditions and an enhancement of catalytic efficiency upon acid addition. Radical pathways are dominant in these reactions.

3. Oxygenation of aromatic C–H bonds

Despite the extensive use of molecular iron complexes for the catalytic oxidation of aliphatic C–H bonds, fewer investigations have been made on the selective oxidation of aromatic substrates.[160] On the one hand this may be due to the higher bond strength of aromatic compared to aliphatic C–H bonds (*e.g.*, $BDE_{C–H}$ of 112.9 kcal mol^{-1} for benzene *versus* 99.5 kcal mol^{-1} for cyclohexane[161]). On the other hand the higher reactivity of the phenolic products compared to the non-activated substrates can lead to undesirable formation of catechols, hydroquinones, benzoquinones or even tars.[162]

Many recent reports deal with mechanistic aspects of biomimetic arene oxygenation reactions catalysed by heme and nonheme iron complexes. The proposed oxidising species all derive from ferric hydroxo intermediates and identify as high-valent iron–oxo complexes in several cases. Taking this as a starting point different reaction pathways have been proposed, which involve either an initial hydrogen atom abstraction (path a, Scheme 7) or the formation of a metal-based intermediate (path b, c, Scheme 7).[163,164] An inverse KIE observed for the competitive oxidation of benzene and d_6-benzene and a negative Hammett ρ value indicate the formation of a cationic or radical σ-complex (path b), whereas a normal kinetic isotope effect points either towards an epoxide formation (KIE ~ 1.2, path c) or an initial hydrogen atom abstraction (path a).[165,166]

Moreover, the observation of NIH shift reactions – named after the National Institute of Health where they were first observed in enzymatic reactions[167] – can be explained by a metal-centred

Scheme 7 Proposed mechanisms for aromatic ring hydroxylation by a high-valent iron–oxo species.[163,164]

oxidation pathway. d_3-Benzene as a probe substrate to detect NIH shifts has been established by Kudrik and Sorokin (Scheme 8).[168] The detection of mono- and trideuterated benzoquinone is used as an indicator for the replacement of a deuterium atom to an adjacent carbon atom.

3.1 Iron heme complexes and related derivatives

Iron heme complexes, bearing substituted porphyrin and phthalocyanine ligands, have been used since the early 1990s for the catalytic oxidation of aromatic substrates.[30,36,169–171] However, the reaction mechanisms for aromatic substrates feature great complexity and in the last decade numerous experimental and theoretical investigations have been made to elucidate the nature of the active oxidising species. Mostly iron(IV)–oxo π-radical cations, analogous to those formed by Cyt P450 enzymes, are believed to be the catalytically active species. Amongst others, this was supported by Jang, Nam and co-workers who performed kinetic measurements of arene hydroxylation reactions under stoichiometric conditions.[163] As catalyst they used an iron(IV)–oxo porphyrin π-radical cation complex, which was generated *in situ* by the reaction of PhIO and an iron(III) complex bearing ligand **1a** (Fig. 2). The authors also observed an inverse KIE and a large negative Hammett ρ value, indicating that the reaction involves an electrophilic attack of the iron species and the formation of a σ-complex (path b, Scheme 7). Further evidence was gained by kinetic experiments under catalytic conditions and ^{18}O labelling studies using *m*CPBA as the oxidant.[172] By DFT methods Kumar *et al.*[173] investigated the influence of axial ligands on the kinetics and mechanism of aromatic hydroxylation reactions mediated by iron(III) porphyrin complexes. They found that the nature of the axial ligand, being a cysteine residue in the naturally occurring enzyme, determines the basicity of the iron centre and thus influences the reaction rate.

Practical use of iron porphyrin complexes can be made for environmental applications. Polycyclic aromatic hydrocarbons (PAHs), which constitute an important class of pollutants and possess carcinogenic properties, can be oxidised to the corresponding quinone derivatives using metalloporphyrin complexes

Scheme 8   Detection of NIH shift with d_3-benzene as a model substrate.[168]

and H_2O_2 as the oxygen source (Scheme 9).[174,175] Giri and Chauhan observed that iron(III) porphyrin complexes bearing electron withdrawing substituents exhibit the highest catalytic efficiency. The mild reaction conditions in the absence of additives and the use of a commercially available and benign oxidant as well as a reusable catalyst renders this process very environmentally friendly.

In addition to metalloporphyrins, structurally related phthalocyanine and porphyrazine iron(III) complexes were found to catalyse the oxidation of aromatic C–H bonds. For example, Kudrik and Sorokin reported the catalytic oxidation of benzene with H_2O_2 by a μ-nitrido bridged iron tetra(tert-butylphthalocyanine) (2a, Fig. 2) complex.[168] 20% of benzene was converted with 12 turnovers and a NIH shift could be detected. The formation of benzene oxide during the reaction and a normal KIE indicate that the mechanism differs from that of iron porphyrin mediated reactions. The use of alternative oxidation

reagents such as PhIO, iodosylbenzene sulfate or tetrabutylammonium oxone enables the oxidation of a variety of aromatic substrates catalysed by μ-oxo diiron complexes bearing phthalocyanine ligands 2b and 2c (Fig. 2).[176,177] The systems prove to be very reactive and benzene can be oxidised to para-benzoquinone with 38% yield and 100% selectivity at a catalyst loading of 5 mol%.[177] A common problem shared by these catalysts is the deactivation via oxidative degradation of the ligand scaffold. By elimination of all ligand C–H bonds, which was achieved using perfluorinated porphyrazine ligand 79 (Fig. 2), the stability under oxidative conditions could be increased.[178]

3.2   Iron nonheme complexes bearing pure N-donor ligands

In analogy to alkane oxidation reactions, nonheme iron complexes have been reported to act as catalysts for ring hydroxylation of aromatic substrates with various oxidants. Many of these contain pure N-donor ligands with varying denticity. Several mononuclear iron complexes with polyazadentate ligands (19c (Fig. 7), 80, 81 (Fig. 13)) catalyse the oxidation of benzene and substituted derivatives.[179,180] Good selectivity for ring oxidation instead of benzylic oxidation in case of toluene or demethylation in case of anisole is observed. De Visser, Nam and co-workers used iron(II) complexes of the pentadentate ligands 13 and 30 to demonstrate that the corresponding iron(IV)–oxo species are active oxidants in arene oxygenation reactions.[164] Similar to the above described iron porphyrin complexes the authors claimed that the reaction mechanism includes an electrophilic attack followed by the formation of a radical or cationic σ-complex (path b, Scheme 7), indicated by an inverse KIE and a large negative Hammett ρ value. An initial proton abstraction mechanism (path a, Scheme 7) could be ruled out on the basis of these findings. This also accounts for aromatic hydroxylation reactions mediated by BPMEN 10-supported iron catalysts as reported by Makhlynets and Rybak-Akimova.[181] In this case, however, the iron(IV)–oxo complex was shown to be catalytically inactive and a different intermediate derived from a well-characterized ferric hydroperoxo species was assumed to be the active oxidant.

Furthermore, iron(II) complexes bearing hexadentate ligands 34a or 34c (Fig. 5) were reported to be efficient catalysts for arene ring hydroxylation reactions with H_2O_2.[182] Using 5 mol% $[Fe^{II}(34a)](PF_6)_2$ as the catalyst benzene is converted to phenol with 46% yield based on the oxidant, which can be enhanced by addition of reducing agents such as 1-naphtol. Complexes containing polyaza-ligands of lower denticity (19c, Fig. 5, 80a and 80b, Fig. 13) on the other hand exhibit reduced catalytic efficiency. In a later study a reaction mechanism was proposed involving the formation of a pair of caged oxidants including an iron(IV)–oxo species and a hydroxyl radical, which perform aromatic hydroxylation in a concerted manner.[183] Che and co-workers demonstrated the versatility of their catalytic system, comprising mono- and diiron complexes with ligands of type 36 (Fig. 7) and oxone as the oxidant, by application to aromatic substrates.[106] Several, mostly electron-rich, benzene derivatives can be oxidised to the corresponding quinones with good selectivity. Naphthoquinone for example is formed from naphthalene in 47% yield with 65% selectivity at a catalyst loading of 5 mol%.
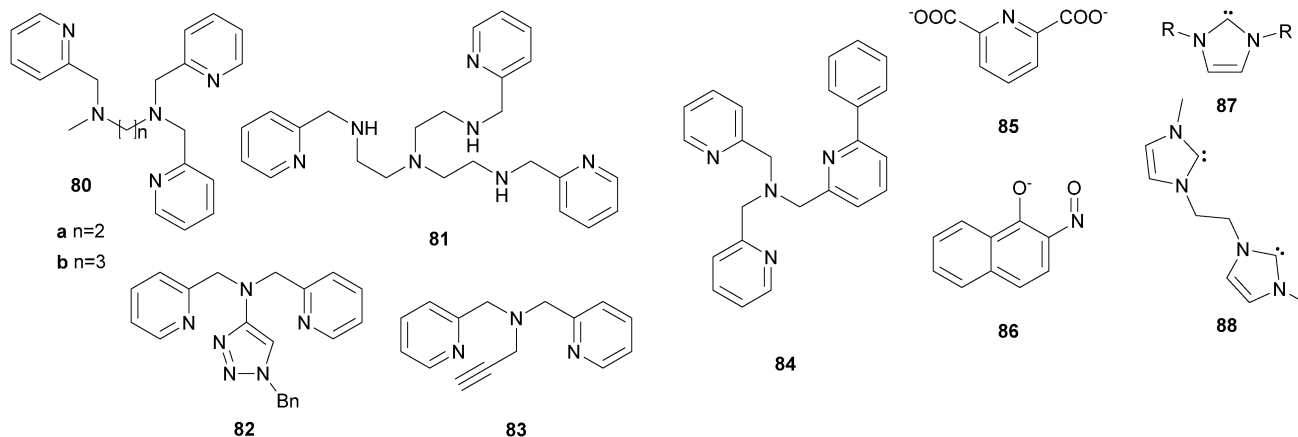

Scheme 9   Oxidation of benzanthracene (top) and pyrene (bottom) by iron(III) porphyrin complexes and H_2O_2.[174]

Fig. 13 Examples of ligands used for iron-based arene oxidation reactions.

In addition to aliphatic C–H bond activation, hexacoordinate iron complexes bearing ligands **35a** or **35b** (Fig. 5) can also be used for the oxidation of anisole with H_2O_2.[105] High affinity for ring hydroxylation is observed as well as a large *ortho/para* selectivity. Liu *et al.*[184] used iron(II) complexes of ligands **7**, **82**, and **83** to relate electronic properties to catalytic performance. It could be shown that complexes with more negative reduction potentials exhibit a higher catalytic efficiency in benzene oxidation with H_2O_2 as oxygen source.

A close resemblance of the reactivity of nonheme aryl amino acid hydroxylases has been identified for iron complexes bearing phenyl derivatised TPA ligands of type **84** (Fig. 13).[185] Intramolecular *ortho*-hydroxylation is observed after addition of *t*BHP and mechanistic investigations revealed that these systems are potent functional models, which support a better understanding of the enzymes' reactivity.[185–187]

3.4 Iron nonheme complexes bearing C-, O- and S-donor ligands

The replacement of nitrogen by other electron donating atoms such as oxygen, sulphur or carbenes allows the synthesis of manifold iron complexes, which can be used as catalysts in aromatic oxygenation reactions. Beller *et al.*[188] observed the *in situ* formation of a catalyst from $FeCl_3$, pyridine-2,6-dicarboxylic acid (**85**, Fig. 13), and a benzyl amine, which mediates the efficient and selective oxidation of non-activated aromatic substrates to the corresponding quinones. Among those were 2,3,5-trimethylbenzoquinone and 2-methylnaphtoquinone, which are industrially important intermediates for vitamin synthesis. An iron(II) complex bearing three bidentate 1-nitroso-2-naphtolate units (**86**, Fig. 13) was reported to be an efficient catalyst for benzene hydroxylation by Li *et al.*[189] Starting with the observation of several by-products, such as hydroquinone and catechol, systematic optimisation of the reaction conditions led to exclusive formation of phenol in 10% yield. Structurally related catalysts containing bidentate quinolinolato ligands **50a–50e** (Fig. 9) cannot reach this high degree of selectivity, although a similar, radical-based reaction mechanism has been proposed.[125]

As already mentioned for alkane oxidation reactions, iron–NHC complex $[Fe^{II}(\textbf{71a})(CH_3CN)_2](PF_6)_2$ was also applied for the oxygenation of aromatic substrates with H_2O_2 as the oxidant.[153,190] In the presence of 1 mol% catalyst benzene and toluene are converted to phenols in yields of 11.2 and 14.7% respectively. In the case of toluene a high selectivity for aromatic instead of benzylic oxidation is observed. Based on reactivity studies and the observation of an inverse KIE the participation of a high-valent iron–oxo species in the catalytic reaction was proposed. Zhang *et al.*[191] used mono- and bidentate carbene ligands **87** and **88** (Fig. 13) to form dinuclear iron complexes, which are further stabilised by a butane-2,3-dithiolate. Oxidation of benzene yields up to 26.7% phenol with H_2O_2 as the terminal oxidant. Again, a correlation between the reduction potential and the catalytic performance was observed, with the complex bearing two carbene donors and the most negative potential being most active.

Pombeiro and co-workers applied the iron(III) complex bearing N_2S_2 ligand **75** not only for alkane but also for arene oxidation.[155] Under mild conditions a yield of 20% phenol and 110 turnovers were reported for the oxidation of benzene with H_2O_2 and PCA as additive. No formation of by-products has been observed.

4. Summary and outlook

The selective oxidation of organic C–H bonds is essential for many industrial and biological processes. Intense research efforts have been made in order to establish more efficient catalyst systems and increase sustainability in the synthesis of both commodity chemicals and organic molecules.

A large number of iron complexes were applied as catalysts for the oxidation of aliphatic hydrocarbons with various oxidants. In particular nonheme iron catalysts bearing tetradentate N-donor ligands have shown potential for high efficiency. The first iron complex reported to catalyse the oxidation of alkanes with H_2O_2 by a metal-centred mechanism, is supported by the tetradentate TPA ligand **1a**.[48] Its reactivity and selectivity was soon surpassed by iron complexes containing ligands BPMEN

(**10**) or ^{Me,Me}PyTACN (**24c**); the latter yielding 65% oxygenated products from the oxidation of cyclohexane with H_2O_2 with an A/K ratio of 12 and a high degree of stereoselectivity.[57,82,83] For these catalysts a coordination geometry exhibiting *cis* labile sites has been considered to be crucial to mediate oxidation with H_2O_2 by a water-assisted mechanism with high selectivity. They are still used as benchmark systems for newly developed catalysts. The successful application of some molecular iron complexes with predictable reactivity for the oxidation of complex organic molecules underlined the potential of iron-based catalysts in oxidation chemistry. It was reported that iron complexes bearing tetradentate N-donor ligands allowed the oxidation of natural products with high regio- and stereoselectivity under reaction conditions feasible for organic synthesis.[42,67,68,73,74] However, catalyst degradation resulting in low turnover numbers (<100 for most systems) and the balance between metal-centred and radical-based reaction pathways pose major difficulties. Often generation of free radicals limits selectivity and leads to the formation of undesirable by-products. Therefore, in the past 10 years numerous investigations have been conducted to elucidate mechanistic aspects, including the nature of the active oxidising species. For selective, metal-centred oxidation pathways typically a high-valent iron–oxo complex has been proposed as the catalytically active species.

Depending on the application, problems regarding the oxidation of aromatic substrates are caused by the enhanced reactivity of the phenolic products. However, iron complexes have been found, which exhibit reactivity distinct from Fenton chemistry and catalyse the selective oxidation of arene C–H bonds. Among those are several catalysts containing N-donor ligands, which are well known for their high efficiency in alkane oxidation, but also other ligand classes have proven high potential.[182] Heme-related phthalocyanine complexes for example also catalyse the selective oxidation of benzene to phenol with H_2O_2 as well as iron complexes bearing O-donor ligands or N-heterocyclic carbene ligands.[168,189,190] Practical applications for environmental purposes, such as the oxidation of polycyclic aromatic hydrocarbons, were also reported.[175] Furthermore, extensive mechanistic investigations contributed to a better understanding of synthetic as well as biological systems regarding reaction pathways and the identity of catalytically active intermediates and thus built a basis for a more rational catalyst design.

Despite those achievements most biomimetic and synthetic catalyst systems still lag behind enzymes with respect to reactivity and selectivity, and only very few practical applications have been realised. Therefore, further improvement is certainly necessary to develop efficient, environmentally friendly catalysts capable of oxidising C–H bonds with benign oxidants as alternatives to traditionally used systems.

Acknowledgements

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