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Heterogeneous Oxidation Catalysis

Site Isolation and Epoxidation Reactivity of a Templated Ferrous Bis(phenanthroline) Site in Porous Silica[**]

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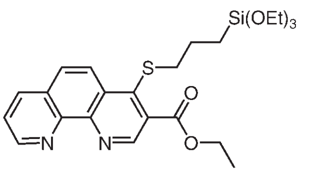
Considerable attention has been devoted recently to the immobilization of olefin oxidation catalysts onto solid supports to increase catalyst stability and allow for catalyst recycling and product separation.[1–3] While the reactivity of many immobilized olefin oxidation catalysts is less than their homogeneous counterparts, some species show enhanced efficiency and/or greater enantioselectivity.[4] The manganese catalysts reported by Jacobs and co-workers benefit remarkably from the site isolation afforded by immobilization: while the homogeneous analogues are prone to forming Mn dimers that decompose H_2O_2, site isolation through immobilization yields more oxidant-efficient and substrate-efficient epoxidation catalysts.[2,5] An additional advantage of such site isolation is the potential to create metal-coordination environments with labile exogenous ligands not readily accessible in a homogeneous medium. Herein, we demonstrate this concept by creating a derivatized Fe^{II}–bis(1,10-phenanthroline) site, referred to hereafter as a Fe^{II}–bisphen site, which contains additional labile ligands. This ligand coordination site is created through a metal-template/metal-exchange procedure on mesoporous silica. Spectroscopic and catalytic oxidative reactivity studies support the formation of such a stabilized Fe^{II}–bisphen binding site, which is only transiently stable in homogenous solution.

Efficient epoxidation of terminal and electron-deficient olefins has been demonstrated recently using catalysts with the related tetra-coordinating nitrogen ligands $[Fe^{II}(mep)]^{2+}$[6] and $[Mn^{II}\{(R,R)\text{-mcp}\}]^{2+}$.[7,8] In the latter case, replacing (*R*,*R*)-mcp, a tetradentate nitrogen ligand, with 2 equivalents of phen provides $[Mn^{II}(phen)_2X_2]^{2+}$ (where X is a weak-field, labile monodentate ligand), which is the most active Mn^{II} catalyst among 20 complexes examined under identical reaction conditions.[9] $[Fe^{II}(phen)_2X_2]^{2+}$ should also be a potential catalyst for olefin epoxidation. While $[Mn^{II}(phen)_2X_2]^{2+}$ complexes form readily upon mixing two equivalents of phen with a variety of Mn^{II} salts in solution, the addition of two equivalents of phen to Fe^{II} salts, such as $Fe^{II}(OTf)_2$ ($OTf = CF_3SO_3^-$), leads rapidly to the highly stable, low-spin $[Fe^{II}(phen)_3]^{2+}$ complex and free Fe^{II}; $[Fe^{II}(phen)_2X_2]^{2+}$ is unstable thermodynamically and kinetically with respect to ligand disproportionation in water as well as in the solvent conditions used for catalysis (see below).[10] Thus, monomeric ferrous bisphen species with accessible coordination sites, which are necessary for most electrophilic oxidation reactions,[9,11] remain unexplored as catalysts.

For this investigation, the micelle-templated silica SBA-15 was selected as a support because of its facile synthesis, large pore diameter (ca. 60 Å), and superior hydrothermal and chemical stability.[3,12] The phenanthroline derivative **1** was synthesized on a multigram scale in an overall yield of 60%. The purposeful incorporation of the sulfur moiety provides an elemental tag for ligand quantification by inductively coupled plasma (ICP) spectroscopy and the trialkoxysilyl group enables facile immobilization on a silica surface. Ligand **2**, which was synthesized in a similar manner, provides metal complexes for comparative studies in homogeneous solution.[13]



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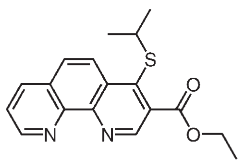

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Two methods were used for the immobilization of **1** onto SBA-15 silica: metal templating and random ligand grafting. The templating method involves the initial formation of the thermodynamically stabilized Cu^I–bisphen complex $[Cu\mathbf{1}_2]^{1+}$, covalent attachment of this discrete complex to the silica, removal of the copper atom template, and final metalation of the immobilized **1** with $Fe(OTf)_2$. Exposing SBA-15 to a brown solution of $[Cu\mathbf{1}_2]PF_6$ yields a material, referred to as Cu^I**T**, which retains its brown color upon filtration and drying in air, thus indicating the presence of a stable Cu^I–bisphen species. More than 95% of the Cu^I is removed from Cu^I**T** by treatment with ethylenediaminetetraacetate (EDTA) to obtain the almost nonmetalated, colorless, templated material **T**.[14] Metalating **T** with $[Cu^I(CH_3CN)_4]PF_6$ reestablishes the 2:1 ligand/metal ratio as determined by ICP analysis, thereby indicating fully reversible metal binding at the templated sites. The random ligand grafting method involves covalent attachment of **1** on SBA-15 in the absence of a metal template to give the grafted material **G**.[15] At a loading of about 0.11 $mmol\,g^{-1}$ of **1** on either **T** or **G**, the average surface area per ligand is 500 $Å^2$, which allows (on average) effective site-isolation of each ligand.[13]

Metalation of **T** and **G** with methanol solutions of $Cu^{II}(OTf)_2$ and $Fe^{II}(OTf)_2$ yields the materials Cu^{II}**T**, Fe^{II}**T**,

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$\mathrm{Cu^{II}}$**G**, and $\mathrm{Fe^{II}}$**G**. The sulfur to metal content confirms the anticipated 2:1 ratio of **1**/metal for $\mathrm{Cu^{II}}$**T** and $\mathrm{Fe^{II}}$**T**, whereas a 1.7:1 **1**/$\mathrm{Cu^{II}}$ ratio and a 2.9:1 **1**/$\mathrm{Fe^{II}}$ ratio were obtained for the grafted materials (Table 1). These results support site isolation for the bis-**1** coordination sphere of **T**, while **G** either forms the highly stable $\mathrm{Fe^{II}}$–(tris-**1**) complex or many of the sites lose weakly associated $\mathrm{Fe^{II}}$ ions upon washing. Incubation of $\mathrm{Fe^{II}}$**T** with 1,10-phenanthroline results in the uptake of one equivalent of this ligand per metal, further supporting the ICP evidence for a site-isolated bis-**1** coordination sphere in $\mathrm{Fe^{II}}$**T** (Table 1).[13]

Table 1: Concentration of metal and ligand in the materials.

Material	**1**[16] [mmol g^{-1}] (±0.01)	Metal [mmol g^{-1}] (±0.002)	**1**/ metal	Phen uptake [mmol g^{-1}] (±0.002)
$\mathrm{Cu^{I}}$**T**	0.11	0.051	2.2:1	–
T	0.11	0.001	–	0.001
$\mathrm{Cu^{II}}$**T**	0.11	0.052	2.1:1	–
$\mathrm{Fe^{II}}$**T**	0.11	0.055	2.0:1	0.055
G	0.10	0.00	–	0.001
$\mathrm{Cu^{II}}$**G**	0.10	0.055	1.7:1	–
$\mathrm{Fe^{II}}$**G**	0.10	0.035	2.9:1	0.020

The copper coordination environments in $[\mathrm{Cu^{II}}$**2**$_2](\mathrm{OTf})_2$, $\mathrm{Cu^{II}}$**T**, and $\mathrm{Cu^{II}}$**G** can be probed readily by X-band EPR spectroscopy.[17] All three systems display characteristic mononuclear axial signals consistent with a $d_{x^2-y^2}$ electronic ground state; the slight signal broadening in $\mathrm{Cu^{II}}$**T** and $\mathrm{Cu^{II}}$**G** as compared to $[\mathrm{Cu^{II}}$**2**$_2](\mathrm{OTf})_2$ is again consistent with site isolation of the complexes in the SBA materials. The spectra of $[\mathrm{Cu}$**2**$_2](\mathrm{OTf})_2$ and $\mathrm{Cu^{II}}$**T** are very similar, with signals corresponding to $g_\perp = 2.06$ and $g_\parallel = 2.270$, while $\mathrm{Cu^{II}}$**G** shows a significant shift to lower field with $g_\parallel = 2.295$ (Figure 1). These results suggest the geometry and coordination around the $\mathrm{Cu^{II}}$ center in the templated material more directly resemble the bisphen environment of $[\mathrm{Cu}$**2**$_2](\mathrm{OTf})_2$ than the grafted material.[13]

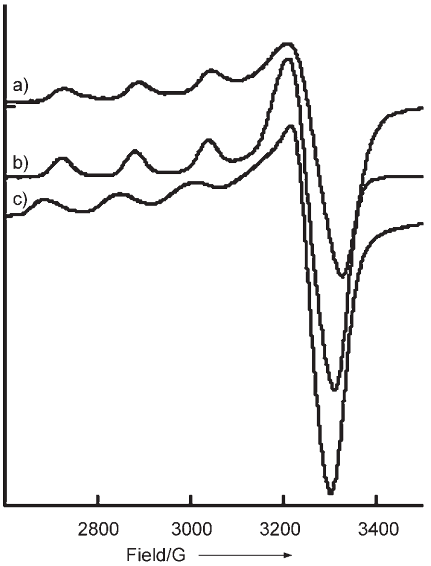

Figure 1. X-band EPR spectrum at 77 K of a) $\mathrm{Cu^{II}}$**T**, b) $[\mathrm{Cu}$**2**$_2](\mathrm{OTf})_2$, and c) $\mathrm{Cu^{II}}$**G**.

The catalytic epoxidation reactivity of $\mathrm{Fe^{II}}$**T**, $\mathrm{Fe^{II}}$**G**, and $[\mathrm{Fe}$**2**$_3](\mathrm{OTf})_2$ with vinylcyclohexane and peracetic acid[18] supports the notion that the most efficient catalyst contains a $\mathrm{Fe^{II}}$–bisphen site (Figure 2). To ensure a fair comparison, the molar ratio of iron to olefin was the same for each reaction, and relevant control experiments were performed.[19] The observed induction period in the case of the homogeneous catalyst $[\mathrm{Fe}$**2**$_3](\mathrm{OTf})_2$[20] presumably corresponds to the dissociation of at least one of the three ligands under the mildly acidic conditions.[21] Indeed, the addition of additional equivalents of **2** to the solution increases the induction period.

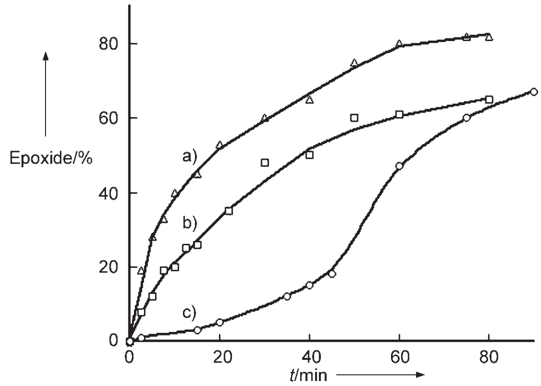

Figure 2. Epoxidation of vinylcyclohexane to 90% conversion with 1 mol% iron and 3 equiv peracetic acid at 2 °C with a) $\mathrm{Fe^{II}}$**T** (△), b) $\mathrm{Fe^{II}}$**G** (□), and c) $[\mathrm{Fe}$**2**$_3](\mathrm{OTf})_2$ (○).[22]

By contrast, $\mathrm{Fe^{II}}$**T** and $\mathrm{Fe^{II}}$**G** present a constant initial reaction rate, which is consistent with labile ligands at the iron center that are exchangeable with the peracetic acid oxidant. While similar vinylcyclohexane conversions are achieved after 60 minutes with each material, $\mathrm{Fe^{II}}$**T** reproducibly exhibits the highest turnover frequency, highest selectivity, and highest yields for all independently prepared materials; $\mathrm{Fe^{II}}$**G** is an inferior epoxidation catalyst under all the conditions explored.

$\mathrm{Fe^{II}}$**T** readily catalyzes the epoxidation of α-olefins such as 1-octene and vinylcyclohexane, but more electron-deficient olefins such as 2-cyclohexen-1-one or allyl acetate react slowly (Table 2).[23] $\mathrm{Fe^{II}}$**T** also reacts more selectively than $[\mathrm{Fe}$**2**$_3]^{2+}$ with each substrate. The olefin substrate scope of $\mathrm{Fe^{II}}$**T** is comparable to that of the homogeneous catalysts $[\mathrm{Fe(mep)}]^{2+}$ with $\mathrm{H_2O_2}$[6] and $[\{\mathrm{Fe(phen)_2(H_2O)}\}_2(\mu\text{-O})]^{4+}$ with peracetic acid,[24] yet very little reactivity is observed with $[\{\mathrm{Fe}($**2**$)_2\mathrm{(H_2O)}\}_2(\mu\text{-O})]^{4+}$, which suggests that the homogeneous catalyst is not acting through a reactive species similar to that of $[\{\mathrm{Fe(phen)_2(H_2O)}\}_2(\mu\text{-O})]^{4+}$.[25]

Table 2: Epoxidations catalyzed by $\mathrm{Fe^{II}}$**T**, $\mathrm{Fe^{II}}$**G**, and $[\mathrm{Fe}$**2**$_3](\mathrm{OTf})_2$.

Substrate	Epoxide yield [%] (selectivity [%])[a]		
	$\mathrm{Fe^{II}}$**T**	$\mathrm{Fe^{II}}$**G**	$[\mathrm{Fe}$**2**$_3](\mathrm{OTf})_2$
vinylcyclohexane	85 (90)	60 (65)	60 (65)
1-octene	80 (95)	75 (95)	65 (80)
allyl acetate	25 (70)	20 (45)	15 (40)
2-cyclohexene-1-one	15 (85)	0 (0)	<5 (<5)

[a] Conditions: 1 mol% Fe, 0.4 M substrate in MeCN, 3 equiv peracetic acid, 2 °C, 60 min.

In essence, by incorporating Fe^{II} centers into an immobilized, site-isolated, bis-**1** coordination sphere on a heterogeneous support we have accessed a species that is only transiently stable in solution. This proposed templated Fe^{II}–(bis-**1**) species has no noticeable induction period and has more selective and efficient catalytic activity for olefin epoxidation with peracetic acid than the analogous homogeneous catalyst or grafted catalyst under similar conditions. The templated bis-**1** sites, though immobilized and site isolated, are flexible enough to coordinate tetrahedral Cu^{I}, tetragonal Cu^{II}, and octahedral Fe^{II} ions. Although the present study is restricted to the reactivity of $[Fe\mathbf{1}_2]^{2+}$ species, the metal-templating method may be adapted to enhance the reactivity of other catalysts that suffer from unreactive, thermodynamically stable species or oligonuclear deactivation pathways in homogeneous solution. Future work will focus on expanding the scope of the reactivity of these materials and developing methods to recycle the catalysts.

Experimental Section

1: 4-Hydroxy-1,10-phenanthroline-3-carboxylic acid ethyl ester (6 g)[26] was mixed with $SOCl_2$ (20 mL) and a catalytic amount of DMF for one hour at 85 °C. After cooling the reaction mixture, the excess $SOCl_2$ was evacuated and the products separated using 10% K_2CO_3 (500 mL) and ethyl acetate (500 mL) to give crude 4-chloro-1,10-phenanthroline-3-carboxylic acid ethyl ester (5.3 g) which was recrystallized from heptanes (70% yield). The recrystallized product was mixed with 3-mercaptopropyltriethoxysilane (1.4 equiv) and K_2CO_3 (1.4 equiv) in THF under N_2 for 12 h at 65 °C. After filtering the mixture, the THF was removed under vacuum, and the product separated by adding pentanes and cooling to 77 K before decanting the solvent. The remaining solvent was then removed under vacuum to leave a yellow oil of **1** that was pure by NMR spectroscopy. ^1H NMR (400 MHz, CD_3Cl, 25 °C, tetramethylsilane): $\delta = 9.20$ (s, 1 H), 9.17 (dd, 1 H), 8.59 (d, 1 H), 8.23 (dd, 1 H), 7.86 (d, 1 H), 7.63 (dd, 1 H), 4.75 (m, 2 H), 3.67 (q, 6 H), 2.96 (t, 2 H), 1.61 (m, 2 H), 1.43 (t, 3 H), 1.08 (t, 9 H), 0.64 ppm (m, 2 H); EI$^+$-HRMS m/z: calculated $[C_{24}H_{32}N_2O_5SSi]$ 488.1801, experimental 488.1787. **2** was prepared in a similar manner except for the thiol used: ^1H NMR (400 MHz, CD_3Cl, 25 °C, tetramethylsilane): $\delta = 9.250$ (s, 1 H), 9.21 (dd, 1 H), 8.66 (d, 1 H), 8.27 (dd, 1 H), 7.90 (d, 1 H), 7.67 (dd, 1 H), 4.51 (m, 2 H), 3.50 (m, 1 H), 1.46 (t, 3 H), 1.23 ppm (d, 6 H).

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[13] See the Supporting Information.

[14] The metal and ligand were quantified with ICP. The ligand was quantified by its sulfur content; see Ref. [13].

[15] Ref. [13] provides further details for templating, grafting, metal removal, and metal incorporation procedures.

[16] The material was analyzed at each stage of development by ICP spectroscopy for metal and sulfur content. The sulfur content of $Cu^{I}\mathbf{T}$ and its nonmetalated species **T** correlate directly to the ligand content of the material before metal-triflate species are added.

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[18] The 18% peracetic acid is synthesized from 50% H_2O_2 and acetic anhydride. Limited epoxidation occurs with commercial peracetic acid solutions; see see Ref. [13].

[19] Control experiments with vinylcyclohexane result in less than 10% epoxide production under the reported reaction conditions; see Ref. [13].

[20] $[Fe\mathbf{2}_3](CF_3SO_3)_2$ is rapidly and quantitatively formed (UV/Vis) by the addition of 2 or 3 equiv of **2** to $Fe^{II}(CF_3SO_3)_2$ in a MeCN/HOAc solution, thus supporting the claim of instability of $[Fe\mathbf{2}_2](CF_3SO_3)_2$ to disproportionation.

[21] $[Fe(phen)_3]^{2+}$ shows similar reactivity to $[Fe\mathbf{2}_3]^{2+}$ under the same conditions: an induction period followed by 60% selectivity for vinylcyclohexane epoxide. During the induction period, red $[Fe\mathbf{2}_3]^{2+}$ is oxidized to blue $[Fe\mathbf{2}_3]^{3+}$, which is detected by a characteristic EPR signal with $g = 2.65$ and by a UV/Vis adsorption band at 600 nm. The Fe^{III} species is more labile towards ligand dissociation than the Fe^{II} species.

[22] Multiple runs of several preparations of the materials consistently resulted in final conversions and selectivities that agree to ± 5%. Multiple runs of the same material consistently resulted in final conversions and selectivities that agree to ± 3%.

[23] In a typical reaction, 18% peracetic acid solution (45 μL, 118 μmol) was added dropwise to a slurry of vinylcyclohexane (6 μL, 44 μmol), acetonitrile (110 μL), and catalyst material (9 mg, 0.45 μmol Fe g^{-1}, 1 mol% Fe) at 2 °C. Aliquots were diluted with diethyl ether and filtered through a silica plug. The products were analyzed by GC and GC-MS, and the yields were determined by integration relative to an alkane internal standard.

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[25] Using **2** as the ligand under the conditions developed for $[\{Fe(phen)_2(H_2O)\}_2(\mu\text{-}O)]^{4+}$ results in 5% conversion of vinylcyclohexane to epoxide in 5 min with no further conversion. The identity of $[\{Fe((\mathbf{2})_2(H_2O)\}_2(\mu\text{-}O)]^{4+}$ was confirmed by comparisons of the absorption spectrum to that of $[\{Fe(phen)_2(H_2O)\}_2(\mu\text{-}O)]^{4+}$ and by ES$^+$-MS. While $[\{Fe(phen)_2(H_2O)\}_2(\mu\text{-}O)]^{4+}$ is an active catalyst under the reaction conditions used herein, the dimer produces only the *cis*-epoxide when treated with *cis*-2-heptene while $[Fe(phen)_3]^{2+}$ produces the *trans*-epoxide.

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