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A novel mononuclear Fe(III) mono(terpyridine) complex having labile solvent ligands and its catalytic activity †

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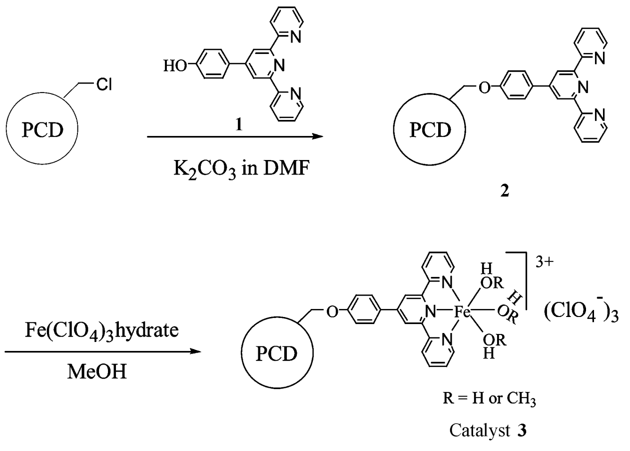
A novel Fe mono(terpyridine) complex was successfully prepared by deliberately choosing the polymer surface-anchored terpyridine as a chelating ligand and it showed an excellent catalytic activity with an easy reusability on the ring-opening reaction of various epoxides by alcohol and water under mild and neutral conditions to give stereospecific and regioselective products.

There has been growing interest in immobilizing (or heterogenizing) conventional homogeneous organometallic catalysts on support materials for simple isolation and recycling processes as well as in developing new organometallic catalysts having high and/or novel specific catalytic activities.[1–4] Although the electrochemical and photochemical features of Ru(II) and Fe(II) poly(pyridyl) complexes have been investigated for many decades, only a few Fe(II) poly(pyridyl) complexes have been studied for their catalytic applications.[5] Furthermore, Fe(III) poly(pyridyl) complexes, that seem to resemble the iron-containing enzymes which play a major role in many metabolically important reactions, have hardly been investigated for catalytic applications. This is probably due to the lack of synthetic methods for preparing a stable Fe(III) poly(pyridyl) complex having labile solvent molecules, which allows exogenous ligands such as substrate to bind during the catalytic reaction,[6] that is believed to be the critical requirement for catalytic processes. Herein, we report on the successful synthesis of the novel mononuclear Fe(III) terpyridine complex with labile solvent, $[Fe(tpy)(solv)_3]^{3+}$ (solv = solvent), by deliberately employing a surface-anchored terpyridine ligand to prevent the generation of the bis(terpyridine) complex, $[Fe(tpy)_2]^{3+}$. Furthermore, the preliminary application of the surface-anchored complex as an immobilized catalyst for the mild hydrolysis and alcoholysis of epoxides at ambient temperature showed very promising results and this novel catalytic system appeared to be very mild and efficient, regioselective, and easily recyclable.

When Fe(III) salts such as $FeCl_3$ or $Fe(ClO_4)_3$ were treated with an excess amount of terpyridine (tpy) a green-colored $[Fe(tpy)_2]^{3+}$ complex was produced immediately. It has already been reported that the formation of the 1 : 1 complex is the rate-determining step of a similar process and higher substituted complexes are easily produced as a major product.[6] Since the spatial arrangement of two tpy ligands in this complex is meridional in conformation (perpendicular to each other), it was expected that the Fe(III) mono(tpy) complex could only be formed if the tpy ligand is attached to a solid surface in a sterically confined rigid manner to prevent the formation of the bis(tpy) complex, $[Fe(tpy)_2]^{3+}$. The functionalized rigid tpy ligand to be anchored on the solid polymer support, therefore, was synthesized by a slightly modified literature method.[7] The insoluble polymer support employed in the present study is a cross-linked modified-polystyrene, poly(chloromethylstyrene-co-divinylbenzene) (PCD, 2.6 mole% divinylbenzene),[8] in which all of the styryl moieties contain chloromethyl groups easily modifiable to other functional groups by simple S_N2 type reactions. PCD-(tpy)Fe complex (**3**) was synthesized as shown in Scheme 1. The mixed solution of polymer support PCD, potassium carbonate and 2,6-bis(2-pyridyl)-4-(*para*-hydroxyphenyl)-pyridine (**1**)† was shaken in DMF at 50 °C for 12 h.† After washing the resultant PCD–terpyridine (PCD-tpy, **2**) in DMF, H_2O, and acetone, it was added to an Fe(III) perchlorate hydrate solution in MeOH. The mixture was shaken for 12 h at room temperature. The pale yellow PCD-tpy (**2**) turned red-brown (*instead of green corresponding to Fe(tpy)$_2$ complex*) due to the formation of the PCD-(tpy)Fe complex **3**, which could also have three additional water and/or methanol ligands. The generation of the Fe mono(tpy) complex with labile solvent ligands could easily be confirmed by adding a solution of free tpy to PCD-(tpy)Fe giving an immediate color change to green (forming PCD-(tpy)Fe(tpy)), or by exchanging the solvent molecule with an excess amount of pure solvent such as H_2O or MeOH followed by IR investigation. The polymer-supported complex **3** was also identified by EPMA (electron probe micro analysis) and elemental analysis.



Scheme 1 Synthesis of polymer-supported PCD-(tpy)Fe catalyst.

PCD-(tpy)Fe complex **3** is, to the best of our knowledge, the first synthesized Fe mono(terpyridine) complex having three coordination sites which are open or loosely bound with labile solvent molecules. Furthermore, PCD-(tpy)Fe complex **3** itself can be considered as a polymer-immobilized catalyst.[9] As expected, the polymer-bound complex **3** effectively catalyzed the epoxide ring-opening reaction[10] with methanol; the results are summarized in Table 1. Cyclohexene oxide was effectively converted to *trans*-1,2-diol monomethyl ether (100% conversion in 1 h) defined as in eqn. (1). More importantly, the catalyst

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/dt/b2/b208413a/

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Table 1 Ring opening results of epoxides (0.6 mmol) by using catalyst **3** in CH_3OH at room temperature

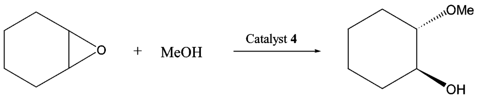
Substrate	Time/h	Conversion yield[a b] (%)
Cyclohexene oxide	1[c]	> 99%
Cyclopentene oxide	5	> 99%
Cyclooctene oxide	48[d]	39
Z-Stilbene oxide	10[e]	> 99%
E-Stilbene oxide	2[e]	> 99%
2-Butene oxide	3	> 99%
Styrene oxide	1	> 99% (exclusively primary alcohol)
1-Hexene oxide	3	> 99% (primary : secondary = 56 : 44)

[a] See ESI † for detailed experimental procedures. All reactions were run at least three times, and the average conversion yields are presented. [b] Based on the consumption of starting epoxide. [c] A mixture of CH_2Cl_2/MeOH (1 : 1) was used instead of MeOH due to insolubility. [d] The reaction was carried out at 50 °C. [e] The moles of *Z*- and *E*-stilbene oxides were 0.2 mmol instead of 0.6 mmol.

Table 2 Hydrolysis of epoxides using catalyst **3** in a mixture of acetone/H_2O (8 : 2 v/v) at room temperature

Substrate	Time/h	Conversion yield[a] (%)
Cyclohexene oxide	2	> 99%
Cyclopentene oxide	32	> 99%
Styrene oxide	48	> 99%
1-Hexene oxide	120	> 99%

[a] Same reaction conditions described in Table 1.



(1)

could be easily recovered by a simple filtration and used repeatedly without any significant change from the original catalytic activity even when used over 20 times consecutively. (*Actually all the reactions in Tables 1 and 2 were performed with the same recycled catalyst.*)

Cyclopentene oxide was also completely converted within 5 h and even cyclooctene oxide, which has been known as one of the most difficult substrates for ring-opening reactions,[10,11] was ring-opened in moderate yield. Furthermore, this novel Fe(III) mono(tpy) catalyst was also very active to acyclic epoxides. *E*- and *Z*-Stilbene oxide, and *Z*-2-butene oxide were completely converted to the corresponding products. All products were determined to have *E*-stereochemistry by NMR, GC and GC/MS analysis, comparing with authentic samples. Styrene oxide was completely converted to 2-methoxy-2-phenyl ethanol within 1 h and the alkoxy group was incorporated exclusively at the benzylic position (α-carbon) instead of the less hindered β-carbon center to generate a primary alcohol. In the case of 1-hexene oxide, however, a mixture of primary and secondary alcohols (56 : 44) was obtained, showing no steric preference for the alcoholic nucleophile. In addition, the reactions with ethanol and propanol have shown similar product patterns as with methanol, but the reaction rates were significantly slower (more than 6 times). These results suggest that the regiochemistry of the ring opening by catalyst **3** would be dependent on the electronic nature of the substrate rather than steric factors.

The more difficult reaction, hydrolysis, has also been carried out with catalyst **3**. Various epoxides could be completely converted to the corresponding *E*-diols that were considered to be valuable (chiral) building blocks for organic synthesis,[12] even though the reaction rate was slower than methanolysis as usual (Table 2). Cyclohexene oxide was also found to be a superb substrate for hydrolysis as shown for methanolysis and the catalyst could be recycled with no observable loss in catalytic activity or selectivity. Further detailed study on the reaction mechanism of various solvolysis reactions with catalyst **3** is in progress.

In conclusion, we have developed a novel synthetic method to prepare a mononuclear Fe mono(tpy) complex with labile solvent ligands by deliberately anchoring the tpy ligand onto a solid support surface. This catalyst system appears to be an efficient, mild, and easily recyclable method for the alcoholysis and hydrolysis of epoxides. This result may also represent an excellent starting point for the development of a new synthetic method to produce metal complexes with labile solvent ligands as recyclable catalysts for many important reactions such as enantioselective solvolysis, hydrogenation, C–H bond oxidation, and various environment-friendly oxidation reactions.

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