

# Novel polymer-supported ruthenium and iron complexes that catalyze the conversion of epoxides into diols or diol mono-ethers: clean and recyclable catalysts†

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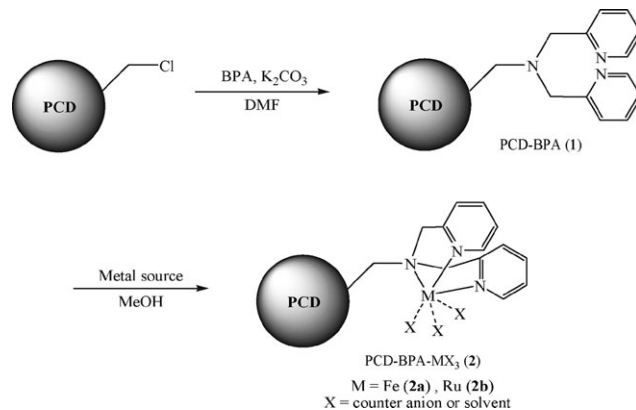
**Polymer-supported metal (Fe or Ru) complexes for epoxide ring opening reactions were successfully prepared by anchoring the bis(2-picoyl)amine ligand onto the polymer poly(chloromethylstyrene-co-divinylbenzene) (PCD); the catalysts showed heterogeneous catalytic activity and easy recyclability in the ring opening reactions of various epoxide substrates with methanol or H<sub>2</sub>O at room temperature under mild and neutral conditions.**

Epoxides are important intermediates in organic synthesis, and the reaction of epoxides with nucleophiles under mild and neutral conditions has been the subject of extensive studies.<sup>1</sup> The 1,2-diol and 1,2-diol mono-ether synthetic intermediates that result from the solvolytic reactions of epoxides have been synthesized by the ring opening methodology of epoxides with various nucleophiles in the presence of metal complexes.<sup>2</sup> More conveniently, the covalent attachment of homogeneous catalysts to insoluble polymer supports has been studied recently as an attractive strategy for extending the practical advantages of heterogeneous catalysis to homogeneous systems,<sup>3</sup> since the catalysts are easily separated from the reagents and products, and can possibly be reused. In contrast, immobilization often results in catalysts with lower efficiencies than their solution phase counterparts.<sup>4</sup> Such approaches frequently lead to partial loss of reactivity. In order to further develop efficient polymer-bound metal complexes, we have synthesized new polymer-bound BPA–metal complexes (BPA = bis(2-picoyl)amine) and studied their reactivity in the ring opening of epoxides. Herein, we report the successful synthesis of novel polymer-bound BPA–metal complexes (metal = Fe (**2a**) or Ru (**2b**)) and their application to the mild ring opening reactions of epoxides by methanol or H<sub>2</sub>O at ambient temperature. In addition, iron catalyst **2a** showed about 10 times better activity than our previous PCD–tpy–Fe(ClO<sub>4</sub>)<sub>3</sub> complex

(PCD = poly(chloromethylstyrene-co-divinylbenzene), tpy = terpyridine).<sup>3m</sup> Moreover, Ru-loaded catalyst **2b** showed a reactivity comparable to iron catalyst **2a**, although Ru is well known as an inert metal.<sup>5</sup>

The insoluble polymer backbone employed in the present study is PCD, a cross-linked polystyrene, in which all the styryl moieties contain chloromethyl groups that can be easily modified to other useful functional groups by simple S<sub>N</sub>2-type reactions (see ESI†).<sup>3m</sup> **2a** and **2b** were synthesized as shown in Scheme 1. PCD, potassium carbonate and BPA were reacted in DMF at 50 °C for 12 h. After washing the crude PCD–BPA (**1**), it was transferred to an MeOH solution of Fe(ClO<sub>4</sub>)<sub>3</sub> or RuCl<sub>3</sub>. The mixture was stirred for 12 h at room temperature. Yellow **1** turned greenish-yellow due to the formation of the PCD–BPA–Fe(ClO<sub>4</sub>)<sub>3</sub> complex **2a**, while RuCl<sub>3</sub> showed a color change from yellow to black. Next, **2a** and **2b** were thoroughly washed with MeOH several times to remove residual metal species.

The attachment of BPA and iron to the PCD was identified by EPMA (Electron Probe Micro Analysis) and elemental analysis. With EPMA, the iron atom coordinating to the ligand showed 2 peaks (*K<sub>α</sub>*, *K<sub>β</sub>*) by X-ray emission, and the nitrogen atoms of BPA were detected using elemental analysis (see ESI†). We found, using the same calculation method as shown in the previous study,<sup>3m</sup> that 50% of the Cl in the PCD was substituted by BPA (2.14 mmol in 1 g PCD; see ESI†). The quantity of metal ions loaded into the catalytic sites of 1 g of the polymer support was determined to be 0.565 mmol for Fe (26% of BPA)



**Scheme 1** Synthesis of PCD-supported BPA–metal catalysts.

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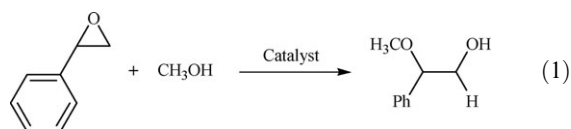
**Table 1** Ring opening reactions of epoxides using catalysts **2a** and **2b** in methanol at room temperature

Entry	Substrate	<b>2a</b> <sup>a</sup>		<b>2b</b> <sup>a</sup>	
		Time/h <sup>b</sup>	Conversion (%) (yield (%)) <sup>c</sup>	Time/h <sup>b</sup>	Conversion (%) (yield (%)) <sup>c</sup>
1	Styrene oxide	1	100 (88.1 ± 1.3; primary alcohol only)	1.5	100 (90.5 ± 1.1; primary alcohol only)
2	Cyclohexene oxide	2.5	100 (86.3 ± 2.5)	4.5	100 (89.4 ± 3.0)
3	Cyclopentene oxide	35	100	24	100
4	<i>cis</i> -2,3-Epoxybutane	8	100	12	100
5	<i>trans</i> -2,3-Epoxybutane	22	100	48	100
6	<i>trans</i> -Stilbene oxide	12	100 ( <i>anti</i> -stereomer : <i>syn</i> -stereomer = 84 : 16) <sup>d</sup>	10	100 ( <i>anti</i> -stereomer : <i>syn</i> -stereomer = 83 : 17) <sup>d</sup>
7	<i>cis</i> -Stilbene oxide	30	100 ( <i>anti</i> -stereomer : <i>syn</i> -stereomer = 93 : 7) <sup>e</sup>	28	100 ( <i>anti</i> -stereomer : <i>syn</i> -stereomer = 93 : 7) <sup>e</sup>
8	1,2-Epoxyhexane	200	100 (1-ol : 2-ol = 57 : 43) <sup>f</sup>	190	100 (1-ol : 2-ol = 57 : 43) <sup>f</sup>

<sup>a</sup> Catalyst 1 mg (0.565 μmol catalytic sites for **2a** and 0.260 μmol for **2b**), substrate 0.5 mmol. All reactions were run at least in triplicate. The data reported represents the average of these reactions. The internal standard was dodecane. <sup>b</sup> Time needed for the complete conversion of epoxide. <sup>c</sup> The yield was based on the starting epoxide and monitored by GC/mass spectroscopy. <sup>d</sup> *Anti*-stereomer means 2-methoxy-1,2-diphenylethanol and *syn*-stereomer means (1*R*,2*R*)-2-methoxy-1,2-diphenylethanol. <sup>e</sup> *Anti*-stereomer means (1*R*)-2-methoxy-1,2-diphenylethanol and *syn*-stereomer means (2*S*)-2-methoxy-1,2-diphenylethanol. <sup>f</sup> 1-ol and 2-ol represent the primary and secondary alcohols, respectively.

and 0.260 mmol for Ru (12% of BPA), respectively, by ICP (inductively coupled plasma) spectrometry.

We have examined the catalytic activity of the newly developed polymer-supported metal complexes **2a** and **2b** in epoxide ring opening reactions (eqn. (1)). Firstly, methanol was examined as a nucleophile for the epoxide ring opening reaction. The treatment of styrene oxide (0.5 mmol) with methanol (1 mL) in the presence of **2a** (1 mg, 0.565 μmol for the quantity of catalytic sites loaded with iron salts) at room temperature produced exclusively and quantitatively a primary alcohol, 2-methoxy-2-phenylethanol, within 1 h under neutral conditions (see entry 1 of Table 1). No epoxide ring opening reaction occurred without catalyst **2a** over the same time period. **2b** also showed a catalytic reactivity similar to that of **2a** (Table 1, entry 1). Importantly, it is worth pointing out that **2a** showed about 10 times better reactivity than our previous catalyst (PCD-tpy-Fe(ClO<sub>4</sub>)<sub>3</sub>).<sup>3m</sup>



Potential benefits of the heterogeneous catalyst include facilitating the separation of the catalyst from the reagents and reaction products, and its recyclability for repeated use.<sup>6</sup> It is critical that catalyst recovery should be simple and efficient, and that the recovered catalyst should retain its original reactivity through multiple cycles. Based on our previous experience,<sup>3m,3n,7</sup> we have examined the reusability of **2a** and **2b** at room temperature. After the ring opening reaction of styrene oxide was complete, the catalysts were recovered by filtration and thoroughly washed with methanol for consecutive runs. The recovered catalysts were used in a new reaction batch of styrene oxide. Our polymer support-immobilized catalysts **2a** and **2b** showed excellent 10 cycle reusability without showing any significant deterioration in catalytic activity (see Table 2).

Next, we performed another control reaction, because in the process of catalysis, the metal species leached from the catalysts might catalyze the ring opening reaction instead of the heterogeneous catalyst.<sup>7</sup> We filtered catalysts **2a** and **2b** after the ring opening reaction of styrene oxide and allowed the filtrates to

react with another aliquot of styrene oxide. We observed that the filtrates showed little catalytic activity (less than 5%) within the same time interval, while the ring opening reactions with the filtered catalysts showed similar reactivities to the initial catalysts. These results strongly suggest that the dominant reactive species are the heterogeneous catalysts **2a** and **2b**, not the other species, such as leached-out metal.

The ring opening reaction of various epoxide substrates catalysed by **2a** and **2b** were also examined, and the results are given in Table 1. Cyclic epoxides, such as cyclohexene oxide and cyclopentene oxide, were effectively converted to *trans*-1,2-diol mono-ethers within 2.5 and 35 h for **2a**, and 1.5 and 4.5 h for **2b**, respectively (Table 1, entries 2 and 3). Acyclic epoxides, such as *cis*- and *trans*-2-butene oxides, were also ring opened efficiently to the corresponding products, respectively. *cis*- and *trans*-Stilbene oxides showed complete conversion to the corresponding product (93 : 7 *anti*-stereomer : *syn*-stereomer for *cis*-stilbene oxide for both **2a** and **2b**, and 84 : 16 *anti*-stereomer : *syn*-stereomer for *trans*-stilbene oxide for both **2a** and **2b**; Table 1, entries 6 and 7). *trans*-Stilbene oxide underwent conversion to the product about three times faster than *cis*-stilbene oxide. All the products were

**Table 2** Catalyst recycling experiments in the ring opening reaction of styrene oxide catalyzed by polymer-supported catalysts **2a** and **2b**<sup>a</sup>

Cycle	<b>2a</b>		<b>2b</b>	
	Time/h <sup>b</sup>	Conversion (%) <sup>c</sup>	Time/h <sup>b</sup>	Conversion (%) <sup>c</sup>
1	1	100	1.5	100
2	1	100	1.5	100
3	1	100	1.5	100
4	1	100	1.5	100
5	1	100	1.5	100
6	1	100	1.5	100
7	1	100	1.5	100
8	1	100	1.5	100
9	1	100	1.5	100
10	1	100	1.5	100

<sup>a</sup> Reaction conditions: Catalyst: 1 mg (0.565 μmol catalytic sites for **2a** and 0.260 μmol for **2b**), styrene oxide : 0.5 mmol, and methanol : 1 mL. <sup>b</sup> Time needed for the whole conversion of styrene oxide. <sup>c</sup> Based on the starting epoxide and monitored by GC/Mass. Dodecane was used as an internal standard.

determined by their characteristic GC retention times and mass spectra, which were obtained and compared with authentic samples.<sup>7</sup>

To further study the regioselectivity of the epoxide conversion, a non-symmetric epoxide, 1,2-epoxyhexane, was used as a substrate (Table 1, entry 8). A mixture of primary (1-ol) and secondary (2-ol) alcohol was obtained (57 : 43 for both **2a** and **2b** for the 1-ol and 2-ol products of 1-hexene oxide), showing no regioselectivity in the reaction with alcohol as the nucleophile. Importantly, the exclusive attack at the benzylic position of styrene oxide (Table 1, entry 1) and the lack of steric preference in 1-hexene oxide shown by the alcoholic nucleophile suggest that the regiochemistry of the ring opening catalysed by **2a** and **2b** is dependent on the electronic nature of the substrate rather than on steric hindrance. On the other hand, it is very surprising that **2b** showed a catalytic reactivity comparable to that of **2a**, because Ru metal is well known to be inert in such catalytic reactions.<sup>5</sup>

The epoxide ring opening mechanism catalysed by **2a** and **2b** could be inferred from the methanolysis of styrene oxide since the methoxy group was incorporated exclusively at the benzylic position ( $\alpha$ -carbon) instead of the less hindered  $\beta$ -carbon to generate the primary alcohol (Scheme 2). Firstly, the substrate styrene oxide substitutes an anion or solvent (X) to give the adduct PCD-BPA-MX<sub>2</sub>(substrate). Next, the more substituted carbon in the intermediate adduct, generated from the catalyst complex **2** and the epoxide, might have significant cationic character. This cationic character could be stabilized by the phenyl group through resonance, and therefore methanol would attack the more positive  $\alpha$ -carbon to give 2-methoxy-2-phenylethanol. Detailed mechanistic studies are currently under investigation.

We also attempted the hydrolysis reaction of epoxide compounds with water to produce diol products, since diol compounds are considered to be valuable building blocks for organic synthesis as intermediates for pharmaceuticals and agrochemicals,<sup>8</sup> and the hydrolysis of epoxide rings is much more difficult than methanolysis.<sup>9</sup> Reactions in the presence of **2b** were carried out under similar conditions in a mixture of H<sub>2</sub>O/acetone (2 : 8) instead of methanol as the solvent. In case of **2a**, Fe metal ions leached-out during the reactions. All the epoxide substrates underwent ring opening by H<sub>2</sub>O to produce the corresponding diol compounds, as shown in Table 3. Styrene oxide proved to be the best substrate for the hydrolysis

**Table 3** Hydrolysis of epoxides using **2b** in a mixture of acetone/H<sub>2</sub>O (8 : 2) at room temperature<sup>a</sup>

Substrate	Time/h <sup>b</sup>	Conversion (%) (yield (%)) <sup>c</sup>
Styrene oxide	1	100 (74.5 $\pm$ 3.3)
Cyclohexene oxide	3	100 (88.7 $\pm$ 2.7)
Cyclopentene oxide	20	100 (90.2 $\pm$ 1.0)
cis-2,3-Epoxybutane	10	100
Trans-2,3-Epoxybutane	30	100

<sup>a</sup> Catalyst 1 mg (0.260  $\mu$ mol catalytic sites for **2b**), substrate 0.5 mmol. All reactions were run at least in triplicate. The data reported represent the average of these reactions. <sup>b</sup> The time needed for the complete conversion of epoxide. <sup>c</sup> Conversion and yield were based on the starting epoxide and monitored by GC/mass spectroscopy. The internal standard was dodecane.

reaction (1 h; Table 3, entry 1). The ring opening reactions of epoxide compounds bearing cyclic and acyclic structures (Table 3, entries 2–5) with **2b** proceeded well at room temperature. All the reactions in Table 3 were performed with the same recycled catalyst. A further detailed study on the various solvolysis reactions with **2a** and **2b** is now in progress.

It deserves to be mentioned that **2a** and **2b** did not catalyze transesterification reactions, while our previous Zn-containing polymer-supported catalysts carried out the reaction efficiently but did not catalyze epoxide ring opening reactions.<sup>3n</sup> These results suggest that the nature of individual metals play an important role when performing specific reactions. For example, transesterification with Zn<sup>3n</sup> vs. epoxide ring opening with Fe and Ru.

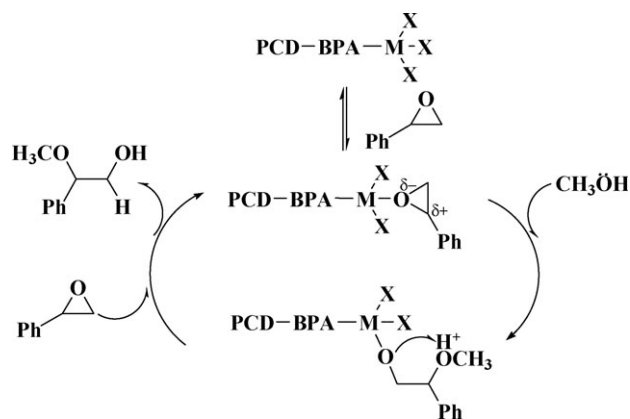
In summary, we have developed new polymer-supported catalysts **2a** and **2b** by deliberately anchoring the tridentate BPA ligand onto a solid support. **2a** and **2b** appear to be efficient, mild and easily recyclable catalysts for the ring opening of epoxides, and these catalysts showed about 10 times better activity than our previous catalyst PCD-tpy-Fe(ClO<sub>4</sub>)<sub>3</sub>. Interestingly, Ru catalyst **2b** showed comparable reactivities to iron catalyst **2a**. This system could also be applied to the preparation of further substituted ether alcohols, which might be exploited immediately for the practical synthesis of a wide range of interesting 1,2-diol mono-ethers. Moreover, this catalytic system is applicable to a wide range of epoxide substrates to prepare various diol compounds. Significantly, these findings may constitute a good starting point for the development of new polymer-supported, efficient and recyclable catalysts for many important reactions, such as enantioselective solvolysis, hydrogenation, C–H bond activation and various environmentally friendly oxidation reactions.

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## Experimental

### Chemicals

PCD (poly(chloromethylstyrene-co-divinylbenzene)) was obtained as by a previous study (see ESI†).<sup>3m</sup> Methanol,



**Scheme 2** A plausible epoxide ring opening mechanism.



acetone, acetonitrile, DMF,  $K_2CO_3$ ,  $Fe(ClO_4)_3$  and  $RuCl_3$  were purchased from Aldrich and used as received. The epoxides and their products, diol mono-ethers and diols, were also obtained from Aldrich and used without further purification.

### Instrumentation

Elemental analysis for carbon, nitrogen and hydrogen was carried out using an EA1108 (Carlo Erba Instruments, Italy) in the Organic Chemistry Research Center of Sogang University, Korea. Product analyses for the ring opening of epoxides were performed on either a Hewlett-Packard 5890 II Plus gas chromatograph interfaced with a Hewlett-Packard model 5989B mass spectrometer or a Donam Systems 6200 gas chromatograph equipped with an FID detector using a 30 m capillary column (Hewlett-Packard HP-1, HP-5 and Ultra 2). Detection of metals was carried out using an electron probe micro analyzer (JEOL JXA-8900R). The amount of metals loaded in **1** was determined by an Inductively Coupled Plasma Spectrometer (IRIS XDL Duo).

### Preparation of catalysts

**Attachment of bis(2-picoly)amine (BPA) onto PCD: PCD-BPA (1).** A mixture of PCD (0.540 g), BPA (0.917 g, 4.6 mmol) and  $K_2CO_3$  (0.829 g, 6 mmol) in DMF (20 mL) was shaken at 50 °C for 12 h. The solid product was filtered and washed with DMF (10 mL for 2 h), water (10 mL for 2 h) and acetone (10 mL for 2 h). It was then further washed with acetonitrile (40 mL) for 1 d by shaking to give a yellow solid. Based on elemental analysis, 50% of the Cl in the PCD was substituted with BPA. The quantity of BPA sites in 1 g of PCD was calculated to be 2.14 mmol (see ESI†).

**Loading of Fe or Ru ions onto BPA ligand: PCD-BPA-M (2).** PCD-BPA (100 mg, 0.214 mmol of BPA sites) and a 10-fold excess of iron(III) perchlorate (779 mg, 2.2 mmol) or  $RuCl_3$  (456 mg, 2.2 mmol) were mixed in MeOH (30 mL) and shaken for 12 h at room temperature. The solid product was filtered and washed with MeOH (30 mL, twice, for 12 h),  $H_2O$  (30 mL for 1 h) and acetone (30 mL for 2 h), and then air dried to give a greenish-yellow solid of PCD-BPA- $Fe(ClO_4)_3$  (**2a**) and a black solid of PCD-BPA- $RuCl_3$  (**2b**), respectively.

**Determination of the amount of metal in 2.** 10 mg of **2** was dissolved in a mixture of  $HNO_3$  (3 mL) and HCl (9 mL), and heated to 100 °C for 12 h. The solution was cooled to room temperature and filtered to remove the undissolved material. The filtrate was transferred to a volumetric flask and water added to make the volume up to 100 mL. Based on standard solutions (0.01, 0.1, 1 and 10 ppm) and using an ICP spectrometer, the amount of metal in **2** was determined to be 0.0565 mmol for Fe (**2a**; 26% of BPA) and 0.0260 mmol for Ru (**2b**; 12% of BPA), respectively.

### Ring opening reactions of epoxides

**Methanolysis.** Epoxides (0.5 mmol) were dissolved in methanol (1 mL), and the polymer-supported catalyst **2** (1 mg,

5.65  $\mu$ mol catalytic sites for **2a** and 2.60  $\mu$ mol for **2b**) was added and shaken at room temperature. Product analysis and characterization were undertaken by the GC/GC mass spectroscopy of 20  $\mu$ L aliquots withdrawn periodically from the reaction mixture. All the products were determined by their characteristic GC retention times and mass spectra, which were obtained and compared with authentic samples.<sup>7</sup>

**Hydrolysis.** The reaction conditions were the same as described above, except that a mixture of  $H_2O$ /acetone (2 : 8) was used as the solvent instead of methanol.

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