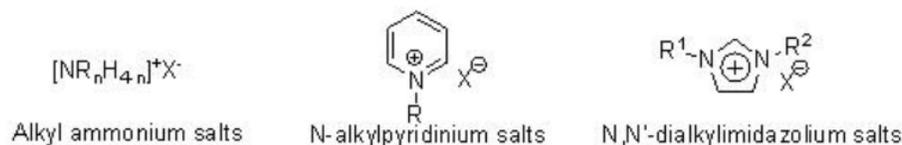


## 7.4: Reactions in Ionic Liquids (IL)

Ionic liquids are composed of ions having melting points below 100°C. They are nonvolatile and facilitate the recovery and recyclability of the catalysts. Scheme 7.4.1 presents some of the typical ILs.



Abbreviations

C<sub>4</sub>C<sub>1</sub>im: R<sup>1</sup> = C<sub>4</sub>H<sub>9</sub>, R<sup>2</sup> = CH<sub>3</sub>

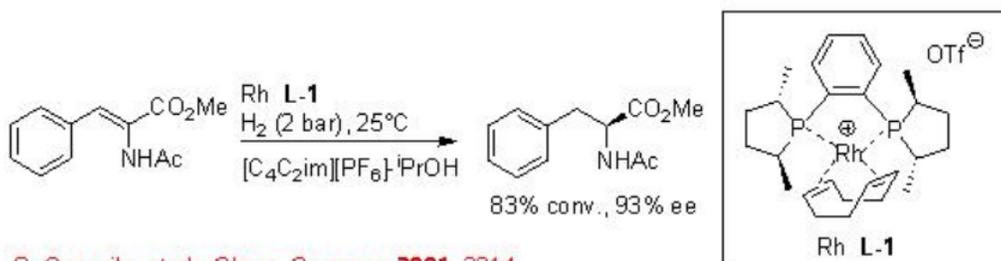
C<sub>4</sub>C<sub>2</sub>im: R<sup>1</sup> = C<sub>4</sub>H<sub>9</sub>, R<sup>2</sup> = C<sub>2</sub>H<sub>5</sub>

C<sub>2</sub>C<sub>1</sub>im: R<sup>1</sup> = C<sub>2</sub>H<sub>5</sub>, R<sup>2</sup> = CH<sub>3</sub>

Scheme 7.4.1

### 7.4.1 Hydrogenation of Alkenes

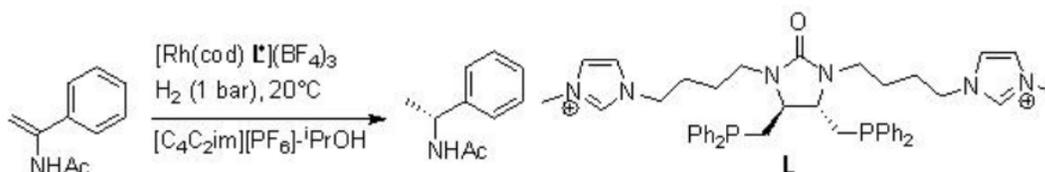
Asymmetric hydrogenation of alkenes using molecular hydrogen as hydrogen source is one of the useful chemical transformation. For example, the chiral rhodium complex Rh **L-1** catalyses the hydrogenation of  $\alpha$ -acetoamide cinnamic acid and related enamides with high enantioselectivity in IL [C<sub>4</sub>C<sub>2</sub>im][PF<sub>6</sub>]. The catalyst can be reused and IL can suppress the catalyst aging in some cases.



S. Guemik, et al., *Chem. Commun.* **2001**, 2314.

Scheme 7.4.2

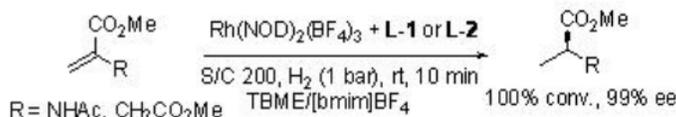
The modified rhodium complex bearing chiral diphosphine with imidazolium moieties has been used as effective catalyst for hydrogen reaction in IL (Scheme 7.4.3). The catalyst can be recovered and recycled without loss of activity and selectivity.



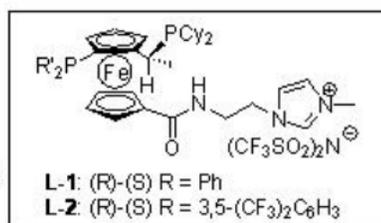
S. Lee, et al., *Chem. Commun.* **2003**, 2624.

Scheme 7.4.3

The asymmetric hydrogenation of methyl acetoamidacrylate can be accomplished in biphasic cosolvent/IL combination in the presence of chiral rhodium complex bearing Josephose with imidazolium tag in *tert*-butyl methyl ether/[bmim]BF<sub>4</sub> (Scheme 7.4.4). The presence of imidazolium tag in the Josephose ligand enhances the affinity of the Rh complex for the IL and suppresses the catalyst leaching. The catalyst can be recycled without loss of activity.

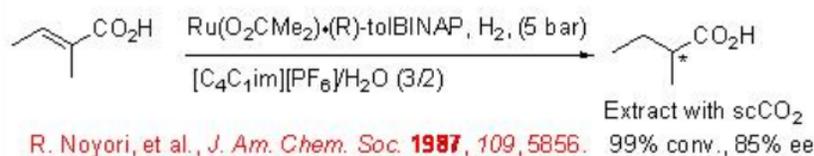


X. Feng et al., *Adv. Synth. Catal.* **2007**, 349, 1803.



Scheme 7.4.4

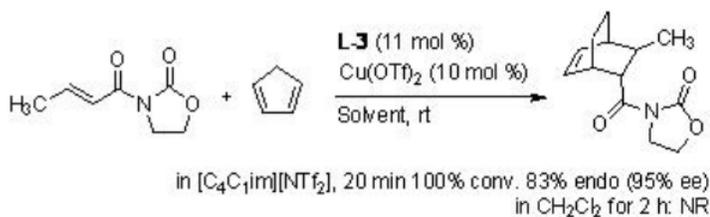
The hydrogenation of tiglic acid has been successful using Ru-BINAP in [bim]PF<sub>6</sub>/H<sub>2</sub>O with good enantioselectivity (Scheme 7.4.5). The enantioselectivity depends on the pressure of the reaction. At high pressure the presence of water increases the enantioselectivity, but low pressure show no effect.



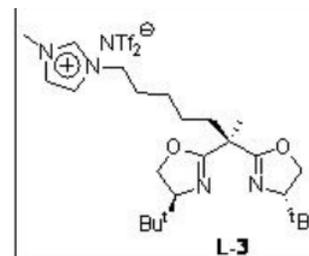
Scheme 7.4.5

### 7.4.2 Diels-Alder Reaction

Copper(II) bisoxazoline complex having imidazolium tag can catalyze the Diels-Alder reaction of *N*-crotonyloxazolidinones with cyclopentadienes in [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>] (Scheme 7.4.6). The catalyst can be recovered and recycled without loss of activity and enantioselectivity at least 10 times. The presence of imidazolium tag to bisoxazoline considerably enhances the recovery and reuse of the catalyst from the IL.



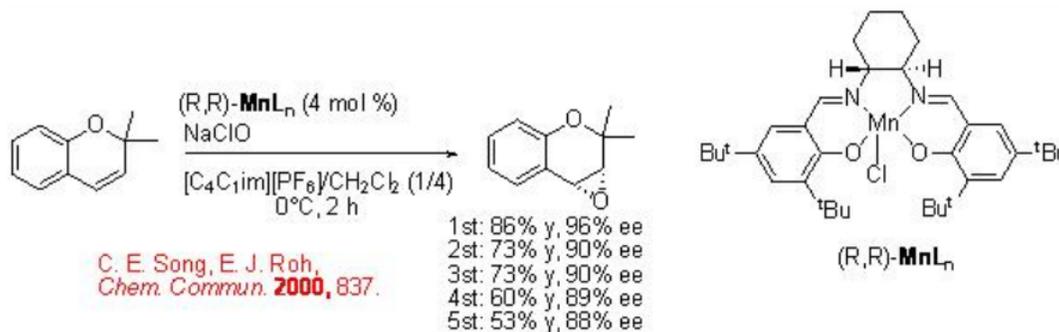
S. Doherty, et al., *Adv. Synth. Catal.* **2007**, 349, 951.



Scheme 7.4.6

### 7.4.3 Epoxidation

The epoxidation of alkenes using chiral Mn(III) salen has been successful in a mixture of [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>]/CH<sub>2</sub>Cl<sub>2</sub> (Scheme 7.4.7). Since IL is solidified at 0°C, the reaction requires CH<sub>2</sub>Cl<sub>2</sub> to form homogeneous solution. The catalyst and IL can be recycled with slight drop in the enantioselectivity.

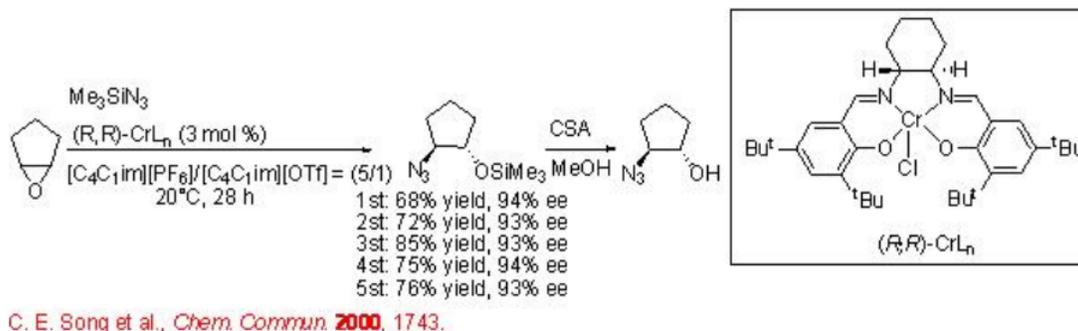


Scheme 7.4.7

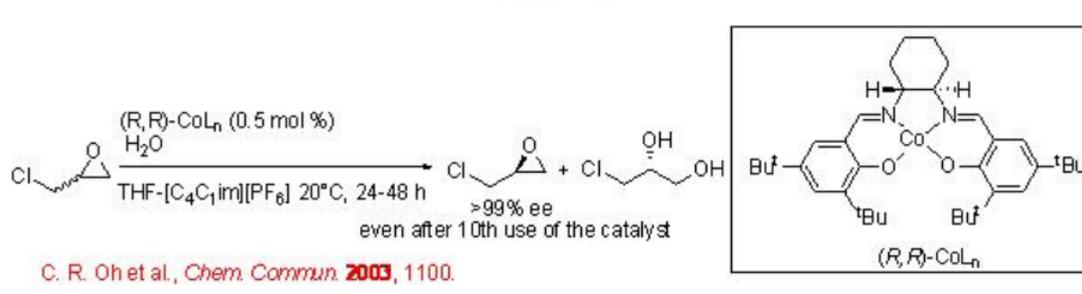
The ring opening of epoxides with  $\text{TMSN}_3$  can be pursued using chiral Cr(III)salen complex in  $[\text{C}_4\text{C}_1\text{im}][\text{OTf}]$  and  $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$  at ambient temperature (Scheme 7.4.8). The catalyst can be recycled up to five times without loss of activity.

#### 7.4.4 Epoxide Opening

Hydrolytic resolution of racemic epoxides is effective using chiral Co(II)salen complex in THF and  $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$  with excellent enantioselectivity (Scheme 7.4.9). In this reaction, Co(II) is oxidized to Co(III) catalyzes the reaction. The catalyst can be recycled 10 times without loss of activity and selectivity.



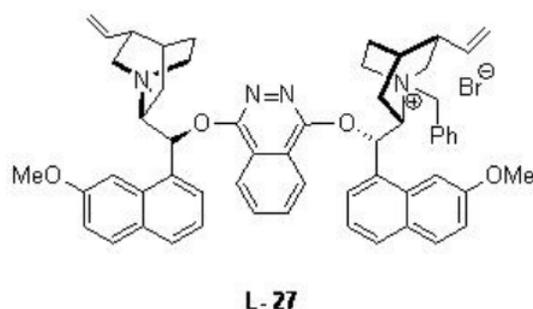
Scheme 7.4.8



Scheme 7.4.9

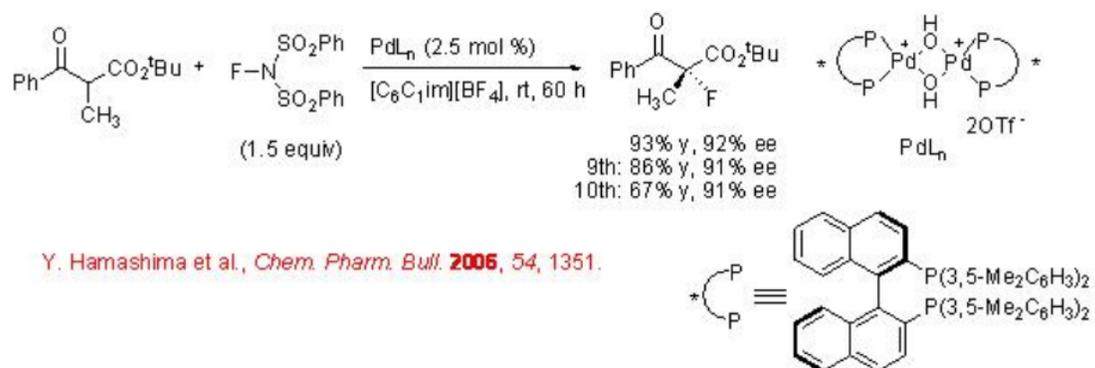
#### 7.4.5 Dihydroxylation Reaction

The asymmetric dihydroxylation of *trans*-stilbene has been done using  $\text{OsO}_4$  (1.5 mol%) and L-3 (2 mol%) in the presence of *N*-methylmorpholine *N*-oxide (NMO) (2.6 mol%) and  $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$  (2 mL) in acetone-water (v/v, 10/1) at  $^\circ\text{C}$ . The catalyst can be recovered in IL and recycled up to three times without significant loss of activity and with a small amount of  $\text{OsO}_4$  leaching from the IL to organic phase.



#### 7.4.6 Fluorination

Fluorination of  $\beta$ -ketoester can be accomplished employing chiral Pd-BINAP in  $[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$ . (Scheme 7.4.10). The reaction proceeds smoothly with good enantioselectivity and the catalyst can be recycled up to 10 times without slight loss of activity.



Scheme 7.4.10

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