

# Ionic Liquids as Solvents for Catalyzed Oxidations of Organic Compounds

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Received: July 12, 2005; Accepted: October 24, 2005

**Abstract:** This review summarizes the oxidation methods of organic compounds carried out in the presence of a catalyst using ionic liquids or molten ammonium salts as solvents. From an ecological point of view, these procedures are particularly interesting when the catalyst is efficiently immobilized in the solvent, thus leading to a reusable system.

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**Keywords:** ammonium salts; catalyst recycling; ionic liquids; organic catalysis; oxidation; transition metal catalysis

## 1 Introduction

Over the last decade, growing attention has been devoted to the use of ionic liquids (ILs) as solvents for organic synthesis, a fact manifested by the increasing rate at which papers on this topic are being published, and also, the number of reviews.<sup>[1–17]</sup> The strong interest in ILs for catalyzed reactions is due to the expected immobilization of the catalyst in the IL that would allow the recycling of the tandem catalyst/solvent. Furthermore, ILs have a rate acceleration effect on some catalytic reactions, and they are often considered as green alternatives to volatile organic solvents although their toxicity and biodegradability are yet to be fully determined.<sup>[18]</sup>

Oxidation reactions are an important topic in organic synthesis. A range of procedures uses stoichiometric and even overstoichiometric amounts of toxic metal oxides; catalytic methods have also been disclosed, but stoichiometric as well as catalytic procedures are mainly carried out in organic solvents. Consequently, the potential of ILs for oxidation reactions has not escaped from the attention of the chemists. Therefore, stoichiometric and catalytic oxidations in ILs have been reported, mainly by adapting the traditional organic solvent methods to

ILs. Since the compatibility with economic and environmental viewpoints is more respected with catalytic processes, the present review focuses on catalyzed oxidations of organic compounds in ILs and includes reactions in molten ammonium salts. For convenience, the structures and abbreviations of the ILs documented in this review are gathered in Scheme 1.

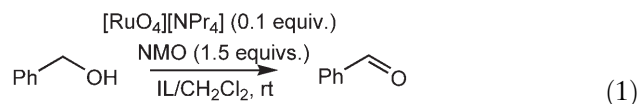
## 2 Alcohol Oxidation

In 2001, Ley et al. have reported the efficient tetra-*N*-propylammonium perruthenate (TPAP)-catalyzed oxidation, at room temperature, of a variety of primary and secondary alcohols, aliphatic, allylic or benzylic, with *N*-methylmorpholine *N*-oxide (NMO) in a mixture of either [C<sub>2</sub>mim][PF<sub>6</sub>] and CH<sub>2</sub>Cl<sub>2</sub> or Et<sub>4</sub>NBr and CH<sub>2</sub>Cl<sub>2</sub> [Eqs. (1)–(4)].<sup>[21]</sup> Oxygen pressure instead of NMO has also been used for the oxidation of *sec*-phenethyl alcohol [Eq. (4)]. Under Ley's experimental conditions, the oxidation products are easily recovered by decanting, and the catalyst/IL system is reusable, the recycling ability depending on the nature of both the starting alcohol and the IL [Eqs. (1)–(4)].

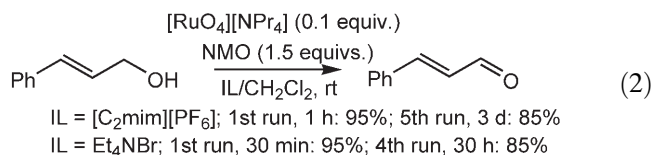
Jacques Muzart was born in 1946, in Vienne la Ville, a small village in the Argonne area, 200 km east of Paris. He studied chemistry at the Université de Champagne-Ardenne and received his degrees (Doctorat de 3<sup>ème</sup> cycle in 1972, Doctorat d'Etat in 1976) for his work with J.-P.



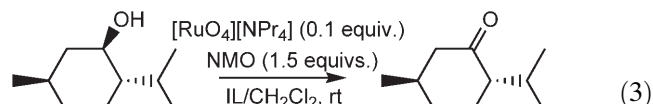
Pête on photochemical rearrangements of  $\alpha,\beta$ -epoxy ketones and  $\beta$ -diketones. He was appointed at the Centre National de la Recherche Scientifique (CNRS) in 1971 as Stagiaire de Recherche and spent 15 months (1977–1978) as a postdoctoral fellow of National Science Foundation working with E. J. Corey at Harvard University on natural product synthesis. On his return to Reims, he mainly studied the photoreactivity of  $\eta^3$ -allylpalladium complexes and anionic activation by supported reagents. In 1988, he was promoted to Directeur de Recherche CNRS. His research interests concentrate on transition metal-catalysis with particular emphasis on oxidations, asymmetric reactions and mechanisms. Since a few years, he is also involved in the valorization of agricultural by-products and in the use of water and molten salts as solvents for organic synthesis.



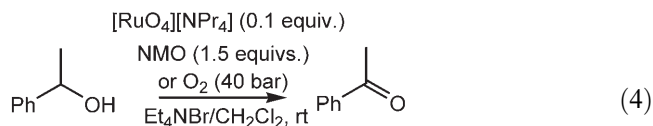
IL = [C<sub>2</sub>mim][PF<sub>6</sub>]; 1st run, 20 min: 96%; 5th run, 40 min: 94%  
IL = Et<sub>4</sub>NBr; 1st run, 5 min: 95%; 5th run, 50 min: 93%



IL = [C<sub>2</sub>mim][PF<sub>6</sub>]; 1st run, 1 h: 95%; 5th run, 3 d: 85%  
IL = Et<sub>4</sub>NBr; 1st run, 30 min: 95%; 4th run, 30 h: 85%

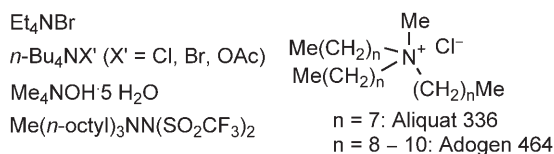
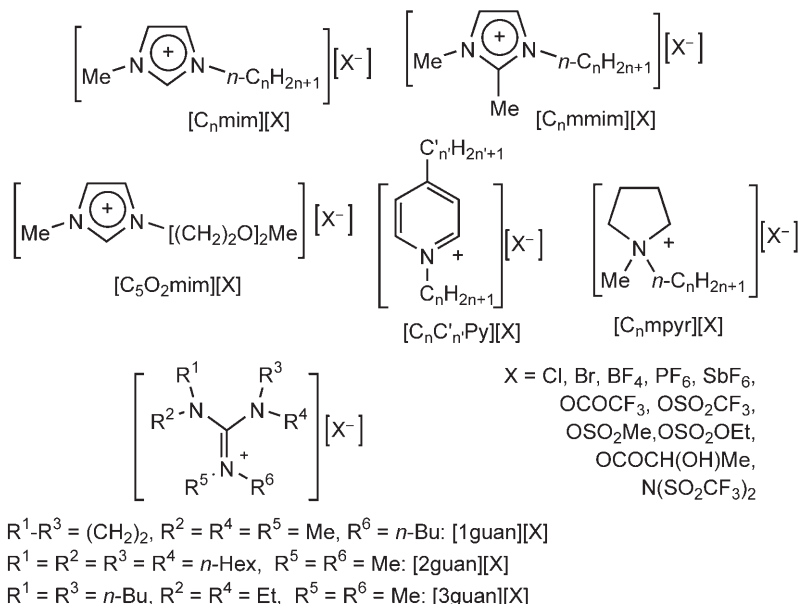


IL = [C<sub>2</sub>mim][PF<sub>6</sub>]; 1st run, 2.5 h: 89%; 2nd run, 24 h: 40%  
IL = Et<sub>4</sub>NBr; 1st run, 2 h: 95%; 3rd run, 3 d: 66%



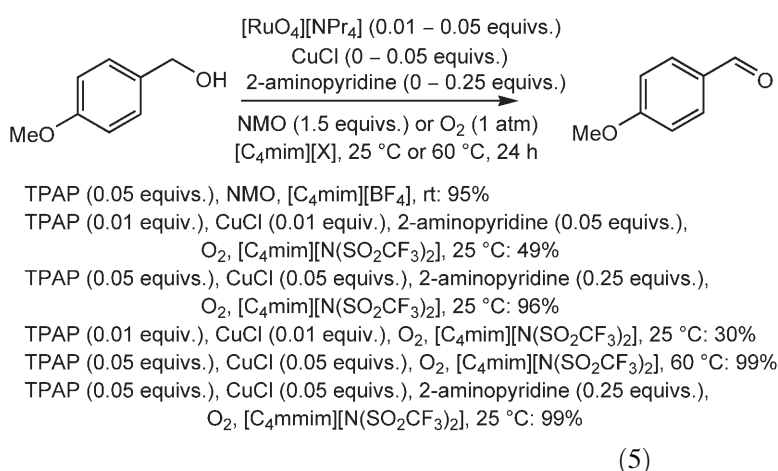
NMO; 1st run, 20 min: 95%; 5th run, 3 d: 33%  
O<sub>2</sub>; 1st run, 6 h 99%; 6th run, 2 d: 96%

The room temperature TPAP-catalyzed oxidation of a variety of alcohols with NMO has been almost simi-

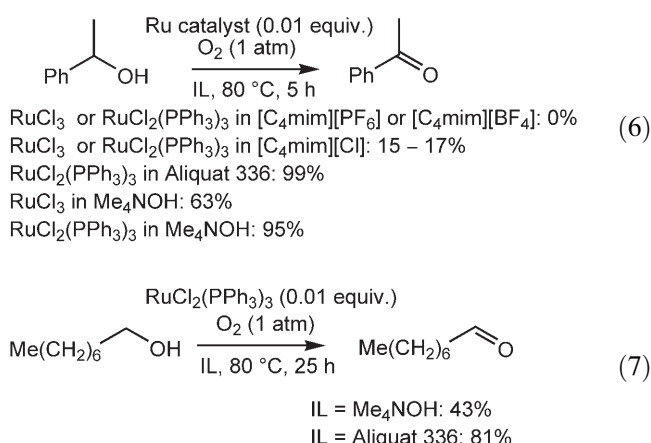


**Scheme 1.** Ionic liquids and ammonium salts used as solvents for oxidation reactions

taneously reported by Welton et al. but using  $[\text{C}_4\text{mim}][\text{BF}_4]$  as IL, and without an organic co-solvent.<sup>[19,20]</sup> The over-oxidation of primary alcohols to acids was not observed even with the addition of one equiv. of water. For aliphatic alcohols that are immiscible in the IL, sonication of the reaction mixture improved the conversion. Welton's team has also used  $\text{O}_2$  instead of NMO. Testing the reactivity of 4-trifluoromethylbenzyl alcohol in  $[\text{C}_4\text{mim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$  under 1 atm of molecular oxygen, a strong increase of the oxidation efficiency has been observed with the addition of CuCl as a co-catalyst. Reactions have been, furthermore, carried out in the presence of 2-aminopyridine and in  $[\text{C}_4\text{mmim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$  [Eq. (5)]. Reactivity lower for aliphatic than for allylic and benzylic alcohols has been demonstrated under the conditions using oxygen as the oxidant.

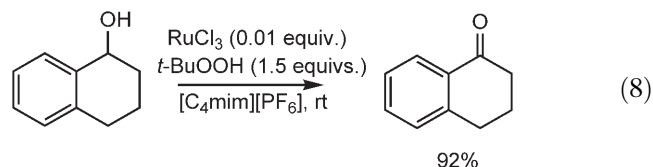


Instead of a Ru(VII) catalyst, Jacobs et al. have used Ru(II) and Ru(III) catalysts under oxygen in various ILs [Eq. (6)], the conversion of aliphatic alcohols being much more pronounced in Aliquat<sup>®</sup> 336 than in  $\text{Me}_4\text{NOH}$  [Eq. (7)].<sup>[22]</sup> A decrease of reactivity was noted under atmospheric air and in recycling experiments.

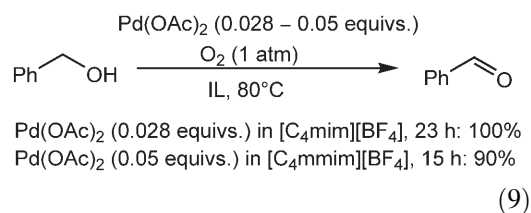


A report written in Chinese relates the efficient  $\text{RuCl}_3$ -catalyzed oxidation, with *t*-BuOOH in  $[\text{C}_4\text{mim}][\text{PF}_6]$ , of

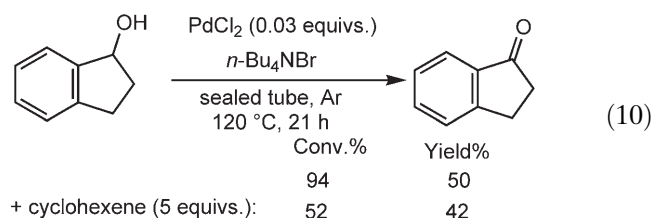
cyclohexanol and 1-tetralol into cyclohexanone and 1-tetralone respectively [Eq. (8)], and the recycling of the IL/catalyst system. Low conversions of cyclohexanol were obtained using  $\text{H}_2\text{O}_2$  instead of *t*-BuOOH.<sup>[23]</sup>



Seddon et al. have studied the  $\text{Pd}(\text{OAc})_2$ -catalyzed oxidation at 80 °C of benzyl alcohol with oxygen in  $[\text{C}_n\text{mim}][\text{X}]$  ( $n = 4, 6$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{BF}_4$ ) and  $[\text{C}_4\text{mmim}][\text{BF}_4]$ , the best results being obtained in  $[\text{C}_4\text{mim}][\text{BF}_4]$  and  $[\text{C}_4\text{mmim}][\text{BF}_4]$  [Eq. (9)] while no reaction was observed in  $[\text{C}_4\text{mim}][\text{Br}]$ . The catalyst/IL system was recyclable but, to preclude the over-oxidation of benzaldehyde to benzoic acid, the recovered catalyst/IL system has to be dried from time to time to remove water that accumulates either as reaction by-product, or by absorption of moisture from the atmosphere during the work-up. According to Seddon's team, their methodology affords quantitatively acetophenone from *sec*-phenethyl alcohol.<sup>[24]</sup>

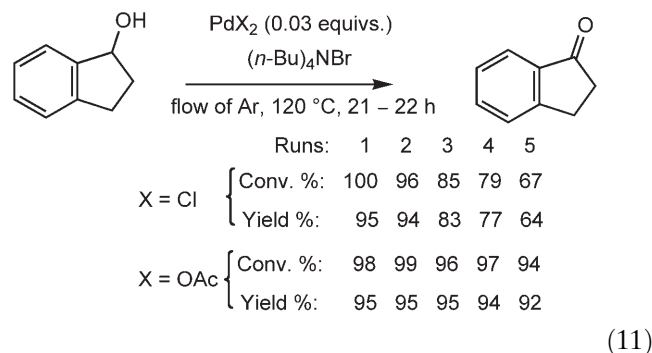


In *n*-Bu<sub>4</sub>NBr as solvent at 120 °C, we have observed the oxidation of indan-1-ol to indan-1-one in the presence of catalytic amounts of  $\text{PdCl}_2$ , but with a low selectivity because of the concurrent hydrogenolysis reaction leading to indane. The use of cyclohexene as hydrogen trap allowed a strong increase in the selectivity, but was detrimental to the conversion probably because of the competitive coordination of the hydrogen acceptor to palladium [Eq. (10)].<sup>[25]</sup>



The selectivity towards the ketone was strongly improved by performing the reaction under a gentle flow of argon, and the system  $\text{PdCl}_2/n\text{-Bu}_4\text{NBr}$  was recyclable but, gradually, loses its oxidative properties

[Eq. (11)].<sup>[25]</sup> The high selectivity also obtained using palladium black instead of  $\text{PdCl}_2$ <sup>[26,27]</sup> indicates a catalysis by  $\text{Pd}(0)$  and the probable formation of nanoparticles<sup>[28]</sup> from  $\text{PdX}_4[\text{N}(n\text{-Bu})_4]_2$  species ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ).<sup>[29]</sup> The selectivity obtained using this protocol is due to the removal of hydrogen gas as soon as it is produced; this implies a low stability under these reaction conditions of the dihydridopalladium formed by dehydrogenation of the alcohol.



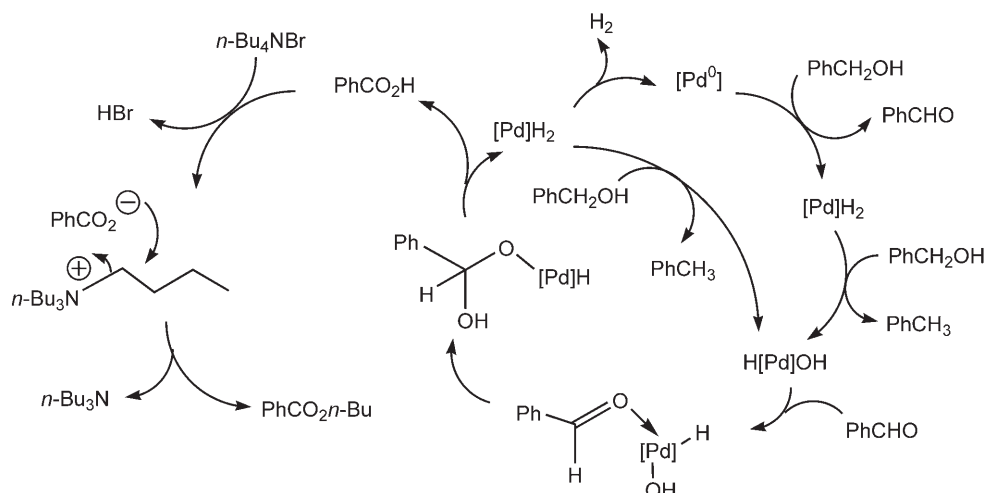
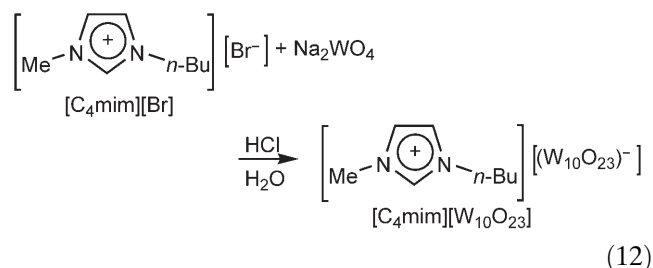
Changing  $(n\text{-Bu})_4\text{NBr}$  for  $(n\text{-Bu})_4\text{NCl}$ ,  $(n\text{-Bu})_4\text{NOAc}$  or Adogen 464<sup>®</sup> was unsatisfactory. High selectivities have been observed with  $\text{PdCl}_2/(n\text{-Bu})_4\text{NBr}$  from a range of secondary, linear or cyclic benzylic alcohols. In contrast, oxidation of primary benzylic alcohols was less satisfactory, naphthalenemethanols suffering from some hydrogenolysis, while benzyl alcohol led to a mixture of benzaldehyde, toluene and *n*-butyl benzoate. The latter compound was the main product and was formed by the reaction of benzoic acid with the ammonium salt (Scheme 2). We have proposed that  $\text{PhCO}_2\text{H}$  was produced by a dismutation-type of reaction from  $\text{PhCH}_2\text{OH}$  mediated by palladium.<sup>[25]</sup> Saturated alcohols were unreactive under these conditions while allylic alcohols yielded mainly saturated ketones *via* the migration of

the  $\text{C}=\text{C}$  bond.<sup>[30]</sup> We have subsequently discovered that  $\text{Pd}(\text{OAc})_2$  as a catalyst improved the efficiency of the oxidation of 1-indanol and also the recycling ability [Eq. (11)].<sup>[26]</sup>

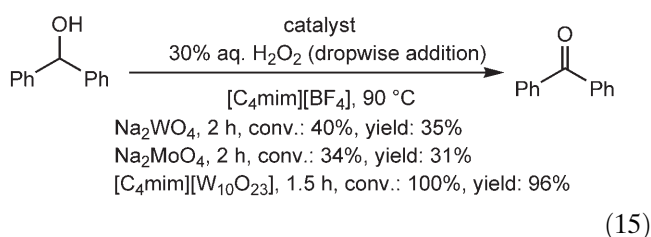
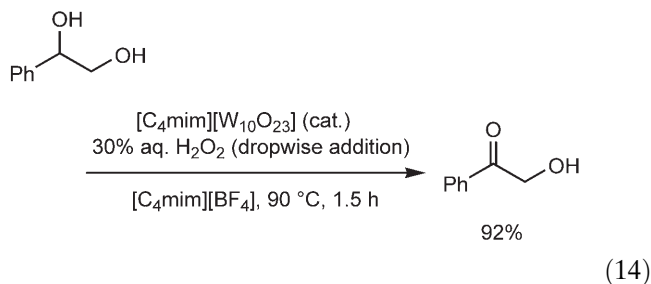
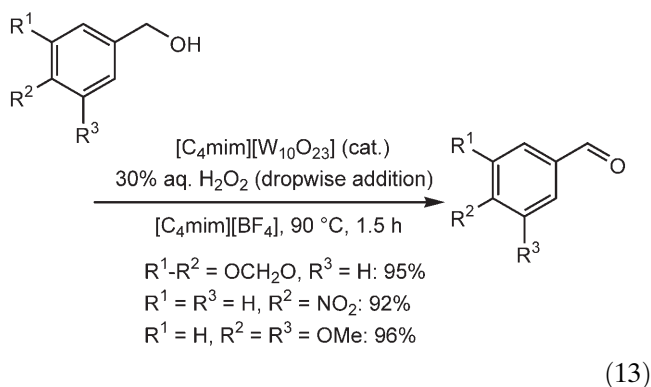
At 80 °C, Hardacre et al. oxidized selectively cinnamyl alcohol into cinnamaldehyde over  $\text{Pd}/\text{Al}_2\text{O}_3$  in  $[\text{C}_4\text{mim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$  using two types of reactors (a rotating disc reactor and a stirred tank reactor) and various concentrations of alcohol and pressures of oxygen.<sup>[31]</sup>

Two IL procedures using  $\text{H}_2\text{O}_2$  associated to catalytic amounts of tungstate complexes have been disclosed by Chhikara et al.

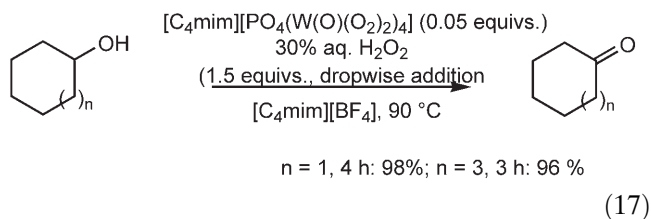
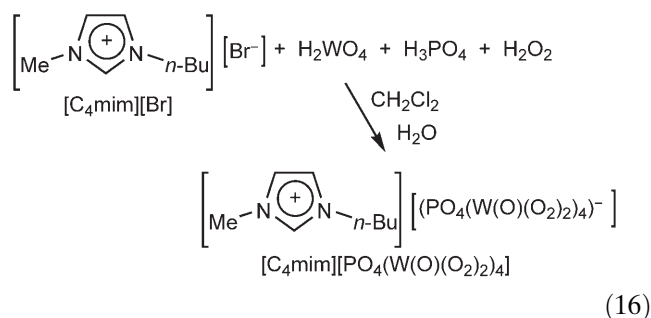
Firstly, a new catalyst,  $[\text{C}_4\text{mim}]_4[\text{W}_{10}\text{O}_{23}]$ , which was obtained from the reaction of sodium tungstate with  $[\text{C}_4\text{mim}][\text{Br}]$  in aqueous  $\text{HCl}$  [Eq. (12)], has been used at 90 °C in  $[\text{C}_4\text{mim}][\text{BF}_4]$  for the catalytic oxidation of a range of aliphatic and benzylic alcohols with 30% aqueous  $\text{H}_2\text{O}_2$  [Eq. (13)].<sup>[32]</sup> Primary aliphatic alcohols are not oxidized under these conditions; this has allowed the selective oxidation of 1-phenyl-1,2-diethanol into  $\alpha$ -hydroxyacetophenone [Eq. (14)]. Changing  $[\text{C}_4\text{mim}]_4[\text{W}_{10}\text{O}_{23}]$  for  $\text{Na}_2\text{WO}_4$  or  $\text{Na}_2\text{MoO}_4$  was detrimental to the conversion of diphenyl carbinol [Eq. (15)]. Five consecutive cycles, using the system  $[\text{C}_4\text{mim}]_4[\text{W}_{10}\text{O}_{23}]/[\text{C}_4\text{mim}][\text{BF}_4]$  for the oxidation of diphenyl carbinol, have successfully been carried out.



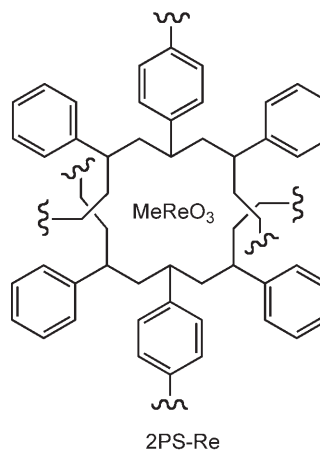
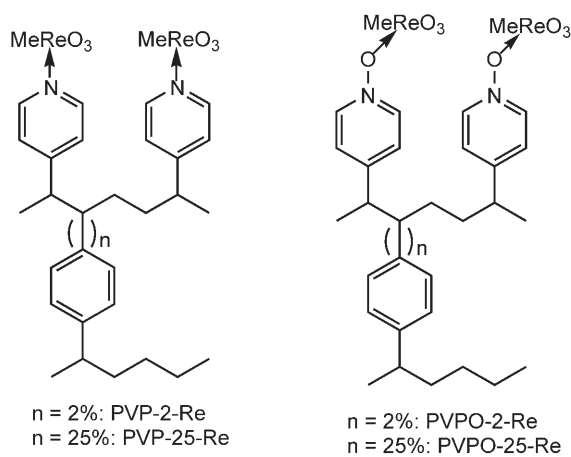
**Scheme 2.** Proposed mechanism of the Pd-catalyzed reaction of benzyl alcohol in molten  $(n\text{-Bu})_4\text{NBr}$ .



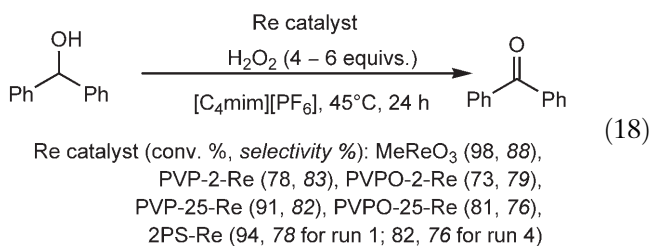
The second procedure involves a catalyst,  $[\text{C}_4\text{mim}]_3[\text{PO}_4(\text{W}(\text{O})(\text{O}_2)_2)_4]$ , also based on imidazolium and tungstate ions, that was obtained from tungstic acid, phosphoric acid and  $[\text{C}_4\text{mim}][\text{Br}]$  in an oxidizing medium [Eq. (16)]. High yields of ketones were usually attained at  $90^\circ\text{C}$  from secondary aliphatic and benzylic alcohols with this catalyst and hydrogen peroxide in  $[\text{C}_4\text{mim}][\text{BF}_4]$  [Eq. (17)], while some over-oxidation occurred with primary alcohols. Each recycling of the catalyst/IL for the oxidation of diphenylmethanol led to a slight decrease in the yield of benzophenone.<sup>[33]</sup>



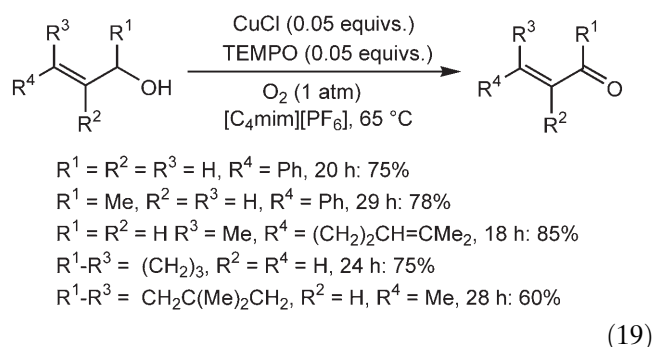
Hydrogen peroxide has also been used by Saladino et al. but with homogeneous and heterogeneous (Scheme 3) rhenium catalysts to carry out the oxidation of benzhydrol and 1-phenylethanol in  $[\text{C}_4\text{mim}][\text{PF}_6]$ .<sup>[34]</sup> The best recycling results have been achieved using the microencapsulated catalyst 2PS-Re [Eq. (18)].



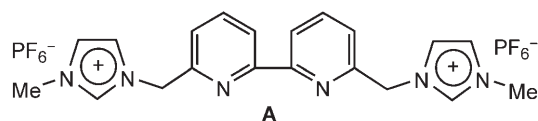
**Scheme 3.** Saladino's heterogeneous rhenium catalysts.



Gree et al. have disclosed a catalytic system, copper(I) chloride + 2,2,6,6-tetramethyl-1-piperidinyloxy (CuCl + TEMPO), for the oxidation of aliphatic, allylic and benzylic alcohols, with oxygen at 65 °C in [C<sub>4</sub>mim][PF<sub>6</sub>] [Eq. (19)]. Instead of molecular oxygen, an air atmosphere can be used but longer reaction times are required. Unfortunately, the catalytic system is either decomposed or not immobilized in [C<sub>4</sub>mim][PF<sub>6</sub>], the IL only being recyclable.<sup>[35]</sup> Under Gree's conditions, the reaction of some aliphatic alcohols is slow, no reaction being obtained from menthol; that contrasts with the above Ru(VII)/NMO system [Eq. (3)].

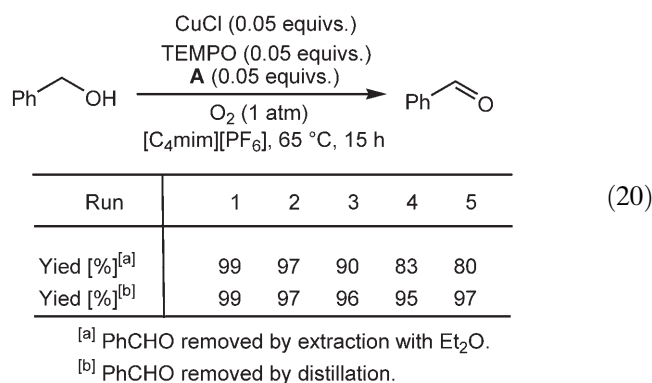


Since the Gree catalytic system is not recoverable, Gao et al. have synthesized the ionic ligand **A**, which contains two 1-methylimidazolium hexafluorophosphate moieties (Scheme 4).

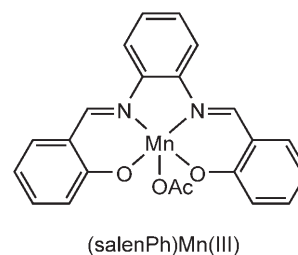


**Scheme 4.** Gao's ionic ligand of copper.

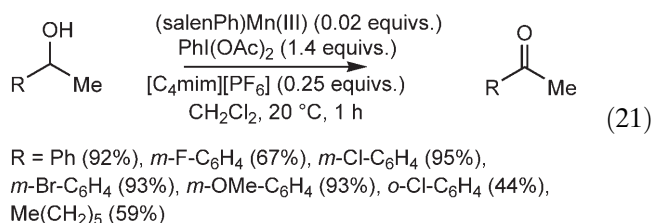
Using exactly Gree's procedure, except for the addition of **A**, the authors observed similar reactivities with the advantage that the catalytic system was recyclable, without notable decrease of yields, especially when the carbonyl compounds were removed by distillation [Eq. (20)].<sup>[36]</sup>



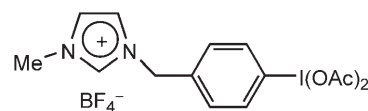
Xia et al. have used PhI(OAc)<sub>2</sub> in association with an Mn(salen) complex (Scheme 5) for the room temperature oxidation of alcohols in a mixture of [C<sub>4</sub>mim][PF<sub>6</sub>] and CH<sub>2</sub>Cl<sub>2</sub>. Benzylic and aliphatic secondary alcohols led to the corresponding ketones, yields being usually better from the benzylic substrates [Eq. (21)]. Some over-oxidation to acids was observed from primary alcohols. Although the IL was used as additive rather than as a real solvent, the effective immobilization of the catalyst in the IL led to a recyclable system.<sup>[37]</sup>



**Scheme 5.** The Mn(salen) catalyst used by Xia's team.



In fact, Y. Zhang et al. have recently reported the efficient oxidation at 30 °C, in the absence of any metal catalyst, of primary and secondary aliphatic or benzylic alcohols in [C<sub>2</sub>mim][BF<sub>4</sub>] with an aryl iodine diacetate bound to an imidazolium ion (Scheme 6). Under these conditions, PhI(OAc)<sub>2</sub> as oxidant led to lower yields. Zhang's team has shown that the reaction is promoted by bromide ion. Consequently, catalysis of the process by the small amount of bromide ion remaining in [C<sub>2</sub>mim][BF<sub>4</sub>] as impurity has been suspected.<sup>[38]</sup>

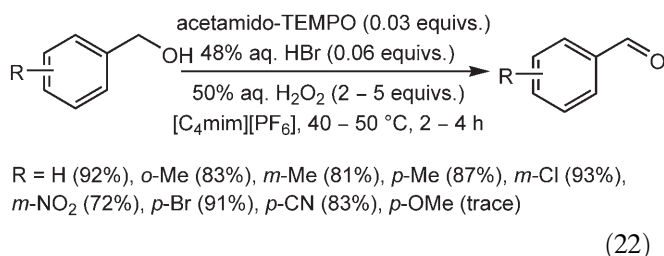


**Scheme 6.** A new oxidant proposed by Zhang's team.

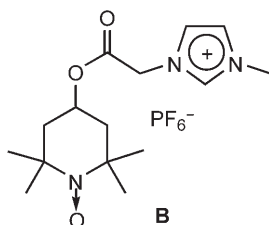
Two catalytic oxidations in ILs, without any metal catalyst, but in the presence of a catalytic amount of a nitroxyl radical, have been recently disclosed.

Firstly, catalytic amounts of both TEMPO and HBr in [C<sub>4</sub>mim][PF<sub>6</sub>] have been used with H<sub>2</sub>O<sub>2</sub> for the efficient oxidation of electron-neutral and electron-deficient benzylic alcohols to the corresponding aldehydes. How-

ever, work-up with diethyl ether led to the extraction of the expensive TEMPO. Fortunately, 4-acetamido-2,2,6,6-tetramethyl-1-piperidinyloxy (acetamido-TEMPO) is soluble in  $[\text{C}_4\text{mim}][\text{PF}_6]$  but not in  $\text{Et}_2\text{O}$ . Consequently, the acetamido-TEMPO/ $[\text{C}_4\text{mim}][\text{PF}_6]$  is recoverable and reusable; only HBr and  $\text{H}_2\text{O}_2$  being consumed in each cycle [Eq. (22)].<sup>[39]</sup>

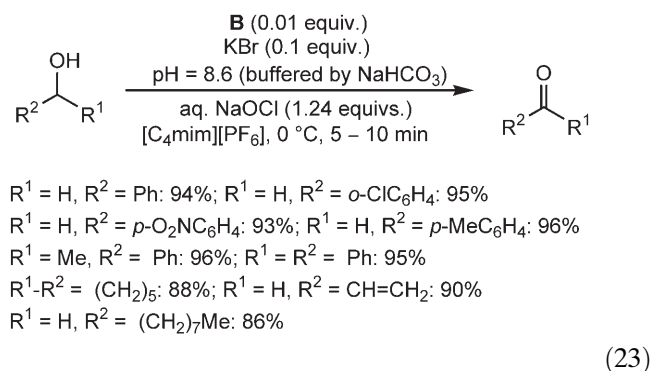


Secondly, Gao et al. have synthesized the nitroxyl radical **B**, which contains an ionic liquid-type appendage (Scheme 7).



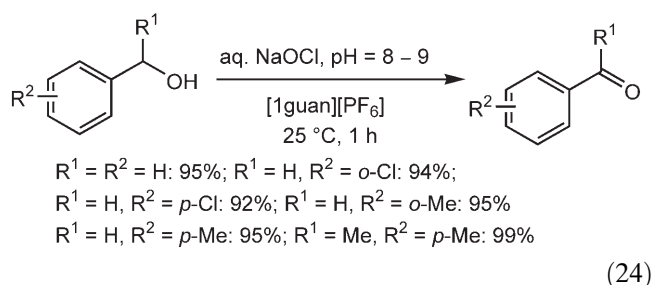
**Scheme 7.** Gao's nitroxyl radical.

In cold buffered  $[\text{C}_4\text{mim}][\text{PF}_6]$  containing slight amounts of KBr, **B** catalyzes the rapid and efficient oxidation with NaOCl of aliphatic, allylic and benzylic alcohols [Eq. (23)]. The reactivity and selectivity with TEMPO and **B** are similar but the advantage of **B** is the recyclability of the **B**/ $[\text{C}_4\text{mim}][\text{PF}_6]$  association.<sup>[40]</sup>

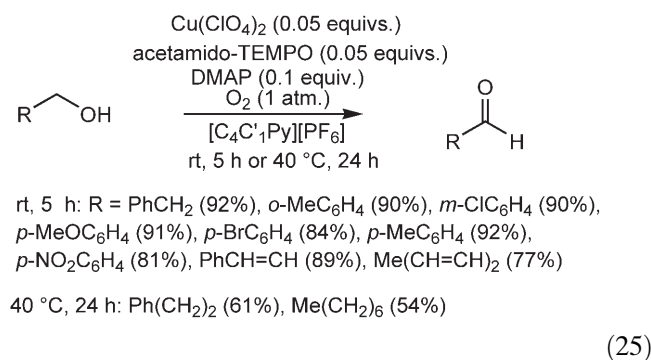


According to S. Zhang et al., benzyl alcohol in  $[\text{C}_4\text{mim}][\text{PF}_6]$  is, in fact, oxidized to benzaldehyde with NaOCl, at room temperature, even in the absence of any trace of a nitroxyl radical (in 1 h: 68% conversion,

65% yield).<sup>[41]</sup> The efficiency of this transformation has been greatly improved using a new IL, i.e., the hexaalkylguanidinium salt  $[\text{1guan}][\text{PF}_6]$  (Scheme 1). Thus, primary and secondary benzylic alcohols are oxidized to the corresponding carbonyl compounds with high yields and the recovered IL has been recycled with no appreciable decrease in efficiency [Eq. (24)].

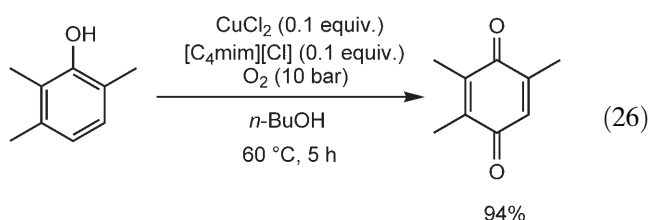


Very recently, Ragauskas et al. have created a three-component catalytic system consisting of acetamido-TEMPO, a copper(II) salt and 4-(dimethylamino)pyridine (DMAP) in ILs to effect the oxidation of primary alcohols to aldehydes with oxygen.<sup>[42]</sup> The best results were obtained using  $\text{Cu}(\text{ClO}_4)_2$  as the Cu salt, and  $[\text{C}_4\text{C}'_1\text{Py}][\text{PF}_6]$  as the ionic liquid [Eq. (25)]. After extraction with pentane, the reuse of the catalytic system and the IL was performed with a slight drop of activity. According to the authors, DMAP may have dual roles, namely as a base to deprotonate the alcohol, and as an N-donor ligand to coordinate to Cu(II).



### 3 Phenol Oxidation

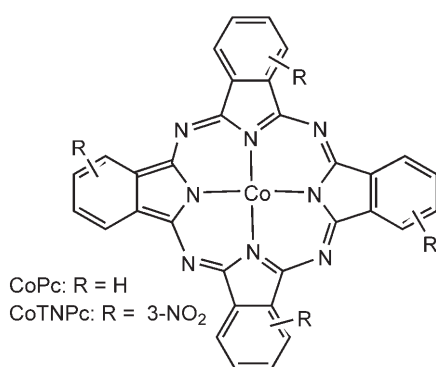
Sun et al. have obtained trimethyl-1,4-benzoquinone from the  $\text{CuCl}_2$ -catalyzed oxidation of 2,3,6-trimethylphenol with oxygen, in *n*-butanol containing  $[\text{C}_4\text{mim}][\text{Cl}]$  and *n*-butanol [Eq. (26)]. The *in situ* formation of 1-*n*-butyl-3-methylimidazolium oxotetracuprate, that is an active catalyst, has been demonstrated.<sup>[43]</sup> Other Cu salts and ILs were less efficient.<sup>[44]</sup> The process has also been used for the oxidation of 2-methyl-1-naphthol to 2-methyl-1,4-naphthoquinone (yield up to 47%).



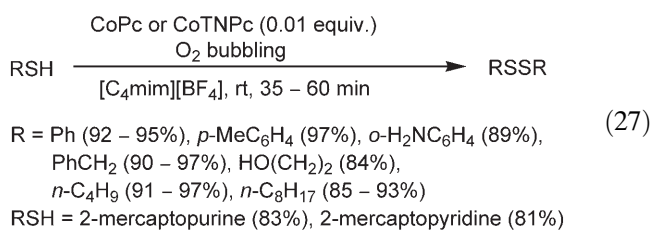
As for some other studies carried out in mixtures of an IL and an organic solvent, in particular in the above example for which a good result was obtained with an equimolecular amount of  $\text{CuCl}_2$  and  $[\text{C}_4\text{mim}][\text{Cl}]$ , we suspect a phase-transfer catalysis role of the IL rather than a reaction occurring really in the IL.

#### 4 Oxidation of Thio Compounds

Chauhan et al. have oxidized thiols to disulfides with oxygen, at room temperature, in  $[\text{C}_4\text{mim}][\text{BF}_4]$  containing catalytic amounts of cobalt(II) phthalocyanines [Scheme 8, Eq. (27)]. Recycling experiments led to a slight decrease in the yields.<sup>[45]</sup>

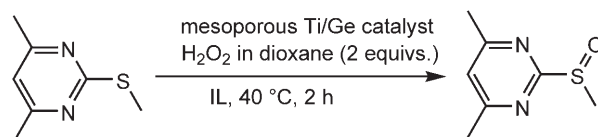


**Scheme 8.** Cobalt(II) phthalocyanines used as catalysts.



Hardacre et al. have studied the heterogeneous oxidation of pyrimidine and alkyl thioethers, with hydrogen peroxide or the urea-hydrogen peroxide adduct, in a range of ionic liquids ( $[\text{C}_n\text{mim}][\text{X}]$ ,  $n = 2, 4, 8$ ;  $[\text{C}_n\text{Py}][\text{X}]$ ,  $n = 4, 6, 8$ ;  $[\text{C}_4\text{mpyr}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ ;  $[(n\text{-octyl})_3\text{MeN}][\text{N}(\text{SO}_2\text{CF}_3)_2]$  over mesoporous Ti or Ti/Ge catalysts. The corresponding sulfoxides can be selectively ob-

tained, even at high conversions. Both the anion and the cation of the IL have an effect on the rate the reactions [Eq. (28)]. Some leaching of the catalyst in the IL occurs from interactions of the catalyst with peroxy species, but leached titanium is also an active catalyst.<sup>[46]</sup> Consequently, recycling experiments can be carried out effectively.<sup>[47,48]</sup>



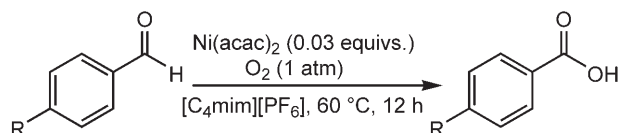
conversion % (selectivity %)

in $[\text{C}_2\text{mim}][\text{X}]$ , X = BF <sub>4</sub> : 77 (95), X = OSO <sub>2</sub> CF <sub>3</sub> : 49 (98)
in $[\text{C}_4\text{mim}][\text{X}]$ , X = BF <sub>4</sub> : 73 (96), X = OSO <sub>2</sub> CF <sub>3</sub> : 53 (96), X = OSO <sub>2</sub> Me: 9 (100)
in $[\text{C}_n\text{Py}][\text{BF}_4]$ , n = 6: 41 (100), n = 8: 44 (99)
in $[\text{C}_4\text{Py}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ : 57 (96)

(28)

#### 5 Oxidation of Carbonyl Compounds

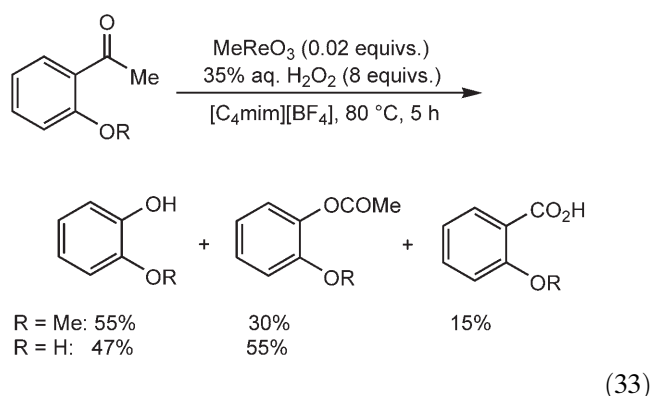
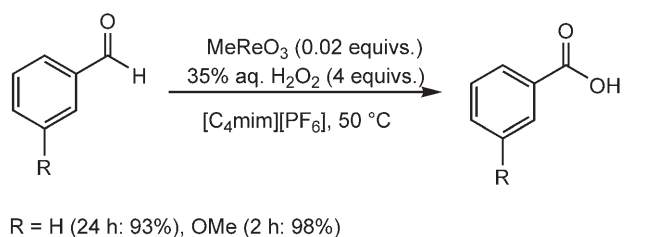
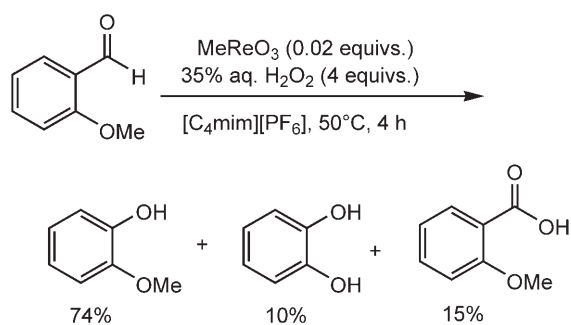
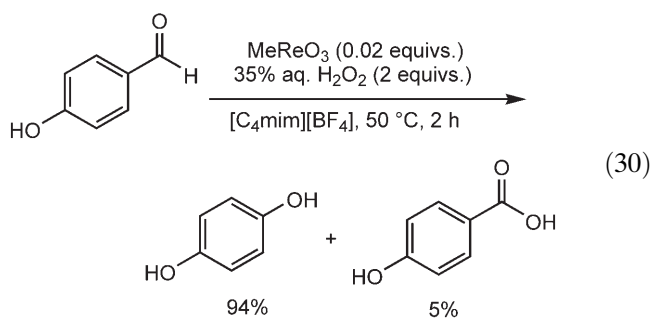
Howarth has oxidized aromatic aldehydes to the corresponding acids, with oxygen at 60 °C, using  $\text{Ni}(\text{acac})_2$  as the catalyst in  $[\text{C}_4\text{mim}][\text{PF}_6]$  [Eq. (29)].<sup>[49]</sup> The reactions have been repeated a further three times using the recovered Ni/IL system without decrease of yields.



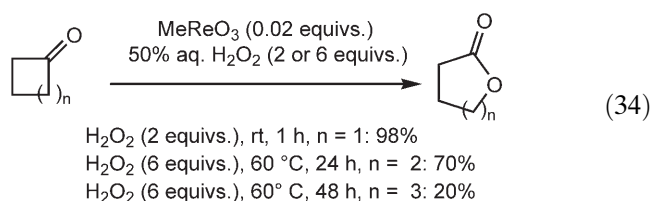
R = H (66%), Me (63%), Cl (57%), Br (60%),  
OMe (64%), OH (65%), CO<sub>2</sub>H (47%)

(29)

Aromatic aldehydes have also been oxidized in  $[\text{C}_4\text{mim}][\text{X}]$  (X = BF<sub>4</sub>, PF<sub>6</sub>) using hydrogen peroxide and catalysis with methyltrioxorhenium, but phenols, i.e., the Dakin products, rather than acids were the main isolated compounds from activated benzaldehydes, as reported by Bernini et al. [Eq. (30)]. Some hydroquinone or catechol was obtained from *p*- or *o*-methoxybenzaldehyde, respectively [Eq. (31)], and the amount of the acid increased with the recycling of the  $\text{MeReO}_3/[\text{C}_4\text{mim}][\text{X}]$  system. Under these conditions, benzaldehyde and the benzaldehydes *meta*-substituted with an electron-donating group led selectively to the acids [Eq. (32)]. The same oxidation system afforded phenols and esters from acetophenones *ortho*- or *para*-substituted with either a hydroxy or a methoxy group [Eq. (33)].<sup>[50]</sup>

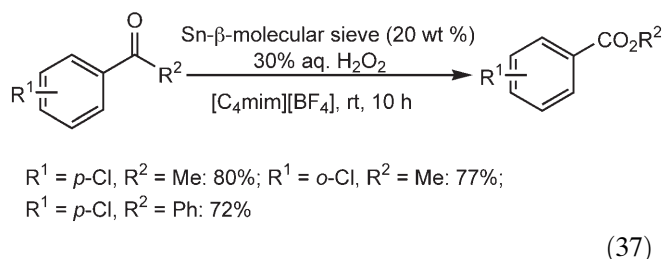
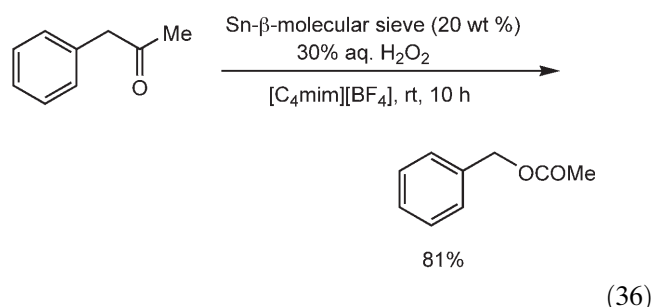
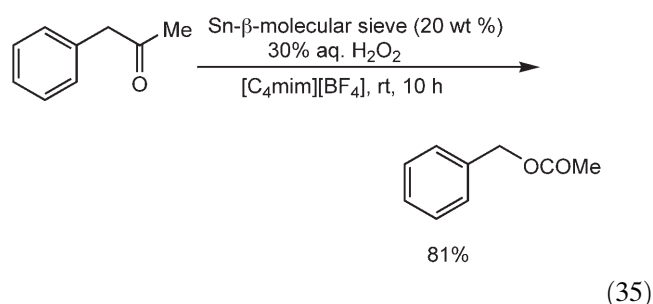


Bernini et al. have also used the  $MeReO_3/[C_4mim][BF_4]$  system for the Baeyer–Villiger oxidation of the cyclic ketones with  $H_2O_2$  [Eq. (34)].<sup>[51]</sup>



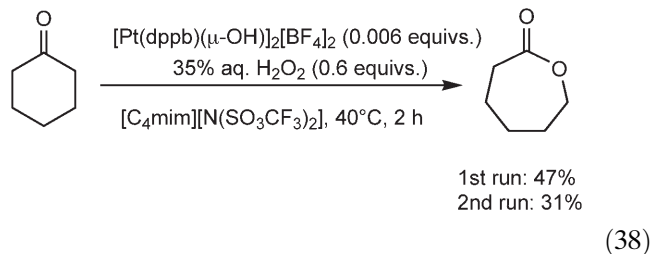
According to Bernini et al., the R-catalyst/IL system can be repeatedly recycled after extraction of the organic compounds with diethyl ether.<sup>[50,51]</sup> Saladino et al. have disagreed about this assertion,<sup>[34]</sup> but the reuse of the Re catalyst/IL solution for at least five times with no loss of activity has been the subject of a recent addendum by Bernini et al.<sup>[52,53]</sup>

Instead of a rhenium catalyst, Kalkote et al. used an Sn- $\beta$ -molecular sieve for the oxidation of 1-phenylpropan-2-one and acetophenone or benzophenone derivatives [Eqs. (35)–(37)]. With this recyclable system, the reaction occurred at room temperature and the formation of phenols was not observed.<sup>[56]</sup>



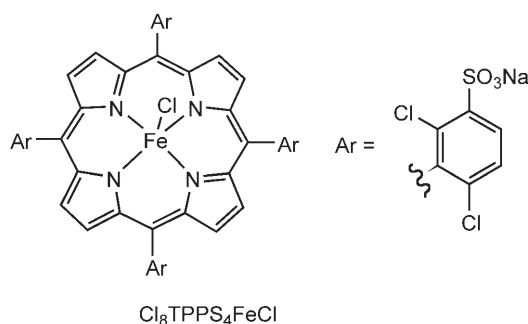
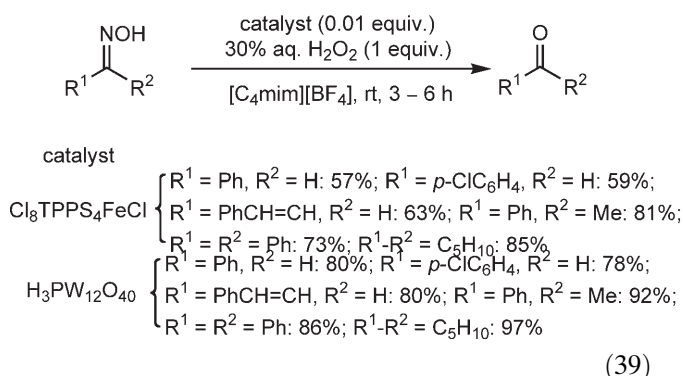
Recently, Conte et al. have investigated the Baeyer–Villiger oxidation of cyclohexanone with aqueous  $H_2O_2$  in a range of ILs under catalysis with  $[Pt(dppb)(\mu-OH)]_2[BF_4]_2$  [dppb = 1,4-bis(diphenylphosphino)butane]. At room temperature, the very low yields obtained using hydrophilic ILs such as  $[C_4mim][X]$  ( $X=BF_4, OSO_2CF_3$ ) were increased up to 25% in hydrophobic ILs such as  $[C_4mim][PF_6]$ ,  $[C_nmim][N(SO_3CF_3)_2]$  ( $n=2, 4, 6$ ) and  $[C_4mmim][N(SO_3CF_3)_2]$ . The best yield was finally obtained at 40 °C in  $[C_4mim][N(SO_3CF_3)_2]$ , but decreased

with the recycling of the catalyst/IL sample [Eq. (38)]. The oxidation of 2-methylcyclohexanone was more efficient since a 50% yield was attained at room temperature.<sup>[57]</sup>



## 6 Oxidation of Oximes

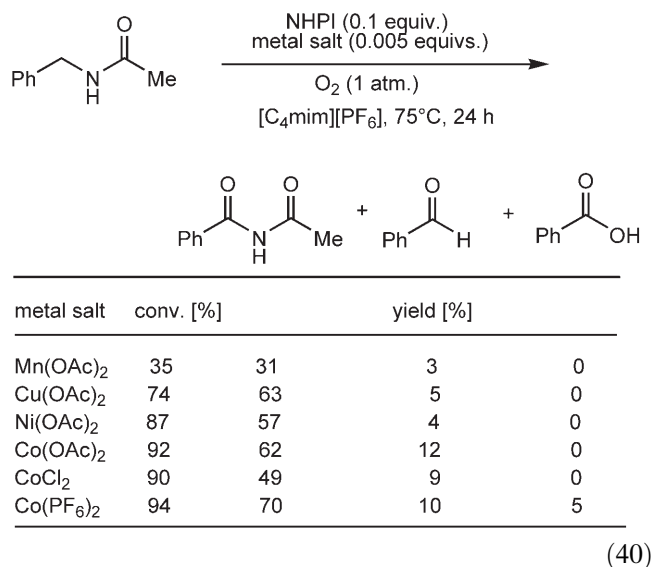
The formation of carbonyl compounds from oximes has been carried out by Chauhan et al. using aqueous H<sub>2</sub>O<sub>2</sub> in [C<sub>4</sub>mim][BF<sub>4</sub>] and catalysis with either a water-soluble iron(III) porphyrin, namely Cl<sub>8</sub>TPPS<sub>4</sub>FeCl (Scheme 9), or phosphotungstic acid (Eq. 39). The H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/[C<sub>4</sub>mim][BF<sub>4</sub>] system is more efficient than the Cl<sub>8</sub>TPPS<sub>4</sub>FeCl/[C<sub>4</sub>mim][BF<sub>4</sub>] one and, furthermore, reusable.<sup>[58]</sup>



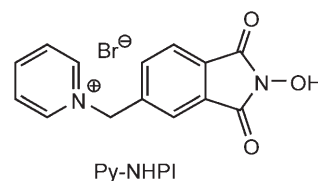
**Scheme 9.** A water-soluble iron(III) porphyrin used as catalyst.

## 7 Oxidation of Imides

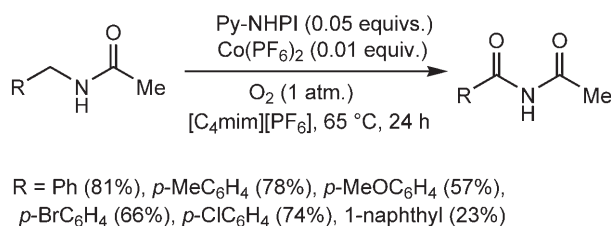
The team of Liu and Guo has studied the oxidation of *N*-benzylacetamide with oxygen in [C<sub>4</sub>mim][PF<sub>6</sub>] using a mixture of *N*-hydroxyphthalimide (NHPI) and a metal salt as the catalytic system, the best result occurring with Co(PF<sub>6</sub>)<sub>2</sub> [Eq. (40)].<sup>[59]</sup>



Surprisingly, no oxidation occurred in [C<sub>4</sub>mim][BF<sub>4</sub>]. The process was extended to a range of *N*-substituted acetamides using an ionic version of NHPI [Scheme 10 and Eq. (41)]. Under these conditions, the ionic liquid can be reused after washing with water.



**Scheme 10.** The ionic derivative of *N*-hydroxyphthalimide used by the team of Liu and Guo.

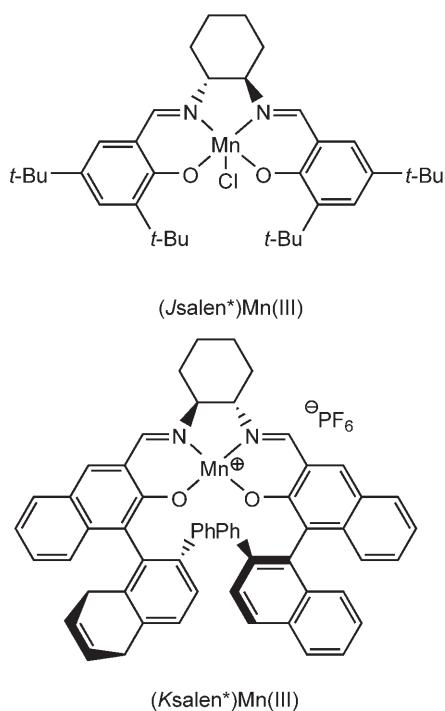
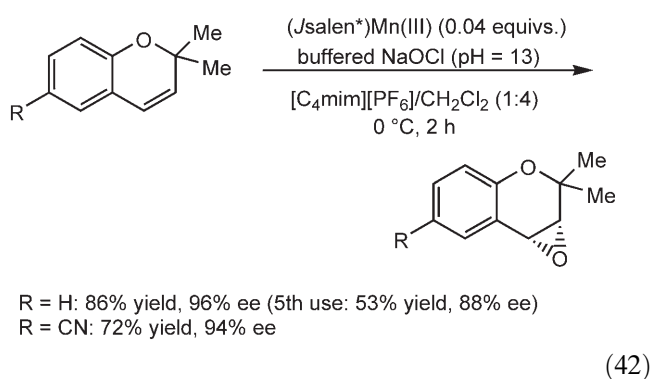


R = Ph (81%), *p*-MeC<sub>6</sub>H<sub>4</sub> (78%), *p*-MeOC<sub>6</sub>H<sub>4</sub> (57%), *p*-BrC<sub>6</sub>H<sub>4</sub> (66%), *p*-ClC<sub>6</sub>H<sub>4</sub> (74%), 1-naphthyl (23%)

## 8 Olefin Oxidation

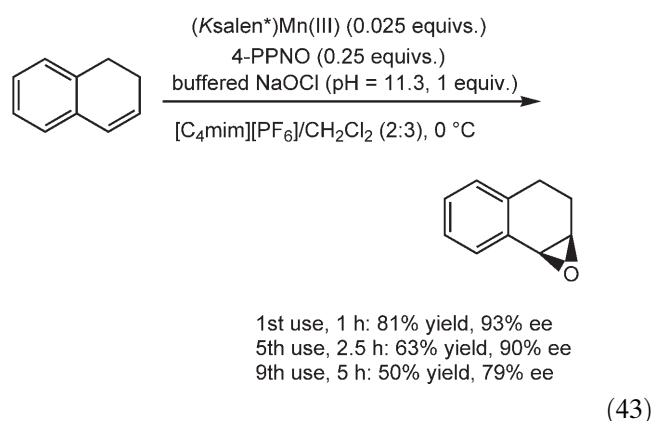
### 8.1 Epoxidation

In 2000, Song et al. disclosed a procedure to recycle the Jacobsen chiral (salen)Mn(III) epoxidation catalyst, namely  $[N,N'$ -bis(3,5-di-*t*-butylsalicylidene)-1,2-cyclohexanediamine]manganese chloride (Scheme 11). The asymmetric epoxidations were carried out at 0 °C in  $[C_4mim][PF_6]$ , with NaOCl as the oxidant, and a co-solvent since the IL solidifies at the reaction temperature [Eq. (42)].<sup>[60]</sup> Subsequently, Bedioui et al. reported the room temperature electro-assisted activation of molecular oxygen by the same Mn(III) catalyst in  $[C_4mim][PF_6]$ , but no epoxidation of a prochiral substrate has been included in their paper.<sup>[61]</sup>

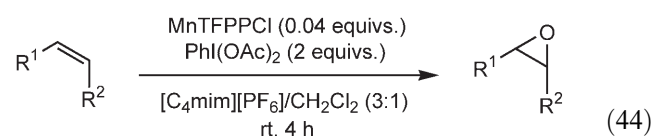


**Scheme 11.** The Jacobsen and Katsuki chiral catalysts used in ILs.

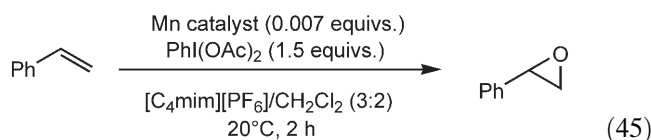
Smith et al. used a chiral Katsuki-type (salen)Mn(III) catalyst (Scheme 11) for the epoxidation at 0 °C of 1,2-dihydronaphthalene with NaOCl, in a mixture of  $[C_4mim][X]$  ( $X = PF_6$  or  $BF_4$ ) and an organic solvent ( $CH_2Cl_2$  or EtOAc), and in the presence of 4-phenylpyridine-*N*-oxide (4-PPNO) [Eq. (43)]. Under identical experimental conditions,  $(Ksalen^*)Mn(III)$  provided a higher yield and a higher enantioselectivity than  $(Jsalen^*)Mn(III)$  but required a longer reaction time. Up to 100% ee was attained under some conditions.<sup>[62]</sup>



Manganese porphyrins (Scheme 12) in a mixture of  $[C_4mim][PF_6]$  and  $CH_2Cl_2$  have been used, at ambient temperature, by Xia et al. for the efficient catalytic epoxidation of various alkenes with iodobenzene diacetate, this latter being more efficient than PhIO.<sup>[63,64]</sup> Effective recycling of the catalytic system, particularly with MnTFPPCl and MnTPPS<sub>4</sub>, has been obtained [Eqs. (44) and (45)].<sup>[64,65]</sup> According to a Chinese patent, Xia's team has also tested Co, Mo, Fe and Cu complexes of various porphyrins as epoxidation catalysts in ILs.<sup>[58]</sup>

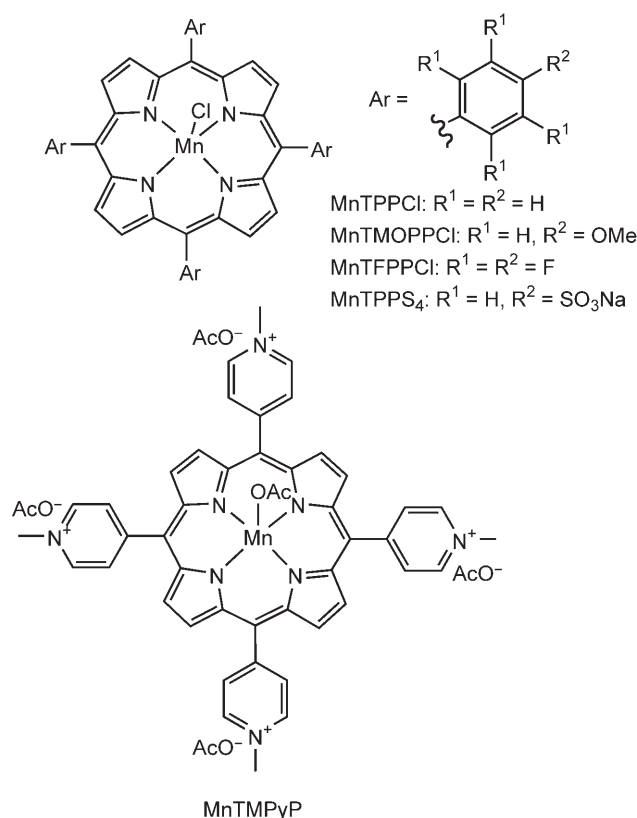


$R^1 = n$ -pentyl,  $R^2 = H$ : 74%, 6th cycle: 86%  
 $R^1-R^2 = C_4H_8$ : 74%, 6th cycle: 56%



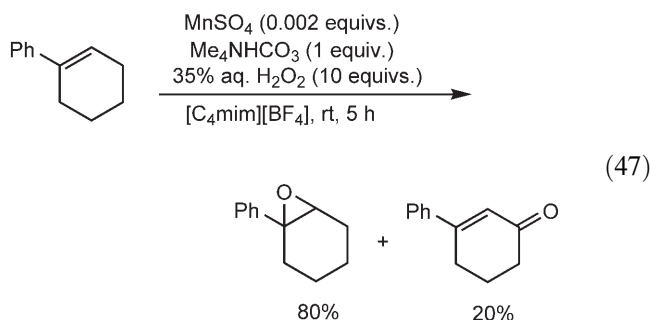
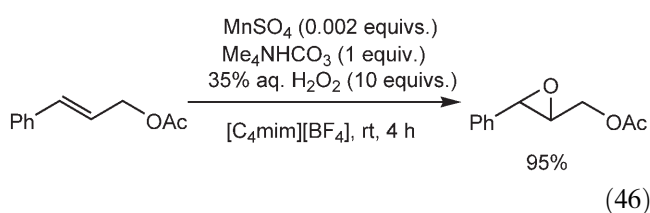
MnTPPCL: 90%; MnTMOPPCl: 92%  
 MnTFPPCl: 99%, 10th cycle: 72%  
 MnTPPS<sub>4</sub>: 98%, 7th cycle: 96%

Effective epoxidation of various alkenes was accomplished at room temperature in  $[C_4mim][BF_4]$  with aqueous hydrogen peroxide, in the presence of catalytic

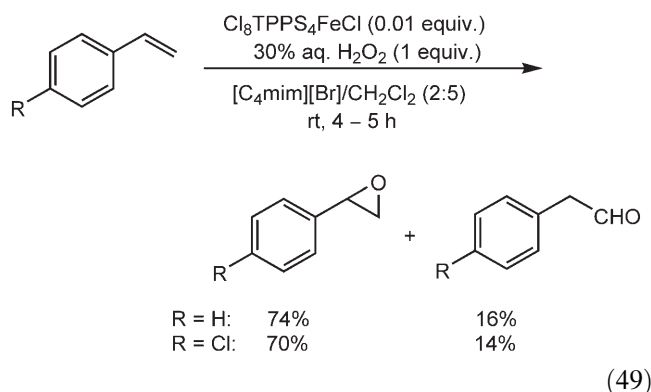
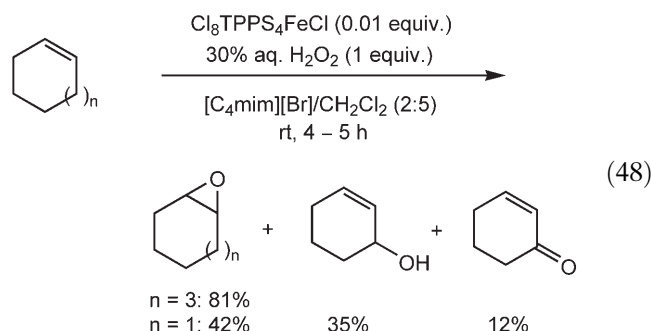


**Scheme 12.** Manganese porphyrins used as catalysts.

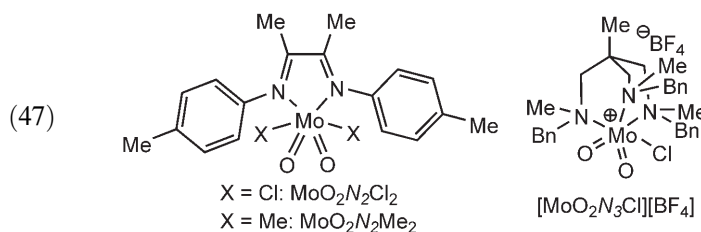
amounts of manganese sulfate and a stoichiometric quantity of tetramethylammonium hydrogen carbonate [Eq. (46)]. Good reactivities and high selectivities were generally obtained, except from an unactivated terminal alkene such as 1-decene which was unmodified, and 1-phenylcyclohexene [Eq. (47)]. For recycling experiments, some  $MnSO_4$  and  $Me_4NHCO_3$  have to be added from time to time to restore the activity of the system.<sup>[67]</sup>



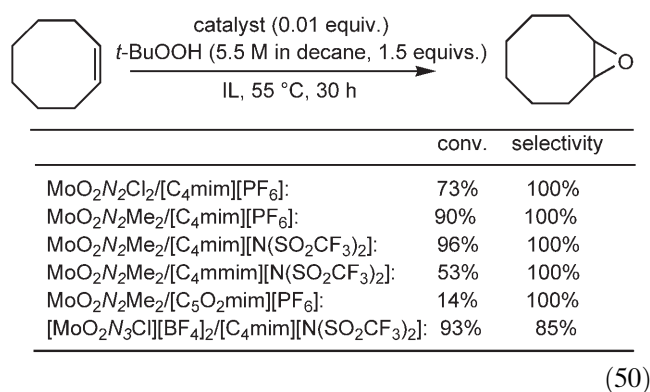
Chauhan et al. have used the water soluble  $Cl_8TPPS_4FeCl$  (Scheme 9) in  $[C_4mim][Br]$  as a recyclable system to epoxide C=C bonds with aqueous  $H_2O_2$ . The reactions were performed at room temperature with  $CH_2Cl_2$  as a co-solvent, but selective epoxidation occurred only from cyclooctene, by-products being obtained from cyclohexene and styrenes [Eqs. (48) and (49)].<sup>[68]</sup>



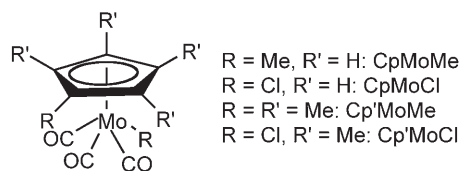
Three dioxomolybdenum(VI) complexes (Scheme 13) in  $[C_nmim][PF_6]$  ( $n=4, 8$ ),  $[C_4mim][N(SO_2CF_3)_2]$ ,  $[C_4mmim][N(SO_2CF_3)_2]$ ,  $[C_5O_2mim][PF_6]$  or  $[2guan][PF_6]$  have been tested by Valente et al. for the epoxidation of cyclooctene with anhydrous  $t-BuOOH$  [Eq. (50)]. The best result was achieved at  $55^\circ C$  with  $MoO_2N_2Me_2$  in  $[C_4mim][N(SO_2CF_3)_2]$ , but the decrease of reactivity with the recycling was less pronounced with  $[MoO_2N_3Cl][BF_4]$  as the catalyst. Nevertheless,  $[MoO_2N_3Cl][BF_4]$  led to a less selective reaction due to the production of 1,2-cyclooctanediol as a by-product.<sup>[69]</sup>



**Scheme 13.** Dioxomolybdenum catalysts.



Subsequently, the teams of Kühn and Romão studied also the epoxidation of cyclooctene with decane solutions of *t*-BuOOH in [C<sub>n</sub>mim][X] [n = 4, 8; X = BF<sub>4</sub>, PF<sub>6</sub>, N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] but with cyclopentadienyl-molybdenum complexes as the catalysts (Scheme 14).<sup>[70]</sup> This

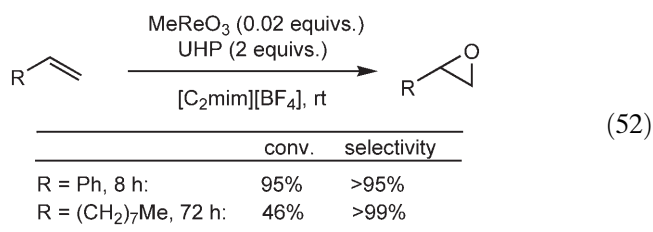
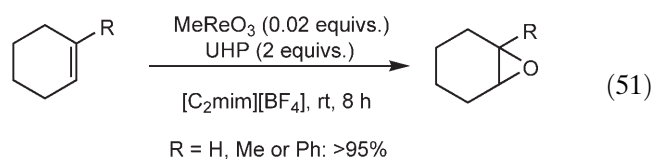


**Scheme 14.** Cyclopentadienyl-molybdenum catalysts.

study brought out the non-innocent role of some ILs, as already pointed out by Dupont et al.<sup>[71]</sup> Indeed, hydrofluoric acid, generated by the degradation of [C<sub>n</sub>mim][PF<sub>6</sub>] (n = 4, 8) promoted the epoxide ring opening by traces of water included in the ILs, leading to the corresponding 1,2-diol. A quantitative yield of cyclooctene oxide was achieved in 24 h at 55 °C in [C<sub>4</sub>mim][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] with 1 mol % of CpMoMe, CpMoCl or Cp'MoCl as the catalyst. Lower yields were obtained from catalysis with Cp'MoMe and in [C<sub>4</sub>mim][BF<sub>4</sub>] or [C<sub>4</sub>mim][PF<sub>6</sub>]. To obtain interesting recycling results, the authors used a 4:1 mixture of [C<sub>4</sub>mim][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] and [C<sub>4</sub>mim][BF<sub>4</sub>].<sup>[70]</sup>

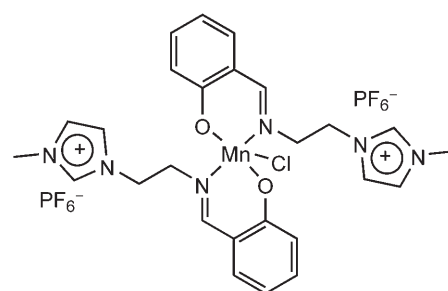
The urea-hydrogen peroxide adduct (UHP) associated to MeReO<sub>3</sub> as the catalyst led, at room temperature in [C<sub>2</sub>mim][BF<sub>4</sub>], to the efficient epoxidation of cycloalkenes, styrene and 1-(*E*-prop-1-enyl)benzene [Eqs. (51) and (52)]. Under these conditions which have been disclosed by Abu-Omar et al., the reaction of 1-decene was sluggish but, nevertheless, afforded selectively the corresponding epoxide [Eq. (52)], while cyclohex-2-enol was converted to 2,3-epoxycyclohexanol (62%) and 2,3-epoxycyclohexanone (32%).<sup>[54]</sup> The reaction between MeReO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> led to the mono- and diperoxo-rhenium complexes MeReO(η<sup>2</sup>-O<sub>2</sub>) and MeReO(η<sup>2</sup>-O<sub>2</sub>).<sup>[72]</sup> Abu-Omar et al. have explored the kinetics and thermodynamics of these reactions in a range of

ILs<sup>[73]</sup> and the kinetics of the oxygen-atom transfer from the peroxo complexes to alkenes.<sup>[74]</sup>



When 30% aqueous H<sub>2</sub>O<sub>2</sub> was used instead of UHP, the MeReO<sub>3</sub>-catalyzed oxidation in [C<sub>2</sub>mim][BF<sub>4</sub>] afforded mainly the corresponding diol,<sup>[54]</sup> because of the ring-opening of sensitive epoxides in the presence of large amounts of water.<sup>[75]</sup> The use of MeReO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> in ILs for the oxidation of alkenes has also been studied by Eckert et al.<sup>[76]</sup>

Although two epoxidation methods recently reported do not use an IL as solvent, it seems that they have to be mentioned here. Mizuno et al. have treated an IL anchored to an SiO<sub>2</sub> surface with an anionic dinuclear peroxotungstate. This led to a reusable heterogeneous W catalyst for the efficient epoxidation of a variety of C=C bonds with aqueous H<sub>2</sub>O<sub>2</sub> in MeCN at 60 °C.<sup>[77]</sup> Song et al. have synthesized an ionic liquid-grafted Mn(III)-Schiff base complex (Scheme 15) which was employed as a recyclable complex for the epoxidation of chalcones with a 1:1 mixture of *m*-chloroperbenzoic acid and NMO in MeCN at –25 °C.<sup>[78]</sup>



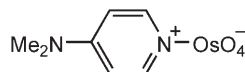
**Scheme 15.** Song's ionic liquid-grafted Mn(III)-Schiff base catalyst.

## 8.2 Dihydroxylation

As mentioned in Section 8.1, 1,2-diols can be a by-product of the epoxidation of olefins but they are rather produced from a subsequent reaction of the epoxides. Di-

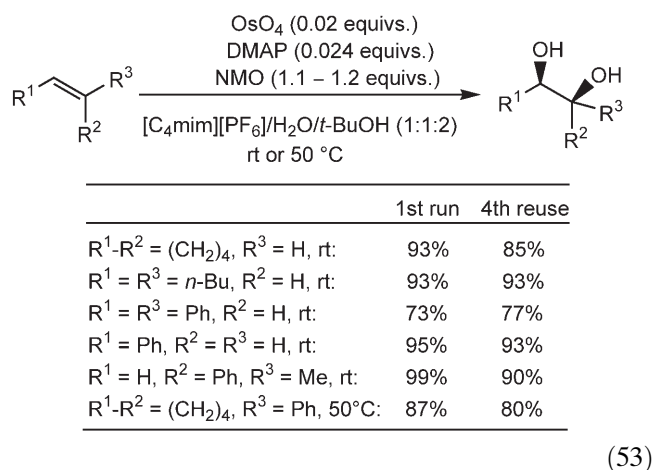
rect dihydroxylation of olefins in ILs are osmium-catalyzed oxidations with mainly *N*-methylmorpholine *N*-oxide (NMO), i.e., methods based on the Upjohn<sup>[79]</sup> and Sharpless<sup>[80]</sup> procedures.

Studying the OsO<sub>4</sub>-catalyzed dihydroxylation of 1-octene with NMO in a [C<sub>4</sub>mim][PF<sub>6</sub>]/H<sub>2</sub>O/*t*-BuOH mixture, Yao observed that the catalyst/IL recycling was much more effective with 4-(dimethylamino)pyridine (DMAP) as additive. According to Yao, this increase of the reuse efficiency is due to the formation of a polar



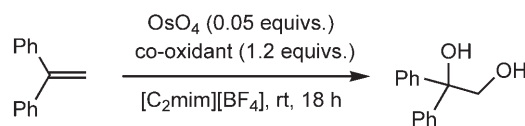
**Scheme 16.** Complex formed from OsO<sub>4</sub> and DMAP.

complex (Scheme 16) between OsO<sub>4</sub> and DMAP, that is better immobilized in the polar IL layer. Yao's protocol is efficient at room temperature to 50 °C for mono-, di- and trisubstituted aliphatic, as well as aromatic, olefins [Eq. (53)].<sup>[81]</sup>



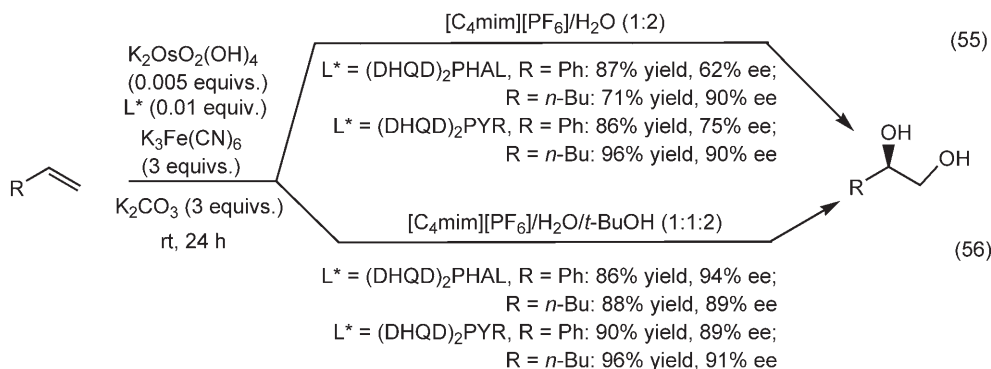
Almost simultaneously to Yao, Yanada et al. studied the OsO<sub>4</sub>-catalyzed dihydroxylation in [C<sub>2</sub>mim][BF<sub>4</sub>] of 1,1-diphenylethylene with various co-oxidants, in the ab-

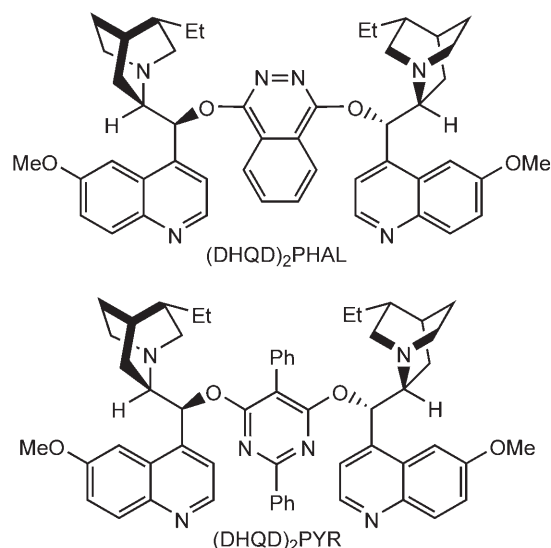
sence of a co-solvent and at room temperature [Eq. (54)].<sup>[82]</sup> They observed that NMO monohydrate as the co-oxidant led to the best results and that these conditions led to four recoveries and reuses of the OsO<sub>4</sub>/[C<sub>2</sub>mim][BF<sub>4</sub>] association without decrease of the yields. With [C<sub>4</sub>mim][PF<sub>6</sub>] as the solvent, the reaction carried out at 70 °C, because the melting point of [C<sub>4</sub>mim][PF<sub>6</sub>] is 61 °C, afforded a complex mixture. Then, the OsO<sub>4</sub>/[C<sub>2</sub>mim][BF<sub>4</sub>]/NMO system was successfully used for other olefins.<sup>[82,83]</sup>



co-oxidant	% of recovered substrate	yield [%] of diol	(54)
NMO	94	6	
NMO·H <sub>2</sub> O	0	100	
30% aq. H <sub>2</sub> O <sub>2</sub>	96	2	
Na <sub>2</sub> CO <sub>3</sub> ·1.5 H <sub>2</sub> O <sub>2</sub>	82	18	
<i>t</i> -BuOOH	18	31	

A few months later, the teams of Afonso and Song reported independently the asymmetric dihydroxylation of olefins in ILs.<sup>[84,85]</sup> The asymmetric dihydroxylation reported by Afonso et al. were carried out at room temperature with K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub>-L\* [L\* = (DHQD)<sub>2</sub>PHAL or (DHQD)<sub>2</sub>PYR] (Scheme 17) as the catalytic system and K<sub>3</sub>Fe(CN)<sub>6</sub> as the oxidant, in [C<sub>4</sub>mim][PF<sub>6</sub>]/H<sub>2</sub>O or [C<sub>4</sub>mim][PF<sub>6</sub>]/H<sub>2</sub>O/*t*-BuOH mixtures containing K<sub>2</sub>CO<sub>3</sub>. The most suitable procedure depended on the nature of the substrate [Eqs. (55) and (56)]. Enantiomeric excesses up to 99% have been obtained from mono-, di-, and trisubstituted olefins, and furthermore, more than 10 successive runs can be performed with the same IL/osmium/ligand without important decrease of the yield and ee. A few examples mentioned in a footnote of Afonso's original communication led us to suspect that the use of OsO<sub>4</sub> as the catalyst and NMO as the oxidant could be less effective.<sup>[84]</sup> Subsequently, the same team has also studied their K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub>-L\* catalytic sys-



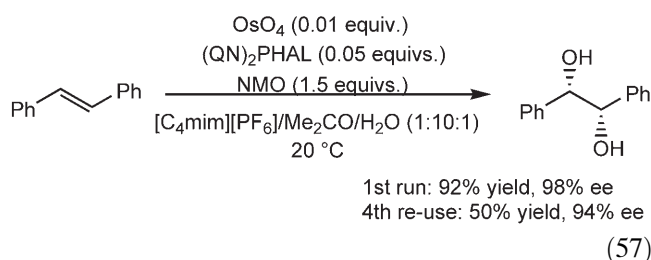


Scheme 17. Quinidine derived ligands.

tem, with  $\text{K}_3\text{Fe}(\text{CN})_6$  and NMO as the oxidants, in a variety of ILs as co-solvents, namely  $[\text{C}_n\text{mim}][\text{PF}_6]$  [ $n=4, 8, 10$ ,  $\text{X}=\text{BF}_4, \text{PF}_6, \text{OCOCF}_3, \text{N}(\text{SO}_2\text{CF}_3)_2$ ],  $[\text{C}_5\text{O}_2\text{mim}][\text{X}]$  ( $\text{X}=\text{BF}_4, \text{PF}_6$ ) and  $[3\text{guan}][\text{X}]$  [ $\text{X}=\text{PF}_6, \text{N}(\text{SO}_2\text{CF}_3)_2$ ]; impressive results were obtained in  $[\text{C}_n\text{mim}][\text{PF}_6]$  ( $n=4$  or  $8$ ) with both oxidants.<sup>[86]</sup> Recently, with the team of Nunes da Ponte who has studied different mixtures of ILs under high pressures of  $\text{CO}_2$ ,<sup>[87]</sup> Afonso et al. have shown the efficiency of the use of  $\text{scCO}_2$  in the separation process, allowing a better recyclability of the catalyst/IL system.<sup>[88]</sup>

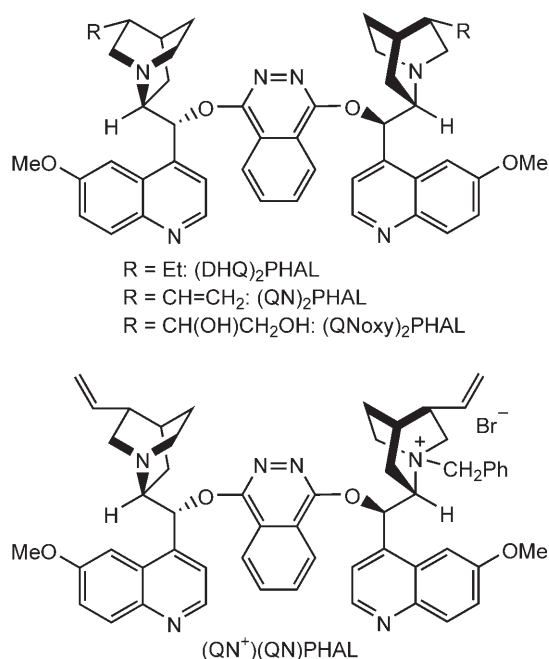
As for Song's team, it observed that the use of  $\text{OsO}_4$  with  $(\text{DHQ})_2\text{PHAL}$  (Scheme 18) and NMO in

$[\text{C}_4\text{mim}][\text{X}]/\text{Me}_2\text{CO}/\text{H}_2\text{O}$  ( $\text{X}=\text{PF}_6, \text{SbF}_6$ ) mixtures was efficient, but that the re-use of the recovered IL resulted in a dramatic decrease in the yields. Better results were obtained with a new bis-*Cinchona* alkaloid,  $(\text{QNOH}_2)_2\text{PHAL}$ , generated *in situ* from  $(\text{QN})_2\text{PHAL}$  (Scheme 18) during the reaction. Nevertheless, some leaching of osmium led to a decrease of the catalytic activity over successive reactions [Eq. (57)].<sup>[85]</sup> These asymmetric dihydroxylation processes, in particular the effect of the ligand structure on recyclability, have subsequently been studied by Sheldon et al.<sup>[89]</sup>

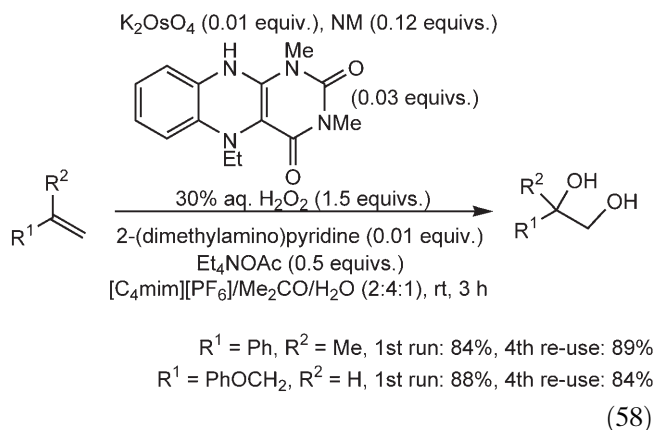


S. Zhang et al. have mono-quaternized Song's ligand to obtain  $(\text{QN}^+)(\text{QN})\text{PHAL}$  (Scheme 18). The use of this chiral ligand under Song's experimental conditions, except for the reaction temperature ( $0^\circ\text{C}$  instead of  $20^\circ\text{C}$ ), allowed a better reusability of the immobilized catalytic system.<sup>[90]</sup>

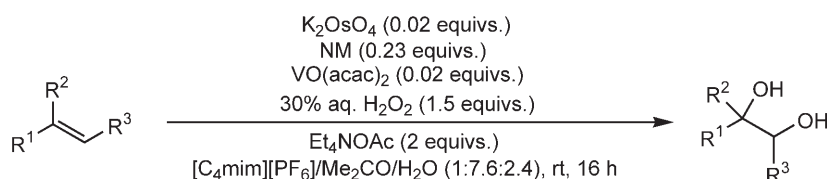
As shown above [Eq. (54)], NMO is a much more effective oxidant than  $\text{H}_2\text{O}_2$  for the Os-catalyzed dihydroxylation of olefins in ILs. However, NMO is much more expensive than  $\text{H}_2\text{O}_2$ . Interestingly, Bäckvall's team has been able, in a  $[\text{C}_4\text{mim}][\text{PF}_6]/\text{Me}_2\text{CO}/\text{H}_2\text{O}/\text{Et}_4\text{NOAc}$  mixture, to use  $\text{H}_2\text{O}_2$  as the stoichiometric oxidant *via* a triple catalytic system, namely  $\text{K}_2\text{OsO}_4/\text{NM}/\text{flavin}$  ( $\text{NM}=\text{N-methylmorpholine}$ ).<sup>[91]</sup> Flavin hydroperoxide generated from flavin and  $\text{H}_2\text{O}_2$  transfers one of its oxygen atoms to NM giving NMO, and the reduced flavin derivative is recycled to the active hydroperoxide *via* a reaction with  $\text{H}_2\text{O}_2$ .<sup>[92]</sup> A variety of olefins has been oxidized, and five successive runs performed without decrease of yields [Eq. (58)].



Scheme 18. Quinine-derived ligands.

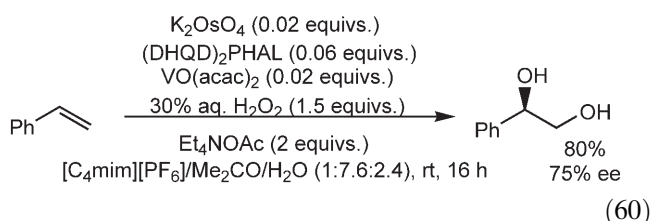


As  $\text{H}_2\text{O}_2$ -activating catalyst, Bäckvall's team has also used  $\text{VO}(\text{acac})_2$ <sup>[55,91]</sup> and  $\text{MeReO}_3$ <sup>[55]</sup> instead of flavin. Although the preliminary results with  $\text{VO}(\text{acac})_2$  were disappointing from aliphatic olefins,<sup>[91]</sup> recent reported experimental conditions were effective for the dihydroxylation of several different alkenes [Eq. (59)], and also mediated the asymmetric oxidation of styrene in the presence of a chiral ligand [Eq. (60)].<sup>[55]</sup> With  $\text{MeReO}_3$ , the dihydroxylation was, in some cases, more efficient using citric acid as additive rather than tetraethylammonium acetate [Eq. (61)]. With this latter additive, some substrates led, however, to the best yields in the absence of NM. Compared to  $\text{VO}(\text{acac})_2$ , recycling experiments were usually less productive with  $\text{MeReO}_3$ .<sup>[55]</sup>

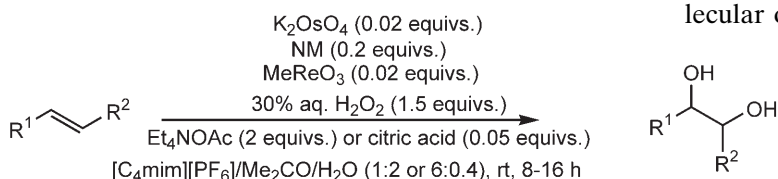


$\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{R}^3 = \text{H}$ : 81%;  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{H}$ ,  $\text{R}^3 = \text{Me}$ : 82%;  
 $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{Me}$ ,  $\text{R}^3 = \text{H}$ : 91%;  $\text{R}^1 = \text{PhOCH}_2$ ,  $\text{R}^2 = \text{R}^3 = \text{H}$ : 81%;  
 $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2\text{-R}^3 = (\text{CH}_2)_4$ : 73%;  $\text{R}^1 = \text{H}$ ,  $\text{R}^2\text{-R}^3 = (\text{CH}_2)_4$ : 91%;  
 $\text{R}^1 = (\text{CH}_2)_5\text{Me}$ ,  $\text{R}^2 = \text{R}^3 = \text{H}$ : 81%;  $\text{R}^1 = (\text{CH}_2)_4\text{Me}$ ,  $\text{R}^2 = \text{Me}$ ,  $\text{R}^3 = \text{H}$ : 86%;  
 $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{H}$ ,  $\text{R}^3 = (\text{CH}_2)_4\text{Me}$ : 80%;  $\text{R}^1 = \text{R}^3 = (\text{CH}_2)_3\text{Me}$ ,  $\text{R}^2 = \text{H}$ : 87%

(59)



(60)



with  $\text{Et}_4\text{NOAc}$ :

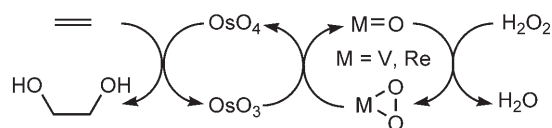
$\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{H}$ : 74%;  $\text{R}^1 = \text{PhOCH}_2$ ,  $\text{R}^2 = \text{H}$ : 68%;  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{Me}$ : 73%;  
 $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{COMe}$ : 48%;  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{CO}_2\text{Et}$ : 56%;  $\text{R}^1 = \text{R}^2 = (\text{CH}_2)_3\text{Me}$ : 85%;  
 $\text{R}^1 = (\text{CH}_2)_5\text{Me}$ ,  $\text{R}^2 = \text{H}$ : 90%;  $\text{R}^1\text{-R}^2 = (\text{CH}_2)_4$ : 72%.

with citric acid:

$\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{H}$ : 94%;  $\text{R}^1 = \text{PhOCH}_2$ ,  $\text{R}^2 = \text{H}$ : 86%;  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{Me}$ : 51%;  
 $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{COMe}$ : 51%;  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{CO}_2\text{Et}$ : 77%;  $\text{R}^1 = \text{R}^2 = (\text{CH}_2)_3\text{Me}$ : 18%;  
 $\text{R}^1 = (\text{CH}_2)_5\text{Me}$ ,  $\text{R}^2 = \text{H}$ : 78%;  $\text{R}^1\text{-R}^2 = (\text{CH}_2)_4$ : 41%.

(61)

The mechanism of the dihydroxylation with the bimetallic catalytic systems has been described as shown in

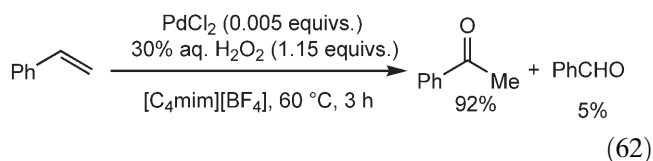


**Scheme 19.** Catalytic cycle proposed by Bäckvall's team for the dihydroxylation of alkenes with bimetallic catalytic systems.

Scheme 19. The re-oxidation of the osmium catalyst can be improved by catalytic amounts of NM. In this latter case, NM is oxidized to the corresponding *N*-oxide (NMO), which would transfer an oxygen atom to osmium.<sup>[55]</sup>

### 8.3 Wacker-Type Reaction

Varma et al. have studied the  $\text{PdCl}_2$ -catalyzed oxidation of styrene with aqueous  $\text{H}_2\text{O}_2$  in  $[\text{C}_4\text{mim}][\text{X}]$  ( $\text{X} = \text{BF}_4$  or  $\text{PF}_6$ ). The optimum reaction temperature was  $60^\circ\text{C}$  and acetophenone was the main product [Eq. (62)]. Benzaldehyde and benzoic acid can be formed as by-products, and their amount increased with the quantity of  $\text{H}_2\text{O}_2$ .<sup>[93]</sup>



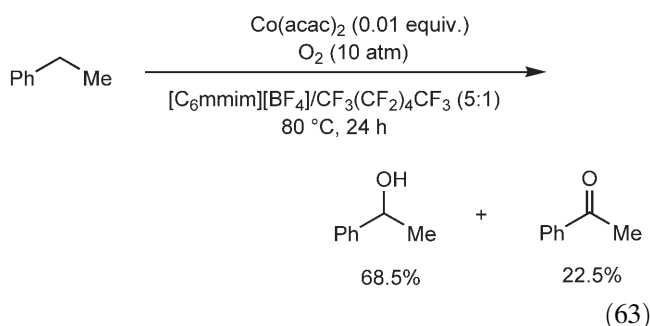
(62)

The  $\text{PdCl}_2$ -catalyzed oxidation of 1-hexene by molecular oxygen (60 to 180 bar) was conducted by Han et al. at  $60^\circ\text{C}$  in  $[\text{C}_4\text{mim}][\text{PF}_6]$  in the presence of methanol and  $\text{CuCl}_2$ . The main products were 2- and 3-hexanones, and it was observed that the selectivity towards 2-hexanone was increased up to *ca.* 95% using a mixture of supercritical  $\text{CO}_2$  and  $[\text{C}_4\text{mim}][\text{PF}_6]$  instead of the pure IL. According to the authors, the change in the properties of the catalytic system is the main reason for the decrease of the conversion with recycling.<sup>[94]</sup>

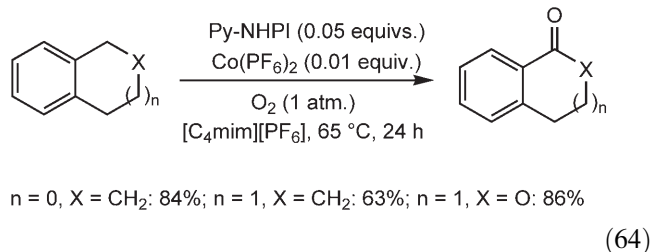
## 9 Benzylic Oxidation

A low conversion of toluene to benzaldehyde and benzyl alcohol was obtained by Seddon et al. in ILs, at  $80^\circ\text{C}$  under 10 atm oxygen, using  $\text{Pd}(\text{OAc})_2$  or  $\text{Co}(\text{ac}$

ac)<sub>2</sub> as the catalyst. Ethylbenzene was more reactive, especially when perfluorohexane was added as a co-solvent to concentrate the dissolved oxygen, the conversion reaching up to 91% in [C<sub>6</sub>mim][BF<sub>4</sub>] [Eq. (63)].<sup>[24]</sup>

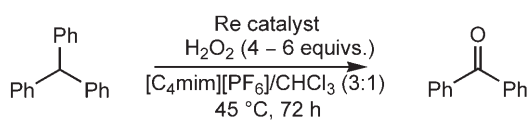


The team of Liu and Guo has used their above-described catalytic system, Co(PF<sub>6</sub>)<sub>2</sub>/Py-NHPI [Eq. (41)], for the aerobic oxidation of benzylic compounds in [C<sub>4</sub>mim][PF<sub>6</sub>] [Eq. (64)].<sup>[59]</sup>



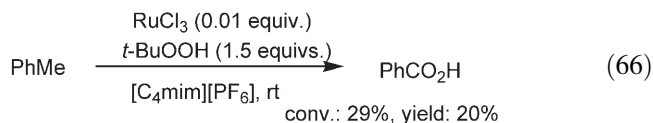
The Co(OAc)<sub>2</sub>-catalyzed oxidation of the side chain of aromatic hydrocarbons by oxygen in ILs/RCO<sub>2</sub>H mixtures has been reported in a Chinese patent, a mixture of benzaldehyde and benzyl acetate being produced from toluene at 115–120 °C with AcOH as the co-solvent.<sup>[95]</sup>

The Re-catalyzed oxidation of triphenylmethane with H<sub>2</sub>O<sub>2</sub> in a mixture of CHCl<sub>3</sub> and [C<sub>4</sub>mim][PF<sub>6</sub>] affords benzophenone.<sup>[34]</sup> This oxidative dearylation occurs with slightly lower conversion and selectivity using the heterogeneous Re catalysts depicted in Scheme 3 rather than MeReO<sub>3</sub>, but, according to Saladino et al.,<sup>[96]</sup> only the heterogeneous catalysts are reusable [Eq. (65)].

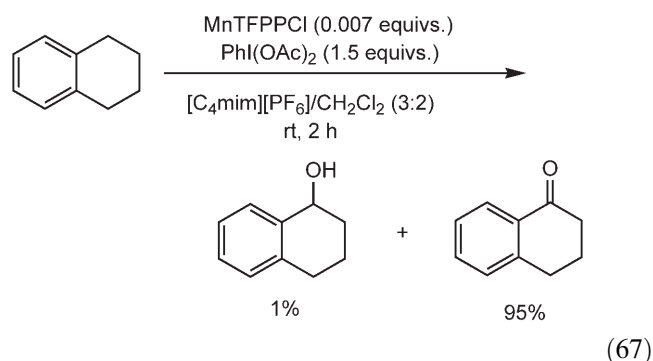


Re catalyst	conv. [%]	selectivity [%]
MeReO <sub>3</sub>	57	93
PVP-2-Re	48	89
PVPO-2-Re	51	81
PVP-25-Re	51	91
PVPO-25-Re	53	80
2PS-Re	49	88 (for run 1)
	45	86 (for run 3)

Benzoic acid was the main compound from the RuCl<sub>3</sub>-catalyzed oxidation of toluene with *t*-BuOOH in [C<sub>4</sub>mim][PF<sub>6</sub>] [Eq. (66)].<sup>[23]</sup>

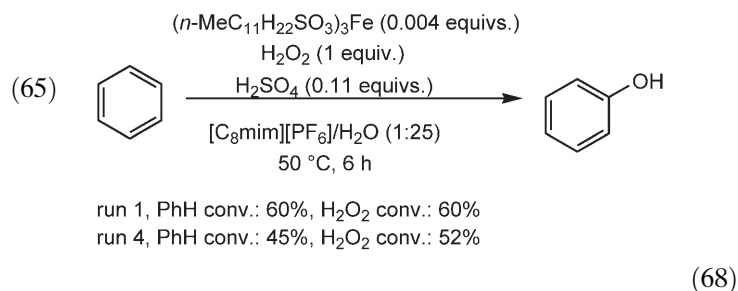


Tetraline has been efficiently oxidized at room temperature, by Xia et al., to mainly 1-tetralone using PhI(OAc)<sub>2</sub> as the oxidant, MnTFPPCl (Scheme 12) as the catalyst, in a mixture of [C<sub>4</sub>mim][PF<sub>6</sub>] and CH<sub>2</sub>Cl<sub>2</sub> [Eq. (67)].<sup>[97]</sup> Other manganese porphyrins, even with an axial ligand, were less active catalysts.<sup>[64]</sup>



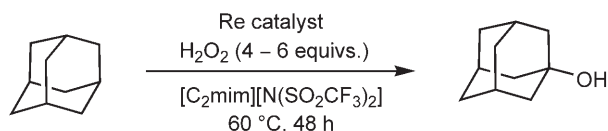
## 10 Benzene Hydroxylation

Deng et al. have carried out the selective aqueous-IL biphasic hydroxylation of benzene using H<sub>2</sub>O<sub>2</sub> and metal dodecanesulfonate salts of Fe(II), Fe(III), Co(II), Cu(II) and Ni(II), in [C<sub>n</sub>mim][X] (n = 4, 8, 10; X = PF<sub>6</sub>, BF<sub>4</sub>).<sup>[98]</sup> Only a stoichiometric amount of H<sub>2</sub>O<sub>2</sub> was used and a high selectivity of H<sub>2</sub>O<sub>2</sub> for benzene conversion was achieved. The use of ferric tri(dodecanesulfonate) as the catalyst in acidic H<sub>2</sub>O/[C<sub>8</sub>mim][PF<sub>6</sub>] led to the best result with almost 100% selectivity for phenol, and allowed recycling experiments with, however, some decrease in efficiency [Eq. (68)]. Only 1% conversion to mainly benzaldehyde was reached with toluene as the substrate. Surprisingly, with the addition of a 0.02 equiv. of benzene to toluene, the conversion was enhanced to 3% and some hydroxylation of the aromatic ring occurred.



## 11 Alkane Oxidation

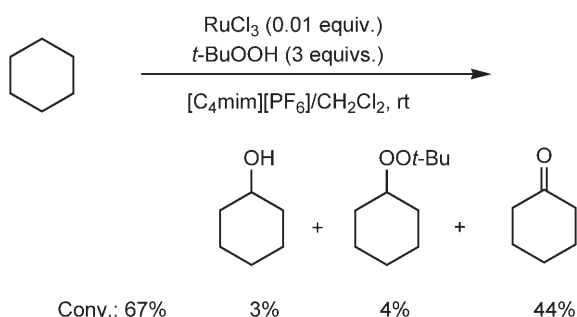
The selective oxidation of a tertiary C–H bond of *cis*-1,2-dimethylcyclohexane and adamantane with H<sub>2</sub>O<sub>2</sub> in [C<sub>4</sub>mim][PF<sub>6</sub>] and [C<sub>2</sub>mim][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>], respectively, has been reported by Saladino et al. using MeReO<sub>3</sub> and the heterogeneous Re complexes depicted in Scheme 3 as catalysts. For the adamantane oxidation, the heterogeneous catalysts provided better results than MeReO<sub>3</sub> [Eq. (69)].<sup>[34]</sup>



Re catalyst	conv. [%]	selectivity [%]
MeReO <sub>3</sub>	43	68
PVP-2-Re	63	79
PVPO-2-Re	78	68
PVP-25-Re	69	75
PVPO-25-Re	79	69
2PS-Re	72	72

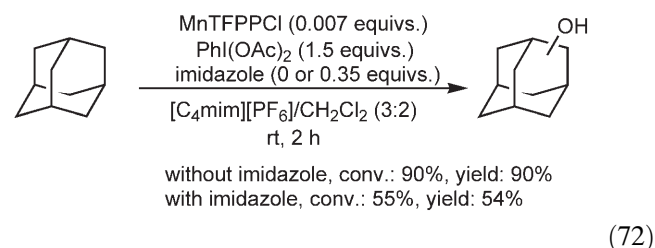
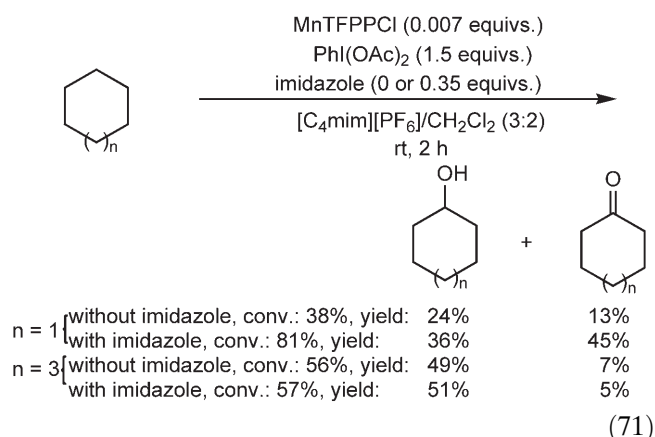
(69)

A report written in Chinese relates the RuCl<sub>3</sub>-catalyzed oxidation of cyclohexane into mainly cyclohexanone with *t*-BuOOH in [C<sub>4</sub>mim][PF<sub>6</sub>]. The conversion was improved using CH<sub>2</sub>Cl<sub>2</sub> as a co-solvent [Eq. (70)], and was very low when H<sub>2</sub>O<sub>2</sub> was the oxidant.<sup>[23]</sup>



(70)

Xia et al. have studied the oxidation of cyclohexane, cyclooctane and adamantane with PhI(OAc)<sub>2</sub> and a variety of manganese porphyrins (Scheme 12) in mixtures of [C<sub>4</sub>mim][PF<sub>6</sub>] and organic solvents.<sup>[64,97]</sup> The beneficial effect of imidazole or pyridine as an axial ligand of the manganese porphyrins depended on the nature of the substrate, the porphyrin and the co-solvent [Eqs. (71) and (72)].



## 12 Conclusions

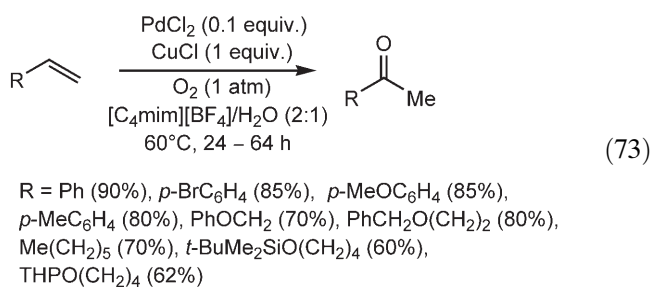
Intensive research over the last few years in the area of catalyzed oxidations in ILs has resulted in the development of a number of processes which, for some of them, are more efficient than those carried out in organic solvents. It is important to note that the oxidation efficiency can be greatly dependent on the nature of the IL and, furthermore, the IL can be a non-innocent solvent. For some studies carried out using IL/organic solvent mixtures, we suspect that the IL could be a phase-transfer catalyst.

Most ILs are expensive and, often, their toxicity as well as their stability remain to be determined. With regards to economic and ecological concerns, of particular interest are the methods allowing the recovery and the re-use of both the catalyst and IL. Although significant progress has been made, further work is necessary to improve the recyclability of the catalyst/IL associations. The use of ILs in organic synthesis is still in its infancy and new ILs are emerging. Consequently, it is likely that new and more efficient procedures will appear in the near future.

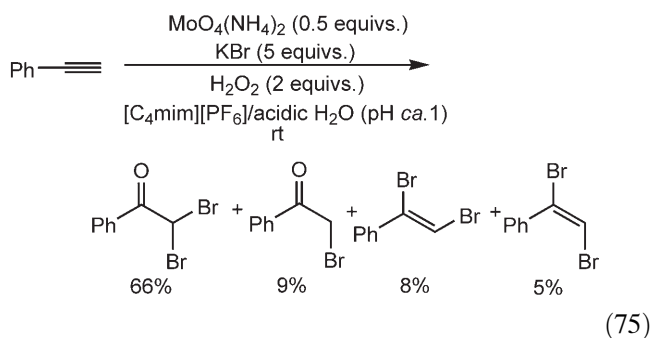
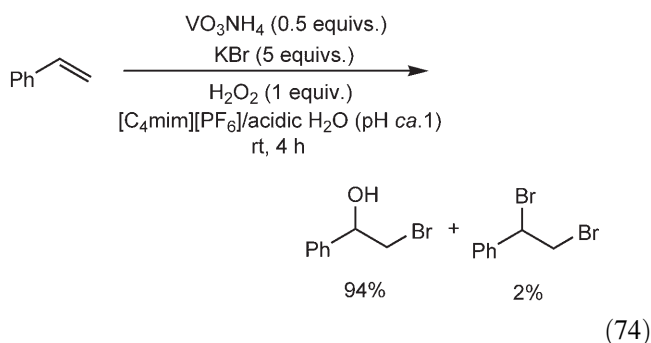
## 13 Addendum

Ansari, Gree et al. have disclosed the Wacker oxidation of a variety of terminal olefins using catalytic amounts of PdCl<sub>2</sub>, a stoichiometric amount of CuCl in a [C<sub>4</sub>mim][BF<sub>4</sub>]/H<sub>2</sub>O mixture at 60 °C under an oxygen atmosphere [Eq. (73)]. The expected ketones were usually accompanied by low amounts of aldehydes. Interesting-

ly, it was possible to recycle the IL and the catalytic system up to eight times with only a slight decrease in the conversion<sup>[99]</sup>



Conte et al. have carried out the vanadium(V)-catalyzed oxybromination of styrene with H<sub>2</sub>O<sub>2</sub> and KBr in IL/H<sub>2</sub>O mixture [Eq. (74)].<sup>[100]</sup> Subsequently, the same team reported the molybdenum(VI)-catalyzed oxybromination of phenylacetylene under similar experimental conditions [Eq. 75].<sup>[101]</sup>



Jakubiak et al. have observed that the selectivity of the oxidation of hydroquinone to *p*-benzoquinone with aqueous H<sub>2</sub>O<sub>2</sub> and catalytic amounts of Cu(II) ions immobilized on acrylic resins increased in the presence of [C<sub>4</sub>mim][BF<sub>4</sub>] (yield up to 66%).<sup>[102]</sup>

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