Imidazolium Ionic Liquid-Grafted 2,2′-Bipyridine—A Novel Ligand for the Recyclable Copper-catalyzed Selective Oxidation of Alcohols in Ionic Liquid [bmim][PF6]

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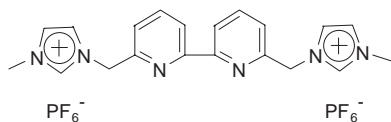
A novel imidazolium ionic liquid-grafted 2,2′-bipyridine ligand has been prepared and successfully employed in the copper-catalyzed selective oxidation of alcohols to the corresponding carbonyl compounds in ionic liquid [bmim][PF6] under mild conditions, and the catalytic ionic liquid solution can be recovered and reused without significant loss of catalytic efficiency.

The use of ionic liquids (ILs), especially those based upon the 1-alkyl-3-methylimidazolium cation, as 'green' solvents in organic synthetic processes has gained recognition because of their solvating ability, negligible vapour pressure, easy recyclability, and reusability.[1] Recent advances in ILs research provided another route for achieving task-specific ionic liquids (TSILs) in which a functional group is covalently tethered to the cation or anion of the ILs.[2] It was expected that these TSILs might further enlarge the application scope of ILs in chemistry.

The oxidation of primary and secondary alcohols into the corresponding carbonyl compounds plays a central role in organic synthesis.[3] Traditionally such transformations have been performed with stoichiometric inorganic oxidants.[4] However, from both economic and environmental viewpoints, there is an urgent demand for green, atom efficient methods that employ clean oxidants, such as O_2 or H_2O_2 and a preferably recyclable catalyst. Recently it has been demonstrated that ILs can be employed in the copper-catalyzed oxidation of alcohols employing O_2 as oxidant.[5] However, the immobilization of the catalytic system in the IL was not successful in their procedure.

In the present communication, we report an efficient synthesis of a new TSIL, see Scheme 1, that contains two 1-methylmidazolium hexafluorophosphate moieties and describe preliminary results of its catalytic efficiency and reusability in the copper(I) chloride and 2,2,6,6-tetramethylpiperidine N-oxyl (TEMPO) catalysed oxidation of alcohols to corresponding aldehydes and ketones using the IL [bmim]PF6 as catalyst solvent. IL [bmim]PF6 has been prepared from [bmim]Cl[6] according to a method described by Fuller et al.[7]

**Scheme 1.** Ionic liquid grafted 2,2′-bipyridine ligand.

The route to the new bipyridine ligand bearing with pending imidazolium tags is depicted in Scheme 2.[8] The 6,6′-bis(bromomethyl)-2,2′-bipyridine (3), easily prepared from commercially available 6,6′-dimethyl-2,2′-bipyridine (2) in one step,[9] was reacted with 1-methylimidazole in acetonitrile at 80 °C for 24 h to give 6,6′-bis(1-methylimidazolium-3-ylmethyl)-2,2′-bipyridine dibromide (4). Further treatment of 4 with KPF6 in acetone for 48 h provides 1.
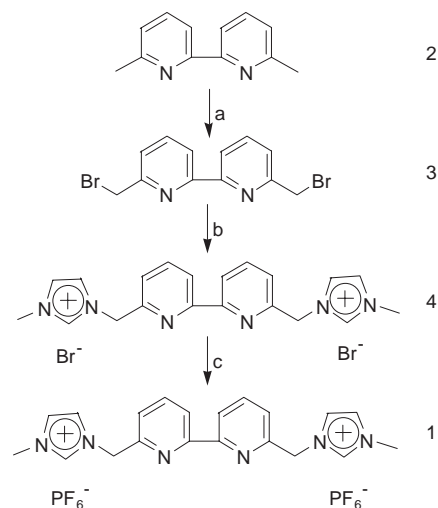
Scheme 2. The synthesis of ligand 1. a) NBS, CCl4, reflux; b) 1-methylimidazole (2.7 equiv.) 80 °C, 24 h in CH3CN, 98%; c) KPF6 (1.2 equiv.), rt, 48 h in acetone, 96%.

The coordination ability of the new IL-ligand has also been briefly studied and it was found that the new IL-ligand 1 could form complex with CuCl. The complex was prepared from CuCl and the IL-bpy ligand in acetonitrile at room temperature and has been confirmed by element analysis and FTIR spectra.[10]
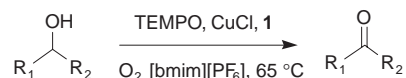
Scheme 3. Oxidation of alcohols in ionic liquid.

For the catalyst, the preferred method was preparation in situ by mixing 49 mg (0.5 mmol) of CuCl and one equivalent of ligand 1 (318 mg, 0.5 mmol) in a 5-mL acetonitrile/[bmim][PF6] (1/1, v/v) mixture. After the acetonitrile was removed in vacuum, a yellow-colored catalyst solution was obtained. With 5 mol % of this catalyst, TEMPO (5 mol %) as co-catalyst, the oxidation reactions were carried out at 65 °C under oxygen atmosphere. The conversion of alcohols was followed by thin layer chromatography (TLC) and gas chromatography (GC) with an internal standard. The products were isolated by simple extraction with diethyl ether. The structures of the products were confirmed by comparison with authentic standards of carbonyl compounds. The IL phase could be separated and reused for further runs.

The results of this study are summarized in Table 1 (Runs 1–

Table 1. Conversion of alcohols to aldehydes and ketones[a]

Run	Alcohol	Product	Time /h	Conversion[a] %
1	Benzyl alcohol	Benzaldehyde	15	>99
2	(4-Methoxy-phenyl)-methanol	4-Methoxy-benzaldehyde	15	95
3	(4-Nitro-phenyl)-methanol	4-Nitro-benzaldehyde	15	98
4	(2-Chloro-phenyl)-methanol	2-Chloro-benzaldehyde	15	98
5	1-Phenyl-ethanol	1-Phenyl-ethanone	15	96
6	Cyclohexanol	Cyclohexanon	48	83
7	Prop-2-en-1-ol	Propenal	15	80
8	Heptan-1-ol	Heptanal	48	70
9	Benzyl alcohol	Benzaldehyde	15	>99[b]

[a]Selectivity >99% based on GC. [b]In the absence of the IL-bpy ligand.

8). As indicated by quantitative GC analysis, aldehydes and ketones were formed in high yields from the corresponding primary and secondary alcohols, respectively. However, aliphatic alcohols react slower than benzyl alcohols and allylic alcohols. This may be due to the poor solubility of aliphatic alcohols in ILs.

The recyclability of the used ILs solution containing the catalyst was demonstrated for the oxidation of benzyl alcohol to benzaldehyde. The results of five consecutive recycling experiments were shown in Table 2. As expected, the reaction was performed five times without a major loss of catalytic activity. The observed loss of activity was maybe due to mechanical losses during the extraction procedure. This problem could be minimized by direct distillation of the carbonyl compounds from the reaction mixture. Indeed, after the carbonyl compounds were removed by distilling from the IL solution directly, the resulting catalytic IL solution could be reused for the oxidation of benzyl alcohol and showed no variation of catalytic activity and selectivity compared to the fresh catalyst, see Table 2.

Table 2. Reuse of the catalyst solution for the oxidation of benzyl alcohol to benzaldehyde

Run	1	2	3	4	5
Yield %[a]	>99	97	90	83	80
Yield %[b]	>99	97	96	95	97

[a]The carbonyl compounds were removed by extraction diethyl ether; [b]The carbonyl compounds were removed by distilling.

For comparison, a reaction for the oxidation of benzyl alcohol was carried out under the same reaction condition in the absence of the IL-bpy ligand, see Table 1 (Run 9). Although similar results were also obtained, it was observed that the copper catalyst was extracted from the IL solution along with the polar products (aldehydes) by the diethyl ether during the extraction process. The conclusion is substantiated by the observation that the ether phase turned blue-green.

In conclusion, we have shown that the imidazolium IL-modified bipyridine is an efficient ligand for the performance of the copper-catalyzed oxidation of various primary and secondary alcohols to their corresponding aldehydes and ketones in hexafluorophosphate IL under mild conditions. The facile recovery of the catalyst is a great advantage of this method. Work is in progress to further address the recoverability and recyclability properties of this new ligand. The approach may therefore be of interest not only for oxidations but also for many other catalytic reactions in ILs. Studies on the imidazolium ionic tag strategy to increase the reusability of the other catalysts in environmentally benign ILs will be continued.

References and Notes
1 Comprehensive information about this field can be found in the many reviews that have appeared on this subject: "Ionic Liquids in Synthesis," ed. by P. Wasserscheid and T. Welton, Wiley-VCH, Weinheim (2002); J. Dupont, R. F. de Souza, and P. A. Z. Suarez, *Chem. Rev.*, **102**, 3667 (2002); C. M. Gordon, *Appl. Catal., A*, **222**, 101 (2001), and references therein.
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8 Detailed information for the IL-ligand synthesis and catalyst preparation see supporting information. **4**: ^{1}H NMR (DMSO, 400 MHz): $\delta = 9.38$ (s, 2H), 8.23 (d, $J = 8.0$ Hz, 2 H), 8.05 (t, $J = 8.0$ Hz, 2 H), 7.90 (s, 2H), 7.79 (s, 2H), 7.57 (d, $J = 8.0$ Hz, 2H), 5.68 (s, 4H), 3.93 (s, 6H); ^{13}C NMR (DMSO, 400 MHz): $\delta = 154.41$, 153.36, 138.78, 137.31, 123.58, 123.12, 122.95, 120.18, 52.81, 35.89. Anal. Calcd. for $C_{20}H_{22}N_6Br_2$: C 47.45, H 4.38, N 16.60, Found C 47.39, H 4.31, N 16.53%. MS (FBA): $m/z = 346$ [M]$^+$. IR (KBr, selected data) 1565.63, 1431.88, 1162.03 cm^{-1}. $T_g = 299.65\,°$C. **1**: ^{1}H NMR (DMSO, 400 MHz): $\delta = 9.28$ (s, 2H), 8.20 (d, $J = 8.0$ Hz, 2 H), 8.03 (t, $J = 8.0$ Hz, 2 H), 785 (s, 2H), 7.75 (s, 2H), 7.55 (d, $J = 8.0$ Hz, 2 H), 5.64 (s, 4H), 3.93 (s, 6H); ^{13}C NMR (DMSO, 400 MHz): $\delta = 154.51$, 153.34, 138.80, 137.38, 123.64, 123.20, 122.92, 120.22, 52.96, 35.85. Anal. Calcd. for $C_{20}H_{22}N_6P_2F_{12}$: C 37.74, H 3.48, N 13.21, P 9.73, Found C 37.69, H 3.41, N 13.20, P 9.68%. MS (FBA): $m/z = 346$ [M]$^+$. IR (KBr, selected data) 1579.73, 1440.07, 1175.23, 832.05 cm^{-1}. mp = 227 °C. $T_g = 285.69\,°$C.
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10 Detailed information for this complex preparation see supporting information. Elemental analysis calcd for $C_{20}H_{22}ClP_2F_{12}N_6Cu$: C 32.67, H 3.02, N 11.43, P, 8.42; found C 53.53, H 4.90, N 18.57%. IR (KBr, selected data) 1605.32, 1580.33, 1469.82, 1438.31, 1183.10, 1169.84, 840.25 cm^{-1}.