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Short Communication

Catalytic oxidation of alcohols by a novel manganese Schiff base ligand derived from salicylaldehyd and l-Phenylalanine in ionic liquids

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ABSTRACT

A selective oxidation of alcohols to corresponding carbonyl compounds in ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate([bmim]BF_4) was achieved by using a novel salicylaldehyd amino acid Schiff base manganese ligand. The catalytic system can be recycled and reused for four runs without any significant loss of catalytic activity.

1. Introduction

The oxidation of alcohols to the corresponding aldehydes, ketones and carboxylic acids is one of the important reactions in organic chemistry both at the laboratory and in industrial synthetic chemistry [1]. Traditionally, this transformation is performed with stoichiometric, toxic and expensive inorganic oxidizing agents (i.e. $KMnO_4$, Cr(VI) compounds, HNO_3, etc.) and in organic solvents which are volatile, toxic, and flammable [2]. Due to the industrial importance of this process and the ever-growing environmental concerns, the development of effective, greener catalytic systems that use inexpensive oxidants is an important challenge.

As one of the alternative approaches for tackling these problems, ambient temperature ionic liquids (ILs) have been employed as the promising alternative green solvents for the above reactions because of their negligible vapor pressure, solvating ability, easy recyclability and reusability. In the last several years, many transition metals such as palladium [3–8], copper [9], ruthenium [10–12], manganese [13], tungsten [14,15], rhenium [16], iron [17] and vanadium [18] have been used as catalysts for alcohol oxidation with ILs as green solvents [19].

The Schiff base transition metal complexes are attractive oxidation catalysts because of their cheap, easy synthesis and their chemical and thermal stability. Considerable attention has been paid to the preparation of transition metal complexes of Schiff bases derived from amino acids because they are considered to constitute new kinds of potential antibacterial and anticancer reagents [20–25]. However, to the best of our knowledge, the cheap and "green" Mn catalytic systems for oxidation of alcohols in ILs have received less attention, especially manganese metal ligands. Jing team [26] reported the oxidation of secondary alcohols with iodobenzene diacetate catalyzed by Mn(Salen) in ionic liquid, but toxic CH_2Cl_2 was also used as the co-solvent in ionic liquid.

Recently, we reported a copper Schiff base ligand derived from acetylacetonate and L-Leucine that can be recycled and reused in [bmim]BF_4. In continuation of our interest in exploring green oxidation of alcohols in ILs by metal ligands, we herein report a mild and effective procedure for the selective oxidation of alcohols using a novel salicylic amino acid Schiff base manganese ligand (Sal–amino acid–Mn)/H_2O_2 system with an IL [bmim]BF_4 as the solvent (Scheme 1).

2. Experimental

2.1. General

Chromatographic analyses were performed on an HP-4890 gas chromatograph, a flame ionization detector, equipped with an HP-Innowax capillary column. The ^1H NMR measurements were carried out on an Inova 500 MHz high-resolution liquid nuclear magnetic resonance spectrometer. IR spectra were obtained with Nicolet Magna-IR 560 SXB and expressed in cm^{-1}. Elemental analyses were performed with a Vanio-EL analyzer and VISTA-MPS.

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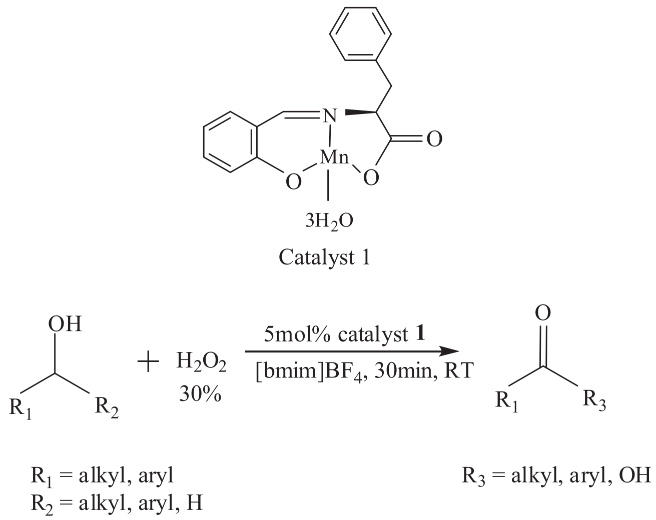


Scheme 1. Salicylic L-Phenylalanine Schiff base manganese complex catalyzed oxidation of alcohols.

Table 1
Optimization of the reaction conditions.[a]

Entry	Solvent	Con (%)[b]/Sel (%)	Yield (%)[c]
1	[bmim]BF$_4$	100/> 98	94
2	[bmim]PF$_6$	34/95	12
3	[bmim]CF$_3$COO	23/98	–
4	CH$_3$CN	47/100	20
5	C$_3$H$_6$O	16/100–	–
6	CH$_3$OH	14/40	–
7	[bmim]BF$_4$	48[d]/> 98	43
8	[bmim]BF$_4$	43[e]/> 98	38
9	[bmim]BF$_4$	65[f]/> 98	56
10	[bmim]BF$_4$	22[g]/> 98	18
11	[bmim]BF$_4$	75[h]/> 98	73
12	[bmim]BF$_4$	58[i]/> 98	56

[a] 2 mmol benzyl alcohol, 5 mol% catalyst 1, 10 mmol 30% H_2O_2, 1 mL [bmim]BF$_4$, room temperature for 30 min.
[b] Based on GC.
[c] Isolated yield by flash chromatography.
[d] 10 mmol 10% aqueous NaClO as the oxidant.
[e] 10 mmol 70% t-BuOOH in 2 ml CH_2Cl_2 as the oxidant.
[f] 10 mmol PhI(OAc)$_2$ as the oxidant.
[g] 2 mmol 30% H_2O_2 was used.
[h] 6 mmol 30% H_2O_2 was used.
[i] The reaction time was 15 min.

2.2. Chemicals

Ionic liquids and other chemicals used without further purification in the present study were of analytical grade and procured from Chemer Chemical Co. Ltd, China and Acros Organics, respectively.

2.3. Synthesis of manganese amino acid Schiff base (catalyst 1)

Sodium hydroxide (8 mmol) and L-Phenylalanine (8 mmol) were stirred in ethanol (100 mL). Once the L-Phenylalanine and sodium hydroxide were dissolved, a further 20 mL of ethanol, containing a dissolved 8 mmol of salicylaldehyd, was added. After refluence for 3 h, an aqueous (8 mmol) Mn(CH$_3$COO)2·H$_2$O (30 mL) solution was added slowly. The color of the solution changed to brown, and the solution was continuously refluxed for 10 h. Left out for one night, the complex was settled out. The precipitate of manganese complex was collected by filtration, washed with water, ethanol and ether, respectively, and dried in a vacuum to afford complex purification (yield 79%). IR(KBr): 3408 cm^{-1}(–OH), 1641 cm^{-1}(C=N), 1601 cm^{-1}(COO–), 1385 cm^{-1}(COO–), 521 cm^{-1}(Mn–N), 437 cm^{-1}(Mn–O). Anal. Calcd for $C_{16}H_{18}NO_6Mn$: C, 51.20; H, 4.80; N, 3.73; Mn, 14.67. Found: C, 51.20; H, 4.83; N, 3.70; Mn, 14.68.

2.4. Representative procedure for the oxidation of alcohols

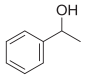
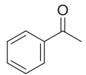
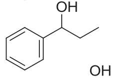
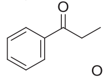
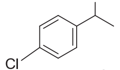
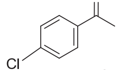
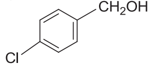
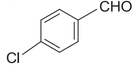
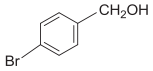
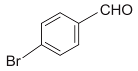
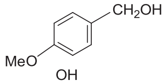
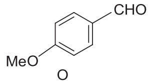
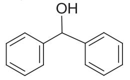
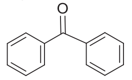
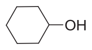
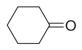
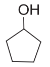
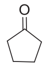
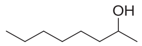
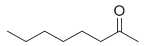
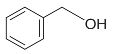
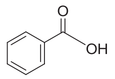
The reactions were performed at room temperature in a batch reactor (glass vial). A mixture of alcohol (2 mmol), catalyst 1 (0.1 mmol) and [bmim]BF$_4$ (1 mL) was added in the micro-reactor stirred for 1 min, after which 30% aqueous H_2O_2 (10 mmol) was added to the mixture. After completion of the oxidation, the mixture was extracted with hexane (3 × 5 mL). The combined hexane phase was concentrated in vacuo and monitored by GC and ^{1}H NMR. The residue was then purified with flash chromatography to afford corresponding carboxylic acids and ketones in 48–94% yield.

3. Results and discussion

The initial investigation was carried out using α-Phenylethanol as the substrate to optimize the reaction conditions, and the results are summarized in Table 1.

First, six different solvents including three kinds of ILs ([bmim]PF$_6$, [bmim]BF$_4$ and [bmim]CF$_3$COO) and acetonitrile, acetone, methanol were tested with the compound 1 as the catalyst for the oxidation. As shown in Table 1, the oxidation proceeded rapidly in BF$_4$-type IL, but far more slowly in acetonitrile, PF$_6$-type and CF$_3$COO-type ILs, and, in acetone and methanol, no reaction occurred at all (Table 1,

Table 2
Oxidation of alcohols.[a]

Entry	Substrate	Products	Time (min)	Con[b]/yield (%)[c]
1			30	> 98/94
2			30	93/86
3			30	99/93
4			30	93/88
5			30	93/89
6			30	95/87
7			30	95/88
8			30	67/62
9			60	53/48
10			60	63/56
11			30	99/62

[a] 2 mmol alcohol, 5 mol% catalyst 1, 10 mmol 30% H_2O_2, 1 mL [bmim]BF$_4$.
[b] Conversion by GC of the crude product complex.
[c] Isolated yield by flash chromatography.

Table 3
Recycling of the catalytic system for the oxidation of benzyl alcohol.[a]

Run	Conversion (%)[b]	Yield (%)[c]
1	100	94
2	94	88
3	89	84
4	88	82

[a] 2 mmol benzyl alcohol, 5 mol% catalyst 1, 10 mmol 30% H_2O_2, 1 mL [bmim]BF_4, room temperature for 30 min.
[b] Conversion by GC of the crude product complex.
[c] Isolated yield by flash chromatography.

Entry 1–6). Next, various types of oxidants were tested as oxygen resource in [bmim]BF_4. It was clear that all the oxidants gave comparable conversions and selections, but H_2O_2 showed to be optimal (Table 1, entries 1, 7, 8, 9). It was noted that the increment of load of H_2O_2 and reaction time led to the increment of yields of acetophenone (Table 1, entries 1, 10, 11, 12).

Having optimized the reaction condition, the oxidation of other alcohols was then examined (Table 2). It was clear that all primary alcohols and secondary alcohols had been selectively oxidized to carboxylic acids and ketones respectively. In addition, the reaction of aromatic alcohols to the corresponding carbonyl compounds was fast and efficient, whereas aliphatic alcohols all reacted more slowly.

Subsequently, the recyclability of the used ILs solution containing the catalyst was demonstrated for the oxidation of α-Phenylethanol. The catalytic system could be reused directly for a new cycle after full extraction of the product three times with 5 mL hexane per extraction. The results shown in Table 3 demonstrated that this oxidative system was readily recyclable for four runs without any significant loss of catalytic activity.

4. Conclusion

In summary, a novel, very mild and efficient protocol for the oxidation of alcohols to corresponding carbonyl compounds with excellent conversions using an salicylic amino acid Schiff base manganese ligand as the catalyst has been developed in the IL [bmim]BF_4. Most importantly, this catalytic system is straightforward and easy to handle, and can be recycled and reused for four runs without any significant loss of the catalytic activity.

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References

[1] S.V. Ley, A. Madin, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, Pergamon, Oxford, 1991, pp. 305–327, Vol. 7.
[2] S.V. Ley, A. Madin, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, Pergamon, Oxford, 1991, p. 251, Vol. 7.
[3] K.R. Seddon, A. Stark, Green Chemistry 4 (2002) 119.
[4] B. Ganchegui, S. Bouquillon, F. Hénin, J. Muzart, Tetrahedron Letters 43 (2002) 6641.
[5] J. Muzart, Tetrahedron 59 (2003) 5789.
[6] S. Bouquillon, A.du Moulinet. d'Hardemare, M.-Th. Averbuch-Pouchot, F. Hénin, J. Muzart, Polyhedron 18 (1999) 3511.
[7] B. Ganchegui, S. Bouquillon, F. Hénin, J. Muzart, Journal of Molecular Catalysis A: Chemical 214 (2004) 65.
[8] C. Hardacre, E.A. Mullan, D.W. Rooney, J.M. Thompson, Journal of Catalysis 232 (2005) 355.
[9] M. Rong, C. Liu, J. Han, Catalysis Letters 125 (2008) 52–56.
[10] A. Wolfson, S. Wuyts, D.E. De Vos, I.F.J. Vankelecom, P.A. Jacobs, Tetrahedron Letters 43 (2002) 8107.
[11] W.M. Tang, C.J. Li, Acta Chimica Sinica 62 (2004) 742.
[12] F.D.S. Roberto, D. Jairton, E.D.L.D. Jeane, Journal of the Brazilian Chemical Society 17 (2006) 48.
[13] J.W. Li, W. Sun, L.W. Xu, C.G. Xia, H.W. Wang, Chinese Chemical Letters 15 (2004) 1437.
[14] B.S. Chhikara, S. Tehlan, A. Kumar, Synlett (2005) 63.
[15] B.S. Chhikara, R. Chandra, V. Tandon, Journal of Catalysis 230 (2005) 436.
[16] G. Bianchini, M. Crucianelli, F. de Angelis, V. Neri, R. Saladino, Tetrahedron Letters 46 (2005) 2427.
[17] A. Kumar, N. Jain, S. Chauhan, Synlett 411 (2007).
[18] J. Nan, J.R. Arthur, Tetrahedron Letters 48 (2007) 273.
[19] J. Muzart, Advanced Synthesis and Catalysis 348 (2006) 275.
[20] T.M. Aminabhavi, N.S. Biradar, S.B. Patil, V.L. Roddabasanagoudar, Inorganica Chimica Acta 107 (1985) 231.
[21] G. Plesch, C. Friebel, O. Svajlenova, J. Kratsmar-Smogrovic, D. Mlynarcik, Inorganica Chimica Acta 151 (1988) 139.
[22] D. Sattari, E. Alipour, S. Shriani, J. Amighian, Journal of Inorganic Biochemistry 45 (1992) 115.
[23] I.A. Ansari, R. Gree, Organic Letters 4 (2002) 1507.
[24] J. Nan, J.R. Arthur, Organic Letters 7 (2005) 3689.
[25] X.E. Wu, L. Ma, M.X. Ding, L.X. Gao, Chemistry Letters 34 (2005) 312.
[26] Se Jing, Li Zhen, Chun-gu Xia, Fenzi Cuihua 22 (2008) 561.