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Short communication

Benzimidazolium sulfonate ligand precursors and application in ruthenium-catalyzed aromatic amine alkylation with alcohols

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ABSTRACT

New benzimidazolium sulfonate salts have been prepared and fully characterized. They have been associated in situ with $[RuCl_2(p\text{-cymene})]_2$ to generate efficient catalytic systems operating at 120 °C under neat conditions in the presence of potassium *tert*-butylate for selective *N*-alkylation of primary aromatic amines into secondary amines.

1. Introduction

Amines constitute a class of organic compounds with a wide range of applications in chemical industry ranging from ammonia, produced in million ton scale, to fine chemicals with biological properties [1]. In this context, the creation of C–N bonds from primary and secondary amines has been investigated for a long time and more recently using the hydrogen borrowing process starting from alcohol as alkylating agent [2–6]. This methodology offers advantages in terms of atom economy and clean reaction over other methods based on organic or organometallic coupling reactions, as only water is formed as byproduct. *N*-alkylation of aromatic amines has been mostly carried out with iridium catalyst precursors such as $[Cp^*IrCl_2]_2$ in the presence of a carbonate or hydrogenocarbonate as mineral base in refluxing toluene. Intermolecular reaction with alcohols [7] and cyclization with diols [8] have thus been successfully achieved. *N*-alkylation of anilines with iridium catalysts has also been carried out without base additive in water in the presence of $[Cp^*IrI_2]_2$ [9] or in neat conditions with dicationic catalysts [10,11]. Catalytic systems based on ruthenium precursors have proved to be also efficient for aniline *N*-alkylation. Initial results were obtained using $RuCl_2(PPh_3)_3$ or $RuCl_3 \cdot xH_2O$ in the presence of phosphine without additional base but at high temperature (180 °C) with or without a solvent, leading to substituted secondary and tertiary anilines [12], *N*-aryl-substituted cyclic amines [13], and heterocycles [14]. Then, new catalysts were designed in order to introduce milder conditions, especially lower temperature conditions or lower amounts of base. In the iridium series, this was done by implementation of bidentate (C, N), (P, N) and tridentate (P, N, P) ligands, which allowed alkylating aniline below 100 °C at low catalyst loading with ^{t}BuOK or CsOH as base [15,16]. Phosphine-sulfonate ligands were also introduced on Cp*Ir(III) complexes to achieve the double *N*-alkylation of primary aniline derivatives with pentanediols [17]. *N*-heterocyclic carbene ligands including chelating ones [18–20] were also used with success. The same strategy was applied to ruthenium catalysts and tridentate nitrogen ligands, (N,N,N) and (P,N,P) pincer ligands were introduced to ruthenium(II) centers but the catalytic *N*-alkylation of aniline still required high temperature [21]. Tridentate (N,N,C) [22] and tetradentate (N,N,N,N) [23] ligands provided efficient catalysts able to operate at 100–110 °C in the presence of a base. More simple ruthenium precursors such as $[Ru(Cl_2(cod)]_n$/1,3,5-triaza-7-phosphaadamantane (PTA), [24] $[RuCl(PPh_3)(MeCN)_3][BPh_4]$ [25] or the in situ generated system based on $[RuCl_2(p\text{-cymene})]_2$ and diphosphine ligand were found efficient for the *N*-alkylation of aniline with catalytic amounts of base [26]. However, only scarce examples of ruthenium complexes bearing a *N*-heterocyclic carbene ligand have been investigated in *N*-alkylation of aromatic amines by alcohols [27]. To our knowledge, $RuX_2(NHC)(p\text{-cymene})$ (X = Cl, I) complexes have revealed good catalytic activity in the reaction of primary aliphatic amines with primary alcohols to form amides but no *N*-alkylation products were formed [28]. Based on the ability of the basic sulfonate group to transfer protons and generate water-soluble species [29], we decided to prepare new *N*-heterocyclic carbene sulfonate ligands constructed on the benzimidazole core and evaluate their activity

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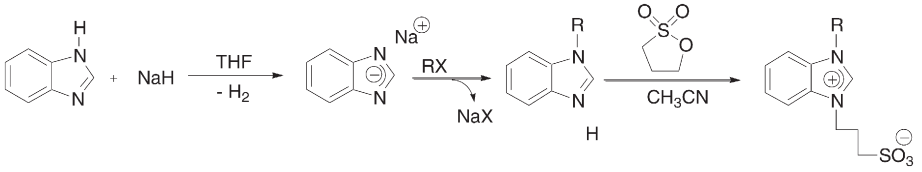


Scheme 1. Synthesis of benzimidazolium sulfonate salts **L1**–**L10.**

in the *N*-alkylation of aniline and 2-aminopyridine in the presence of ruthenium catalysts.

2. Experimental

2.1. Preparation of benzimidazolium sulfonates

The zwitterionic carbene precursors **L1**–**L10** were obtained in a three step procedure according to Scheme 1. The *N*-alkyl or *N*-benzyl benzimidazole was first prepared by deprotonation of benzimidazole by NaH in THF at room temperature for 1 h. The resulting sodium benzimidazolate was reacted with the appropriate alkyl or benzyl halide in refluxing THF during 24 h. The resulting *N*-alkyl or *N*-benzyl-benzimidazole was isolated and purified as a white solid. 1-Substituted benzimidazole and 1,3-propanesultone were then dissolved in acetonitrile and refluxed during 72 h. The benzimidazole sulfonate salts **L1**–**L10** were isolated as solids in good to excellent yields.

2.2. Catalytic reactions

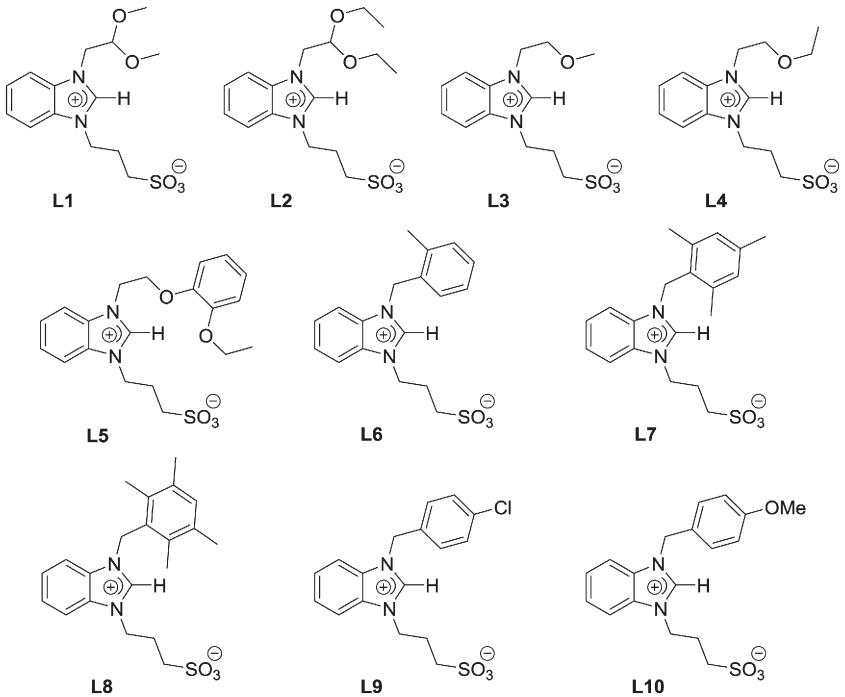
The alcohol derivative (1.6 mmol) was added to a stirred solution of aromatic amine (1 mmol) in a Schlenk tube. Subsequently, ^{t}BuOK (1 mmol), the preligand (**L**) (1 mol%) and $[RuCl_2(p\text{-cymene})]_2$ (0.5 mol%) were added and the sealed Schlenk tube was stirred at 120 °C for 24 h. The crude mixture was collected by the addition of CH_2Cl_2 (2 ml) for GC analysis, and the product was then purified by column chromatography (petroleum ether/Et_2O or EtOAc) to afford the pure secondary amine.

3. Results and discussion

3.1. Preparation of benzimidazolium sulfonate salts

A library of 10 benzimidazolium sulfonate salts **L1**–**L10** has been prepared (Scheme 2). Each of them is equipped with a 1-*n*-propylsulfonate group linked to one nitrogen atom. The other nitrogen atom is substituted either by an aliphatic ether or an acetal functionality, or a benzylic group diversely substituted on the phenyl ring. The acetal groups are in principle stable in basic conditions and the oxygen atoms might be useful for hydrogen bonding or transfer. As far as the phenyl groups are concerned it has been previously shown that they can easily substitute a coordinated *p*-cymene ligand on a ruthenium(II) center upon thermal treatment [30].

L1–**L10** are soluble in water and protic solvents; they were characterized by ^{1}H and ^{13}C NMR, and gave satisfactory elemental analysis. The benzimidazolium fragment showed characteristic C(2)–*H* proton chemical shift at 8.86–9.64 ppm associated to the ^{13}C NMR chemical shift of the C(2) carbon atom deshielded at 140–150 ppm (Table A.1). These chemical shifts are typical of all types of benzimidazolium salts including less functionalized ones. The ^{1}H NMR spectra of the linear *n*-propylsulfonate group are clearly identified by a triplet at 4.5–4.8 ppm for NCH_2, another triplet at 2.8–3.0 ppm for CH_2SO_3, and a



Scheme 2. Library of benzimidazolium sulfonates.