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Metal triflates combined with caffeine based imidazolium salts: A new family of highly efficient and reusable catalysts

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Abstract

The direct alkylation of caffeine (**1**), by ethyl triflate gave 1,3,7-trimethyl-9-ethylxanthinium triflate (**2**) which led to 1,3,7-trimethyl-9-ethylxanthinium bis(trifluoromethanesulfonyl)amide (**3**) after methathesis with $LiNTf_2$; **3** proved to be an ionic solid which can be used for the recovery of metal triflates ($M(OTf)_n$ with M = Sc, La, Yb, Cu, Hf, Bi). These reusable catalysts proved to be efficient Lewis acids for Diels–Alder reactions leading to very little or no polymerisation of the diene. In the case of bismuth (III) triflate, the catalyst can be recovered and reused at least 10 times without loss of activity.

Keywords: Imidazolium salts; Metal triflates; Catalysis; Diels–Alder reaction; Caffeine

1. Introduction

The catalyst separation from products is a key problem within the development of a sustainable commercial process. It is of great interest to recover and reuse costly and/or toxic catalysts for economical and environmental reasons as well as to reduce the amounts of catalysts or its components in many products in order to respect defined specifications [1].

The use of bio-available, cheap and non-toxic sources of compounds is highly desirable for the design of any green synthesis or process. Caffeine (**1**) is a natural product which can be found in more than 60 plant species whose biosynthesis results from the purine nucleotide pool [2]. Our approach was based on caffeine (**1**), a cheap source of *N*-methyl imidazole resulting from the decaffeination of coffee. Use of caffeine has been recently reported for the synthesis and structural characterization of *N*-heterocyclic carbenes [3,4] but, to our knowledge, caffeine has not yet been used in the preparation of reusable catalysts. Alkyl triflates are commercially available compounds known for their high alkylating power [5,6]. Moreover, the replacement by anion exchange of triflate by bis-trifluoromethanesulfonyl amide anion (Tf_2N^-) is known to confer hydrophobicity and a lower melting point [7]. We now wish to report our first results related to the synthesis and the uses of 1,3,7-trimethyl-9-ethylxanthinium bis(trifluoromethanesulfonyl)amide (**3**).

2. Experimental

2.1. Preparation of 1,3,7-trimethyl-9-ethylxanthinium triflate (2)

Into a 250 mL round bottomed flask was placed **1** (4.54 g, 23.4 mmol) in 60 mL of anhydrous nitrobenzene. The suspension was heated to 100 °C in an oil bath for 15 min until all **1** dissolved. Then, ethyl triflate (5.0 g,

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28.07 mmol) was added via syringe as one portion and the solution was stirred for 16 h. After this time, the cooled brown solution was subjected to reduced pressure distillation to remove nitrobenzene and unreacted EtOTf (the distillate can be kept and reused for another reaction) to give pure **2** as a deep brown viscous oil. ^{1}H NMR (300 MHz, acetone-d_6) δ 1.70 (t, $J = 7.3$ Hz, 3H, Me), 3.34 (s, 3H, Me), 3.89 (s, 3H, Me), 4.22 (s, 3H, Me), 4.79 (q, $J = 7.3$ Hz, 2H, CH_2), 9.23 (s, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 14.9, 27.9, 31.4, 35.6, 45.6, 108.7, 121.0 (q, $J(^{13}C/^{19}F) = 320.9$ Hz), 138.4, 139.6, 150.7, 153.7; ^{19}F NMR (188 MHz, acetone-d_6) δ −79.1.

2.2. Preparation of 1,3,7-trimethyl-9-ethylxanthinium bis(trifluoromethanesulfonyl)amide (3)

To the amount of **2** prepared above was added distilled water (30 mL). Then, under good stirring, a solution of $LiNTf_2$ (6.72 g, 23.4 mmol) in distilled water (10 mL) was gradually added at room temperature to the solution of **2** which led to the instantaneous formation of **3**. Then water (60 mL) was added and after 20 min under stirring, the brown solution was filtered to give **3** (11.66 g, 91% overall yield starting from **1**) as a white solid. Mp: 111–112 °C; IR (compressing cell with diamond windows) 3166, 3102, 2963, 1724, 1678, 1633, 1582, 1548, 1467, 1417, 1336, 1198, 1139, 1052, 762 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6) δ 1.72 (t, $J = 7.3$ Hz, 3H, Me), 3.35 (s, 3H, Me), 3.90 (s, 3H, Me), 4.24 (s, 3H, Me), 4.81 (q, $J = 7.3$ Hz, 2H, CH_2), 9.19 (s, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 14.9, 27.9, 31.4, 35.7, 45.7, 108.8, 120.0 (q, $J(^{13}C/^{19}F) = 321.3$ Hz), 138.0, 139.5, 150.6, 153.5; ^{19}F NMR (188 MHz, acetone-d_6) δ −79.8; MS/DCI: 521 $[C_{12}H_{15}F_6N_5O_6S_2 + NH_4]^+$, 242 $[C_{10}H_{15}N_4O_2 + NH_4]^+$, 223 $[C_{10}H_{15}N_4O_2]^+$, 280 $[C_2NO_4F_6S_2]^-$; TGA analysis revealed that **3** starts to decompose around 280 °C (TGA plot not shown). X-ray diffraction study carried out on monocrystals of **3** obtained from cold acetone showed the nitrogen in the NTf_2 anion to be located in the center of the imidazolium ring (structure not shown).

2.3. Preparation of the catalytic systems metal triflates/3

For $Bi(OTf)_3 \cdot 4H_2O$/**3** system (1/10 molar ratio): a mixture of **3** (1.062 g, 2.1 mmol) and bismuth(III) triflate (0.153 g. 0.21 mmol) was dissolved in acetone (6 mL); the addition of heptane (18 mL) precipitated the salts which were dried under vacuum. ^{1}H NMR (300 MHz, acetone-d_6) δ 1.68 (t, $J = 7.3$ Hz, 3H, Me), 3.22 (s, 3H, Me), 3.87 (s, 3H, Me), 4.21 (s, 3H, Me), 4.77 (q, $J = 7.3$ Hz, 2H, CH_2), 9.17 (s, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 16.3, 29.3, 32.8, 37.1, 47.1, 110.2, 121.4 (q, $J(^{13}C/^{19}F) = 321.3$ Hz, $N(SO_2CF_3)_2$), 121.9 (q, $J(^{13}C/^{19}F) = 320.0$ Hz, OSO_2CF_3), 139.5, 140.9, 155.0, 155.3; ^{19}F NMR (188 MHz, acetone-d_6) δ −79.8 (s; $N(SO_2CF_3)_2$), −79.0 (s, OSO_2CF_3), the ratio between these two signal was respectively 6.7:1.

2.4. Typical procedure for Diels–Alder reaction

Into a 50 mL flask at room temperature were successively added the system $Bi(OTf)_3 \cdot 4H_2O$/**3** (0.256 g, which corresponds to 0.044 mmol of $Bi(OTf)_3 \cdot 4H_2O$) and dichloromethane (4.5 mL). Then, with magnetic stirring, ethyl vinyl ketone (0.363 g, 4.4 mmol) and 2,3-dimethylbuta-1,3-diene (0.363 g, 4.4 mmol) were added and the mixture was stirred for 3 h. After this time of reaction heptane was added (9 mL). The suspension was filtered and the filtrate was concentrated under vaccum to afford 1-(3,4-dimethylcyclohex-3-enyl)propan-1-one (0.722 g, 99% yield) as a pale yellow liquid characterized by NMR and GC/MS [8].

The analytical data for other Diels–Alder adducts were in agreement with those reported in the literature: Table 3, entries 1 [9], 2 [8], 3 [10], 4 [11], 5 [8], 6 [10]; for entry 7, Mp: 51 °C; IR (compressing cell with diamond windows) 3141, 2978, 2920, 2856, 1710, 1567, 1456, 1424, 1381, 1114, 1018, 809 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (t, $J = 7.3$ Hz, 3H), 2.47 (q, $J = 7.3$ Hz, 2H), 2.73 (m, 2H), 2.87 (m, 2H), 5.86 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.8, 22.3, 36.0, 40.5, 105.6, 153.1, 210.1; MS (EI) *m/z* 236 $[C_{14}H_{20}O_3]^+$, 165, 107, 57.

2.5. Reusability of the catalyst

At the end of the reaction $Bi(OTf)_3 \cdot 4H_2O$/**3** was recovered by simple filtration and washed with a 1:2 CH_2Cl_2:heptane solution (15 mL). The recovered $Bi(OTf)_3 \cdot 4H_2O$/**3** (0.254 g, 99.2%) was used for subsequent experiments.

3. Results and discussion

The synthesis of **3** started by the direct alkylation of **1** by EtOTf which was quantitatively carried out in nitrobenzene, as previously reported for other such type of reactions [4] (see Scheme 1). After removal of the solvent under reduced pressure, a viscous brown oil of 1,3,7-trimethyl-9-ethylxanthinium triflate (**2**) was obtained which was dissolved in pure water. The addition of $LiNTf_2$, a salt developed for lithium batteries [12], to this solution led instantaneously to the quantitative precipitation of **3** as a white powder in not optimized 91% overall yield starting from **1**.

We then decided to study the catalytic efficiency of **3** in Diels–Alder reactions since other catalysts such as $LiNTf_2$ in acetone [13] or $Sc(OTf)_3$ in [BMIM][PF_6] [14] proved to be active for this reaction. For this study we chose the reaction of 1,3-dimethylbutadiene with ethyl vinyl ketone as a model reaction since these two compounds do not react spontaneously without any catalyst. Our results are summarized in Table 1.

While under our conditions **3** proved to be inactive (Table 1, entries 1 and 8), metal triflates (1% towards the reactants) combined with **3** (see Sections 2.3 and