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Communication

One-pot synthesis of α-aminonitriles using a highly efficient and recyclable silica-based scandium (III) interphase catalyst

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ABSTRACT

Both aryl and alkyl imines, which formed in situ from aldehydes and amines undergo smooth nucleophilic addition with trimethylsilyl cyanide in the presence of a catalytic amount of a silica-based scandium (III) interphase catalyst under mild reaction condition to furnish the corresponding α-aminonitriles in good to excellent yields. The catalyst shows high thermal stability (up to 300 °C) and it could also be recovered and reused for at least 6 reaction cycles without considerable lose of its reactivity.

1. Introduction

α-Aminonitriles are very important intermediate, particularly in the preparation of α-aminoacids [1], nitrogen containing heterocycles [2,3], and other biologically active molecules. There are many reported protocols in the literature for the preparation of α-aminonitriles [4–13], among them the classical Strecker reaction represents one of the simplest and most economical method for this purpose through a nucleophilic addition of cyanide anion to imines [14]. Moreover, enantioselective Strecker reaction is one of the prominent tool for the synthesis of enantiomerically pure α-aminoacids and their analogs [15]. Although, a variety of cyanating agents and methods such as alkaline cyanides [14,16], diethylphosphoro cyanidate [17] Bu_3SnCN [18], and Et_2AlCN [19] have been used to carry out the Strecker reaction, it has been shown that trimethylsilyl cyanide (TMSCN) is a very effective, relatively safe and easy-to-handle cyanide source for this purpose [20–28]. However, most of the existing TMSCN-based protocols involve the use of expensive or unrecoverable catalyst, harsh acidic conditions, and tedious work-up procedure leading to copious amount of toxic wastes. Therefore, it seems that there is still much room to develop new improved and recyclable catalyst for this transformation, which works under economically appropriate conditions. Interest in scandium has increased recently due to the successful application of its compounds in organic chemistry [29,30]. Along this line, scandium triflate has been introduced as a promising mild, powerful and selective Lewis acid for a variety of functional group transformations [31–34]. While most of Lewis acids are decomposed or deactivated in the presence of water or protic solvents, $Sc(OTf)_3$ is quite stable in aqueous work-up conditions and its recovery is often possible [35]. However, the most popular recycling methods for recovery of $Sc(OTf)_3$ are time consuming and include the successive extraction of organic reaction mixture using deionized water [31–35]. Therefore, there is a need for the design and preparation of new version of scandium-based catalysts to circumvent this problem without considerable loss of its catalytic power. One way to attain this goal is to immobilize one or more components of the catalytic systems onto a large surface area solid carrier to create new *organic–inorganic hybrid* (interphase) catalysts [36,37]. An interphase is defined as a *region* within a material in which a stationary (organic–inorganic hybrid catalyst) and mobile component (solvent and reactants) penetrate each other on a molecular level. In these types of solid catalysts the reactive center is highly mobile similar to homogeneous catalysts and at the same time it has the advantage of recyclability. Recently, Kobayashi and his co-workers have prepared a new styrene-based hydrophobic polymer supported scandium triflate to combine the advantage of both homogeneous and heterogeneous catalysts in a number of carbon–carbon bond forming reactions in water [38]. While, this work can be considered as the first example of heterogeneous scandium, however, the polymer backbone in this catalyst is very expensive and the catalyst loading and its durability are not yet satisfactory. Therefore, it seems that there is still much room for design and preparation of new recoverable and efficient scandium-based catalysts which work under mild and more appropriate conditions.

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2. Experimental

General remarks: Chemicals were either prepared in our laboratories or purchased from Merck, Fluka and Aldrich Chemical Companies. All yields refer to isolated products unless otherwise stated. The products were characterized by comparison of their physical data with those of known samples or by their spectral data. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 500 MHz spectrometer in $CDCl_3$ as the solvent and TMS as internal standard. Most of the products are known and all of the isolated products gave satisfactory IR and NMR spectra.

2.1. Preparation of aminopropyl silica (AMPS)

Mesoporous silica gel (average pore diameter 60 Å) was activated by refluxing in concentrated hydrochloric acid (6 M) for 24 h and then washed throughly with the deionized water and dried before undergoing chemical surface modification. The activated silica gel (10 g) was refluxed with 3-aminopropyltrimethoxysilane in dry toluene for 18 h. The solid materials were filtered off and washed with hot toluene for 12 h in a continuous extraction apparatus (Soxhelet) and then dried in oven at 110 °C overnight to give the surface bound amine (AMPS) group at a loading *c.a.* 0.30–0.31 mmol g^{-1} (by elemental analysis and back titration).

2.2. Preparation of surface bound bidentate ligand **1**

The resulting AMPS were subject to react with and equimolar of 2-hydroxybenzaldehyde in absolute EtOH for 18 h. The solid was filtered off and was washed throughly with absolute ethanol. The solvent was evaporated and dried over Mg for another application. The resulting deep yellow solid was allowed to react with an excess $NaBH_3CN$ (5-fold excess, 1.5 mmol/g of solid) in super dry MeOH for 72 h. The resulting material was filtered off and was washed with hot dry MeOH for 18 h in a continuous extraction apparatus (Soxhelet) and then dried in oven at 120 °C overnight to furnished the corresponding surface bound bidentate ligand **1** at a loading *c.a.* 0.30 mmol g^{-1} (determined by TGA analysis). The methanol was recovered and dried using Mg techniques for another application.

2.3. Preparation of silica-based scandium interphase catalyst **2**

To a solution of an equimolar $Sc(OTf)_3$ (1.5 mmol) in dry CH_3CN (150 mL), the solid **1** was added in one portion and the resulting pale yellow slurry was stirred vigorously for 18 h. The solvent was evaporated and the solid was washed continuously with large volume of CH_3CN (700 mL). The solvent was evaporated and reused for another application. The solid pale yellow solid was dried in an oven at 120 °C overnight to furnish the corresponding catalyst **2** at a loading *c.a.* 0.30 mmol g^{-1} (Determined by TGA analysis and atomic absorption spectroscopy (AA).

2.4. General procedure for the three-component Strecker reaction

To a solution of aldehyde (2 mmol) and amine (2 mmol) in CH_2Cl_2 (4 mL), catalyst **2** (167–200 mg, 5–6 mol% of Sc) was added and the resulting mixture was stirred at room temperature for 0.5 h. To this mixture, TMSCN (2.4 mmol) was added drop-wise while stirring was continued and the progress of the reaction was monitored by TLC. After completion, the mixture was filtered and the catalyst rinsed two times with a fresh aliquot of CH_2Cl_2 (2×15 mL). The organic filtrate was dried over anhydrous Na_2SO_4 and evaporation of the solvent under reduced pressure gave almost pure product. Further purification was achieved by flash column chromatography on silica gel or recrystallization from an appropriate solvent to give the desired product(s) in good to excellent yield(s) (Table 1).

All the compounds embodied in Table 1 as isolated products were characterized by IR, ^{1}H and ^{13}C NMR. Spectral data for selected compounds are as follows:

2.4.1. 2-(N-anilino)-2-phenyl acetonitrile

IR (KBr): *v* 3336, 3028, 2941, 2237, 1598, 1507, 1444, 1281, 1241, 924, 880, 753 cm^{-1}; ^{1}H NMR (500 MHz; $CDCl_3$; TMS): δ_H = 7.58–7.60 (m, 2H), 7.41–7.47 (m, 3H), 7.25–7.28 (t, *J* = 7.7 Hz, 2H), 6.88–6.91 (t, *J* = 7.4 Hz), 6.76–6.78 (d, *J* = 7.7 Hz, 2H), 5.42 (s, 1H), 4.10 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ_C = 144.60, 133.93, 129.58, 129.55, 129.34, 127.28, 120.38, 118.16, 114.27, 50.28.

2.4.2. 2-(N-anilino)-2-(4-isopropylphenyl) acetonitrile

IR (KBr): *v* 3375, 3025, 2960, 2899, 2238, 1602, 1515, 1414, 1275, 920, 815, 746 cm^{-1}, ^{1}H NMR (500 MHz; $CDCl_3$; TMS): δ_H = 7.47–7.49 (d, *J* = 8.0 Hz, 2H), 7.28–7.28 (d, *J* = 8.0 Hz, 2H), 7.23–7.28 (t, *J* = 8.0 Hz, 2H), 6.85–6.88 (t, *J* = 7.3 Hz, 1H), 6.73–6.75 (d, *J* = 8.0 Hz, 2H), 5.35 (s, 1H), 4.05 (bs, 1H), 2.90–2.96 (septet, *J* = 6.9 Hz, 1H), 1.25–1.26 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ_C = 150.46, 144.79, 131.33, 129.52, 127.36, 127.29, 120.11, 118.38, 114.10, 49.94, 33.87, 23.86.

2.4.3. 2-(N-anilino)-2-(2-naphthyl) acetonitrile

IR (KBr): *v* 3323, 3061, 3026, 2928, 1600, 1511, 1254, 922, 780 cm^{-1}; ^{1}H NMR (500 MHz; $CDCl_3$; TMS): δ_H = 8.11 (s, 1H), 7.86–7.91 (m, 3H), 7.58–7.61 (dd, *J* = 8.5 Hz, *J* = 1.6 Hz, 1H), 7.53–7.56 (m, 2H), 7.25–7.29 (dt, *J* = 8.5 Hz, *J* = 0.8 Hz, 2H), 6.89–6.92 (t, *J* = 7.5 Hz, 1H), 6.79–6.81 (d, *J* = 8.5 Hz, 2H), 5.56 (s, 1H), 3.90 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ_C = 144.63, 133.52, 133.12, 131.14, 129.61, 129.42, 128.24, 127.79, 127.17, 126.99, 126.65, 124.40, 120.44, 118.20, 114.33, 50.43.

2.4.4. 2-(N-anilino)-2-(4-methoxyphenyl) acetonitrile

IR (KBr): *v* 3345, 3027, 2926, 2239, 1598, 1503, 1292,1120, 1050, 915, 760 cm^{-1}; ^{1}H NMR (500 MHz; $CDCl_3$; TMS): δ_H = 7.47–7.49 (d, *J* = 8.3 Hz, 2H), 7.24–7.27 (t, *J* = 7.6 Hz, 2H), 6.93–6.95 (d, *J* = 8.3 Hz, 2H), 6.87–6.90 (t, *J* = 7.6 Hz, 1H), 6.75–6.76 (d, *J* = 7.6 Hz, 2H), 5.34 (s, 1H), 4.00 (bs, 1H), 3.81 (s, 3H); ^{13}C NMR

Table 1
Synthesis of α-aminonitriles using a three-component procedure catalyzed by Silica-based scandium (III) interphase catalyst **2**

Entry	R^1	R^2	Time (h)	Yield%[a]
1[b]	C_6H_5	C_6H_5	24	0
2	C_6H_5	C_6H_5	14	94
3	4-*i*-Pr–C_6H_4	C_6H_5	14	92
4	3-MeO–C_6H_4	C_6H_5	14	94
5	4-MeO–C_6H_4	C_6H_5	14	88
5	4-Cl–C_6H_4	C_6H_5	14	91
6	3-Cl–C_6H_4	C_6H_5	14	93
7	3-Me–C_6H_4	C_6H_5	14	92
8	2-Me–C_6H_4	C_6H_5	14	91
9	2-Naphthyl	C_6H_5	14	86
10	2-Thienyl	C_6H_5	14	95
11	C_6H_5	4-Br–C_6H_4	14	92
12[c]	C_6H_5	$C_6H_5CH_2CH_2CH_2$	14	>99
13[c]	4-MeO-C_6H_4	$C_6H_5CH_2CH_2CH_2$	14	74
14[c]	4-Cl-C_6H_4	$C_6H_5CH_2CH_2CH_2$	14	93
15[c]	$CH_3(CH_2)_4CH_2$	$C_6H_5CH_2CH_2CH_2$	14	>99
16[c]	2-Furyl	$C_6H_5CH_2CH_2CH_2$	14	93
17[d]	Ph	Morpholine	14	97[d]

[a] Isolated yields unless otherwise stated.
[b] The reaction was conducted in the absence of catalyst **2**.
[c] Conversion based on NMR, the products were not isolated.
[d] The major product was the corresponding cyanohydrin trimethylsilyl ether.

(125 MHz, $CDCl_3$, 25 °C, TMS): δ_C = 160.44, 144.68, 129.55, 128.63, 125.94, 120.22, 118.42, 114.21, 114.21, 55.42, 49.70.

2.4.5. 2-(N-anilino)-2-(3-chlorophenyl) acetonitrile

IR (KBr): ν 3356, 3104, 3053, 2901, 2223, 1601, 1500, 1259, 884, 827, 750 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$; TMS): δ_H = 7.60 (s, 1H), 7.48–7.49 (d, J = 7.4 Hz, 1H), 7.36–7.41 (m, 2H), 7.25–7.28 (t, J = 8.0 Hz, 2H), 6.89–6.92 (t, J = 7.4 Hz, 1H), 6.74–6.76 (d, J = 8.0 Hz, 2H), 5.40 (s, 1H), 4.10 (sb, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ_C = 144.33, 135.86, 135.31, 130.58, 129.76, 129.62, 127.42, 125.33, 120.63, 117.67, 114.37, 49.74.

2.4.6. 2-(N-anilino)-2-(4-chlorophenyl) acetonitrile

IR (KBr): ν 3299, 3099, 3023, 2948, 2241, 1599, 1490, 1308, 1273, 1240, 890, 755 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$; TMS): δ_H = 7.52–7.53 (d, J = 7.6 Hz, 2H), 7.41–7.43 (d, J = 7.6 Hz, 2H), 7.24–7.28 (t, J = 7.4 Hz, 2H), 6.92–6.89 (t, J = 7.4 Hz, 1H), 6.74–6.76 (d, J = 7.4 Hz, 2H), 5.40 (s, 1H), 4.05 (sb, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ_C = 144.38, 135.59, 132.45, 129.61, 129.52, 128.59, 120.58, 117.84, 114.36, 49.66.

2.4.7. 2-(N-anilino)-2-(2-methylphenyl) acetonitrile

IR (KBr): ν 3346, 3025, 2924, 2234, 1598, 1509, 1443, 1282, 1242, 918, 878, 756 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$; TMS): δ_H = 7.36–7.40 (m, 2H), 7.31–7.34 (t, J = 7.5 Hz, 1H), 7.22–7.28 (m, 3H), 6.87–6.90 (t, J = 7.5 Hz, 1H), 6.75–6.77 (d, J = 7.5 Hz, 2H), 5.36 (s, 1H), 3.99 (sb, 1H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ_C = 144.72, 139.31, 133.88, 130.27, 129.56, 129.21, 127.90, 124.33, 120.24, 118.31, 114.16, 50.22, 21.38.

2.4.8. 2-(N-anilino)-2-(3-methoxyphenyl) acetonitrile

IR (KBr): ν 3352, 3089, 3065, 3028, 2934, 2225, 1595, 1093, 1016, 918, 820, 742 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$; TMS): δ_H = 7.31–7.34 (t, J = 8.0 Hz, 1H), 7.22–7.26 (t, J = 8.0 Hz, 2H), 7.14–7.15 (d, J = 8.0 Hz, 1H), 7.09 (s, 1H), 6.92–6.94 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 6.86–6.89 (t, J = 8.0 Hz, 1H), 6.73–6.74 (d, J = 8.0 Hz, 2H), 5.35 (s, 1H), 4.10 (sb, 1H), 3.78 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ_C = 160.22, 144.68, 135.39, 130.38, 129.52, 120.19, 119.32, 118.22, 115.08, 114.16, 112.74, 55.38, 50.09.

2.4.9. 2-(N-anilino)-2-(3-methylphenyl) acetonitrile

IR (KBr): ν 3351, 3049, 2923, 2231, 1598, 1271, 935, 753 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$; TMS): δ_H = 7.68–7.70 (d, J = 7.4 Hz, 1H), 7.22–7.36 (m, 5H), 6.88–6.91 (t, J = 7.4 Hz, 1H), 6.76–6.78 (d, J = 7.4 Hz, 2H), 5.46 (s, 1H), 3.84 (sb, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ_C = 144.84, 136.48, 132.08, 131.33, 129.75, 129.62, 127.57, 126.93, 120.16, 118.38, 113.88, 48.09, 18.66.

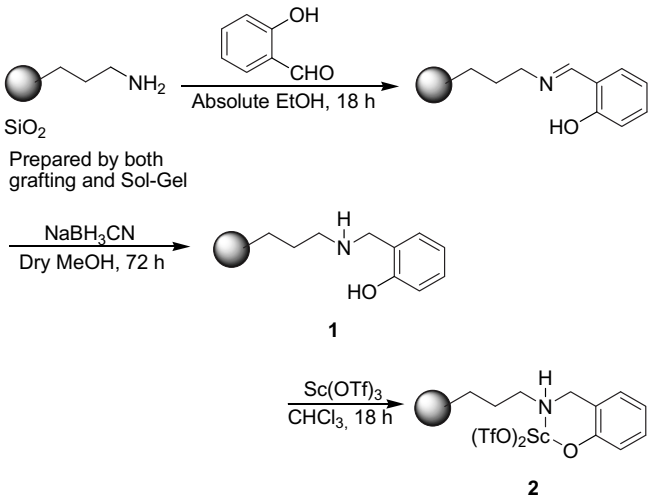
2.4.10. 2-(4-Bromophenylamino)-2-phenylacetonitrile

IR (KBr): ν 3320, 3061, 3028, 2933, 2230, 1599, 1273, 918, 748 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$; TMS): δ_H = 7.52–7.53 (d, J = 4.0 Hz, 2H), 7.42–7.43 (d, J = 4.0 Hz, 3H), 7.30–7.32 (d, J = 8.4 Hz, 2H), 6.60–6.62 (d, J = 8.4 Hz, 2H), 5.34 (s, 1H), 4.16 (sb, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ_C = 143.64, 133.40, 132.27, 129.62, 129.36, 127.15, 117.89, 115.77, 112.16, 50.04.

3. Results and discussion

Very recently, we addressed this issue by designing and preparing of a novel silica-based scandium (III) interphase catalyst (catalyst **2**, Scheme 1) [39].

Quantitative determination of the functional group contents of the surface bound compound **1** was performed with thermogravimetric analysis/differential thermal analysis (TGA/DTA). Typically,

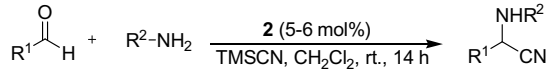


Scheme 1. Preparation of silica-based scandium (III) interphase catalyst **2**.

a loading at *c.a.* 0.3 mmol g^{-1} was obtained [40]. Similarly, TGA/DTA analyses of immobilized scandium **2** were performed and shows a first peak due to the desorption of water (centered at 110 °C). This is followed by a second peak at 375 °C, corresponding to the loss of triflate groups accompanied by a third peak centered at 535 °C, which corresponds to the loss of the surface bound bidentate ligand. Typical loading of scandium was determined using atomic spectroscopy (AA) and shows a loading 0.29 ± 0.01 mmol g^{-1}. This result in combination with TGA analyses demonstrates that **2** corresponds to a 1:1 and 2:1 complex between surface bound and triflate ligands with scandium, respectively (Scheme 1) [40]. We have also demonstrated that **2** is an efficient heterogeneous catalyst for cyanosilylation of carbonyl compounds and could be easily recovered and reused for at least ten reaction cycles without significant loss of its reactivity [39].

In continuation of our investigations into the development of new efficient and recyclable solid-based catalyst for functional group transformations [41–51], herein, we wish to present that catalyst **2** (5–6 mol% equivalent to Sc) is a highly powerful catalyst for the three-component Strecker synthesis of α-aminonitrilesin in excellent yields at ambient temperature and in the absence of any chemical dehydrating agent (Scheme 2).

First, we examined the Strecker reaction of benzaldehyde with aniline and TMSCN (1.2 equiv.) in the absence of **2**. In this case, the reaction did not proceed even after 24 h (Table 1, entry 1). However, the same reaction in the presence of a catalytic amount of **2** (equivalent to 5 mol% Sc) smoothly afforded the corresponding 2-(*N*-anilino)-2-phenyl acetonitrile in 94% isolated yield (Table 1, entry 2) [19]. Similarly, various types of structurally diverse aromatic aldehydes with either electron-withdrawing or electron-donating groups were converted to the corresponding α-aminonitriles in good to excellent yields (Table 1, entries 3–10). It is also worth mentioning that using **2** as catalyst various types of aldehydes including aliphatic ones underwent the one-pot three-component Strecker reaction with 3-phenylpropylamine and TMSCN giving the corresponding α-aminonitriles in good to excellent yields (Table 1, entries 11–16). We have also studied a possible one-pot three-component Strecker reaction with aid of secondary amines like morpholine. Interestingly, we found that



Scheme 2. One-pot Strecker reaction of carbonyl compounds using **2**.

under this conditions the major product (97%) is the corresponding cyanohydrin trimethylsilyl ether (Table 1, entry 17).

The lifetime and leaching of active metal species into solution are important issues to consider when heterogeneous catalysts are used, particularly for practical applications of the Strecker reaction. Our preliminary investigations demonstrated that catalyst **2** is very stable to air and moisture. Moreover, in a separate experiment the catalyst was filtered off after ~50% conversion at the reaction temperature. Further treatment of the filtrate under similar reaction condition did not proceed significantly. On the other hand, atomic absorption spectroscopy of the filtrate also confirmed that the Sc content solution was below the detection limit. Therefore, we may conclude that any scandium species that leached into the reaction mixture is not an active homogeneous catalyst and that the observed catalysis is truly heterogeneous in nature.

After the first run, which gave the corresponding 2-(*N*-anilino)-2-phenyl acetonitrile in 94% isolated yield (100% conversion), after recovery, the catalyst rinsed two times with an aliquot of fresh CH_2Cl_2 (2×15 mL), dried, and then was subjected to a second Strecker reaction from which it also gave the Strecker products in 100% conversion (95% isolated yield); the average chemical yield for 6 consecutive runs was 93%, which clearly demonstrates the practical recyclability of **2**.

4. Conclusion

In conclusion, the novel silica-based scandium (III) interphase catalyst **2**, which can be prepared by simple operation from commercially available and relatively cheap starting materials, efficiently catalyzes the three-component Strecker reaction of a variety of aldehydes. The catalyst shows high thermal stability (up to 300 °C) and also is stable in both organic and in the presence of by-produced water during the imine formation stage. It can also be recovered and reused for at least six reaction cycles without considerable loss of reactivity. Owing to the bidentate model of the surface bound ligand in **2**, it might be possible to prepare chiral analogs of **2** using a chiral bidentate ligand. The work on other application of **2** and also preparation of its chiral analogs is currently ongoing in our laboratories.

5. Supplementary material

TGA diagram of and the detailed experimental procedure for the preparation of silica-based scandium (III) interphase catalyst **2,** and ^1H and ^{13}C NMR spectra images for isolated products are available online with the paper in science direct.

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