

# General Synthesis of Alkyl Amines via Borrowing Hydrogen and Reductive Amination

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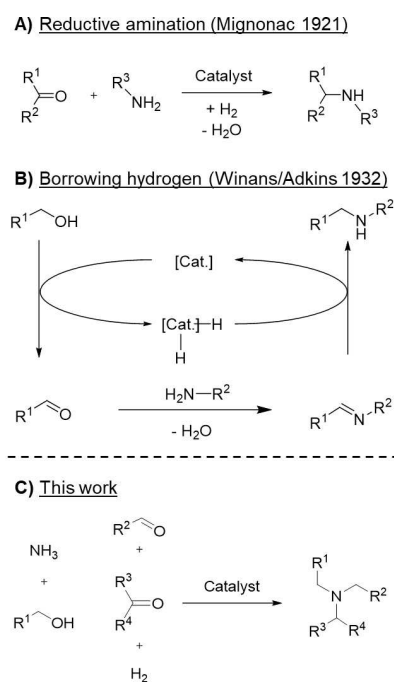
**Abstract:** Amines are a very important class of compounds and the selective synthesis of differently substituted primary, secondary and tertiary alkyl amines is challenging. Here we present the synthesis of primary, secondary, and tertiary alkyl amines from ammonia and alcohols, aldehydes, ketones and hydrogen by combining borrowing hydrogen or hydrogen autotransfer and reductive amination with hydrogen. The key is a nanostructured, bimetallic Co/Sc catalyst able to mediate both reactions or concepts efficiently. We observe a broad product scope, a very good functional group tolerance, upscaling is easily accomplished and our catalyst is reusable.

**Keywords:** amines; borrowing hydrogen; cobalt; reductive amination; scandium

## Introduction

Amines are one of the most important classes of chemical compounds and are present in many bulk and fine chemicals,<sup>[1]</sup> drugs,<sup>[2]</sup> agro chemicals and materials.<sup>[3]</sup> The selective synthesis of differently substituted primary, secondary and tertiary alkyl amines is especially challenging since the alkylated product amine is a better nucleophile and more reactive than the amine or ammonia starting material. Two broadly applied and green or sustainable and selective methods have been developed a century ago namely

the reductive amination<sup>[4]</sup> (Scheme 1A) introduced by Mignonac in 1921<sup>[5]</sup> and the borrowing hydrogen<sup>[6]</sup> or the hydrogen auto-transfer<sup>[7]</sup> (BH HA) concepts<sup>[8]</sup> (Scheme 1B) introduced by Winans and Adkins in 1932.<sup>[9]</sup> Both methods have strengths and weaknesses in comparison to each other. The BH HA approach is highly selective in the first alkylation step while an already alkylated primary or secondary amine is challenging to be modified. The reductive amination is rather unselective in the primary alkylation step if ammonia is employed but selective and efficient regarding the introduction of an already alkylated



**Scheme 1.** Combination of reductive amination employing hydrogen (A) and borrowing hydrogen (B) permits the general synthesis of alkyl amines (C).

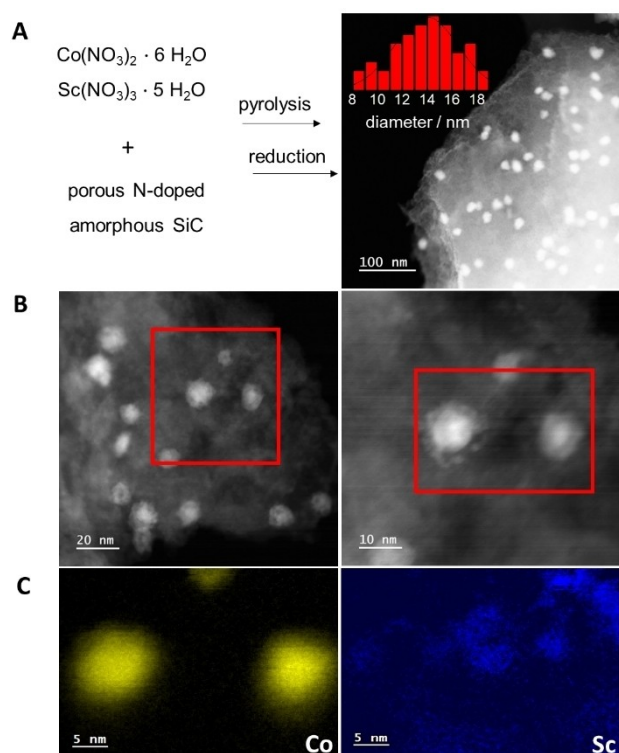
amine. We concluded that a catalyst mediating both reactions would permit to use the one or the other reaction or concept if they are strong and could give rise to a general catalytic access to primary, secondary, and tertiary alkyl amines. We have introduced the first Co<sup>[10]</sup> and Cr<sup>[11]</sup> catalyst for BH HA and highly efficient and selective nanostructured catalysts for the synthesis of primary amines via reductive amination employing hydrogen.<sup>[12,13]</sup> A nanostructured Co catalyst for the synthesis of alkyl amines via BH HA has been introduced by Beller and Jagadeesh and coworkers recently.<sup>[14]</sup> No potential use of that catalyst in reductive amination employing hydrogen has been reported. Furthermore, nanostructured Co catalysts for the general synthesis of primary alkyl amines via reductive amination from carbonyl compounds and ammonia employing hydrogen as the reducing agent have been disclosed.<sup>[13,15]</sup> Here, the potential use as catalysts in BH HA based amine alkylation has not been disclosed. Furthermore, Beller and Jagadeesh and coworkers introduced a general alkyl amine synthesis namely the nickel mediated hydrogenative coupling of nitriles and amines recently.<sup>[16]</sup> We report here on the synthesis of primary, secondary, and tertiary alkyl amines from ammonia and alcohols, aldehydes, and ketones with hydrogen as a reducing agent for the amination step (Scheme 1C). The key is a nanostructured, bimetallic Co/Sc catalyst able to mediate BH HA and reductive amination with hydrogen efficiently. Our catalyst is based on 3d metals with a

high abundance in the earth's crust with Sc being more abundant than Co.<sup>[17]</sup> Our catalyst is easy to synthesize and based on a N-doped and Si-doped porous carbon support developed by us.<sup>[18]</sup> While numerous catalysts that mediate reductive amination employing hydrogen or borrowing hydrogen-based amine alkylation are known, the combination of both approaches seems not been reported yet. We observe a broad product scope, a very good functional group tolerance, upscaling is easily accomplished and our catalyst is reusable.

## Results and Discussion

### Catalyst Synthesis and Characterization

The synthesis of the catalyst support follows an already published procedure, based on the crosslinking of the commercially available polycarbosilane precursor SMP-10 and acrylonitrile applying azobisisobutyronitrile as an initiator.<sup>[13,18]</sup> The resulting greenbody was pyrolyzed at 1000 °C under nitrogen atmosphere (see Supporting Information 2.1). By means of this process a microphase separated, silicon rich NC-material is created. To obtain the final N–SiC support material, an activation step is required. By treatment with 1 M NaOH at 85 °C overnight, a significant percentage of the Si rich domains are washed out and thus creating free C–N–H<sub>x</sub> groups.<sup>[13]</sup> The metal nanoparticles could be introduced via wet impregnation of the N–SiC support and the two metal salts Co(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O and Sc(NO<sub>3</sub>)<sub>3</sub>·5 H<sub>2</sub>O in water, pyrolysis (700 °C, N<sub>2</sub>) and subsequent reduction (550 °C, N<sub>2</sub>/H<sub>2</sub>). The measured metal content, identified via inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis, showed no significant deviation from the theoretical metal content of 2 wt% for Sc and Co. Scanning transmission electron microscopy in combination with high-angle annular dark-field imaging (HAADF-STEM) analysis (Figure 1A and B) revealed homogeneously distributed Co nanoparticles with an average particle size of 13.9 nm. In combination with electron energy loss spectroscopy (EELS, Figure 1C), the STEM analysis could also show that the scandium particles are smaller by orders of magnitude than the cobalt ones with the former finely distributed over the support material. Scanning electron microscopy (SEM) in combination with energy dispersive X-ray spectroscopy (EDX) also confirmed the homogeneously distributed cobalt nanoparticles and revealed, that the remaining silicon, which was not removed from the support material, is allocated in the same way as the scandium particles (see Supporting Information Figure S2). To further explore the nature of our catalyst material, X-ray Photoelectron Spectroscopy (XPS) was performed. The spectra of the support without metal particles (black) and the metal particles on the support (green) are shown in Figure 2. In Figure 2A, a wide



**Figure 1.** Synthesis and characterization of the Co catalyst: (A) Synthesis of the crosslinked material, followed by pyrolysis and NaOH treatment to obtain the support material; wet impregnation, pyrolysis and reduction led to the active Co/Sc catalyst. (B) HAADF-STEM analysis of the nanoparticles combined with STEM-EELS analysis (C) revealed the size difference of cobalt and scandium particles with the latter being significantly smaller and finely distributed over the support material.

scan with the expected signals for both, the support material (Si 2p, N 1s, C 1s, O 1s) and the supported catalyst particles (Si 2p, C 1s, O 1s, Sc 2p, Co 2p) and carbon and oxygen impurities, are shown. Additional ghost signals, originating from Ga  $L\alpha$  radiation and shifted by 155.7 eV, are marked with a “\*”. In Figure 2B, the Co 2p<sub>3/2</sub> region is shown. For the support, as expected, no signals are visible. For the supported Sc/Co catalyst, a broad signal arises at 780 eV. Two binding energies at 780.6 and 786.4 eV for Co oxides and their shake-ups, respectively, are indicated.<sup>[19]</sup> The splitting is characteristic for Co<sub>2</sub>O<sub>3</sub> and/or Co(OH)<sub>2</sub>. Additionally, a third energy at 777.3 eV for metallic Co is indicated.<sup>[17,20]</sup> The binding energies suggest that the surface Co is oxidized. The Sc 2s region is shown in Figure 2C. A single species with a binding energy of 501.1 eV is found, indicating oxidized Sc when considering the literature binding energy for metallic Sc of 499 eV.<sup>[18]</sup> Comparing the corrected signal areas of the Co 2p and the Sc 2s region, the amount of Sc detected by XPS is 10 times higher than that of Co (9.6 : 1.3 at%, Sc : Co), albeit

the same concentration is expected from ICP-OES results. Because of the high surface sensitivity of XPS and additional information from microscopy; we conclude that Sc is finely dispersed on the outer layer, while Co is present as or inside of bigger particles. We assume that the close proximity of the Co and Sc oxide centres are beneficial for the combination of (de)hydrogenation and condensation steps needed in both catalytic reactions - reductive amination and BH HA.

### Optimization of the Reaction Conditions

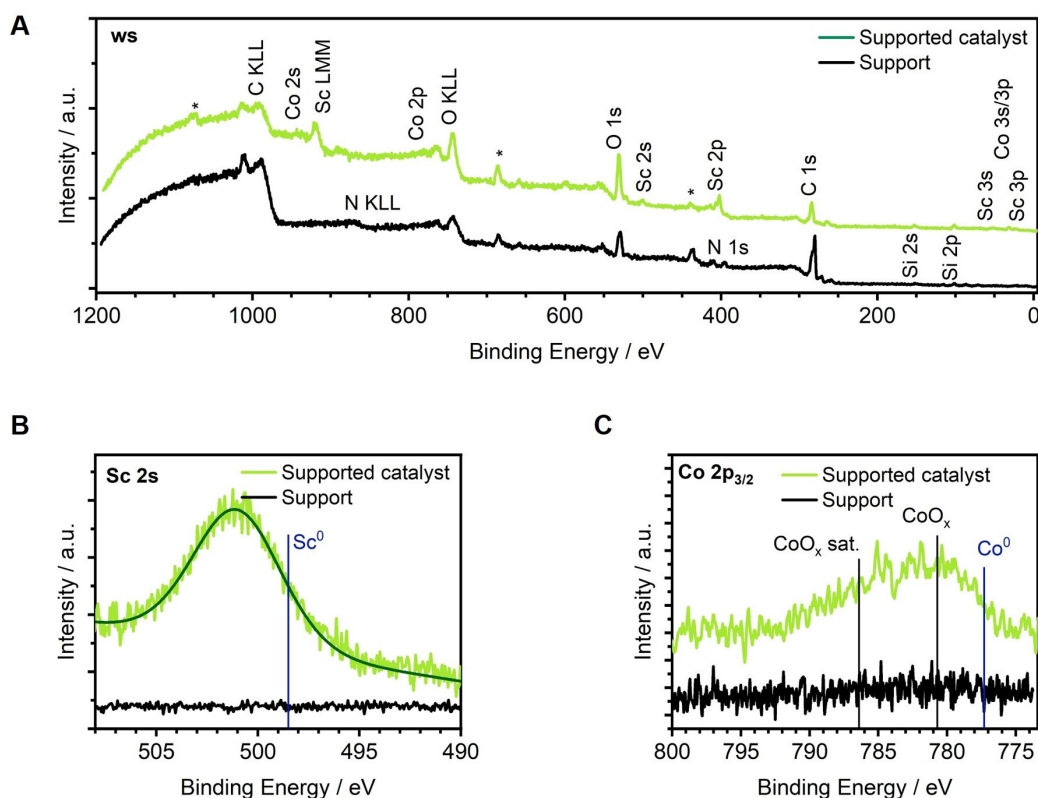
To determine the optimal reaction conditions, the BH HA reaction of benzyl alcohol with gaseous ammonia has been selected as a benchmark for all screenings (see Supporting Information 2.4). The solvent screening revealed that toluene was the most suitable. The toluene amount was set to 2.0 mL since this delivered the maximum yield of benzyl amine. Furthermore, potassium hydroxide in equimolar amounts as well as a temperature of 160 °C were determined. The ammonia pressure was kept at 20 bar. For the comparison to other catalysts, the rare earth metal was varied (Table 1). It could be shown that the selectivity of the catalyst is higher the smaller the used rare earth metal is, which led us to Sc as the most active. Neither Co nor Sc as monometallic catalysts could deliver the

**Table 1.** Catalyst Screening.<sup>[a]</sup>

Entry	Metal(s)	Support	Yield/%
1	Co/La	N-SiC	5
2	Co/Gd	N-SiC	9
3	Co/Lu	N-SiC	54
4	<b>Co/Sc</b>	<b>N-SiC</b>	<b>99</b>
5	Fe/Sc	N-SiC	7
6	Ni/Sc	N-SiC	33
7 <sup>[b]</sup>	Fe	N-SiC	0
8 <sup>[b]</sup>	Ni	N-SiC	12
9 <sup>[b]</sup>	Co	N-SiC	16
10 <sup>[b]</sup>	Sc	N-SiC	32
11	Co/Sc	Activated C	67
12	Co/Sc	Al <sub>2</sub> O <sub>3</sub>	2
13	Co/Sc	TiO <sub>2</sub>	0
14	Co/Sc	SiO <sub>2</sub>	0
15	–	N-SiC	0

<sup>[a]</sup> Reaction conditions: 1.5 mol% Co/Fe/Ni, 0.85 mol% La, 0.74 mol% Gd, 0.66 mol% Lu, 0.49 mol% Sc, pyrolyzed at 700 °C, 0.5 mmol benzyl alcohol, 2.0 mL toluene, 0.5 mmol KOH, 160 °C, 44 h, 20 bar NH<sub>3</sub>. Yields were determined by GC using *n*-dodecane as an internal standard.

<sup>[b]</sup> 1.5 mol% Fe/Ni/Co/Sc.



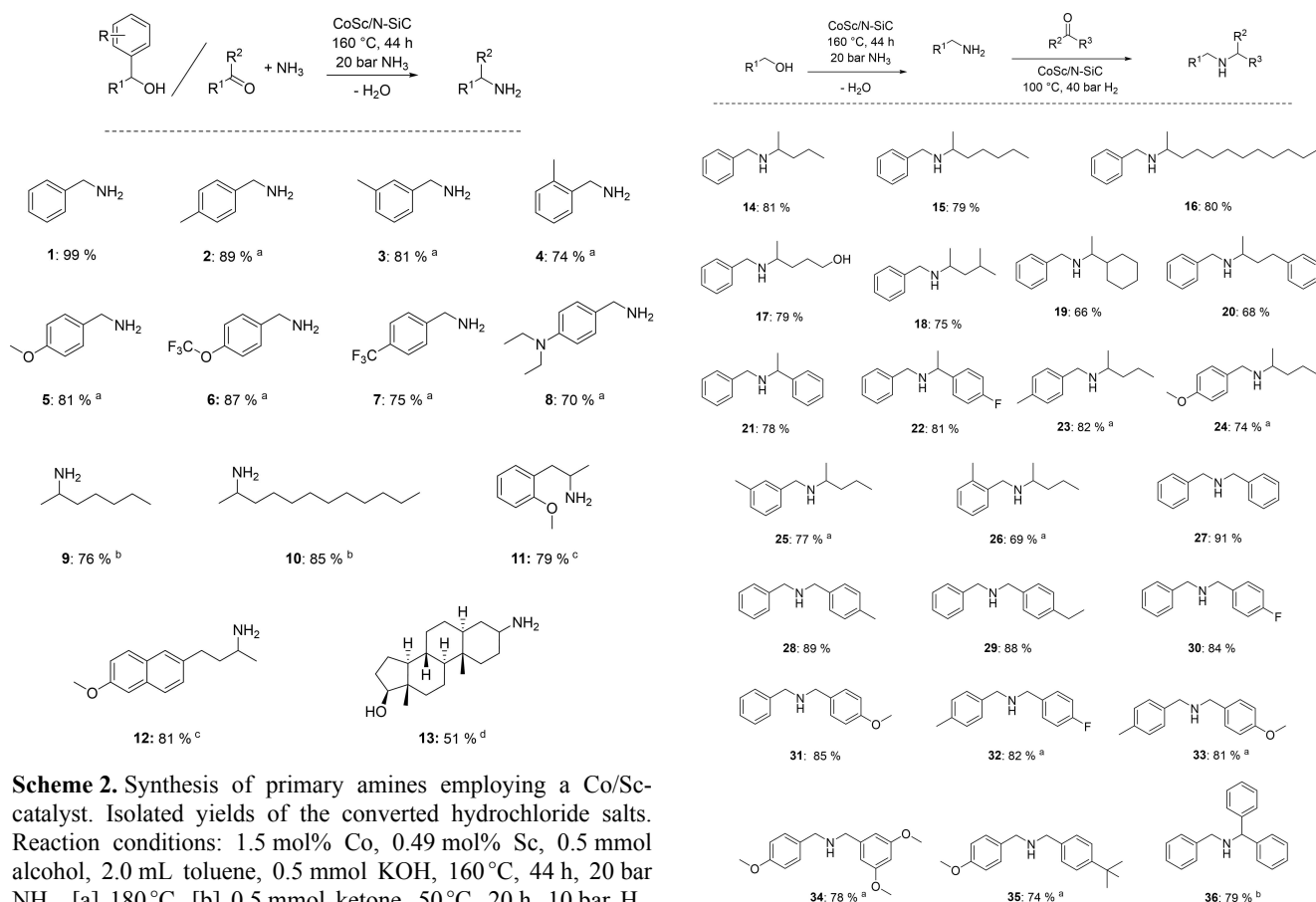
**Figure 2.** XPS spectra: (A) wide scan (ghost peaks from Ga  $L\alpha$  excitation (\*)), (B) Co 2p, (C) Sc 2s.

outstanding activity of the bimetallic material. The variation of the support material revealed that only activated carbon could show a decent activity while  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$  and N–SiC without a metal loading indicated little to no conversion of benzyl alcohol. The superiority of the N–SiC material as a catalyst support is based on its unique structure with free C–N– $\text{H}_x$  functionalities and an Si coating.<sup>[13]</sup>

### Substrate Scope

After the optimized reaction conditions have been determined, we became interested in the applicability of our catalyst system and investigated the substrate scope. The product yields are given for the isolated corresponding hydrochloride salts of the synthesized amines. For better clarity, we split the substrate scope in three parts, one for primary, secondary, and tertiary amines each. First, we wanted to show that the catalyst permits the synthesis of different primary amines (Scheme 2). We discovered that as soon as the aromatic ring of the benzyl alcohol derivate was substituted, we had to raise the reaction temperature from 160 to 180 °C. With that done, several electron donating substituents in various ring positions (products **2–5**) as well as electron withdrawing substituents (**6, 7**) could be tolerated. Unfortunately, there is too

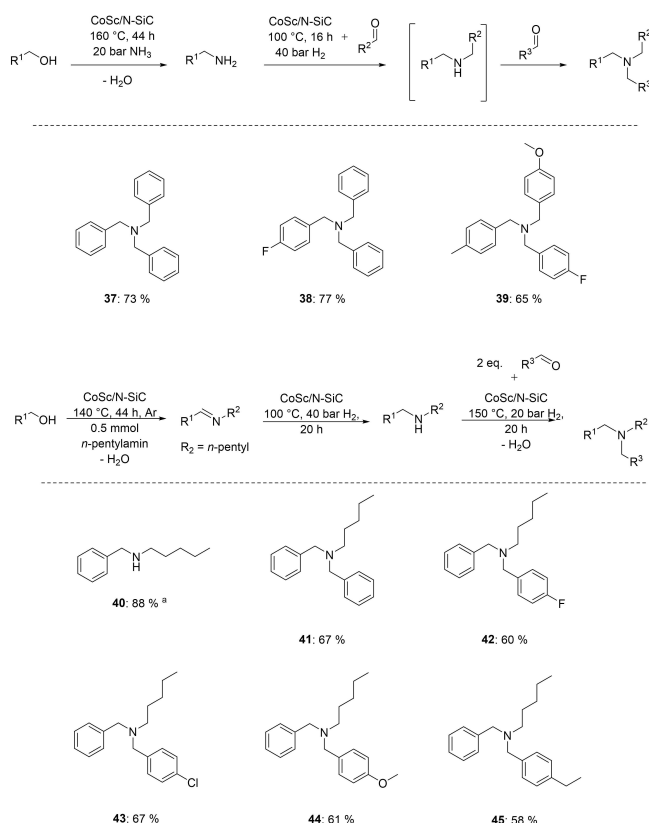
much steric hindrance to the reaction if the  $\text{CF}_3$  group is placed in the ortho position.  $\text{NO}_2$ , CN and  $\text{CONR}_2$  groups were also not tolerated due to numerous side reactions. A second amine function within the alcohol did not pose any problem (**8**). To further show the applicability of our catalyst we synthesized two completely aliphatic amines (products **9** and **10**) from ketones like we did in our previous work with a single metal Co/N–SiC catalyst employed in the reductive amination.<sup>[13]</sup> The conversion of three biologically active molecules (**11–13**) could also be accomplished. As it can be seen, the bimetallic CoSc/N–SiC catalyst could also mediate the reductive amination of these ketones with aqueous ammonia. Next, we explored the synthesis of secondary amines. Since we already showed above that the catalyst can permit the reductive amination of carbonyl compounds, we combined borrowing hydrogen and reductive amination as a consecutive reaction to give rise to more complex amine structures. The same catalyst is reused for the second step and beside neutralization, 0.8 mmol carbonyl compound was added (Scheme 3). The reductive amination part then proceeds at 100 °C and 40 bars of hydrogen pressure. Under these conditions, short, medium and long aliphatic moieties could be introduced (Scheme 3, substrates **14–16**). The presence of a terminal hydroxy group on the carbonyl compound



did not present any difficulties for our catalyst (**17**). Even double branched (**18**) or alicyclic ketones (**19**) could be tolerated in good to median yields. Combining an aliphatic part with a terminal aromatic ring led to substrate **20**. Furthermore, acetophenone and its fluoro-substituted derivative could be employed in the reductive amination step (**21** and **22**). Note that the difficulty to introduce halogenide substituted educts in the borrowing hydrogen step due to dehalogenation under these harsh conditions could thus be compensated. When varying the benzyl alcohol side of the amine (**23–26**), the temperature had to be raised to 180 °C again. Hence, a methyl group in all ring positions as well as a methoxy group could be tolerated. Moving forward, we switched the carbonyl compound of the reductive amination step from ketones to aldehydes. Besides dibenzyl amine (**27**), its methyl- (**28**), ethyl- (**29**), fluoro- (**30**) and methoxy-substituted (**31**) derivatives could be synthesized with very good yields. Varying both sides was also possible at 180 °C for the first step and gave rise to multiple products (**32–35**) with small to more bulkier substituents. Lastly, the addition of benzophenone as an educt

**Scheme 3.** One pot synthesis of secondary amines employing a Co/Sc-catalyst. Isolated yields of the converted hydrochloride salts. Reaction conditions for first step: 1.5 mol% Co, 0.49 mol% Sc, 0.5 mmol alcohol, 2.0 mL toluene, 0.5 mmol KOH, 160 °C, 44 h, 20 bar NH<sub>3</sub>. [a] 180 °C. Reaction conditions for second step: 1.5 mol% Co, 0.49 mol% Sc, 0.8 mmol carbonyl compound, 2.0 mL toluene, 100 °C, 20 h, 40 bar H<sub>2</sub>, 0.05 mL 32% HCl. [b] 150 °C.

could also be accomplished by increasing the temperature of the second step from 100 to 150 °C (**36**). To complete our work, we studied the synthesis of (differently substituted) tertiary amines, which presented a major challenge overall. For the synthesis of tertiary amines with three benzylic alkyl substituents (Scheme 4, upper half), we extended our consecutive synthesis by a third step, which involves the addition of 1.0 mmol of a further aldehyde as well as an increase in temperature to 140 °C. The addition of 0.05 mL concentrated hydrochloric acid was necessary since it supports the tertiary imine formation of the secondary amine with the aldehyde. Utilizing this three-step synthesis protocol we were able to synthesize three tertiary amines with one, two and three different moieties in good to very good yields (**37–39**). Next, we established a workarround approach (Scheme 4, lower half). For the borrowing hydrogen



**Scheme 4.** One pot synthesis of tertiary amines employing a Co/Sc-catalyst. Isolated yields of the converted hydrochloride salts. Substrates 37–39: Reaction conditions for first step: 1.5 mol% Co, 0.49 mol% Sc, 0.5 mmol alcohol, 2.0 mL toluene, 0.5 mmol KOH, 160 °C, 44 h, 20 bar NH<sub>3</sub>. Reaction conditions for second step: 1.5 mol% Co, 0.49 mol% Sc, 0.8 mmol aldehyde, 2.0 mL toluene, 100 °C, 20 h, 40 bar H<sub>2</sub>, 0.05 mL 32% HCl. Reaction conditions for third step: 1.5 mol% Co, 0.49 mol% Sc, 1.0 mmol aldehyde, 2.0 mL toluene, 140 °C, 20 h, 40 bar H<sub>2</sub>, 0.05 mL 32% HCl. Substrates 40–45: Reaction conditions for first step: 2.0 mol% Co, 0.65 mol% Sc, 0.5 mmol alcohol, 0.5 mmol *n*-pentylamine, 2.0 mL toluene, 0.5 mmol KOH, 140 °C, 44 h, Ar atmosphere. Reaction conditions for second step: 2.0 mol% Co, 0.65 mol% Sc, 2.0 mL toluene, 100 °C, 20 h, 40 bar H<sub>2</sub>. Reaction conditions for third step: 2.0 mol% Co, 0.65 mol% Sc, 1.0 mmol aldehyde, 2.0 mL toluene, 150 °C, 20 h, 20 bar H<sub>2</sub>, 0.05 mL 32% HCl. [a] Product isolated after second step.

step we switched the gaseous ammonia with *n*-pentylamine. By increasing the catalyst loading to 2.0 mol% Co and lowering the temperature to 140 °C under argon atmosphere, the catalyst was able to generate the imine, but not to hydrogenate it further to the corresponding amine. Thus, we had to implement an extra hydrogenation step by applying 40 bars of hydrogen pressure at 100 °C for 20 h, which led to the desired product (40). By then adding 1.0 mmol aldehyde and 0.05 mL of concentrated hydrochloric acid as well as slightly adjusting the reaction con-

ditions (150 °C, 20 bar H<sub>2</sub>), five more tertiary amines could be isolated (41–45) with products 39 and 42–45 not yet known to literature. Unfortunately, the synthesis of tertiary alkyl amines carrying one branched alkyl substituent (resulting from a ketone educt) failed due to steric overloading. For the synthesis of such secondary alkyl amines, see Scheme 3. Although our reaction protocol alone confirms the reusability of our bimetallic catalyst system, we investigated it further for five consecutive runs of the first reaction step - the borrowing hydrogen reaction of our model substrate benzyl alcohol. Five consecutive runs without any loss of activity could be accomplished (see Supporting Information 2.4.3). Furthermore, we confirmed the upscaling capabilities of our catalyst by carrying out the above reaction and the consecutive reductive amination to give rise to product 14 (Scheme 3) again - but this time with ten times the amount of all compounds involved. This led to 76% yield of the isolated product (see Supporting Information 2.4.4). Finally, a hot filtration test was performed and the filtrate did not show any catalytic activity (see Supporting Information 2.4.5). In addition, competition experiments have been conducted for BH HA and the reductive amination (see Supporting Information 2.4.6).

## Conclusion

In conclusion, we report on the synthesis of primary, secondary, and tertiary alkyl amines combining the borrowing hydrogen or hydrogen auto-transfer concept and the concept of reductive amination employing hydrogen. We use green or sustainable starting materials namely ammonia and alcohols or aldehydes and ketones and hydrogen for our amine synthesis. The key is a nanostructured, bimetallic Co/Sc catalyst able to mediate both reactions or concepts. Both metals are of high abundance in the Earth's crust with Sc being the more abundant 3d metal. We observe a broad product scope with five examples not known to literature yet, a very good functional group tolerance, upscaling is easily accomplished and our catalyst is reusable.

## Experimental Section

### Synthesis of the Support Material

For the preparation of the N–SiC support material 0.200 g SMP-10 (StarPCS™), 0.987 mL (0.800 g, 15.08 mmol) acrylonitrile and 45 mg (0.28 mmol) azobis(isobutyronitrile) were dissolved in 4 mL dimethylformamide and crosslinked for 16 h at 75 °C. After solvent removal under reduced pressure, the obtained greenbody was pyrolyzed at 1000 °C under nitrogen flow. After ball mining for 40 min, 0.400 g of the ceramic were washed by stirring in solution of 5.3 mL aq. NaOH (1 M) and 4 mL MeOH at 85 °C for 24 h. Afterwards the material was washed until neutrality and dried at room temperature.

## Synthesis of the Catalyst

1000 mg N-SiC were impregnated with 98.75 mg  $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  and 143 mg  $\text{Sc}(\text{NO}_3)_3 \cdot 5 \text{H}_2\text{O}$  in 20 mL  $\text{H}_2\text{O}$  and stirred at  $110^\circ\text{C}$  until the solvent was completely removed. Afterwards, the material was pyrolyzed at  $700^\circ\text{C}$  under nitrogen atmosphere and reduced at  $550^\circ\text{C}$  under forming gas (90:10,  $\text{N}_2:\text{H}_2$ ).

## Catalytic Procedures

The first step of the catalytic reaction (borrowing hydrogen/hydrogen autotransfer) of benzyl alcohol and its derivatives was carried out after the procedure described in the following: A magnetic stirring bar, 0.5 mmol alcohol, 2.0 mL toluene (freeze pumped), 0.5 mmol KOH (28 mg) and 28.8 mg of cobalt/scandium-catalyst (2.0 wt% Co, 1.5 mol% Co, 0.58 mg Co, 2.0 wt% Sc, 0.49 mol% Sc, 0.58 mg Sc) were placed directly into a 130 mL high pressure autoclave (Parr Instruments) and flushed with argon for 10 seconds. The autoclave was placed in a liquid nitrogen bath for 5 min whereafter gaseous ammonia was condensed inside for 5 s. The autoclave was then heated to the desired temperature and the reaction was stirred for 44 h. After cooling to room temperature and release of the ammonia pressure, the autoclave was opened and 0.8 mmol of the carbonyl compound as well as one drop of concentrated hydrochloric acid for the neutralization of the remaining ammonia was added. The autoclave was then flushed three times with 10 bars of  $\text{H}_2$ , pressurized with 40 bars of  $\text{H}_2$  and heated to  $100^\circ\text{C}$  for 20 h. In case of the synthesis of tertiary amines, the autoclave was opened again after cooldown and pressure release and 1.0 mmol of aldehyde as well as one drop of concentrated hydrochloric acid were added. The autoclave was flushed again three times with 10 bars of  $\text{H}_2$ , pressurized with 20 bars of  $\text{H}_2$  and heated to  $140^\circ\text{C}$ . To obtain the amine hydrochloride salts, the remaining solution was filtrated into a round bottom flask to remove the catalyst. After the addition of 30 mL of diethyl ether and 0.5 mL HCl in ether (2 M) the precipitate was filtrated, dried under reduced pressure and the resulting solid was then further analyzed by NMR spectroscopy. This was carried out after every step from which the product should be obtained for characterization. For the synthesis of amines with a non-branched aliphatic moiety a slightly different method was used. For the first step, a magnetic stirring bar, 0.5 mmol benzyl alcohol or its derivatives and 0.5 mmol of *n*-pentylamine together with 0.5 mmol of KOH (28 mg), 2 mL of freeze pumped toluene and 38.4 mg of cobalt/scandium-catalyst (2.0 wt% Co, 2.0 mol% Co, 0.77 mg Co, 2.0 wt% Sc, 0.65 mol% Sc, 0.77 mg Sc) were placed inside a pressure tube and flushed with argon. The tube was heated to  $140^\circ\text{C}$  for 44 h. After cooling, the whole content was transferred to an autoclave, flushed with 10 bars of  $\text{H}_2$  three times and pressurized with 40 bars of  $\text{H}_2$  to hydrogenate the remaining double bond. After cooldown, 1.0 mmol of aldehyde as well as one drop of concentrated hydrochloric acid were added. The autoclave was flushed with 10 bars of  $\text{H}_2$  three times, pressurized with 20 bars of  $\text{H}_2$  and heated to  $150^\circ\text{C}$  for 20 h. To obtain the amine hydrochloride salts, the remaining solution was filtrated into a round bottom flask to remove the catalyst. After the addition of 30 mL of diethyl ether and 0.5 mL HCl in ether (2 M) the precipitate was filtrated, dried under reduced

pressure and the resulting solid was then further analyzed by NMR spectroscopy.

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