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Imidazolium-based ionic liquid-catalyzed hydrosilylation of imines and reductive amination of aldehydes using hydrosilane as the reductant†

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The first imidazolium-based ionic liquid-catalyzed hydrosilylation of imine and reductive amination of aldehydes with primary amines using a catalytic amount of 1-butyl-3-methylimidazolium tetrachloride iron [BMIm][FeCl₄] and Ph₂SiH₂ as a reductant were performed under mild conditions. Good yields of secondary amines with high chemoselectivity and a tolerance for a wide range of functional groups were obtained.

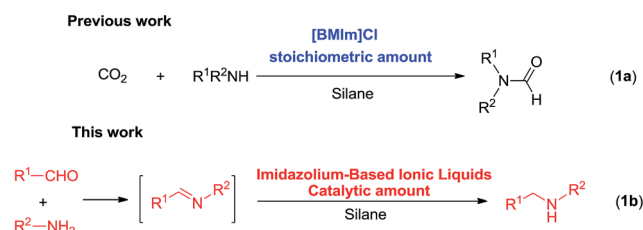
The formation of amines is one of the most important transformations in chemistry because amines are versatile building blocks for various organic molecules and essential precursors to a variety of biologically active compounds.¹ Although several methods are known for amine synthesis, catalytic reduction of imines or direct reductive amination of carbonyl derivatives in the presence of primary amines *via* sequential condensation/catalytic reduction are some of the most efficient methods through hydrogenation,^{2,3} or hydrogen transfer reactions.^{4,5} Recently, transition metal-catalyzed hydrosilylations have attracted attention as a competitive alternative method to the classical stoichiometric reduction, hydrogenation or hydrogen transfer reaction due to their mild conditions and good chemoselectivities.^{6,7} In contrast, although some catalysts have been included in the amine synthesis *via* hydrosilylation of imine^{8–12} and the synthetic method of more green direct reductive amination from primary amines with carbonyl derivatives under hydrosilylation conditions has some examples in the literature,^{13–17} the IL-catalyzed hydrosilylation of imines or direct reductive amination has not yet been developed.

Ionic liquids (ILs), composed of organic cations and organic/inorganic anions, have attracted attention as a competitive alternative green solvent to the classical solvents mainly because of its unique features such as high thermal and chemical stability, negligible vapor pressure, easy separation, and tunable properties.¹⁸ ILs have been applied in many areas, especially in catalysis.¹⁹ On the other hand, ILs can provide specific functions as a result of cooperative or synergistic effects

between ions due to the designable cations and anions from ILs.²⁰ However, only few studies have been reported on IL-catalyzed hydrosilylations. Recently, Liu's group has shown that using a stoichiometric amount of imidazolium-based ionic liquids [BMIm]Cl, high efficiency for the synthesis of formamides of amines and carbon dioxide under hydrosilylation conditions was obtained (Scheme 1, **1a**).²¹

Following our continuous efforts to perform selective reduction *via* hydrosilylation,²² herein, we report the first simple commercially available 1-alkyl-3-methylimidazolium-based ionic liquids and their use in catalytic amount for hydrosilylation of imines or reductive amination of aldehydes and primary amines (Scheme 1, **1b**).

Initial studies focused on the reduction of imine **1a** with several stoichiometric amounts of commercially available imidazolium-based ionic liquids and diphenylsilane (1.5 equiv.) as the hydride donor (Scheme 2). Preliminary tests on the ionic liquid **1** (IL **1**: [AMIm]OAc) 1-allyl-3-methylimidazolium acetate indicated low conversion to the secondary amine **4a** at room temperature. In contrast, 1-butyl-3-methylimidazolium tetrachloride iron (IL **2**: [BMIm]FeCl₄) was very efficient for this reaction, affording secondary amine **4a** in 83% yield within 16 h at room temperature. The other five imidazolium-based ionic

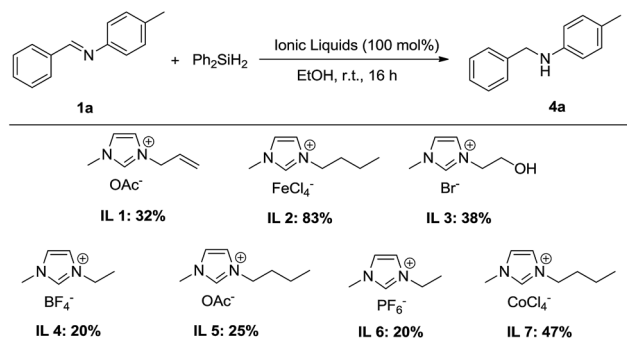


Scheme 1 Comparison of different ionic liquid-catalyzed hydrosilylation.

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Scheme 2 Imidazolium-based ionic liquid-catalyzed hydrosilylation of imines.

liquids **IL 3–7** were also examined for catalyzing this reaction, but lower catalytic activity was observed. These findings indicated that different cations and anions have a significant influence on the activity of the ILs and on the catalytic hydrosilylation.

After the ionic liquids were tested in this catalytic system, **IL 2** was determined to be the best catalyst and applied in this catalytic hydrosilylation of imine. The reaction could proceed in acetonitrile, toluene, even under neat conditions, but provided the desired product in lower yield (Table 1, entries 1–3). Among the variety of silanes tested in ethanol at room temperature for 16 h in the presence of 1 equiv. of [BMIm]FeCl₄, PhSiH₃, TMDS (1,1,3,3-tetramethylhydroxysiloxane), and PMHS (poly-methylhydroxysiloxane) were optimal hydrogen sources towards

the formation of the secondary amine **4a** (Table 1, entries 4–7). As PMHS is a less expensive and greener hydrosilylation reagent than other hydrosilanes, it was then evaluated for optimizing the conditions. When the reaction temperature increased to 80 °C, a 94% yield of amine **4a** was obtained (Table 1 entry 8). Decreasing the amount of **IL 2** to 20 mol% led to 66% yield (Table 1, entry 13). However, when this reaction was performed with Ph₂SiH₂ (1.5 equiv.) instead of PMHS (4 equiv.) in the presence of 20 mol% of **IL 2** [BMIm]FeCl₄, 91% yield of amine **4a** was still obtained (Table 1, entry 15). Decreasing the amount of **IL 2** to 10 mol% led to a lower yield using Ph₂SiH₂ as a hydrogen source (Table 1, entry 16).

The scope and limitations of this first imidazolium-based-catalyzed hydrosilylation of imines with Ph₂SiH₂ were then explored using 20 mol% of [BMIm][FeCl₄] to produce the secondary amines **4** at 80 °C under an air atmosphere (Table 1, entry 24). Various imines, **1**, were applied to synthesize the secondary amines **4**, as shown in Table 2.

As shown in Table 2, secondary amine **4a**, which was produced from imine **1a** with a *p*-methyl group on the imine R² aryl, was isolated in 85% yield (entry 1). The reaction could be

Table 2 [BMIm][FeCl₄]-catalyzed hydrosilylation of imines^a

Entry	Product		Yield (%)
1		4a : R ¹ = H	85
2		4b : R ¹ = <i>p</i> -OMe	84
3		4c : R ¹ = <i>m</i> -Me	88
4		4d : R ¹ = <i>p</i> -NO ₂	36
5		4e : R ¹ = <i>p</i> -CN	52
6		4f : R ¹ = H	94
7		4g : R ¹ = <i>p</i> -Br	70
8		4h : R ¹ = <i>p</i> -CO ₂ Me	75
9		4i : R ¹ = H	86
10		4j : R ¹ = <i>p</i> -Me	90
11		4k : R ¹ = H	70
12		4l : R ¹ = <i>p</i> -Me	72
13		4m	77
14		4n	75

Table 1 Optimization of [BMIm][FeCl₄] catalyzed hydrosilylation of imine^a

Entry	Amount of IL 2 (mmol)	Silane	Solvent (mL)	Temp. (°C)	GC-yield ^b (%)
1	0.5	Ph ₂ SiH ₂	—	r.t.	51
2	0.5	Ph ₂ SiH ₂	CH ₃ CN (2 mL)	r.t.	50
3	0.5	Ph ₂ SiH ₂	Toluene (2 mL)	r.t.	Trace
4	0.5	PhSiH ₃	EtOH (2 mL)	r.t.	97
5	0.5	Ph ₃ SiH	EtOH (2 mL)	r.t.	25
6	0.5	PMHS	EtOH (2 mL)	r.t.	83
7	0.5	TMDS	EtOH (2 mL)	r.t.	91
8	0.5	PMHS	EtOH (2 mL)	80	94
9	0.5	PMHS	EtOH (2 mL)	90	91
10	0.4	PMHS	EtOH (2 mL)	80	93
11	0.3	PMHS	EtOH (2 mL)	80	89
12	0.2	PMHS	EtOH (2 mL)	80	75
13	0.1	PMHS	EtOH (2 mL)	80	66
14	—	PMHS	EtOH (2 mL)	80	—
15	0.1	Ph ₂ SiH ₂	EtOH (2 mL)	80	91 (85 ^c)
16	0.05	Ph ₂ SiH ₂	EtOH (2 mL)	80	86

^a Imine (0.5 mmol), [BMIm][FeCl₄], silane (0.75 mmol), solvent (2 mL), 16 h. ^b Determined by GC. ^c Isolated yield of **4a**.

^a Typical conditions: [BMIm][FeCl₄] (20 mol%), aldimine (0.5 mmol), Ph₂SiH₂ (0.75 equiv), EtOH (2 mL), 80 °C, 16 h.



carried out with *p*-OMe and *m*-Me substituents on the imines R^1 aryl in 84% and 86% isolated yield, respectively (entries 2 and 3). However, the hydrosilylation was more difficult to perform with the nitro group and cyano group, where only 36% and 52% yield of the corresponding amines were obtained (entries 4 and 5), respectively. No dehalogenation occurred in this hydrosilylation of imine **1g** and the corresponding amine **4g** was generated in 70% yield (entry 7). More importantly, hydrosilylation tolerated the functional ester group of imine **1h**, and the corresponding amine **4h** (75%) was directly obtained without alteration of the carbonyl moieties (entry 8). The results of entries 9–12 indicated that the electronic effects of the donating group on the imine R^2 aryl resulted in slightly better reactivity than those of the withdrawing group. The steric effect of the *o*-methyl group on the imine R^2 aryl did not hamper the reaction (entry 13). Moreover, the hydrosilylation of the cyclohexane carboxaldehyde **1n** successfully led to the corresponding amine **4n** with 75% isolated yield (entry 14).

In addition, direct reductive amination from carbonyl derivatives in the presence of primary amines *via in situ* generated imine and catalytic reduction shows a more green process in the amine synthesis than reduction of imines, which eliminated one condensation and imine isolation step. The reductive amination of aldehydes **2** and anilines **3** with Ph_2SiH_2 was also explored using 20 mol% of [BMIm][FeCl₄] under similar conditions, but with some molecular sieves (Table 3). Various aromatic aldehydes **2** successfully reacted with aniline **3a** to produce the secondary amine **4** bearing the *p*-OMe, *p*-Me,

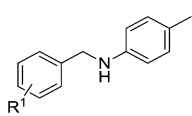
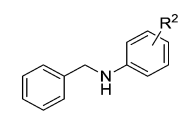
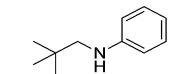
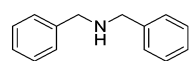
m-Me, *p*-NO₂, *p*-CN, and *p*-Br group on the amine R^1 aryl in moderate to good yields (48–86%) (entries 1–7). Several anilines bearing a functional group, such as *p*-OMe, *p*-Cl, and *o*-F, were tested under similar conditions, leading to the corresponding amines **4i**, **4q**, and **4r** in 78%, 75%, and 88% isolated yields, respectively (entries 8–10). Additionally, the aliphatic aldehyde could also be applied to synthesize a secondary amine under these hydrosilylation conditions (entry 11). The reductive product dibenzylamine **4t** obtained from the reaction of benzylamine with benzaldehyde was produced and isolated in 76% yield.

For the imidazolium-based catalytic hydrosilylation, Wang and co-workers reported that imidazolium preferred to activate the Si–H bond of hydrosilane as the first step, as obtained from the calculated results.²³ Moreover, the Liu's group also demonstrated that the ionic liquid [BMIm]Cl favored the activation of the Si–H bond of phenylsilane then proceeded for the next transformation.²¹ To obtain more clear information about the mechanism of this catalytic system, some control experiments were performed (Scheme 3). When [BMIm]Cl instead of [BMIm][FeCl₄] was used as a catalyst, the secondary amine **4a** was also obtained, but with 37% GC-yield under the same conditions. Moreover, 76% GC-yield of secondary amine **4a** was detected using only FeCl₃ as a catalyst. However, while mixing both [BMIm]Cl and FeCl₃, the GC-yield of the secondary amine **4a** was increased to 88%. These results indicate that imidazolium and FeCl₃ interact to effect the transformation.

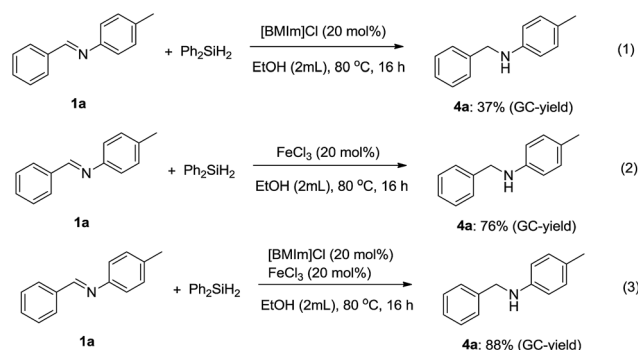
Based on the previous works^{21,23} and the abovementioned control experiments, we proposed a mechanism (Scheme 4) for the [BMIm][FeCl₄]-catalyzed reductive amination. First, [BMIm][FeCl₄] interacts with silane silicone, making the Si–H bond of diphenylsilane insert into the *in situ* generated imine much easier, resulting in the formation of the *N*-silylamine; the resulting product is then generated *via* hydrolysis with H₂O or EtOH.

In summary, we developed the first imidazolium-based ionic liquid-catalyzed hydrosilylation of imine using catalytic amount of 1-butyl-3-methylimidazolium tetrachloride iron [BMIm][FeCl₄]. Moreover, this catalytic system was also applied in the reductive amination of aldehydes to access secondary amines with diphenylsilane. Furthermore, many functional groups, such as nitro, cyano, halide, and ester, were tolerated under this

Table 3 [BMIm][FeCl₄]-catalyzed reductive amination of aldehydes and anilines under hydrosilylation conditions^a

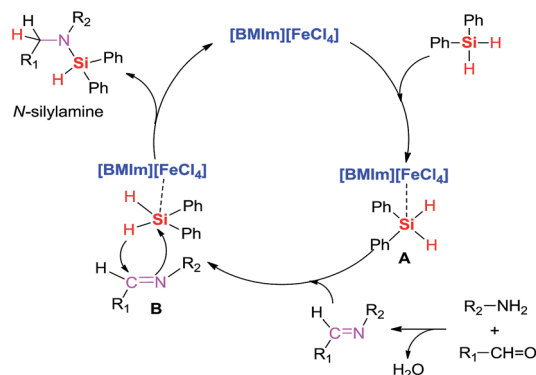
$R^3-CHO + H_2N-R^4 \xrightarrow[\text{EtOH (2 mL), 80 }^\circ\text{C, 16 h, under air}]{[BMIm][FeCl_4] (20 \text{ mol\%}), \text{Molecular sieves (200 mg)}} R^3-CH_2-NH-R^4$		
2	3	4
Entry	Product	Yield (%)
1		4a: $R^1 = H$ 80
2		4b: $R^1 = p\text{-OMe}$ 83
3		4o: $R^1 = p\text{-Me}$ 86
4		4c: $R^1 = m\text{-Me}$ 85
5		4d: $R^1 = p\text{-NO}_2$ 48
6		4e: $R^1 = p\text{-CN}$ 55
7		4p: $R^1 = p\text{-Br}$ 82
8		4i: $R^2 = p\text{-OMe}$ 78
9		4q: $R^2 = p\text{-Cl}$ 75
10		4r: $R^2 = o\text{-F}$ 88
11		4s 80
12		4t 76

^a Typical conditions: [BMIm][FeCl₄] (20 mol%), aldehydes (0.6 mmol), aniline (0.5 mmol), Ph_2SiH_2 (0.75 equiv.), 4 Å molecular sieves (200 mg), EtOH (2 mL), 80 °C, 16 h.



Scheme 3 Control experiments.





Scheme 4 Proposed catalytic cycle for the [BMIm][FeCl₄]-catalyzed direct reductive amination of aldehyde and aniline.

catalytic process. A possible mechanism for the [BMIm][FeCl₄]/Ph₂SiH₂ catalytic system has been demonstrated.

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