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ARTICLE

Calcium-catalysed synthesis of amines through imines hydrosilylation: an experimental and theoretical study

Yougourthen Boumekla,^a Fengjie Xia,^a Lucas Vidal,^a Cédric Totée,^a Christophe Raynaud*^a and Armelle Ouali*^a

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A method to reduce aldimines through hydrosilylation is reported. The catalytic system involves calcium triflimide (Ca(NTf₂)₂) and potassium hexafluorophosphate (KPF₆) shown to act in a synergistic manner. The expected amines are obtained in fair to very high yields (40-99%) under mild conditions (room temperature in most cases). To illustrate the potential of the method, a bioactive molecule with antifungal properties was prepared in gram scale and high yield in environmentally friendly 2-methyltetrahydrofuran. Moreover, it was shown on this example that the imine can be prepared in situ from the aldehyde and the amine without isolating the imine. The mechanism involved has been explored experimentally and through DFT calculation, and the results are in accordance with an electrophilic activation of the silane by the calcium catalyst.

Introduction

Amines constitute highly important building blocks in organic synthesis due to their omnipresence in natural products, polymers,¹ pharmaceuticals² or agrochemicals.^{3,4} Among the synthetic strategies towards these key compounds, catalytic reduction of imines including hydrogenation, hydrogen transfer or hydrosilylation, appear as efficient methodologies. Within the last few years, hydrosilylation processes involving silanes as the H source, significantly contributed to the preparation of amines.^{5,6} Hydrosilanes, readily produced on an industrial scale, indeed constitute useful reducing agents due to their air- and water stability, ease of handling and ability to be activated in mild conditions. They thus appear as an attractive alternative to molecular hydrogen often requiring high temperature and pressure conditions as well as specific set-up. Although ytterbium-, aluminium-, boron^{7,8}- even ionic liquid⁹-based or organic¹⁰ catalysts have been shown to promote imine hydrosilylations, the most ubiquitous catalysts for these transformations involve transition metals. Historically, the first systems reported involved noble ones (ruthenium, rhodium, iridium, palladium) and later on, some catalysts based on more earth abundant metals such as copper,¹¹ zinc,¹² nickel,¹³ or iron¹⁴⁻¹⁷ have been developed.⁵ Some of the complexes required multi-step ligand synthesis and/or are air- or moisture sensitive. Our objective consisted in providing the actual toolbox for imine hydrosilylation with a catalytic system involving a benign metal and attractive for the organic chemist namely readily available and easy to handle (air- and moisture stable). We then turned

our attention to calcium. Generally, alkaline earth metals (Ae = Mg, Ca, Sr, Ba) attracted much attention over the last decade and catalytic systems have been reported to promote a wide range of processes including ring-opening polymerizations,¹⁸ C-C or C-heteroatom bond-forming transformations,¹⁹⁻²⁰ dehydrocouplings²¹⁻²⁴ or hydroelementations of C=C, C=O or C=N bonds.²⁵⁻²⁸ Along these lines, alkaline earth complexes were shown to promote hydrosilylation of olefins²⁹⁻³¹ or pyridines.³²⁻³⁵ Interestingly, concerning non-activated C=N bonds, Sarazin et al reported stoichiometric hydrosilylation of imine ligands in barium complexes.³⁶ In addition, a recent breakthrough by Harder et al demonstrated for the first time the ability of calcium, strontium and barium complexes involving amide and/or benzyl ligands to catalyse the hydrosilylation of aldimines and one ketimine with phenylsilane.³⁷⁻³⁸

In this report, a commercial and moisture stable calcium salt Ca(NTf₂)₂ is shown to act in a synergistic manner with KPF₆ and in the absence of any additional ligands to catalyse hydrosilylation of aldimines under mild conditions. DFT studies have been carried out to get insight into the involved mechanism. To the best of our knowledge, if calcium-based Lewis acids emerged as important catalysts in green chemistry, Ca(NTf₂)₂ has not been used yet to promote imines hydrosilylation.^{20,28} In addition, it is the first time that calcium triflimide is shown to activate Si-H bonds which opens new prospects in the fields of hydrosilylation reactions as well.

Results and Discussion

Imine **1a**, which results from the condensation of 4-bromobenzaldehyde and 4-iodoaniline, was chosen as the model substrate. The performance of several commercial calcium salts was evaluated in the hydrosilylation of **1** with phenylsilane at room temperature. Although calcium hydroxide and alkoxides revealed inefficient (no **1a** conversion), Ca(NTf₂)₂,

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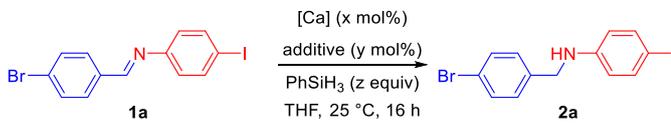
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a calcium precursor that carries a strong electron-withdrawing and weakly coordinating counter anion, allowed the formation of expected amine **2a**, with low yield (10%) however (Table 1, entry 1). The addition of catalytic amounts of KPF_6 (20 mol%) enabled to significantly increase the performances (entry 2), **2a** being quantitatively obtained. It is noteworthy that $\text{Ca}(\text{NTf}_2)_2$ and KPF_6 acted in a synergistic manner, KPF_6 being inefficient when used alone (entry 3). It has previously been shown that $\text{Ca}(\text{NTf}_2)_2$ and PF_6 salts underwent anion metathesis to form KNTf_2 and $\text{Ca}(\text{NTf}_2)\text{PF}_6$.²⁰ The latter salt, more Lewis acidic than $\text{Ca}(\text{NTf}_2)_2$ and displaying two binding sites available on the calcium center, was reported to activate a wide range of substrates such as cyclopropanes,³⁹⁻⁴⁰ carbonyl compounds,⁴¹⁻⁴² alcohols,⁴³⁻⁴⁸ alkenes^{49,50} or more recently sulfonyl^{51,52} fluorides.^{20,28,53} $\text{Ca}(\text{NTf}_2)\text{PF}_6$, whose Lewis acidity has been evaluated by the Childs method,⁴¹ has also been associated with hexafluoroisopropanol as the solvent and the resulting system shown by Gandon and Leboeuf to be highly active in various transformations including Aza-Piancatelli,^{54,55} hydroarylation,⁵⁶ or hydroamidation⁵⁷ or hydroacyloxylation⁵⁸ reactions. It is noteworthy that under our conditions, KNTf_2 itself was unable to promote imine **1a** hydrosilylation (entry 4), suggesting that $\text{Ca}(\text{NTf}_2)\text{PF}_6$ is the catalytically active species. Furthermore, triflimic acid was unable to promote hydrosilylation, which ruled out the possibility that traces of Tf_2NH were at the origin of the observed activity and confirmed that the calcium center played a role in the catalytic process.

Table 1: Optimisation study for the reduction of imine **1a** with calcium pre-catalysts



Entry	[Ca] (mol %)	Additive (mol %)	Eq PhSiH ₃	Yield 2a <i>a,b</i>
1	$\text{Ca}(\text{NTf}_2)_2$ (20)	-	4	10
2	$\text{Ca}(\text{NTf}_2)_2$ (20)	KPF_6 (20)	4	99
3	-	KPF_6 (20)	4	0
4	-	KNTf_2 (20)	4	0
5	$\text{Ca}(\text{NTf}_2)_2$ (10)	KPF_6 (10)	4	99
6	$\text{Ca}(\text{NTf}_2)_2$ (10)	KPF_6 (10)	2	99 (86 ^c)
7	$\text{Ca}(\text{NTf}_2)_2$ (5)	KPF_6 (5)	2	87

^a Typical procedure: $\text{Ca}(\text{NTf}_2)_2$, KPF_6 , PhSiH_3 and THF (1 mL) were stirred at 25 °C for 10 minutes before adding the aldimine **1a** (0.25 mmol) and THF (0.5 mL). The reaction mixture was stirred at 25 °C for 16 h and next hydrolysed with MeOH (1.5 mL) and NaOH (2M, 1.5 mL). ^b Yield determined by NMR using 1,3,5-trimethoxybenzene as the standard (selectivity > 99%). ^c after 6h instead of 16.

The amounts of catalyst and additive could be successfully decreased to 10 mol % without significant change (entry 5). Under these conditions, by decreasing the amount of silane by two (2 equiv instead of 4, entry 6), amine **2a** could be obtained quantitatively when the reaction was stopped after 16 hours at 25 °C (entry 6). It is worthy to note that **2a** is formed in 86% yield after only 6 hours, suggesting that the conversion is attained before 16 h. Decreasing the amount of $\text{Ca}(\text{NTf}_2)\text{PF}_6$ /

KPF_6 (1:1) from 10 to 5 mol% only lead to a slight decrease of the yield of amine **2a** from 99 to 87% (entry 7).

With these optimized conditions in hand, phenylsilane was replaced by several cheaper counterparts including diphenylsilane, triphenylsilane, dimethylphenylsilane, triethylsilane and 1,1,3,3-tetramethyldisiloxane. However, none of the tested silanes allowed to observe the conversion of imine **1a** at 25 °C.

Next, the scope of the method was investigated on aromatic aldimines using $\text{Ca}(\text{NTf}_2)_2$ / PF_6 (1:1) (10 mol%) as the catalytic system (Figure 1).

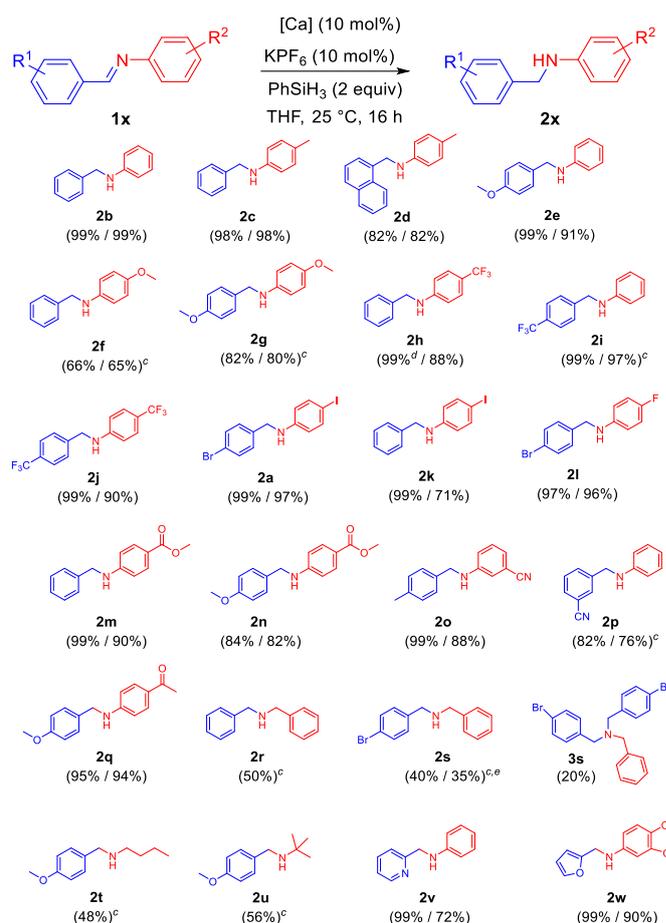


Figure 1: Scope of the catalytic system (NMR yield^a / isolated yield^b)

a. Typical procedure (NMR yields): $\text{Ca}(\text{NTf}_2)_2$ (0.025 mmol), KPF_6 (0.025 mmol), PhSiH_3 (0.5 mmol), THF (1 mL) were stirred at 25 °C for 10 minutes before adding aldimine **1x** (0.25 mmol) and THF (0.5 mL). The reaction mixture was stirred at 25 °C for 16 h and then hydrolysed with MeOH (1.5 mL) and NaOH (2M, 1.5 mL). Yield determined by NMR using 1,3,5-trimethoxybenzene as the standard. **b.** Typical procedure (isolated yields): $\text{Ca}(\text{NTf}_2)_2$ (0.1 mmol), KPF_6 (0.1 mmol), PhSiH_3 (2 mmol), THF (4 mL) were stirred at 25 °C for 10 minutes before adding the aldimine **1x** (1 mmol) and THF (2 mL). The reaction mixture was stirred at 25 °C for 16 h and then hydrolysed with MeOH (6 mL) and NaOH (2M, 6 mL). **c.** 65 °C. **d.** Quantitative NMR yield after 6h. **e.** Formation of *N,N*-di(4-bromobenzyl)benzylamine **3s** (20% isolated yield, see ESI).

(Benzylidene)phenylamine **1b** was quantitatively transformed into amine **2b**. Imines **1c** and **1d**, both derived from toluidine, underwent hydrosilylation in good yields as well (98 and 82% isolated yields for **2c** and **2d** respectively), even in the case of bulkier ortho-substituted naphthyl derivative **1d**. Substrates **1e**-

g bearing electron-donating methoxy substituents were converted in fair to high yields (66, 82 and 99% for **2f**, **2g** and **2e** respectively). While imine **1e** was fully converted within 16 h at 25 °C, **2f** and **2g** derived from electron-rich *p*-methoxyaniline revealed less reactive and an increase in temperature to refluxing THF (65 °C) was required to improve the conversions. The hydrosilylation of imines **1h-j** bearing electron-withdrawing trifluoromethyl groups was then investigated. Amines **2h**, **2i** and **2j** could be formed quantitatively and isolated in very high yields (88, 97 and 90% respectively). Here again, the effect of the substituent revealed dependent on its position: while **1h** and **1j** issued from electron-poor *p*-trifluoromethylaniline were fully converted at 25 °C within 6 and 16h respectively, imine **1d** bearing the CF₃ substituent on the "aldehyde" side required higher temperature to be reduced (refluxing THF instead of 25 °C). As in the case of **1a**, the halogenated imines **1k** and **1l** were quantitatively transformed into the corresponding amines **2k** and **2l** under standard conditions. The method revealed compatible with several functional groups including esters (90% and 82% isolated yields for **2m** and **2n**), cyano substituents (88% and 76% isolated yields for **2o** and **2p**) or ketones (94% yield for **2q**). Significantly lower yields were obtained for amines **2r-u** bearing alkyl substituents at N in refluxing THF. Increasing the amount of calcium catalyst from 10 to 20 mol% did not significantly improve the performances. Therefore, this system appears as complementary to the one reported by Harder, that has been shown to be particularly efficient for imines bearing an alkyl group at N and aryl substituents at C.³⁷ Interestingly, in addition to expected amines **2r** and **2s**, tertiary amines were formed and as an example, *N,N*-di(4-bromobenzyl)benzylamine **3s**, isolated in 20% yield (see ESI p. S12), represents an appealing starting compounds towards pharmaceuticals or sensors.⁵⁹ The synthetic pathway to explain the formation of this by-product is still unclear. The heteroaromatic imines **1v** and **1w** were quantitatively reduced and the expected amines were isolated in good to very high yields (72 and 90% for **2v** and **2w** respectively). While **2v** represents a potential ligand finding application in catalysis, **2w** has potential applications in medicinal chemistry for its antifungal properties and also as a precursor for antitubercular agents.^{60,61}

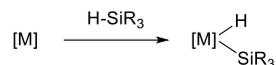
At this stage, we were keen to get insights into the processes involved in the previously described hydrosilylation.

From a mechanistic point of view, two main hydrosilane activation pathways have been previously proposed (Scheme 1): (i) the Chalk-Harrod and modified Chalk-Harrod mechanism occurring for e. g. with rhodium or platinum catalysts and relying on two-electron oxidative addition and reductive elimination steps (Scheme 1, A); (ii) a ionic mechanism in which a Lewis acidic catalyst enhances the electrophilic character of the silicon center through activation of the Si-H bond (Scheme 1, B).

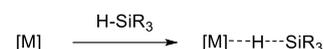
In Ae-catalyzed C=C or C=N hydrosilylation, metal hydride species play a key role in the mechanism and are proposed to be the active species.^{29-32,37,62} In some of these reactions, the pre-catalyst involves the metal-hydrogen bond. The calcium hydrido complexes can also be generated from amide/alkyl/benzyl calcium precursors and silanes through σ -

bond metathesis (Scheme 1, C). This process has been widely described and exploited in catalytic reactions including hydrogenation or hydro-elementations,⁶² and more recently redistribution of hydrosilanes⁶³ or dehydrogenative silylation of aromatic ethers.⁶⁴

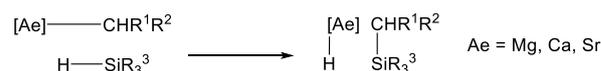
A- Chalk-Harrod and modified Chalk-Harrod mechanisms



B- Lewis acid mechanisms (electrophilic Si-H activation)



C- Mechanisms involving σ -bond metathesis: case of Ae-alkyl/amide complexes

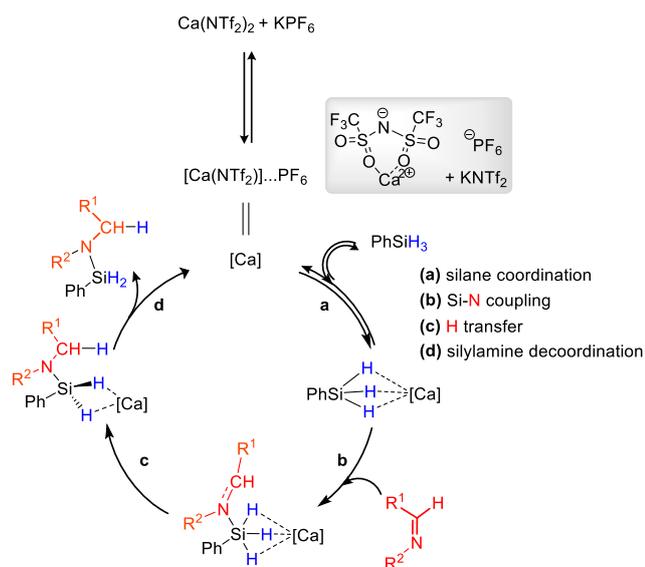


Scheme 1: Main mechanisms for silane activation pathways

In our conditions, calcium hydroxide, alkoxides and even calcium triflimidate Ca(NTf₂)₂ alone are not efficient to promote the hydrosilylation of imine **1a**. The fact that hydrosilylation only occurs in the presence of the highly Lewis acidic calcium salt Ca(NTf₂)PF₆ might suggest that the mechanism involves an electrophilic activation of the Si-H bond (Scheme 1, B). Such pathway was reported for ketones and imines hydrosilylation promoted by perfluoroarylborane such as B(C₆F₅)₃ (Scheme 1, B).⁶⁵⁻⁶⁹ In these processes, hydrosilylation proceeded more rapidly in the case of least basic substrates.⁶⁷ In our conditions, the electronic properties of the substituents were shown to have an effect on the catalytic performances. For example, electron-poor imine **1h** with a CF₃ group in the para position of the imine nitrogen revealed significantly more reactive than imine **1f** with an electron-donating methoxy group in the same position. Indeed, while **1h** was quantitatively converted into **2h** within 6h at room temperature (Figure 1, note d), **1f** required heating to reach a conversion of 66% after 16h.

Next the interaction between the Ca(NTf₂)PF₆ catalyst and each of the substrates, imines and silane, have been investigated. For this and in first intention, the evolution of a stoichiometric mixture of calcium catalyst and imine **1h** in deuterated THF was monitored by ¹H NMR at different temperatures (25 °C to -65 °C and back to 25 °C). No obvious change could be observed on the imine spectrum whatever the temperature, suggesting that the presence of the hydrosilane is required for the two substrates to react together. The same behaviour was observed in the case of more electron-rich imine **1f**. The same NMR experiment was then done in the case of phenylsilane. The addition of one equivalent of Ca(NTf₂)PF₆ to phenylsilane did not induce any change on the ¹H NMR spectrum of the silane at room temperature. Next ¹H NMR spectra were collected at lower temperatures, from 25 °C to -65 °C. At -25 °C (ESI § 4.1). Interestingly, the appearance of broad signals at around 6-6.4 ppm was observed and the signals were becoming increasingly sharp when decreasing the temperature to -65 °C (ESI, Figure S1 p. S14). The phenomenon was shown to be reversible when coming back to room temperature (ESI, Figure S2 p. S14). These observations suggest a weak coordination of the silane to calcium.^{67,70}

From all these experimental observations, we propose a putative catalytic cycle (Scheme 2). The process starts with the generation of the catalytic active species and highly Lewis acidic $\text{Ca}(\text{NTf}_2)\text{PF}_6$ (represented as $[\text{Ca}]$), where the PF_6^- counteranion is not expected to be in the first coordination sphere.^{20,71} The first step of the catalytic cycle would consist in the coordination of the silane to the calcium center $\text{Ca}(\text{NTf}_2)^+$ (Scheme 2, step a). Subsequent intermolecular nucleophilic attack of imine on the silicon center may lead to a silyliminium intermediate (Scheme 2, step b), by analogy with the mechanism proposed in the case of $\text{B}(\text{C}_6\text{F}_5)_3$.⁶⁹ In the following step c, the H-transfer may occur. The last decoordination step d would enable the release of the expected silylamine and the regeneration of the calcium catalytic active species **3**.



Scheme 2: Mechanism for the Ca-catalyzed hydrosilylation of imines proposed by analogy with $\text{B}(\text{C}_6\text{F}_5)_3$

To gain a better understanding of the mechanism of this catalytic hydrosilylation, DFT studies were carried out with a dispersion corrected hybrid functional and an implicit model for the solvent (THF). Natural Bond Orbital (NBO) analyses of the stationary points of the potential energy surface have been carried out. Full computational details are given in the ESI.

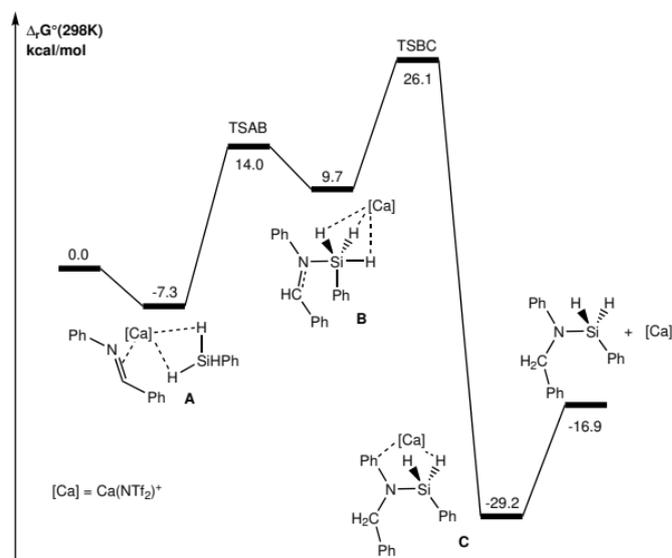


Figure 2: Gibbs energy profile ($\text{kcal}\cdot\text{mol}^{-1}$) for the hydrosilation of **2b** imine catalysed by $\text{Ca}(\text{NTf})^+$

The Ca^{2+} complex with the NTF⁻ ligand, and the substrates (**2b** imine and PhSiH_3) were represented in full. The PF_6^- counteranion was supposed to be non-coordinated and was not taken into account for the modelisation.

The overall reaction is found to be exergonic ($\Delta_r G^0 = -16.9 \text{ kcal}\cdot\text{mol}^{-1}$) and requires a Gibbs activation energy of $26.1 \text{ kcal}\cdot\text{mol}^{-1}$ relative to the separate reagents (Figure 2). The driving force of the reaction relies on the C-H and Si-N bonds, which are slightly stronger than the broken Si-H and C=N bonds. The reaction mechanism is found to be the succession of two elementary steps.

The reaction sequence begins with the coordination of the imine and PhSiH_3 to the metal cation, leading to adduct **A**. The first step requires a low activation barrier ($\Delta G^\ddagger = 21.3 \text{ kcal}\cdot\text{mol}^{-1}$, relative to adduct **A**, *i.e.* $14.0 \text{ kcal}\cdot\text{mol}^{-1}$ relative to the energy reference), and corresponds to the step during which the Si-N bond is formed, leading to intermediate **B** ($d_{\text{Si-N}} = 2.181 \text{ \AA}$ and 2.019 \AA for **TSAB** and **B**, respectively). Noteworthy for this intermediate **B**, the Si atom is found pentavalent and at the center of a trigonal bipyramid. The NBO analysis for this intermediate shows that its relative stability is essentially based on favorable donor-acceptor interactions, on the one hand between the N lone-pair and the three $\sigma_{\text{Si-H}}^*$ antibonds (mainly with the $\sigma_{\text{Si-H}}^*$ trans to N) and on the other hand between the three $\sigma_{\text{Si-H}}$ and the vacant $3s$ orbital of Ca (see ESI § 5.3). It is also important to note that all attempts to optimize the structure of such a reaction intermediate, where Si is hypervalent, *in the absence of $\text{Ca}(\text{NTf}_2)^+$ catalyst*, have been unsuccessful: the stability of this intermediate is a key-step of the process and can only be ensured with the electrophilic assistance of Ca. This intermediate **B** also has a characteristic ^1H NMR signature: calculations suggest an isotropic chemical shift δ for the H in alpha from the C functional of imine to 9.0 ppm and shifts for the 3 H bonded to the Si and in interactions with Ca, between 5.0 and 5.8 ppm (ESI § 5.4); these calculated values are

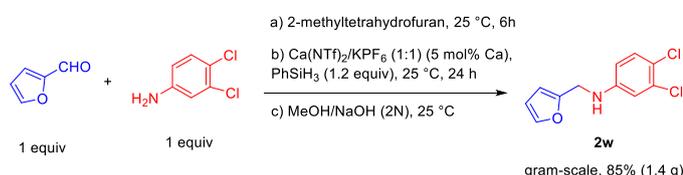
consistent with the transiently experimentally observed values of chemical shift (see ESI Figure S3 p. S15).

The second step corresponds to the transition from this intermediate **B** to the product **C** and is the kinetic determining step ($\Delta G^\ddagger = 26.1 \text{ kcal}\cdot\text{mol}^{-1}$ with respect to the reference energy). This step corresponds to a β -migration of one of the three H carried by the Si towards the imine C atom. An NBO analysis of the electronic structure of this **TSBC** transition state shows clearly that the transferred H has a strong hydride character (the corresponding NBO charge is $-0.81e$); this electrophilic nature allows to better understand the greater efficiency of the process for imines substituted by an electron-withdrawing group with respect to imines substituted by electron-donating groups (**2h** vs **2f**, Fig. 2), which enable respectively the stabilisation/destabilisation of this transition state (see ESI § 5.3).

The final step corresponds to the decoordination of the silylamine to the metal (adduct **C**), leading to the free $\text{Ca}(\text{NTf}_2)^+$ complex and the reaction product without interactions.

The proposed mechanism, consistent with the experimental observations previously presented, is in favor of an electrophilic Si-H activation pathway.

Lastly and to illustrate the interest of the method for organic chemistry, the catalytic system reported here was applied to the synthesis of bioactive amine **2w** on gram-scale through reductive amination and by optimizing the conditions (solvent, amount of metal and of silane, Scheme 3). Therefore, in this synthesis, equimolar amounts of 2-furfural, chemical obtained from biomass,⁷² and 3,4-dichloroaniline (7 mmol) were allowed to react in 2-methyltetrahydrofuran, a renewable and more eco-friendly solvent.⁷³ After 6h, 5 mol% of the Ca catalyst and 1.2 equiv of silane were added and the mixture stirred for 24 h at 25 °C before achieving basic hydrolysis. ¹H NMR of the crude confirmed the complete conversion of both reactants, the absence of intermediate imine and the quantitative formation of **2w**. The latter was isolated in 85% yield after column chromatography, which is in the same order of magnitude than at 1 mmol scale from imine **1w** (90%, Figure 1). It is worth noting that for this substrate, the amount of catalyst could be decreased from 10 to 5 mol% and the excess of silane from 2 to 1.2 equivalents, while keeping good performances. Under these conditions, more than 1.4 g of the expected amine could be obtained with high purity.



Scheme 3: Application of the method for gram-scale synthesis of an amine with anti-fungal activity

Conclusions

This method reports a simple and efficient method for imine hydrosilylation using a catalytic system based on non-toxic calcium, the fifth most frequent element in the Earth crust. The

proposed catalyst is based on $\text{Ca}(\text{NTf}_2)_2$ and KPF_6 , which act in a synergistic manner. Both precursors are readily available and easy-to-handle salts that can be stored on the shelves, open to air and used for several months without loss of activity. This catalytic system is able to promote the hydrosilylation of a variety of aldimines under mild conditions (25–65 °C, 6–16 h) without requiring an inert atmosphere, and shows tolerance to functional groups including halides (I, Br, F), trifluoromethyl, ketones, esters or nitriles. Expected amines are obtained in fair to excellent yields.

The value of the method has been shown on the synthesis of a bioactive amine with antifungal properties, that was prepared in gram scale and high yield in environmentally friendly 2-methyltetrahydrofuran. It was shown on this example that the imine can be generated in situ from the corresponding aldehyde and amine without isolating the imine, which is interesting from a practical point of view. Overall, due to the nature of the metal (calcium is non-toxic even in large amounts) and the mild reaction conditions, the reported methodology contributes to the search for sustainable syntheses of amines, highly important building blocks in many application fields. The resulting amines are obtained free from transition metal traces, which is of great interest in the field of pharmaceuticals for which the metal contaminants are strictly regulated. No tedious and costly purification is thus needed. In addition, experimental data and DFT calculations are in accordance with an electrophilic Si-H activation pathway by the $\text{Ca}(\text{NTf}_2)^+$ catalyst shown to promote imine hydrosilylation for the first time. To the best of our knowledge, such an electrophilic activation of the Si-H bond, well-known for boron catalysts, is not common in alkaline earth chemistry where a Ae-hydride complex is generally generated from calcium precursors and silanes through σ -bond metathesis (Scheme 1, C). $\text{Ca}(\text{NTf}_2)^+$ being shown to activate Si-H bonds for the first time, studies to enlarge the scope of this catalyst to other challenging hydrosilylation reactions are currently underway.

Author Contributions

Yougourthen Boumekla: Investigation, Methodology. Fengxie Xia: Investigation. Lucas Vidal: Investigation. Cédric Totee: Methodology. Christophe Raynaud: Methodology, Software, Formal analysis, Writing–Review and Editing. Armelle Ouali: Conceptualization, Methodology, Writing original draft, Review and Editing, Supervision.

Conflicts of interest

There are no conflicts to declare.

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