New generation of nitrenium salts: catalytic hydrosilylation of imines and a mechanism of action of nitrogen Lewis acids

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ABSTRACT: Nitrogen Lewis acids (NLAs) are emerging as a powerful tool in strong bond activation and catalysis. Till now, N,N-dialkyl-nitrenium salts were known and utilized in chemical transformations. In this article, we report on the synthesis and characterization of a new generation of nitrenium-based Lewis acids – N,N-diaryl-substituted naphthotriazinium salts, which open a door to libraries of stereoelectronically modifiable catalysts. We exemplify the potency of these new Lewis acidic catalysts in a gram-scale hydrosilylation of various ketimines and aldimines in yields up to 99% and a catalyst loading as low as 0.1mol%. Notably, dialkyl-nitrenium salts proved inefficient in this reaction. Based on our experimental and theoretical studies, we elucidated, for the first time, the mechanistic action of nitrenium Lewis acids in such reduction-type reactions, demonstrating a unique hydridic behavior of N-H bonds in triazanes.

KEYWORDS: Organocatalysis, Nitrogen, Nitrenium, Lewis acids, Hydrosilylation, Imines, Silanes.

INTRODUCTION

Lewis acids (LAs) based on main group elements have found paramount applications in all areas of chemistry encompassing synthesis, supramolecular chemistry, biochemistry and materials.¹ Particularly, such metal-free LAs have been employed as strong bond activators and catalysts for myriads of chemical transformations.² Typical main group element LAs, possessing free low-lying orbitals for substrate interaction and activation, are based on boron, aluminum, tin, silicon and phosphorous.¹

The use of nitrenium-based compounds³ – divalent stabilized nitrogen cations – for chemical bond activation and catalysis is an emerging concept in organic chemistry. In our initial study of nitrenium salts, we discovered their capability to serve as π -accepting ligands in transition metal complexes.⁴ In a following study, we examined the Lewis acidity of the central nitrogen atom in triazolium and triazinium salts, which enables their coordination to a plethora of Lewis bases, forming stable acid-base adducts (Scheme 1 a).⁵ Subsequently, Stephan et al. synthesized cyclic (alkyl)(amino)nitrenium (CAAN) cations and combined them with tBu₃P to create an FLP capable of cleaving S-S bonds in disulfides (Scheme 1 b).⁶ Goicoechea et al. demonstrated the capability of *N*,*N*-dimethyl naphthotriazinium salts to serve as Lewis acid catalysts in several organic transformations at ambient conditions (Scheme 1 c).⁷

Scheme 1. Evolution of nitrenium-based Lewis acids.



Recently, we have reported the cleavage of Si-H bonds by a FLP composed of *t*Bu₃P and a CF₃decorated dialkyl-substituted nitrenium ion (Scheme 1 a).⁸ This modified naphthotriazinium ion experimentally proved to possesses enhanced Lewis acidity, which was corroborated through DFT calculations. Accordingly, a new stable N-H triazane had formed, which showed potential in hydride transfer reactions.

We were interested to comprehensively examine naphthotriazinium ions and the corresponding N-H triazanes in catalytic reactions, which presumably include Si-H bond activation and a hydride transfer as a key step. We have selected the hydrosilylation of imines as a benchmark reaction.⁹ Notably, employing the known *N*,*N*-dialkyl-substituted naphthotriazinium salts 1,3-dimethylnaphthotriazinium BArF **1** and 1-methyl-3-(2,2,2-trifluoroethyl)naphthotriazinium BArF **2** (Scheme 1 a) in this process, we observed only very low reactivity (Table 1, entries A and B). In their seminal study, Piers et al. have demonstrated that the highly Lewis acidic

tris(pentafluorophenyl)borane B(C_6F_5)₃ can efficiently catalyze the hydrosilylation of carbonyl functions¹⁰ and imines.¹¹ Therefore, we assumed that conceptually new and more acidic triazinium ions are required to facilitate the catalysis of reactions, which proved challenging with *N*,*N*-dialkyl substituted counterparts.

We envisioned that the introduction of aryl groups as substituents on the flanking nitrogen atoms should lower the LUMO energy of the molecule, making the nitrenium significantly more acidic, and accordingly, more reactive in LA catalysis. Involvement of the flanking N-lone pairs in a conjugation, as well as a possibility to introduce electron-withdrawing groups on the aryl rings should make a conceptually new subset of nitrenium catalysts.

In this article, we report on a new generation of nitrenium-based Lewis acids – diarylnaphthotriazinium salts (Scheme 1 d). We demonstrate both experimentally and theoretically that these novel and highly modifiable nitrenium ions indeed possess higher acidity and can efficiently catalyze the hydrosilylation of various imines in excellent yields, with a catalyst loading as low as 0.1mol%. Additionally, the mechanism of nitrenium and N-H triazane action was, for the first time, investigated by experimental and computational methods for the example of imine reduction. Our conclusions further ratify the mechanism of the Lewis acid-catalyzed hydrosilylation reaction conceived by Piers et al. and establish N-H triazane as a powerful hydride donating species.

RESULTS AND DISCUSSION

In the previous studies we used **1** and **2** as Lewis acids and as FLP partners with tBu_3P for Si-H bond activation.⁸ We were wondering whether nitrenium ions (and, accordingly, N-H triazanes formed during Si-H cleavage) could be utilized for the catalytic hydrosilylation of N=C bonds.

However, combining catalytic amounts of either 1 or 2 with our model imine

N-(1-phenylethylidene)aniline **3** and PhSiH₃, after optimization of the reaction conditions, did not lead to the desired result: the product silylamine **4** and the hydrolyzed product amine **5** were detected in unsatisfactory yield, (less than 10% combined, by ¹H NMR) and most of imine **3** remained unreacted. An inclusion of molecular sieves (M.S.) into the reaction mixture led to some increase in the reaction rate, providing silylamine **4** (and then amine **5** after hydrolysis) in 28% yield in 8h (Table 1). Employing higher temperatures than the optimized 60°C generated a mixture of compounds. In a control experiment, no reaction was detected when molecular sieves were used without nitrenium catalyst; thus, we are certain the molecular sieves do not possess any catalytic activity in this process.

Since the unhydrolyzed silylamine **4** went through rapid decomposition when concentrated by vacuum evaporation of the solvent, we were not able to isolate it, thus only the hydrolyzed counterpart amine **5** was isolated. Nevertheless, utilizing the ¹⁵N-labeled imine **3'** as a starting material, we were able to observe the ¹⁵N-labeled silylamine product **4'** by ¹H NMR, ¹⁵N NMR (a singlet at -314.46 ppm with ²⁹Si satellites, ¹ $J_{N-Si} = 19.7$ Hz) and ²⁹Si NMR (a doublet at -32.57 ppm, ¹ $J_{Si-N} = 19.7$ Hz).

We presumed that the relatively low acidity of catalysts **1** and **2** might be a reason for their low activity in the imine hydrosilylation. To increase the acidity and, likely, activity of our nitrenium-based Lewis acids, we decided to replace the alkyl "arms" on the flanking nitrogen atoms with aryl substituents. Our hypothesis was that aryl "arms" would be able to partially conjugate with the lone electron pairs of the flanking nitrogen atoms, thus decreasing their ability to donate electron density to the central nitrogen atom through the π -conjugation. This would in turn decrease the electron density on the central nitrogen atom, thus "expose" its empty *p* orbital

and increase the Lewis acidity. Moreover, the aryl substituents can be facilely and versatilely decorated by various functional groups, including electron withdrawing motifs, thus further allowing to tune Lewis acidity of the catalyst via inductive effect.

Since such molecules are unknown, we started from developing efficient synthetic pathways, which would allow for a preparation of a versatile library of *N*,*N*-diaryl-naphthotriazinium ions. We employed two different approaches for the coupling of 1,8-diaminonaphthalene with an aryl group, depending on its electronic nature. For electron donating or neutral aryl groups, we utilized a Cu-catalyzed C-N coupling between the amine and aryl iodides,¹² and for electron withdrawing aryl units we employed an aromatic nucleophilic substitution of the amine on aryl fluorides (Scheme 2).¹³ Subsequently, an employment of NaNO₂ (or Na¹⁵NO₂ for the ¹⁵N-labelled variants) and acetic acid generates a diazonium salt, which reacts intramolecularly with the secondary amine moiety to generate a 1,2,3-triazine ring. Lastly, we utilized a Cu(OAc)₂·H₂O-catalyzed C-N coupling reaction¹⁴ with an appropriate aryl-iodonium salt¹⁵ and replaced the anion using NaBAr^F to afford the desired nitrenium Lewis acid **6**.

Scheme 2. Preparation of diaryl-naphthotriazinium salts.



R = 4-MeOPh 6a, 4-Tol 6b, Ph 6c, 4-FPh 6d, 4-ClPh 6e

[I] Conditions: DMSO, 90°C, overnight; Reaction used for: **6a-c**; 42% yield. [II] Conditions: DMSO, 90°C, overnight; Reaction used for: **6d-e**; 30% yield. [III] Conditions: EtOH, room temperature, 4h; 82% yield [IV] Conditions: DMF, 60°C, 48-120h; For **6c**: R' = Ph, $X' = PF_6$; For

all else: R' = 2,4,6-trimethoxyphenyl, $X^- = TsO^-$; 78% yield. [V] Conditions: Toluene, room temperature, overnight; 99% yield.

All the aryl-substituted nitrenium Lewis acids **6a-e** were characterized by ¹H and ¹³C NMR (and ¹⁹F NMR for **6d**). The ¹⁵N-labelled variants **6c'** and **6e'** were also characterized by ¹⁵N NMR, revealing chemical shifts of 13.1 ppm and 12.7 ppm respectively. Acids **6c** and **6e*** (with the anion BPh₄⁻ (using NaBPh₄) instead of BAr^{F-} since crystallizing **6e** with BAr^{F-} was unsuccessful) were further characterized by single crystal X-ray crystallography (Figure 1).



Figure 1. POV-ray depictions of the X-ray structures of a) cation of **6c** and b) cation of **6e***. Anisotropic displacement ellipsoids set at 50% probability. The BAr^{F-} anion of **6c**, BPh₄⁻ anion of **6e*** and all H atoms are omitted for clarity. Selected bond lengths: a) N-N 1.299 Å. b) N-N 1.300 Å. Selected bond angles: a) N-N-N: 119.08°. b) N-NN: 119.28°.

Having in hand a new class of aryl-substituted nitrenium Lewis acids, we have examined them as catalysts in the hydrosilylation of imines (Table 1). Gratifyingly, catalyst **6e**, bearing 4-ClPh N-substituents generated product **5** in 99% yield within 8h under the optimized conditions (See SI Tables S1 and S2). Remarkably, the yield was retained (99%) when the reaction was scaled up to 1 gr of the starting imine **3**, while decreasing the catalyst loading to 0.1mol% (0.001 eq), demonstrating the high potency of nitrenium **6e** as a Lewis acid catalyst.

Ph 3	Ph + PhSiH ₃ $\xrightarrow{R_1^1, N_1 + N_1^2}_{Me} \xrightarrow{R_2^1}_{1mol\%} \xrightarrow{1mol\%}_{M.S. 4Å}_{DCM, 60°C, 8h}$	PhH ₂ Si N Ph	, Ph <u>H₂</u> O `Me	HN ^{∕P} ≻ Ph 5	h R ¹ N	P ⁺ Me ₃ N R ²	$\Delta G R$ ΔH Me_3P	
Entry	R^1, R^2	%Yield ^a	AN	ΔG [kcal mol ⁻¹]	ΔH [kcal mol ⁻¹]	E _{LUMO} [eV]	GEI [eV]	$\begin{array}{l} Hammett \\ \sigma_p{}^{19} \end{array}$
А	Me, Me $(1)^b$	28%	21.2	4.2	17.5	-3.50	4.05	-
В	Me, $CH_2CF_3(2)^{b}$	15%	22.2	11.4	24.7	-3.76	4.56	-
С	4-MeOPh, 4-MeOPh (6a)	18%	21.2	11.2	25.5	-3.63	4.32	-0.27
D	4-MePh, 4-MePh (6b)	9%	21.2	12.2	26.9	-3.65	4.36	-0.17
Е	Ph, Ph (6c)	52%	21.4	14.0	28.3	-3.70	4.45	0
F	4-FPh, 4-FPh (6d)	22%	22.0	13.6	28.4	-3.78	4.59	0.06
G	$4-ClPh, 4-ClPh (6e)^{c}$	99%	22.0	14.6	30.0	-3.80	4.64	0.23

Table 1. Yields of NLA-catalyzed hydrosilylation of imine **3**; Acidity number (AN) by the Gutmann-Beckett method; Dissociation energies of Lewis adducts of NLAs and Me₃P

^{*a*}Measured by ¹H NMR. ^{*b*}AN, Δ G, Δ H, E_{LUMO} and GEI for **1** and **2** were taken from our previous work.⁷ ^{*c*}99% yield was also obtained for 0.1 mol% catalyst loading.

The scope of ketimines and aldimines undergoing hydrosilylation using catalyst **6e** was thoroughly investigated. As seen in Scheme 3, Lewis acid **6e** can catalyze the hydrosilylation of a broad scope of ketimines and aldimines, carrying various substituents with electron withdrawing or donating groups, exhibiting good to excellent isolated yields of the final amine, yet with some notable exceptions. These exceptions, together with some clear trends for the reaction times of the differently substitutes imines, assisted us in elucidating the mechanism for the reaction (*vide infra*).



Scheme 3. Scope of the hydrosilylation of ketimines and aldimines catalyzed by NLA 6e.

We explored several physical organic parameters of our nitrenium catalysts and investigated the mechanistic details of the reaction to better understand the experimental data. Firstly, we employed the Gutmann-Beckett (G-B) method to experimentally examine the Lewis acidity of our newly synthesized nitrenium salts.¹⁶ Each acid was combined with Et₃PO in a 3:1 ratio in CD₂Cl₂ and the ³¹P NMR of the resulting solution was measured.¹⁷ The obtained acidity numbers (ANs) are provided in Table 1. Additionally, we utilized DFT computations to calculate the E_{LUMO} and Global Electrophilicity Index (GEI)¹⁸ of these Lewis acids in addition to the energy of dissociation (Δ G, Δ H) of the adducts formed by these acids and trimethylphosphine (Me₃P) (Table 1, see SI for the computational details).

According to all the tested parameters, nitrenium **1** has the lowest Lewis acidity of all the acids examined, including aryl-substituted acids which contain electron neutral and even electron donating groups, such as p-MeOPh. Consequently, it seems aryl-substituted nitrenium Lewis acids are inherently more Lewis acidic than their alkyl-substituted counterparts. As expected, nitrenium acids which are substituted with electron-withdrawing aryl groups, such as 4-FPh and 4-ClPh, possess higher Lewis acidity parameters than those substituted with electron-neutral or donating groups, such as Ph, 4-MePh and 4-MeOPh. Notably, the most effective catalyst **6e**, is also the most Lewis acidic nitrenium cation, thus it is evident that the Lewis acidity of the catalyst indeed plays a considerable role in the success of the reaction. Markedly, the deduced parameters show a good correlation to the Hammett substituent constant σ_p (Table 1 and Figures S3-S4 in the SI).¹⁹

To further investigate the Lewis acidity and hydride donor/acceptor ability of these new compounds, each of the acids **6c'** and **6e'** were separately combined with the ¹⁵N-labelled 1,3-dimethyl-2-*H*-naphthotriazane **1'-H** in an equimolar amount at room temperature (Scheme

10

4). In both experiments, a complete hydride transfer was observed by ¹H and ¹⁵N NMR after a few minutes of stirring, generating the triazanes **6c'-H** or **6e'-H** and nitrenium ion **1'**. This experiment demonstrates the facile hydride transfer capability of these nitrenium acids, while indicating the higher hydride affinity and Lewis acidity of the aryl-substituted nitrenium Lewis acids compared to their methyl-substituted counterpart. Additionally, our DFT calculation showed that the 4-ClPh-substituted acid **6e** possesses a significantly higher hydride affinity than the dimethyl-substituted acid **1** by a margin of 10.4 kcal/mol (Scheme 4).

Scheme 4. An experimental and calculated hydride transfer reaction between N-H triazane 1'-H and NLAs 6c' and 6e'.



To further confirm their molecular structures, triazanes **6c'-H** and **6e'-H** were independently prepared by direct reduction of the nitrenium acids **6c'** and **6e'** with NaBH₄. Both triazanes were isolated and fully characterized in solution by ¹H, ¹³C and ¹⁵N NMR. The ¹H NMR spectra of **6c'-H** and **6e'-H** exhibited a doublet at 6.68 ppm (${}^{1}J_{\text{H-N}} = 77 \text{ Hz}$) and 6.71 ppm (${}^{1}J_{\text{H-N}} = 78 \text{ Hz}$) respectively, corresponding to the nitrogen-bound H atoms. This clearly demonstrates a distinct de-shielding effect compared to the same chemical shift in **1'-H** of 5.5 ppm (${}^{1}J_{\text{H-N}} = 66 \text{ Hz}$).⁸ Additionally, compounds **6c'-H** and **6e'-H** were crystallized and their structures were confirmed by single-crystal X-ray diffraction (Figure 2).



Figure 2. POV-ray depictions of the X-ray structures of a) **6c-H** and b) **6e-H**. Anisotropic displacement ellipsoids set at 50% probability. All carbon-bound H atoms are omitted for clarity. Selected bond lengths: a) N1-N2 1.437 Å, N2-N3 1.422 Å, N2-H 0.965 Å. b) N1-N2 1.430 Å, N2-N3 1.425 Å, N2-H 0.917 Å. Selected bond angles: a) N1-N2-N3: 110.32°, N1-N2-H: 109.26°, N3 N2 H: 101.60°. b) N1-N2-N3: 110.88°, N1-N2-H: 107.58°, N3-N2-H: 105.75°.

The crystallographic analysis revealed that in both **6c-H** and **6e-H** the central nitrogen atom is out of plane with respect to the naphthalene ring and the two flanking nitrogen atoms, as expected for a pyramidalized saturated N-atom in the N-N-N motif.

We sought to gain some mechanistic clues of the nitrenium action in such type of catalytic reactions. Firstly, we performed the hydrosilylation with PhSiD₃ to confirm that the silane is indeed responsible for the formal hydride donation (Scheme 5a). Satisfyingly, when the deuterium-labeled silane reacted with imine **3** in the presence of a catalytic amount of nitrenium **6e**, the deuterated amine **5**" was detected in 76% yield by ²H (broad singlet at 4.48 ppm), ¹³C (1:1:1 triplet at 53.05 ppm for the *C*-D motif) and ¹H NMR.

Scheme 5. Mechanism study



a) Reaction of imine **3** with PhSiD₃: labelling experiment. b) Hydrosilylation of imines **24a** and **25a**: no cyclization products. c) Preparation of the silyl-iminium intermediate **41** in situ and a hydride transfer from **6e-H**.

We can contemplate at least three different mechanisms for the nitrenium-catalyzed hydrosilylation of imines. The first one is a direct activation of imines by the nitrenium Lewis acid catalyst, followed by a hydride transfer from the silane. As seen in Scheme 3, ketimines were generally found to react much faster than aldimines. Since aldimines are stronger Lewis bases than ketimines, the nitrenium should coordinate and thus activate the formers more efficiently according to this mechanism. Therefore, a direct activation of imines by the nitrenium ion should dictate a faster hydrosilylation reaction for aldimines, however, our results exhibited the opposite trend. Moreover, no changes were detected by NMR when catalyst **6e** was combined with a typical imine **3** in equimolar ratio (without the silane), indicating they do not form a strong Lewis adduct. Thus, this mechanism could likely be ruled out. Notably, these findings agree with the mechanistic conclusions of Piers for his hydrosilylation reaction of imines catalyzed by $B(C_6F_5)_3$.¹¹

The second scenario is a radical-based pathway in which an imine reduces the nitrenium ion by single electron transfer to result in an iminyl radical²⁰ cation $(R_2C=N^-R)^+$ as intermediate, which in turn induce a hydrogen atom transfer from the silane. To investigate this option, we have prepared the two imines **24a** and **25a** (Scheme 5b). These substrates smoothly undergo hydrosilylation to generate amines **24** and **25** in excellent yields (98% and 96% respectively) at a relatively moderate rate (9h). If the N- or C-centered radical species, substituted with butenyl or pentenyl units (iminyl radical cations derived from **24a** or **25a**), would be generated during the reaction, the fast intramolecular ring-closing process and the formation of the corresponding cyclization products would be expected. As no such products were observed, the suggested radical-type mechanism is most likely irrelevant. Moreover, we followed the reaction by EPR spectroscopy and no signal was detected on EPR, affirming this conclusion.

We believe that our nitrenium-catalyzed reaction is best explained by the FLP-type mechanism, analogous to the one described by Piers *et al.* for the $B(C_6F_5)_3$ -catalyzed hydrosilylation of carbonyls¹⁰ and imines,¹¹ which was corroborated in subsequent studies.²¹ The process starts with a simultaneous Si-H bond activation of the silane by the Lewis acidic nitrenium and Lewis basic imine (Scheme 6, **TS1**). This induces the cleavage of the Si-H bond, generating the N-H triazane **6-H** and a silyl-iminium intermediate **41A**. It should be noted that no reaction or any changes were observed by NMR when the catalyst was mixed with PhSiH₃ only, in the absence of imine. Importantly, we have recently demonstrated that nitrenium ions can serve as Lewis acids for the Si-H bond cleavage of silanes in a FLP-manner once combined with Lewis bases, generating the N-H triazanes.⁸ A hydride transfer between species **6-H** and **41A** completes the catalytic cycle to afford the silylamine product and regenerate the catalyst.

14

Scheme 6. Proposed catalytic cycle for the hydrosilylation of imines catalyzed by nitrenium Lewis acids



To test whether a triazane **6-H** can induce a hydride transfer to a silyl-iminium intermediate **41A** as the boron-ate anion $HB(C_6F_5)_3^{-1}$ does in the Piers mechanism,¹⁰⁻¹¹ we independently prepared the silyl-iminium species **41** *in situ* by combining PhSiH₂OTf and imine **3** (Scheme 5c). To this solution, we added the ¹⁵N-labelled **6e'-H**, and after stirring at room temperature overnight, a distinct amount of silylamine **4** was detected by the ¹H NMR in the reaction mixture. Moreover, the ¹⁵N NMR spectrum exhibited the formation of nitrenium acid **6e'**. This clearly demonstrates the feasibility of this mechanistic step (see Scheme 6). Since the hydride transfer from triazane **6e'-H** to silyl iminium cation **41** takes place at room temperature (Scheme 5c), whereas the whole process of hydrosilylation of amines requires elevated temperatures (60°C), we can presume that the Si-H bond cleavage is a rate limiting step in the catalysis. This hypothesis is confirmed by our DFT studies (*vide infra*).

This mechanism seamlessly explains the general tendency of ketimines to react faster than aldimines (Scheme 3). The larger Lewis basicity of aldimines causes their relatively strong

association to the nitrenium catalyst, thus they obstruct it, leading to a slower reaction overall. A special exception to this trend was observed for the reaction generating amine **23** ($R^2 = CF_3$), for which the rate was extremely low (91% yield after 5 days). Since the electron withdrawing CF₃ group is located so close to nitrogen atom, it renders the corresponding ketimine much less Lewis basic, thus it probably coordinates (activates) very weakly to the silane, greatly inhibiting the reaction rate.

Another important trend ratified by the suggested mechanism is that imines bearing electron withdrawing substituents, such as CF_3 or Cl on either R^1 or R^3 (which generate amines 7-9, 27-**29**; Scheme 3), react faster than imines carrying electron donating groups, such as OMe or tBu (which generate amines 11-13, 31-33). The electron withdrawing groups render the imine less basic, causing its possible reversible coordination to the nitrenium catalyst to be weaker, thus freeing the Lewis acid to react with the silane and therefore increase the reaction rate. Accordingly, electron donating groups have the opposite effect and thus decrease the reaction rate. For amines **21** ($R^3 = Bn$) and **35** ($R^1 = 4$ -Me₂NPh) the hydrosilylation reaction did not occur at all. We hypothesized that the corresponding imines might be excessively Lewis basic and thus coordinate too strongly to the nitrenium catalyst. To test this, we combined each of these imines separately with 0.01 eq of 6e in DCM without silane, and indeed, NMR spectrometry showed a complete disappearance of the original signals of catalyst 6e within a few minutes. As such, the Lewis basicity of the imine substrate likely plays a substantial role in the reaction since it interacts competingly with both the Lewis acidic nitrenium and the silane. Therefore, for the reaction to proceed effectively, the imine must be in a suitable nucleophilicity/basicity window.

We further investigated the proposed mechanism through a computational analysis. We also attempted to calculate the energy barrier for a direct activation of the imine by the nitrenium, however a local minimum for a nitrenium-imine adduct and a saddle point for the respective transition state could not be detected, thus this mechanism was further invalidated. Regarding our suggested mechanism, we calculated the free energy (ΔG) and enthalpy (ΔH) of the various materials, intermediates, and transition states for the hydrosilylation of imine **3** by PhSiH₃, catalyzed by nitrenium catalyst **1** (Scheme 7, see SI for the computational details). Catalyst **1** was chosen to simplify the calculation since it consists of a relatively simple nitrenium structure (methyl "arms"). Calculations for the reaction with catalyst **6** were performed only for the proposed rate limiting step (shown in red in Scheme 7).





As seen in scheme 7, the reaction is both exergonic $-\Delta G = -16.4$ kcal/mol and exothermic $-\Delta H = -30.5$ kcal/mol. As expected, the initial Si-H bond cleavage step is indeed the rate limiting step, possessing a relatively large energy barrier. Accordingly, with nitrenium **1** as the catalyst: $\Delta G^{\dagger} = 34.8$ kcal/mol, $\Delta H^{\dagger} = 9.2$ kcal/mol and with nitrenium **6e** as the catalyst: $\Delta G^{\dagger} = 32.5$ kcal/mol, $\Delta H^{\dagger} = 4.9$ kcal/mol. The smaller energy barrier calculated for nitrenium **6e** compared to its

counterpart **1** is consistent with our hypothesis that **6e** is the superior catalyst due to its stronger Lewis acidity. In addition, the calculations show that the *E* isomer of imine **3** leads to a slightly lower energy barrier than the *Z* isomer. We propose that the relatively large energy barrier ΔG^{\dagger} for the first step can be rationalized by the well-established overestimation of calculated free energies in solution.²² The currently ubiquitous procedure for calculation of free energy in solution utilizes gas phase formulae (ideal gas/rigid rotor/harmonic oscillator - IGRRHO). This approach overestimates entropic effects for reactions in solution, especially when molecularity is changed ($\Delta n \neq 0$). The current state of this challenge does not provide a simple solution (See SI for more details). Therefore, we realize that the real potential free energy surface lies between the calculated enthalpy and the calculated free energy surfaces, thus the real energy barrier ΔG^{\dagger} is presumably lower than the calculated figure.

CONCLUSIONS

In conclusion, we have revealed and developed a synthesis of a new generation of N-heterocyclic nitrenium Lewis acids – diaryl-substituted naphthotriazinium cations. The prepared Lewis acids as well as their reduced form, diaryl-N-H triazanes, were fully characterized by multinuclear NMR and X-ray techniques. We demonstrated the enhanced Lewis acidity and hydride affinity of this new class of nitrenium acids over the dialkyl-substituted variant both experimentally and computationally. These Lewis acids were utilized for the hydrosilylation of various ketimines and aldimines in yields up to 99%, while employing a modest catalyst loading of as low as 0.1 mol%. Notably, the dialkyl-substituted naphthotriazinium acids proved inefficient in this reaction. We elucidated, for the first time, the mechanistic action of the nitrenium Lewis acids in such reduction-type reactions. Our experimental and computational studies indicate that it likely involves the FLP-type activation of the Si-H bond in silane following by a hydride transfer from

18

the generated N-H triazane to the silyl-iminium cation. This confirms our hypothesis that the N-H triazanes can be considered as "molecular hydrides" and serve as unusual reducing agents. In our view, aryl-substituted nitrenium-based Lewis acids possess high potential for small molecule activation and catalysis, superior to the alkyl-substituted analogues. Studies for further applications are currently underway in our lab.

ASSOCIATED CONTENT

Supporting Information. Full experimental details, synthetic procedures, characterization data, copies of NMR spectra, crystallographic data, and computational methods and data are available (PDF).

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Notes

The authors declare no competing financial interest.

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 Up to 99% yield
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