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Authors: Meera Mehta and Jose Manuel Goicoechea

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Nitrenium Salts in Lewis Acid Catalysis

Meera Mehta* and Jose M. Goicoechea*

Abstract: Molecular compounds featuring nitrogen atoms are typically regarded as Lewis bases and are extensively employed as donor ligands in coordination chemistry or as nucleophiles in organic chemistry. By contrast, electrophilic nitrogen-containing compounds are much rarer. Nitrenium cations are a new family of nitrogen-based Lewis acids, the reactivity of which remains largely unexplored. In this work, nitrenium ions are explored as catalysts in five organic transformations. These reactions are the first examples of Lewis acid catalysis employing nitrogen as the site of substrate activation. Moreover, these compounds are readily accessed from commercially available reagents and exhibit remarkable stability toward moisture, allowing for benchtop transformations without the need to pretreat solvents.

Traditional examples of main-group Lewis acid catalysts involve group 13 and 14 elements as the central locus of reactivity, as they feature a low-lying orbital for substrate activation.^[1] Over the last decade there has been increasing interest in studying pnictogens, often considered Lewis basic given the availability of an energetically accessible lone pair, in this unconventional role. This work has been expanded to include compounds of phosphorus, ^[2-11] arsenic, ^[12] antimony, ^[13-20] and bismuth. ^[21-23] By contrast, the reactivity of nitrogen-containing compounds as Lewis acids has been investigated to a much lesser extent, largely due to the dearth of such species. Chloramines, nitrenes, diazocarboxylates, azides, and diazonium salts have been shown to possess N-centered electrophilic behavior. However, further reactivity of these compounds with nucleophiles often led to unstable intermediates and subsequent decomposition rather than adduct formation. [24-28]

Nitrenium cations, nitrogen-based Lewis acids that are isoelectronic with carbenes (R₂C:), were first reported in 1996 by Boche et al.^[29] It was found that bis(amino) ligands were necessary to isolate stable crystalline ions, as previously observed by Arduengo with imidazol-2-ylidenes.^[30] Related silyene, germylene, phosphenium and arsenium ions have also been reported.^[12,31–34] In 2011, Gandelman demonstrated that nitrenium cations can serve as ambiphilic ligands on rhodium and that they behave as weak σ -donors but considerable π -acceptors.^[36] Stoichiometric investigations of these ions with Lewis bases were also undertaken by Gandelman, demonstrating that the Lewis acidic centre is primarily located on the internal nitrogen (Figure 1).^[36] In 2018, Stephan and co-workers reported

 [a] Dr. Meera Mehta and Prof. Dr. Jose M. Goicoechea Department of Chemistry University of Oxford Chemistry Research Laboratory, Mansfield Rd., Oxford, OX1 3TA E-mail: meera.mehta@chem.ox.ac.uk; jose.goicoechea@chem.ox.ac.uk

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on the cyclic(alkyl)(amino)nitrenium ions and explored their reactivity in FLP chemistry.^[37,38] This display of Lewis acidity



prompted us to investigate these ions in Lewis acid catalysis.

Figure 1. N-heterocyclic nitrenium cations.

Lewis acid catalysts function by accepting electron density from a nucleophilic substrate, activating the substrate for subsequent reactivity. Some of the earliest reports of Lewis acid catalysts were based on titanium and zirconium.^[39] After this work, there was a movement to use boron and aluminium based compounds for similar chemistry.^[40,41] Generally, moving away from metal-based systems to main group catalysts reduces operational costs, particularly when separation of the catalyst from the product is necessary. Perhaps the most widely employed system in this category is tris(pentafluorophenylborane) [B(C6F5)3; BCF] due to its high Lewis acidity and ubiquitous use in frustrated Lewis pair (FLP) chemistry.^[42-45] It is worth noting however, that catalytic reactions employing BCF are often performed under inert conditions given its propensity to form a stable adduct with water and undergo further hydrolysis at elevated temperatures.[45-47] Herein, we prepared the nitrenium salts 1 and 2 (Scheme 1), and probed their Lewis acidity in an effort to benchmark them relative to more conventional Lewis acids. Next, we employed these salts to affect the Friedel-Crafts dimerization of 1,1-diphenylethylene, hydrodefluorination of 1-fluoroadamantane, deoxygenation of ketones, transfer hydrogenation of olefins, and dehydrocoupling of alcohols and amines with silanes.

In line with literature reports, compound **1** was prepared in moderate yield, by oxidation of diaminonapthalene and subsequent methylation.^[48] Noted in both this report by Bohle et al. and the crystallographic data acquired by us, a weak interaction between the Lewis acidic nitrogen centre and the trifluoromethanesufonate anion could be observed.



Scheme 1. Synthesis of nitrenium salts 1 and 2.

Counter-ion exchange with K[B(C₆F₅)₄] yielded an analytically pure sample of the novel salt **2** (Scheme 1). While ¹H and ¹³C NMR spectroscopy showed little change, single crystal X-ray diffraction studies revealed the absence of any significant cationanion interaction in compound **2**, shown in Figure 2.

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Figure 2. Molecular structure of **2**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms have been omitted for clarity, fluorine atoms pictured as spheres of arbitrary radius.

The Gutmann-Beckett test and global electrophility index DFT investigations were undertaken to assess the relative Lewis acidity of **1** and **2**.^[49,50] Both studies revealed them to be weak Lewis acids (see Supporting Information). Undeterred by these results, we focused our efforts on reactivity by studying **1** and **2** in five benchmark catalytic reactions (Figure 3).

First, the Friedel-Crafts dimerization of 1,1-diphenylethylene (**3a**) was examined. It was found that compound **1** did not act as a catalyst for this transformation even at 50 °C over 24h, whereas compound **2** afforded 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene (**3b**) in 20% conversion as determined by ¹H NMR spectroscopy. Under similar conditions, employing BCF as a catalyst resulted in 48% conversion. However, catalyst **2** gave similar conversion (26%) when stored on the bench for several weeks and the Friedel-Crafts dimerization of 1,1-diphenylethylene (**3a**) could be performed in air without the use of pre-dried solvents (Karl Fisher titrations of CH₂Cl₂ revealed 21.7 ppm of H₂O).

Next, the hydrodefluorination of 1-fluoroadamantane (**4a**) was examined. Catalyst **1** was able to affect this transformation; however complete conversion was observed only at 50 °C over 24h. By contrast, **2** gave complete conversion to adamantane (**4b**) after 5 hours under ambient conditions. This reaction was monitored by ¹⁹F NMR spectroscopy by probing the signal corresponding to **4a** (–128 ppm) which diminished over time accompanied by the appearance of a resonance for Et₃SiF (–175 ppm). BCF also gave complete conversion under similar conditions. We suspect that for this particular transformation all three catalysts act as initiators for silylium catalysis, consistent with a recent report by Stephan and Oestreich.^[51]

1 and **2** were also explored in the catalytic deoxygenation of benzophenone (**5a**) with triethylsilane to give diphenylmethane (**5b**) and the hexamethyldisiloxane. Consistent with the reactivity noted for reaction **A** (Figure 3) it was found that **1** did not catalyze this reduction even at 50 °C (only starting material was observed in the ¹H NMR spectrum). Catalyst **2** gave complete conversion within 5 hours under ambient conditions. Interestingly, Stephan and co-workers reported that in the same transformation BCF gave 9% conversion to diphenylmethane (**5b**) and 91% conversion to (benzhydryloxy)triethylsilane at 50 °C.^[8] As noted previously, catalyst **2** was able to affect this transformation in high

yield using standard bench techniques and wet solvent. This transformation serves to highlight both the unique stability and selectivity of **2** relatively to BCF.



Figure 3. Catalytic reactions explored with the nitrenium salts 1, 2 and BCF. Conversions determined by ¹H or ¹⁹F NMR spectroscopy. Isolated yields given in parenthesis.

Following these observations, catalysts **1** and **2** where investigated in the transfer hydrogenation of 1,1-diphenylethylene (**3a**) with 1,4-cyclohexadiene to yield ethane-1,1-diyldibenzene (**3c**). Again, the counter-ion played a significant role in the catalytic activity of **1** relative to **2**, with **1** being unable to catalyze this reaction while **2** yielded complete conversion within 5 hours. In 2017, Oestreich reported that 10 mol% of BCF affected this transfer hydrogenation after 16 hours to give 92% conversion to give ethane-1,1-diyldibenzene (**3c**), however a more decorated cyclohexadiene was employed as an H₂ source.^[52] Unlike the observations made by Oestreich, in the absence of substrate catalyst **2** did not dehydrogenate 1,4-cyclohexadiene to yield benzene. Consistent with the observations made for reaction **A** and **C**, catalyst **2** retained catalytic activity using standard bench techniques.

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Finally, both 1 and 2 were explored as catalysts for the dehydrocoupling of phenol (6a) with triethylsilane on the bench to give triethyl(phenoxy)silane (6b). As expected, catalyst 2 displayed high activity with complete conversion observed by ¹H NMR spectroscopy after 5 hours under ambient conditions. Similar reactivity has been reported for BCF by Piers and coworkers.^[53] While the air stability of compound 1 has been noted in the literature previously, it is interesting to note the naked nitrenium cation retains this property on exchange of the trifluoromethansulfonate ion for [B(C₆F₅)₄]⁻. Thus, no decomposition of 2 could be observed in CD₂Cl₂ over several weeks in air. Furthermore, no decomposition of either catalyst 1 or 2 could be observed by NMR spectroscopy during catalytic reactions A-E (Figure 3).

BCF mediated hydrosilylation of carbonyls was first reported by Piers and co-workers in 1996,[54] however there are few examples which result in the complete reduction of the carbonyl to a methylene group.^[8,55,56] Given the benchtop activity observed for nitrenium ion 2 to affect this reaction, we were interested in expanding this work. We found the hexamethyldisiloxane byproduct was not trivial to remove after this reduction and were interested in moving to a protocol with an easier work-up. Triethylsilane was replaced with polymethylhydrosiloxane (PMHS), a milder reducing agent with greater bench-top stability commonly used in organic and industrial laboratories. Upon deoxygenation of benzophenone (5a) to diphenylmethane (5b) with 10 mol% of 2 the polymeric silane cross-links to form a gel (see Supporting Information). Using the violet colour of the catalyst as an indicator, the siloxane gel was washed until clear allowing for the isolation of the final product in 98% yield.

Table 1. Deoxgenation reactions of ketones with catalytic amounts of 2.

R ¹	+ 2.5 eq PMHS $-rt$ R ²	10 mol% 2 , DCM, 24 h air R ¹	H, H R ²
Entry	substrate ^[a]	conv.(%) ^[b]	product
1	5a : R ¹ /R ² = H	>99 (98)	5b
2	7a : R ¹ = CI, R ² = H	97	7b
3	8a : R ¹ = Br, R ² = H	89	8b
4	9a : R ¹ = F, R ² = H	66	9b
5	10a : R ¹ = CF ₃ , R ² = H	73	10b
6	11a: R ¹ /R ² = Cl	98	11b
7	12a : R ¹ = CH ₃ , R ² = H	61	12b
8	13a : R ¹ = CH ₂ Br, R ² = H	64	13b

^[a] 2 (10 mol%, 10 mg) was added to a solution of ketone (0.1 mmol) and PMHS (17 mg, 0.3 mmol) in DCM (1.2 mL) at ambient temperature on the bench. ^[b] Determined by ¹H or ¹⁹F NMR spectroscopy (CD₂Cl₂, based on ketone). Isolated yields given in parenthesis.

In order to establish functional group tolerance, the deoxygenation of ketones with 10 mol% catalyst loading of compound **2** was explored (Table 1). It was found that both chloro- and bromo- substituents were well tolerated (**7a**, **8a**, **11a**) to give products **7b**, **8b** and **11b** in high conversion,

whereas moderate conversion was observed with a *para*fluoro subsistent (**9a**). Para-trifluoromethane substitution of substrate **10a** resulted in 73% conversion to **10b**, with no evidence of C–F bond activation. This is consistent with the observed C–F bond activation for 1-fluoroadamantane being a result of silylium catalysis, a process not possible in air. Furthermore, electron donating groups like *para*-methyl of **12a** were also tolerated to give **12b**. Similar to **10a**, carbonyl **13a** was reduced in moderate yield to give **13b** with no dehalogenation. Benzophenone derivatives functionalized with methoxy, cyano or amino groups displayed little to no conversion to the corresponding deoxygenated products. The presence of competing donors, either in the form of a counterion (as with compound **1**) or functional groups on the substrate, resulted in lower conversions.

Table 2. Transfer hydrogenation reactions of alkenes with catalytic amounts of 2.



Entry	substrate ^[a]	conv.(%) ^[b]	produc t
1	3a : R ¹ /R ² = Ph, R ³ /R ⁴ = H	>99(89)	3c
2	14a : R ¹ = 3-CIPh, R ² = Ph, R ³ /R ⁴ = H	91	14b
3	15a : R ¹ /R ⁴ = Ph, R ² /R ³ = H	0	15b
4	16a : R ¹ /R ³ = Ph, R ² /R ⁴ = H	0	16b
5	17a : R ¹ /R ² = Ph, R ³ = Ph, R ⁴ = H	84	17b
6	18a : R ¹ /R ² = Ph, R ³ = 4-BrPh, R ⁴ = H	46	18b
7	19a : R ¹ /R ² = 4-CIPh, R ³ /R ⁴ = CI	0	19b
8	20a : R ¹ /R ² = Ph, R ³ /R ⁴ = Ph	0	20b

^[a] 2 (10 mol%, 10 mg) was added to a solution of olefin (0.1 mmol) and 1,4-cyclohexadiene (14 mg, 0.2 mmol) in DCM (0.7 mL) at ambient temperature on the bench. ^[b] Determined by ¹H NMR spectroscopy (CD₂Cl₂, based on olefin). Isolated yields given in parenthesis.

Transfer hydrogenation, formal transfer of an H₂ molecule, from an organic reagent allows for reduction of a substrate without the inconvenience and hazards of using gaseous H₂. We were interested in exploring the utility of air stable catalyst 2 to mediate this reaction (Table 2). Yet again, to increase conversion a 10 mol% catalyst loading was used. As expected, 1,1diphenylethylene (3a) gave complete conversion to 3c upon benchtop reduction with catalyst 2. Additionally, meta-chloro substitution in compound 14a was tolerated and gave high conversion to 14b. By contrast, moving to 1,2-diaryl substituted alkenes like cis- and trans-stilbene gave no conversion. This transfer hydrogenation is thought to go through FLP- like activation of the 1,4-cyclohexadiene resulting in protonation of the olefin to give a carbocation and nitrenium-hydride complex. Thus, the stilbene derivatives would yield the less stable secondary carbocation, whereas 1,1-diarylsubsituted would yield a more stable tertiary carbocation. This mechanism is also consistent as

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no reaction is observed when nitrenium cation 2 is exposed to 1,4cyclohexadiene in the absence of substrate. Both tri-substituted alkenes 17a and 18a were converted to 17b and 18b in high to moderate yields. Finally, both tetrasubstituted alkenes 19a and 20a showed no conversion to 19b and 20b, presumably due to steric encumbrance.

Table 3. Dehydrocoupling reactions of alcohols and diphenylamine with catalytic amounts of $\ensuremath{2}.$

$$R^{1}EH + HSiR^{2}_{3} \xrightarrow{5 \text{ mol}\% 2} R^{1}ESiR^{2}_{3}$$

E = O, N air

Entry	substrate (RE ¹ H) ^[a]	silane (HSiR ² ₃)	conv.
1	PhOH (6a)	HSiBu₃	>99 (41)
2	4-CIC ₆ H ₄ OH (21a)	HSiEt₃	>99 (54)
3	4-MeC ₆ H ₄ OH (22a)	HSiEt₃	>99 (62)
4	4- <i>t</i> BuC₀H₄OH (23a)	HSiEt₃	95%
5	Ph ₂ NH (24a)	HSiEt₃	>99 (31)

 $^{[s]}$ **2** (5 mol%, 5 mg) was added to a solution of substrate (0.1 mmol) and silane (Et₃SiH: 13 mg, 0.1 mmol, Bu₃SiH: 23 mg, 0.1 mmol) in DCM (1 mL) at ambient temperature on the bench. $^{[b]}$ Determined by ¹H NMR spectroscopy (CD₂Cl₂, based on R¹H). Isolated yields given in parenthesis.

Finally, the benchtop catalytic dehydrocoupling of alcohols with silanes to eliminate hydrogen gas and form an O-Si was expanded on. Catalytic benchtop transformations of this nature are of importance because silanes are employed as protecting groups for alcohols and amines in organic laboratories. This transformation has been previously reported with the more airsensitive Lewis acid BCF by Piers, however they observed diminished reactivity with bulky silanes such as HSiBu3 and HSi[/]Pr₃.^[53] We found that this reactivity could be expanded to HSiBu3 with phenol to afford PhOSiBu3 (6c) under ambient conditions with 5 mol% 2, but not HSiⁱPr₃. Furthermore, under similar reaction conditions both the electron-withdrawing substituent, in the case of 21a, and electron-donating substituents, in the case of 22a and 23a, were well tolerated and afforded 21b, 22b, or 23b in high conversion. Finally, diphenylamine (24a) was dehydrocoupled with triethylsilane to give 24b in complete conversion.

In conclusion, we report the preparation of the naked nitrenium cation **2** by a salt metathesis reaction of **1** with K[B(C₆F₅)₄]. Despite the difficulties with benchmarking these N-based Lewis acids using classical techniques like the Gutmann-Beckett test and the GEI we explored these systems in five catalytic transformations. Although direct comparison to boron-based systems is still inconclusive, it was found that moving to the less-coordinating anion [B(C₆F₅)₄]⁻ had a remarked impact on catalytic activity. Furthermore, catalyst **2** retained catalytic activity using traditional benchtop techniques and wet solvent. The deoxygenation of ketones, transfer hydrogenation of olefins, and dehydrocoupling of alcohols was expanded on. Investigations into this new class of Lewis acids in catalysis and as a counterpart in FLP chemistry to affect small molecule activation is currently underway.

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Keywords: Nitrenium ions • Lewis acids • Catalysis • Ketone deoxygenation • Transfer hydrogenation

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Entry for the Table of Contents

Layout 2:

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We explore the use of nitrenium salts as Lewis acid catalysts in five organic transformations. Despite their weakly acidic character, these species proved competent catalysts in a number of benchmark transformations. The moisture-stability of the salts allows for the reactions to be carried on the benchtop without the need for pre-dried solvents.

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