



Fasano, V., Radcliffe, J. E., Curless, L. D., & Ingleson, M. J. (2017). N-Methyl-Benzothiazolium Salts as Carbon Lewis Acids for SiH -Bond Activation and Catalytic (De)hydrosilylation. *Chemistry - A European Journal*, 23(1), 187-193. <https://doi.org/10.1002/chem.201604613>

Publisher's PDF, also known as Version of record

License (if available):
CC BY

Link to published version (if available):
[10.1002/chem.201604613](https://doi.org/10.1002/chem.201604613)

[Link to publication record in Explore Bristol Research](#)
PDF-document

This is the final published version of the article (version of record). It first appeared online via Wiley at <https://doi.org/10.1002/chem.201604613> . Please refer to any applicable terms of use of the publisher.

University of Bristol - Explore Bristol Research

General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available:
<http://www.bristol.ac.uk/pure/about/ebr-terms>

Frustrated Lewis Pairs | Hot Paper |

N-Methyl-Benzothiazolium Salts as Carbon Lewis Acids for Si–H σ -Bond Activation and Catalytic (De)hydrosilylationValerio Fasano, James E. Radcliffe, Liam D. Curless, and Michael J. Ingleson^{*[a]}

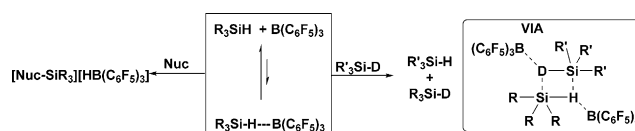
Abstract: *N*-Me-Benzothiazolium salts are introduced as a new family of Lewis acids able to activate Si–H σ bonds. These carbon-centred Lewis acids were demonstrated to have comparable Lewis acidity towards hydride as found for the triarylboranes widely used in Si–H σ -bond activation. However, they display low Lewis acidity towards hard Lewis bases such as Et₃PO and H₂O in contrast to triarylboranes. The *N*-Me-benzothiazolium salts are effective catalysts for

a range of hydrosilylation and dehydrosilylation reactions. Judicious selection of the C2 aryl substituent in these cations enables tuning of the steric and electronic environment around the electrophilic centre to generate more active catalysts. Finally, related benzoxazolium and benzimidazolium salts were found also to be active for Si–H bond activation and as catalysts for the hydrosilylation of imines.

Introduction

The use of hydridophilic main-group Lewis acids, particularly B(C₆F₅)₃, in Si–H bond activation,^[1] and more broadly in “frustrated Lewis pair” (FLP) chemistry,^[2] has generated significant recent breakthroughs.^[3] This includes their use as versatile catalysts for dehydrosilylation and hydrosilylation reactions.^[4] Generally, the Lewis acids employed are tri(fluoroaryl)boranes which have sufficient Lewis acidity towards hydride to heterolytically cleave Si–H bonds (in combination with an appropriate Lewis base) and generate borohydrides that are able subsequently to reduce electrophilic substrates. Mechanistic studies revealed that Si–H heterolysis is an S_N2 type process proceeding via a “partially” activated Si–H bond, which can be viewed as a “Si–H–B” 3c–2e interaction,^[5,6] with one example recently crystallographically characterised.^[7] In the absence of an appropriate nucleophile no silylium ions are formed from combining B(C₆F₅)₃ and R₃SiH, although silane H/D scrambling still proceeds via a four-membered transition state (inset Scheme 1).^[7]

In more recent studies, weaker boron Lewis acids, such as BPh₃, also have been shown also to be effective in Si–H bond activation.^[8] Nevertheless, the high oxophilicity of boron Lewis acids requires rigorously dried conditions (or an excess of hy-



Scheme 1. Silane activation with B(C₆F₅)₃.

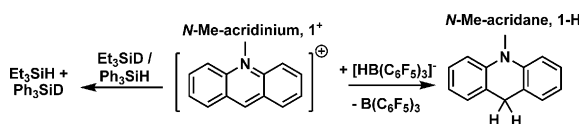
dride)^[9] and leads to substrate scope limitations.^[10] Consequently, the development of new Lewis acids that have low oxophilicity but retain sufficient Lewis acidity towards hydride to activate E–H (E=H or R₃Si) bonds is desirable.^[11] Lewis acids in which carbon is the locus of electrophilic character have significant potential in this area as the higher electronegativity of carbon (relative to boron) results in a reduction in “hard” Lewis acidity.^[12] Trityl salts are amongst the most widely utilised carbon Lewis acids including in catalytic applications. However, these catalytic transformations generally proceed by activation of the substrate by coordination to the electrophilic carbon centre in trityl and not by an FLP-type mechanism.^[12,13] The use of trityl salts and other carbon Lewis acids in FLP chemistry, including the activation of H₂, has significantly less precedent, although a limited number of examples have been recently reported.^[14]

Carbocations including trityl, are well documented to irreversibly cleave Si–H bonds to form silylium cations and Ph₃CH.^[15] In contrast, carbon Lewis acids that “partially” activate Si–H bonds (e.g., exhibit analogous reactivity to B(C₆F₅)₃) are extremely rare to the best of our knowledge. One recent example from our group are *N*-methyl-acridinium salts which activate Si–H bonds (Scheme 2) as indicated by Si–H/Si–D scrambling experiments but no silylium cations are observed in solution.^[16] However, the Lewis acidity of the *N*-Me-acridinium cation (1⁺) towards hydride is greater than that of B(C₆F₅)₃.^[17] This makes the conjugate organic hydride, *N*-Me-acridane (1-

[a] V. Fasano, Dr. J. E. Radcliffe, Dr. L. D. Curless, Dr. M. J. Ingleson
School of Chemistry, University of Manchester
Manchester, M13 9PL (UK)
E-mail: Michael.ingleson@manchester.ac.uk

Supporting information for this article and ORCID(s) from the authors can be found under:
<http://dx.doi.org/10.1002/chem.201604613>.

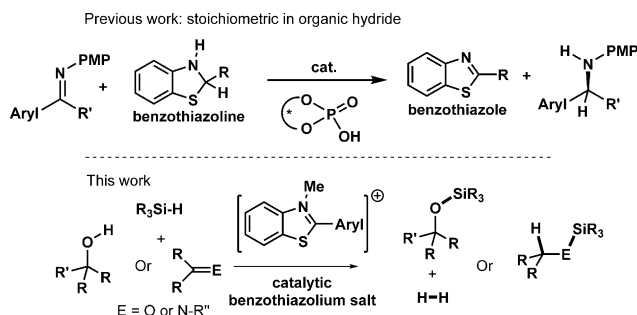
© 2016 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.



Scheme 2. E–H bond activation using $[N\text{-Me-acridinium}]^+$.

H), formed for example on Si–H heterolysis by 1^+ and an appropriate nucleophile, a poor reductant. This fact combined with the propensity of *N*-Me-acridinium salts to initiate photo-activated radical reactivity^[18] led us to search for other carbon Lewis acids able to “partially” activate Si–H bonds but that are weaker Lewis acids towards hydride than 1^+ .

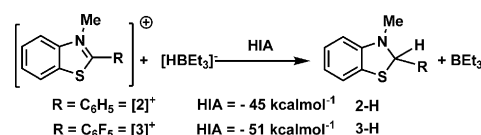
Previous work has shown that C2 substituted benzothiazolines are highly effective organic hydrides for the reduction of imines catalyzed by phosphoric acids (Scheme 3, top).^[19] Based on this precedence, we targeted the oxidised form, the benzothiazole, as a potential carbon Lewis acid after methylation at nitrogen to increase the electrophilicity at the C2 position. *N*-Me-2-*R*-benzothiazolium cations are attractive Lewis acids as they are simple to make using established routes and can be readily fine-tuned e.g., by altering the C2 substituent.^[19] Furthermore, they represent a hitherto underexplored class of Lewis acid in FLP-type catalysis, namely a Lewis acid based on an iminium cation, a moiety which is generally considered as a substrate for reduction and not as a catalyst. Herein we demonstrate that *N*-Me-2-aryl-benzothiazolium salts are able to activate Si–H bonds and are effective as catalysts for dehydrosilylation and hydrosilylation reactions.



Scheme 3. Top, Brønsted acid catalyzed transfer hydrogenation of imines using stoichiometric benzothiazoline. Bottom, benzothiazolium cation catalyzed hydrosilylation and dehydrosilylation using stoichiometric silane.

Results and Discussion

Initially, the hydride ion affinity (HIA)²⁰ of the *N*-methyl-2-phenylbenzothiazolium cation (2^+) relative to BEt_3 was computationally determined and found to be $-45 \text{ kcal mol}^{-1}$ (Scheme 4). This is comparable to that calculated previously for $\text{B}(\text{C}_6\text{F}_5)_3$ ($-41 \text{ kcal mol}^{-1}$ M06-2X/6-311G(d,p) with dichloromethane (DCM) solvation (Polarizable Continuum model, PCM). Furthermore, this HIA value is less than that found for 1^+ ($-53 \text{ kcal mol}^{-1}$)^[15] suggesting 2^+ is a more appropriate Lewis acid for use in catalytic imine reductions as its conjugate organic hydride will be more reducing than 1-H . The C2-penta-



Scheme 4. Relative (to BEt_3) HIA values of 2^+ and 3^+ .

fluorophenyl analogue, 3^+ , also was calculated and found to have an HIA of $-51 \text{ kcal mol}^{-1}$ indicating it is less suitable for use in catalytic reductions (as its conjugate hydride, 3-H , will be a poorer reductant).

Due to its suitable calculated HIA value *N*-methyl-2-phenylbenzothiazolium iodide was synthesized and metathesized with AgOTf , NaBPh_4 and NaBARCl ($\text{BARCl} = [\text{B}(\text{3,5-Cl}_2\text{-C}_6\text{H}_3)_4]^-$) to afford $2^+[\text{Anion}]$ (Anion = OTf , BPh_4 , BARCl , respectively) in moderate to good yields in each case. Single crystals of the triflate salt were obtained from MeCN/ *ortho*-dichlorobenzene (*o*-DCB) which revealed a non-planar cation with an angle of 47.8° between the plane of the phenyl ring and that of the thiazole ring, with the *N*-Me group preventing a co-planar arrangement (Figure 1). The closest cation/anion contact involv-

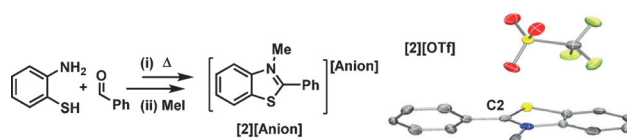
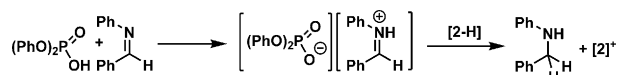


Figure 1. Synthesis and X-ray structure of $2^+[\text{Anion}]$. Red = oxygen, yellow = sulfur, grey = carbon, blue = nitrogen, light green = fluorine.

ing the electrophilic C2 position is long and involves a triflate oxygen located at 3.324 \AA , a distance that is significantly greater than the combined covalent radii of carbon and oxygen.^[21] The low oxophilicity of 2^+ indicated by this structure was confirmed by the lack of any evidence for binding of H_2O to $2^+[\text{BARCl}]$; furthermore, no O–H heterolytic cleavage was observed on addition of 2,6-lutidine and H_2O to a DCM solution of $2^+[\text{BARCl}]$ (in contrast to what is observed with $\text{B}(\text{C}_6\text{F}_5)_3$ and other Lewis acidic boranes).^[22] The combination of one equivalent of Et_3PO and three equivalents of $2^+[\text{BARCl}]$ only led to a small downfield shift in the $^{31}\text{P}\{^1\text{H}\}$ resonance ($\Delta\delta = 4.4 \text{ ppm}$) confirming the weak Lewis acidity of 2^+ towards hard Lewis bases (for comparison $\text{B}(\text{C}_6\text{F}_5)_3$ gives a $\Delta\delta$ of 33.7 ppm).^[23]

Seeking to experimentally assess the relative Lewis acidity of 2^+ towards hydride, compound 2-H and $\text{B}(\text{C}_6\text{F}_5)_3$ were combined in DCM. This led to rapid (< 5 minutes) hydride transfer and formation of $2^+[\text{HB}(\text{C}_6\text{F}_5)_3]$, thus $\text{B}(\text{C}_6\text{F}_5)_3$ is a stronger Lewis acid towards hydride than 2^+ . In contrast, combining 2-H and BPh_3 led to no hydride transfer, suggesting the Lewis acidity of 2^+ towards hydride lies between that of BPh_3 and $\text{B}(\text{C}_6\text{F}_5)_3$. Both these boranes can activate H_2 and Si–H bonds,^[1,8b,24] thus analogous bond activations using $2^+[\text{Anion}]$ should be thermodynamically viable. The activation of H–H or Si–H is only the initial step in a putative catalytic cycle, with subsequent hydride transfer to the substrate also required.

Recent studies have highlighted the importance of correctly balancing the electrophilicity of the substrate (e.g., an iminium cation) and the reducing power of the organic hydride to achieve successful transfer hydrogenation.^[25] Thus, we investigated the diphenylphosphoric acid initiated reduction of *N*-benzylidene-aniline, employing [2-H] as the hydride source (Scheme 5). Using equimolar ratios this produced *N*-benzylaniline in around 50% conversion, with conversion limited due to the amine product deprotonating the iminium cation (full imine reduction can be achieved by using >2 equivalent of the phosphoric acid). These reactions confirm that 2-H is a more accessible source of hydride for reductions than 1-H.



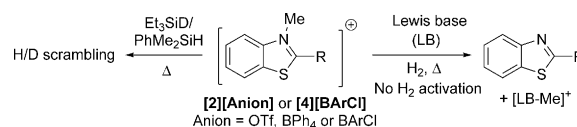
Scheme 5. Phosphoric acid initiated *N*-benzylidene-aniline reduction with 2-H.

E–H bond activation studies

Compounds [2][BPh₄] and [2][BArCl] (5 mol %) both induced H/D scrambling between Et₃SiD and PhMe₂SiH, albeit only at raised temperatures (80 °C in MeCN for the former and at 60 °C in DCM for the latter in sealed tubes). In contrast, no scrambling was observed between Ph₃SiH and Et₃SiD using [2][BArCl] (at 60 °C in DCM for 24 h) presumably due to the greater steric bulk of Ph₃SiH. This is consistent with the less bulky silane Ph₂MeSiH, that has a similar kinetic nucleophilicity to Ph₃SiH (*N* parameter values of 2.72 and 2.65, respectively),^[26] undergoing H/D exchange with Et₃SiD in the presence of [2][BArCl]. Triarylboranes are also competent at activating Si–H bonds,¹ therefore control reactions were performed to preclude the possibility that a Lewis acidic borane, potentially formed in situ by anion decomposition by trace protic impurities,^[27] is leading to Si–H activation. Notably, utilising the identical batch of NaBPh₄ used to prepare [2][BPh₄] no H/D scrambling between Et₃SiD and PhMe₂SiH was observed under identical conditions (at 5 mol % NaBPh₄ loading for 20 h at 80 °C in MeCN), thus silane H/D scrambling is being mediated by the carbon Lewis acid [2]⁺. This is further confirmed by [2][OTf] also resulting in H/D scrambling between PhMe₂SiH and Et₃SiD (at 80 °C in MeCN) albeit more slowly than observed with both borate anions. The requirement for raised temperatures for H/D scrambling with [2]⁺ may in part be attributed to strong anion cation interactions which need to be overcome before silane activation occurs. Indeed the diffusion coefficients (by diffusion ordered spectroscopy (DOSY) experiments) are identical for the cationic and anionic components of [2][BArCl] in DCM and in acetone, consistent with the existence of intimate ion pairs in these solvents.^[28]

FLPs were generated by combining [2][BArCl] with equimolar 2,6-lutidine, 1,8-bis(dimethylamino)naphthalene and 4-DMAP. The absence of any observable Lewis adduct between [2]⁺ and 4-DMAP is notable and in contrast to the reactivity of both [1]⁺ and B(C₆F₅)₃ towards 4-DMAP,^[16,29] further indicating

the low Lewis acidity of [2]⁺ towards hard Lewis bases. A modified benzothiazolium salt containing a *para*-*t*Bu-phenyl C2-substituent, [4][BArCl], was also explored in FLPs with these three amine Lewis bases in an attempt to use the steric bulk provided by a *t*Bu substituent to weaken cation–anion interactions. However, combinations of [2][BArCl] or [4][BArCl] and these amines resulted in no H₂ activation (100 °C in *o*-DCB for 16 h, ca. 4 atm. of H₂). FLPs containing [4]⁺ and stronger Lewis bases, such as PtBu₃ and Verkade's base also showed no propensity to activate H₂ (ca. 4 atm. at 60 °C or 100 °C). In these cases slow demethylation of the benzothiazolium salt proceeded to form, for example, [Me–PtBu₃]⁺ (Scheme 6).



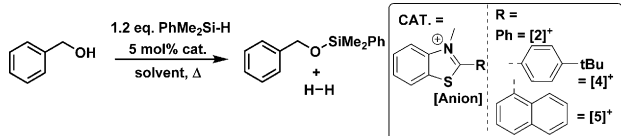
Scheme 6. Activation of E–H bonds using benzothiazolium salts. LB for example = PtBu₃.

Catalytic studies

Three different benzothiazolium cations containing phenyl ([2]⁺), *p*-*t*Bu-phenyl ([4]⁺) and 1-naphthyl ([5]⁺) C2-substituents were evaluated as catalysts in dehydrosilylation and hydrosilylation reactions. Cations [4]⁺ and [5]⁺ were selected to alter steric bulk distal (in the case of [4]⁺) and proximal ([5]⁺) to the C2 electrophilic centre relative to that in [2]⁺. It should be noted that the incorporation of a *para*-*t*Bu substituent will also affect the electrophilicity at the C2 position, an effect confirmed by HIA calculations which revealed that [4]⁺ is 1 kcal mol⁻¹ less Lewis acidic towards hydride relative to [2]⁺. The initial reaction studied was the dehydrosilylation of benzyl alcohol using PhMe₂SiH.^[30] Although the parent iodide salts (e.g. [2][I]) resulted in no dehydrosilylation using the [OTf] and [BPh₄] salts dehydrosilylation occurred in DCM but was extremely slow (Table 1, entries 1–3). Dehydrosilylation could be accelerated to some extent for the [BPh₄] salts by using a more polar solvent (e.g., MeCN, Table 1, entries 4,5). The [BArCl] salts were significantly more active catalysts and thus only salts containing this anion were studied hereon. The three benzothiazolium [BArCl] salts showed minimal differences as catalysts for benzyl alcohol (BnOH) dehydrosilylation (entries 6–9) which proceeded rapidly at 20 °C in DCM in each case.

A number of control reactions were performed to ensure that protonolysis of the borate anion is not leading to an active borane catalyst under these conditions. Anion decomposition has been previously reported on heating NaBPh₄ in wet solvents which led to the formation BPh₃.^[27,31] Using 5 mol% Na[BPh₄] (at 80 °C for 24 h in MeCN) or 5 mol% Na[BArCl] (20 h at 20 °C or 5 h at 80 °C in MeCN) no dehydrosilylation of BnOH was observed. In contrast, under identical conditions both [2][BPh₄] and [4][BArCl] lead to significant dehydrosilylation (entries 4 and 10). Moreover, BPh₃ was confirmed to be an active catalyst for the dehydrosilylation of BnOH in MeCN under these conditions (40% in 20 h at 80 °C), consistent with

Table 1. Dehydrosilylation of benzyl alcohol with benzothiazolium salts.



Entry	Catalyst	Solvent	Time [h]	Temp [°C]	Yield [%] ^[a]
1	[2][BPh ₄]	DCM	40	60	8
2	[5][BPh ₄]	DCM	40	60	13
3	[5][OTf]	DCM	45	60	12
4	[2][BPh ₄]	MeCN	24	80	76
5	[5][BPh ₄]	MeCN	24	80	72
6	[2][BArCl]	DCM	1	20	94
7	[2][BArCl]	MTBE	1	20	94
8	[5][BArCl]	DCM	1	20	86
9	[4][BArCl]	DCM	1	20	84
10	[4][BArCl]	MeCN	24	20	60

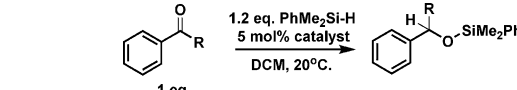
[a] Conversion by NMR spectroscopy versus mesitylene as an internal standard.

Okuda's original observation of EtOH dehydrosilylation catalyzed by BPh₃.^[8b] Thus the complete absence of BnOH dehydrosilylation using Na[B(Aryl)₄] in MeCN indicates that B(Aryl)₃ (or any other borane able to initiate dehydrosilylation) is not being formed by anion decomposition. These results combined confirm that under these conditions catalytic BnOH dehydrosilylation is initiated by the benzothiazolium salts and not by Lewis acidic boranes derived from anion decomposition.^[32]

[5][BArCl] also catalyzes the dehydrosilylation of BnOH in DCM with Ph₃SiH with 57% conversion at 60 °C after 24 h. This is slower than with B(C₆F₅)₃^[30] using the same silane/alcohol which proceeds at room temperature. This indicates a significantly greater kinetic barrier using the benzothiazolium salt as catalyst. Phenol also underwent dehydrosilylation catalyzed by [4][BArCl] (76% conversion after 2 h at 20 °C in DCM) precluding an alcohol dehydrogenation/ carbonyl hydrosilylation mechanism. Benzothiazolium salts also dehydrosilylate water to form the respective siloxane, thus alcohol dehydrosilylation proceeds using non-purified solvents (using excess silane) and also in more environmentally friendly solvents such as methyl *tert*-butyl ether (MTBE).

Another established B(C₆F₅)₃ catalyzed reaction is the hydrosilylation of carbonyls reported by Piers and co-workers.^[5] Using the three benzothiazolium[BArCl] salts for carbonyl hydrosilylation led to differences in the rate of benzaldehyde (Table 2 entries 1–3) and acetophenone (Table 2 entries 4–6) hydrosilylation. With both substrates the C2-(1-naphthyl) substituted catalyst [5][BArCl] results in the slowest rate of hydrosilylation suggesting that either greater steric hindrance around the C2 centre or stronger cation–anion interactions are retarding the rate of hydrosilylation using this catalyst. HIA calculations on [5]⁺ revealed it has an effectively identical Lewis acidity towards hydride as found for [2]⁺ (–45.5 and –45.4 kcal mol^{–1}, respectively) precluding the reactivity disparity originating from different degrees of Lewis acidity to hydride (which in turn would lead to differing degrees of silane activation and differing reducing powers of 5-H and 2-H).

Table 2. Hydrosilylation of benzaldehyde and acetophenone.



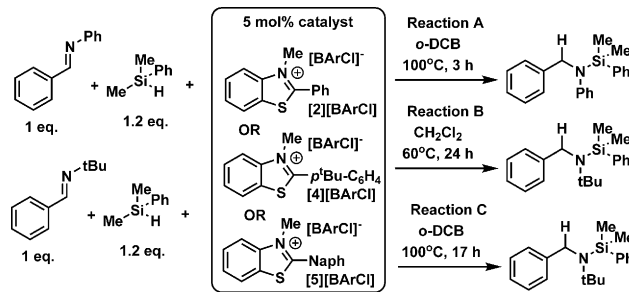
Entry	Catalyst	R	Time [min]	Yield [%] ^[a]
1	[2][BArCl]	H	60	92
2	[5][BArCl]	H	60	10
3	[4][BArCl]	H	60	90
4	[2][BArCl]	Me	15	> 99
5	[5][BArCl]	Me	15	40
6	[4][BArCl]	Me	15	> 99

[a] Conversion by NMR spectroscopy versus mesitylene as an internal standard.

Other features of carbonyl hydrosilylation using benzothiazolium salts are comparable to that reported for B(C₆F₅)₃. For example, an equimolar mixture of acetophenone/benzaldehyde/PhMe₂SiH led to hydrosilylation of the more nucleophilic substrate, benzaldehyde, preferentially in the presence of 5 mol% [4][BArCl]. Moreover, attempts to selectively hydrosilylate ethyl benzoate using 1.2 equivalents of PhMe₂SiH in the presence of [4][BArCl] led to mixtures of products consistent with the silyl acetal product undergoing further reduction competitively to ester hydrosilylation, again analogous to that observed using B(C₆F₅)₃.^[5] Finally, a control reaction using 5 mol% NaBArCl in the hydrosilylation of acetophenone resulted in no reaction (after 60 minutes at 20 °C in DCM) indicating that catalytic activity is again due to the benzothiazolium salt.

Benzothiazolium[BArCl] salts were also effective catalysts for the hydrosilylation of imines, albeit at raised temperatures. Whilst all three benzothiazolium catalysts reduced *N*-benzylidene aniline at 100 °C in *o*-DCB (Table 3) considerable disparities in catalyst activity were observed in the hydrosilylation of the less electrophilic imine *N*-benzylidene-*tert*-butylamine. Both [2][BArCl] and [5][BArCl] were inactive for the hydrosilylation

Table 3. Imine hydrosilylation using [n][BArCl] as catalyst.

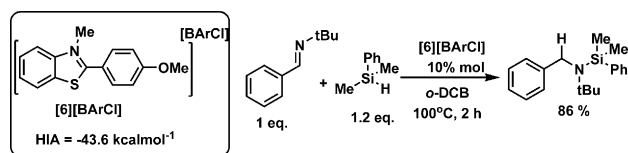


Catalyst	HIA [kcal mol ^{–1}]	Yield [%] ^[a]		
		Reaction A	Reaction B	Reaction C
[2][BArCl]	–45.4	76	0	24
[4][BArCl]	–44.4	60	97	76
[5][BArCl]	–45.5	54	0	20

[a] Conversion by NMR spectroscopy versus mesitylene as an internal standard.

of *N*-benzylidene-*tert*-butylamine with PhMe₂SiH at 60 °C, whilst catalysis did proceed at 100 °C it was extremely slow with both salts. In contrast, [4][BARCl] was able to catalyse the hydrosilylation of both of these imines, including *N*-benzylidene-*tert*-butylamine at 60 °C in DCM. The disparities in activity between the benzothiazolium salts are attributed to the lower HIA of [4]⁺ relative to [2]⁺ and [5]⁺. This results in the conjugate hydride of [4]⁺, 4-H, being a stronger reducing agent thus more effective at reducing the silylated iminium cation derived from *N*-benzylidene-*tert*-butylamine. The effectiveness of benzothiazolium salts in catalytic imine hydrosilylation is therefore dependent on the difference in electrophilicity between the silylated iminium cation and the benzothiazolium cation.

A decrease in the HIA of the benzothiazolium cation (relative to [4]⁺) was explored targeting more rapid iminium cation reduction by increasing the reducing power of the conjugate hydride.^[26] Thus [6][BARCl] (Scheme 7, left), containing a MeO



Scheme 7. Imine hydrosilylation using [6][BARCl].

group in the *para* position of the C2-phenyl substituent was synthesized using standard procedures. HIA calculations on [6]⁺ confirmed a reduced HIA value, with [6]⁺ being 0.8 kcal mol⁻¹ less Lewis acidic towards hydride than [4]⁺, indicating the conjugate hydride 6-H should be more reducing than 4-H. Utilizing 5 mol% of [6][BARCl] the hydrosilylation of *N*-benzylidene-*tert*-butylamine led to more rapid hydrosilylation relative to [4][BARCl], with around 50% conversion after 3 h at 100 °C. However, heating this reaction for longer did not lead to any further imine hydrosilylation. This is attributed to a catalyst deactivation process as the use of 10 mol% of [6][BARCl] led to 86% hydrosilylation of *N*-benzylidene-*tert*-butylamine in 2 hours (at 100 °C in *o*-DCB).

With [4][BARCl] identified as the more robust catalyst (relative to [6][BARCl]) a brief substrate scope exploration was performed. This revealed that using the less bulky silane PhMe₂SiH in place of PhMe₂SiH led to more rapid imine hydrosilylation (Table 4, entries 1 and 2), whilst the bulkier silane Ph₂MeSiH significantly retarded the rate of hydrosilylation (entries 3,4). The hydrosilylation of the less hindered imines *N*-benzylidenebenzylamine and *N*-benzylidene-methylamine were both extremely slow using [4][BARCl] (entry 5 and 6). The ¹H NMR spectra for [4][BARCl] revealed no significant changes to the resonances for [4][BARCl] before and after addition of *N*-benzylidene-methylamine, even with 20 equivalents of *N*-benzylidene-methylamine, precluding any appreciable Lewis adduct formation. In contrast, mixtures of B(C₆F₅)₃ and this imine form a strong Lewis adduct.^[10] However, when [4][BARCl] was combined with 1 or 5 equivalents of this imine the *N*-Me ¹H NMR

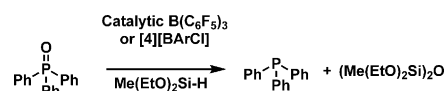
Table 4. Imine hydrosilylation using [4][BARCl] as catalyst.

Entry	R	R ¹	R ²	Time [h]	Yield [%] ^[a]
1	<i>t</i> Bu	Me	Me	17	76
2	<i>t</i> Bu	Me	H	17	98
3	Ph	Me	Me	3	60
4	Ph	Ph	Me	44	73
5	CH ₂ Ph	Me	Me	72	43 ^[b]
6	Me	Me	Me	48	22 ^[b]

[a] % Conversion by NMR spectroscopy versus mesitylene as an internal standard. [b] Imine consumption.

resonance was significantly broadened suggesting a non-covalent interaction (e.g., H-bonding or π -stacking) between the imine and [4]⁺ which maybe impacting its rate of hydrosilylation. Although [4][BARCl] catalyses the hydrosilylation of carbonyls and imines it does not catalyse the hydrosilylation of alkynes (e.g., phenylacetylene or 1-phenyl-1-propyne) with PhMe₂SiH (even at 100 °C), consistent with the lower Lewis acidity of the [4]⁺ towards hydride (relative to B(C₆F₅)₃) leading to a lower degree of silane activation and thus a weaker silicon electrophile.^[8a]

To compare the catalytic activity of [4][BARCl] in another reaction involving a nucleophile that forms a Lewis adduct with B(C₆F₅)₃ the reduction of a phosphine oxide was investigated. Oestreich, Stephan and co-workers have recently utilized B(C₆F₅)₃ to reduce phosphine oxides with silanes.^[33] Replacing B(C₆F₅)₃ with [4][BARCl] under identical conditions led to the quantitative reduction of Ph₃PO to Ph₃P (Scheme 8), although at a slower rate relative to that catalyzed by B(C₆F₅)₃. This is despite the absence of any observable Lewis adduct on combining equimolar [4]⁺ and Ph₃PO. A control reaction using 5 mol% NaBARCl resulted in no significant phosphine oxide reduction under identical conditions again indicating catalytic activity is initiated by [4]⁺.



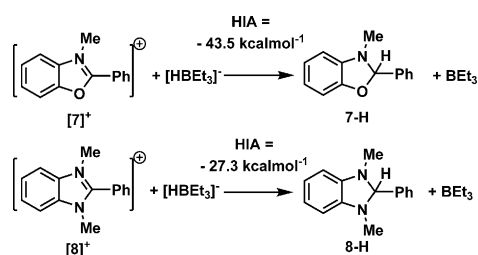
Scheme 8. Ph₃PO reduction using [4][BARCl].

Benzoxazolium and benzimidazolium cations as Lewis acids

With an understanding of the catalytic ability of *N*-Me-benzothiazolium[BARCl] salts in hand the related cations, *N*-Me-2-phenyl-benzoxazolium, [7]⁺, and *N,N*-Me₂-2-Ph-benzimidazolium, [8]⁺ were investigated. From previous calorimetry studies *N*-Me-2-Ph-benzoxazoline, 7-H, is reported to have a significantly lower, and *N,N*-Me₂-2-Ph-benzimidazoline, 8-H, a significantly higher hydride donating ability relative to 2-H.^[34] The latter was consistent with HIA calculations (Scheme 9), however, [8]⁺

and $[2]^+$ were calculated to have HIA values within 2 kcal mol⁻¹ of each other. In fact, the only major significant calculated difference between $[2]^+$ and $[7]^+$ is related to the charge distribution, with a more polarized σ -bonding framework in $[7]^+$ leading to a greater positive NBO charge localized at C2 in $[7]^+$ relative to $[2]^+$ (+0.56 and +0.20, respectively).

Salts $[7][I]$ and $[8][I]$ were obtained by methylating the neutral precursors with MeI. Subsequent metathesis with NaBARCl provided $[7][BARCl]$ and $[8][BARCl]$. Confirmation of the greater hydride donating ability of **8-H** relative to **2-H** and **7-H** was confirmed by the combination of **8-H** with $[2][BARCl]$ (or $[7][BARCl]$). This led to complete consumption of **8-H** and the formation of $[8][BARCl]$ and **2-H** (or **7-H**), after heating to 60 °C for 2 h in DCM (Scheme 9). Despite the increased magnitude



Scheme 9. Calculated (relative to BEt₃) hydride ion affinity values of $[7]^+$ / $[8]^+$.

of positive charge at C2 in $[7][BARCl]$ there is no evidence for binding of H₂O or one equivalent of Et₃PO (by NMR spectroscopy) indicating $[7]^+$ is a weak Lewis acid toward hard Lewis bases. Consistent with this the combination of $[7][BARCl]$ with 2,6-lutidine, 4-DMAP and PtBu₃ resulted in FLP formation with no evidence for any coordination to $[7]^+$. However, no H₂ activation was observed for any of these FLP combinations. In contrast, both $[7][BARCl]$ and $[8][BARCl]$ were effective for the activation of silanes, with H/D exchange observed between Et₃SiD and PhMe₂SiH. To assess the catalytic activity of $[7][BARCl]$ and $[8][BARCl]$ relative to $[2][BARCl]$ (the latter selected as it has an identical C2-substituent) the hydrosilylation of *N*-benzylidene-*tert*-butylamine was explored (Table 5). This was selected as it is a reaction that was found to be sensitive to

variation in the C2-substituents of the benzothiazolium salts. Both $[7][BARCl]$ and $[8][BARCl]$ were active for the hydrosilylation of imines confirming that they are also effective Lewis acid catalysts, with conversions similar to that observed for $[2][BARCl]$. The small differences in relative conversions are attributed to different degrees of silane activation (lower with the less Lewis acidic $[8]^+$) and reducing powers of the conjugate hydride (higher in **8-H**).

Conclusion

N-Me-C2-Aryl-benzothiazolium cations represent a new family of readily tuned Lewis acids that show activity in frustrated Lewis pair (FLP) chemistry. They are based on cationic iminium moieties containing an electrophilic carbon centre that has a Lewis acidity towards hydride comparable to the triarylboranes widely used in FLP reactivity. However, in contrast to the triarylboranes these cations show little propensity to bind hard Lewis bases such as, H₂O, Et₃PO and 4-DMAP. A range of benzothiazolium salts “partially” activate the Si–H bond of silanes, as indicated by H/D scrambling. Furthermore, they are effective catalysts^[35] in a range of established FLP-type (de)hydrosilylation reactions with rational tuning of the C2-aryl substituent enhancing catalytic activity. The ability of a cationic iminium moiety to initiate catalytic (de)hydrosilylation reactions by activation of silane σ -bonds is notable as these moieties are viewed generally as substrates for reduction in FLP chemistry and not as catalysts themselves.

Experimental Section

Supporting Information for this article includes experimental details, spectra, computational and crystallographic data. CCDC 1501133 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Acknowledgements

This work was made possible by financial support from the EPSRC (EP/K03099X/1 and EP/M023346/1), and the Royal Society (for the award of a University Research Fellowship). Dr Alex Pulis is thanked for useful discussions. Additional research data supporting this publication are available as supplementary information accompanying this publication.

Keywords: benzothiazolium salts · frustrated Lewis pairs · hydrosilylation · Lewis acids · organocatalysis

Table 5. Imines hydrosilylation using $[n][BARCl]$ as catalyst.

Entry	E (Catalyst)	Conversion [%] ^[a]
1	S ($[2][BARCl]$)	24
2	O ($[7][BARCl]$)	25
3	NMe ($[8][BARCl]$)	38

[a] conversion by NMR spectroscopy versus mesitylene as an internal standard.

[1] W. E. Piers, A. J. V. Marwitz, L. G. Mercier, *Inorg. Chem.* **2011**, *50*, 12252–12262.

[2] a) G. Erker, D. W. Stephan in *Frustrated Lewis Pairs I, Uncovering and Understanding*, (Eds.: G. Erker, D. W. Stephan), Springer, Heidelberg, Germany, **2013**; b) G. Erker, D. W. Stephan in *Frustrated Lewis Pairs II, Expanding the Scope*, (Eds.: G. Erker, D. W. Stephan), Springer, Heidelberg, Germany, **2013**.

[3] For the original report on using B(C₆F₅)₃ to activate Si–H bonds see: D. J. Parks, W. E. Piers, *J. Am. Chem. Soc.* **1996**, *118*, 9440–9441.

- [4] For a recent review see: a) M. Oestreich, J. Hermeke, J. Mohr, *Chem. Soc. Rev.* **2015**, *44*, 2202–2220; b) for the use of electrophilic phosphonium cations in analogous chemistry see: M. Pérez, Z.-W. Qu, C. B. Caputo, V. Podgorny, L. J. Hounjet, A. Hansen, R. Dobrovostsky, S. Grimme, D. W. Stephan, *Chem. Eur. J.* **2015**, *21*, 6491–6500 and references therein.
- [5] D. J. Parks, J. M. Blackwell, W. E. Piers, *J. Org. Chem.* **2000**, *65*, 3090–3098.
- [6] S. Rendler, M. Oestreich, *Angew. Chem. Int. Ed.* **2008**, *47*, 5997–6000; *Angew. Chem.* **2008**, *120*, 6086–6089.
- [7] A. Y. Houghton, J. Huralmainene, A. Mansikkamaki, W. E. Piers, H. M. Tuononen, *Nat. Chem.* **2014**, *6*, 983–988.
- [8] For the use of non-fluorinated and partially fluorinated triarylboranes in FLP-type chemistry: a) S. Keess, A. Simonneau, M. Oestreich, *Organometallics* **2015**, *34*, 790–799; b) D. Mukherjee, D. F. Sauer, A. Zanardi, J. Okuda, *Chem. Eur. J.* **2016**, *22*, 7730–7733; c) F. Bertini, V. Lyaskovskyy, B. J. J. Timmer, F. J. J. de Kanter, M. Lutz, A. W. Ehlers, J. C. Slootweg, K. Lammertsma, *J. Am. Chem. Soc.* **2012**, *134*, 201–204; d) D. Mukherjee, S. Shirase, K. Mashima, J. Okuda, *Angew. Chem. Int. Ed.* **2016**, DOI: 10.1002/anie.201605236.
- [9] J. W. Thomson, J. A. Hatnean, J. J. Hastie, A. Pasternak, D. W. Stephan, P. A. Chase, *Org. Process Res. Dev.* **2013**, *17*, 1287–1292.
- [10] For example, unhindered imines do not undergo hydrosilylation using $B(C_6F_5)_3$: J. M. Blackwell, E. R. Sonmor, T. Scoccitti, W. E. Piers, *Org. Lett.* **2000**, *2*, 3921–3923.
- [11] For a review on Lewis acids in that are not based on boron in FLPs see: a) S. A. Weicker, D. W. Stephan, *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1003–1016; b) For a recent publication highlighting the importance of lower oxophilicity/moisture stability see: c) S. Postle, V. Podgorny, D. W. Stephan, *Dalton Trans.* **2016**, *45*, 14651–14657.
- [12] V. R. Naidu, S. Ni, J. Franzen, *ChemCatChem* **2015**, *7*, 1896–1905.
- [13] For a recent example see: E. Mosafieri, D. Ripsman, D. W. Stephan, *Chem. Commun.* **2016**, *52*, 8291–8293.
- [14] a) G. D. Frey, V. Lavallo, B. Donnadiu, W. W. Schoeller, G. Bertrand, *Science* **2007**, *316*, 439–441; b) B. Inés, S. Holle, R. Goddard, M. Alcarazo, *Angew. Chem. Int. Ed.* **2010**, *49*, 8389–8391; *Angew. Chem.* **2010**, *122*, 8567–8569; c) J. W. Runyon, O. Steinhof, H. V. Rasika Dias, J. C. Calabrese, W. J. Marshall, A. J. arduengo III, *Aust. J. Chem.* **2011**, *64*, 1165–1172; d) M. P. Boone, D. W. Stephan, *J. Am. Chem. Soc.* **2013**, *135*, 8508–8511; e) E. R. Clark, M. J. Ingleson, *Organometallics* **2013**, *32*, 6712–6717; f) K. F. Kalz, A. Brinkmeier, S. Dechert, R. A. Mata, F. Meyer, *J. Am. Chem. Soc.* **2014**, *136*, 16626–16634; g) J. Auth, J. Padevet, P. Mauleon, A. Pfaltz, *Angew. Chem. Int. Ed.* **2015**, *54*, 9542–9545; *Angew. Chem.* **2015**, *127*, 9678–9681.
- [15] a) J. B. Lambert, L. Kania, S. Zhang, *Chem. Rev.* **1995**, *95*, 1191–1201; b) C. A. Reed, *Acc. Chem. Res.* **1998**, *31*, 325–332; c) H. F. T. Klare, M. Oestreich, *Dalton Trans.* **2010**, *39*, 9176–9184.
- [16] E. R. Clark, M. J. Ingleson, *Angew. Chem. Int. Ed.* **2014**, *53*, 11306–11309; *Angew. Chem.* **2014**, *126*, 11488–11491.
- [17] E. J. Lawrence, E. R. Clark, L. D. Curless, J. M. Courtney, R. J. Blagg, M. J. Ingleson, G. G. Wildgoose, *Chem. Sci.* **2016**, *7*, 2537–2543.
- [18] D. J. Wilger, J.-M. M. Grandjean, T. R. Lammert, D. A. Nicewicz, *Nat. Chem.* **2014**, *6*, 720–726 and references therein.
- [19] C. Zhu, K. Saito, M. Yamanaka, T. Akiyama, *Acc. Chem. Res.* **2015**, *48*, 388–398.
- [20] For HIA calculations on main group Lewis acids see: a) E. R. Clark, A. Del Grosso, M. J. Ingleson, *Chem. Eur. J.* **2013**, *19*, 2462–2466; b) Z. M. Heiden, A. P. Lathem, *Organometallics* **2015**, *34*, 1818–1827.
- [21] B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan, S. Alvarez, *Dalton Trans.* **2008**, 2832–2838.
- [22] a) S. J. Geier, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 3476–3477; b) D. J. Scott, T. R. Simmons, E. J. Lawrence, G. G. Wildgoose, M. J. Fuchter, A. E. Ashley, *ACS Catal.* **2015**, *5*, 5540–5544; c) V. Fasano, J. E. Radcliffe, M. J. Ingleson, *ACS Catal.* **2016**, *6*, 1793–1798.
- [23] A. E. Ashley, T. J. Herrington, G. G. Wildgoose, H. Zaher, A. L. Thompson, N. H. Rees, T. Krämer, D. O'Hare, *J. Am. Chem. Soc.* **2011**, *133*, 14727–14740.
- [24] S. Mummadi, D. K. Unruh, J. Zhao, S. Li, C. Krempner, *J. Am. Chem. Soc.* **2016**, *138*, 3286–3289.
- [25] I. Chatterjee, M. Oestreich, *Org. Lett.* **2016**, *18*, 2463–2466.
- [26] M. Horn, L. H. Schappele, G. Lang-Wittkowski, H. Mayr, A. R. Ofial, *Chem. Eur. J.* **2013**, *19*, 249–263.
- [27] For the decomposition of $NaBPh_4$ on heating in wet benzene see: M. H. Chisholm, J. C. Gallucci, H. Yin, *Dalton Trans.* **2007**, 4811–4821.
- [28] P. S. Pregosin, *Prog. Nucl. Magn. Reson. Spectrosc. Spec.* **2006**, *49*, 261–288.
- [29] M. J. G. Lesley, A. Woodward, N. J. Taylor, T. B. Marder, I. Cazenobe, I. Ledoux, J. Zyss, A. Thornton, D. W. Bruce, A. K. Kakkar, *Chem. Mater.* **1998**, *10*, 1355–1365.
- [30] J. M. Blackwell, K. L. Foster, V. H. Beck, W. E. Piers, *J. Org. Chem.* **1999**, *64*, 4887–4892.
- [31] In related work MCl_2 salts activated with $Na[B(Aryl)_4]$ have been used to activate silane Si–H bonds and the possibility of anion decomposition leading to catalytically active borane Lewis acids was considered. See: Q. Yin, H. F. T. Klare, M. Oestreich, *Angew. Chem. Int. Ed.* **2016**, *55*, 3204; *Angew. Chem.* **2016**, *128*, 3256–3207.
- [32] Using 5 mol% $NaBArCl$ in DCM a small amount of dehydrosilylation of $BnOH$ was observed ($<10\%$ 1 h, $20^\circ C$ in DCM). This is much slower than dehydrosilylation using benzothiazolium $[BArCl]$ salts, indicating that the benzothiazolium cation is also the key initiating species in DCM. Analysis of the as synthesized $NaBArCl$ revealed extremely minor levels of impurities (identified as 3,5-dichlorobromobenzene and tetrachlorobiphenyl at $<1\%$ levels) with no observable $B(Aryl)_3$. Therefore the low activity observed in DCM is attributed to protic species (H_2O or ROH) leading to slow $NaBArCl$ decomposition to form the respective triarylborane. Presumably in MeCN coordination of MeCN to Na^+ (in preference to $BnOH/H_2O$) prevents anion protonolysis by a $[Na(ROH)]^+$ species and the formation of a boron Lewis acid.
- [33] M. Mehta, I. Garcia de la Arada, M. Perez, D. Porwal, M. Oestreich, D. W. Stephan, *Organometallics* **2016**, *35*, 1030–1035.
- [34] X.-Q. Zhu, M.-T. Zhang, A. Yu, C.-H. Wang, J. P. Cheng, *J. Am. Chem. Soc.* **2008**, *130*, 2501–2516.
- [35] Whilst the initial silane activation step requires the carbon Lewis acid we acknowledge it is feasible that subsequent catalytic cycles are mediated by a silicon electrophile, for a related example using a strong Bronsted acid see: Q.-A. Chen, H. F. T. Klare, M. Oestreich, *J. Am. Chem. Soc.* **2016**, *138*, 7868.

 Manuscript received: September 29, 2016

Accepted Article published: October 25, 2016

Final Article published: November 22, 2016