Synthetic Methods

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N-Methylacridinium Salts: Carbon Lewis Acids in Frustrated Lewis Pairs for σ-Bond Activation and Catalytic Reductions**

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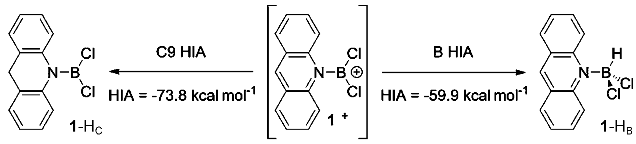
Abstract: *N-methylacridinium salts are Lewis acids with high hydride ion affinity but low oxophilicity. The cation forms a Lewis adduct with 4-(N,N-dimethylamino)pyridine but a frustrated Lewis pair (FLP) with the weaker base 2,6-lutidine which activates H_2, even in the presence of H_2O. Anion effects dominate reactivity, with both solubility and rate of H_2 cleavage showing marked anion dependency. With the optimal anion, a N-methylacridinium salt catalyzes the reductive transfer hydrogenation and hydrosilylation of aldimines through amine–boranes and silanes, respectively. Furthermore, the same salt is active for the catalytic dehydrosilylation of alcohols (primary, secondary, tertiary, and ArOH) by silanes with no observable over-reduction to the alkanes.*

Frustrated Lewis pairs (FLPs), pioneered by Stephan and co-workers,[1] represent a versatile new method for small-molecule activation, and have been successfully applied to the catalytic hydrogenation of a range of substrates.[2] Related systems also activate the Si–H bond in silanes, thus enabling catalytic (*de*)hydrosilylation.[3,4] Fluoroaryl boranes, typified by $B(C_6F_5)_3$, are the most commonly studied Lewis acids within the field. Despite their clear utility, these boranes are not without drawbacks, the principal ones being cost and high oxophilicity which can limit their utility and stability in wet solvents and tolerance to functional groups.[5] Other main-group Lewis acids, including aluminum,[6] silicon,[7] and phosphorus[8] systems, have been exploited in FLPs, but these remain extremely oxophilic and in many cases the H_2-activation products are not amenable to further catalytic application. Thus there is a demand for cheaper, less oxophilic Lewis acids for FLP applications.

Softer carbon-centered Lewis acids were shown by the groups of Bertrand[9] and Arduengo[10] to activate H_2, but the high hydride ion affinities (HIA) of these compounds preclude application in reduction processes. Alcarazo and co-workers have used electron-poor allenes as weaker carbon Lewis acids,[11] which do activate RS–SR bonds but are incapable of H_2 activation. The realization of carbon Lewis acid based FLPs for catalyzing reductions was first reported by Stephan and co-workers using $[((Ph_2PC_6H_4)_2B(\eta^6\text{-}C_6H_5))RuCl][B(C_6F_5)_4]$.[12] This compound, whilst able to activate H_2 with an appropriate base, still contains a precious metal. Thus the goal of utilizing a metal-free, inexpensive carbon Lewis acid for FLP-based reductions remains to be realized.

In our prior work, the borocation $\mathbf{1}^+$ (Scheme 1) was found to act as a Lewis acid either at boron or at the C9-position of the acridine moiety, depending upon the reaction



Scheme 1. Hydride ion affinities of $\mathbf{1}^+$ (relative to Et_3B).

conditions.[13] Computational determination of HIAs confirmed that the C-centered HIA is greater than that at boron by 13.9 kcal mol^{-1}. The high HIA of $\mathbf{1}^+$ at the carbon atom is not surprising, as N-alkyl acridinium species have been investigated as model compounds for the biological hydride transfer system NADH/NAD$^+$.[14,15] *N*-Methylacridinium salts ($\mathbf{2}^+$; see Table 1 for structure) are particularly attractive Lewis acids as they: a) are easy to synthesize, b) are indefinitely air and moisture stable,[14] and c) show little propensity to coordinate H_2O, thus indicating low oxophilicity. Herein we report the incorporation of $\mathbf{2}^+$ into FLPs which activate H–H, Si–H, and B–H bonds and are catalysts for the reduction of imines, as well as the dehydrosilylation of alcohols.

Initially the HIA of $\mathbf{2}^+$ was quantified[16] and computationally determined to be -53.3 kcal mol^{-1} (Table 1), 20.5 kcal mol^{-1} less than the C-centered value for $\mathbf{1}^+$. The marked difference is ascribed to the additional stabilization afforded by significant B=N bond character in **1**-H$_C$ (Scheme 1). The HIA of $\mathbf{2}^+$ was nevertheless found to exceed that of the model compounds of the conjugate Lewis acids of known hydride donors, that is, Hantzsch ester ($\mathbf{3}^+$) and a NADH model ($\mathbf{4}^+$). Significantly, $\mathbf{2}^+$ has a considerably lower HIA than Ph_3C^+ (consistent with the experimental observation of hydride abstraction from *N*-methylacridane by Ph_3C^+),[14b] essential for transferring a hydride to substrates post H_2 activation. It is however, still 12.3 kcal mol^{-1} greater than that of $B(C_6F_5)_3$, thus indicating that H_2 activation in a FLP with an appropriate base will be thermodynamically favored.[17]

A range of [**2**]X salts [X = I, SbF_6, BPh_4, tetra(3,5-dichlorophenyl)borate (hereafter BAr^{Cl})][18] were readily available in excellent yield by methylation of acridine with

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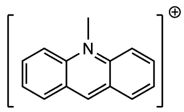
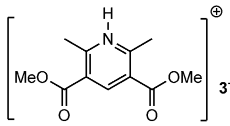
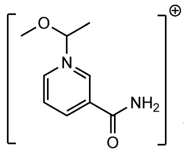
Table 1: HIAs (relative to Et_3B) at the M06-2X/6-311G(d,p), PCM(DCM) level.

Lewis Acid	HIA [kcal mol^{-1}]
$[Ph_3C]^+$	−75.3
 2^+	−53.3
 3^+	−43.1
$B(C_6F_5)_3$	−41.0
 4^+	−39.6

methyliodide and subsequent anion exchange with the appropriate metathesis reagent. [**2**]SbF_6, [**2**]BPh_4, and [**2**]BAr^{Cl} were crystallographically characterized as well-separated ion pairs, and show good correlation with calculated structural metrics of $\mathbf{2}^+$. The crystal structure of [**2**]SbF_6 is shown in Figure 1 as an example.

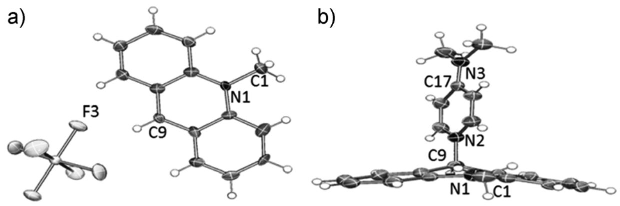


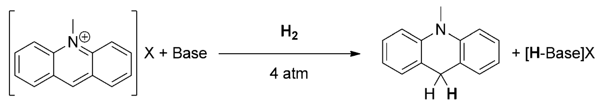
Figure 1. a) Molecular structure of **2**[SbF_6] and b) molecular structure of [**2**-(4-DMAP)]BAr^{Cl}, **6** (only one molecule from the asymmetric unit is shown, and counterions and disordered solvent are omitted for clarity). Thermal ellipsoids are drawn at 50% probability. Selected bond lengths [Å]: For **2**[SbF_6]: C(1)-N(1) 1.487(14), closest C-$FSbF_5$ distance C(9)-F(3) 3.348(15). For [**2**-(4-DMAP)]BAr^{Cl}, **6**: C(1)-N(1) 1.471(4), C(9)-N(2) 1.525(4), C(17)-N(3) 1.335(3).

Experimental confirmation for the predicted higher HIA relative to $B(C_6F_5)_3$ was obtained by the abstraction of hydride from [(2,6-lutidine)H][$HB(C_6F_5)_3$] by [**2**]BAr^{Cl} to yield *N*-methylacridane (**5**) and $B(C_6F_5)_3$. Upon combination of 3 equivalents of [**2**]BAr^{Cl} with Et_3PO, to determine Lewis acidity by the Gutmann–Beckett method,[19] a $\Delta\delta^{31}$P of 4.3 ppm was determined, which is much lower than that of $B(C_6F_5)_3$ (at $\Delta\delta^{31}$P 26.8 ppm).[20] The addition of crotonaldehyde to [**2**]BAr^{Cl} in CH_2Cl_2 (the Childs' method for assessing Lewis acidity)[21] resulted in a minimal downfield shift of the H3 proton with a $\Delta\delta^{1}$H of 0.02 ppm. Thus $\mathbf{2}^+$ is a significantly weaker Lewis acid towards Et_3PO and crotonaldehyde than $B(C_6F_5)_3$, in marked contrast to the ordering of the HIAs. These remarkable differences, coupled with the observations that [**2**]BAr^{Cl} exhibits no observable H_2O coordination (by ^{1}H NMR spectroscopy) and that the halide salts [**2**]X (X = Cl, Br, I) exist as well-separated ion pairs[21] (closest C9-X contact of 3.896(3) Å for [**2**]Cl·H_2O), indicates that the Lewis acidity of these species may be regarded as soft and orbital controlled, and thus hydride selective.

[**2**]BAr^{Cl} forms FLP systems with oxidation-resistant nitrogen-donor bases with moderate steric demand (e.g. 2,6-lutidine). In contrast, a 1:1 admixture of [**2**]BAr^{Cl} and 4-DMAP results in adduct formation between acid and base in solution, typified by the upfield shift of the N-methyl resonance in the ^{1}H NMR spectra from δ_{1H} 4.50 ppm (for free acridinium cation) to δ_{1H} 3.67 ppm (δ_{1H} = 3.35 ppm in **5**). The adduct [**2**-(4-DMAP)]BAr^{Cl} (**6**) can be isolated in good yield and crystallizes with two metrically similar ion pairs in the asymmetric unit (thus only one is discussed herein). C9 in **6** is strongly pyramidalized (the sums of non-N bond angles about C9 are 328.20°) and the acridinium moiety folds along the C(1)-N(1)-C(9) axis by 20.99° (trans-annular folding of 1.22° in [**2**]SbF_6). The donor-acceptor N−C bonds are comparable to those of other alkylated 4-DMAP compounds consistent with strong dative bonding.[23]

The FLPs of **2**[anion] and 2,6-lutidine were exposed to four atmospheres of H_2 and slow H_2 bond cleavage occurred at 60 °C, with significant dependency of the rate of the reaction upon the anion (Table 2). [**2**]SbF_6 was found to undergo minimal H_2 activation (entry 1) as a result of anion decomposition, thus leading to a complex and intractable mixture of degradation products. Whilst [**2**]BPh_4 is almost completely insoluble in CH_2Cl_2, it nevertheless displayed the greatest rate of H_2 activation at 60 °C (entry 2), albeit still taking over five days to approach completion. From this data we conclude that the rate of activation is in fact rapid compared to that of [**2**]BAr^{Cl} (entry 3), but severely limited by solubility. [**2**]BAr^{Cl} was chosen for further experiments by virtue of its improved solubility, and overall anion and

Table 2: FLP activation of H_2.[a]



2 **5**

Entry	Lewis acid	Lewis base	*T* [°C]	Completion (*t*)[b]
1	[**2**]SbF_6	2,6-lutidine	60[c]	13% (135 h)[f]
2	[**2**]BPh_4	2,6-lutidine	60[c]	92% (135 h)[g]
3	[**2**]BAr^{Cl}	2,6-lutidine	60[c]	97% (234 h)
4	[**2**]BAr^{Cl}	2,6-lutidine	100[d]	98% (23 h)
5	[**2**]BAr^{Cl}	2,6-lutidine	100[e]	62% (72 h)
6	[**2**]BAr^{Cl}	**7**	100[d]	25% (72 h)[h]

[a] Reaction conditions: 0.1 mmol each of acid and base in 0.8 cm^3 solvent sealed under about 4 atmospheres H_2. [b] Reaction progress assigned by relative intensities of the ^{1}H NMR resonances of the acridinium and acridane N-methyl groups, except where noted. No products were isolated. [c] Reaction performed in CH_2Cl_2. [d] Reaction performed in *o*DCB. [e] Reaction performed in undried *o*DCB. [f] Anion degradation to give intractable insoluble material. [g] Because of low solubility of [**2**]BPh_4 in CH_2Cl_2, completion was assessed by relative intensity of the *N*-methylacridane resonance to that of lutidine.
[h] Calculated by relative intensities of imine CH and amine CH_2 resonances.

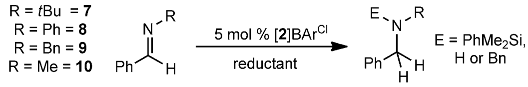
thermal stability. The carbon-centered Lewis acidity was unambiguously confirmed by studies with D_2, with incorporation of ^{2}D into the C9-position of the resultant **5** as monitored by ^{1}H and ^{2}D NMR spectroscopy. H_2 activation by [**2**]BAr^{Cl}/2,6-lutidine proceeds more rapidly at 100 °C in *ortho*-dichlorobenzene (*o*DCB; entry 4), thus indicating a significant kinetic barrier to H_2 bond cleavage, which in light of the anion dependence observed, is attributed to anion/cation interactions in solution. Importantly, there is no decomposition of [**2**]BAr^{Cl} at 100 °C after 2 days, thus precluding H_2 activation via a $B(3,5\text{-}Cl_2C_6H_3)_3$/2,6-lutidine FLP.[24] Given the utility of N-alkyl acridinium salts as photoredox catalysts in a wide range of transformations,[25] [**2**]BAr^{Cl}/2,6-lutidine was exposed to dihydrogen and heated in the absence of light, with dihydrogen activation still proceeding in the dark. Pleasingly, the FLP systems are stable to water at room temperature, although slow H_2O activation is observed at higher temperatures (60 °C) to form N-Me-9-OH acridane and the 2,6-lutidinium cation. Performing H_2 activation in wet *o*DCB with [**2**]BAr^{Cl}/2,6-lutidine (entry 5) remarkably resulted in H_2 activation, however heterolytic O–H cleavage of H_2O was also observed to give a minor product.

With H_2 activation unequivocally demonstrated, the reduction of the unsaturated substrate *N*-benzylidene-*tert*-butylamine (**7**) was explored in a FLP with [**2**]BAr^{Cl}. This FLP slowly activated H_2 with reduction of the imine to the corresponding amine after heating to 100 °C (Table 2, entry 6). To improve reduction kinetics, the ability of $\mathbf{2}^+$ to activate the inexpensive dihydrogen surrogate Me_2NHBH_3 was investigated for transfer-hydrogenation applications. [**2**]BAr^{Cl} reacts with Me_2NHBH_3 by rapid hydride transfer to generate **5** and a cationic boron species. Repeating the reaction in the presence of **7** resulted in formation of $(Me_2NBH_2)_2$, **5** and the protonated imine [**7**H]$^+$, which upon heating abstracted hydride from **5** to regenerate [**2**]BAr^{Cl} and lead to overall reduction of the imine to an amine. The observation of **5** and [**7**H]$^+$ indicates that it is the hydride-transfer step that is the rate-limiting step. Catalyst-free, direct reduction of **7** with Me_2NHBH_3 does occur,[26] but this background reaction is slow in CH_2Cl_2 at 60 °C, thus taking 69 h to reach only 78 % conversion. In comparison, a 5 mol % loading of [**2**]BAr^{Cl} gave complete reduction of **7** in the presence of $Me_2NH\text{-}BH_3$ after 18 hours at 60 °C (Table 3, entry 1), thus confirming catalysis of the transfer hydrogenation by the carbon Lewis acid [**2**]BAr^{Cl}.

The applicability of [**2**]BAr^{Cl} for the activation of Si–H bonds was next investigated. The direct 1:1 combination of [**2**]BAr^{Cl} and $PhMe_2SiH$ resulted in no observable reaction and no loss of $^3J_{H\text{-}H}$ coupling between the Si–H fragment and the adjacent methyl groups, as observed for analogous systems with $B(C_6F_5)_3$.[3] Nevertheless, mixing Ph_3SiH and Et_3SiD with 5 mol % [**2**]BAr^{Cl} resulted in H–D exchange at room temperature, thus confirming activation of the Si–H bond. Consistent with this, the hydrosilylation of a number of aldimines was achieved using catalytic [**2**]BAr^{Cl}. Whilst hydrosilylation of **7** is slow at 60 °C it is complete within 4 hours at 100 °C, giving the desired amine post hydrolysis. Hydrosilylation was also observed for the N-Ph (**8**) and N-Bn (**9**) imines (Table 3, entries 3 and 4). More remarkable, is the hydrosilylation of the unhindered imine **10**, catalyzed by [**2**]BAr^{Cl} (entry 6). **10** is incompatible with $B(C_6F_5)_3$-catalyzed hydrosilylation because of the formation of a strong Lewis adduct.[3b,27] In contrast, [**2**]BAr^{Cl} shows no significant propensity to bind **10** in CH_2Cl_2 (the N-Me resonance of [**2**]$^+$ remains at $\delta_{1H} = 4.50$ ppm post addition of excess imine **10**).

Finally, we investigated the utility of this species in other $B(C_6F_5)_3$-catalyzed reactions. [**2**]BAr^{Cl} catalyzes the dehydrosilylation of aromatic, primary, secondary, and tertiary alcohols (Table 4). A range of silanes can be utilized as reductants, though steric bulk precludes the use of triisopropylsilane, and triphenylsilane causes anion degradation as a minor competitive pathway (entry 2). Dehydrosilylation proceeds unimpeded in the absence of light (entry 3 versus 4). The reaction evolves dihydrogen gas using R_3SiH (observed by ^{1}H NMR spectroscopy). When Et_3SiD is used, a mixture of

Table 3: Catalytic reduction of aldimines.



Entry	Substrate	Reductant	T [°C]	Conv. [%]	t [h]
1[b]	7	Me_2NHBH_3	60	> 99	18
2[a]	7	$PhMe_2SiH$	60	98	296
3[a,b]	7	$PhMe_2SiH$	100	> 98[c]	4
4[a,b]	8	$PhMe_2SiH$	100	> 98[c]	4
5[a,b]	9	$PhMe_2SiH$	100	> 98[d]	24
6[a,b]	10	$PhMe_2SiH$	100	45[d]	24

[a] Reactions were performed on a 0.2 mmol scale with 50% excess silane in 0.8 cm^3 dry CH_2Cl_2 except where noted. [b] Reaction in *o*DCB [c] Calculated by integration of ^{1}H NMR peaks using cyclohexane as an internal standard. [d] Consumption of starting imine determined by integration of ^{1}H NMR peaks using cyclohexane as an internal standard. Concomitant transimination occurred under reaction conditions consuming BnN(SiMe$_2$Ph)R to form a range of other amines; see the Supporting Information for details.

Table 4: Catalytic dehydrosilylation of alcohols.[a]

$$ROH + R'_3SiH \xrightarrow[\text{[2]BAr}^{Cl}]{\text{cat.}} ROSiR'_3 + H\text{-}H$$

Entry	Substrate	Silane	Catalyst Loading [%]	t [h]	Conv. [%]
1	*i*PrOH	Et_3SiH	5	< 2	86[b]
2	*i*PrOH	Ph_3SiH	10	16	75[c]
3	BnOH	$PhMe_2SiH$	5	< 1	> 99
4	BnOH	$PhMe_2SiH$	5	< 1	> 99[d]
5	BnOH	$PhMe_2SiH$	0.5	72	80
6	BnOH	$PhMe_2SiH$	0.5	2	93[e]
7	CyOH	$PhMe_2SiH$	5	< 1	> 99
8	1-AdOH	$PhMe_2SiH$	5	< 1	> 99
9	Phenol	$PhMe_2SiH$	5	< 1	> 99

[a] Reactions were performed at room temperature on 0.2 mmol scale with 5% excess silane in 0.8 cm^3 dry DCM except where noted. Yields assessed by ^{1}H NMR spectroscopy. [b] Total consumption of silane observed, but competitive siloxane formation from the presence of H_2O in *i*PrOH. [c] Heated to 60 °C for reaction duration; total decomposition of anion observed. [d] Identical reaction conditions to those in entry 4 but performed in total darkness. [e] Heated to 60 °C. Ad = adamantyl.

H_2 and HD is evolved, with no ^{2}D incorporation into the product observed, thus demonstrating that no carbonyl intermediates derived from alcohol dehydrogenation are involved. This data is further supported by the facility with which phenol is silylated, thus implicating an analogous mechanism to that with $B(C_6F_5)_3$ involving heterolytic activation of Si–H to form **5** and $[RO(H)SiR_3]^+$, which undergoes dehydrocoupling to release H_2 (or mixtures of H_2 and HD when Et_3SiD is used and [D]-**5** is formed).[3] Unlike $B(C_6F_5)_3$-catalyzed dehydrosilylation of alcohols,[3] no over-reduction to alkanes with concomitant siloxane formation is observed, even in the presence of a large excess of silane and with prolonged heating, presumably as a result of the lower reducing power of *N*-methylacridane versus that of $[HB(C_6F_5)_3]^-$. This reactivity allows the reaction to be performed under ambient atmosphere, with no need to pre-dry solvents. The catalyst rapidly converts H_2O into the appropriate siloxane under the reaction conditions (confirmed by deliberate siloxane synthesis), and any excess silane poses no threat of over-reducing the $R_3Si{-}OR'$ product. This reaction was demonstrated in the bulk synthesis of $BnOSiPh_3$ using unpurified solvents in air with 64% (unoptimized) conversion despite the use of the challenging silane Ph_3SiH (from anion decomposition side reactions).

In summary, N-alkylated acridinium salts are introduced as simple carbon Lewis acids for FLP-based σ-bond activations. They were shown computationally and experimentally to have an appropriate HIA to be useful carbocationic Lewis acids in FLPs for H_2 activation and for reduction (hydride transfer) chemistry. The former was confirmed by *N*-methylacridinium salts being effective in H_2 activation, dehydrogenation of amine–boranes, and silane activation, subject to anion dependence upon reactivity. Their application in proof-of-concept catalytic transfer hydrogenation and catalytic hydrosilylation of imines has been demonstrated. Furthermore, the low Lewis acidity of $[\mathbf{2}]^+$ towards hard Lewis bases enables the catalytic hydrosilylation of unhindered imines which are incompatible with hydrogenation/hydrosilylation catalyzed by $B(C_6F_5)_3$. [**2**]BAr^{Cl} is also a cheap, air- and moisture-stable catalyst for the dehydrosilylation of alcohols, thus functioning with excellent turnover and good (unoptimized) yield in bench-grade solvents. Current work involves extending this family of carbon Lewis acids by developing FLPs containing other N-alkylated pyridinium salts with lower HIAs and different anionic components.

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