

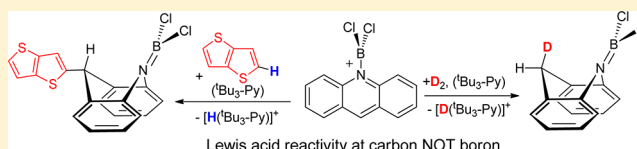
[(acridine)BCl₂]⁺: A Borenium Cation That Is a Strong Boron- and Carbon-Based Lewis Acid

Ewan R. Clark and Michael J. Ingleson*

School of Chemistry, University of Manchester, Manchester, U.K. M13 9PL

Supporting Information

ABSTRACT: [(acridine)BCl₂][AlCl₄] was synthesized by halide abstraction from (acridine)BCl₃ with AlCl₃. The hydride ion affinity of the C9 position in [(acridine)BCl₂]⁺ was calculated to be 14 kcal mol⁻¹ greater than that at boron. [(acridine)BCl₂][AlCl₄] reacts with 1 equiv of acridine to form the strained boronium cation [(acridine)₂BCl₂][AlCl₄] and with P(mesityl)₃ by photoinduced one-electron transfer to form the 9,9'-biacridane moiety by radical coupling. A stable frustrated Lewis pair (FLP) was formed on combining [(acridine)BCl₂][AlCl₄] and 2,4,6-tri-*tert*-butylpyridine (TBP), which heterolytically activated H₂ at 100 °C. The ultimate location of the hydride from H₂ activation was the C9 position of acridine and not boron. Carbon Lewis acid based reactivity also occurred when thieno[3,2-*b*]thiophene was added to the [(acridine)BCl₂][AlCl₄]/TBP FLP or to [(acridine)₂BCl₂][AlCl₄], with arylation of acridine at C9 observed for both.



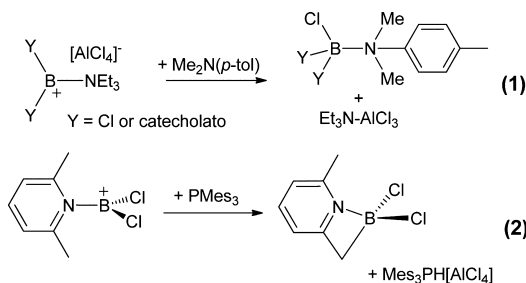
Borenium cations, three-coordinate borocations,^{1,2} are of significant topical interest due to their utility in an increasing number of synthetic applications.^{3,4} Recent notable developments use borenium cations as Lewis acid catalysts⁴ for hydrogenation, hydrosilation, and hydroboration^{5–8} and as stoichiometric reagents for effecting intermolecular arene borylation^{3,9–12} and haloboration.¹³ For successful H₂ and certain arene C–H bond activation reactions it was essential to combine a borenium cation with 1 equivalent of a Lewis base that had sufficient steric bulk to ensure “frustration” of Lewis adduct formation.^{7,14} Lewis pair frustration enables the synergic, or sequential, reactivity of the Lewis acid and base necessary for heterolytic σ bond cleavage.^{15–17} In addition to preventing strong dative bond formation, frustrated Lewis pair (FLP) combinations have to be resistant to other deactivation pathways; for example, hydride abstraction from Et₃N and related aliphatic amines by the neutral borane B(C₆F₅)₃ can complicate or even preclude FLP reactivity.¹⁸ The use of cationic main group Lewis acids in FLPs presents additional challenges to FLPs containing neutral borane Lewis acids including; anion decomposition (eq 1), a greater susceptibility

judicious design silicon²⁶ and boron⁷ cationic Lewis acids have been incorporated into FLPs and subsequently used to activate H₂.

We are interested in generating FLPs that contain highly Lewis acidic borenium cations, especially examples compatible with simple weakly coordinating anions, e.g., [AlCl₄][–], and derived from inexpensive Lewis bases. [(2,6-disubstituted pyridyl)BCl₂]⁺ cations are an attractive motif for constructing FLPs, as steric bulk at the 2,6-positions induces a perpendicular arrangement of the pyridyl and {BCl₂}⁺ moieties.^{19,27} This orthogonality maximizes steric shielding of the boron center, particularly the formally empty p_z orbital, essential for FLP formation. The *ortho* substituents on 2,6-disubstituted pyridyls are also important to facilitate halide abstraction from (2,6-R₂-pyridyl)BCl₃ due to steric effects lowering the chloride ion affinity.¹⁹ Replacing 2,6-lutidine with 2,6-dichloropyridine or acridine will prevent the deprotonation observed in FLPs containing [(2,6-lutidine)BCl₂][AlCl₄], **1**[AlCl₄] (eq 2), thereby facilitating the formation of stable borenium cation containing FLPs. Herein we report on the Lewis acidity and synthetic accessibility of [(2,6-Cl₂-pyridine)BCl₂][AlCl₄] and [(acridine)BCl₂][AlCl₄] and, in the latter case, its subsequent reactivity toward H₂ and an arene nucleophile.

RESULTS AND DISCUSSION

Initially the Lewis acidity of the target cations, [(2,6-Cl₂-pyridine)BCl₂]⁺ and [(acridine)BCl₂]⁺ (**[2]**⁺ and **[3]**⁺, respectively), was assessed by calculations at the M06-2X/6-311G(d,p) level with a solvation model (PCM, CH₂Cl₂). The



of the cation to undergo deprotonation (eq 2),^{12,19–21} dealkylation,^{22,23} and even C–H insertion reactions.^{24,25} With

Special Issue: Applications of Electrophilic Main Group Organometallic Molecules

Received: May 24, 2013

Published: June 26, 2013



relative (to BEt_3) hydride ion affinity (HIA) was calculated using a previously reported protocol^{19,28} and confirmed that $[2]^+$ would be a strong Lewis acid ($\text{HIA} = -64.6 \text{ kcal mol}^{-1}$) comparable to $[1]^+$ ($\text{HIA} = -61.7 \text{ kcal mol}^{-1}$). The situation for $[3]^+$ is more complex, as addition of a hydride to the C9 position of acridinium salts is well documented;^{29–31} thus, the hydride ion affinity of boron and C9 were both calculated for $[3]^+$. While the HIA of the Lewis acidic boron center in $[3]^+$ was comparable to that calculated for $[1]^+$ and $[2]^+$, the HIA of the C9 position was surprisingly found to be considerably greater (Figure 1). The addition of hydride to C9 forms an

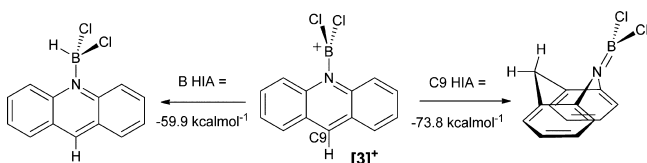


Figure 1. Relative (to BEt_3) HIA of the boron and C9 positions of $[3]^+$.

acridane with a boat conformation for the central six-membered ring and significant multiple-bond character between the amido N and boron ($\text{N}=\text{B} = 1.40 \text{ \AA}$).³² The development of considerable $\text{B}=\text{N}$ character presumably contributes to the large HIA calculated for the C9 position. For comparison the HIA of the C9 position in protonated acridine was $-51.8 \text{ kcal mol}^{-1}$, considerably lower than that for $[3]^+$. The HIA values of the C9 position in $[3]^+$ and, to a lesser extent, $[\text{H}-(\text{acridinium})]^+$ are both greater than that of $\text{B}(\text{C}_6\text{F}_5)_3$,¹⁹ suggesting that these cations may react as carbon-based Lewis acids in FLP chemistry.^{33–35}

The calculated relative (to AlCl_3) chloride ion affinities (CIA) of the boron centers of $[2]^+$ and $[3]^+$ were also determined and both found to be within 1 kcal mol^{-1} of that for $[1]^+$ (CIA values (kcal mol^{-1}): $[1]^+$, +20.7; $[2]^+$, +20.0; $[3]^+$, +20.2).¹⁹ For comparison purposes the relative CIA values of the C9 position of $[3]^+$ were calculated to be +27.9 and +31.4 kcal mol^{-1} (for chloride in cis and trans positions of the boat isomer, respectively), indicating that the C9 position is less Lewis acidic than the boron center toward harder bases such as chloride. The disparity between the relative HIA and CIA of B and C9 in $[3]^+$ is attributed in part to the different electrostatic contributions to bonding; this will be larger in the $\text{B}=\text{N}$ bond than in the $\text{C}=\text{N}$ bond on the basis of relative electronegativities. The CIA values for both $[2]^+$ and $[3]^+$ indicated that halide abstraction using AlCl_3 is feasible, provided that (pyridyl) BCl_3 adducts are accessible. However, all attempts to form $[2][\text{AlCl}_4]$ by combining BCl_3 , 2,6-dichloropyridine, and AlCl_3 were unsuccessful. The absence of dative bond formation

between BCl_3 and poorly nucleophilic 2,6-dichloropyridine presumably precludes halide abstraction, a rationale supported by the ^{11}B NMR spectra showing no change on addition of equimolar 2,6-dichloropyridine to BCl_3 .

In contrast, the acridine analogue (acridine) BCl_3 , termed **3-Cl**, is readily accessible as an extremely poorly soluble but analytically pure material. A single-crystal X-ray diffraction study confirmed Lewis adduct formation. There is significant structural distortion in **3-Cl** due to steric effects (Figure 2, left) which are best exemplified by (i) boron projecting out of the plane of the central pyridyl moiety ($\text{C9}=\text{N}=\text{B} = 161.45^\circ$) and (ii) acridine deviating away from planarity (the angle between the planes of the two outer six-membered rings of acridine is 16.6°). As predicted by the calculated CIA, halide abstraction by AlCl_3 cleanly converts **3-Cl** to $3[\text{AlCl}_4]$. There is no evidence for the competing formation of acridine(AlCl_3), which is observed when AlCl_3 is added to 9-chloro-9-borafluorene/acridine mixtures.³⁶ The NMR chemical shifts of $3[\text{AlCl}_4]$ are fully consistent with an ionic borenium formulation (including δ_{B} 49.3 ppm and a sharp ^{27}Al resonance at δ_{Al} 103.8 ppm consistent with $[\text{AlCl}_4]^-$). An alternative resonance form for $[3]^+$ containing an amido group, $\text{B}=\text{N}$ character, and a carbocationic center at C9 is disfavored, as the chemical shift for the C9 carbon nucleus for $3[\text{AlCl}_4]$ was observed at 154.6 ppm. This shift is considerably upfield from that reported for the 9-($\text{B}(\text{Mes})_2$)-*N*-Me-acridinium cation (δ_{C9} 175 ppm), which does possess significant carbocation character at C9.^{37,38} A borenium cation formulation for $3[\text{AlCl}_4]$ was corroborated by X-ray diffraction studies. The solid-state structure has angles at boron summing to 360° and $\text{Cl}_3\text{AlCl}\cdots\text{B}$ contacts $>4 \text{ \AA}$, while the planes defined by $\{\text{BCl}_2\}^+$ and the central ring of acridine are approaching orthogonality (77.3°), as expected, precluding any significant $\text{N} \rightarrow \text{B}$ π donation (Figure 2, right). Structural distortions arising from sterics in $3[\text{AlCl}_4]$ are now minimal, with acridine effectively planar and a $\text{C9}=\text{N}=\text{B}$ angle of 174.5° .

While small nitrogen Lewis bases (e.g., pyridine) coordinate to boron in $3[\text{AlCl}_4]$, it was envisaged that $3[\text{AlCl}_4]$ would form FLPs with bulkier bases, including acridine. Surprisingly, addition of 1 equivalent of acridine to $3[\text{AlCl}_4]$ resulted in an upfield shift of the ^{11}B resonance (to δ_{B} +7.8 ppm). The presence of only one set of acridine proton resonances and a ^{27}Al NMR spectrum confirming the persistence of $[\text{AlCl}_4]^-$ indicated the formation of the borenium salt $[(\text{acridine})_2\text{BCl}_2][\text{AlCl}_4]$ (**4** $[\text{AlCl}_4]$). On standing in CH_2Cl_2 , **4** $[\text{AlCl}_4]$ spontaneously precipitated as a crystalline solid suitable for X-ray diffraction. The asymmetric unit of **4** $[\text{AlCl}_4]$ contained two metrically similar equivalents; thus, only one is discussed herein. The structure of **4** $[\text{AlCl}_4]$ exhibits considerable distortion (Figure 3), exemplified by the $\text{C9}=\text{N}=\text{B}$ angles

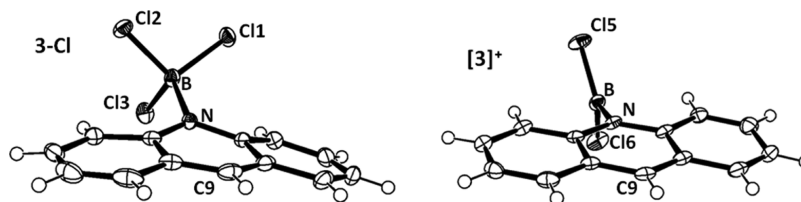


Figure 2. ORTEP representations of **3-Cl** (left) and the cationic portion of $3[\text{AlCl}_4]$ (right), with thermal ellipsoids at the 50% probability level. Selected bond distances (\AA) and angles ($^\circ$): for **3-Cl**, $\text{B}=\text{N} = 1.603(2)$, $\text{B}=\text{Cl}_2 = 1.859(2)$, $\text{N}=\text{C} = 1.380(1)$ and $1.380(2)$, $\text{N}=\text{B}=\text{Cl}_2 = 110.57(11)$; for $[3]^+$, $\text{B}=\text{Cl}_5 = 1.717(3)$, $\text{B}=\text{Cl}_6 = 1.721(3)$, $\text{B}=\text{N} = 1.503(3)$, $\text{N}=\text{C} = 1.372(4)$ and $1.382(4)$, $\text{N}=\text{B}=\text{Cl}_5 = 120.1(2)$, $\text{N}=\text{B}=\text{Cl}_6 = 118.5(2)$, $\text{Cl}_5=\text{B}=\text{Cl}_6 = 121.3(2)$.

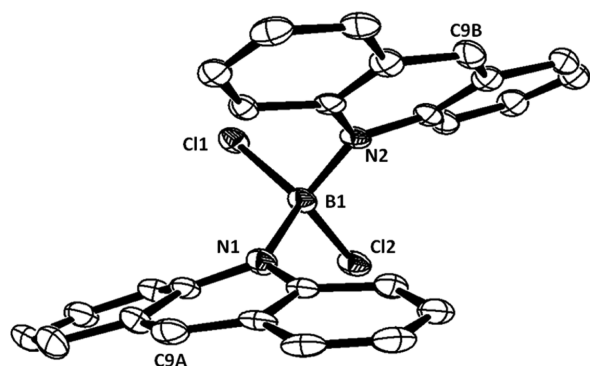


Figure 3. ORTEP representation of $4[\text{AlCl}_4]$, with thermal ellipsoids at the 50% probability level and hydrogens and $[\text{AlCl}_4]^-$ omitted for clarity. Selected bond distances (Å) and angles (deg): Cl1–B1 = 1.826(6), Cl2–B1 = 1.863(6), N1–B1 = 1.598(7), N2–B1 = 1.608(7), N2–B1–N1 = 108.4(4).

(161.2 and 162.4°) and a hinging of each acridine along the N–C9 axis to minimize steric repulsion between the two acridines (the average angle between the planes of the outer six-membered rings of acridine is 16.4°). The two significantly distorted acridines in $4[\text{AlCl}_4]$ clearly indicate some degree of sterically derived destabilization, suggesting that B–N dissociation may be thermally accessible. However, attempts to use $4[\text{AlCl}_4]$ as a thermally induced FLP³⁹ to activate H_2 resulted in no observable reaction (at 100 °C). In contrast to the case for $4[\text{AlCl}_4]$, equimolar $\text{B}(\text{C}_6\text{F}_5)_3/\text{acridine}$ is sterically prevented from B–N dative bond formation and this FLP rapidly activates H_2 at 20 °C. The calculated HIA of $3[\text{AlCl}_4]$ as a boron-based Lewis acid is 19 kcal mol^{−1} greater than that of $\text{B}(\text{C}_6\text{F}_5)_3$; thus, the failure of $4[\text{AlCl}_4]$ to activate H_2 is consistent with considerable FLP “preparation energy” being required to cleave a strong dative bond in $4[\text{AlCl}_4]$.⁴⁰

Borocation-containing FLPs are accessible with $3[\text{AlCl}_4]$ by using the bulky phosphine $\text{P}(\text{mesityl})_3$ (PMes_3), but this FLP undergoes undesired reactivity initiated by photoinduced one-electron transfer from the phosphine to $[\text{3}]^+$. At 20 °C the ^1H NMR spectrum showed rapid consumption of $3[\text{AlCl}_4]$ and PMes_3 and formation of $[\text{Mes}_3\text{PH}]^+$ and multiple acridine resonances, with BCl_3 observed as the major soluble boron-containing product by ^{11}B NMR spectroscopy. A yellow crystalline solid precipitated during the course of the reaction, enabling identification by X-ray diffraction as a dicationic bis-borenium salt, $5[\text{AlCl}_4]_2$ (Figure 4, left). $5[\text{AlCl}_4]_2$ is derived from a photoinduced radical dimerization through the C9 position of acridine (Figure 4, right); a related photoinduced dimerization of $[\text{N-methylacridinium}]^+$ in the presence of PPh_3 as the one-electron donor has been reported.⁴¹ Post-dimerization ligand scrambling with $3[\text{AlCl}_4]$ will produce BCl_3 and $5[\text{AlCl}_4]_2$, a less Lewis acidic borenium cation stabilized by an amido π donor (B–N_{amido} distances are consistent with multiple-bond character). Support for this proposed mechanism is provided by the observation of a radical attributable to $\text{Mes}_3\text{P}^{\bullet+}$ in the X-band EPR spectrum during the course of the reaction.³² Furthermore, a comparable ligand scrambling proceeded on combination of $1[\text{AlCl}_4]$ and $^i\text{Pr}_2\text{N}(\text{BCl}_2)$ to form BCl_3 and $[(^i\text{Pr}_2\text{N})\text{B}(\text{Cl})(2,6\text{-lutidine})][\text{AlCl}_4]$. The instability of the $3[\text{AlCl}_4]/\text{PMes}_3$ FLP necessitated the generation of a FLP between $3[\text{AlCl}_4]$ and a nonoxidizable Lewis base.

2,4,6-Tri-*tert*-butylpyridine (TBP) is sufficiently bulky and resistant to oxidation and thus forms a stable FLP with $3[\text{AlCl}_4]$. This FLP did not activate H_2 at 20 °C, but after it was heated at 100 °C for 16 h in 1,2- $\text{C}_6\text{H}_4\text{Cl}_2$, the resultant ^1H NMR spectrum (at 20 °C) showed that 50% of TBP was transformed to $[\text{HTBP}]^+$ and concomitantly a new resonance appeared consistent with a substituted acridane.⁴² Repeating

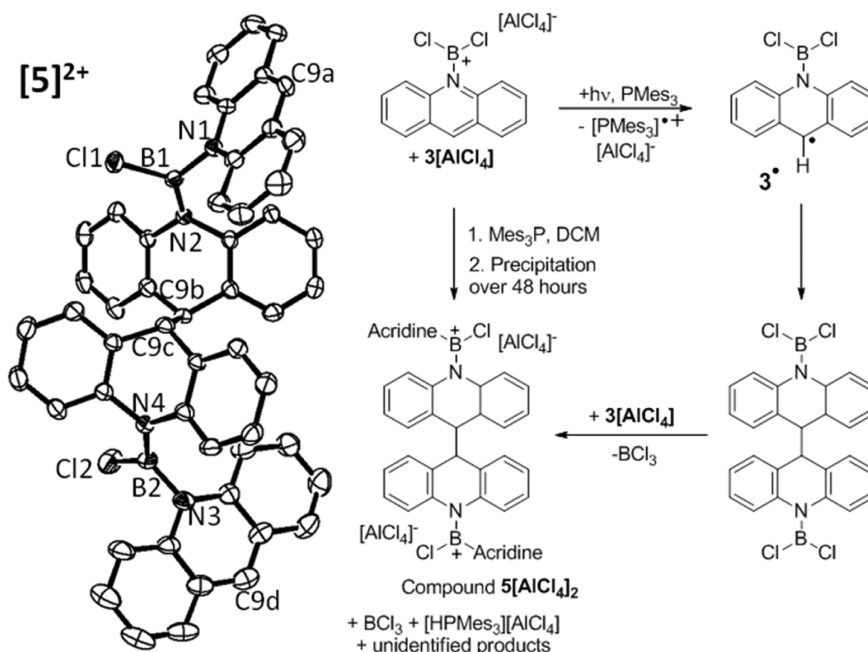
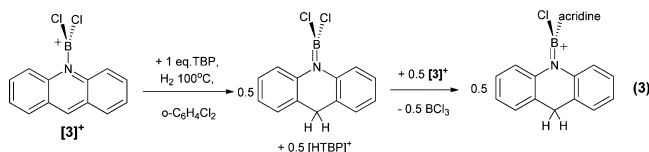


Figure 4. (left) ORTEP representation of the dicationic portion of $5[\text{AlCl}_4]_2$, with thermal ellipsoids at the 50% probability level and hydrogens omitted for clarity. Selected bond distances (Å) and angles (deg): Cl1–B1 = 1.757(5), Cl2–B2 = 1.780(6), N1–B1 = 1.522(6), N2–B1 = 1.391(6), N3–B2 = 1.524(6), N4–B2 = 1.370(7). N2–B1–N1 = 122.3(4), N4–B2–N3 = 123.7(4). (right) Postulated mechanism for the formation of $5[\text{AlCl}_4]_2$.

the reaction under D_2 resulted in deuterium incorporation at both of these positions, confirming dihydrogen activation by $3[AlCl_4]/TBP$. The ^{11}B NMR spectrum after complete consumption of $3[AlCl_4]$ consisted of a broad resonance centered at 32 ppm and the resonance of BCl_3 , consistent with ligand scrambling. The ^{27}Al NMR spectrum confirmed no anion decomposition, while the aromatic region was complex in the 1H NMR spectrum, suggesting >1 acridine environment. We assign the broad $\delta^{11}B$ resonance at 32 ppm to $[(acridine)-B(Cl)(acridane)]^+$ (eq 3), consistent with $[5]^{2+}$ and literature



values.^{42,43} The observed 1:1 ratio of $[HTBP]^+$ and TBP is also fully consistent with rapid ligand scrambling, as the formed amido stabilized borenium cation (right, eq 3) will be insufficiently Lewis acidic to activate H_2 in an FLP with TBP.

The formation of an acridane confirms that the ultimate location for the hydride derived from heterolytic cleavage of H_2 with $3[AlCl_4]/TBP$ is not boron but instead is the C9 position. This is consistent with the relative HIA values of C9 and boron in $[3]^+$ (-73.8 and $-59.9 \text{ kcal mol}^{-1}$, respectively) and suggests that the C9 position of $[3]^+$ may be acting as the Lewis acid in an FLP for H_2 activation. Unambiguous H_2 activation by carbon Lewis acids is rare, with a notable exception being Bertrand's electrophilic carbenes, where the empty p orbital is functioning as a carbon Lewis acid;⁴⁴ trityl cations, fullerenes, and an amidine dication may also be acting as carbon Lewis acids to cleave H_2 .^{45–47} While carbon Lewis acids have been used in bimolecular FLPs, to date their reactivity has been limited, e.g., to heterolytic activation of S–S, with no H_2 activation observed.^{35,48,49} However, we cannot definitely assign the initial position of hydride addition to $[3]^+$ to C9, as heating $BHCl_2(acridine)$ even to only $60^\circ C$ led to complete consumption of $BHCl_2(acridine)$ within 1 h (by 1H NMR spectroscopy) and the appearance of resonances consistent with a substituted acridane. Therefore, an alternative scenario of slow H_2 activation at $100^\circ C$ involving the boron center/TBP followed by rapid hydride transfer from boron to C9 (intra- or intermolecular) is also feasible. In an attempt to

unambiguously observe H_2 cleavage with a carbon Lewis acid, equimolar $[H(acridine)][AlCl_4]/acridine$ was heated at $100^\circ C$ under 4 atm of H_2 (or D_2), but this led to no H_2 activation. $[H(acridine)]^+$ has been demonstrated to be a strong Lewis acid toward hydride,³⁰ as demonstrated by the reduction of acridine using $H_2/B(C_6F_5)_3$, which involves transfer of hydride from $[HB(C_6F_5)_3]^-$ to the C9 of $[H(acridine)]^+$ to produce acridane and $B(C_6F_5)_3$.²⁹ As the C9 position in protonated acridine has a greater HIA than $B(C_6F_5)_3$, H_2 activation using $[H(acridine)][AlCl_4]/acridine$ is thermodynamically favored overall, but its absence indicates a significant kinetic barrier, the origin of which is currently unclear.

To probe the propensity of the C9 position in $[3][AlCl_4]$ to react as an electrophile, the electrophilic aromatic substitution of thieno[3,2-*b*]thiophene was investigated with and without the base TBP. Importantly, while protonated acridines are sufficiently electrophilic at C9 to react with highly nucleophilic arenes, such as indoles and anilines,⁵⁰ there was no reaction between $[H(acridine)][AlCl_4]$ and the less nucleophilic arene thieno[3,2-*b*]thiophene at $100^\circ C$ even in the presence of additional acridine, thereby simplifying our subsequent studies. In the absence of a base $[3][AlCl_4]$ borylates thieno[3,2-*b*]thiophene at $20^\circ C$ to give the α -borylated (thienyl) BCl_2 as the major product (Figure 5, top) after 2 h. However, when the FLP $3[AlCl_4]/TBP$ was used, borylated thieno[3,2-*b*]thiophene was only a minor product. The major product was associated with a broad resonance at 32 ppm in the ^{11}B NMR spectrum, while the 1H NMR spectrum revealed formation of $[HTBP]^+$, substitution of the α position of thieno[3,2-*b*]thiophene, and a resonance attributable to the C9 position of an aryl-substituted acridane.³² These observations are consistent with arylation of $[3]^+$ at C9 enabled by deprotonation of the intermediate arenium cation by TBP (Figure 5, bottom). The absence of significant borylation when using the FLP $3[AlCl_4]/TBP$ indicates that the kinetic position for addition of a heteroarene to $[3][AlCl_4]$ is at C9 but that without a base this interaction is reversible (Figure 5, left). In contrast, attack of thieno[3,2-*b*]thiophene at boron in $3[AlCl_4]$ is ultimately irreversible, as steric pressure at boron in the four-coordinate intermediate leads to acridine dissociation and subsequent deprotonation (Figure 5, top): this was previously found for heteroarene borylation with the related borenium salt $[1][AlCl_4]$.¹⁴ The C9 functionalization of $3[AlCl_4]$ observed in the presence of TBP also confirms that coordination of $\{BCl_2\}^+$

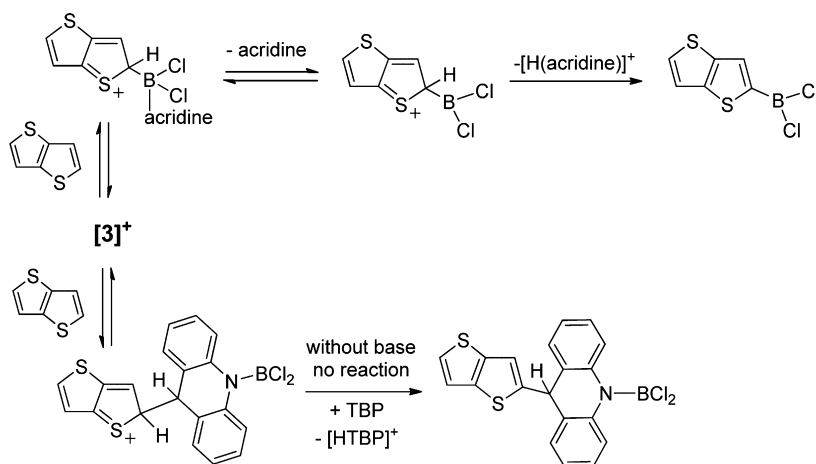


Figure 5. Schematic for the reaction of $[3]^+$ with thieno[3,2-*b*]thiophene with and without TBP.

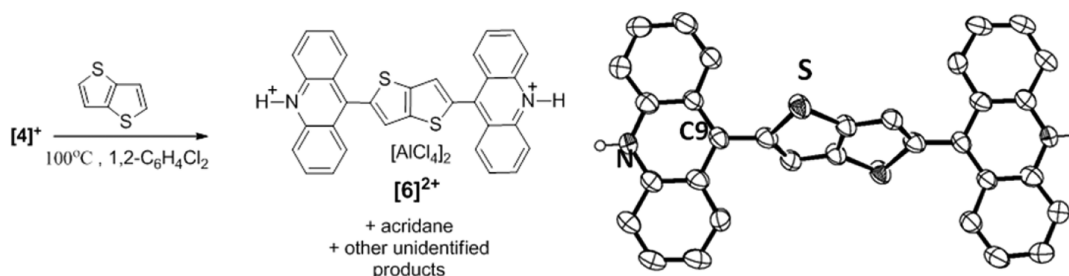


Figure 6. (left) Formation of $[6]^{2+}$ from $[4]^+$ /thieno[3,2-*b*]thiophene. (right) ORTEP representation of the dicationic portion of $6[AlCl_4]_2$, with thermal ellipsoids at the 50% probability level and hydrogens omitted for clarity apart from those bound to nitrogen.

to acridine activates the C9 position of the heterocycle toward nucleophilic attack to a greater extent than simply protonation at nitrogen.

Further confirmation for the functionalization of the C9 position of acridine was forthcoming from heating equimolar $4[AlCl_4]$ and thieno[3,2-*b*]thiophene to 100 °C in 1,2- $C_6H_4Cl_2$. This resulted in the formation of an acridane and the growth of a resonance at 32 ppm in the ^{11}B NMR spectrum. Over 16 h a red crystalline solid precipitated in 46% yield, which was identified as the dication $6[AlCl_4]_2$ (Figure 6). Identical reactivity was observed, including precipitation of $6[AlCl_4]_2$, when the reaction was repeated in the dark, precluding photoinduced radical pathways.³⁰ While the presence of other unidentified products in the reaction mixture precludes a detailed mechanistic discussion, the isolation of $6[AlCl_4]_2$ confirms the ability of the C9 position to be extremely electrophile when acridine is bound to a borocation fragment.

CONCLUSIONS

An acridine-stabilized borenium cation, $[(acridine)BCl_2]^+$, can be incorporated as the Lewis acidic component of a frustrated Lewis pair (FLP), provided the base is extremely bulky and resistant to oxidation. Remarkably, $[(acridine)BCl_2]^+$ exhibits electrophilic reactivity at both boron and the C9 position of acridine, with the presence of an added base allowing control of the mode of reactivity. The C9 position in $[(acridine)BCl_2]^+$ has a hydride ion affinity (HIA) 14 kcal mol⁻¹ greater than that at boron and 22 kcal mol⁻¹ greater than that for $[H(acridine)]^+$, making it an extremely strong carbon Lewis acid. Carbon-based Lewis acids are currently underutilized as components of frustrated Lewis pairs for small-molecule activation and catalysis. With the HIA of $[H(acridine)]^+$ being greater than that of $B(C_6F_5)_3$ (by calculations and experimental reactivity), acridinium and related cations may be suitable as carbon Lewis acids in FLP-based small-molecule activations.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed using standard Schlenk techniques or in an argon-filled MBraun glovebox (O_2 levels below 0.5 ppm). Solvents used were purified by an Innovative Technology PS-MD-5 solvent purification system or distilled from appropriate drying agents, degassed, and stored over molecular sieves. Deuterated solvents were distilled from appropriate drying agents and degassed. All materials were purchased from commercial vendors and used as received. Elemental analysis of air-sensitive compounds was performed by the London Metropolitan University service.

Synthesis of 3-Cl. BCl_3 (1.0 M in DCM, 7.85 cm³, 7.85 mmol) was added as a single portion to a suspension of acridine (1.4 g, 7.81 mmol) in DCM (5 cm³), generating a bright yellow solution and

resulting in immediate formation of a bright yellow precipitate. The reaction mixture was stirred overnight, giving a bright yellow precipitate and a dark supernatant. The solid was isolated by filtration, washed with DCM (3 cm³), and dried in vacuo to give the product (1.96 g, 6.6 mmol, 85% yield). The resultant product, though too insoluble in DCM or 1,2- $C_6H_4Cl_2$ to allow NMR characterization, was found to be of good purity by elemental analysis. Anal. Calcd for $C_{13}H_9NBCl_3$: C, 52.68; H, 3.06; N, 4.73. Found: C, 52.69; H, 3.17; N, 4.68.

Synthesis of 3[AlCl₄]. 3-Cl (87 mg, 0.3 mmol) and $AlCl_3$ (40 mg, 0.3 mmol) were combined as solids, DCM (3 cm³) was added, and the mixture was stirred to generate an intense yellow solution. Crystals were grown by slow diffusion of hexanes into the reaction mixture. The supernatant was decanted, and the crystals were washed with hexane (5 cm³) and then dried in vacuo to give 3[AlCl₄] (82 mg, 0.19 mmol, 63% yield). 1H NMR (d_2 -DCM, room temperature): δ 10.08 (1H, s); 8.73 (2H, d, J = 8.5 Hz); 8.53 (2H, ddd, J = 8.6, 7.0, 1.6 Hz), 8.14 (2H, m). ^{11}B NMR (d_2 -DCM, room temperature): δ 49.3 (bs). ^{13}C NMR (d_2 -DCM, room temperature): δ 154.55 (s), 141.38 (s), 139.50 (ws), 133.23 (s), 129.78 (s), 126.55 (ws), 118.67 (s). ^{27}Al NMR (d_2 -DCM, room temperature): δ 103.8 (s, $AlCl_4$). Anal. Calcd for $C_{13}H_9AlBCl_6N$: C, 36.34; H, 2.11; N, 3.26. Found: C, 36.41; H, 2.12; N, 3.32.

Synthesis of 4[AlCl₄]. 3-Cl (58 mg, 0.2 mmol) and $AlCl_3$ (28 mg, 0.2 mmol) were combined in a J. Young Schlenk and dissolved in DCM (1 cm³), forming a yellow solution. Acridine (36 mg, 0.2 mmol) was dissolved in DCM (1 cm³) and added in one portion to the reaction mixture, resulting in a darkening toward amber. The mixture was stirred and then allowed to stand for 1 week. The volume was then reduced by 50% in vacuo and the reaction mixture allowed to stand for 1 week, during which time orange crystals of 4[AlCl₄] grew. The mother liquor was removed, and the crystals were washed with hexane (2 cm³) and dried in vacuo, giving 4[AlCl₄] (51 mg, 0.084 mmol, 42% yield). Anal. Calcd for $C_{26}H_{18}AlBCl_6N_2$: C, 51.28; H, 2.98; N, 4.60. Found: C, 51.43; H, 2.89; N, 4.69.

Synthesis of 5[AlCl₄]. 3-Cl (145 mg, 0.5 mmol) and $AlCl_3$ (67 mg, 0.5 mmol) were combined in a J. Young Schlenk and DCM (1.6 cm³) added, the whole mixture being stirred to produce an intense yellow solution. To this solution was added trimesitylphosphine (390 mg, 1 mmol) in DCM (1.2 cm³) in one portion, with immediate formation of a black color. The mixture was sealed and allowed to stand for 10 days, over which time the solution became less dark and yellow crystals grew. The supernatant was decanted, and the crystals were washed with DCM (1 cm³) and hexane (2 cm³) then dried in vacuo, giving 5[AlCl₄]₂ (64 mg, 0.056 mmol, 44% yield by 3-Cl). Anal. Calcd for $C_{52}H_{36}Al_2B_2Cl_{10}N_4$ (solvent of crystallization lost on drying): C, 54.45; H, 3.16; N, 4.88. Found: C, 54.61; H, 3.07; N, 4.96.

Reaction of 4[AlCl₄] + Thieno[3,2-*b*]thiophene. 3-Cl (60 mg, 0.2 mmol) and $AlCl_3$ (27 mg, 0.2 mmol) were combined in a NMR tube fitted with a J. Young tap and preloaded with a d_6 -DMSO capillary. 1,2- $C_6H_4Cl_2$ (1 cm³) was added and the tube inverted until dissolution was complete, generating a yellow solution. Acridine (26 mg, 0.2 mmol) was added and the tube inverted to ensure mixing; the tube was then heated briefly to 100 °C to ensure complete dissolution and reaction, forming 4[AlCl₄]. The tube was cooled (yellow crystals

of 4[AlCl₄] formed upon cooling) and thieno[3,2-*b*]thiophene (28 mg, 0.2 mmol) added. The tube was again inverted to ensure mixing and dissolution and then heated at 100 °C for 16 h. Upon removal, the reaction mixture was a blood red color and contained copious red precipitate. The supernatant was removed, the solid was washed with 1,2-C₆H₄Cl₂ (1 cm³), and the residual solvent was removed in vacuo to give 6[AlCl₄]₂ (38 mg, 0.046 mmol, 46% yield by 3-Cl) as a microcrystalline red solid. Crystals suitable for single-crystal X-ray diffraction were grown by repeating the reaction and slowly cooling the NMR tube from 100 °C to room temperature over 2 h. 6[AlCl₄]₂ is essentially insoluble in chlorinated NMR solvents at room temperature, with no dissolution in *d*₂-DCM even upon addition of excess Et₃N to achieve deprotonation to facilitate solubility. Anal. Calcd for C₃₁H₂₀Al₂Cl₈N₂S₂: C, 45.28; H, 2.45; N, 3.41. Found: C, 46.29; H, 2.53; N, 3.28.

■ ASSOCIATED CONTENT

■ Supporting Information

Text, figures, tables, and CIF files giving full experimental information, including NMR spectra, computational data, and crystallographic details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for M.J.I.: Michael.ingleson@manchester.ac.uk.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Royal Society (M.J.I.) and the Leverhulme Trust (E.R.C.). We also acknowledge the use of the EPSRC UK National Service for Computational Chemistry Software (NSCCS) and Dr. Daniel Sells and Dr. Stephen Sproules at the EPSRC UK National Electron Paramagnetic Resonance Service at The University of Manchester and Dr. J. Hatnean (University of Toronto) for EPR observations.

■ REFERENCES

- (1) Koelle, P.; Nöth, H. *Chem. Rev.* **1985**, *85*, 399.
- (2) Piers, W. E.; Bourke, S. C.; Conroy, K. D. *Angew. Chem., Int. Ed.* **2005**, *44*, 5016.
- (3) De Vries, T. S. D.; Prokofjevs, A.; Vedejs, E. *Chem. Rev.* **2012**, *116*, 4246.
- (4) Corey, E. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2100.
- (5) Prokofjevs, A.; Boussoumiere, A.; Li, L.; Bonin, H.; Lacôte, E.; Curran, D. P.; Vedejs, E. *J. Am. Chem. Soc.* **2012**, *134*, 12281.
- (6) Eisenberger, P.; Bailey, A. M.; Crudden, C. M. *J. Am. Chem. Soc.* **2012**, *134*, 17384.
- (7) Farrell, J. M.; Hatnean, J. A.; Stephan, D. W. *J. Am. Chem. Soc.* **2012**, *134*, 15728.
- (8) Chen, J.; Lalancette, R. A.; Jäkle, F. *Chem. Commun.* **2013**, *49*, 4893.
- (9) Del Grosso, A.; Helm, M. D.; Solomon, S. A.; Caras-Quintero, D.; Ingleson, M. J. *Chem. Commun.* **2011**, *47*, 12459.
- (10) Del Grosso, A.; Singleton, P. J.; Murny, C. A.; Ingleson, M. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 2102.
- (11) Prokofjevs, A.; Kampf, J. W.; Vedejs, E. *Angew. Chem., Int. Ed.* **2011**, *50*, 2098.
- (12) De Vries, T. S.; Prokofjevs, A.; Harvey, J. N.; Vedejs, E. *J. Am. Chem. Soc.* **2009**, *131*, 14679.
- (13) Lawson, J. R.; Clark, E. R.; Cade, I. A.; Solomon, S. A.; Ingleson, M. J. *Angew. Chem., Int. Ed.* **2013**, DOI: 10.1002/anie.201302609.
- (14) Bagutski, V.; Del Grosso, A.; Ayuso Carrillo, J.; Cade, I. A.; Helm, M. D.; Lawson, J. R.; Singleton, P. J.; Solomon, S. A.; Marcelli, T.; Ingleson, M. J. *J. Am. Chem. Soc.* **2013**, *135*, 474.
- (15) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46.
- (16) Welch, G. C.; San-Juan, R. R.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124.
- (17) Stephan, D. W. *Org. Biomol. Chem.* **2012**, *10*, 5740.
- (18) Focante, F.; Mercandelli, P.; Sironi, A.; Resconi, L. *Coord. Chem. Rev.* **2006**, *250*, 170.
- (19) Clark, E. R.; Del Grosso, A.; Ingleson, M. J. *Chem. Eur. J.* **2013**, *19*, 2462.
- (20) Solomon, S. A.; Del Grosso, A.; Clark, E. R.; Bagutski, V.; McDouall, J. J. W.; Ingleson, M. J. *Organometallics* **2012**, *31*, 1908.
- (21) Schmidt, R. K.; Muether, K.; Mueck-Lichtenfeld, C.; Grimme, S.; Oestreich, M. *J. Am. Chem. Soc.* **2012**, *134*, 4421.
- (22) Kovacevic, L. S.; Idziak, C.; Markevicius, A.; Scullion, C.; Corr, M. J.; Kennedy, A. R.; Tuttle, T.; Murphy, J. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 8516.
- (23) Corr, M. J.; Roydhouse, M. D.; Gibson, K. F.; Zhou, S.; Kennedy, A. R.; Murphy, J. A. *J. Am. Chem. Soc.* **2009**, *131*, 17980.
- (24) Tsang, C.-W.; Rohrick, C. A.; Saini, T. S.; Patrick, B. O.; Gates, D. P. *Organometallics* **2004**, *23*, 5913.
- (25) Prokofjevs, A.; Vedejs, E. *J. Am. Chem. Soc.* **2011**, *133*, 20056.
- (26) Schäfer, A.; Reissmann, M.; Schäfer, A.; Saak, W.; Haase, D.; Müller, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 12636.
- (27) Mansaray, H. B.; Rowe, A. D. L.; Phillips, N.; Niemeyer, J.; Kelly, M.; Addy, D. A.; Bates, J. I.; Aldridge, S. *Chem. Commun.* **2011**, *47*, 12295.
- (28) Mock, M. T.; Potter, R. G.; Camaioni, D. M.; Li, J.; Dougherty, W. G.; Kassel, W. S.; Twamley, B.; DuBois, D. L. *J. Am. Chem. Soc.* **2009**, *131*, 14454.
- (29) Geier, S. J.; Chase, P. A.; Stephan, D. W. *Chem. Commun.* **2010**, 4884.
- (30) Sliwa, W. *Heterocycles* **1994**, *38*, 897.
- (31) Srikrishna, A.; Reddy, T. J.; Viswajani, R. *Tetrahedron* **1996**, *52*, 1631.
- (32) See the Supporting Information.
- (33) Iglesias-Siguenza, J.; Alcarazo, M. *Angew. Chem., Int. Ed.* **2011**, *51*, 1523.
- (34) Cabrera, L.; Welch, G. C.; Masuda, J. D.; Wei, P.; Stephan, D. W. *Inorg. Chim. Acta* **2006**, *359*, 3066.
- (35) Ines, B.; Holle, S.; Goddard, R.; Alcarazo, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 8389.
- (36) Narula, C. K.; Nöth, H. *Inorg. Chem.* **1985**, *24*, 2532.
- (37) Chiu, C.-W.; Gabbai, F. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 1723.
- (38) Chiu, C.-W.; Gabbai, F. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 6878.
- (39) Geier, S. J.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 3476.
- (40) Rokob, T. A.; Hamza, A.; Papai, I. *J. Am. Chem. Soc.* **2009**, *131*, 10701.
- (41) Yasui, S.; Ohno, A. *Tetrahedron Lett.* **1991**, *32*, 1047.
- (42) Casanova, J.; Geisel, M. *Inorg. Chem.* **1974**, *13*, 2783.
- (43) Wang, Y.; Robinson, G. H. *Inorg. Chem.* **2011**, *50*, 12326.
- (44) Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439.
- (45) Runyon, J. W.; Steinhof, O.; Rasika Dias, H. V.; Calabrese, J. C.; Marshall, W. J.; Arduengo, A. J. *Aust. J. Chem.* **2011**, *64*, 1165.
- (46) Li, B.; Xu, Z. *J. Am. Chem. Soc.* **2009**, *131*, 16380.
- (47) Corr, M. J.; Gibson, K. F.; Kennedy, A. R.; Murphy, J. A. *J. Am. Chem. Soc.* **2009**, *131*, 9174.
- (48) Palomas, D.; Holle, S.; Ines, B.; Bruns, H.; Goddard, R.; Alcarazo, M. *Dalton Trans.* **2012**, *41*, 9073.
- (49) After the submission of this article, Stephan et al. reported a Ru- η^6 -arene complex which despite containing a three-coordinate boron center reacts as a carbon Lewis acid in the FLP-based activation of H₂ with PMes₃; Boone, M. P.; Stephan, D. W. *J. Am. Chem. Soc.* **2013**, *135*, 8508.
- (50) Chiron, J.; Galy, J.-P. *Synthesis* **2004**, 313.