Fundamental and Applied Properties of Borocations

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Contents

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E. Fernández, A. Whiting (eds.), *Synthesis and Application of Organoboron Compounds*, Topics in Organometallic Chemistry 49,
DOI 10.1007/978-3-319-13054-5_2

Abstract The past 5 years has witnessed considerable growth in the field of borocation chemistry with a multitude of new cations containing 2, 3 and 4 coordinate boron centres reported. Perhaps more significant has been the expansion in the synthetic utility of borocations as stoichiometric reagents and catalysts. It is these new applications of borocations that are the primary focus of this article which concentrates on reports from 2009 to the end of June 2014. The correlation between structure and reactivity in these recent studies will be emphasised to aid in the future design of new borocations for specific targeted outcomes.

Keywords Borenium • Borinium • Borocations • Boronium • Borylation • Dehydroboration • Electrophiles • Haloboration • Hydroboration • Lewis acid catalysis

Abbreviations

$[NTf_2]^-$	Triflimide $^-N(SO_2CF_3)_2$
$[OTf]^-$	Triflate $^-OSO_2CF_3$
BBN	9-Borabicyclo[3.3.1]nonane
Cat	Catecholato ($[o\text{-}C_6H_4O_2]^{2-}$)
$CatS_2$	Thiocatecholato ($[o\text{-}C_6H_4S_2]^{2-}$)
CIA	Chloride ion affinity
DABCO	Diazabicyclo[2.2.2]octane
DIPP	2,6-Disopropylbenzene
DOSY	Diffusion-ordered NMR spectroscopy
FIA	Fluoride ion affinity
FLP	Frustrated Lewis pair
HIA	Hydride ion affinity
KIE	Kinetic isotope effect
Mes	Mesityl (2,4,6-Me_3-C_6H_2)
NHC	*N*-Heterocyclic carbene
PCM	Polarisation continuum model
Pin	Pinacolato ($[OC(Me)_2C(Me)_2O]^{2-}$)
S_EAr	Electrophilic aromatic substitution
X-DMAP	*N*,*N*-Dimethylaminopyridine ($x = 2$ or 4)

1 Introduction

The fundamental chemistry of borocations was first summarised in the seminal review by Koelle and Nöth nearly 30 years ago [1]. This included defining the terminology for borocations of varying coordination number at boron as boronium, borenium and borinium for four, three and two coordinate, respectively (Fig. 1). In 2005, Piers and co-workers provided an updated review and emphasised the

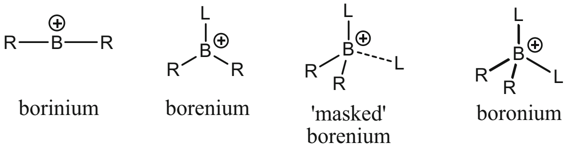

Fig. 1 The terminology for borocations of varying coordination number (where L is formally a neutral two-electron donor and R is formally a monoanionic substituent)

potential of borocations in synthesis and materials applications [2]. In addition to these two articles that cover the fundamental aspects of borocation chemistry in depth, a comprehensive review of the chemistry of borocations from an organic perspective (covering the literature up to the end of 2011) was produced by Vedejs and co-workers [3]. To avoid excessive overlap with these previous reviews, this chapter only briefly discusses the fundamental and early chemistry of borocations. Instead, it focuses on the applications of borocations reported in the last 5 years and emphasises how structural variation of the borocation controls electrophilicity at boron and subsequent reactivity. Current mechanistic hypotheses, limitations and future challenges will also be discussed. Due to space limitations, this article is limited to (i) the condensed phase reactivity of borocations (for gas phase reactivity, see Piers and co-workers [2]), (ii) metal-free borocations (for cationic transition metal borylenes, see references in [4]), and (iii) borocations directly bound to two R groups (Fig. 1), with R_3B with peripheral cationic groups also beyond the scope of this review [5].

As expected for a compound class that carries a unit positive charge and for borinium and borenium cations are formally electron deficient at boron, the reactivity of borocations is dominated by electrophilicity at boron. The majority of this review focuses on the recent applications of borenium cations as these cations combine significant electrophilicity at boron with relatively simple synthetic accessibility. However, it is important to note that a number of boronium cations are also useful electrophiles, particularly examples containing weakly bound Lewis bases in the fourth coordination site. A continuum of electrophilic reactivity with borinium cations at one extreme can be proposed in which boronium cations play an important role either as masked forms of borenium cations (via dissociation of L) or as electrophiles in their own right reacting via a S_N2-type process. Furthermore, anion-coordinated species can also exhibit borenium-type reactivity provided the anion is sufficiently weakly coordinating and readily displaced by another nucleophile, thus these neutral species are included where appropriate. Finally, we acknowledge that representing the positive charge throughout this review as localised at boron in borenium cations is a simplification and that charge is inherently diffuse. However, we feel that this representation is useful as it emphasises that the locus of electrophilic reactivity is consistently at boron and that boron generally possesses the greatest magnitude of positive charge in these cations (by NBO calculations) [6].

2 Fundamentals

2.1 Select Synthetic Considerations

The major synthetic routes to borenium and "masked" borenium cations remain as outlined originally by Koelle and Nöth, specifically (i) B–Y bond heterolysis (Y=halide or hydride), (ii) anion displacement by a neutral donor and (iii) coordination of an electrophile to a nucleophilic moiety in a neutral borane (Fig. 2). As noted by Vedejs and co-workers [7] for the latter when the electrophile (E) is neutral, this does not actually generate a compound with an overall positive charge. However, a borocation subunit can be identified (e.g. Fig. 2, inset) in these species; furthermore, they are often strong boron-based Lewis acids, thus their inclusion herein has validity [8]. Whilst a more comprehensive discussion of the synthetic routes to borocations is provided in previous reviews, some key observations of particular importance are discussed below.

The dominant synthetic route to borocations utilised in the recent literature is by B–Y bond heterolysis (Y=halide or hydride, route (i)). This can be effected by the addition of a metathesis agent (e.g. Ag^+/$[Ph_3C]^+$ salts), a strong Brønsted acid (e.g. $HNTf_2$) or a neutral strong Lewis acid, such as $AlCl_3$. The latter was in fact the methodology used to generate the first well-characterised borenium cation [9]. For successful borocation formation by route (i), a number of interrelated factors must be considered: (a) the donor L has to bind sufficiently strongly to boron in the neutral precursor to prevent rapid dissociation of L and competitive coordination of L to M on the addition of M[anion] or MX_n. Likewise, strong L → B bonds are necessary to prevent the protonation of L when a strong Brønsted acid reagent is used. (b) The coordination of L to the neutral borane has to weaken the B–Y bond to

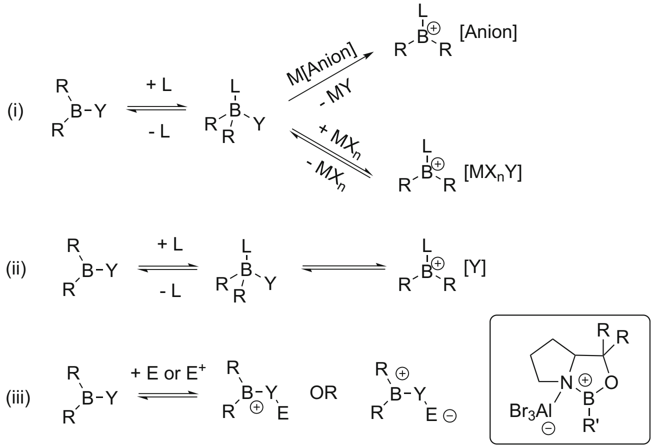

Fig. 2 Common synthetic routes to borenium cations. *Inset*, an example of a neutral compound that can be considered a borenium equivalent [8]

energetically favour B–Y bond heterolysis either on addition of MX_n/M^+ (route (i)) or without any further reagents (route (ii)). (c) L has to provide enough stabilisation, either kinetically through significant L steric bulk and/or electronically (e.g. by π donation), to disfavour strong anion/solvent binding. With borenium cations that have considerable Lewis acidity, B–Y bond heterolysis from the neutral precursor often only proceeds with the strongest MX_n Lewis acids, even when L is bulky and electron donating. Furthermore, B–Y bond heterolysis can be reversible, leading to complex dynamic mixtures in the solution phase that can complicate subsequent reactivity [6, 10].

The anion compatibility of borocations is also an important consideration and is obviously also dependent on the steric and electronic environment around boron. The production of the most electrophilic borocations necessitates the use of extremely robust and weakly coordinating anions, with simple fluorinated anions (e.g. $[BF_4]^-$, $[SbF_6]^-$) susceptible to anion decomposition by fluoride abstraction [11–15]. Many recently synthesised borenium cations utilise anions previously proven to be robust and weakly coordinating with the valence isoelectronic silicenium cations [16]. $[B(C_6F_5)_4]^-$ is a popular example, with reports of its decomposition when partnering borocations being extremely rare [7, 17]. It is notable that the $[B(C_6H_3(CF_3)_2)_4]^-$ anion is much more susceptible to decomposition by fluoride abstraction by highly electrophilic borocations due to the weaker sp^3 C–F bond [12]. Other classic "weakly" coordinating anions, particularly $[OTf]^-$, often interact strongly with boron in the absence of considerable steric crowding/electronic stabilisation of boron. This can effectively quench the Lewis acidity at boron, precluding subsequent synthetic applications.[1] In contrast, weak anion coordination can actually be beneficial, with stabilising $B\cdots Cl–AlCl_3$ and $B\cdots NTf_2$ interactions often observed in the solid state and solution. These weak interactions may well be essential for facilitating the simple synthesis of many borenium equivalents whilst maintaining significant electrophilicity at boron [18]. The determination of a borenium ions position on the continuum between a strongly bound ion pair and a solvent-separated ion pair in solution is complex. The most widely used method is the value of $\delta^{11}B$; however, this has limitations and is generally only able to unambiguously distinguish between 3 and 4 coordination at boron. This has recently been supplemented by the use of DOSY experiments, with the difference between anion and cation diffusion coefficients, an established method to assess the degree of ion association in solution [19, 20]. This approach was used to confirm the solvent-separated ion pair nature of [BBN(IMes)][OTf], whose existence as a borenium cation demonstrates that with sufficient steric bulk around boron even triflate can fulfil the role of a "non"-coordinating anion towards a borenium cation [19].

The coordinating ability of all other possible nucleophiles present in solution also needs to be considered if highly electrophilic borocations are the synthetic

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[1] A CCDC search (June 2014) revealed 21 structures with the formula $[R_2BL][OTf]$ where the B–O bond distance is consistent with a significant interaction between the triflate anion and boron.

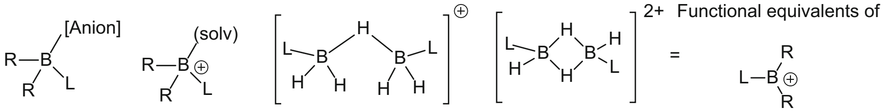


Fig. 3 Functional equivalents, or masked versions, of borenium cations

goal; this includes further equivalents of the neutral boron precursors. For example, Vedejs and co-workers have demonstrated the propensity of $(R_3N)BH_3$ to coordinate to the highly electrophilic borocations $[(R_3N)BH_2]^+$ forming hydride-bridged cations (Fig. 3 centre). More remarkably, borenium cations have been recently reported to dimerise to form dications (Fig. 3), further confirming the considerable electrophilicity of weakly stabilised borenium cations [21]. Nevertheless, all the species shown in Fig. 3 can be considered as functional equivalents, or masked versions, of borenium cations for reactivity purposes, and in this review they will all be termed borenium cations. Whether these species react via a true borenium cation intermediate or via S_N2 processes is generally unknown.

Finally, reaction solvent is another important variable. The avoidance of strongly coordinating solvents and the use of a solvent that is stable towards cationic boron electrophiles are obviously essential requirements for harnessing borenium ion reactivity in solution. Whilst ethers unsurprisingly decompose in the presence of many borocations [22, 23], even CH_2Cl_2 will react with certain borocations [24]. One specific example is from attempts to form $[(\text{amine})BBr_2]^+$ borocations in CH_2Cl_2 which instead led to halide exchange and formation of $[(\text{amine})BCl_2]^+$ [25]. Solvent polarity can also significantly effect borocation formation particularly equilibrium positions when using B–Y bond heterolysis effected by neutral Lewis acids as the synthetic route. In these reactions, low-polarity solvents often favour neutral species over the borocation [26]. Therefore, the solvents of last resort for synthesising the most electrophilic borocations are the halogenated arenes which combine sufficient polarity and low nucleophilicity with robustness (e.g. resistance to C–X cleavage). When all the above considerations are met, a multitude of highly electrophilic borenium cations, or functional equivalents, can be readily synthesised thus allowing their electrophilicity to be harnessed in the condensed phase.

2.2 *Electrophilicity of Borocations*

Borocation reactivity is dominated by Lewis acidity at boron. However, reactivity studies have demonstrated that electrophilicity at boron spans a considerable range. It is therefore important to summarise the key factors controlling Lewis acidity in these cations. Analogous to the neutral boranes [27], the Lewis acidity of borenium cations is dominated by three factors: (i) the degree of positive charge localised at boron ("hard" Lewis acidity using Pearson's HSAB terminology which is particularly important when the electrostatic contribution to bonding is significant), (ii) the energy of the lowest unoccupied molecular orbital with significant boron character ("soft" Lewis acidity) and (iii) the substituent steric bulk which effects the energy required to pyramidalise at boron and to increase the coordination number at boron from three to four. Intuitively, the unit positive charge present in a borocation would be expected to lead to higher Lewis acidity towards hard Lewis bases relative to neutral borane Lewis acids. This is consistent with experimental observations that many borocations abstract fluoride from $[BF_4]^-$ [11–15], whilst $[CatB(NEt_3)]^+$, **1**, even abstracts fluoride from $[SbF_6]^-$ [13]. Cation **1** therefore has a greater fluoride ion affinity (FIA) than SbF_5 (FIA of $SbF_5 = 489$ KJ mol^{-1}), making it considerably more fluorophilic than the neutral borane, $B(C_6F_5)_3$ (FIA = 444 KJ mol^{-1}) [28]. In contrast, the relative Lewis acidity of **1** and $B(C_6F_5)_3$ towards hydride is reversed, with $B(C_6F_5)_3$ able to abstract hydride from $CatB(H)(NEt_3)$ to form **1** and $[HB(C_6F_5)_3]^-$. This indicates an enhanced "hard" Lewis acidity in **1** due to increased magnitude of positive charge localised at boron (supported by NBO calculations).

As the Lewis acidity comparison between **1** and $B(C_6F_5)_3$ clearly demonstrates no absolute scale of borocation Lewis acidity can be provided due to the inherent dependence on the probe Lewis base. However, two probe nucleophiles have been widely used to assess electrophilicity, Et_3PO (Gutmann–Beckett method) [29] as a "hard" nucleophile and crotonaldehyde (Childs methods) as a "softer" nucleophile [30]. Piers and co-workers found that the dipyrrinato-ligated borenium cation (Fig. 4, **2**) has a Lewis acidity towards crotonaldehyde comparable to BF_3 [31]. The planar chiral borenium cation, **3**, had a Lewis acidity towards Et_3PO that was slightly lower than $B(C_6F_5)_3$ [32]. Our laboratory found that the binding of Et_3PO to **1** produced a greater deshielding of the ^{31}P nucleus than Et_3PO bound to $B(C_6F_5)_3$ indicating greater Lewis acidity for **1** towards Et_3PO, consistent with the relative FIAs [13]. Vedejs and co-workers reported that the non-stabilised borenium cation $[(Me_3N)BH_2]^+$ has a comparable Lewis acidity towards Et_3PO to that reported for **1** (based on comparable δ_{31P} values) [33]. This result can again be attributed to the large degree of positive charge localised at boron in **1**, which is generated by the bonding of boron to three highly electronegative atoms. Finally, Brunker and co-workers used the Gutmann–Beckett method to probe the Lewis acidity of a number of pentamethylazaferrocene ligated borenium cations including **4** and **5** [14]. Cation **4** was found to be more Lewis acidic towards Et_3PO than **5**, consistent with the reduced electronic stabilisation of boron bonded to two hydride substituents relative to two chloride π donor substituents. Despite the significant B=N double bond character in cation **4**, it was still more Lewis acidic than $B(C_6F_5)_3$ towards Et_3PO in competitive binding experiments. The Lewis acidity of compounds **4** and **5** can also be assessed by the magnitude of the dip angle (the ring centroid – N – B angle), with **5** having a dip angle of −9.6° compared to that of −12.3° for $Cp^*Fe(C_5H_4BBr_2)$, indicating a greater interaction between Fe and boron for the neutral borane [14]. These results again suggest an enhanced hard Lewis acidity for borocations due to the unit positive charge.

The paradigm of a soft nucleophile is hydride; thus the hydride binding propensity of borocations is an informative indication of "soft" Lewis acidity. Trityl salts are extremely hydridophilic and will abstract hydride from a multitude of L-BY_2H species to generate borenium cations or their functional equivalents. This is exemplified by hydride abstraction from LBH_3 with $[Ph_3C][B(C_6F_5)_4]$ (L=tertiary amines or NHCs) proceeding effectively, producing the transient weakly stabilised borenium cation, $[LBH_2]^+$, which rapidly dimerises or interacts with an equivalent of LBH_3 to form $[(LBH_2)_2(\mu\text{-}H)]^+$ [7, 21]. Another informative comparison is to benchmark borenium cation hydridophilicity against that of $B(C_6F_5)_3$, the ubiquitous Lewis acid used for H_2/R_3SiH activation in frustrated Lewis pair chemistry [34]. A number of $[PinB(L)]^+$ and $[CatB(L)]^+$ (L=DABCO, $PhNMe_2$, Et_3N, 2,6-lutidine or P^tBu_3) cations have been synthesised by hydride abstraction from the neutral four-coordinate hydroborane using $B(C_6F_5)_3$, thus these cations all have lower HIA values than $B(C_6F_5)_3$. The lower Lewis acidity of these cations towards hydride is partly due to the stabilisation of the p_z orbital on boron by O → B π donation [13, 35–37]. Enhancing π donation by using C → B π donation from a carbodiphosphorane even enabled isolation of a $(L)BH_2^+$ borenium cation (Fig. 4, **7**) by hydride abstraction from LBH_3 with $B(C_6F_5)_3$ [38]. π donation to boron and positive charge delocalisation is also important for stabilising highly unusual borocations, as exemplified by the use of a carbodicarbene enabling isolation of the dication, $[\text{bis(carbodicarbene)BH}]^{2+}$ [39]. In addition to electronic effects, steric bulk can also greatly modulate HIA, with borocation **8** (Fig. 4) also having a lower hydride ion affinity than $B(C_6F_5)_3$. In this case, the lower HIA can be attributed in part to significant steric crowding producing a large pyramidalisation energy [40]. Borenium cations with a greater Lewis acidity towards hydride than $B(C_6F_5)_3$ are accessible provided there is only weak electronic stabilisation of boron and limited substituent steric bulk. For example, the boron centre in [(2,6-lutidine)

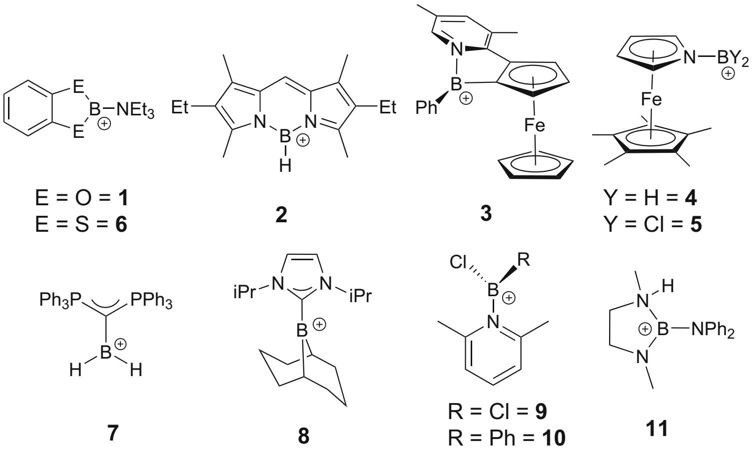


Fig. 4 Borenium cations whose Lewis acidity has been probed experimentally or computationally

$BCl_2]^+$, **9** (Fig. 4), is electronically stabilised by Cl → B π donation, with the pyridyl and BCl_2 moieties orthogonal precluding significant N → B π donation [25]. This cation abstract hydride from $[HB(C_6F_5)_3]^-$ forming (2,6-lutidine)$BHCl_2$ and $B(C_6F_5)_3$, confirming that borocations can be extremely strong Lewis acids towards both hard and soft nucleophiles [13].

Alongside these experimental observations, several computational studies have been performed evaluating the Lewis acidity of borenium cations towards various Lewis bases. The binding enthalpy of NH_3 to borocations was probed at the M06-2X/6-311++G(3df,2p)//M06-2X/6-31+G(d,p) level by Vedejs and co-workers [3]. This revealed a considerable range of NH_3 affinities with borenium cations containing good π donor amido substituents, such as **11** (Fig. 4), being at one extreme displaying minimal Lewis acidity towards NH_3 (ΔH for NH_3 binding = -2.3 kcal mol^{-1}). At the other extreme, the weakly stabilised and sterically unhindered borocation $[(Me_3N)BH_2]^+$ is highly Lewis acidic towards NH_3 (ΔH for NH_3 binding = -48.8 kcal mol^{-1}). Related trends were found for the calculated chloride ion affinity (CIA, Eq. 1) of borocations (at the M06-2X/6-311G(d,p) level with a PCM (DCM)), with the steric environment around boron and π donor ability of substituents important factors effecting Lewis acidity (e.g. **10** is considerably less Lewis acidic towards chloride than **9**, Fig. 4) [13].

$$[R_2BL]^+ + [AlCl_4]^- \xrightarrow{\Delta H_{CIA}} R_2ClBL + AlCl_3 \tag{1}$$

$$[R_2BL]^+ + [HBEt_3]^- \xrightarrow{\Delta H_{HIA}} R_2HBL + BEt_3 \tag{2}$$

One point worth reemphasising is the key effect the degree of positive charge localised at boron has on Lewis acidity towards hard bases, including chloride, due to the high electrostatic contribution to bonding. Two related borocations based on catechol and thiocatechol, **1** and **6** (Fig. 4), were found to have calculated relative Lewis acidities towards chloride that was the reverse of the expected order based on π donor ability (calculated CIA of **1** > **6**). The relative CIA was confirmed by reactivity studies. The greater O → B π donation relative to S → B π donation would suggest that **6** would be a weaker Lewis acid; however, the significantly greater polarisation of the σ bonding framework in **1** leads to a larger magnitude of positive charge localised at boron in **1** thus contributing to a greater CIA (NBO charges at boron for **1** = +1.338e, for **6** = +0.396e at the MPW1K/6-311++G(d,p) level) [6]. The importance of electrostatics in increasing the binding strength of Lewis bases containing highly electronegative donor atoms towards borocations is not limited to borenium cations; Frenking and co-workers reported analogous trends for the borinium cation $[H_2B]^+$ with EC_5H_5 (E=N, P, As, Sb, Bi) [41].

The methodology for assessing relative CIA was extended to determining HIA relative to BEt_3 (Eq. 2). Calculated relative HIA values were found to be consistent with the experimental reactivity observed between borocations and $B(C_6F_5)_3$ [13]. Whilst Lewis acidity trends were broadly analogous to those observed for CIA, there are a number of important distinctions: (i) HIA is less effected by steric

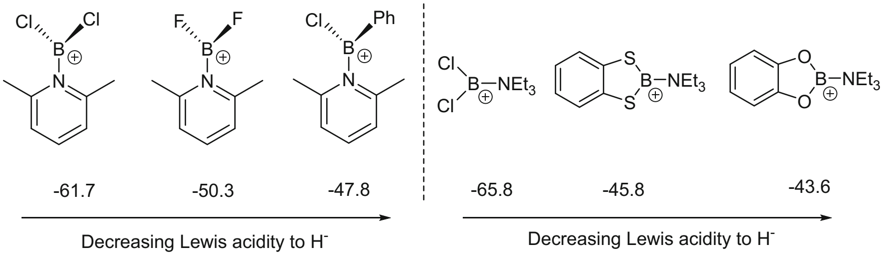


Fig. 5 HIA values of a range of borenium cations. HIA values are relative to BEt_3 (kcal mol^{-1}) calculations at the M06-2X/6311G(d,p) (PCM=DCM) level [13]

bulk around boron relative to CIA due to the smaller size of hydride versus chloride and (ii) the degree of positive charge localised at boron has a lower effect on Lewis acidity as expected for forming a B–H bond in which the electrostatic contribution to overall bond strength will be smaller. Thus **6** is a stronger Lewis acid towards hydride than **1** in contrast to relative CIA. Overall, the effect of altering the halide/chalcogen substituents on the HIA of borenium cations (Fig. 5) mirrors that observed for the Lewis acidity of neutral boranes [27]. A general correlation between the LUMO energy of the borocations in Fig. 5 and HIA was also observed, a trend analogous to that reported for the neutral boranes BF_3 and BCl_3 [42].

2.3 General Reactivity Pathways of Borocations with Nucleophiles

When a sufficiently electrophilic borenium cation, or its functional equivalent, interacts with a nucleophile, the primary product is generally a Lewis adduct. With π nucleophiles (the major area of recent studies), a number of subsequent reaction pathways are followed that are dependent on borocation structure. These can be grouped into three distinct classes: (i) L → B bond cleavage, which generates a new borenium cation, containing an activated nucleophile and an equivalent of a Lewis base (useful for subsequent deprotonations resulting in overall dehydroboration of the nucleophile); (ii) R–B bond cleavage, e.g. leading to intramolecular transfer of an anionic R group to the nucleophile (representing elemento-boration); and (iii) No L–B or R–B cleavage, in which the activated nucleophile in the Lewis adduct can be attacked by an additional nucleophile (which if the product dissociates from boron represents Lewis acid catalysis) (Fig. 6).

Before discussing recent examples of each type, pathway (i) warrants more attention. The addition of a nucleophile to a borenium cation followed by dissociation of L generates $[R_2B(Nuc)]^+$. This is an equivalent outcome to that from reacting a nucleophile directly with a borinium cation, but importantly avoids having to synthesise the borinium cation, which can often be extremely challenging. Borinium cations are in general more electrophilic than borenium cations and

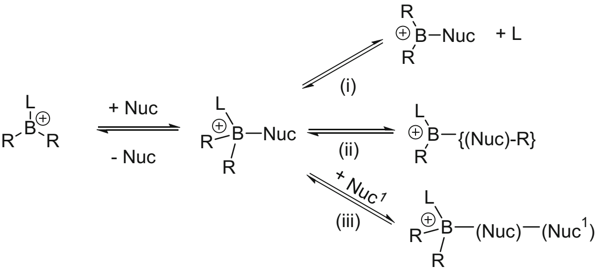


Fig. 6 Possible reaction pathways after initial combination of a borenium cation and a nucleophile (Nuc)

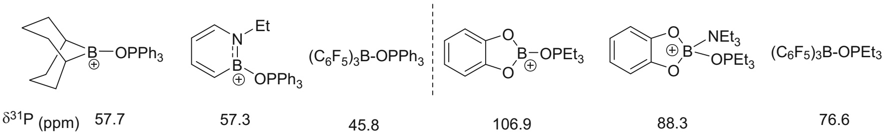


Fig. 7 ^{31}P NMR chemical shifts of phosphine oxide adducts of borocations and $B(C_6F_5)_3$

therefore will activate the coordinated nucleophile to a greater extent [27]. Indeed, the greater downfield shift observed in the ^{31}P NMR spectra of R_3PO coordinated to $[R_2B]^+$ species relative to R_3PO coordinated to $B(C_6F_5)_3$ and to borenium cations confirms the considerable Lewis acidity of borinium cations (Fig. 7) [13, 17, 43, 44]. Thus borenium cations can also be considered as masked borinium cations provided they dissociate L at some point during the reaction with a nucleophile.

Specific examples of reactions between borocations and nucleophiles from the recent literature are presented in Sects. 3–5.

3 Borocations in Dehydroboration

The addition of a nucleophile containing a Brønsted acidic moiety to a borenium cation, or a borenium cation equivalent, can ultimately result in the dehydroboration of the nucleophile. The most obvious example of dehydroboration is the reactivity of borocations with ROH generating B–OR moieties (for a recent example, see [45]). More useful products can be accessed from the dehydroboration of C–H bonds in unsaturated hydrocarbons, and this is the primary focus of this section. Direct electrophilic borylation, the conversion of C–H to C–B, is an appealing synthetic conversion installing a highly versatile functional group onto a hydrocarbyl framework. However, this reaction requires significant Lewis acidity at the boron centre towards soft (π) nucleophiles, with neutral boranes, such as BCl_3, not sufficiently strong Lewis acids [10]. In one mechanistic sequence, L is evolved at some point from boron post binding of the nucleophile (Fig. 8 left) and

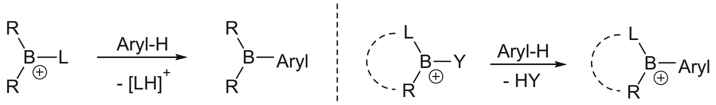


Fig. 8 Two distinct dehydroboration reactions using borenium cations

subsequently acts as a Brønsted base. An alternative dehydroboration pathway that leads to different primary products utilises the anionic substituent on the borocation as a Brønsted basic moiety, generating HY (Y=halide or hydride) as the by-product and producing a new borocation (Fig. 8, right). The latter process dominates particularly when the datively bound L substituent is part of a chelating group, thereby disfavouring dissociation of L from boron.

Historically, multiple intramolecular dehydroborations may proceed via borocations, but the intermediacy of these species was generally not considered [3]. This section therefore predominantly focuses on more recent work where the key role of borocations in C–H borylation has been considered and in some cases unambiguously confirmed.

3.1 Intramolecular Electrophilic Aromatic Borylation

To the best of our knowledge, the first possible observation of a borenium cation in intramolecular electrophilic borylation came from the work of Nagy and co-workers in 2000. In this work, cation **12** (Fig. 9, left) was proposed as an intermediate based on ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. However, the borenium formulation was not definitive due to the absence of ^{11}B NMR spectroscopic data. On warming to 0°C **12** (or its functional equivalent) was converted into the cyclic borylated structure with loss of HCl [46].

Subsequently, Vedejs and co-workers performed more extensive studies on a related intramolecular borylation proceeding via borocation **13** (Fig. 9, right), or its functional equivalent, to form **15** with H_2 as the only by-product [7]. This dehydroboration reaction could be extended to a number of other amine boranes, including for the formation of six-membered boracycles. Anions Weakly coordinating towards borocations were found to be essential, with $[OTf]^-$ preventing dehydroboration, whereas $[NTf_2]^-$ and $[B(C_6F_5)_4]^-$ proving compatibility with borylation. The authors proposed a C–H insertion mechanism where C–B and H–H bond formations were concerted via a four-membered transition state, a hypothesis supported by high-level calculations. Experimental evidence for a C–H insertion mechanism was provided by using the ^{t}Bu containing borocation **14**, which exclusively borylated at the *ortho* C–H position, with no products derived from loss of ^{t}Bu$^+$ observed. The evolution of the *tert*-butyl cation would be expected if the reaction proceeded via an arenium cation and a S_EAr process. The extreme electrophilicity of boron in **13** is presumably essential for generating an interaction between the borocation and the C–H σ bond on the pathway to C–H insertion. It is

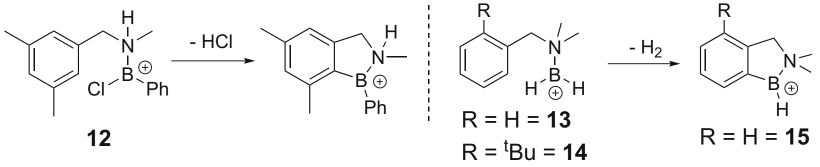


Fig. 9 Intramolecular dehydroboration using borenium cations (or functional equivalents)

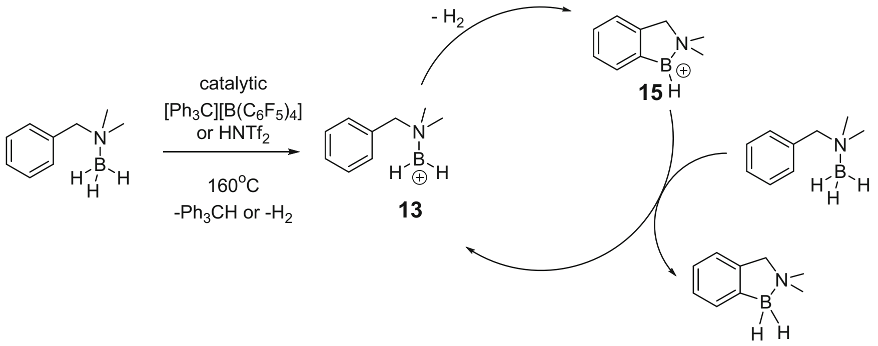
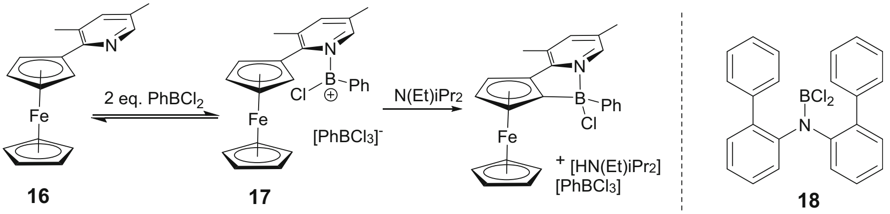


Fig. 10 Catalytic (in cationic activator) intramolecular dehydroboration of arenes

also noteworthy that a related C–H insertion process occurs for the dehydroboration of benzene with BH_3 which produces Ph_3B and H_2 [47, 48]. Catalytic (in activators such as $HNTf_2$) variants using borenium equivalents were concurrently developed (Fig. 10) [7, 49]. The key step in the catalytic cycle involves hydride transfer from (amine)BH_3 to **15** to regenerate **13** (or its functional equivalent). Catalytic turnover proceeded effectively at raised temperatures down to catalyst loadings of 5 mol% $HNTf_2$.

Since Vedejs and co-worker's seminal report in 2009, a number of other intramolecular borylations have been reported where borocations have been proposed as intermediates; this includes pyridyl- [50–52] and phosphinite [53]-directed dehydroborations. In the pyridyl-directed borylation, excess BBr_3 and the hindered base, $NEt^{i}Pr_2$, were both essential; the base required either to deprotonate an arenium intermediate if the reaction proceeds by an S_EAr mechanism or sequester HBr to prevent protodeboronation. Borenium cation intermediates have also been proposed in pyridyl-directed borodestannylation of a stannylated ferrocene and the related dehydroboration of **16** [54]. Compound **16** underwent dehydroboration at −70°C only in the presence of two equivalents of $PhBCl_2$, which the authors suggest supports the intermediacy of **17** (Fig. 11). Borocations (or their equivalent) are also probable intermediates in the synthesis of BN-fused polycyclic aromatics from **18** (and related compounds) by double intramolecular dehydroboration. The addition of $AlCl_3$ and a hindered base were essential for the dehydroboration of **18**, with $AlCl_3$ presumably required to generate borenium equivalents by binding to nitrogen or by abstract halide [55, 56].



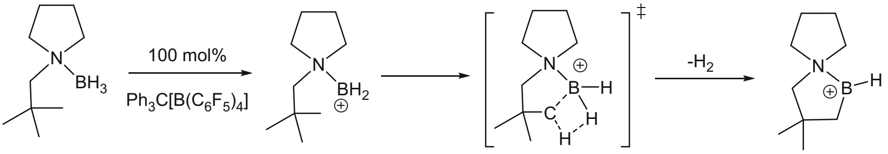
16 17 18

Fig. 11 *Left*, intramolecular borylation proposed to be mediated by borenium cation **17**. *Right*, the precursor **18** used for double electrophilic dehydroboration

3.2 Intramolecular Electrophilic Aliphatic Borylation

The observation of a C–H insertion mechanism in intramolecular electrophilic aromatic borylation using borocations was significant [7], as it had been reported that BH_3 will dehydroborate both arenes and alkanes via a related mechanism [48]. Thus Vedejs and co-workers demonstrated that intramolecular aliphatic C–H borylation using highly electrophilic $[(R_3N)BH_2]^+$ borenium cations, or their equivalents, was also possible. Activation of amine borane **19** with $[Ph_3C][B(C_6F_5)_4]$ led to the evolution of H_2 and formation of the *spiro* borenium cation **20** (which was subsequently characterised by X-ray diffraction studies) [49, 57]. A C–H insertion mechanism was proposed proceeding via a four-membered transition state. (Fig. 12). Figure 12 displays the mechanistic pathway assuming monoboron intermediates.

Vedejs and co-workers extended intramolecular aliphatic borylation to other $[(NR_3)BH_2]^+$ systems and in internal competition studies determined that the formation of five-membered boracycles is preferred over six membered, whilst the dehydroboration of aromatic and aliphatic C–H bonds was kinetically comparable [49]. Finally, they demonstrated that the replacement of $[Ph_3C][B(C_6F_5)_4]$ with $HNTf_2$ was possible and that catalytic (in electrophilic activator) aliphatic C–H borylation was also feasible. Braunschweig et al. reported a related intramolecular C–H borylation from the addition of a ^{t}Bu-substituted NHC to BBr_3 [58]. This rapidly evolved HBr and formed the five-membered boracycle, with the intermediacy of a borenium cation feasible due to ligand steric bulk inducing spontaneous bromide dissociation as previously observed [59]. To date, the dehydroboration of nonactivated aliphatic C–H positions has been limited to the use of highly electrophilic borenium cations (or their functional equivalents). A less remarkable aliphatic intramolecular C–H dehydroboration has been observed starting from **9**, with the addition of a hindered Brønsted base leading to deprotonation of the activated *ortho* methyl group of 2,6-lutidine leading to C–B bond formation and generation of a neutral boracycle [13].



19 **20**

Fig. 12 Intramolecular aliphatic C–H borylation mediated by a borocation

3.3 Intermolecular Electrophilic Aromatic Borylation

The first intermolecular dehydroboration reactions involving borocations or their equivalents came from Muetterties and Lappert [60–63]. Independently, they activated boron trihalides with Lewis acids in arene solvents and observed intermolecular dehydroboration. In both cases, the removal of the Brønsted acidic by-product from S_EAr (either as gaseous HX or as H_2 from the reaction of HX with Al, X=halide) was essential [64]. The active boron electrophile(s) was not observed, but two plausible candidates were proposed (Fig. 13, left) [65]. More recently, Ingleson et al. reported that Muetterties-type dehydroborations are viable with hindered amines in place of aluminium as HX scavengers [10]. Furthermore, Wagner and co-workers proposed an analogous intramolecularly activated electrophile **21** in the dehydroboration of arenes [66].

In 2010, Del Grosso and Ingleson activated CatBCl with extremely halophilic silicenium cations partnered with robust weakly coordinating anions and observed intermolecular borylation of arenes, including the deactivated arene *ortho*-dichlorobenzene. The activation of CatBH [17] (or 1-hydrido-1,3,2-benzodiazaboroles) [6] was also reported using trityl salts or the Brønsted superacidic by-product from arene dehydroboration. The latter reaction enabled electrophilic borylation to be catalytic in the initial electrophilic activator with H_2 the only by-product. The active electrophile in each of these reactions was again transient, eluding observation by low-temperature NMR spectroscopy, but related electrophiles to those proposed for the Muetterties/Lappert systems are feasible (Fig. 14, left) [17]. An alternative electrophile where $\{CatB\}^+$ is stabilised by weak interactions with the $[CB_{11}H_6Br_6]^-$ anion is also feasible, and this can be viewed as a masked form of a borinium cation. A related "quasi-borinium" cation, **22**, derived from [μ-8,8′-I-3,3′-Co(1,2-$C_2B_9H_{10})_2$] has been proposed by Sivaev and co-workers to be the active electrophile in the dehydroboration of arenes [67, 68]. Other carborane compounds with "naked boron vertices" have been used by Michl et al. to effect the borodesilation of arylsilanes [69].

For the catecholato- and halide-substituted monoboron systems, the active boron electrophile is short-lived preventing its unambiguous characterisation, whilst the extremely Lewis/Brønsted acidic reaction mixtures limited substrate scope [63]. Less electrophilic and more well-defined borocations were subsequently utilised that enabled the expansion of electrophilic arene dehydroboration to heterocycles. These cations included catecholato borenium cations and more

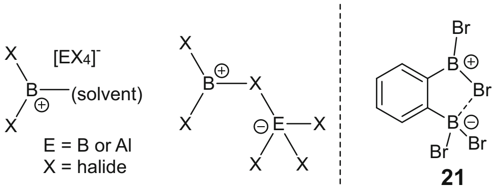


Fig. 13 *Left*, borocation species proposed for Muetterties/Lappert dehydroborations. *Right*, a related boron electrophilic proposed by Wagner and co-workers for intermolecular dehydroboration

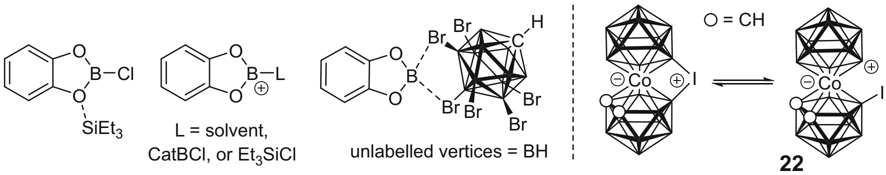


Fig. 14 *Left*, potential boron electrophiles for the intermolecular dehydroboration of arenes using CatBH or CatBCl. *Right*, ring opening of an iodonium cation to generate a "quasi-borinium" cation for arene dehydroboration

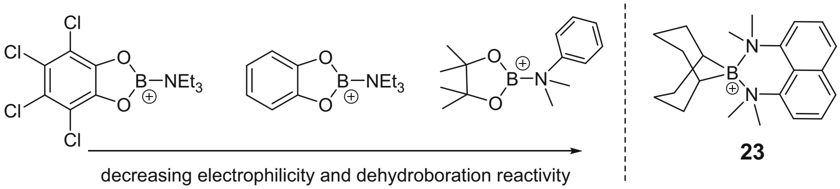


Fig. 15 *Left*, relative reactivity of borenium cations in intermolecular dehydroboration of heteroarenes. *Right*, the boronium cation **23** that dehydroborates activated *N*-heterocycles

electrophilic tetrachlorocatecholato analogues, both generally used as the tetrachloroaluminate salts. As expected based on the lower π donor ability of the aryloxy groups, the tetrachlorocatecholato substituted congener demonstrated an increased arene substrate scope consistent with enhanced electrophilicity at boron (Fig. 15). The solution NMR data and the solid state structure of a tetrachlorocatecholato borenium cation were most consistent with a 3-coordinate boron centre with only weak interactions with the $[AlCl_4]^-$ anion [37]. Related amine-ligated pinacolato borenium cations (Fig. 15) did not borylate activated heterocycles, such as *N*-Me-pyrrole, indicating a considerable reduction in electrophilicity at boron towards π nucleophiles on replacing aryloxide for alkoxide substituents. This was confirmed by calculations which revealed that $[PinB(NEt_3)]^+$ had an HIA relative to BEt_3 (-23 kcal mol^{-1}) (Unpublished results) considerably lower than the catecholato congener (-43 kcal mol^{-1}).

Concurrently, Vedejs and co-workers synthesised the boronium cation, **23**, from the addition of 1,8-bis(dimethylamino)naphthalene to 9-BBN(NTf_2), with the NTf_2

anion essential for high conversion (9-BBNOTf was in equilibrium with **23** + amine with ca. 50% conversion to **23**) [70]. The significantly elongated B–N bonds in **23** relative to other boronium cations indicated strain in the azaboracycle and suggested that **23** would be a reactive electrophile, possibly through a boronium–borenium equilibrium. The well-defined borenium cations, $[9\text{-BBN(NEt}_3)]^+$ and $[9\text{-BBN(4-DMAP)}]^+$, were also reported with strong π donation from pyridyl to boron in the latter apparent from the 18.6 ppm upfield shift observed in the ^{11}B NMR spectra for the 4-DMAP congener relative to the Et_3N congener. Both **23** and $[9\text{-BBN(NEt}_3)]^+$ borylated activated *N*-heterocycles; however, the 4-DMAP analogue did not presumably due to the lower Lewis acidity at boron. In both the catecholato and BBN systems, the borylation proceeded with excellent regioselectivity and the protic by-product from S_EAr was sequestered by the amine initially bound to boron.

Seeking to expand the substrate scope to less nucleophilic heteroarenes, more electrophilic, yet still well-defined, borenium cations containing the poorer π donors (relative to aryloxide) Cl^- and $ArylS^-$ were investigated. A range of $[Cl_2B(\text{amine})]^+$ and $[(CatS_2)B(\text{amine})]^+$ cations were synthesised, and arene dehydroboration studies revealed a borylation reactivity order of $[Cl_2B(\text{amine})]^+ > [(CatS_2)B(\text{amine})]^+ > [CatB(\text{amine})]^+$[6]. This ordering is consistent with relative π donor abilities and calculated HIA [13]. Dichloroborenium cations were not only more reactive but they also enabled installation of a wider range of protecting groups on boron post dehydroboration, including diols and *N*-Me-diiminoacetate (MIDA). A full substrate scope screening was performed using a number of $[Cl_2B(\text{amine})][AlCl_4]$ species [10]. Electrophilic borylation reactivity was generally found to increase as amine nucleophilicity decreased, provided there was not excessive steric bulk around the boron centre [59]. However, due to the complex nature of the equilibrium mixtures derived from $BCl_3/AlCl_3/\text{amine}$ (Fig. 16), it is not possible to unambiguously attribute enhanced borylation reactivity to greater electrophilicity of the respective borenium cation [25, 71]. For example, whilst combination of 2,6-lutidine and BCl_3 followed by addition of $AlCl_3$ provides solution ^{11}B NMR spectra consistent with a borenium cation ($\delta_{11B} = 46.9$ ppm), the use of pyridine or *N*,*N*,4-trimethylaniline (DMT) led to broad resonances (δ_{11B} between 18 and 26 ppm) considerably upfield of that expected for borenium cations. This disparity was attributed to different equilibrium positions, but borenium cations are definitely present in these mixtures as

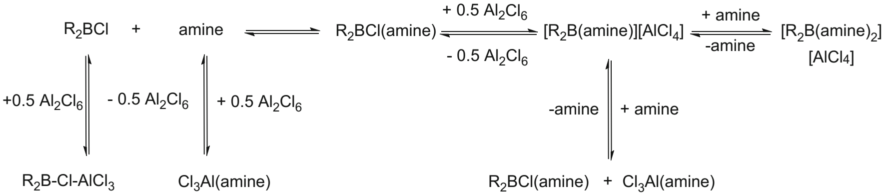


Fig. 16 The multiple equilibria feasible in the formation of borenium cations from mixtures of $R_2BCl/AlCl_3$ and an amine

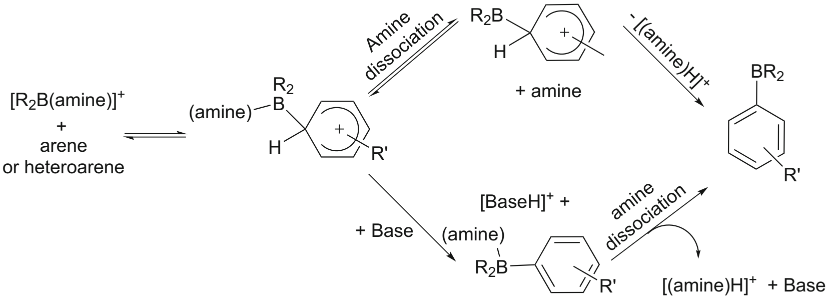


Fig. 17 Mechanisms for the dehydroboration of arenes using $[R_2B(amine)]^+$ varying based on the deprotonation step (R=catecholato or Cl)

$[(pyridine)BCl_2][AlCl_4]$ could be isolated as a solid and crystallographically characterised [71]. *Ortho* disubstituted 2,6-lutidine is particularly effective in reducing the chloride ion affinity of the borenium **9**; therefore, **9[AlCl₄]** is the dominant species on combination of 2,6-lutidine/BCl_3 and $AlCl_3$. Related equilibria are also present in $[CatB(amine)][AlCl_4]$ as evidenced by low-temperature NMR spectroscopy and reactivity studies [37].

To simplify mechanistic studies, a number of borenium cations were synthesised using robust and weakly coordinating anions, $[CB_{11}H_6Br_6]^-$ and $[B(C_6H_3Cl_2)_4]^-$, that do not participate in any halide transfer equilibria. According to a combined experimental and computational study, the borylation of activated arenes at 20°C proceeds through a S_EAr mechanism with borenium cations as the key electrophiles [10]. For catecholato-borocations, two amine-dependent reaction pathways were identified: (i) with $[CatB(NEt_3)]^+$, an additional base is necessary to accomplish borylation by deprotonation of the borylated arenium cation, which otherwise would rather decompose to the starting materials than liberate the amine from boron to effect deprotonation (Fig. 17, bottom). (ii) When the amine component of the borocation is less nucleophilic (e.g. 2,6-lutidine), no additional base is required due to more facile amine dissociation from the boron centre in the borylated arenium cation intermediate (Fig. 17, top).

Surprisingly, given their high electrophilicity $[Cl_2B(amine)]^+$, borenium cations do not dehydroborate weakly activated arenes (e.g. toluene) to any significant degree even at high temperatures [10]. Instead, the key electrophile for the borylation of less activated arenes is presumably derived from the interaction of $AlCl_3$ with R_2BCl, with the amine fulfilling the roll of proton scavenger. Despite the mechanistic complexity of arene dehydroboration using BCl_3-derived boreniums or their functional equivalents, it is an attractive one-step methodology for converting C–H to C–B and is complementary in selectivity to iridium-catalysed direct borylation (electronic control versus predominantly steric control) [72].

Recently, Oestreich, Tatsumi and co-workers developed a route to dehydroborate activated heteroarenes directly using pinacol-ligated borenium cations [73]. In contrast to previous studies using amine-ligated pinacol borenium cations that were ineffective for dehydroborations, they used a cationic Ru(II)–SR compound that was bound to $[PinB]^+$ through sulphur. Presumably, the lower

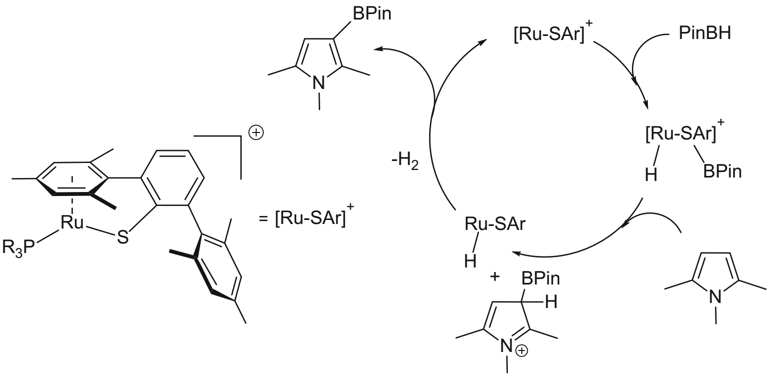


Fig. 18 Catalytic (in cationic ruthenium complex) dehydroboration

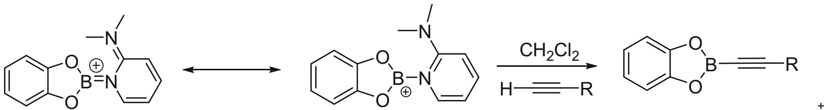


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Fig. 19 The dehydroboration of alkynes using borenium cation **24**

nucleophilicity of the cationic Ru–SR moiety relative to the amine Lewis bases previously studied enhances electrophilicity at boron sufficiently to borylate certain activated heteroarenes. It is also noteworthy that borylation is catalytic in the ruthenium complex, with H_2 loss regenerating the key ruthenium complex (Fig. 18), making this an extremely atom-efficient and elegant process. However, the substrate scope reported to date for this process has been limited to highly activated nitrogen heteroarenes, with *N*,*N*-dimethylaniline and *N*-^{i}Pr$_3$Si-indole not borylated. This indicates that electrophilicity at boron in $[PinB(Ru(H)\text{-}SR)]^+$ is still significantly lower than the catecholato borenium cations which do borylate these substrates [37].

The expansion of dehydroboration to other unsaturated hydrocarbons is in its infancy. Our laboratory has recently reported [CatB(2-DMAP)][$AlCl_4$], **24**, which is a borenium cation in the solid state (by X-ray crystallography) and solution (based on δ_{11B}) despite the presence of two nucleophilic nitrogens in 2-DMAP. This can be attributed to $O \rightarrow B$ π donation and significant B=N double bond character reducing the electrophilicity at boron thereby disfavouring chelation by 2-DMAP. Despite the significant B=N character, **24** is still sufficiently electrophilic to dehydroborate terminal alkynes to produce alkynyl boronic esters (Fig. 19) in moderate to good yields [74]. Whether the pendant NMe_2 basic site plays a role in the deprotonation step is currently unclear, but the related borocation, $[CatB(NEt_3)]^+$, only produced alkyne-dehydroborated products in low yields even in the presence of noninteracting bases to effect deprotonation.

4 Borocations in Elemento-Boration

Elemento-boration is the addition of a B–X bond across an unsaturated moiety. Sections 4.1 and 4.2 discuss the borocation analogues of the venerable (with neutral boranes) hydroboration and haloboration reactions.

4.1 Hydroboration

The intermediacy of borenium cations (or their functional equivalents) in hydroboration was first considered by Vedejs and co-workers when studying the reactivity of (L)BH_2X (X=I or OTf, L=amine or phosphine) [75–77]. Importantly, the hydroboration reactivity of the (L)BH_2X species was distinct to that of the free borane, particularly in providing improved regioselectivity. The authors concluded that an S_N2-type process involving concerted attack by the π nucleophile/B–X heterolysis was proceeding. In this case, LBH_2X is therefore a functional equivalent of a borenium rather than a true borenium cation. More recently, this approach was extended by Vedejs, Curran, Lacôte and co-workers to the borenium equivalents (NHC)BH_2NTf_2 and [((IMe)BH_2)$_2$(μ-H)][NTf_2], **25** (IMe = 1,3-dimethylimidazol-2-ylidene) [78]. In contrast to amine borane adducts, NHCs do not dissociate from boron even under forcing conditions. Therefore, NHC–borane hydroboration is unequivocally due to borenium-type character engendered by the weakly coordinating NTf_2 (or (μ-H) moiety). The product distribution from mono- and di-hydroboration (forming (IMe)B(R)(H)NTf_2 and (IMe)B(R)$_2NTf_2$, respectively, Fig. 20) of a range of alkenes with these borenium cation equivalents was assessed. Interestingly, hydroboration of a number of internal alkenes resulted in rapid migration and final reaction mixtures in which boron at C2 is the dominant product. In contrast, hydroboration with neutral boranes undergoes slower migration and converges to give primary alkylboranes (boron at C1) [78].

Curran and co-workers subsequently extended this approach to the iodide congener, (IMe)BH_2I. This was more selective for mono-hydroboration and enabled the alkene substrate scope to be expanded [79], particularly towards tri- and tetra-substituted alkenes for which the triflimide analogue gave complex mixtures of products. It is noteworthy that in the presence of excess (IMe)BH_3, the iodide congener (IMe)BH_2I does not react to form **25** confirming the greater coordinating power of iodide versus NTf_2 towards boron. In the same paper, the

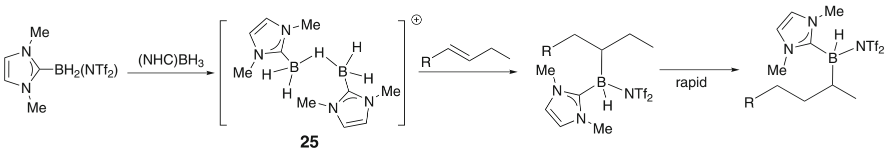


Fig. 20 Hydroboration of alkenes using borenium cation equivalent **25**

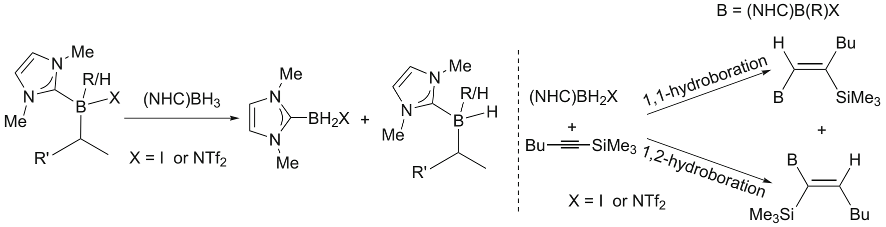


Fig. 21 *Left*, key hydride transfer step in catalytic (in activator) hydroboration. *Right*, 1,1- and 1,2-hydroboration of silyl substituted alkynes

variation of steric bulk on the *N*-substituent of the NHC was investigated, with the most notable effect being bulky aryl groups on nitrogen (mesityl, 2,6-diisopropylbenzene) preventing hydroboration, consistent with an increased barrier for an S_N2-type process. Hydroboration can be made catalytic in $HNTf_2$ or I_2 activators (typical loadings are ca. 10 mol%), with a hydride transfer step again key for transferring borenium-type character (Fig. 21 left).

The hydroboration of a range of allyl and alkenyl silanes produced the 1,2 hydroboration products exclusively under stoichiometric and catalytic activation of $(NHC)BH_3$ with I_2 [80]. The hydroboration of alkynyl silanes was more complex with both syn-1,2- and 1,1-hydroborated products observed (Fig. 21, right). The latter isomer was formed by silicon migration prior to B–H cleavage as it did not form from isomerisation of the 1,2-hydroboration products in the presence of borenium equivalents. 1,1-Hydroboration is related to the “Wrackmeyer reaction” which includes the 1,1-carboboration of alkynyl silanes with BEt_3 [81]. Mesoionic carbene boranes were also effective for the hydroboration of allylbenzene on activation with $[Ph_3C][B(C_6F_5)_4]$, presumably proceeding via borenium cations or their functional equivalents [82]. Brunker and co-workers also utilised a borenium cation produced by hydride abstraction, in this case from pentamethylazaferrocene-BH_3, to hydroborate 1,5-cyclo-octadiene to generate [pentamethylazaferrocene-$BBN]^+$ [14]. In contrast to the reactive borenium hydroborating agents discussed above, the B–H containing borenium cation **2** did not hydroborate phenylacetylene, an indication of considerable π delocalisation reducing Lewis acidity towards soft nucleophiles [31]. Finally, the combination of PinBH/THF and $B(C_6F_5)_3$ is essential for hydroboration catalysed by an Rh complex, with a borenium ion intermediate proposed to facilitate the formal oxidative addition of PinBH to Rh [36].

4.2 *Other Elemento-Boration Reactions*

Haloboration of alkynes using trihaloboranes is well documented but is restricted to terminal alkynes due to limited electrophilicity at boron [83–85]. Calculations on haloboration indicated that increasing electrophilicity at boron results in haloboration becoming more exothermic, and the key transition state barrier also becomes lower in

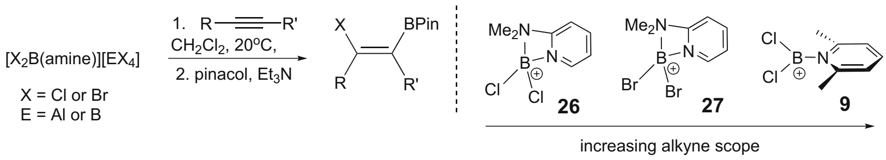


Fig. 22 Haloboration and esterification of alkynes with borenium and boronium cations

energy [86]. Therefore our laboratory investigated the reactivity of alkynes with a series of dihaloborocations, $[X_2B(\text{amine})]^+$ (X=Cl or Br), ligated by 2-DMAP or 2,6-lutidine. $[X_2B(\text{2-DMAP})]^+$ (**26** and **27**, Fig. 22) exist as boronium cations with 2-DMAP a bidentate ligand in contrast to the catechol analogue, **24**. This disparity is presumably due to the lower degree of stabilisation from halide π donation to boron in the ring-opened borenium isomers of **26** and **27** relative to **24** [74]. The chelation of 2-DMAP to boron results in the formation of a significantly strained four-membered boracycle, “consistent with a low calculated barrier to ring opening, was calculated. However, currently, it is not known if $[X_2B(\text{2-DMAP})]^+$ cations react via a borenium cation intermediate or via an S_N2-type process.

Cation **26** only haloborated terminal alkynes, with 1,2-haloboration the exclusive mode of reaction and the initial vinylBCl_2 product in situ esterified to the pinacol boronate ester. Increasing the electrophilicity at boron by replacing chloride for bromide increased the scope of 1,2-haloboration, but only to include internal dialkyl alkynes. The use of 2,6-lutidine in place of 2-DMAP increases electrophilicity at boron further, with **9** haloborating a range of internal alkynes. Throughout, haloboration occurred with excellent regio- and stereoselectivity, predominantly controlled by electronic effects. It is noteworthy that attempts to use another boron electrophile highly effective in arene dehydroboration, specifically that derived from DMT/BCl_3/$AlCl_3$, in place of $[(2,6\text{-lutidine})BCl_2][AlCl_4]$ led to complex mixtures with little haloborated product observed. Presumably the different halide transfer equilibrium positions observed when using DMT compared to 2,6-lutidine lead to significant quantities of aluminium Lewis acids which are well documented to react with alkynes to give oligomers/polymers.

Attempts to extend elemento-boration to the carboboration of terminal alkynes using $[Ph(Cl)B(\text{2-DMAP})][AlCl_4]$ led instead to 1,2-haloborated products, with chloride migrating in preference to phenyl. Modification of the substituents on boron to permit only the migration of phenyl was achieved by using the chelating monoanionic ligand, 8-hydroxyquinoline [87]. The borenium cation **28** was accessed in two steps from $PhBCl_2$, whereas the 5-hexylthienyl congener, **29**, was prepared from 5-hexylthiophene using electrophilic dehydroboration to form the thienylBCl_2. Both **28** and **29** reacted with the 3-hexyne to give products from 1,2-carboboration (Fig. 23). In contrast, **28** reacted with 1-pentyne to effect alkyne cyclotrimerisation forming 1,3,5-tripropylbenzene. The cyclotrimerisation observed with **28** was attributed to the generation of Lewis acidic “$AlCl_3$” species which rapidly cyclotrimerises terminal alkynes but only slowly cyclotrimerises internal alkynes [88]. The support for the presence of Lewis acidic “$AlCl_3$” species

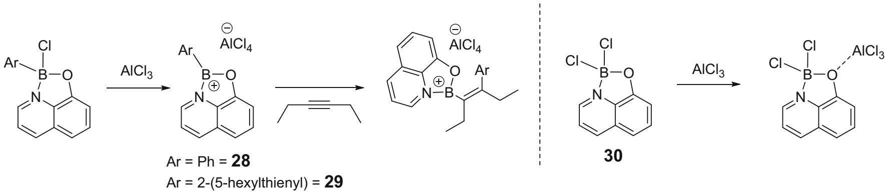


Fig. 23 *Left*, synthesis of borocations **28** and **29** and the 1,2-carboboration of 3-hexyne. *Right*, coordination of $AlCl_3$ to oxo functionality instead of the expected mode of reactivity, halide abstraction

was provided by the addition of $AlCl_3$ to **30** (Fig. 23, right). Instead of borenium cation and $[AlCl_4]^-$ formation, $AlCl_3$ interacts with the weakly nucleophilic oxygen. The formation of an $O\cdots AlCl_3$ interaction can be disfavoured simply by installing a methyl group *ortho* to oxygen, with the addition of $AlCl_3$ now forming a borenium cation.

Recently, the remarkable carboboration of CO_2 with a borinium cation has been reported. The dimesityl borinium cation, $[(Mes)_2B]^+$, **31**, was readily accessed by fluoride abstraction from Mes_2BF with a triethylsilicenium salt. **31** is a linear (at boron) cation stabilised by π donation from the two orthogonally orientated mesityl groups. Cation **31** reacts with CO_2 by 1,2-carboboration, ultimately forming aroyl cations, $[MesCO]^+$ and MesBO, with the latter undergoing oligomerisation and further reactions with **31** to give a complex mixture of boron-containing products [89, 90].

5 Borocations in Catalysis

The previous two sections have discussed the chemistry of borocations with a range of nucleophiles that lead to the loss/transfer of one of the substituents originally bound to boron. The final major class of reactions that borocations have been utilised for retains all three substituents on boron throughout with the borocation centre acting as a Lewis acid catalyst or as an intermediate in hydride "shuttling" reactions.

The paradigms of borocations as Lewis acid catalysts come from seminal studies by Corey and co-workers on chiral cations derived from oxazaborolidines. The two major applications are BH_3-activated oxazaborolidines for chiral hydroborations (the Corey–Bakshi–Shibata reaction, Fig. 24, left) and using $AlBr_3$ or H^+ activation for catalytic enantioselective cycloadditions (Fig. 24, right). Whilst unambiguous borenium formation is not confirmed by ^{11}B NMR spectroscopy for the majority of these systems, it is clear from reactivity studies that borenium equivalents, if not actual borenium cations, are present in solution (an in-depth discussion on the solution species present in activated oxazaborolidine chemistry is provided by Vedejs and co-workers) [3]. It is noteworthy that oxazaborolidines are both extremely weak

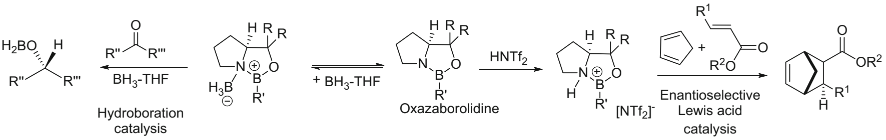


Fig. 24 Oxazaborolidine-derived Lewis acid catalysts for hydroboration and cycloadditions

bases and weak nucleophiles at nitrogen, with Corey and co-workers reporting that there was no significant protonation by methane sulfonic acid and no coordination of $AlCl_3$ or $GaCl_3$ observed. Finally, significant reactivity differences are again observed when using $[OTf]^-$ and $[NTf_2]^-$ as counterions, with $[OTf]^-$ giving drastically inferior catalytic activity due to strong coordination of triflate to boron. The considerable body of work in this area is summarised in two reviews by Corey and co-workers, which readers are directed to for further information [8, 91]. Subsequent to these reviews, high-level calculations were reported that support Corey's proposed mechanistic pathways with Lewis or Brønsted acids interacting with nitrogen giving lower energy species and lower barrier processes than the activation of the oxazaborolidines through coordination of acids to oxygen [92, 93].

Concurrently, Yamamoto developed related oxazaborolidines and demonstrated that the most active catalyst was formed by protonating at nitrogen with $C_6F_5CH(SO_2CF_3)_2$. This produced a catalyst that outperformed both the HOTf- and $HNTf_2$-activated congeners in Diels–Alder reactions. The authors attributed this reactivity trend to the greater steric bulk of the $[C_6F_5C(SO_2CF_3)_2]^-$ anion which weakens its coordination to boron relative to $[OTf]^-$ and $[NTf_2]^-$ ([94]; [95] and references therein). Finally, catalysis of the allylboration of aldehydes may also proceed via related "borenium-type" intermediates generated from Brønsted/Lewis acid coordination to the oxo functionality present in pinacol allylboronates. This extensive and well-developed area was reviewed in depth in 2011 by Elford and Hall [96]. Furthermore, a detailed discussion of this and other synthetic applications of activated oxazaborolidines has been recently provided by Vedejs and co-workers [3].

The most recent catalytic applications of borenium cations are in the activation of σ bonds, particularly H_2. The first suggestion that borocations can activate H_2 came from Olah and co-workers who proposed that $[B_2H_5]^+$ can reversibly coordinate and cleave H_2 [97]. This area lays unexplored until Vedejs and co-workers heated **13[B(C_6F_5)$_4$]** under a D_2 atmosphere and observed H/D exchange concomitant with anion decomposition [7]. Due to the complex/heterogeneous nature of both these examples, H_2 activation by a borocation could not be unambiguously confirmed. Subsequently, Stephan and co-workers unequivocally demonstrated that the borenium cation **8** (Fig. 25, left) activates H_2 in a frustrated Lewis pair (FLP) [40]. Frustrated Lewis pairs use unquenched Lewis acidity/basicity to heterolytically activate H_2 in a concerted manner and have become a highly topical area [34]. Cation **8** forms an FLP with P^tBu_3 due to the combined steric bulk precluding dative bond formation. This FLP when exposed to H_2 (4 atm.)

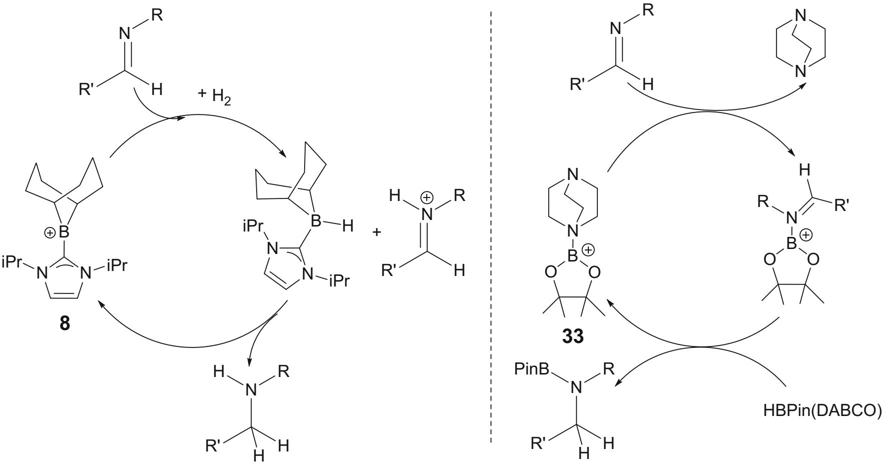


Fig. 25 *Left*, catalytic (in cationic activator) hydrogenation and *right*, hydroboration mediated by borenium cations

heterolytically cleaves H_2. More significantly, **8** is a catalyst for the hydrogenation of imines and enamines via an FLP mechanism, with a functional group tolerance broader than the ubiquitous neutral borane used for FLP reductions, $B(C_6F_5)_3$. For example, **8** tolerates diarylketones, *ortho*-substituted pyridyls and ethyl benzoates. The lack of reaction between **8** and these oxo functionalities is remarkable given the high Lewis acidity of borocations to hard Lewis bases previously discussed. This is presumably due to the severely sterically congested environment around boron.

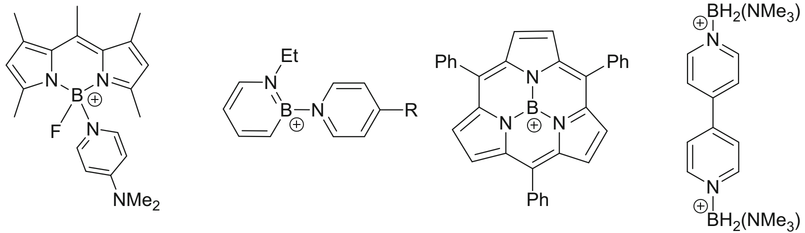
Ingleson and co-workers reported two other borocation-based FLPs that were capable of activating H_2, albeit with competitive reactions observed alongside heterolytic H_2 cleavage [13]. This was followed by the observation that the borenium cation $[(\text{acridine})BCl_2]^+$, **32**, formed an FLP with hindered pyridines that activated H_2 [98]. Surprisingly, the position of hydride addition to **32** was not at boron, but at the C9 carbon of acridine, consistent with this position being the most Lewis acidic towards hydride by HIA calculations. Concurrent to Stephan's borenium-catalysed hydrogenation work, Crudden and co-workers reported a related reduction (hydroboration followed by hydrolysis of the N–B bond) of imines, nitriles and *N*-heterocycles with HBpin catalysed by $[\text{PinB(DABCO)}]^+$, **33** (Fig. 25, right) [99]. The DABCO Lewis base in the borenium cation is proposed to be displaced by an imine to form $[\text{PinB(imine)}]^+$; however, a boronium, $[\text{PinB(DABCO)(imine)}]^+$, is an alternative intermediate. Regardless, the activated imine is subsequently reduced by HBPin(DABCO), regenerating the borenium cation. Consistent with HIA calculations (the conjugate Lewis acid $[\text{PinB(amine)}]^+$ has a lower HIA than $B(C_6F_5)_3$), HBPin(amine) was found to be a better reductant than $[HB(C_6F_5)_3]^-$. The aldimine substrate scope reduced with $[\text{PinB(DABCO)}]^+$ was greater when compared to hydrogenations using $B(C_6F_5)_3$ containing FLPs, indicating improved functional group tolerance of the borocation relative to $B(C_6F_5)_3$.

Alongside H_2 activation, there is considerable current interest in using boron Lewis acids for the activation of Si–H bonds via B-(μ-H)-Si intermediates [100]. Borocations also form sigma complexes with silanes, with Vedejs and co-workers observing a significant upfield shift in the ^{11}B NMR spectrum for **13** on addition of $^{i}Pr_3SiH$ [7]. Jäkle and co-workers also reported that the chiral borenium cation **3** interacts with Et_3SiH via B-(μ-H)-Si interactions (as indicated by loss of $^3J_{HH}$ H-Si-CH_2 coupling) and catalyses the hydrosilylation of carbonyls with only modest 20% *ee* [32]. Denmark and co-workers subsequently demonstrated than [9-BBN(2,6-lutidine)]$^+$, **34**, catalysed the hydrosilylation of a range of ketones to silyl ethers [44]. In contrast to the hydrosilylation of ketones with Et_3SiH catalysed by 9-BBN(NTf_2) and $B(C_6F_5)_3$, cation **34** does not catalyse the over reduction of the silyl ether to the alkane under identical conditions. An analogous hydrosilylation mechanism to that elucidated for $B(C_6F_5)_3$ was proposed [101]; this was based in part on the observation that the addition of Et_3SiH to [33][**NTf₂**] led to the formation of 9-BBN-H and Et_3SiNTf_2.

6 Miscellaneous Applications of Borocations

6.1 Materials Applications

In 1998, Atwood and co-workers reported the use of a boronium cation that reacted as a masked borenium to initiate the polymerisation of propylene oxide [102]. Since then, one of the major materials applications of borocations is to modify photophysical properties by converting neutral boranes into borenium and boronium cations. Notable examples are the modification of the BODIPY framework independently by the groups of Piers and Gabbai, with the latter demonstrating that a BODIPY boronium cation, **35**, can be used as a switch on fluoride sensor [31]. The use of borocations in this area is discussed in more depth in a number of review articles [3, 5, 103]. More recently, 1,2-azaborine-containing borenium cations, **36** (Fig. 26), have been synthesised that are emissive in the solid state with high quantum yields and narrow emission bands [43]. A subporphyrin



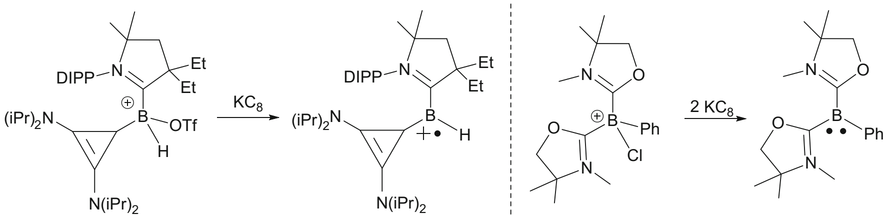
35 **36** **37** **38**

Fig. 26 Select borocations whose photophysical or electrochemical properties have been assessed borenium cation, **37**, has also been isolated indicating the viability of these species as intermediates in facile boron axial ligand exchange in this class of porphyrinic pigments [104]. The subporphyrin borenium cations were found to have similar absorption and emission spectra to the neutral four coordinates at boron, B-methoxy precursors. Calculations indicate that this is due to a comparable stabilisation of the LUMO+1, LUMO, HOMO and HOMO-1 all by ca. 3.6 eV. Boronium cations have also been demonstrated to be highly emissive, with $[(4\text{-DMAP})_2(9\text{-borafluorene})]^+$ emitting in the blue in halogenated solvents when excited with UV light [105].

A number of boronium-containing polymers were also synthesised [106], with boronium incorporation enabling reversible reduction (by CV) [107], whilst the controlled cleavage of a boron–pyridine bond was used for stoichiometric Brønsted acid–base reactivity [108]. Boronium cations have also been incorporated into ionic liquids to be used as extremely stable electrolytes for lithium batteries [109] and as hypergolic fluids [110]. Finally, Davis Jr. and co-workers have synthesised **38** (Fig. 26), a diboronium dicationic analogue of viologens, and demonstrated its rich redox behaviour indicating its potential as an electroactive material [111]. The nature of related reduced boronium species is discussed further in Sect. 6.2.

6.2 Borocations as Precursors to Borylenes and Boryl Radicals

Borocations have proved to be useful precursors for the synthesis of a range of radicals. For example, 2,2′-bipyridyl (bipy)-ligated boronium cations undergo one-electron reduction to form radicals with the amount of spin density localised on boron that is highly dependent on the other substituents. For example, the radical from one electron reduction of the Lewis acid / base adduct between 2,2′-bipyridine and 9-bora-9,10-dihydroanthracene has significant boron character [112], whilst the calculated Mulliken spin density at boron is only 0.15% for the (2,2′-bipyridyl)BCl_2 radical analogue [113]. A bis-carbene boronium cation, **40**, can be reduced by one and two electrons to give an unusual radical cation (Fig. 27), **41**, and a bis(carbene) borylene, respectively [114]. A related approach was recently utilised by Vidovic



40 **41** **42** **43**

Fig. 27 Reduction of boronium cations to radical cation **41** (*left*) and to the carbene-stabilised borylene **43** (*right*) and co-workers with the two-electron reduction of boronium cation **42** leading to the bis(oxazol-2-ylidene)borylene, **43**, which can be protonated at boron to form a new boronium cation [115].

Borenium cations also undergo one-electron reductions, and these occur at distinctly more positive potentials than neutral boranes, for example, $[(\mathrm{Mes})_2\mathrm{B}(\mathrm{L})]^+$ (L = 4-DMAP and IMe) have $E_{\mathrm{peak}} = -2.03$ V and $E_{1/2} = -1.81$ V, respectively (versus $\mathrm{Fc}^+/\mathrm{Fc}$) [114, 115]. The latter can be chemically reduced with magnesium to give a persistent radical that has significant spin density at boron [116, 117].

6.3 Structural Rearrangement of Borocations

Carbocations are well documented to undergo skeletal rearrangements, e.g. 1,2-sigmatropic shifts (Wagner–Meerwein rearrangements), but despite the isoelectronic relationship between carbocations and borenium cations, related conversions in borocations are significantly less common. One example from Braunschweig and co-workers who observed 1,2-halide/mesityl exchange was induced by Lewis base coordination in diborane(4) compounds [118]. This process may involve ionic or zwitterionic borocation intermediates and halide bridge adducts, e.g. **44** (Fig. 28). It is also noteworthy that the replacement of mesityl for NMe_2 leads to the formation of unusual borenium cations based on a diborane(4) backbone, **45** (inset Fig. 28). Himmel and co-workers have also recently synthesised a borenium cation based on a diborane backbone and found that it rapidly undergoes a remarkable B–B coupling reaction to form a tetraborane dication [20].

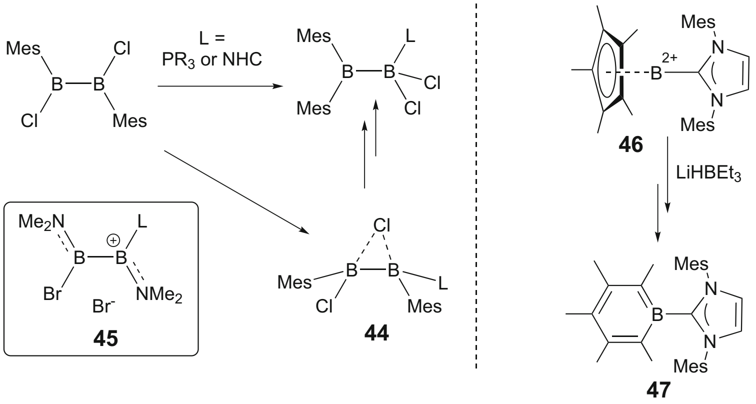


Fig. 28 The inorganic analogue of the Wagner–Meerwein rearrangement (*left*). *Inset bottom left*, a borenium cation based on a diborane(4) backbone. *Right*, the hydride-induced conversion of a dicationic boron compound to an NHC-stabilised borabenzene

A limited number of other structural rearrangements of borocations have also been reported, for example, heating the boronium cation [B,B-(*N*-Me-imidazole)$_2$(BC$_5$H$_5$-2-SiMe$_3$)]Cl under vacuum produced the borabenzene complex B-(*N*-methyl-imidazole)BC$_5$H$_5$ [119]. The borenium cation [(η^1-C$_5$Me$_5$)B(Cl)(IMes)]$^+$ undergoes halide abstraction with AlCl$_3$ to form the dication [(η^5-C$_5$Me$_5$)B(IMes)]$^{2+}$, **46** (Fig. 28). Subsequent addition of Li[HBEt$_3$] induces the remarkable ring expansion conversion to IMes-stabilised borabenzene, **47** [120].

7 Conclusions and Future Outlook

At the end of 2005 Piers and co-workers predicted that the chemistry of cationic boron compounds was on the verge of a “quantum leap” in activity [2]. This prediction proved prescient with a multitude of synthetic applications using borocations developed over the past 5–6 years. A significant factor in enabling this surge in interest is the considerable versatility of borocations. The myriad of structural permutations for borocations allows for the controlled modulation of electrophilicity and steric environment at boron. This flexibility allows for bespoke borocations to be designed and readily synthesised for targeted applications. For example, the activation of aliphatic C–H bonds requires the extreme electrophilicity of weakly stabilised borocations [49], whilst more functional group-tolerant hydrogenations require combining moderate electrophilicity (to activate H$_2$) with considerable substituent steric bulk at boron [40]. The structural versatility not only controls key properties but it can also be used to fundamentally alter the reaction pathway followed post combination of a borocation and a nucleophile. This has considerable potential as exemplified by simple structural changes to the borocation enabling selective dehydroboration, haloboration and carboboration of alkynes [74, 87].

Borenium cations are isoelectronic to neutral boranes and carbocations, and Vedejs and co-workers have previously highlighted the similarities and disparities in the fundamental chemistry of carbocations and borenium cations [3]. As synthetic applications of borocations increase, reactivity disparities between neutral boranes and borenium ions are also becoming apparent. Whilst a number of the synthetic applications mentioned throughout this review are conceivable (or have already been reported) with neutral boranes, a considerable proportion require the unique properties of borocations. Most examples require the enhanced electrophilicity of borocations which can surpass that of the neutral boranes BBr$_3$ and B(C$_6$F$_5$)$_3$. This is demonstrated in the intermolecular dehydroboration of arenes, a reaction that utilises two components of the borocation in distinct steps: (i) the strongly Lewis acidic borocation forms the borylated arenium cation and (ii) the evolved Brønsted base acts as a proton scavenger [10]. Related dehydroborations using neutral boranes (particularly B(C$_6$F$_5$)$_3$)/noninteracting base combinations are known but are much more limited in arene scope [121]. In addition to the dramatic reactivity differences derived from extremely electrophilic borocations, there are also more subtle distinctions emerging between the chemistry of neutral boranes and borocations (or their equivalents). One notable example is the alkene hydroboration product distribution observed by Vedejs and Curran and co-workers; with borenium equivalents, this results in predominantly C2-borylated hydroboration products after migration, whereas neutral boranes lead to C1-borylated hydroboration products post migration [78, 79].

The advances discussed herein highlight the burgeoning utility of borocations in synthesis, but this field is still in its infancy. Simply defining the reactivity of borocations towards π nucleophiles other than arenes and alkynes is in itself a vast research area, whilst the ability to activate sigma bonds opens up a multitude of possibilities, both stoichiometric and catalytic in borocation. Furthermore, the recent development of a simple route to the highly electrophilic borinium cation, $[(Mes)_2B]^+$, and the subsequent unusual reactivity with CO_2 suggests that even the most reactive member of the borocation family, the borinium, is poised for wider exploitation [89]. In comparison to synthetic applications, the incorporation of borenium and boronium ions into functional materials is less developed and opportunities abound in using the unique properties of borocations to produce desirable photophysical properties. Consequently, the next decade should see a continuation of the recent "quantum leap" in activity and see borocations assume a place alongside neutral boranes as widely used reagents and catalysts, rather than simply being niche reagents and curiosities.

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Synthesis and Application of Organoboron Compounds
Fernández, E.; Whiting, A. (Eds.)
2015, VII, 331 p. 492 illus., 14 illus. in color., Hardcover
ISBN: 978-3-319-13053-8