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Protonolysis and Thermolysis Reactions of Functionalised NHC-carbene Boranes and Borates

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A set of β-ketoimidazolium and β-ketoimidazolinium salts of the general formula $[R^1C(O)CH_2\{CH[NCR^3CR^3N(R^2)]\}]X$ (R^1 = ^{t}Bu, naphth; R^2 = ^{i}Pr, Mes, ^{t}Bu; R^3 = H, Me, $(H)_2$; X = Cl, Br) show contrasting reactivity with superhydride bases $MHBEt_3$; two are reduced to chiral β-alcohol carbene-boranes $R^1CH(OH)CaH_2\{C(BEt_3)[NCR^3CR^3N(R^2)]\}$ **2** (R^1 = ^{t}Bu; R^2 = ^{i}Pr, Mes; R^3 = H), two with bulky R^2 substituents are reduced to chiral β-borate imidazolium salts $[R^1CH(OBEt_3)CH_2\{CH[NCR^3CR^3N(R^2)]\}]X$ **3** (R^1 = ^{t}Bu, naphth; R^2 = Mes, ^{t}Bu; R^3 = H, Me; X = Cl, Br), and the two saturated heterocycle derivatives remain unreduced but form carbene-borane adducts $R^1C(O)CH_2\{C(BEt_3)[NCR^3CR^3N(R^2)]\}$ **4** (R^1 = ^{t}Bu, naphth; R^2 = Mes; R^3 = $(H)_2$). Heating solutions of the imidazolium borates **3** results in the elimination of ethane, in the first example of organic borates functioning as Brønsted bases and forming carbene boranes $R^1CH(OBEt_2)CH_2\{C[NCR^3CR^3N(R^2)]\}$ **5** (R^1 = naphth; R^2 = Mes; R^3 = Me). The 'abnormal' carbene borane of the form **2** $R^1CH(OH)CH_2\{CR^2[NC(BEt_3)CR^3N(R^2)]\}$ (R^1 = ^{t}Bu; R^2 = ^{t}Bu; R^3 = H), is also accessible by thermolysis of **3**, suggesting that the carbene-borane alcohol is a more thermodynamically stable combination than the zwitterionic imidazolium borate. High-temperature thermolysis also can result in complete cleavage of the alcohol arm, eliminating *tert*-butyloxirane and forming the B-N bound imidazolium borate **7**. The strong dependence of reaction products on the steric and electronic properties of each imidazole precursor molecule is discussed.

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Introduction

Carbene-boranes derived from N-heterocyclic carbenes (NHCs) and possessing the general formula $[HCN(R)]_2C:BR'_3$ (R, R' = hydrocarbyl), such as **a** in Chart 1, are receiving increasing levels of attention due to recent displays of some interesting reactivity.[1-4] For example, the B-H bond in NHC-BH_3 compounds is significantly weakened (compared to those in R_3NBH_3) and can be removed as H^+ by a base[5] or as H^- by treatment with phosphine-boranes $PhH_2PB(C_6F_5)_3$ (**b** in Chart 1).[4] Frustrated Lewis Pair (FLP) combinations of NHCs and perfluorinated aryl boranes (**c** in Chart 1) have been shown to activate and cleave dihydrogen, THF, and amines, [6-8,9] although the rearrangement to the 'abnormal' carbene–borane adduct (**d** in Chart 1) provides a route to shut down further small molecule reactivity.[6, 8] Despite this Tamm has noted reactivity between a bulky NHC-borane FLP and white phosphorus which yields the 'abnormal' NHC.P_4.$B(C_6F_5)_3$ adduct (**e** in Chart 1).[10]

Yamaguchi has previously described the reactivity of imidazolium salts towards $LiHBEt_3$ yielding triethylborohydride-NHC adducts.[11, 12] Notably the triethylborane group was shown to exchange with BH_3, BF_3 and with $[M(\eta^3\text{-allyl})\{\eta^2\text{-}(NPh)_2CH\}(CO)_2(py)]$ (M = W, Mo) reflecting the similarities between the Lewis acidic boron and early transition metal cations.

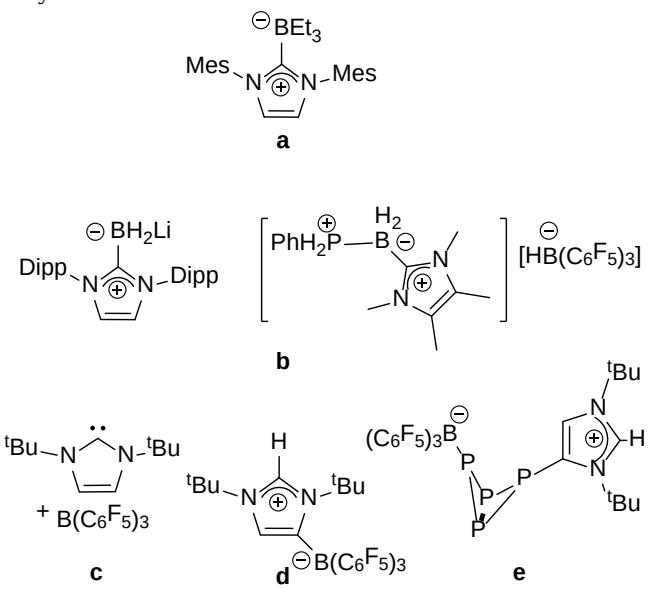


Chart 1: Carbene-borane adducts, frustrated pairs, and selected reaction products

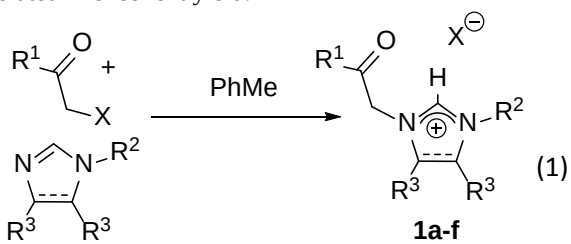
Carbenes have also previously been shown to be catalysts for the reduction of ketones with borane, for which only a few examples of organocatalysts exist.[13-15] Other NHC-borane catalysed reactions include radical hydrogenation reactions, hydroboration of alkynes,[16] and the reduction of xanthates.[17] We have studied a range of alkoxy tethered carbenes for Lewis acidic metals and have previously demonstrated the reactivity of the labile carbene-metal bonds towards boranes.[18, 19] More recently we became interested in further functionalisation of the pendant alkoxide arm of these ligands with sterically demanding and potentially reactive BR_3 group. However, in the development of these new carbene proligands some unexpected reactivity was observed.

Herein we report the different chemistry of a range of β-ketoimidazolium and imidazolinium (for saturated heterocyclic derivatives) salts towards superhydride bases and seek to rationalise their relative susceptibility towards either ketone reduction or imidazolium deprotonation. We also describe previously unseen intramolecular acid-base alkane elimination chemistry of the imidazolium-borate species.

Results and Discussion

Proligand Synthesis

In a modification of a literature preparation, a range of alkyl-ketone N-functionalised imidazolium salts can be accessed from mono-N-substituted alkyl or aryl imidazoles by treatment with an equimolar quantity of a 2-haloketone in refluxing toluene solution, eq 1.[20-24] The resultant β-ketoimidazolium (or imidazolinium for saturated backbone derivatives) salt **1** precipitates as a colourless solid and can be isolated by filtration. Salts **1a-f** ($[R^1C(O)CH_2\{CH[NCR^3CR^3N(R^2)]\}]X$ (R^1 = ^{t}Bu, naphth; R^2 = ^{i}Pr, Mes, ^{t}Bu; R^3 = H, Me, $(H)_2$; X = Cl, Br) See Eq. 1) containing a range of different substituents were isolated in excellent yield.



(1)

	R^1	R^2	R^3	X	δ (NCH^N)	Ref.
1a	^{t}Bu	^{i}Pr	H	Cl	10.53	21
1b	^{t}Bu	Mes	H	Cl	10.01	22
1c	^{t}Bu	^{t}Bu	H	Cl	10.79	23
1d	Napth	Mes	CH_3	Br	9.78	24
1e	^{t}Bu	Mes	H_2	Cl	9.68	-
1f	Napth	Mes	H_2	Cl	9.27	

In the ^{1}H NMR spectra of **1a-c** the imidazolium protons resonate at 10.94, 10.22 and 10.79 ppm respectively whereas in **1d** the same proton appears at 9.78 ppm and at 9.68/9.37 ppm in **1e/f**. The FTIR C=O stretching frequencies in solutions of **1b** and **1e** are 1724 and 1719 cm^{-1}; un-shifted from the solid state values of 1721 and 1715 cm^{-1} respectively, suggesting minimal hydrogen bonding between the ketone oxygen and acidic imidazolium proton. Accordingly, the value of the high-frequency imidazolium ^{1}H NMR resonance may be taken as a measure of the different acidity of the imidazolium protons in these compounds. From these data and comparisons with the literature,[25] we estimate the order of acidity to be **1a**~**1b**~**1c**>**1d**>**1e**~**1f**.

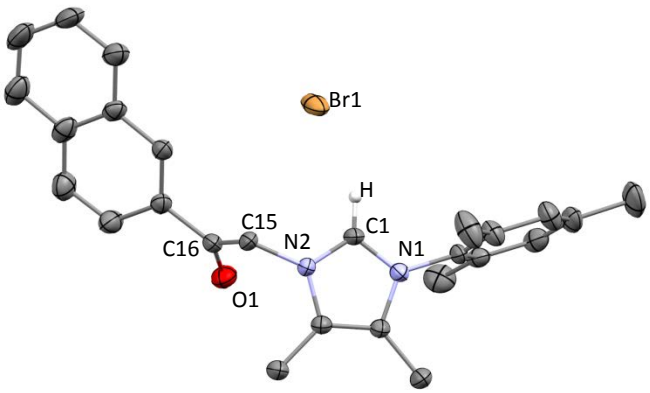
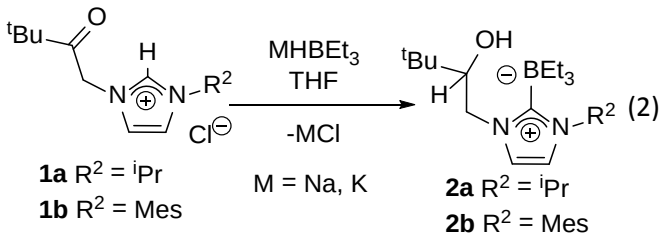


Figure 1: Solid-state structure of **1d**. For clarity, all hydrogen atoms except the imidazolium CH, and all solvent molecules are omitted (displacement ellipsoids are drawn at 50% probability). Selected distances (Å) and angles (°): O1-C16 1.216(3), C1-N1 1.334(3), C1-N2 1.328(3), C1-Br1 3.456(2), N1-C1-N2 108.6(2).

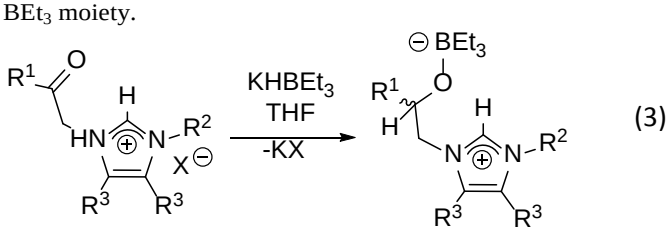
X-ray quality crystals of **1d** were grown by slow cooling of a methanol solution at -30°C, Figure 1. The molecular structure shows a C=O distance of 1.216(3) Å and in the solid state a long C1 – Br distance of 3.456(2) Å suggests a weak hydrogen bonding interaction between the bromide anion and the acidic imidazolium CH.

Reduction with Group 1 metal borohydrides



Treatment of **1a** with either $KHBEt_3$ or $NaHBEt_3$ affords a colourless precipitate, and after workup of the filtrate, an orange oil, characterised as the alcohol-functionalised carbene-borane **2a** ((tBu)CH(OH)CH$_2${C(BEt$_3$)[NC(H)C(H)N(iPr)]}), eq. 2. The ^{1}H NMR spectrum of **2a** shows no imidazolium CH proton confirming carbene formation. In addition an AB$_2$ coupling system is evident at 4.80, 3.41, and 3.39 ppm (1H each) assigned as the C(H)OCH$_2$ protons in the N-alkyl arm resulting from reduction of the ketone group. The ^{13}C NMR spectrum contains a four line resonance at 175.3 ppm indicative of a carbene borane. Regardless of the number of equivalents of borohydride used or reaction temperature **2a** is the only organic product formed.

The reaction between equimolar amounts of **1b** and $KHBEt_3$ proceeded similarly, yielding a pale yellow solid after workup which was characterised as the analogue, **2b** ((tBu)CH(OH)CH$_2${C(BEt$_3$)[NC(H)C(H)N(Mes)]}), eq. 2. Similarly, a doublet of doublets at 4.95 ppm demonstrates reduction of the ketone bond has occurred. Additionally, desymmetrisation of the mesityl methyl groups is now evident in the NMR spectra implying hindered rotation about the C-N bond as a result of the coordination of the carbene to the bulky BEt_3 moiety.



1c R^1 = ^{t}Bu, R^2 = ^{t}Bu, R^3 = H, X=Cl
1d R^1 = napth, R^2 = Mes, R^3 = Me, X=Br
3c R^1 = ^{t}Bu, R^2 = ^{t}Bu, R^3 = H
3d R^1 = napth, R^2 = Mes, R^3 = Me

In contrast, treatment of **1c** or **1d** with $KHBEt_3$ yielded a colourless or pale yellow solid respectively after workup, which were characterised as the imidazolium borates **3c** (tBu)CH(OBEt$_3$)CH$_2${CH[NC(H)C(H)N(tBu)]} and **3d** ((tBu)CH(OBEt$_3$)CH$_2${CH[NC(CH$_3$)C(CH$_3$)N(Mes)]}), eq 3. The ^{1}H NMR spectrum of **3c** contains a resonance at 10.24 ppm which is shifted to only a slightly lower frequency than the imidazolium CH of **1c** (10.95 ppm). Similarly, the ^{13}C NMR spectrum shows a resonance at 137.2 ppm corresponding to the imidazolium CH carbon which contrasts with the carbene carbon resonance in **2a** of 175.3 ppm. However, three multiplets at 3.52, 3.88 and 4.10 ppm (1H each) confirm reduction of the ketone group. In the ^{1}H NMR spectrum of **3d** the imidazolium H1 proton appears at 9.24 ppm. The presence of three sets of resonances at 5.63, 4.14 and 3.65 (1H each) confirms this reduction and the formation of a chiral centre at the ketone carbon. A ^{13}C NMR spectral resonance at 145.3 ppm is also indicative of an imidazolium CH, similar to that in **3c** (137.2 ppm).

The presence of a CH imidazolium proton in **3c**, rather than the carbene species observed in **2a** and **2b** is likely due to the steric bulk of the tert-butyl imidazolium substituent (R^2) which is able to effectively block coordination of the BEt_3 fragment to the adjacent carbene carbon.

The difference between **b** and **d** is electronic and not steric: the pK$_a$ of the acidic proton in **1d** is higher than in **1b** due to the 4,5-dimethylimidazolium ring substituents in **d**.

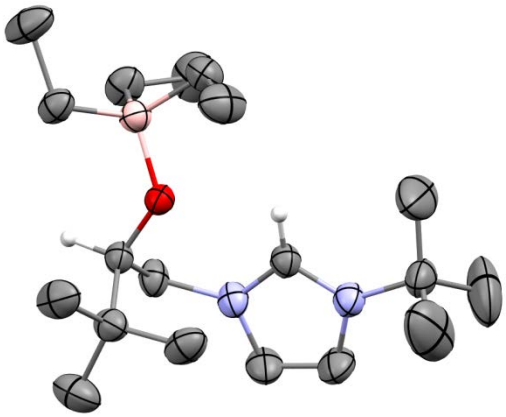


Figure 2: Solid-state structure of **3c**. For clarity, all hydrogen atoms except the imidazolium CH, and all solvent molecules are omitted (displacement ellipsoids are drawn at 50% probability). Selected distances (Å) and angles (°): B1-O1 1.544(3), O1-C9 1.385(3), C1-N1 1.329(3), C1-N2 1.328(3), C9-O1-B1 123.64(16), N1-C1-N2 109.0(2).

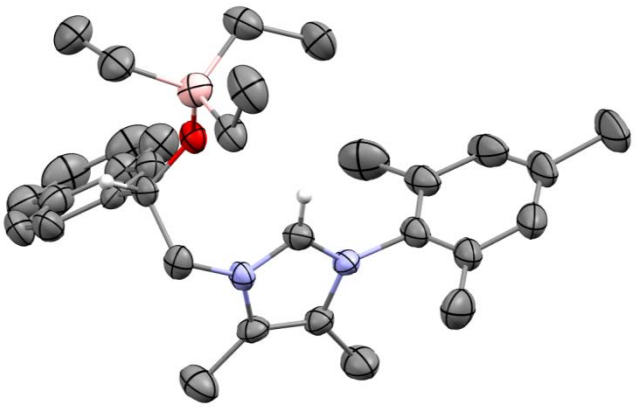


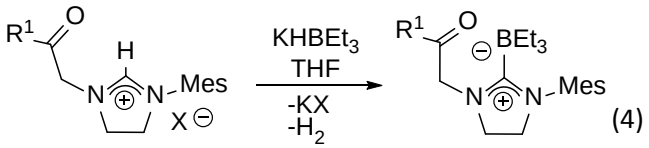
Figure 3: Solid-state structure of **3d**. For clarity, all hydrogen atoms except the imidazolium CH, and all solvent molecules are omitted (displacement ellipsoids are drawn at 50% probability). Selected distances (Å) and angles (°):B1-O1 1.536(7), O1-C16 1.386(6), C1-N1 1.327(6), C1-N2 1.324(6), C16-O1-B1 120.7(4), N1-C1-N2 108.7(5)

Crystals of **3c** suitable for X-ray diffraction were grown by slow cooling a toluene solution to -30°C, Figure 2. The structure confirms the assignment as an O-functionalised imidazolium borate with a C-O distance of 1.385(3) Å, within the expected range for a single bond (1.33 – 1.54 Å) and significantly longer than the C=O bond in **1d** (1.216(3) Å). The angles around the C9 carbon are also indicative of a sp^3 hybridised carbon centre, confirming reduction of this bond. The identity of the imidazolium proton H1 can also be inferred in the structure from the absence of a counter-ion.

X-ray quality crystals of **3d** were grown by slow cooling of a toluene solution (-30°C). The molecular structure is shown in Figure 3. The C-O distance of 1.386(6) Å is significantly longer than that in **1d** (1.216Å) confirming the reduction of the ketone bond. The B-O bond 1.536(7) Å is within the expected range (1.324-1.590 Å).

Formation of NHC-BR_3 instead of ketone reduction

The pKas of the saturated imidazolinium C-H group (the conjugate acid of the strongly basic 4,5-dihydroimidazol-2-ylidene) are higher than those of unsaturated imidazolium salts (conjugate acids of imidazole-2-ylidenes), so **1e-f** should be harder to deprotonate, but no significant electronic effect on the ketone group was anticipated. Surprisingly, treatment of either **1e** or **1f** with one equivalent of $KHBEt_3$ in THF yielded a colourless powder after workup, characterised as the ketone-functionalised carbene-borane **4e** ((tBu)C(O)CH_2{CH[NCH_2CH_2N(Mes)]}) and **4f** ((naphth)C(O)CH_2{CH[NCH_2CH_2N(Mes)]}) respectively eq. 4.



(4)

1e R^1 = ^{t}Bu **4e** R^1 = ^{t}Bu

1f R^1 = nap **4f** R^1 = nap

The ^{1}H NMR spectrum contains no resonances above 7 ppm indicating loss of the imidazolinium proton (9.68 ppm in **1e**). In addition the α-keto methylene group appears as a sharp singlet at 4.56 ppm (2H) demonstrating that no reduction of the ketone has occurred. In spite of this, a triplet at 1.19 ppm (9H) and a quartet at 0.51 ppm (6H) demonstrate the presence of a BEt_3 group. The ^{13}C NMR spectrum also shows a four-line resonance at 201.6 ppm indicative of carbene-borane formation. The ^{11}B NMR spectrum contains a singlet at -14.1 ppm, close to that exhibited by **2a** (-12.1 ppm). The spectral data for **4f** are comparable to those of **4e**.

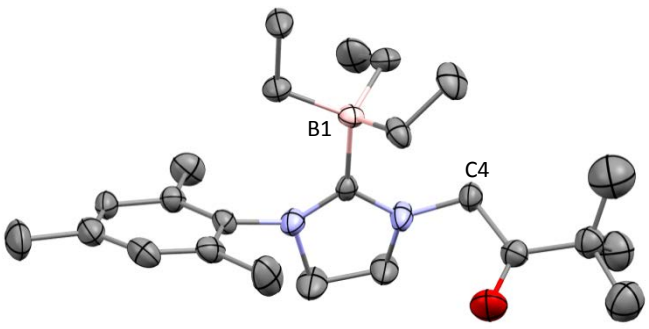


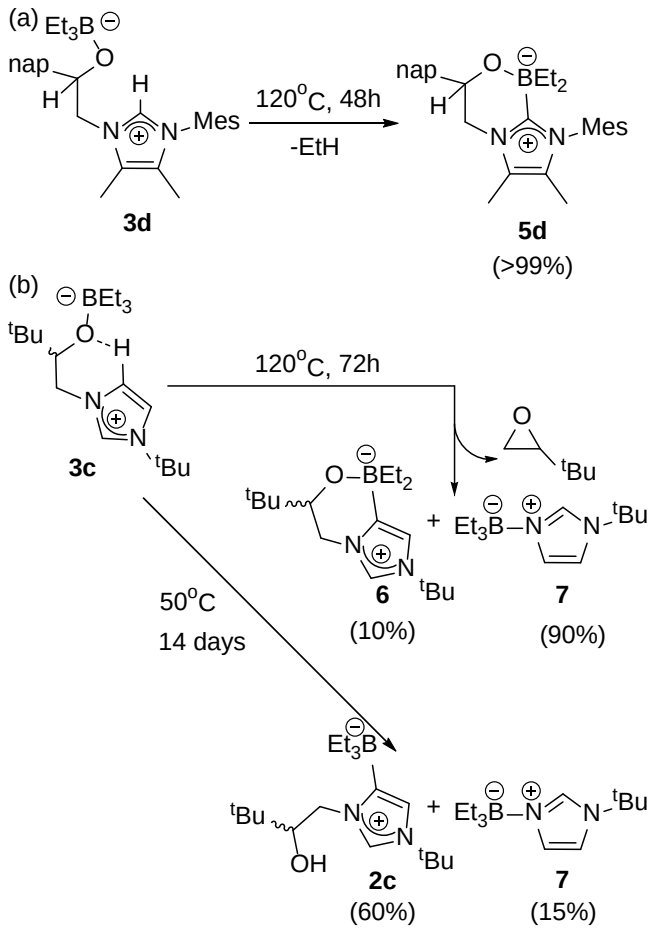
Figure 4: Solid-state structure of **4e**. For clarity, all hydrogen atoms, are omitted (displacement ellipsoids are drawn at 50% probability). Selected distances (Å) and angles (°):B1-C1 1.664(8), O1-C5 1.207(7), C1-N1 1.344(7), C1-N2 1.328(5), O1-C5-C4 120.2(5), N1-C1-N2 108.0(4)

X-ray quality crystals of **4e** were grown from slow cooling of a toluene solution, Figure 4. The refined structure contains a

short C=O bond of 1.207(7) Å indicative of the unreacted ketone and a C-B bond length (1.664(8) Å) within the expected range (ca. 1.55-1.68 Å).[26] X-ray quality crystals of **4f** were also grown from slow diffusion of a solution of **4f** in toluene and the refined structure is shown in the ESI.

Thermally induced alkane elimination

Attempts to deprotonate the imidazolium CH group of **3d** using a variety of strong bases including $KN(SiMe_3)_2$, KCH_2Ph and KH proved unsuccessful (see ESI). However, heating a toluene solution of **3d** to reflux for 48 hours in a teflon-valved NMR tube resulted in a loss of the characteristic imidazolium proton, formerly at 9.21 ppm in the ^{1}H NMR spectrum, and the formation of a new species which has been assigned as the carbene borane **5d** ($(tBu)CH(OBEt_2)CH_2\{C[NC(CH_3)C(CH_3)N(Mes)]\}$) resulting from the intramolecular deprotonation of the imidazolium moiety by a BEt_3 group, Scheme 1.



Scheme 1: Intramolecular ring closure of **3c** to form the carbene borane **5c** which at higher temperatures forms the 'abnormal' carbene **6** and the degradation product **7**.

A resonance at 0.81 ppm in the ^{1}H NMR spectrum was assigned as ethane and is no longer visible in spectra recorded after freeze-pump-thaw degassing of the solution. Two triplets in the ^{1}H spectrum of **5d** at 1.44 and 1.39 ppm (3H each) are assigned to the ethyl CH_3 groups and two doublets of doublets at 1.11 and 0.47 ppm, the ethyl CH_2 protons. The ^{11}B NMR spectrum contains a singlet at -1.10 ppm which, compared with the chemical shift in **3d** of 2.23 ppm, suggests a more electron rich boron centre in **5d**.

X-Ray quality crystals of **5d** were grown by slow cooling of a toluene/THF solution to -30°C, Figure 5. The molecular structure confirms the presence of a carbene-borane bond which is significantly longer (1.651(4) Å) than the mean C-B NHC-borane distance in the CCDC (1.609 Å) although shorter than in Yamaguchi's di*iso*-propylimidazolyltriethylborane, (1.683 Å).[11]

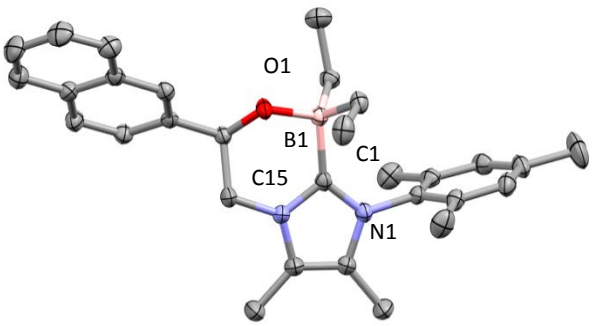


Figure 5: Solid-state structure of **5d**. For clarity, all hydrogen atoms except the imidazolium CH, and all solvent molecules are omitted (displacement ellipsoids are drawn at 50% probability). Selected distances (Å) and angles (°):B1-C1 1.651(4), B1-O1 1.513(3), O1-C16 1.393(3), C1-N1 1.344(3), C1-N2 1.353(3), O1-B1-C1 105.62(19), C16-O1-B1 117.32(18), N1-C1-N2 104.6(2).

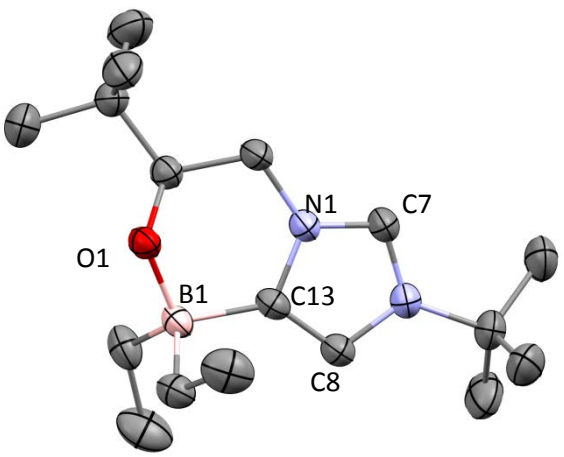


Figure 6: Solid-state structure of **6**. For clarity, all hydrogen atoms are omitted (displacement ellipsoids are drawn at 50% probability). Selected distances (Å) and angles (°): C13-N1 1.3872(19), N1-C7 1.3353(19), C13-C8 1.362(2), C13-B1 1.643(2), B1-O1 1.519(2), O1-B1-C13 106.24(12), C8-C13-B1 135.56(14)

Heating a solution of **3c** in d_8-toluene to reflux in a teflon-valved NMR tube for 72 h affords two imidazolyl-containing compounds according to ^{1}H NMR spectroscopy, Scheme 1. The

minor product (ca. 10%) of this reaction was crystallised and shown to be the abnormal carbene **6** ((tBu)CH(OBEt$_2$)CH$_2${CH[NCCHN(tBu)]}), Figure 6. The ^{1}H NMR spectra of crystals of **6** showed two resonances in the aromatic region at 6.44 (1H) and 6.33 (1H) ppm as well as two multiplets at 3.76 (1H) and 3.38 (2H). The BEt$_2$ groups are characterised by two triplets at 1.60 (3H) and 1.45 (3H) and complex overlapping multiplets between 1.22 and 0.89 ppm.

The major product **7** (Et$_3$B{CH[NCHCHN(tBu)]}, ca. 90%) is the N-B bonded imidazolium borate, identified initially by X-ray diffraction since X-ray quality single crystals were isolated by slow cooling of a hot hexane solution (Figure 7). The ^{1}H NMR spectra of **7** show three high-frequency ring protons at 7.52, 7.02 and 6.08 ppm indicative of a protonated imidazolium rather than a carbene functionality. In addition a triplet and quartet at 1.26 (9H) and 1.01 (6H) ppm confirmed the presence of a BEt$_3$ moiety. Careful analysis of the ^{1}H NMR spectrum of the reaction mixture shows the presence of two resonances at 2.46 (1H) and 2.27 (2H) ppm representing the known epoxide 2-*tert*-butyloxirane (see ESI). The ^{13}C NMR spectrum also showed resonances representing the free epoxide. This suggests that degradation of **3c** occurs by cleavage of the imidazole tether to eliminate the epoxide.

To avoid extensive epoxide loss, heating solutions of **3c** at only 50°C for 14 days shows the formation of an alcohol-functionalised carbene borane complex, **2c** ((tBu)CH(OH)CH$_2${CH[NC(BEt$_3$)C(H)N(tBu)]}) identified by NMR spectroscopy as containing the 'abnormal' rather than 'normal' carbene group. This mirrors the chemistry seen for the systems **a** and **b**, but the bulky **c** substituents allow this to be isolated, and favour the 'abnormal' carbene formation. This is also reasonable since the ultimate alkane elimination product is 'abnormal' in this system.

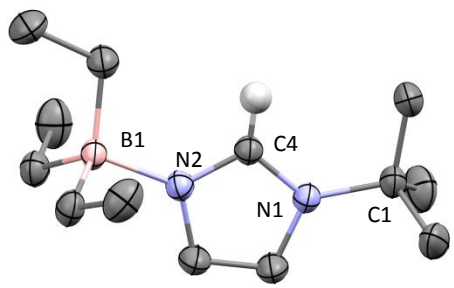
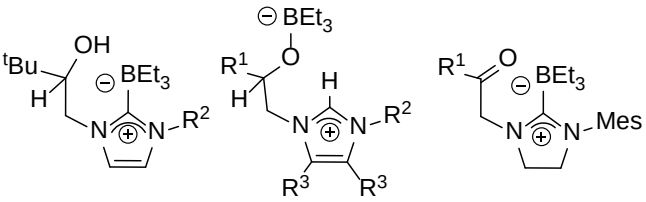


Figure 7: Solid-state structure of **7**. For clarity, all hydrogen atoms except the imidazolium CH are omitted (displacement ellipsoids are drawn at 50% probability). Selected distances (Å) and angles (°): N1-C4 1.345(2), N2-C4 1.325(2), B1-N2 1.635(2), N1-C1 1.501(2), N2-C4-N1 110.88(12).

Discussion

The reduction of this set of six similar β-ketoimidazolium (or imidazolinium) salts described above yield a range of different products depending on the alkyl and N-atom substituents, and on the degree of unsaturation of the carbene-precursor, summarised in Chart 2. Further heating of the neutral complexes in some cases shows alkane elimination from the BEt$_3$ group in what is the first example of a borate group acting as a Brønsted base. Comparisons of the reactivity allow us to make some tentative conclusions.



2a R^2 = ^{i}Pr **3c** R^1 = ^{t}Bu R^2 = ^{t}Bu R^3 = H **4e** R^1 = ^{t}Bu
2b R^2 = Mes **3d** R^1 = nap R^2 = Mes R^3 = Me **4f** R^1 = nap

Chart 2. Comparison of the products isolated from the reaction of **1** with superhydride base.

Firstly, the reaction with the superhydride reagent MBHEt$_3$ in the cases **1a-d** results in a reduction of the ketone and addition of the BEt$_3$ group, although in **1a-b** the product is an alcohol-carbene-borane, and in **1c-d** the product is a boronate imidazolium, whilst the ketone in **1e-f** is untouched, forming the ketone-carbene-borane. The pattern of these reactions does not simply follow a trend according to the relative pK$_a$s of the imidazol(in)ium; we estimate this order is **1a**~**1b**~**1c**>**1d**>**1e**~**1f** from comparisons with the literature and analysis of spectral data. It depends also on the steric demands of the peripheral groups and the degree of carbene saturation.

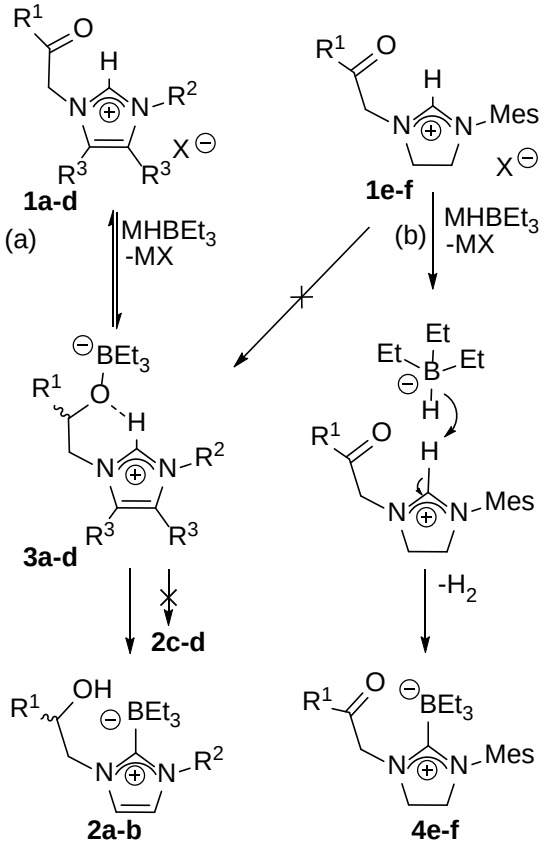
Compounds **a-d** have the most acidic imidazolium CH group, arguing against the deprotonation of the imidazol(in)ium CH as the first step. Compounds **a-b** have lower steric crowding around the C1 position. These yield carbene borane species of type **2**. However if either the sterics at the N1 position or the pK$_a$ of the C1 proton are increased then the imidazolium borate species **3** is favoured. With compounds **e-f** (β-ketoimidazolinium), reduction of the ketone bond was not observed suggesting an alternative mechanism for non-aromatic heterocycles to yield the β-ketocarbene borane species **4**.

Assuming the initial kinetic products do not rearrange once formed, two different reactions with the [HBEt$_3$]$^-$ anion are proposed:

1. The unsaturated β-ketoimidazolium salts **1a-d** likely follow the pathway (a) shown in Scheme 2. First, reduction of the ketone occurs forming the zwitterionic imidazolium borate **3a-d**, for which **3a-b** were not observed directly but instead are presumed to be intermediates in the formation of **2a-b**. If the N-R^2 substituent is small or the pK$_a$ of the C1 proton is low, rearrangement occurs to afford the alcohol and carbene-borane groups in **2**. Thereafter, a 1,5 sigmatropic shift of the highly acidic imidazolium proton allows a strong carbene-borane bond to form, unless the steric bulk of the R^2 position is sufficiently high to prevent coordination of the BEt$_3$ fragment, see **3c**. If the imidazolium CH has a higher pK$_a$ (as for the dimethylimidazolium in **1d**) the rearrangement is also disfavoured, see **3d**.

By these arguments, proligands **1e-f** would be expected to form the imidazolinium analogues **3e-f** based on their high CH pK_a. Therefore the isolation of **4e-f** suggests an alternate mechanism for these saturated backbone-derivatives:

2. In the solid state, the structure of **3c** (Figure 2) shows a short O···H distance of 2.286 Å (d(O···H)/d(O···C1) = 2.774(2) Å) suggesting a weak hydrogen bonding interaction may stabilise this intermediate. The X-ray structure of **3d** (Figure 3) shows a longer interaction (d(O···H)/d(O···C1) = 2.467 Å/2.825(5) Å respectively) reflecting the lower acidity of the 4,5-dimethylimidazolium C1 proton. The C1 proton in **1e-f** is significantly less acidic than in **1a-d** which may result in the destabilisation of pathway (a, Scheme 2) for imidazolinium based species relative to the deprotonation pathway (b, Scheme 2) which yields **4e-f** in a process rendered irreversible due to the evolution of dihydrogen in this pathway.

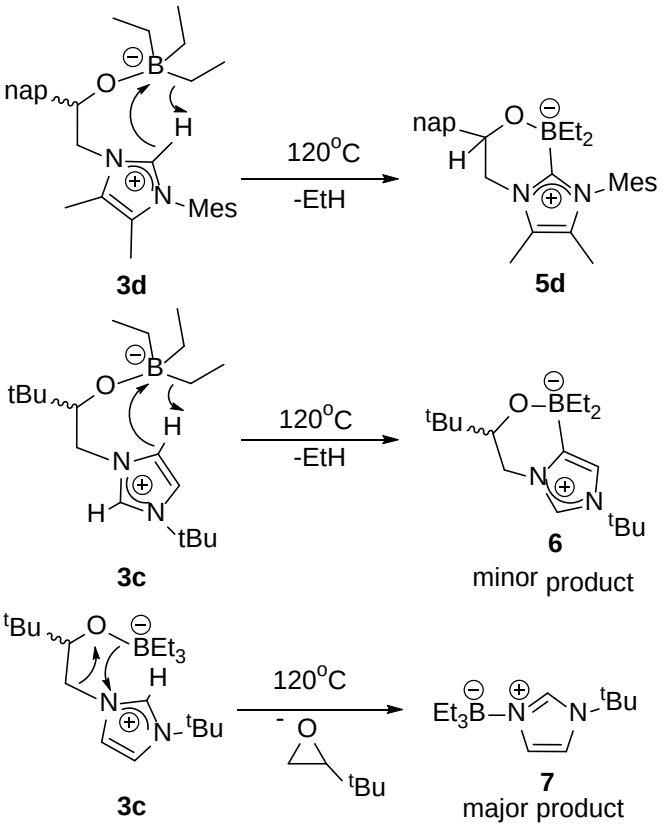


Scheme 2: Proposed routes for the different reactivities of **1a-f** with $MHBEt_3$.

The reactions are summarised in Scheme 3. The thermolysis of imidazolium borates **3** results in the highly unusual extrusion of ethane, in which the imidazolium group functions as a Brønsted acid. To our knowledge, this is the first example of this type of acid-base reactivity with a simple borane although Köster has noted that elimination of ethane occurs on heating the salt $Na[HOBEt_3]$ to yield $NaOBEt_2$.[32] The authors proposed that this was catalysed by $NaHBEt_3$ but control reactions of **3** with additional $NaHBEt_3$ do not result in ethane elimination, arguing against the involvement of any metal ions in the ethane elimination process in this system (see ESI). In particularly sterically crowded compounds (for example where R^2 = ^{t}Bu **3c**) the 'abnormal' carbene-borane **6** is formed from ethane elimination.

Although the C-B bond is relatively long in both **5d** (1.651 Å) and **6** (1.634 Å) compared with the mean NHC-B distance in the CSD[26] of 1.609 Å we have been unable to elicit further B-C insertion chemistry from either **5** or **6** to date.

Higher-temperature treatments of the most electron-rich and bulkiest complexes (**3c**) results in an equally unusual thermal degradation involving elimination of the alcohol arm, replacing a B-O bond with a B-N bond in the formation of the imidazolium borate **7** in preference to **6**. It may be that elimination of the epoxide is facilitated since it can readily polymerise to the polyether at these reaction temperatures, which would drive any equilibrium process towards the formation of **7**.



Scheme 3: Summary of reactions that thermally eliminate ethane or *tert*-butyloxirane.

Conclusions

The reaction between β-ketoimidazolium salts and an alkali metal triethylborohydride yields a range of products which depend strongly upon both the steric and electronic properties of the imidazole. Highly acidic imidazoles with low steric

crowding around the C1 position yield carbene borane species of type **2**, probably *via* the zwitterionic imidazolium borate **3**, which can be isolated when the imidazolium N-substituent is sufficiently large. However if either the sterics at the N1 position or the pK_a of the C1 proton are increased then the imidazolium borate species **3** is favoured. With β-ketodihydroimidazolium salts reduction of the ketone bond was not observed suggesting an alternative mechanism for non-aromatic imidazoles to yield the β-ketocarbene borane species **4**. Heating of imidazolium borates of type **3** can result in the formation of closed ring carbene boranes such as **5** which contains a relatively long C-B bond, suggesting reactions in which it behaves as a carbene-borane Lewis acid-base pair may be possible. In the case of **3c** where there is significant steric hindrance around the C1 carbon the 'normal' carbene species **5c** is not observed with the 'abnormal' species **6** being isolated instead, albeit in low yield. The unexpected degradation to the imidazole borane **7**, *via* extrusion of a molecule of epoxide, occurs at very high temperatures in a rare example of a process that cleaves a B-O bond to form a B-N bond. This suggests that the variety of resonance forms that can be drawn for the bonding in **7** are able to provide a significant additional stabilisation to this molecule. Work is in progress to identify the coordination chemistry of the complexes and the ability of small molecules and organometallic fragments to re-open the boracycles **5** and **6** to afford new carbene compounds.

Experimental Details

All reactions were carried out under an atmosphere of dry, oxygen–free dinitrogen, using standard Schlenk techniques or in a MBraun glovebox. Solvents were distilled and dried by standard methods or used directly from a Glass Contour solvent purification system. Mass spectra were recorded on a MAT 900 XP (EI/FAB), Thermo–Fisher LCQ Classic (ESI). NMR spectra were recorded either on 400 MHz, 500 MHz or 600 MHz Bruker Advance III spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to $SiMe_4$ (δ = 0) and were referenced internally with respect to the protio solvent impurity or the ^{13}C resonances respectively. ^{11}B chemical shifts are reported in ppm relative to $BF_3.OEt_2$ (δ = 0). Infra–red spectra were recorded from solution or a nujol mull using cells with NaBr windows or as neat solids using a Perkin–Elmer Spectrum 65. Elemental analyses were carried out by Mr Stephen Boyer at London Metropolitan University.

The compounds N-mesitylimidazole,[33] N-tert-butylimidazole,[34] N-isopropylimidazole,[35] 4,5-dimethyl-N-mesitylimidazole[36] and N-mesitylimidazoline[37] were synthesised according to literature procedures. All other chemicals were obtained from Sigma–Aldrich and used as received.

General synthesis of β-ketoimidazol(in)ium salts 1

The imidazole $CH[NCR^3CR^3N(R^2)]$ (R^2 = ^{i}Pr, Mes, ^{t}Bu; R^3 = H, Me, $(H)_2$) (4 mmol) was dissolved in toluene and the 2-haloketone $[R^1C(O)CH_2X$ (R^1 = ^{t}Bu, naphth; X = Cl, Br) (one equiv.) was added, affording a cloudy solution. The mixture was heated to reflux for 8 hours during which time a colourless precipitate formed. After allowing the suspension to cool to room temperature, the precipitate was isolated by filtration and washed with hot hexane to yield $[R^1C(O)CH_2\{CH[NCR^3CR^3N(R^2)]\}]X$ (R^1 = ^{t}Bu, naphth; R^2 = ^{i}Pr, Mes, ^{t}Bu; R^3 = H, Me, $(H)_2$; X = Cl, Br) **1** as a colourless solid.

1a: $[(tBu)C(O)CH_2\{CH[NC(H)C(H)N(iPr)]\}]Cl$
Yield: 80%; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.53 (s, 1H, NC<u>H</u>N); 7.48 (s, 1H, NC<u>H</u>CHN); 7.39 (s, 1H, NCHC<u>H</u>N); 5.91 (s, 2H, NC<u>H$_2$</u>CO); 4.66 (sept., J = 6.7 Hz, 1H, C<u>H</u>$(CH_3)_2$); 1.56 (d, J = 6.7 Hz, 6H, CH(C<u>H$_3$</u>)$_2$); 1.24 (s, 9H, C(C<u>H$_3$</u>)$_3$); ^{13}C NMR (500 MHz, $CDCl_3$): 206.9 (NCH$_2$<u>C</u>O), 137.3 (N<u>C</u>N), 124.2 (N<u>C</u>HCHN), 118.9 (NCH<u>C</u>HN), 54.2 (N<u>C</u>H$_2$), 53.3 (N<u>C</u>$(CH_3)_2$), 43.5 (<u>C</u>$(CH_3)_3$), 26.2 (C(<u>C</u>H$_3$)$_3$), 23.0 (C(<u>C</u>H$_3$)$_2$); ESI (+ve) M^+ 209.1 m/z [M^+-Cl]; Anal. Calcd. $C_{12}H_{21}ClN_2O$ (244.76), %C = 58.89; %H = 8.65; %N = 11.45; Found, %C = 58.62, %H = 8.73, %N = 11.34.

1b: $[(tBu)C(O)CH_2\{CH[NC(H)C(H)N(Mes)]\}]Cl$
Yield: 86%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 10.01 (s, 1H, NC<u>H</u>N); 7.60 (s, 1H, NC<u>H</u>CHN); 7.13 (s, 1H, NCHC<u>H</u>N); 7.02 (s, 2H, Ph<u>H</u>); 6.29 (s, 2H, NC<u>H$_2$</u>CO); 2.36 (s, 3H, Ph(C<u>H$_3$</u>)); 2.12 (s, 6H, Ph(C<u>H$_3$</u>)$_2$); 1.35 (s, 9H, C(C<u>H$_3$</u>)$_3$); ^{13}C NMR (500 MHz, $CDCl_3$) δ 207.0 (<u>C</u>O), 141.5 (N<u>C</u>N), 139.1 (N<u>C</u>CN), 134.6 (NC<u>C</u>N), 130.9 (Ph), 125.0 (Ph), 122.1 (Ph), 55.6 (N<u>C</u>CO), 43.6 (Ph(<u>C</u>H$_3$), 26.5 (C(<u>C</u>H$_3$)$_3$), 21.1 (<u>C</u>$(CH_3)_3$), 17.7 (Ph(<u>C</u>H$_3$)$_2$); ESI (+ve) M^+ = 285.1 m/z [M^+-Cl]. IR (CH_2Cl_2) ν_{max}/cm^{-1} 1724 (s); IR (neat) ν_{max}/cm^{-1} 1721 (s).

1c: $[(tBu)C(O)CH_2\{CH[NC(H)C(H)N(tBu)]\}]Cl$
Yield: 93%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.79 (s, 1H, NC<u>H</u>N), 7.37 (s, 1H, NC<u>H</u>CHN), 7.35 (s, 1H, NCHC<u>H</u>N), 5.98 (s, 2H, CH_2), 1.67 (s, 9H, C$(CH_3)_3$), 1.28 (s, 9H, C$(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 207.1 (CO), 137.2 (CH), 124.2 (CH), 118.4 (CH), 60.2 (C_q), 54.2 (CH_2), 43.5 (C_q), 30.0 (CH_3), 26.3 (CH_3).

1d: $[(naphth)C(O)CH_2\{CH[NC(CH_3)C(CH_3)N(Mes)]\}]Br$
Yield: 0.3707g (80%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.78 (s, 1H, NC<u>H</u>N), 8.86-7.55 (m, 7H, CH), 7.02 (s, 2H, CH), 6.74 (s, 2H, CH_2), 2.35 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.07 (s, 6H, CH_3), 2.00 (s, 3H, CH_3).

1e: $[(tBu)C(O)CH_2\{CH[NCH_2CH_2N(Mes)]\}]Cl$
Yield: 83 %; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.68 (s, 1H), 6.92 (s, 2H, CH), 5.44 (s, 2H, CH_2), 4.16 (s, 4H, CH_2), 2.32 (s, 6H, CH_3), 2.27 (s, 3H, CH_3), 1.25 (s, 9H, C$(CH_3)_3$).^{13}C NMR (126 MHz, CDCl3) δ 208.6 (C=O), 161.5 (CH), 140.1 (Cq), 135.1 (Cq), 130.5 (Cq), 129.8 (CH), 52.9 (N<u>C</u>H$_2$), 51.0 (N<u>C</u>H$_2$CH$_2$N), 49.9 (NCH$_2$<u>C</u>H$_2$N), 43.1 (<u>C</u>$(CH_3)_3$), 26.1 (C(<u>C</u>H$_3$)$_3$), 20.9 (<u>C</u>$(CH_3)_3$), 17.7 (Ph(<u>C</u>H$_3$)$_2$); ESI (+ve) M^+ = 287.21 m/z [M^+-Cl]; Anal. Calcd $C_{18}H_{27}ClN_2O$ (322.88): %C = 66.96; %H, 8.43; %N, 8.68; Found: %C = 67.10; %H, 8.36; %N, 8.61; IR (CH_2Cl_2) ν_{max}/cm^{-1} 1719 (s); IR (neat) ν_{max}/cm^{-1} 1715(s).

1f $[(naphth)C(O)CH_2\{CH[NCH_2CH_2N(Mes)]\}]Cl$
Analytically pure material was obtained by recrystallisation from chloroform. Yield: 90 %; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.27 (s, 1H), 8.52 (s, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.90 (d, J =

8.4, 1H), 7.65 (dd, J = 8.4, 8.4 Hz, 2H), 7.43 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 6.75 (s, 2H), 5.84 (s, 2H), 4.27 (t, J = 10.6 Hz, 2H), 4.13 – 4.00 (t, J = 10.6 Hz, 2H), 2.19 (s, 6H), 2.12 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.7 (CO), 161.1 (CH), 140.3 (C_q), 136.0 (C_q), 135.3 (C_q), 132.4 (C_q), 131.1 (CH), 130.5 (Cq), 130.0 (CH), 129.2 (CH), 128.9 (CH), 127.7 (CH), 127.0 (CH), 123.3 (CH), 54.8 (N<u>C</u>H$_2$), 51.2 (N<u>C</u>H$_2$CH$_2$N), 50.5 (NCH$_2$<u>C</u>H$_2$N), 21.0 (<u>C</u>(CH$_3$)$_3$), 18.0 (Ph(<u>C</u>H$_3$)$_2$); ESI (+ve) M^+ = 357.2 m/z [M^+-Cl]; Anal. Calcd $C_{24}H_{25}BrN_2O.CHCl_3$ (556.75): %C = 53.93; %H, 4.71; %N, 5.03; Found: %C = 54.14; %H, 5.29; %N, 5.02.

General procedure for reaction of 1 with KHBEt$_3$

A solution of compound **1** in THF was treated with a 1M solution of $KHBEt_3$ in THF. If a precipitate formed then the solution was filtered and the solvent removed from the filtrate *in vacuo*.

2a: (tBu)CH(OH)CH$_2${C(BEt$_3$)[NC(H)C(H)N(iPr)]}

Product isolated as a viscous orange oil. Yield: 72%; ^{1}H NMR (C_6D_6, 400 MHz) δ 6.72 (s, 1H, NC<u>H</u>CHN); 6.25 (s, 1H, NCHC<u>H</u>N); 5.48 (sept., J = 6.7 Hz, 1H, C<u>H</u>(CH$_3$)$_2$); 4.82 (m, 1H, CH$_2$C<u>H</u>(^{t}Bu)OH); 3.41 (m, 2H, NCH<u>H</u>C); 3.39 (s, 1H, NC<u>H</u>HC) 1.12 (t, J = 7.7 Hz, 9H, B(CH$_2$C<u>H</u>$_3$)$_3$); 1.05 (dd, J = 6.7 Hz, 6H, CH(C<u>H</u>$_3$)$_2$); 0.93 (m, 6H, B(C<u>H</u>$_2$CH$_3$)$_3$); 0.86 (s, 9H, C(C<u>H</u>$_3$)$_3$); ^{13}C NMR (500 MHz, C_6D_6) δ 175.7 (N<u>C</u>(B)N), 123.5 (NC<u>C</u>N), 115.0 (N<u>C</u>CN), 74.4 (<u>C</u>H(^{t}Bu)OH), 51.0 (N<u>C</u>H$_2$CO), 49.2 (N<u>C</u>H(CH$_3$)$_2$), 35.2 (<u>C</u>(CH$_3$)$_3$), 26.2 (B(CH$_2$<u>C</u>H$_3$)$_3$), 23.6 (C(<u>C</u>H$_3$)$_2$), 23.3 (C(<u>C</u>H$_3$)$_2$), 15.3 (B(<u>C</u>H$_2$CH$_3$)$_3$), 12.6 (C(<u>C</u>H$_3$)$_3$); ^{11}B (C_6D_6, 160.5 MHz) δ -12.1; EI M^+ = 308.3 m/z; Anal. Calcd. $C_{18}H_{37}BN_2O$ (308.32), %C = 70.12; %H = 12.10; %N = 9.09; Found, %C = 69.85, %H = 12.27, %N = 8.86; IR (neat) ν_{max}/cm^{-1} 3426 (br, O-H).

2b: (tBu)CH(OH)CH$_2${C(BEt$_3$)[NC(H)C(H)N(Mes)]}

Trituration with Et_2O yielded a colourless sticky foam which could not be crystallised. Yield: 69 %; ^{1}H NMR (C_6D_6, 400 MHz): δ 6.96 (s, 1H, NC<u>H</u>CHN); 6.69 (s, 2H, Ph<u>H</u>); 5.80 (s, 1H, NCHC<u>H</u>N); 3.66 (dd, 1H, NC<u>H</u>HCO); 3.42(dd, 1H, NCH<u>H</u>CO); 2.08 (s, 6H, Ph(C<u>H</u>$_3$)$_2$); 2.04 (s, 3H, Ph(C<u>H</u>$_3$)); 1.20 (t, 9H, B(CH$_2$C<u>H</u>$_3$)$_3$); 0.83 (s, 9H, C(CH$_3$)$_3$); 0.73 (q, 6H, B(C<u>H</u>$_2$CH$_3$)$_3$); ^{13}C NMR (500 MHz, C_6D_6) δ 179.0 (N<u>C</u>(B)N), 138.6 (C_q), 137.6 (C_q), 135.3 (C_q), 135.1 (C_q), 129.1 (CH), 129.0 (CH), 122.4 (NC<u>C</u>N), 120.9 (N<u>C</u>CN), 78.5 (<u>C</u>H(^{t}Bu)OH); 51.0 (<u>C</u>(CH$_3$)$_3$), 35.1 (NCH$_2$), 25.8 (C(<u>C</u>H$_3$)$_3$), 21.0 (CH$_3$), 18.2 (CH$_3$), 18.1 (CH$_3$), 15.3 (B(<u>C</u>H$_2$CH$_3$)$_3$), 12.6 (C(<u>C</u>H$_3$)$_3$); ^{11}B (C_6D_6, 160.5 MHz) δ -13.2; HRMS (EI) Calcd. for $C_{24}H_{41}ON_2B$ [M^+] requires m/z 384.32770, found m/z = 384.33065.

3c: (tBu)CH(OBEt$_3$)CH$_2${CH[NC(H)C(H)N(tBu)]}

Trituration with Et_2O yielded a colourless foam. Yield: 61%; ^{1}H NMR (C_6D_6, 500 MHz) δ 10.07 (s, 1H), 6.03 (d, J = 1.5 Hz, 1H), 5.98 (d, J = 1.5 Hz, 1H), 4.10 (dd, J = 13.6, 4.0 Hz, 1H), 3.83 (d, J = 4.0 Hz, 1H), 3.62 (d, J = 13.6 Hz, 1H), 1.49 (t, J = 7.7 Hz, 9H), 1.00-0.75 (m, 6H) 0.93 (s, 9H), 0.83 (s, 9H); ^{13}C NMR (C_6D_6, 126 MHz) δ 136.3 (CH), 122.6 (CH), 116.2 (CH), 75.1 (<u>C</u>H(^{t}Bu)OBEt$_3$), 58.8 (C_q), 53.2 (NCH$_2$), 36.2 (C_q), 29.2 (CH$_3$), 27.6 (CH$_3$), 17.0 (BCH$_2$), 12.6 (C(<u>C</u>H$_3$)$_3$); ^{11}B (C_6D_6, 160.5 MHz,) δ 1.1; EI M+ = 307.2 m/z [M^+-H]; Anal. Calcd. $C_{19}H_{39}BN_2O$ (322.34), %C = 70.80; %H = 12.20; %N = 8.69; Found, %C = 70.71, %H = 12.10, %N = 8.67.

3d: (tBu)CH(OBEt$_3$)CH$_2${CH[NC(CH$_3$)C(CH$_3$)N(Mes)]}

The pure product was obtained after recrystallisation from toluene at -30 ^{o}C. Yield: 68%; ^{1}H NMR (C_6D_6, 400 MHz): δ 9.24 (s, 1H, <u>H</u>$_{imidazole-2}$), 7.98-7.21 (m, 7H, naphthyl-C<u>H</u>), 6.58 (s, 1H, Ph<u>H</u>), 6.46 (s, 1H, Ph<u>H</u>), 5.63 (dd, 1H, naphthyl-C<u>H</u>O), 4.16-4.11 (dd, 1H, naphthyl-CHO-C<u>H</u>$_2$), 3.67-3.63 (dd, 1H, naphthyl-CHO-C<u>H</u>$_2$), 1.97 (s, 3H, imidazole-C<u>H</u>$_3$), 1.93 (s, 3H, imidazole-C<u>H</u>$_3$), 1.58-1.54 (t, 9H, CH$_2$C<u>H</u>$_3$), 1.40 (s, 3H, para-PhC<u>H</u>$_3$), 1.11-1.04 (m, 6H, B-C<u>H</u>$_2$), 0.76 (s, 3H, ortho-PhC<u>H</u>$_3$), 0.74 (s, 3H, ortho-PhC<u>H</u>$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 400 MHz): δ 145.3 (N<u>C</u>HN), 141.3 (C_q), 135.9 (C_q), 134.7 (C_q), 134.3 (C_q), 133.5 (C_q), 129.7 (C_q), 127.5 (C_q), 124.5 (C_q), 136.3 (CH), 130.4 (CH), 130.0 (CH), 127.7 (CH), 126.3 (CH), 126.1 (CH), 126.0 (CH), 125.7 (CH), 70.3 (naphthyl-<u>C</u>HO), 56.6 (N<u>C</u>H$_2$), 21.3 (B<u>C</u>H$_2$CH$_3$), 17.9 (CH$_3$), 17.2 (CH$_3$), 12.9 (B-CH$_2$<u>C</u>H$_3$), 7.9 (CH$_3$), 7.2 (CH$_3$). ^{11}B NMR (C_6D_6, 400 MHz): δ 2.2. Anal. Calcd. for $C_{32}H_{43}BN_2O$: C, 79.66; H, 8.98; N, 5.81. Found: C, 79.80; H, 9.06; N, 5.74. IR (neat): ν_{max}/cm^{-1} 1124 (C-O).

4e (tBu)C(O)CH$_2${CH[NCH$_2$CH$_2$N(Mes)]}

^{1}H NMR (C_6D_6, 500 MHz) δ 6.66 (s, 2H), 4.56 (s, 2H), 3.06 – 2.97 (m, 2H), 2.97 – 2.86 (m, 2H), 2.22 (s, 6H), 2.10 – 1.99 (m, 3H), 1.19 (t, J = 7.7 Hz, 9H), 1.01 (s, 9H), 0.51 (q, J = 7.7 Hz, 6H); ^{13}C NMR (126 MHz, C_6D_6) δ 208.8 (C=O), 202.0 (C-B), 137.8 (C_q), 137.6 (C_q), 135.6 (C_q), 129.5 (CH), 53.4 (CH$_2$), 51.9 (CH$_2$), 48.2 (CH$_2$), 43.1 (C_q), 26.5 (CH$_3$), 21.0 (CH$_3$), 18.21 (CH$_3$), 14.98 (CH$_2$), 12.46 (CH$_3$); ^{11}B NMR (C_6D_6, 400 MHz): δ -14.1; Anal. Calcd. $C_{24}H_{41}BN_2O$ (384.42), %C = 74.99; %H = 10.75; %N = 7.29; Found, %C = 75.13, %H = 10.72, %N = 7.40.

4f: (naphth)C(O)CH$_2${C(BEt$_3$)[NCH$_2$CH$_2$N(Mes)]}

^{1}H NMR (C_6D_6, 500 MHz) δ 8.45 (s, 1H), 8.11 – 8.00 (dd, J = 8.6, 1.7 Hz, 1H), 7.55 (d, J = 8.1 Hz, 1H), 7.52 (d, J = 8.6 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.23 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.18 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 6.68 (s, 2H), 3.25 (ddd, J = 13.5, 9.9, 1.7 Hz, 2H), 3.12 (ddd, J = 13.5, 9.9, 1.7 Hz, 2H), 2.28 (s, 6H), 2.06 (s, 3H), 1.30 – 1.09 (t, J = 7.7 Hz, 9H), 0.60 (q, J = 7.7 Hz, 6H); ^{13}C NMR (126 MHz, C_6D_6) δ 193.1 (CO), 137.5 (C_q), 137.2 (C_q), 135.8 (C_q), 135.3 (CH), 132.6 (C_q), 132.4 (C_q), 129.6 (CH), 129.4 (CH), 129.2 (CH), 128.8 (CH), 128.4 (CH), 126.7 (CH), 123.4 (CH), 54.3 (CH$_2$), 51.7 (CH$_2$), 48.7 (CH$_2$), 20.6 (CH$_3$), 17.9 (CH$_3$), 12.1 (CH$_3$); ^{11}B NMR (C_6D_6, 400 MHz): δ -13.9; Anal. Calcd. $C_{30}H_{39}BN_2O$ (440.44), %C = 79.08; %H = 8.47; %N = 6.36; Found, %C = 79.33, %H = 8.78, %N = 6.05.

Thermolysis of imidazolium borates

5d: (tBu)CH(OBEt$_2$)CH$_2${C[NC(CH$_3$)C(CH$_3$)N(Mes)]}

3d (9.6 mg, 0.02 mmol) was dissolved in dry toluene in a J. Young's tap NMR tube. The NMR tube was placed in an oil bath and heated to 120 ^{o}C for 2 days. After cooling to the room temperature, the colour of the solution had changed from white to pale yellow. The solvent was removed *in vacuo* to afford a yellow solid. The pure product **5** was obtained after

recrystallisation from toluene/THF at -30 °C. Yield: 9 mg (100%).

^{1}H NMR (C_6D_6, 400 MHz): δ 8.29-7.29 (m, 7H, naphthyl-C<u>H</u>), 6.74 (s, 1H, Ph<u>H</u>), 6.73 (s, 1H, Ph<u>H</u>), 5.38-5.35 (dd, 1H, naphthyl-C<u>H</u>O), 3.65-3.62 (dd, 1H, naphthyl-CHO-C<u>H</u>$_2$), 3.52-3.46 (dd, 1H, naphthyl-CHO-C<u>H</u>$_2$), 2.05 (s, 3H, imidazole-C<u>H</u>$_3$), 2.03 (s, 3H, imidazole-C<u>H</u>$_3$), 1.93 (s, 3H, para-PhC<u>H</u>$_3$), 1.46-1.43 (t, 3H, B-CH$_2$-C<u>H</u>$_3$), 1.41-1.37 (t, 3H, B-CH$_2$-C<u>H</u>$_3$), 1.35 (s, 3H, ortho-PhC<u>H</u>$_3$), 1.29 (s, 3H, ortho-PhC<u>H</u>$_3$), 1.23-1.14 (m, 1H, B-C<u>H</u>$_2$), 1.09-1.00 (m, 1H, B-C<u>H</u>$_2$), 0.58-0.49 (m, 1H, B-C<u>H</u>$_2$), 0.44-0.35 (m, 1H, B-C<u>H</u>$_2$). ^{13}C{^{1}H} NMR (500 MHz, C_6D_6): δ 142.9 (N<u>C</u>N), 139.6 (C_q), 136.7 (C_q), 136.6 (C_q), 134.6 (C_q), 134.0 (C_q), 133.2 (C_q), 124.0 (C_q), 123.6 (C_q), 129.7 (CH), 129.7 (CH), 128.8 (CH), 128.7 (CH), 126.4 (CH), 126.0 (CH), 125.8 (CH), 125.8 (CH), 70.8 (naphthyl-<u>C</u>HO), 53.2 (HCO-<u>C</u>H$_2$), 21.4 (B-<u>C</u>H$_2$), 18.5, 18.3 (imidazole-<u>C</u>H$_3$), 12.6 (B-CH$_2$-<u>C</u>H$_3$), 11.0, 8.1 (Phenyl-<u>C</u>H$_3$). ^{11}B NMR (C_6D_6, 400 MHz): δ 1.2.

6: (tBu)CH(OBEt$_2$)CH$_2${CH[NCCHN(tBu)]} and

7: Et$_3$B{CH[NCHCHN(tBu)]}

3c (0.1925g, 0.60 mmol) was dissolved in dry toluene (4mL) in an ampoule and heated in an oil bath at 120°C under reflux for 72h. The reaction mixture was cooled to room temperature and the solvent removed in vacuo. The residue was redissolved in hexane and crystals of **7** formed at room temperature. Filtration and cooling to -30°C yielded a few crystals of **6**.

6 ^{1}H NMR (C_6D_6, 400 MHz) δ 6.44 (d, J = 1.8 Hz, 1H), 6.33 (d, J = 1.8 Hz, 1H), 3.76 (t, J = 6.5 Hz, 1H), 3.37 (d, J = 6.5 Hz, 2H), 1.61 (d, J = 7.5 Hz, 3H), 1.48 (dd, J = 7.5 Hz, 3H), 1.26 (s, 9H), 1.22 – 0.89 (m, 6H), 0.65 (t, J = 6.5 Hz, 9H); ^{13}C (126 MHz, C_6D_6) δ 116.5 (CH), 115.4 (CH), 75.8 (CH), 59.2 (C_q), 48.6 (C_q), 34.5 (C_q), 29.0 (CH_3), 26.8 (CH_3), 11.6 (CH_3), 11.5 (CH_3); ^{11}B NMR (C_6D_6, 400 MHz): δ 0.4; HRMS (EI) Calcd. for $C_{17}H_{33}O_1N_2B$ [M^+] requires m/z 292.26805, found m/z = 292.26795.

7 ^{1}H NMR (C_6D_6, 400 MHz) δ 7.53 (t, J = 1.5 Hz, 2H), 7.02 (t, J = 1.5 Hz, 2H), 6.15 (t, J = 1.5 Hz, 2H), 1.22 (t, J = 7.7 Hz, 19H), 0.97 (q, J = 7.7 Hz, 13H), 0.69 (s, 18H); ^{13}C (126 MHz, C_6D_6) δ 131.9 (CH), 125.7 (CH), 116.7 (CH), 59.5 (C_q), 29.4 (CH_3), 15.8 (BCH_2), 11.5 (CH_3); ^{11}B NMR (C_6D_6, 400 MHz): δ 2.1; Anal. Calcd. $C_{13}H_{27}BN_2$ (222.18), %C = 70.28; %H = 12.25; %N = 12.61; Found, %C = 70.06, %H = 12.25, %N = 12.45;

2c: (tBu)CH(OH)CH$_2${CH[NC(BEt$_3$)C(H)N(tBu)]}

3c was dissolved in C_6D_6 and heated to 50°C for 21 days yielding ~60% conversion to **2c** along with ca. 25% **3c** and ca. 15% **7**.

^{1}H NMR (500 MHz, C_6D_6) δ 7.63 (d, J = 2.0 Hz, 1H), 6.76 (d, J = 2.0 Hz, 1H), 5.00 – 4.89 (m, 1H), 3.47 – 3.37 (m, 2H), 1.33 (t, J = 7.7 Hz, 9H), 1.03 – 0.95 (m, 6H), 0.88 (s, 9H), 0.84 (s, 9H); ^{13}C NMR (126 MHz, C_6D_6) δ 162.7 (C-B), 130.9 (CH), 119.1 (CH), 77.8 (<u>C</u>H(^{t}Bu)OBEt$_3$), 55.8 (C_q), 49.3 (NCH_2), 34.9 (C_q), 29.3 (CH_3), 25.9 (CH_3), 17.4 (BCH_2), 16.0 (BCH_2) 12.0 (C(<u>C</u>H$_3$)$_3$); ^{11}B NMR (C_6D_6, 400 MHz): δ -15.2; Anal. Calcd. $C_{19}H_{39}BN_2O$ (322.34), %C = 70.80; %H = 12.20; %N = 8.69; Found, %C = 70.68, %H = 12.04, %N = 8.78;

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Notes and references

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