Counterion Dependence on the Synthetic Viability of NHC-stabilized Dichloroboreonium Cations

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Abstract

The synthetic viability of several N-heterocyclic carbene-stabilized dichloroboreonium cations $[\text{NHC} \cdot \text{BCl}_2]^+$ ($\text{NHC} = (\text{RC})_2(\text{NR}')_2\text{C}$; **1**: $\text{R} = \text{R}' = \text{Me}$; **2**: $\text{R} = \text{H}$, $\text{R}' = ^i\text{Pr}$; **3**: $\text{R} = \text{Me}$, $\text{R}' = ^i\text{Pr}$; **4**: $\text{R} = \text{H}$, $\text{R}' = ^t\text{Bu}$; **5**: $\text{R} = \text{H}$, $\text{R}' = 2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3$) in the presence of Cl^- , AlCl_4^- , OTf^- ($\text{Tf} = \text{O}_2\text{SCF}_3$), NTf_2^- and $[\text{BAr}^{\text{Cl}}_4]^-$ ($\text{Ar}^{\text{Cl}} = 3,5\text{-Cl}_2\text{-C}_6\text{H}_3$) was investigated. None of the target borocations could be synthesized in the presence of Cl^- as only neutral $\text{NHC} \cdot \text{BCl}_3$ compounds were observed. On the other hand, it was not surprising that all targeted cations were synthetically viable in the presence of AlCl_4^- but a different degree of inter-ion interaction was

evident from ^{11}B NMR experiments. This was confirmed by X-ray analyses of $[\mathbf{1}\cdot\text{BCl}_2]^+$, $[\mathbf{2}\cdot\text{BCl}_2]^+$ and $[\mathbf{3}\cdot\text{BCl}_2]^+$ in the presence of AlCl_4^- counterions as the degree of cation-anion interaction was dependent on the steric encumbrance of the corresponding NHCs. Apart from $[\mathbf{4}\cdot\text{BCl}_2]^+$, no borocation was synthetically viable when OTf^- and NTf_2^- were used as the counterions. Finally, we were able to show that only $[\mathbf{4}\cdot\text{BCl}_2]^+$ could be synthetically viable without the counterion stabilization effect(s) as the preparation of $[\mathbf{4}\cdot\text{BCl}_2][\text{BAr}^{\text{Cl}}_4]$ was achieved. Even though the presence of $[\mathbf{3}\cdot\text{BCl}_2][\text{BAr}^{\text{Cl}}_4]$ was detected, this compound appeared not to be thermally stable as it decomposed in solution after 48 h. Thermal stability of $[\mathbf{4}\cdot\text{BCl}_2]^+$ and instability of $[\mathbf{3}\cdot\text{BCl}_2]^+$ in the presence of $[\text{BAr}^{\text{Cl}}_4]^-$ was attributed to the presence and absence, respectively, of very weak intra-ion (agostic) interactions in these two borocations.

Introduction

The inherent electron deficiency of boron (including other group 13 elements) plays a key role in the synthesis and reactivity of various Lewis acids.¹ One of the most promising approaches to further increase the Lewis acidic properties of compounds, in general, is to prepare related cationic or polycationic complexes. With respect to boron, monocation species are well-developed and they are classified based on the coordination number, namely borinium, borenium and boronium (Fig. 1).² On the other hand, rare cases of polycationic boron compounds have been limited to four-coordinate complexes.³

Figure 1. Different borocations.

Borenium cations, stabilized by a single neutral two-electron donor substituent L (Figure 1.), seem to be the most appealing borocations in terms of synthetic and reactivity investigations. They are not as difficult to synthesize as borinium and are certainly more reactive than boronium cations.⁴ Furthermore, borenium cations are isoelectronic with neutral boranes (BR₃), which are probably the most commonly used boron species in general synthetic chemistry.⁵ Thus, borenium cations having one or two halogen/hydrido substituents could prove to be invaluable for extending borocation reactivity studies including, for instance, ligand substitution.

Even though several examples of mono- and di-halo/hydrido borenium cations have been reported,^{4a-e,6} a majority of them were characterized in the presence of EX₄⁻ (E = B, Al or Ga; X = F, Cl or Br) or OTf (Tf = O₂SCF₃) counterions, which were shown to associate considerably with various counter-cations in solution.⁷ This is significant as these anions could not only provide additional stability but also interfere with the cation's further reactivity. Recently, the preparation of dibromo- and dihydridoborenium cations were attributed to electronic properties of the neutral donor ligands.^{6f,g} Therefore, we wanted to explore the synthetic viability of several N-heterocyclic carbene (NHC) stabilized dichloroborenium cations by assessing the degree of the cation-anion interaction in these species.

Results and Discussion

The degree of the inter-ion interaction between the target dichloroborenium cations [NHC·BCl₂]⁺ (NHC = **1**, **2**, **3**, **4**, **5**; Scheme 1) and various anions X⁻ (X⁻ = Cl⁻, AlCl₄⁻, OTf⁻, NTf₂⁻, [BAr^{Cl}₄]⁻; Tf = O₂SCF₃; Ar^{Cl} = 3,5-Cl₂-C₆H₃) could be assessed by considering (i) the δ_B values for these compounds and/or (ii) the position of the equilibrium between the neutral NHC·BCl₂X and cationic [NHC·BCl₂][X] species. Furthermore, based on these experimental observations it might

be possible to evaluate if any of the target borocations could be synthesized without the counterion influence.

In the presence of Cl⁻

To probe whether the target borocations will be synthetically viable in the presence of a chloride anion, 1.0 equiv of BCl₃ was added to a toluene solution containing the corresponding NHC. The ¹¹B NMR signals for these five reactions were observed between δ_B 2 (**1**·BCl₃) and 3 (**4**·BCl₃) ppm, which is consistent with the formation of NHC·BCl₃ adducts (Table 1), suggesting that spontaneous chloride ejection has not happened as previously observed for similar systems.^{6f} **2**·BCl₃, **3**·BCl₃, **4**·BCl₃ and **5**·BCl₃ were characterized by single crystal X-ray diffraction confirming the 4-coordinate nature of these species (Figure 2). Interestingly, the difference between the shortest and longest B-Cl bonds for **4**·BCl₃ (0.039 Å, Table 2) is at least twice as large with respect to **2**·BCl₃ (0.010 Å), **3**·BCl₃ (0.014 Å) and **5**·BCl₃ (0.019 Å). Furthermore, the values for (i) the angle defined by centroid_(C3N2)-C_(carbene)-B and (ii) the sum of the Cl-B-Cl angles are the smallest for **4**·BCl₃ (167.3(4) and 320.2(3)°, respectively) than for the rest of the characterized compounds (see Table 2). In view of the abovementioned solid state analysis it can be concluded that there exist a greater steric hindrance around boron for **4**·BCl₃ and possibly hinting at an easier formation of the corresponding borocation with regard to the other compounds. Nonetheless, it was evident that target borocations were not synthetically viable in the presence of chloride anions i.e. it could be postulated that the equilibrium described in Scheme 1 lies completely towards the neutral species when Cl⁻ is the anion.

Scheme 1. Targeted equilibrium.

Table 1. Summary of ¹¹B NMR signals for various compounds/reactions explored.^a

X =	Cl ⁻	AlCl ₄ ⁻	OTf	NTf ₂ ⁻	BAr ^{Cl} ₄ ⁻
[1·BCl ₂][X]	2.0	45.9	2.2	3.8	2.8 ^b
[2·BCl ₂][X]	2.5	38.6	3.2	4.6	2.5 ^b
[3·BCl ₂][X]	2.6	51.9	3.0	7.1	3.0 ^b
[4·BCl ₂][X]	2.9	51.9	3.0, 51.9 ^c	51.9	51.9 ^b
[5·BCl ₂][X]	2.3	47.6	1.5	2.8	1.6 ^b

^aThe spectra for compounds when X = Cl⁻ were obtained in C₆D₆ while for the rest in CD₂Cl₂.

^bApart from the BAr^{Cl}₄⁻ signal, this signal is the major one in solution after 48 hours. ^cThe neutral (δ_B = 3.0) and cationic (δ_B = 51.9) species are involved in a solvent dependent equilibrium.

Figure 2. Molecular structures for **2·BCl₃**, **3·BCl₃**, **4·BCl₃** and **5·BCl₃** (left to right) drawn at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) for **2·BCl₃**: B(1)-C(1) 1.629(2), B(1)-Cl(1) 1.866(2), B(1)-Cl(2) 1.869(2), B(1)-Cl(3) 1.858(2), C(1)-N(1) 1.359(2), C(1)-N(2) 1.358(2), N(1)-(C1)-N(2) 105.7(1) Cl(1)-B(1)-

Cl(2) 110.8(2), Cl(1)-B(1)-Cl(3) 106.3(2) Cl(2)-B(1)-Cl(3) 108.2(2); **3·BCl₃**: B(1)-C(1) 1.644(6), B(1)-Cl(1) 1.873(4), B(1)-Cl(2) 1.859(4), B(1)-Cl(3) 1.863(4), C(1)-N(1) 1.365(5), C(1)-N(2) 1.362(5), N(1)-(C1)-N(2) 106.2(3), Cl(1)-B(1)-Cl(2) 110.0(2), Cl(1)-B(1)-Cl(3) 104.6(2), Cl(2)-B(1)-Cl(3) 108.1(2); **4·BCl₃**: B(1)-C(1) 1.642(6), B(1)-Cl(1) 1.846(5), B(1)-Cl(2) 1.885(5), B(1)-Cl(3) 1.868(4), C(1)-N(1) 1.381(5), C(1)-N(2) 1.379(5), N(1)-(C1)-N(2) 104.7(3), Cl(1)-B(1)-Cl(2) 109.9(2), Cl(1)-B(1)-Cl(3) 109.7(2), Cl(2)-B(1)-Cl(3) 101.0(2); **5·BCl₃**: B(1)-C(1) 1.636(4), B(1)-Cl(1) 1.855(3), B(1)-Cl(2) 1.848(3), B(1)-Cl(3) 1.867(3), C(1)-N(1) 1.352(4), C(1)-N(2) 1.355(4), N(1)-(C1)-N(2) 105.0(2), Cl(1)-B(1)-Cl(2) 107.2(2), Cl(1)-B(1)-Cl(3) 108.3(2), Cl(2)-B(1)-Cl(3) 109.5(2).

Table 2. Selected structural parameters.

X =	Bond Distance (Å)		Bond Angles (°)				
	Cl B-Cl	AlCl ₄ B...Cl	Cl Cl-B-Cl (sum)	Cent-C(1)- B(1) ^a	Cl...B...Cl ^b	AlCl ₄ BCl ₂ - BCl ₂ (contacts) ^c	NHC _(backbone) -BCl ₂ ^d
[1·BCl₂][X]	N/A 1.866(2)	3.309(6) 3.259(6)	N/A	N/A	173.4	88.3	25.0
[2·BCl₂][X]	1.869(2) 1.858(2)	3.493(3) 3.359(3)	325.2(5)	175.1(4)	172.1	89.2	32.9
[3·BCl₂][X]	1.873(4) 1.859(4) 1.863(4)	3.926(3)	322.7(3)	175.0(4)	1.326	90	90
[4·BCl₂][X]	1.846(5) 1.885(5) 1.868(4)	4.190(4) ^e	320.2(3)	167.3(4)	N/A	N/A	81.3 ^e
[5·BCl₂][X]	1.855(3) 1.848(3) 1.867(3)	N/A	325.0(3)	175.9(5) 177.1(6)	N/A	N/A	N/A

^aThis angle is defined by the centroid of the carbene C₃N₂ backbone, the carbene carbon (C(1)) and the boron atom (B(1)). ^bFor compound **[1·BCl₂][AlCl₄]** this angle is defined by Cl(3)-B(1)-Cl(3A) as seen in Figure 3. ^cFor compound **[1·BCl₂][AlCl₄]** this angle is measured between a plane defined by B(1), Cl(1) and Cl(2) (the BCl₂ plane) and a plane defined by B(1), Cl(3) and

Cl(3A) (the $\text{BCl}_{2(\text{contacts})}$ plane) as seen in Figure 3.^dThis angle is measured between a plane defined by the carbene backbone ($\text{NHC}_{(\text{backbone})}$) and the BCl_2 plane. ^eMeasured for $\text{X} = [\text{BAr}^{\text{Cl}}_4]^-$.

In the presence of AlCl_4^-

As halide abstraction using a group 13 trihalide (e.g. AlCl_3 , GaCl_3) seems to be the most exploited procedure for the synthesis of various borocations,² it was then not surprising to observe successful formation of $[\text{NHC}\cdot\text{BCl}_2]^+$ ($\text{NHC} = \mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4}$ and $\mathbf{5}$) having AlCl_4^- counterions. However, the ^{11}B NMR experiments suggested either different positions of the $\text{NHC}\cdot\text{BCl}_3\cdots\text{AlCl}_3/[\text{NHC}\cdot\text{BCl}_2][\text{AlCl}_4]$ equilibria or varying extent of cation-anion interactions for these systems as δ_{B} ranged from 38.6 ppm for $[\mathbf{2}\cdot\text{BCl}_2]^+$ to 51.9 ppm for $[\mathbf{3}\cdot\text{BCl}_2]^+$ and $[\mathbf{4}\cdot\text{BCl}_2]^+$ (Table 1). As the δ_{B} value for $[\mathbf{2}\cdot\text{BCl}_2]^+$ did not vary with temperature the equilibrium for this and other systems explored in this work could be ruled out (See Figure S1). It then follows that different degrees of cation-anion interactions are mainly responsible for the observed δ_{B} values. Thus, based on the ^{11}B NMR spectroscopic results $[\mathbf{2}\cdot\text{BCl}_2][\text{AlCl}_4]$ showed the highest extent of inter-ion interaction in solution, while $[\mathbf{3}\cdot\text{BCl}_2][\text{AlCl}_4]$ and $[\mathbf{4}\cdot\text{BCl}_2][\text{AlCl}_4]$ the least if any at all.

Additionally, the crystal packing of $[\mathbf{1}\cdot\text{BCl}_2][\text{AlCl}_4]$, $[\mathbf{2}\cdot\text{BCl}_2][\text{AlCl}_4]$ and $[\mathbf{3}\cdot\text{BCl}_2][\text{AlCl}_4]$ revealed the presence of close contacts between the $\text{B}(2p)$ orbital and the chloride atoms of AlCl_4^- (Figure 3). In fact, these contacts were formed by two chloride atoms, originating from two different anions, positioned above and below the cationic BCl_2 plane. More importantly, these two $\text{Cl}_{(\text{anion})}$ atoms were situated along the $\text{B}(2p)$ orbital as the values for the BCl_2 - $\text{BCl}_{2(\text{contacts})}$ torsion angles for these three species are virtually 90° (Table 2). Even the vast difference in the $\text{NHC}_{(\text{backbone})}$ - BCl_2 torsion angles (Table 2), presumably due to the relative size

of the NHCs, did not influence the formation of these inter-ion contacts. Furthermore, the values for the B...Cl short contact distances and the $\text{BCl}_{2(\text{contacts})}$ angles (Table 2) are closely related to the steric hindrance of the NHC ligand;⁸ an increase in the steric hindrance yields longer B...Cl inter-ion contacts and more acute corresponding angles leading to a lower degree of cation-anion interactions (see Table 2). Thus, the extent of inter-ion interaction in the solid state seemed to be governed by the steric hindrance of the NHCs, while the solution state indicated a slightly different scenario.

Figure 3. Molecular structures for $[\mathbf{1} \cdot \text{BCl}_2][\text{AlCl}_4]$, $[\mathbf{2} \cdot \text{BCl}_2][\text{AlCl}_4]$ and $[\mathbf{3} \cdot \text{BCl}_2][\text{AlCl}_4]$ (from left to right) including inter-ion close contacts. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for $[\mathbf{1} \cdot \text{BCl}_2][\text{AlCl}_4]$: B(1)-C(1) 1.565(7), B(1)-Cl(1) 1.738(6), B(1)-Cl(2) 1.741(5), C(1)-N(1) 1.354(6), C(1)-N(2) 1.351(6), B(1)...Cl(3) 3.309(6), B(1)...Cl(3A) 3.259(6), Cl(1)-B(1)-Cl(2) 121.4(4), N(1)-C(1)-N(2) 106.2(4), Cl(3)...B(1)...Cl(3A) 173.4(2); $[\mathbf{2} \cdot \text{BCl}_2][\text{AlCl}_4]$: B(1)-C(1) 1.568(4), B(1)-Cl(1) 1.727(4), B(1)-Cl(2) 1.740(3), C(1)-N(1) 1.357(4), C(1)-N(2) 1.361(4), B(1)...Cl(3) 3.493(3), B(1)...Cl(4A) 3.359(3), Cl(1)-B(1)-Cl(2) 121.3(2), N(1)-C(1)-N(2) 106.6(2), Cl(3)...B(1)...Cl(4A) 172.1(2); $[\mathbf{3} \cdot \text{BCl}_2][\text{AlCl}_4]$: B(1)-C(1) 1.571(7), B(1)-Cl(1)

1.719(3), C(1)-N(1) 1.339(3), B(1)···Cl(3) 3.926(3), Cl(1)-B(1)-Cl(1A) 120.7(3), N(1)-C(1)-N(1A) 108.5(4), Cl(3)···B(1)···Cl(3C) 132.6(2).

In the presence of OTf⁻ and NTf₂⁻

In order to obtain more insights about the inter-ion interactions, the synthesis of the target dichloroboreonium cations in the presence of OTf⁻ and NTf₂⁻ was attempted. According to ¹¹B NMR spectroscopy the formation of the borocations employing **1**, **2**, **3** and **5** as NHC ligands did not materialize but a simple ligand exchange and the formation of neutral NHC·BCl₂X (X = OTf, NTf₂) compounds occurred (Table 1). Structural elucidation of **5·BCl₂OTf** confirmed ligand exchange and the formation of a neutral species (Figure 4). On the other hand, formation of [4·BCl₂]⁺ was observed by utilizing NTf₂⁻, while in the presence of OTf⁻ this particular borocation was involved in a solvent dependant equilibrium with its neutral analogue **4·BCl₂OTf** (See Figures S2 and S3). This observation could be explained by the relative nucleophilic character of these two anions i.e. when a less nucleophilic anion (NTf₂⁻) was used, the equilibrium was favored towards the ion pair. In addition, the δ_B values for [4·BCl₂]⁺ in the presence of AlCl₄⁻, NTf₂⁻ and, to some extent, OTf⁻ imply the existence of inter-ion interactions with equal magnitude or their complete absence. The same conclusion could be drawn for [3·BCl₂][AlCl₄] as its δ_B value was also observed at 51.9 ppm. However, it could also imply that [3·BCl₂]⁺ contained a lesser degree of intra-ion contacts with respect to [4·BCl₂]⁺ (based on the X-ray analysis the NHC ligand in **4·BCl₃** imposed a greater steric hindrance around the boron centre compared to **3·BCl₃**) resulting in a different degree of inter-ion contacts for these two

respective borocations with their δ_B values coincidentally being observed at 51.9 ppm (*vide infra*). Thus, in order to shed some light onto this specific issue and to gain more evidence whether any of the target cations could be synthesized without the counterion's stabilization effect(s), the synthesis of the proposed borocations was attempted in the presence of a non-coordinating anion $[\text{BAr}^{\text{Cl}}_4]^-$.⁹

Figure 4. Molecular structure for **5·BCl₂OTf** drawn at 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): B(1)-C(1) 1.616(4), B(1)-Cl(1) 1.855(3), B(1)-Cl(2) 1.850(3), C(1)-N(1) 1.359(3), C(1)-N(2) 1.356(3), B(1)-O(1) 1.500(3), O(1)-S(3) 1.527(2), O(2)-S(3) 1.418(2), O(1)-S(3) 1.425(2), N(1)-(C1)-N(2) 105.4(2).

In the presence of $[\text{BAr}^{\text{Cl}}_4]^-$

¹¹B NMR spectroscopy showed that room temperature preparation of only $[\mathbf{4}\cdot\text{BCl}_2]^+$ was viable when $[\text{BAr}^{\text{Cl}}_4]^-$ was used as the anion (Table 1). Single crystal X-ray diffraction showed inter-ion independence for $[\mathbf{4}\cdot\text{BCl}_2][\text{BAr}^{\text{Cl}}_4]$ (Figure 5) as the value for the shortest B...Cl_{anion} contact (4.190(4) Å) is well outside the sum of van der Waals radii for B and Cl (3.73 Å),¹⁰ and it is not pointing along the B(2p) orbital. In view of the X-ray analysis and the identical δ_B values for $[\mathbf{4}\cdot\text{BCl}_2][\text{X}]$ (X = AlCl₄⁻, NTf₂⁻ and $[\text{BAr}^{\text{Cl}}_4]^-$; Table 1), it could be concluded that $[\mathbf{4}\cdot\text{BCl}_2]^+$ is synthetically viable without the counterion assistance. Agostic (intra-ion) interactions between

C-H fragment(s) of the ^tBu substituents and the B(2p) orbital could be essentially responsible for the absence of close inter-ion contacts between [4·BCl₂]⁺ and anions such as AlCl₄⁻, NTf₂⁻ or [BAr^{Cl}₄]⁻. In fact, C(6) and C(11) atoms of [4·BCl₂]⁺ (Figure 5) are located virtually along the B(2p) orbital suggesting the presence of σ-C-H → B(2p) agostic interactions analogous to those described for solid state 4·AlMe₃.¹¹ Considering that theoretical investigations placed the strength of similar contacts between 1.7 and 2.5 kcal/mol¹² it was not surprising that low temperature ¹H and ¹¹B NMR spectroscopy yielded no evidence to support their existence.

Figure 5. Molecular structure for [4·BCl₂][BAr^{Cl}₄] drawn at 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): B(1)-C(1) 1.576(5), B(1)-Cl(1) 1.736(4), B(1)-Cl(8) 1.734(4), B(1)···Cl(5) 4.190(4), C(1)-N(1) 1.358(4), C(1)-N(2) 1.356(4), Cl(1)-B(1)-Cl(8) 120.5(2), N(1)-C(1)-N(2) 107.5(3).

Furthermore, the attempted synthesis of [NHC·BCl₂]⁺ (NHC = **1**, **2**, **3** and **5**) in the presence of [BAr^{Cl}₄]⁻ resulted in the formation of alleged four-coordinate boron species as judged by ¹¹B NMR spectroscopy (Table 1). Interestingly, the initial mixture of **3**·BCl₃ and 1.5 equiv of Na[BAr^{Cl}₄]¹³ in DCM revealed the presence of a signal around δ_B 54.6 ppm suggesting the formation of [3·BCl₂][BAr^{Cl}₄]. Additional evidence for the existence of [3·BCl₂][BAr^{Cl}₄] came from the ¹H NMR spectrum, obtained immediately after mixing the starting materials, as only one major set of signals corresponding to the NHC ligand and the anion was observed. Other

minor signals were also evident hinting at the onset of cation/anion decomposition. Indeed, the signal at δ_B 54.6 ppm was replaced by a new signal at around δ_B 3 ppm after about 48 h (Figure 6). The presence of multiple products, as judged by 1H NMR spectroscopy, confirmed the decomposition of the initial species. One could only assume that the anion was involved in the decomposition pathways as examples of borate anion decompositions in the presence of reactive cationic species had already been reported.¹⁴ However, it was possible to thwart the decomposition for at least 8 days by keeping the sample at $-40^\circ C$ (See SI).

Figure 6. Reaction progress for the $3 \cdot BCl_3/Na[BAr^{Cl}_4]$ system as monitored by ^{11}B NMR spectroscopy.

Nevertheless, the most intriguing observation regarding the abovementioned experiments is the value of δ_B 54.6 ppm for the proposed formation of $[3 \cdot BCl_2]^+$ in the presence of $[BAr^{Cl}_4]^-$ as it is the most downfield shifted signal with respect to any borocation system prepared in this work. Based on the accumulated ^{11}B NMR spectroscopic evidence, this particular observation indicated

that (i) AlCl_4^- was weakly coordinated to $[\mathbf{3}\cdot\text{BCl}_2]^+$ in the corresponding ion pair ($\delta_{\text{B}} = 51.9$ ppm) and (ii) $[\mathbf{3}\cdot\text{BCl}_2]^+$ presumably exhibited intra-ion contacts to a lesser extent (if any at all) in comparison to $[\mathbf{4}\cdot\text{BCl}_2]^+$. This is in good agreement with the respective solution state stabilities observed for $[\mathbf{3}\cdot\text{BCl}_2]^+$ and $[\mathbf{4}\cdot\text{BCl}_2]^+$ in the presence $[\text{BAr}^{\text{Cl}}_4]^-$. In view of these observations, it is postulated that the coincidentally same δ_{B} values for $[\mathbf{3}\cdot\text{BCl}_2][\text{AlCl}_4]$ and $[\mathbf{4}\cdot\text{BCl}_2][\text{X}]$ ($\text{X} = \text{AlCl}_4^-$, NTf_2^- and $[\text{BAr}^{\text{Cl}}_4]^-$) are predominantly influenced by *inter*- and *intra*-ion contact(s), respectively.

Conclusion

The synthesis of five NHC-supported dichloroboreonium cations has been attempted in the presence of Cl^- , AlCl_4^- , OTf^- , NTf_2^- and $[\text{BAr}^{\text{Cl}}_4]^-$ counterions. ^{11}B NMR spectroscopy appears to be an adequate analytical tool to assess inter- and possibly intra-ion contact(s). AlCl_4^- and possibly other group 13 tetrahalide anions (based on their frequent use) seem to be the most attractive counterion for the synthesis of main group coordinatively unsaturated cation. Nevertheless, these anions are not innocent as they could form small (in terms of magnitude) but important inter-ion contacts with the corresponding cations. Interestingly, the most downfield δ_{B} value of 54.6 ppm was observed for the formation of $[\mathbf{3}\cdot\text{BCl}_2][\text{BAr}^{\text{Cl}}_4]$ seemingly due to the lack of any inter- and intra-ion contacts. It is believed that the absence of these contacts is in turn responsible for the thermal instability of this particular borocation with respect to $[\mathbf{4}\cdot\text{BCl}_2]^+$. In fact, $[\mathbf{4}\cdot\text{BCl}_2]^+$ appeared to be the only cation that did not require counterion close contacts to be synthetically viable at room temperature possibly due to the existence of very weak intra-ion close contacts (agostic interactions). However, this does not suggest that $[\mathbf{4}\cdot\text{BCl}_2]^+$ was

completely counterion independent as only **4·BCl₃** was observed in the attempted synthesis of **[4·BCl₂]⁺** in the presence of Cl⁻.

Lastly, we encourage the researchers preparing main group coordinatively unsaturated cations (or anions) to attempt the synthesis of the target species in the presence of a range of dissimilar anions (or cations). Solid state analysis (single crystal X-ray diffraction) might not always show the inter-ion close contacts. Thus, the use of different anions should unambiguously confirm whether these inter-ion contacts exist and their (un)importance in the synthesis of the charged species.

Experimental Section

(i) General Considerations: All manipulations were carried out under dry argon atmosphere using standard Schlenk line or glovebox techniques. Solvents (dichloromethane, fluorobenzene, toluene, and hexane) were distilled over CaH₂ or sodium-benzophenone and stored over molecular sieves. *d*₆-benzene and *d*₂-dichloromethane were dried over molecular sieves prior to use. BCl₃, AlCl₃ and AgOTf were purchased from commercial sources and used without further purification. 1,3-di-isopropylimidazol-2-ylidene (**2**),^{15a} 1,3-di-*tert*-butylimidazol-2-ylidene (**4**),^{15b} and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**5**)^{15c} were synthesized from their corresponding imidazolium salts using the literature procedures. 1,3-di-isopropyl-4,5-dimethylimidazol-2-ylidene (**3**) and 1,3,4,5-tetramethylimidazol-2-ylidene (**1**) were prepared from their corresponding imidazol-2(3H)-thiones using reported methods.¹⁶ AgNTf₂ and NaBAr₄^{Cl} were also synthesized using literature reports.¹⁷ The NMR spectra were recorded on a Bruker AV300 MHz (¹H NMR at 300 MHz; ¹³C NMR at 75 MHz, ¹¹B NMR at 96 MHz and ¹⁹F NMR at 282 MHz) instrument. Tetramethylsilane was used as reference for ¹H and ¹³C NMR, while ¹¹B and ¹⁹F NMR spectra were recorded with respect to Et₂O·BF₃ and CFCl₃, respectively.

Mass spectrometry was performed by Waters Q-Tof Premier Micromass instrument, using the electro spray ionization (ESI) mode.

(ii) Crystallographic Methods: Single crystals were mounted on quartz fiber and the X-ray intensity data were collected at 103(2) K on a Bruker X8 APEX system, using Mo K α radiation, with the SMART suite of programs.¹⁸ Data were processed and corrected for Lorentz and polarization effects with SAINT¹⁹ and for absorption effects with SADABS.²⁰ Structural solution and refinement were carried out with the SHELXTL suite of programs.²¹ The structure was solved by direct method and refined for all data by full-matrix least-squares methods on F^2 . All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters. Details for each data collection, structure solution and refinement are summarized in Table S1.

General Procedure for the synthesis of NHC·BCl₃ adducts:

BCl₃ (1M solution in hexanes) was added to a toluene solution containing 1 equiv of the corresponding free N-heterocyclic carbene at room temperature. The solution was then immediately filtered to another Schlenk flask. The remaining solid was extracted with toluene three times. All toluene solutions were combined and solvents were evaporated to obtain the target NHC·BCl₃ adducts.

1·BCl₃: 0.250 g free carbene (2 mmol) and 2.0 mL (1M BCl₃ in hexane); white solid, 0.224 g (46% yield). ¹H NMR (CD₂Cl₂): δ 2.11 (s, 6H, CH₃), 3.83 (s, 6H, N-CH₃) ppm. ¹³C NMR (CD₂Cl₂): δ 8.90 (CH₃), 31.63 (N-CH₃), 120.64 (MeC=CMe), 161.03 (C_{carbene}) ppm. ¹¹B NMR (CD₂Cl₂): δ 2.0 (bs) ppm. MS (ESI): m/z calcd for C₇H₁₃BCl₃N₂ ([**1·BCl₃** + H]⁺) 241.0237; found 241.0251.

2·BCl₃: 0.250 g carbene (1.8 mmol) and 1.8 mL (1M BCl₃ in hexane); white solid 0.325 g (67% yield). ¹H NMR (CD₂Cl₂): δ 1.45 (d, *J* = 6.4 Hz, 12H, CH₃), 5.92 (sept, 2H, *J* = 6.6 Hz, CH(CH₃)₂) and 7.17 (s, 2H, HC=CH) ppm. ¹³C NMR (CD₂Cl₂): δ 23.18 (CH₃), 51.20 [CH(CH₃)₂], 118.06 (HC=CH), ¹¹B NMR : δ 2.5 ppm. MS (ESI): *m/z* calcd for C₉H₁₇BCl₃N₂ ([**2·BCl₃** + H]⁺) 269.0550; found 269.0506.

3·BCl₃: 0.250 g carbene (1.4 mmol) and 1.4 mL (1M BCl₃ in hexane); White solid 0.284 g (69% Yield). ¹H NMR (CDCl₃): δ 1.52 (d, *J* = 7.0 Hz, 12H, CH(CH₃)₂), 2.32 (s, 6H, CH₃), 6.27 (sept, *J* = 7.0 Hz, 2H, CH(CH₃)₂); ¹³C NMR (CDCl₃): δ 11.00 (CH(CH₃)₂), 21.32 (CH₃), 50.71(CH(CH₃)₂), 126.96 (MeC=CMe) ppm; ¹¹B NMR (CDCl₃): δ 2.35 ppm. MS (ESI): *m/z* calcd for C₁₁H₂₁BCl₃N₂ ([**3·BCl₃** + H]⁺) 297.0863; found 297.0830.

4·BCl₃: 0.250 g carbene (1.4 mmol) and 1.4 mL (1M BCl₃ in hexane); off white solid 0.266 g (64% yield). ¹H NMR (CD₂Cl₂): δ 1.93 (s, 18H, C(CH₃)₃), 7.38 (s, 2H, HC=CH) ppm. ¹³C NMR (CD₂Cl₂): δ 32.35 (C(CH₃)₃), 66.49 (C(CH₃)₃) and 121.22 (HC=CH) ppm. ¹¹B NMR (CD₂Cl₂): δ 3.31 ppm. MS (ESI): *m/z* calcd for C₇H₁₃BCl₃N₂ ([**4·BCl₃** + H]⁺) 297.0863; found 297.0852.

5·BCl₃: 0.250 g carbene (0.6 mmol) and 0.6 mL (1M BCl₃ in hexane); off white solid 0.272 g (84% yield). ¹H NMR (C₆D₆): δ 1.09 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 1.51 (d, *J* = 6.7 Hz, 12H, CH(CH₃)₂), 2.89 (m, 4H, CH(CH₃)₂), 6.44 (s, 2H, HC=CH), 7.14 to 7.34 (m, 6H, ArH) ppm. ¹³C NMR (C₆D₆): δ 22.55 (CH(CH₃)₂), 25.48 (CH(CH₃)₂), 29.30 (CH(CH₃)₂), 123.97 (HC=CH), 127.62, 128.00, 134.84 and 145.36 (ArC) ppm. ¹¹B NMR (C₆D₆): δ 2.3 ppm. MS (ESI): *m/z* calcd for C₂₇H₃₇BCl₃N₂ ([**5·BCl₃** + H]⁺) 505.2164; found 505.2115.

General procedure for the synthesis of [NHC·BCl₂][AlCl₄]:

Borenium complexes containing aluminium tetrachloride as counter ion were synthesized using the following procedure unless otherwise mentioned. Solid NHC·BCl₃ and anhydrous

aluminium trichloride, a 1:1 mol ratio, were mixed in DCM. The solution was then stirred at room temperature for about 30 min., and layered with hexane to get the corresponding borenium products.

[**1·BCl₂**][AlCl₄]: 0.250 g of **1·BCl₃** (1.0 mmol) and 0.138 g of AlCl₃ (1.0 mmol); white solid 0.173 g (45% yield). ¹H NMR (CD₂Cl₂): δ 2.42 (s, 6H, CH₃), 4.08 (s, 6H, N-CH₃) ppm; ¹³C NMR (CD₂Cl₂): δ 9.84 (CH₃), 36.26 (N-CH₃), 134.49 (MeC=CMe) ppm; ¹¹B NMR: δ 45.8 ppm; ²⁷Al NMR: δ 103.3 ppm. MS (ESI): *m/z* calcd for C₇H₁₂BCl₂N₂ ([**1·BCl₂**]⁺) 205.0471; found 205.0451.

[**2·BCl₂**][AlCl₄]: 0.250 g of **2·BCl₃** (0.9 mmol) and 0.124 g of AlCl₃ (0.9 mmol); white solid 0.210 g (56% yield). ¹H NMR (CD₂Cl₂): δ 1.69 (d, *J* = 6.6 Hz, 12H, CH₃), 4.99 (sept, *J* = 6.6 Hz, 2H, CH(CH₃)₂) and 7.76 (s, 2H, HC=CH) ppm. ¹³C NMR (CD₂Cl₂): δ 23.46(CH₃), 54.63 [CH(CH₃)₂], 123.09 (HC=CH) ppm. ¹¹B NMR (CD₂Cl₂): δ 38.6 (bs) ppm. ²⁷Al NMR (CD₂Cl₂): δ 103.9 (s) ppm. MS (ESI): *m/z* exact mass calcd for [**2·BCl₂**]⁺ 233.0796; found 233.0784.

[**3·BCl₂**][AlCl₄]: 0.250 g of **3·BCl₃** (0.8mmol) and 0.112 g of AlCl₃ (0.8mmol); white solid 0.192 g (53% yield). ¹H NMR (CD₂Cl₂): δ 1.68 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 2.43 (s, 6H, CH₃), 4.62 (sept, *J* = 6.7 Hz, 2H, CH(CH₃)₂); ¹³C NMR (CD₂Cl₂): δ 10.37 (CH(CH₃)₂), 21.97(CH₃), 54.27 (CH(CH₃)₂), 130.42 (MeC=CMe) ppm; ¹¹B NMR (CD₂Cl₂): δ 52.1 (bs) ppm; ²⁷Al NMR (CD₂Cl₂): δ 103.4 (s) ppm. MS (ESI): *m/z* calcd for C₂₇H₃₆BCl₂N₂ ([**3·BCl₂**]⁺) 261.1097; found 261.1126.

[**4·BCl₂**][AlCl₄]: Carried out in a J. Young NMR tube by mixing 0.025 g of **4·BCl₃** (0.08mmol) and 0.012 g of AlCl₃ (0.08 mmol) in CD₂Cl₂ which resulted in quantitative conversion as judged by multinuclear NMR. ¹H NMR (CD₂Cl₂): δ 1.83 (s, 18H, C(CH₃)₃), 7.71 (s, 2H, HC=CH) ppm. ¹³C NMR (CD₂Cl₂): δ 31.23 (C(CH₃)₃), 63.65 (C(CH₃)₃), 122.87 (HC=CH) ppm; ¹¹B NMR

(CD₂Cl₂): δ 52.3 (bs) ppm. ²⁷Al NMR (CD₂Cl₂): δ 106.3 (s) ppm. MS (ESI): m/z calcd for C₂₇H₃₆BCl₂N₂ ([**4**·BCl₂]⁺) 261.1097; found: 261.1051.

[**5**·BCl₂][AlCl₄]: Carried out in a J. Young NMR tube 0.025 g of **5**·BCl₃ (0.04 mmol) and 0.007 g of AlCl₃ (0.04 mmol) in CD₂Cl₂ which resulted in quantitative conversion as judged by multinuclear NMR. ¹H NMR (CD₂Cl₂): δ 1.27 (d, J = 6.8 Hz, 12H, CH(CH₃)₂), 1.35 (d, J = 6.8 Hz, 12H, CH(CH₃)₂), 2.43 (m, 4H, CH(CH₃)₂), 7.47 (m, 4H, HC=CH, ArH), 7.71 (m, 4H, HC=CH, ArH); ¹³C NMR (CD₂Cl₂): δ 23.04 (CH(CH₃)₂), 24.94 (CH(CH₃)₂), 29.51 (CH(CH₃)₂), 125.51 (HC=CH), 130.40, 133.08, 144.31 (ArC) ppm. ¹¹B NMR (CD₂Cl₂): δ 47.6 (bs) ppm. ²⁷Al NMR (CD₂Cl₂): δ 107.3 (s) ppm. MS (ESI): m/z calcd for C₂₇H₃₆BCl₂N₂ ([**5**·BCl₂]⁺) 469.2349; found 469.2371.

General procedure for the reaction between NHC·BCl₃ and either AgOTf or AgNTf₂:

Reactions of NHC·BCl₃ with either AgOTf or AgNTf₂ were carried out using the general procedure described here, unless otherwise mentioned. Solid NHC·BCl₃ and anhydrous AgOTf or AgNTf₂, in a 1:1 mol ratio and absence of light, were mixed in a J. Young NMR tube, followed by addition of CD₂Cl₂. The resulting reaction mixture was then shaken well and collected NMR data after 30min in case of AgNTf₂ and overnight in case of AgOTf. Complete conversion to the target product was observed by ¹H and ¹³C NMR. Attempts to isolate most of these compounds were unsuccessful due to progressive decomposition/hydrolysis.

1·BCl₂OTf: 0.025 g (0.1 mmol) of **1**·BCl₃ and 0.026 g (0.1 mmol) of AgOTf (1:1 ratio) in CD₂Cl₂. ¹H NMR (CD₂Cl₂): δ 2.16 (s, 6H, CH₃), 3.93 (s, 6H, N-CH₃). ¹³C NMR (CD₂Cl₂): δ 9.29 (CH₃), 35.24 (N-CH₃), 126.87 (MeC=CMe) ppm. ¹¹B NMR: δ 2.1 ppm; ¹⁹F NMR (CD₂Cl₂): δ -79.27 ppm. MS (ESI): m/z calcd for C₈H₁₂BCl₂F₃N₂O₃S ([**1**·BCl₂OTf + H]⁺) 355.0069; found 353.0331.

2·BCl₂OTf: 0.025 g (0.09 mmol) of **2·BCl₃** and 0.024 g (0.09 mmol) of AgOTf in (1:1 ratio) CD₂Cl₂. ¹H NMR (CD₂Cl₂): δ 1.51 (d, *J* = 6.6 Hz, 12H, CH(CH₃)₂), 5.95 (sept, *J* = 6.6 Hz, 2H, CH(CH₃)₂), 7.23 (s, 2H, HC=CH) ppm. ¹³C NMR (CD₂Cl₂): δ 23.17(CH₃), 51.20 [CH(CH₃)₂], 118.09 (HC=CH), 118.27 (q, CF₃) ppm. ¹¹B NMR (CD₂Cl₂): δ 1.28 (bs) ppm. ¹⁹F NMR (CD₂Cl₂): δ -77.62 (s) ppm. MS (ESI): *m/z* calcd for C₁₀H₁₇BCl₂F₃N₂O₃S ([**2·BCl₂OTf** + H]⁺) 383.0382; found 383.0310.

3·BCl₂OTf: 0.025 g (0.08 mmol) of **3·BCl₃** and 0.022 g (0.08 mmol) of AgOTf in (1:1 ratio) CD₂Cl₂. ¹H NMR (CD₂Cl₂): δ 1.56 (d, *J* = 7.0 Hz, 12H, CH(CH₃)₂), 2.35 (s, 6H, CH₃), 5.69 (sept, *J* = 7.0 Hz, 2H, CH(CH₃)₂); ¹³C NMR (CD₂Cl₂): δ 10.78 (CH(CH₃)₂), 20.96 (CH₃), 50.89 (CH(CH₃)₂), 127.64 (MeC=CMe) ppm; ¹¹B NMR (CD₂Cl₂): δ 3.02 (bs) ppm; ¹⁹F NMR (CD₂Cl₂): δ -78.83 (s) ppm. MS (ESI): *m/z* calcd for C₁₀H₁₇BCl₂F₃N₂O₃S ([**3·BCl₂OTf** + H]⁺) 411.0695, found 411.0829.

5·BCl₂OTf: Solid 5·BCl₃ adduct (0.250 g, 0.5 mmol) and anhydrous AgOTf (0.130 g, 0.5 mmol) were mixed together, in a 1:1 mol ratio and absence of light, in a Schlenk flask followed by the addition of DCM. The resulting solution was then stirred at room temperature overnight. Finally, the solution was filtered to another flask and layered with hexane to get the pure product as white solid (0.165 g; 54% yield) ¹H NMR (CD₂Cl₂): δ 1.11 (d, *J* = 5.0 Hz, 12H, CH(CH₃)₂), 1.32 (d, *J* = 7.0 Hz, 12H, CH(CH₃)₂), 2.55 (m, 4H, CH(CH₃)₂), 7.17 (s, 2H, HC=CH), 7.31 (m, 4H, *m*-Ar), 7.50 (m, 2H, *p*-Ar); ¹³C NMR (CD₂Cl₂): δ 21.90 ((CHCH₃)₂), 25.51 ((CHCH₃)₂), 29.22 ((CHCH₃)₂), 124.26, 124.89, 131.04, 133.30 and 145.10 (Ar) ppm; ¹¹B NMR (CD₂Cl₂): δ 1.49 (bs) ppm; ¹⁹F NMR (CD₂Cl₂): δ -77.13 (s) ppm. MS (ESI): *m/z* calcd for C₂₈H₃₇BCl₂F₃N₂O₃S ([**5·BCl₂OTf** + H]⁺) 619.1947, found 619.1876.

1·BCl₂(NTf₂): 0.025 g (0.1 mmol) of **1·BCl₃** and 0.040 g (0.1 mmol) of AgNTf₂ (1:1 ratio) in

CD₂Cl₂. ¹H NMR (CD₂Cl₂): δ 2.18 (s, 6H, CH₃), 3.86 (s, 6H, N-CH₃) . ¹³C NMR (CD₂Cl₂): δ 8.81 (CH₃), 34.42(N-CH₃), 118.95 (q, -CF₃), 127.29 (MeC=CMe) ppm. ¹¹B NMR : δ 2.21 ppm; ¹⁹F NMR (CD₂Cl₂): δ -79.89 ppm MS (ESI): *m/z* calcd for C₉H₁₃BCl₂F₆N₃O₄S₂ ([**1·BCl₂(NTf₂)** + H]⁺) 485.9722; found 485.9799.

2·BCl₂(NTf₂): 0.025 g (0.09 mmol) of **2·BCl₃** and 0.036 g (0.09 mmol) of AgNTf₂ (1:1 ratio) in CD₂Cl₂. ¹H NMR (CD₂Cl₂): δ 1.46 (d, *J* = 6.4 Hz, 12H, CH(CH₃)₂), 5.45 (sept, *J* = 6.2 Hz, 2H, CH(CH₃)₂) and 7.24 (s, 2H, HC=CH) ppm. ¹³C NMR (CD₂Cl₂): δ 23.09 (CH₃), 51.54 [CH(CH₃)₂], 118.75 (HC=CH), 118.88 (q, CF₃) ppm. ¹¹B NMR (CD₂Cl₂): δ 3.45 (bs) ppm. ¹⁹F NMR (CD₂Cl₂): δ -77.89 (s) ppm. MS (ESI): *m/z* calcd for C₁₁H₁₇BCl₂F₆N₃O₄S₂ ([**2·BCl₂(NTf₂)** + H]⁺) 514.0035; found 513.9553.

3·BCl₂(NTf₂): 0.025 g (0.08 mmol) of **3·BCl₃** and 0.033 g (0.08 mmol) of AgNTf₂ (1:1 ratio) in CD₂Cl₂. ¹H NMR (CD₂Cl₂): δ 1.60 (d, *J* = 5.3 Hz, 12H, CH(CH₃)₂), 2.38 (s, 6H, CH₃), 5.58 (sept, *J* = 6.3 Hz, 2H, CH(CH₃)₂); ¹³C NMR (CD₂Cl₂): δ 10.73 (CH(CH₃)₂), 21.01 (CH₃), 51.33 (CH(CH₃)₂), 118.94 (q, CF₃), 128.26 (MeC=CMe) ppm; ¹¹B NMR (CD₂Cl₂): δ 2.97(bs) ppm; ¹⁹F NMR (CD₂Cl₂): δ -78.25 (s) ppm. MS (ESI): *m/z* calcd for C₁₃H₂₁BCl₂F₆N₃O₄S₂ ([**3·BCl₂(NTf₂)** + H]⁺) 542.0348; found 542.0294.

[4·BCl₂][NTf₂]: 0.025 g (0.08 mmol) of **4·BCl₃** and 0.033 g (0.08 mmol) of AgNTf₂ (1:1 ratio) in CD₂Cl₂. ¹H NMR (CD₂Cl₂): δ 1.82 (s, 18H, C(CH₃)₃), 7.77 (s, 1H, HC=CH) ppm. ¹³C NMR (CD₂Cl₂): δ 31.07 (C(CH₃)₃), 63.53 (C(CH₃)₃), 118.38 (q, -CF₃), 123.04 (HC=CH) ppm. ¹¹B NMR (CD₂Cl₂): δ 51.93. *m/z* calcd for C₂₇H₃₆BCl₂N₂ ([**4·BCl₂]**⁺) 261.1097; found: 261.1051.

5·BCl₂(NTf₂): 0.025 g (0.05 mmol) of **5·BCl₃** and 0.019 g (0.05 mmol) of AgNTf₂ (1:1 ratio) in CD₂Cl₂. ¹H NMR (CD₂Cl₂): δ 1.24 (d, *J* = 5.2 Hz, 12H, CH(CH₃)₂), 1.32 (d, *J* = 5.1 Hz, 12H, CH(CH₃)₂), 2.42 (sept, 4H, CH(CH₃)₂), 7.37 (s, 2H, HC=CH), 7.71 (m, 4H, ArH); ¹³C NMR

(CD₂Cl₂): δ 21.80 (CH(CH₃)₂), 23.49 (CH(CH₃)₂), 23.97 (CH(CH₃)₂), 25.50 (CH(CH₃)₂), 29.40 (CH(CH₃)₂), 124.91 (HC=CH), 126.02, 128.02, 144.92 (ArC)ppm; ¹¹B NMR (CD₂Cl₂) : δ 2.77 (bs) ppm; ¹⁹F NMR (CD₂Cl₂) : δ -79.56 (s) ppm. MS (ESI): *m/z* calcd for C₂₉H₃₇BCl₂F₆N₃O₄S₂ ([**4**·**BCl₂**(NTf₂) + H]⁺) 750.1600; found 750.1745.

The reaction involving **4**·**BCl₃** and 1 equiv of AgOTf resulted in a solvent dependent equilibrium between **4**·**BCl₂**OTf and [**4**·**BCl₂**][OTf] (Figure S2 and S3). Attempts to purify this reaction mixture were unsuccessful.

General Procedure for the reaction between NHC·BCl₃ and Na[BAr₄^{Cl}]:

Reactions between NHC·BCl₃ and NaBAr₄^{Cl} were carried out using the general procedure described here, unless otherwise mentioned. Solid NHC·BCl₃ and NaBAr₄^{Cl}, in a 1:1 mol ratio, were added to a J. Young NMR tube followed by CD₂Cl₂. Multinuclear NMR was recorded within the first 15 min of mixing.

Reactions involving NHC·BCl₃ (NHC = **1**, **2**, **3** and **5**) resulted in a mixture of product as observed by ¹H and ¹¹B NMR. The reaction progress involving **3**·**BCl₃**/Na[BAr₄^{Cl}] in 1:1 and 1:1.5 ratios was followed by ¹H and ¹¹B NMR and it is summarized in Figures 6, s3, s4 and s5.

[**3**·**BCl₂**][BAr₄^{Cl}]: Not isolated. ¹H NMR (CD₂Cl₂): δ 1.54 (d, 12H, *J* = 5.5 Hz CH(CH₃)₂), 2.22 (s, 6H, CH₃), 4.60 (br, 2H, CH(CH₃)₂), 6.97 (s, 1H, *p*-Ar^{Cl}), 7.02 (s, 2H, *o*-Ar^{Cl}); ¹¹B NMR (CD₂Cl₂): δ 54.6 (bs) ppm; MS (ESI): *m/z* calcd for C₂₇H₃₆BCl₂N₂ ([**3**·**BCl₂**]⁺) 261.1097; found 261.1126.

[**4**·**BCl₂**][BAr₄^{Cl}]: Solid **4**·**BCl₃** (0.250 g, 0.8 mmol) and NaBAr₄^{Cl} (0.519 g, 0.8 mmol) were weighed inside the glove box in a 1:1 mol ratio and taken in a dry Schlenk flask. The flask was taken out and dry dichloromethane was added under argon atmosphere. The solution was then stirred at room temperature for overnight, filtered and layered with hexane to get the pure

product as a white solid 0.410 g (57% yield). ^1H NMR (CD_2Cl_2): δ 1.73 (s, 18H, $\text{C}(\text{CH}_3)_3$), 7.23 (m, 12H, ArH), 7.45 (s, 2H, $\text{CH}=\text{CH}$) ppm. ^{13}C NMR (CD_2Cl_2): δ 31.12 ($\text{C}(\text{CH}_3)_3$), 63.76 ($\text{C}(\text{CH}_3)_3$), 122.23 ($\text{HC}=\text{CH}$), 123.09, 133.12, 164.07-165.25 (ArC) ppm, ^{11}B NMR (CD_2Cl_2): δ -7.9 (s), 52.02 (bs) ppm. MS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{36}\text{BCl}_2\text{N}_2$ ($[\mathbf{4}\cdot\text{BCl}_2]^+$) 261.1097; found: 261.1051.

ASSOCIATED CONTENT

Supporting Information. Figures of the VT ^{11}B NMR spectra for $[\mathbf{2}\cdot\text{BCl}_2][\text{AlCl}_4]$ and $\mathbf{3}\cdot\text{BCl}_3/\text{Na}[\text{BAR}^{\text{Cl}}_4]$ (in 1:1 and 1:1.5 ratios), $\mathbf{4}\cdot\text{BCl}_3/\text{AgOTf}$ reaction mixture and the progress of $[\mathbf{3}\cdot\text{BCl}_2][\text{BAR}^{\text{Cl}}_4]$ decomposition.

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

ACKNOWLEDGMENT

We thank A*STAR (grant # 1220703062) and NTU-SMPS-CBC (SUG grant) for the support.

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