Unraveling the reactivity of a cationic iminoborane: avenues to unusual boron cations†

Rui Guo,a Xin Zhang,b Tong Li,a Qianli Li,c David A. Ruiz,b Liu Leo Liu,b Chen-Ho Tung a and Lingbing Kong*a,d

A cationic terminal iminoborane $\text{[Mes}^*\text{N}=\text{B}^+\text{IPr}_2\text{Me}_2\text{][AlBr}_4\text{]}^3+$ (Mes* $\text{=} 2,4,6$-tri-tert-butylphenyl and IPr2Me2 $\text{=} 1,3$-diisopropyl-$4,5$-dimethylimidazol-$2$-ylidene) has been synthesized and characterized. The employment of an aryl group and N-heterocyclic carbene (NHC) ligand enables $\text{[AlBr}_4\text{]}^3+$ to exhibit both B-centered Lewis acidity and BN multiple bond reactivities, thus allowing for the construction of tri-coordinate boron cations $5^+–12^+$. More importantly, initial reactions involving coordination, addition, and $[2 + 3]$ cycloadditions have been observed for the cationic iminoborane, demonstrating the potential to build numerous organoboron species via several synthetic routes.

Introduction

Exploration of boron cations has attracted extensive attention not only due to their unique bonding environments and electronic configurations but also due to their potential applications in bond activation and catalysis.1,2 Generally, boron cations can be classified into borinium $[\text{R}_2\text{B}]^+$, borenium $[\text{R}_2\text{BL}]^+$, and boronium $[\text{R}_2\text{BL}_2]^+$ cations based on the coordination number of boron (Fig. 1a). By installing π-donating ligands at the boron atom to compensate for the inherent electron deficiency, a few borinium ions have been isolated since the first report of diamido-substituted boron cations I and II by the Nöth group (Fig. 1b).3 Subsequently, Stephan and co-workers obtained the persistent borinium ion III supported by phosphoramidinate groups.4 In 2014, a seminal report on the synthesis of dimesityl boron cation IV was published by Shoji et al.5 IV exhibits high Lewis acidity and electrophilic reactivity towards CO2, CS2, H2 and Et3SiH.6 In addition, twofold 1,2-carboration of diphenylacetylene with IV afforded divinyloborinium ion V, in which the positive charge is delocalized over the entire π-conjugated system.7 More recently, the Inoue group demonstrated the asymmetric borinium ion VI ligated by imidazolin-2-imino and silyl substituents.8

Cationic boron species of type $[\text{R}_n\text{E}=\text{B}]^+$ possess different bonding characters from classical boron cations and should be versatile reagents for organic synthesis through the functionalization of multiple bonds.9,10 Nevertheless, such species are still hitherto unknown. Even with Lewis base stabilization, only two corresponding $[\text{R}_n\text{E}=\text{BL}]^+$ and $[\text{R}_n\text{E}=\text{BL}_2]^+$ derivatives,
exemplified by iminoboryl-CAAC adducts VII and cationic thioxoborane VIII, have been described by the Bertrand, Stephan and Inoue groups, respectively (Fig. 1c).11,12 VII-I with an iodide counter anion is in equilibrium with the neutral idodoinimino-
orborane in solution, which alternatively served as a dipole to 
cyclize with CO₂. Comparatively, VII-BPh₄ and VII-B(C₆F₅)₄ retaining the cationic structure both in the solid-state and in 
solutions do not exhibit dipole reactivity and are inert toward 
CO₂. Neutral iminoboranes are extensively employed as syn-
thons for constructing organoboron compounds through addi-
ion and cycloaddition reactions.13 Therefore, development of 
persistent yet highly reactive cationic counterparts and 
unravelling their reactivity would provide new avenues to 
cationic boron species. Herein, we report the access to the 
caticonic iminoborane IX supported by an NHC, as well as its 
utility for constructing unusual B-containing frameworks 
(Fig. 1d).

Results and discussion

**Synthesis and characterization of 3⁺[AlBr₄]⁻**

Recently, we demonstrated a facile approach for the synthesis of 
iminoborane-NHC complexes by employing NHCs as Bronsted 
bases and ancillary ligands.14 In an analogous fashion, addition 
of two equiv. of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidine 
(IPr₂Me₂) into Mes*NHBBr₃ in toluene afforded compound 2 
as colorless crystals in 56% yield (Scheme 1). The multi-nuclear 
NMR spectroscopic studies coupled with single crystal X-ray 
diffraction confirmed the formulation of 2 to be Mes*N≡B(Br) 
IPr₂Me₂⁺ (1¹B NMR: 9.4 ppm). In the solid state, the boron center 
of 2 adopts a planar geometry with the sum of angles at 359.9°. 
The Mes* and IPr₂Me₂ groups are located on the opposite sides 
of the B1=N1 double bond (Fig. 2a).

Halide abstraction of 2 was next examined. We reacted 2 with 
an equal molar amount of AlBr₃ in toluene at ambient 
temperature for 5 minutes to obtain colorless solids of 
3⁺[AlBr₄]⁻ quantitatively. The 1¹B NMR spectrum of 3⁺ shows 
a broad signal at 6.9 ppm, which is close to the chemical shifts 
seen for the iminoboranes ArB≡NR (2.8–4.3 ppm),15,16 boroni-
nium III (11.1 ppm)⁴ and cationic iminoboranes VII (7.7 and 
7.4 ppm), but strongly upfield-shifted with respect to those of 
two-coordinate boron cations I, II, IV and V (36.7, 38.7, 93.3 and 
74.0 ppm, respectively).¹⁵,¹⁷ A sharp singlet peak at 80.8 ppm 
assigned to [AlBr₄]⁻ was observed in the ²⁷Al NMR spectrum, 
demonstrating the smooth bromide abstraction of 2 by AlBr₃. 
Species 3⁺[AlBr₄]⁻ exhibits high thermal stability under an inert 
atomosphere and does not decompose even upon heating at 80 
°C for 24 h in C₆D₆ (Fig. S71†).

Single crystal X-ray diffraction unambiguously confirmed the 
ionic nature of 3⁺[AlBr₄]⁻ (Fig. 2b). The B1 atom is ligated with 
IPr₂Me₂ and well-separated from the counterion [AlBr₄]⁻ with 
distance of 4.2575(3) Å between the B1 and the closest 
bromine atom of the [AlBr₄]⁻ anion, which is much longer than 
the sum of the van der Waals radii (2.04 Å).¹⁶ The structure of 3⁺ 
shows an essentially linear C1–N1–B1–C19 core with slight 
bending at the N1 (178.6(4)°) and B1 (173.6(4)°) atoms, indica-
tive of sp-hybridization of these two atoms. The B1–N1 bond 
length of 1.224(5) Å in 3⁺ was found to be identical to those of 
VII⁺ (1.229(3), 1.218(4) and 1.192(5) Å) within experimental 
uncertainty. In addition, the contracted B1–C19 (1.527(5) Å) and 
similar C1–N1 (1.389(4) Å) bond lengths in comparison to those 
in 2 (1.605(6) Å and 1.379(5) Å, respectively) were observed.

To further understand the electronic structure of 3⁺, DFT 
calculations at the B3LYP/6-311G* level of theory were 
 performed. The calculated geometrical parameters agree well 
with those observed for the crystal structure of 3⁺. The ¹³B NMR 
chemical shift (5.8 ppm) obtained from GIAO calculations is 
consistent with the experimental value (6.9 ppm, Fig. S82†). The 
Wiberg Bond Index (WBI) for the B-N bond in 3⁺ is 1.98 (Table 
S2†), which is smaller than that of VII (2.10, Table S3†). The 
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Fig. 3 (a) Natural population analysis for $3^+$. (b) Selected molecular orbitals for $3^+$. Isovalue = 0.03.

analysis confirmed the electronic conjugation between the B=N triple bond and Mes* as well as imidazole rings with stabilization energies of 13.9 and 6.9 kcal mol$^{-1}$, respectively (Fig. S85†).

The HOMO and HOMO–2 of $3^+$ represent out-of-plane and in-plane B–N π-bonding orbitals, with contributions from π orbitals of Mes* or imidazole moieties, whereas the LUMO and LUMO+1 predominately involve their π*-components (Fig. 3b). The UV/Vis and IR spectroscopic analyses of $3^+[^{11}AlBr_4]$ were also carried out. The former showed no detectable absorption between 240 and 400 nm (Fig. S15†), whereas the signal at a shorter wavelength (<240 nm) was too noisy or saturated for a reliable assignment. The latter measured in the solid state exhibited a characteristic peak at $\nu = 2004$ cm$^{-1}$ for the B≡N stretching vibration (Fig. S16†), which is comparable to that for $^7$BuB≡NBu (2018 cm$^{-1}$) and is in agreement with the calculated result (2008 cm$^{-1}$, Fig. S84†).

Examination of the Lewis-acidity of $3^+[^{11}AlBr_4]$–

The Lewis-acidity of $3^+[^{11}AlBr_4]$– was first evaluated by computing its global electrophilicity index (GEI). The GEI value at the B3LYP/def2-TZVP level of theory was calculated to be 2.467 (Fig. S89†), which is slightly smaller than that for BCl$_3$ (2.766).¹⁸ Next, the reactivity of $3^+[^{11}AlBr_4]$– towards different Lewis bases was probed. It was demonstrated that hard halide ions such as chloride and bromide readily add to the boron center of $3^+[^{11}AlBr_4]$–. Specifically, treatment of $3^+[^{11}AlBr_4]$– with one equiv. of [PPN]Cl ([PPN = Ph$_3$P=] in toluene at ambient temperature gave the respective B-halogen substituted iminoboranes 4 and 2 smoothly (Scheme 2). The boron atom in 4 was observed at 12.8 ppm in the $^{11}$B NMR spectrum and the single-crystal X-ray analysis elucidated that 4 adopts a formal Z configuration similar to compound 2 (Fig. 4a). The B1–N1 bond length (1.305(7) Å) in 4 compares well with that for 2 (1.296(6) Å). Both values are longer than the B≡N triple bond length in $3^+$ (1.224(5) Å), illustrating the decreased B-N bond strength in iminoborane-NHC complexes 2 and 4.

As for the neutral Lewis bases, 4-dimethylaminopyridine (DMAP) and trimethylphosphine (PMe$_3$) were employed (Scheme 2). Addition of DMAP quantitatively afforded the corresponding cationic terminal iminoborane $5^+[^{11}AlBr_4]$– ($^{11}$B NMR: 15.4 ppm) in the coordination sphere of two different Lewis bases. The solid-state structure of $5^+$ revealed that the DMAP coordination causes the B1 and N1 atoms to be sp$^2$-hybridized and results in a twisted C1–N1–B1–C19 skeleton ($\angle$ C1–N1–B1 = 139.9(3)°; $\angle$ N1–B1–C19 = 123.2(3)°; Fig. 4b). Accordingly, the B1–N1 bond length of 1.332(4) Å is markedly longer than that of $3^+$ (1.224(5) Å) and its WBI is calculated to be 1.55 (Table S6†). In sharp contrast, the coordination of PMe$_3$,

Scheme 2

Reactivity of $3^+[^{11}AlBr_4]$– toward bases ($^*$/NMR yield; NHC = IPr$_2$Me$_2$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene; PPN = Ph$_3$P=) in toluene at r.t.

<table>
<thead>
<tr>
<th>Base</th>
<th>NMR Yield (%)</th>
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<tr>
<td>[PPN]Cl (1 eq)</td>
<td>4 (50%)</td>
</tr>
<tr>
<td>Ph$_3$PBr (1 eq)</td>
<td>2 (90%)</td>
</tr>
<tr>
<td>DMAP (1 eq)</td>
<td>6 (98%)</td>
</tr>
<tr>
<td>PMe$_3$ (1 eq)</td>
<td>6 (95%)</td>
</tr>
<tr>
<td>Dimethylphosphine</td>
<td></td>
</tr>
<tr>
<td>Tris(trimethylphosphine)</td>
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Fig. 4 Solid-state structures of 4 (a) and 5$^+$ (b). The counterion and hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level.
1,2-Addition of $3^+\text{[AlBr}_4]^-$

The addition of unactivated C–H bonds across iminoboranes to form aminoboranes is extremely challenging. It was found that in the presence of sodium cyanate (NaOCN), $3^+\text{[AlBr}_4]^- $ converted into the product $7^+\text{[AlBr}_4]^- $ (11B NMR: 40.8 ppm) at 50 °C (Scheme 3). Both NMR spectroscopic and X-ray single-crystal diffraction studies confirmed $7^+\text{[AlBr}_4]^- $ to be a cyclic amino-borenium formed via an intramolecular C–H bond addition across the B=NN triple bond (Fig. 5a). NaOCN likely acts as a Lewis-base for coordination activation of the B=NN bond to enhance the basicity of N for capturing a proton from the methyl group. Note that a neutral three-coordinate borane enabled intramolecular C–H activation affording borocycles has been described by the Knochel research group. In addition, intermolecular addition proceeded smoothly between $3^+\text{[AlBr}_4]^- $ and more acidic acetonitrile at ambient temperature to give the acyclic aminoborenium $8^+\text{[AlBr}_4]^- $ (11B NMR: 37.2 ppm; Fig. 5b). It was proposed that this transformation may occur in successive steps involving acetonitrile complexation, proton migration and rearrangement of an aza-allene intermediate (Fig. S81†). Both reactions formed anti-addition products.

Inspired by a few successful examples of catalyst-free transfer hydrogenation (TH) of unsaturated compounds,21 the reactions of $3^+\text{[AlBr}_4]^- $ with H2N-BH3 or Me2HN-BH3 were also conducted. The conversions were complete within half an hour at ambient temperature, generating the corresponding aminoborenium salt $9^+\text{[AlBr}_4]^- $ (11B NMR: 34.1 ppm) with concomitant formation of the respective borazine and cycloborazane as the by-products (Fig. S72 and S73†). The solid-state structure of $9^+\text{[AlBr}_4]^- $ revealed its trans stereochemistry (Fig. 5c), which is consistent with Braunschweig’s results on TH of neutral iminoboranes with H2N-BH3.22 Deuterium labelling experiments using H2N-BD3, D2N-BH3 and D2N-BD3 resulted in deuterium incorporation at boron, nitrogen and both boron and nitrogen atoms, respectively, as evidenced by 2H NMR with characteristic peaks at 6.64 ppm (N–D) and 3.58 ppm (B–D) (Fig. S74†). This confirmed the polarity match mechanism of TH to $3^+\text{[AlBr}_4]^- $. This is different from the aminoborane iPr2N=BH2, which readily undergoes reverse TH with Me2N-BH3 and no further hydrogenation of species $9^+\text{[AlBr}_4]^- $ to amineboronium could be observed in the presence of excess H2N-BH3 or Me2N-BH3 under heating conditions (Fig. S75†).

**[2 + 3] cycloaddition of $3^+\text{[AlBr}_4]^- $**

The polar B=NN bond also enables the cycloaddition of $3^+\text{[AlBr}_4]^- $. Nitroene-, azide- and diazomethane-type 1,3-dipolar systems were thus employed.24 Treatment of $3^+\text{[AlBr}_4]^- $ with one equiv. of N-tert-butyl-alpha-phenylnitroine smoothly resulted in the formation of colorless crystals of $10^+\text{[AlBr}_4]^- $ (11B NMR: 25.2 ppm; Scheme 4), which were elucidated to be a cationic oxadiazaborolidine species with the newly formed C=N and B–O bonds (Fig. 6a).

When $3^+\text{[AlBr}_4]^- $ was treated with trimethylsilyl azide (Me3SiN3) in toluene, a white precipitate of 11 was formed immediately. The 11B NMR of 11 showed a signal at 26.0 ppm, whereas $^1\text{H}$ NMR revealed that no Me3Si– group was in the product. Single crystal X-ray diffraction revealed 11 to be a zwitterionic tetraazaborole species with cationic boron and
anionic aluminium centers (Fig. 6b), resulting from a [2 + 3] cycloaddition and subsequent Al/Si exchange as well as Me₃SiBr elimination. With respect to those of 1,4-diphenyl-5-terphenyltetraazaborole reported by the Braunschweig group, features comparable B–N bond lengths (avg. 1.432 Å) and N–N double bond length (1.276(6) Å) as well as an essentially planar BN₅ five-membered ring (the mean deviation from the plane is 0.0186 Å).

Moreover, 3⁺[AlBr₄]⁻ also cyclized with diazomethyl-trimethylsilane to give product 12⁺[AlBr₄]⁻ (¹³B NMR: 22.6 ppm). Its solid structure confirmed the migration of the trimethylsilyl group from carbon to the nitrogen atom after cycloaddition to form an unprecedented cationic triazaborole skeleton (Fig. 6c). The B1–C30 bond length is 1.462(5) Å and its WBI value is 1.2978, thus confirming the typical double bond character. All five atoms of the BCN₅ ring are perfectly coplanar with the sum of internal pentagon angles of 540°, and the calculated nucleus-independent chemical-shift values of NICS(0) and NICS(1) are −11.0 and −28.2, respectively, supporting its aromatic character. The computational studies reveal that the generation of aromatic 12⁺ from isomerization of the non-migrated intermediate is strongly exergonic (−37.1 kcal mol⁻¹) and thus is thermodynamically favorable (Fig. S91†).

Conclusions

Collectively, this work unravels the elementary reactions of a cationic iminoborane, laying the foundation for efficient alternatives to build organoboron species. Employment of aryl and NHC ligands afforded isolable cationic iminoborane 3⁺. Both the boron atom and B≡N triple bond in 3⁺ could behave as reactive sites for derivatization enabling coordination, addition, and cycloaddition leading to a facile access to three-coordinate boron cations. This clearly confirms that substituent modification could boost the reactivity of cationic iminoboranes since analogous VII-BPh₄ lacks the dipole reactivity toward CO₂, CH₃CN, H₂N-BH₃ and Me₃SiN₃ (Figs. S76–S78†). These systematic results indicate that unsaturated boron cations, which integrate both Lewis-acidity and multiple bond reactivities, are attractive synthons in organic synthesis. Investigations on the isolation and applications of more functional boron cations are continuously underway in our laboratory.

Data availability

Experimental and computational data has been provided as ESI†.

Author contributions

L. K. designed the study and supervised the project. R. G. synthesized the complexes and conducted most of the measurements. X. Z., L. L. L. and L. K. performed the theoretical calculations. T. L. collected the crystal structures. Q. L. conducted the HRMS measurement. D. A. R., L. L. L., C.-H. T. and L. K. wrote the manuscript. All authors discussed the experimental results and commented on the manuscript.

Conflicts of interest

The authors declare no competing financial interests.
Acknowledgements

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Notes and references


