Investigation on reactivity of non-classical carbenes with sterically hindered Lewis acid, $B(C_6F_5)_3$ under inert and open conditions

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Abstract. Reactions of $B(C_6F_5)_3$ with *abnormal* N-heterocyclic carbene (*a*NHC), **L1** and cyclic (alkyl)(amino) carbene (*c*AAC), **L2** in the presence of moisture as well as in its absence, have been investigated in toluene. Reaction of *a*NHC with 1 equivalent of $B(C_6F_5)_3$ under inert condition produced classical Lewis acid-base adduct, [**L1**.$B(C_6F_5)_3$], **1**. Further, probing the same reaction with cyclic (alkyl)(amino) carbene (*c*AAC), having different electronic property, led to the isolation of [**L2**.$B(C_6F_5)_3$], **2** under inert condition. Interestingly, reaction of *a*NHC or *c*AAC with 1 equivalent of $B(C_6F_5)_3$ in the presence of moisture resulted in water splitting leading to the formation of [**L1**-H][(OH)$B(C_6F_5)_3$], **3** and [**L2**-H][(OH)$B(C_6F_5)_3$], **4**. All these compounds (**1**-**4**) were characterized in solution by ^{1}H, ^{13}C, ^{19}F and ^{11}B NMR spectroscopy. Additionally, the solid-state structures were unambiguously established by crystallographic analysis of compounds **1**-**4**.

Keywords. Borane; water splitting; tris(pentafluoro phenyl) borane; abnormal NHC; cyclic (alkyl)(amino) carbene.

1. Introduction

The first isolation of a stable carbene by Bertrand in 1989[1] and the subsequent generation of N-heterocyclic carbenes (NHCs) by Arduengo and co-workers[2] in 1991 are important achievements in modern chemistry. Since then, NHCs have been extensively utilized in various fields including transition-metal chemistry,[3] catalysis[4] and main group chemistry[5] because of their strong two-electron σ-donor ability. In 2001, Crabtree and co-workers discovered that 2-pyridylmethylimidazolium salts react with $IrH_5(PPh_3)_2$ to give a complex with the imidazole ring bound the "wrong way," at C5 and not at C2 position like classical carbene.[6] Since then, a few other complexes of the type featuring the so-called *abnormal* (or non-classical) NHCs (*a*NHCs) as ligands have been prepared.[7] However, the first isolable *abnormal* N-heterocyclic carbene (*a*NHC) derived from 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium salt in 2009[8] was reported by Bertrand and co-workers, and thus the chemistry of isolated *abnormal* NHCs still remains in infancy. Another fascinating class of stable non-classical carbenes, cyclic (alkyl)(amino)carbenes, having more σ-donor ability than normal NHCs, was further developed from Bertrand laboratory.[9] Since the discovery of *c*AAC,

they have been widely used as a metal-free system for stabilizing low valent main group elements[10] which was a challenging task for transition metal based ligand systems. Most recently, due to the striking similarity between electron-rich organophosphines and nucleophilic carbenes, Tamm and co-workers have reported use of nucleophilic normal NHCs as a Lewis base partner for the preparation of frustrated Lewis pairs (FLPs).[11] In contrast, utilization of these non-classical carbenes (*abnormal* NHC and/or cyclic (alkyl)(amino)carbene) as Lewis base counterpart in the formation FLPs and their further applications in small molecule activation have not been reported so far. Furthermore, previous theoretical calculation[12a] on *c*AAC and *a*NHC indicated that they can act as better donors than normal NHCs in general and this fact is further manifested by its (*a*NHC) superior catalytic activity compared to *n*NHC.[12b−d] Hence, their reactivity was further investigated towards sterically encumbered borane *i.e.*, $B(C_6F_5)_3$ to check whether they can form suitable FLP and their further utilization for small molecules activation. Tris(pentafluorophenyl)borane is a well known strong Lewis acid, and extensively used to promote the formation of highly active cationic catalysts for olefin polymerization[13−20] as well as a Lewis acid partner for making frustrated Lewis pairs (FLPs). The use of tris(pentafluorophenyl)borane

requires elimination of water present in the reaction media, due to the occurrence of equilibrium 1 as shown below.[21] Moreover, it has been reported that water coordinated to the strong Lewis acid $B(C_6F_5)_3$ becomes a strong Bronsted acid,[22,23] which is able to protonate alkyl groups bound to metal centres.

$$B(C_6F_5)_3 + H_2O \rightleftharpoons \left[(C_6F_5)_3B.(OH_2)\right] \qquad (1)$$

As a part of our ongoing research interest in *a*NHC chemistry,[24] the present study reports the reactivity of the strongly acidic, sterically encumbered borane $B(C_6F_5)_3$ towards non-classical carbenes as Lewis bases. Herein we report the isolation and characterization of four new boron compounds resulted by the reaction between $B(C_6F_5)_3$ and *a*NHC(**L1**)/*c*AAC (**L2**) under dry as well as moistured conditions, respectively. Although the combination of *a*NHC/*c*AAC and $B(C_6F_5)_3$ did not provide a suitable FLP system, however, they have shown a unique property towards water splitting when the reaction was performed under moistured condition and provides a Lewis acid-base adduct under inert condition.

2. Experimental

2.1 *General procedures and instrumentation*

Unless stated otherwise, reactions were performed in flame-dried glassware under oxygen-free atmosphere (Argon) using standard Schlenk techniques or inside a M Braun Glove box maintained below 0.1 ppm of O_2 and H_2O level. All solvents were distilled using appropriate drying agent prior to use. All chemicals were purchased from Sigma-Aldrich and used as received. ^1H, ^{13}C, ^{11}B, ^{19}F NMR spectra were recorded on a JEOL ECS 400 MHz spectrometer and on a Bruker Avance III 500 MHz spectrometer. ^{11}B and ^{13}C NMR spectra of compound 4 were recorded on a Bruker Advance III 500 MHz spectrometer. All chemical shifts are reported in ppm using tetramethylsilane as a reference. Chemical shifts (δ) downfield from the reference standard were assigned positive values. Elemental analysis were carried out using a Perkin-Elmer, series 2, 2400 CHN analyzer and samples were prepared by keeping under reduced pressure (10^{-2} mbar) for overnight. Infrared spectra were obtained on a Perkin Elmer FT-IR Spectrometer Spectrum RXI spectrometer. *Abnormal* NHC[8] and *c*AAC[25] were prepared according to the literature procedure.

2.2 *Synthesis of **L1**.$B(C_6F_5)_3$, 1*

A 1:1 mixture of $B(C_6F_5)_3$ (0.196 mmol, 0.100 g) and *a*NHC (**L1**) (0.196 mmol, 0.106 g) were dissolved in 20 mL of dry toluene. The green solution immediately changed to pale yellow solution and the resulting solution was stirred for 30 min at room temperature under N_2, leading to the formation of a colourless solution. The solvent was removed in vacuum, and the remaining solid was washed three times with 10 mL of hexane to afford a white solid and dried in vacuum. Crystals of **1** were obtained from a mixture of CH_2Cl_2/ hexane at $-30°C$. Yield: 0.164 g (86%); ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.58–7.54 (t, J = 7.6 Hz, 1H), 7.50-7.46 (t, J = 7.6 Hz, 1H), 7.29-7.11 (m, 8H), 7.06-7.02 (t, J = 7.6 Hz, 3H), 6.87-6.85 (d, J = 7.8 Hz, 3H), 3.86-3.84 (m, 1H), 3.11-3.07 (m, 1H), 2.68-2.61 (m, 1H), 2.60-2.58 (m, 1H), 1.42-1.40 (d, J = 6.9 Hz, 3H), 1.32-1.30 (d, J = 6.9 Hz, 3H), 1.24-1.23 (d, J = 6.9 Hz, 3H), 1.0-0.98 (d, J = 6.9 Hz, 6H), 0.77-0.75 (d, J = 7 Hz, 3H), 0.27-0.25 (d, J = 6.9 Hz, 3H), 0.14-0.12 (d, J = 6.9 Hz, 3H) ppm; ^{11}B NMR (96 MHz, $CDCl_3$, 25°C): δ = −16.3 (s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 147.2, 145.4, 144.8, 144.5, 143.2, 139.2, 137.3, 133.9, 131.4, 131.3, 131.1, 130.6, 128.9, 128.1, 127.7, 126.3, 126.2, 125.4, 125.2, 123.6, 123.0, 31.5, 28.3, 28.2, 27.9, 24.3, 24.1, 23.9, 23.6, 23.1, 23.0, 22.6, 21.6 ppm; ^{19}F NMR (178 MHz, $CDCl_3$, 25°C): δ = −116.1, −124.9, −126.7, −131.6, −133.3, −133.6, −159.5, −160.0, −160.7, −165.1, −165.8, −166.0, −166.4, −168.3 ppm; Anal. Calcd. (%) for $C_{57}H_{44}BF_{15}N_2$: N 2.66, C 65.02, H 4.21, found (%): N 2.63, C 64.59, H 4.18.

2.3 *Synthesis of [**L2**.$B(C_6F_5)_3$] adduct, 2*

A 1:1 mixture of $B(C_6F_5)_3$ (0.14 mmol, 0.072 g) and *c*AAC carbene (**L2**) (0.14 mmol, 0.040 g) was dissolved in 10 mL of dry toluene at −78°C under N_2 atmosphere. The solution immediately changed to pale yellow colour and the resulting solution was stirred for 30 min at room temperature under N_2, leading to the formation of a colourless solution. The solvent was removed in vacuum and the remaining solid was washed three times with 10 mL of hexane to afford a white solid and dried in vacuum. Crystals of **2** were obtained from a mixture of CH_2Cl_2/ hexane at −30°C. Yield: 0.099 g (80%). ^1H NMR (500 MHz, $CDCl_3$, 25°C): δ = 7.30–7.29 (m, 2H), 6.87-6.84 (m, 1H), 2.94-2.90 (m, 2H), 2.51 (d, J = 12.5 Hz, 1H), 2.01 (d, J = 12.5 Hz, 1H), 1.56-1.55 (m, 3H), 1.50 (s, 3H), 1.46 (d, J = 3 Hz, 3H), 1.30-1.27 (m, 6H), 1.10 (d, J = 6.5 Hz, 3H), 1.03 (s, 3H), 0.90-0.88 (m, 3H) ppm; ^{11}B NMR (120 MHz, $CDCl_3$, 25°C): δ = −14.3 (s) ppm; ^{13}C NMR (125 MHz, $CDCl_3$, 25°C): δ = 149.10, 149.07, 145.6, 133.4, 130.3, 126.5, 125.8, 124.5, 82.9, 56.9, 56.5, 33.2, 30.3, 29.4, 28.7,

28.4 ppm; ^{19}F NMR (225 MHz, CDCl$_3$, 25°C): δ = −108.2, −120.9, −121.3, −128.5, −131.2, −132.4, −155.0, −156.8, −158.6, −158.8, −163.2, −164.1, −165.5, −165.9, −166.6 ppm; Anal. calcd (%) for C$_{39}$H$_{33}$BF$_{15}$NCl$_2$: N 1.59, C 53.08, H 3.77, found (%): N 1.82, C 53.25, H 3.46.

2.4 Synthesis of [L1.H][(OH)B(C$_6$F$_5$)$_3$], 3

A 1:1 mixture of B(C$_6$F$_5$)$_3$ (0.196 mmol, 0.100 g) and aNHC (L1) (0.196 mmol, 0.106 g) was dissolved in 20 mL of toluene. The green solution immediately changed to pale yellow solution and the resulting solution was stirred for 30 min at room temperature under open atmosphere, leading to the formation of a colourless solution. The solvent was removed in vacuum, and the remaining sticky solid was immediately washed three times with 10 mL of hexane to afford a white solid and dried in vacuum. X-ray quality crystals of 3 were obtained from a mixture of CH$_2$Cl$_2$/ hexane at −30°C. Yield: 0.104 g (54%); ^{1}H NMR (500 MHz, CDCl$_3$, 25°C): δ = 7.86 (s, 1H), 7.81-7.76 (m, 2H), 7.65-7.59 (m, 2H), 7.53-7.51 (m, 4H), 7.49 (s, 1H), 7.47 (s, 1H), 7.43-7.41(m, 2H), 7.29-7.28 (d, J = 8 Hz, 2H), 7.13- 7.11(d, J = 8 Hz, 2H), 2.68-2.63 (m, 2H), 2.59-2.54 (m, 2H), 1.44-1.42 (d, J = 7 Hz, 6H), 1.20-1.18 (d, J = 7 Hz, 6H), 1.03-1.01 (m, 12H) ppm; ^{11}B NMR (120 MHz, CDCl$_3$, 25°C): δ = −3.5 (s) ppm; ^{13}C NMR (125 MHz, CDCl$_3$, 25°C): δ = 148.9, 148.8, 147.0, 147.9, 146.2, 144.8, 144.4, 137.6, 133.3, 132.7, 131.4, 129.7, 129.6, 129.4, 128.2, 127.8, 126.2, 125.7, 124.0, 121.3, 120.2, 29.5, 29.3, 25.2, 23.6, 23.2, 22.3 ppm; ^{19}F NMR (225 MHz, CDCl$_3$, 25°C): δ = −135.3, −167.4, −170.2 ppm; Anal. calcd (%) for C$_{57}$H$_{46}$BF$_{15}$N$_2$O: N 2.62, C 63.93, H 4.33, found (%): N 2.69, C 62.89, H 4.25.

2.5 Synthesis of [L2.H][(OH)B(C$_6$F$_5$)$_3$], 4

A 1:1 mixture of B(C$_6$F$_5$)$_3$ (0.14 mmol, 0.072 g) and cAAC carbene (L2) (0.14 mmol, 0.040 g) was dissolved in 10 mL of toluene at −78°C. The solution immediately changed to pale yellow solution and the resulting solution was stirred for 30 min at room temperature under open atmosphere, leading to the formation of a colourless solution. The solvent was removed in vacuum and the remaining solid was washed three times with 10 mL of hexane to afford a white solid and dried in vacuum. Crystals of 4 were obtained from a mixture of CH$_2$Cl$_2$/ hexane at −30°C. Yield: 0.084 g (74%); ^{1}H NMR (400 MHz, CDCl$_3$, 25°C): δ = 8.57 (s, 1H), 7.61 (t, J = 7.64 Hz, 1H), 7.41 (d, J = 7.64 Hz, 2H), 2.61-2.57 (m, 2H), 2.46 (s, 2H), 1.60 (d, J = 7.64 Hz, 12H), 1.39 (d, J = 6.12 Hz, 6H), 1.09 (d, J = 6.88 Hz, 6H) ppm; ^{11}B NMR (96 MHz, CDCl$_3$, 25°C): δ = −5.5 (s) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, 25°C): δ = 149.0, 147.1, 144.1, 133.0, 129.1, 128.4, 126.0, 125.4, 85.3, 48.8, 47.8, 30.0, 28.4, 26.3, 26.1, 22.0 ppm; ^{19}F NMR (178 MHz, CDCl$_3$, 25°C): δ = −133.6, −135.5, −162.3, −163.7, −166.0, −166.9 ppm. Anal. calcd (%) for C$_{38}$ H$_{33}$BF$_{15}$NO: N 1.72, C 55.96, H 4.08, found (%): N 1.83, C 55.59, H 3.94.

2.6 X-ray structure determination

Suitable single crystals of 1–4 were selected and an intensity data were collected on a Super Nova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2,[26] the structure was solved with the Superflip[27] structure solution program using Charge Flipping and refined with the SHElXL[28] refinement package and Least Squares minimization. Crystallographic information for compounds 1–4 are given in table 1.

3. Results and Discussion

3.1 Synthesis and characterization of 1 and 2

As shown in scheme 1(a), reaction of aNHC (L1) with 1 equiv. of B(C$_6$F$_5$)$_3$ in toluene at room temperature for 5 min under inert atmosphere resulted in the formation of a classical Lewis acid-base adduct [L1.B(C$_6$F$_5$)$_3$] (1) in good yield. Anologous to the reaction pathway shown in scheme 1a, reaction of cAAC (L2) with 1 equiv. of B(C$_6$F$_5$)$_3$ in toluene under the similar reaction condition resulted in the formation of another Lewis acid-base adduct [L2.B(C$_6$F$_5$)$_3$] (2) in good yield (scheme 1b). Both the reactions were monitored by ^{11}B NMR spectroscopy, which revealed the formation of new four coordinated boron compounds, as indicated by the sharp resonances in the decoupled ^{11}B NMR spectrum at δ = −16.3 ppm and −14.3 ppm for 1 and 2, respectively. In addition, 1 and 2 were characterized by ^{1}H, ^{13}C, ^{19}F NMR spectroscopy and X-ray diffraction studies.

Compound 1 was isolated as a white solid in 86% yield. The ^{11}B{^{1}H} NMR spectrum of 1 shows the presence of a four coordinated boron giving rise a singlet at δ = −16.3 ppm. The ^{1}H NMR spectrum of 1 reveals four types of isopropyl CH protons in the ratio of 1:1:1:1.The ^{19}F NMR spectrum provides 15

**Table 1.** Crystallographic data for compounds **1–4**.

	C$_{57}$H$_{44}$BF$_{15}$N$_2$, **1**	C$_{39}$H$_{33}$BF$_{15}$NCl$_2$, **2**	C$_{57}$H$_{46}$BF$_{15}$N$_2$O, **3**	C$_{38}$H$_{33}$BF$_{15}$NO, **4**
CCDC Number	1052864	1052866	1052865	1052867
Formula weight	1052.75	882.37	1070.81	815.46
Crystal system	Monoclinic	monoclinic	triclinic	orthorhombic
Space group	P2$_1$/n	P2$_1$/n	P-1	P2$_1$/n
a (Å)	12.2212(5)	10.6273(2)	10.2867(3)	11.2760(3)
b (Å)	23.0961(9)	19.7950(5)	13.3935(4)	18.8351(5)
c (Å)	19.3645(7)	17.5470(4)	18.7612(5)	17.0893(5)
α (°)	90.000	90.00	101.534(2)	90.00
β (°)	99.943(4)	95.180(2)	93.568(2)	100.348(3)
γ (°)	90.000	90.00	97.639(2)	90.00
V(Å^3)	5383.8(4)	3676.23(14)	2499.63(12)	3570.46(17)
Z	4	4	2	4
D_{calc}(g/cm^3)	1.299	1.594	1.423	1.517
F (000)	2160.0	1792.0	1100.0	1664.0
μ (mm^{-1})	0.112	2.578	1.065	0.144
θ Range (°)	3.52–50.06	6.74–130.78	6.82–132.74	3.24–52.74
Goodness-of-fit	1.041	1.053	1.053	1.071
R1, wR2 [$I > 2\sigma(I)$]	0.0462, 0.1165	0.0581, 0.1591	0.0350, 0.0870	0.0419, 0.1115
Ri ndexes [all data]	0.0593, 0.1233	0.0642, 0.1675	0.0430, 0.0901	0.0491, 0.1165
Largest difference in peak and hole (e/ Å^3)	0.24 and −0.24	0.74 and −0.73	0.25 and −0.23	0.39 and −0.29
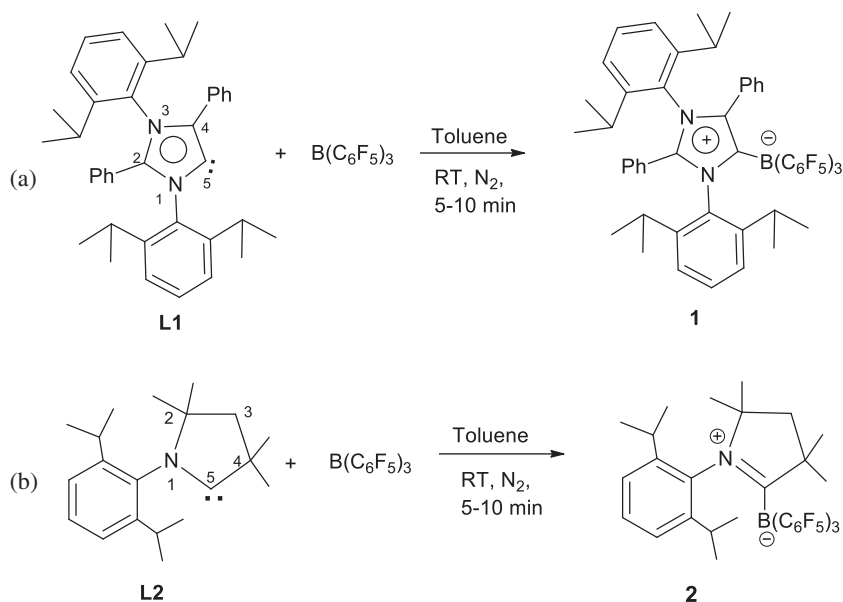
Scheme 1. Formation of *a*NHC-borane (a) and *c*AAC-borane adducts (b).

lines which indicate that all 15 fluorine nuclei are magnetically inequivalent. This can be attributed to the hindered rotation around all four B-C bonds due to the bulky di-isopropyl group attached to the phenyl group bound to N1 and phenyl group at C4 centre. As a result, all the 15 fluorine nuclei became inequivalent at room temperature on the NMR time scale to provide 15 different signals in ^{19}F NMR spectrum.

The ^{1}H and ^{13}C NMR spectra of **1** indicate the presence of four different isopropyl groups. Crystallization from CH$_2$Cl$_2$/hexane solution afforded single crystals suitable for X-ray diffraction analysis, and the molecular structure confirms the formation of the adduct **1**. The NMR data of **1** are consistent with the solid-state X-ray structure which is shown in figure 1. The B-C2 distance was measured as 1.674 (3) Å and is almost identical to
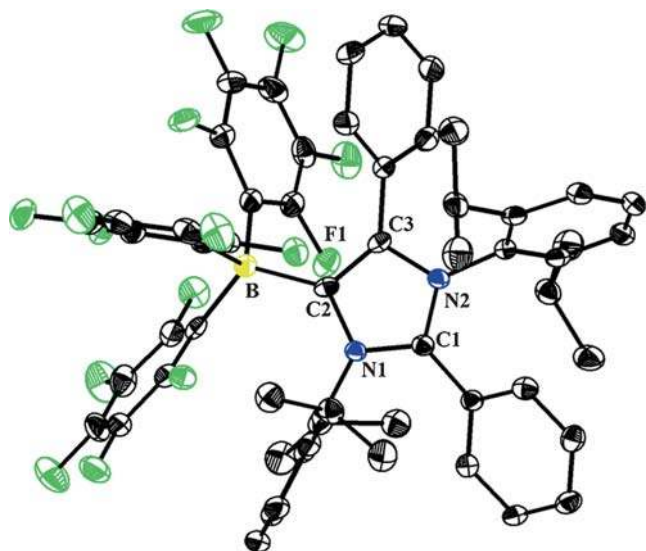
Figure 1. ORTEP diagram of **1** with thermal ellipsoids drawn at 50% probability. The hydrogen atoms are omitted for the sake of clarity. Selected bond lengths [Å] and angles [°] are: C2-B 1.674 (3), N1-C2 1.417(2), C2-C3 1.370(3), N2-C1 1.349(2), N1-C1 1.358(2); C3-C2-B 125.44(16), N1-C2-B 130.26(16), C2-C3- N2 108.90(16), N2-C1-N1 106.86(16), C1-N1-C2 110.92(14).

that found in the related normal NHC-borane adduct of tris(pentafluorophenyl) borane and sterically less-encumbered carbene, 1,3,4,5-tetramethylimidazolin-2-ylidene[29] as well as B-C distance (1.649 (3) Å) in *abnormal* NHC–borane adduct which is formed by rearrangement of normal NHC.[11]

It is well established that *c*AAC is having different electronic property as compared to normal NHCs[10,12a] and *a*NHC[8] and hence it is worthwhile to investigate its reactivity towards sterically encumbered borane to form Frustrated Lewis pairs (FLP). Reaction of *c*AAC with 1 equiv. of $B(C_6F_5)_3$ in toluene followed by hexane wash afforded the 1:1 adduct, **2** in 80% yield and this was confirmed by the signature sharp peak in the ^{11}B NMR spectrum at $\delta = -14.3$ ppm. Furthermore, the ^{1}H NMR spectrum showed one isopropyl CH proton in the range of $\delta = 2.94$–2.89 ppm. The di-isopropylphenyl group at nitrogen atom and two methyl groups at C5 may restrict the free rotation around the B-C axis. As a result, the ^{19}F NMR spectrum exhibits 15 peaks at room temperature on the NMR time scale due to 15 inequivalent fluorine nuclei as observed for compound **1**. The single crystals suitable for X-ray diffraction analysis of **2** were obtained from a CH_2Cl_2/hexane solution at $-30°C$ and the molecular structure reveals the formation of an 1:1 adduct of *c*AAC and borane. The solid-state X-ray structure of **2**, shown in figure 2, is consistent with the NMR data. The B-C1 distance was measured as 1.702 (3) Å which is slightly longer than the B-C2
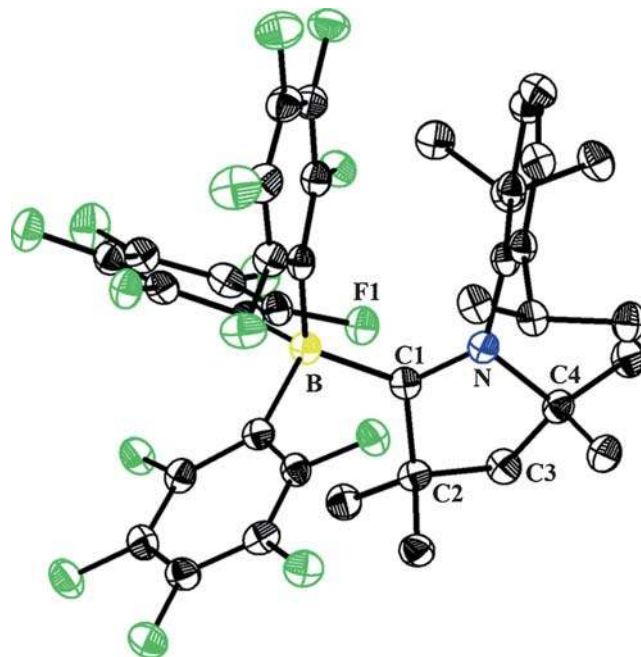

Figure 2. ORTEP diagram of **2** with thermal ellipsoids drawn at 50% probability. The hydrogen atoms and CH_2Cl_2 are omitted for the sake of clarity. Selected bond lengths [Å] and angles [°] are: C1-B 1.702(4), N-C1 1.316(3), N-C4 1.560(3), C1-C2 1.573(3), C3-C4 1.522(4); N-C1-B 131.7(2), C2-C1-B 119.9(2), N-C1-C2 108.4(2), C1-N-C4 113.7(2),C4-C3-C2 106.0(2).

bond distance measured in **1**. This may be attributed to the less σ donor and more π-acceptor property of *c*AAC as compared to *a*NHC. Further, N-C1 bond distance of 1.316(3) Å is significantly shorter than that of N-C4 bond distance of 1.560(3) Å due to double bond character of N-C4 bond.

3.2 *Synthesis and characterization of 3 and 4*

Exploring the reaction of $B(C_6F_5)_3$ with *a*NHC (**L1**) in wet toluene under open atmosphere at room temperature and subsequent evaporation of the toluene and cold hexane wash afforded a white solid in 54% yield, which was characterized by spectroscopic data and X-ray diffraction analysis, clearly indicating the formation of water splitted product, $[\textbf{L1}.H][(OH).B(C_6F_5)_3]$ (**3**, scheme 2a). Remarkably, the reaction when carried out in the presence of 1 equiv. of water also afforded the same water splitted product, $[\textbf{L1}.H][(OH)B(C_6F_5)_3]$ (**3**). The formation of **3** can be rationalized by assuming that in the presence of water, $B(C_6F_5)_3$ forms the adduct$[H_2O.B(C_6F_5)_3]$ as also reported earlier by Danopoulos *et al*.[30] This adduct formation of water and $B(C_6F_5)_3$ further activates the H_2O molecule which becomes a strong Brønsted acid,[22,23] as demonstrated
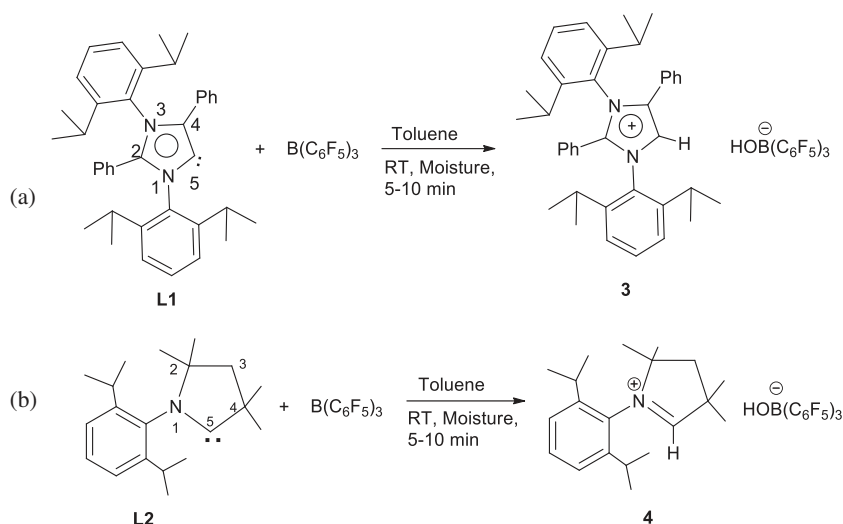
**Scheme 2.** Formation of water splitted products, **3**(a) and **4**(b).
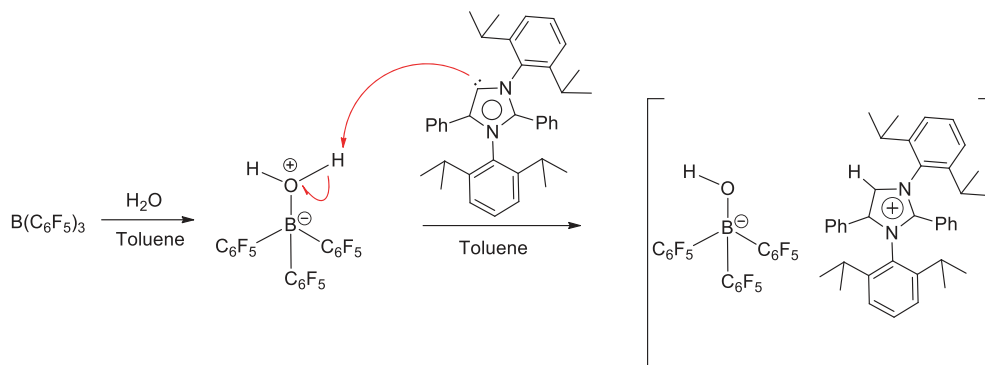
Scheme 3. Schematic representation of formation of water splitting product, **3**.

by previous report on its ability to protonate the metal alkyl group. Further, abstraction of the proton in this activated H_2O molecule by nucleophilic *a*NHC results in the H_2O splitting (scheme 3).

Further description of the characterization of **3** from X-ray diffraction studies and various spectroscopic data are presented below. The $^{11}B\{^1H\}$ NMR spectrum of **3** rationalized the presence of oxygen bonded four coordinated boron atom at $\delta = -3.5$ ppm.[31] Furthermore, the ^1H NMR spectrum of **3** clearly shows the presence of a unique proton attached at the C5 centre at 7.86 ppm. The ^{19}F NMR spectrum exhibits three singlet peaks which may be assigned for the *ortho*, *meta* and *para* fluorine nuclei. Further, IR-spectrum of **3** revealed absorption at 3321 cm^{-1} confirming the presence of −OH group. The NMR data of **3** are consistent with the solid-state X-ray structure, shown in figure 3. The B-O bond distance was measured as 1.462(2) Å and it is comparable with other B-O bond distances observed in $t-Bu_2(H)P(CH_2)_4OB(p-C_6F_4H)_3$ (1.465(16) Å) and

$C_5H_3Me_2N(CH_2)_4OB(C_6F_5)_3$ (1.458(14) Å)[31] and in boronic acid.[32]

The corresponding reaction of *c*AAC with the $B(C_6F_5)_3$ in wet toluene under open atmosphere provided the salt, **4** which was isolated in 74% yield (scheme 2b). Evaporation of the toluene followed by washing with cold hexane afforded a white solid, which was characterized by spectroscopic data and X-ray diffraction analysis, clearly indicating the formation of **4**. As observed for **L1**, the same reaction in the presence of 1 equiv. of water also afforded water splitted product, $[\textbf{L2}.H][(OH)B(C_6F_5)_3]$, **4**. The $^{11}B\{^1H\}$ NMR spectrum of **4** rationalized the presence of oxygen bonded four coordinated boron atom at $\delta = -5.5$ ppm.[31,32] Furthermore, the ^1H NMR spectrum of **4** clearly shows the presence of a proton attached at the C5 carbon at $\delta = 8.57$ ppm. Further, IR-spectrum of **4** confirms the presence of −OH group displaying a strong absorbance at 3415 cm^{-1}. The NMR data of **4** are consistent with the solid-state X-ray structure, shown in figure 4. The
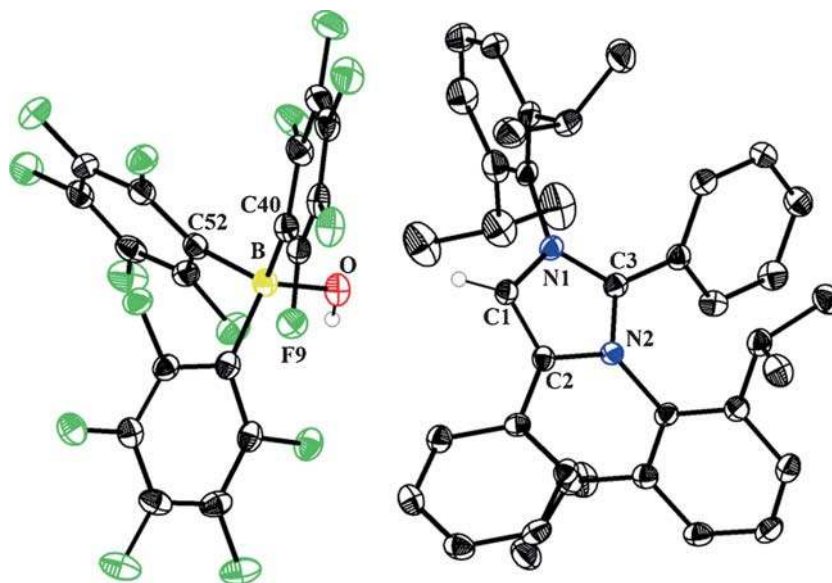
Figure 3. ORTEP diagram of **3** with thermal ellipsoids drawn at 50% probability. The hydrogen atoms are omitted for the sake of clarity. Selected bond lengths [Å] and angles [°] are: O-B 1.462(2), N1-C1 1.378(2), N1-C3 1.344(2), C2-C1 1.357(2), N2-C2 1.399(2), N2-C3 1.353(2); C40-B-O 103.19(13), C40-B-C52 112.84(13), C2-C1-N1 107.91(13), C3-N1-C1 109.66(13), C3-N2-C2 109.54(12), N1-C3-N2 106.88(13).
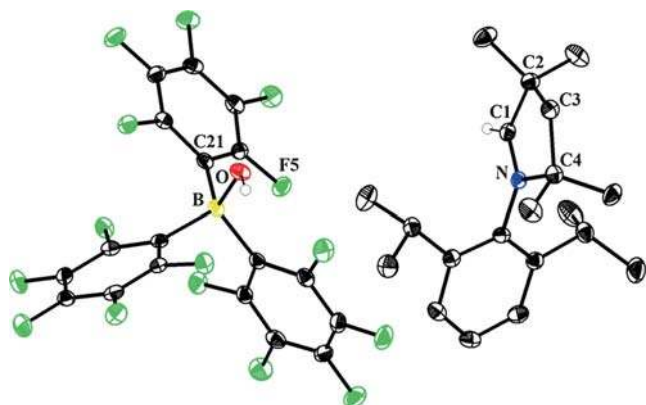
Figure 4. ORTEP diagram of **4** with thermal ellipsoids drawn at 50% probability. The hydrogen atoms are omitted for the clarity. Selected bond lengths [Å] and angles [°] are: O-B 1.477(2), N-C11.277(2), C1-C2 1.493(2), C3-C2 1.549(2), C3-C4 1.537(2); O-B-C21 101.89(13), C1-N-C4 113.00(14), C3-C4-N 100.21(13), N-C1-C2 114.22(14), C1-C2-C3 101.44(14).

O-B bond distance is 1.477(2) Å and it is comparable with other B-O bond distance[31] and in boronic acid.[32]

4. Conclusions

In conclusion, we have demonstrated the reactivity of non-classical carbenes (*a*NHC and *c*AAC) with Lewis acid $B(C_6F_5)_3$ under inert as well as under open condition to afford classical Lewis acid-base adducts (**1** and **2**) and water splitting products (**3** and **4**), respectively. To the best of our knowledge, the formation of *a*NHC-$B(C_6F_5)_3$ and *c*AAC-$B(C_6F_5)_3$ adducts using *a*NHC and *c*AAC as a Lewis base partner and non-classical carbenes mediated water splitting have not been reported earlier. These results clearly demonstrated the potential of these systems towards water activation under very mild conditions. Furthermore, judicious modulation of the steric demand of *a*NHC/*c*AAC is in process at our laboratory to make suitable FLP systems and their utilization for small molecule activation.

Supplementary Information (SI)

Spectroscopic data for compounds **1-4**. CCDCs 1052864–1052867 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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