Supporting Information for:

Tricationic Analogues of Boroxines and Polyborate Anions.

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Contents:

Computational Details

General Considerations: All manipulations were performed using standard Schlenk techniques or in an argon-filled MBraun glovebox (O_2 levels below 0.5 ppm). Glassware was dried in a hot oven overnight and heated under vacuum before use. Solvents were distilled from Na/benzophenone, CaH_2 or P_2O_5 and degassed prior to use. [(2,6-lutidine)BCl_2][$AlCl_4$] was prepared as previously reported.[1] All other materials were purchased from commercial vendors and used as received. NMR spectra were recorded with a Bruker AV-400 spectrometer (400 MHz ^{1}H; 100 MHz ^{13}C; 128 MHz ^{11}B; 162 MHz and ^{27}Al 104.3 MHz). ^{1}H NMR chemical shifts are reported in ppm relative to protio impurities in the deuterated solvents and ^{13}C NMR using the centre line of CD_2Cl_2 (or $CDCl_3$ etc. as appropriate) as internal standard. ^{11}B NMR spectra were referenced to external $BF_3{:}Et_2O$, and ^{27}Al to $Al(NO_3)_2$ in D_2O ($Al(H_2O)_6{}^{3+}$). Unless otherwise stated all NMR are recorded at 293 K. Elemental analysis of air sensitive compounds were performed by London Metropolitan University service. Broad features in the ^{11}B and ^{27}Al NMR spectra are due to boron materials present in the spectrometer probe/NMR tube glass.

BCl_3 purchased as a 1M solution in CH_2Cl_2 or heptanes was found to be of variable molarity. Therefore an excess of reagents can be used or the molarity of BCl_3 solutions was approximately quantified by titration with PPh_3 (using ^{11}B and ^{31}P{^{1}H} NMR spectroscopy).

Synthesis of $[(2,6\text{-lutidine})_4B_5O_6][AlCl_4]_3$, Compound **2**.

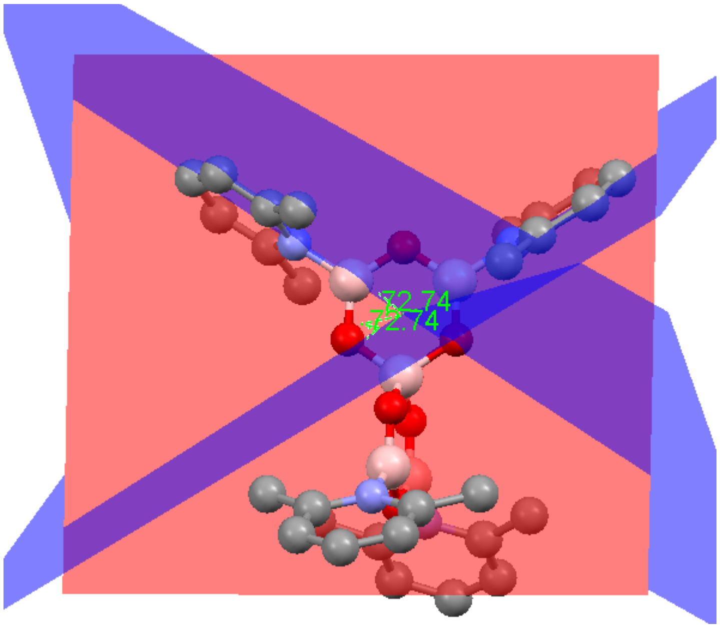
A Schlenk fitted with a J. Youngs valve was charged with $[(2,6\text{-lutidine})BCl_2][AlCl_4]$ (0.032 mgs, 0.09 mmol) this was suspended/partially dissolved in o-$C_6H_4Cl_2$ (1 ml) and one equivalent of $(Me_3Si)_2O$ (19 μl, 0.09 mmol) added. The mixture was heated to 80 ^{o}C to produce a homogenous solution. Further heating for 18 hours produced a crystalline solid that was suitable for single crystal X-ray diffraction studies. The crystalline material was isolated by decanting the o-$C_6H_4Cl_2$ and washing with one 1 ml batch of o-$C_6H_4Cl_2$. Subsequent prolonged drying (16 hours 0.02 mbar) produced compound **2** analytically pure in 52 % isolated yield (10 mgs). Attempts to dissolve **2** in hot (140^{o}C) o-$C_6H_4Cl_2$, CH_2Cl_2, THF and $PhNO_2$ all failed.

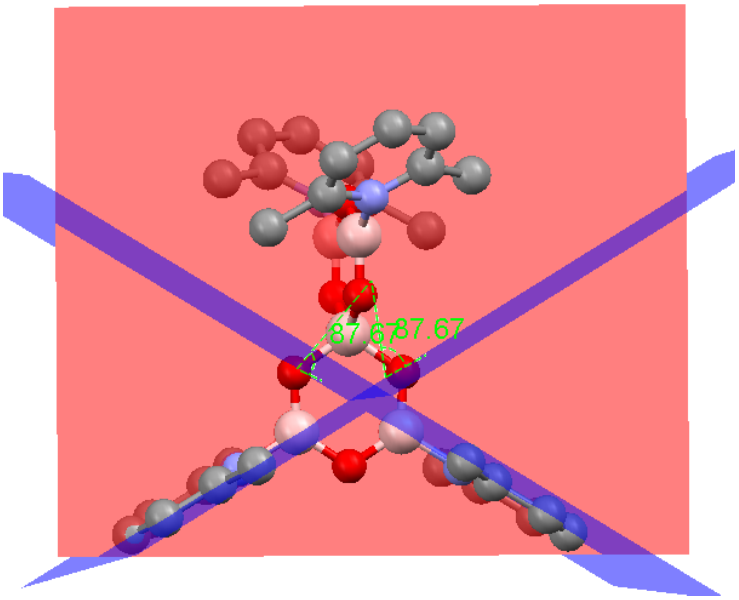
Elemental Analysis: Expected for $C_{34}H_{40}B_5O_6Al_3Cl_{14}N_4$; C = 31.11, H = 3.36, N = 5.18. Found C = 31.12, H = 3.26, N = 5.07.

Crystallographic Details of Compound **2**

$C_{34}H_{40}B_5O_6Al_3Cl_{14}N_4$,M = 1231.99, orthorhombic, a = 23.9228(10), b = 25.3459(10), c = 38.9296(16) Å, V = 23604.8(17) Å^3, T = 100(2) K , space group Fddd, Z = 16, R_{int} = 0.0724 (for 5219 measured reflections), R_1 = 0.0470 [for 2740 unique reflections with >2s(I)], wR^2 = 0.1077 (for all 5219 unique reflections).

Below schematics of the cationic portion of **2** showing the interplane angles between the B_3O_3 and lutidine rings, red plane = B_3O_3, blue = pyridyl (atom colours: pink = boron, dark grey = carbon, blue = nitrogen, red = oxygen)





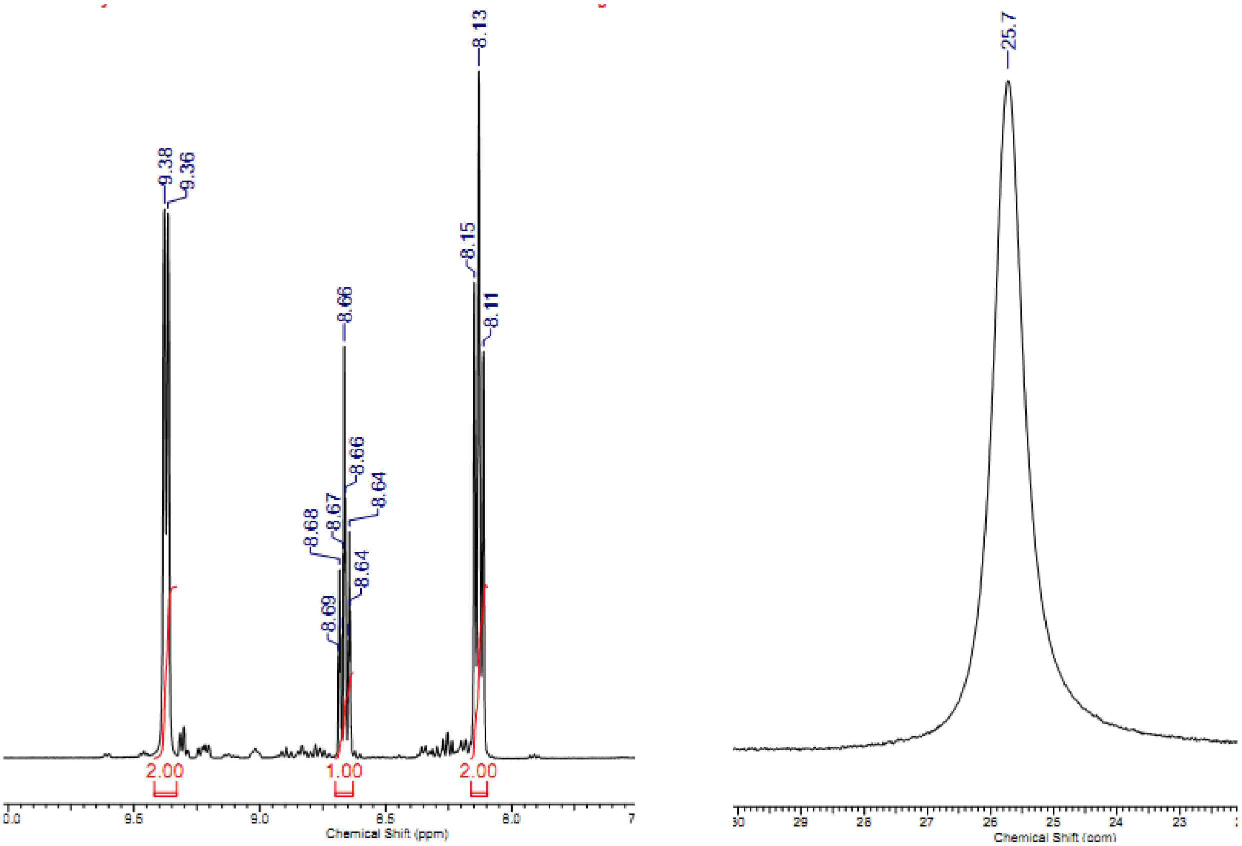
Synthesis of [(pyridine)BCl_2][$AlCl_4$], Compound **3**:

In an oven dried Schlenk tube fitted with a J. Young's tap pyridine (32 µl, 0.4 mmol, 1 equiv.) was added to anhydrous CH_2Cl_2 (3 ml). This solution was cooled to 0 °C, BCl_3 (0.8 M in dichloromethane, 0.5 ml, 0.4 mmol, 1 equiv.) was then added dropwise and allowed to warm to room temperature. After stirring the reaction mixture for 1 hour at room temperature $AlCl_3$ (53 mg, 0.4 mmol, 1 equiv.) was added. The reaction mixture was allowed to react for 2 hours, layered with anhydrous pentane and placed in a freezer at -20 °C. Slow pentane diffusion yielded yellow crystalline needles suitable for X-ray analysis (115 mg, 87 %).

Elemental Analysis: Expected for C_5H_5 $AlBCl_6N$; C = 18.22, H = 1.53, N = 4.25. Found C = 18.25, H = 1.58, N = 4.09.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.13 (t, *J* = 7.2 Hz, 2H), 8.66 (tt, *J* = 7.7, 1.5 Hz, 1 H), 9.35 (d, *J* = 5.8 Hz, 2 H).
^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 128.2, 146.0, 149.6.
^{11}B NMR (128 MHz, CD_2Cl_2): δ 25.7.
^{27}Al NMR (104 MHz, CD_2Cl_2): δ 103.6 (FWHH = 526 Hz)

Representative ^{1}H and ^{11}B NMR Spectra at 20 ^{o}C

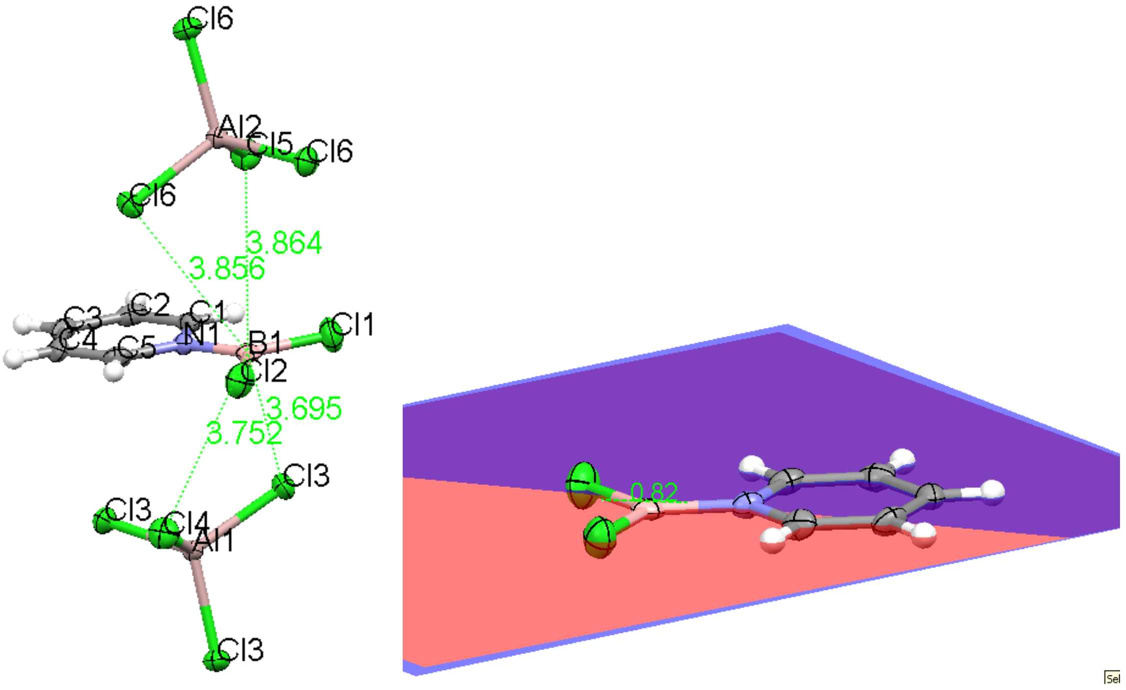


Left: ^{1}H NMR spectra at 20 °C. Right: ^{11}B NMR spectra at 20 °C

Crystallographic Details of Compound **3**

$C_5H_5B_1Al_1Cl_4N_1$,M = 329.59, trigonal, a = 12.708(5), b = 12.708(5), c = 13.720(5) Å, V = 1918.8(19) $Å^3$, T = 100(2) K , space group P3c1, Z = 6, R_{int} = 0.0506 (for 2621 measured reflections), R_1 = 0.0327 [for 2187 unique reflections with >2s(I)], wR^2 = 0.0718 (for all 2621 unique reflections).

Below ORTEP diagrams of **3** (ellipsoids at 50 % probability level). Left showing the closest anion---cation contacts, right showing the interplane angles between the Cl-C-Cl plane and the pyridine ring, red plane = B_3O_3, blue = lutidine (atom colours: pink = boron and aluminium, dark grey = carbon, blue = nitrogen, chlorine = green)



Selected bond lengths (Å) and angles (º):

N1-B1	1.487(5)	N1-B1-Cl2	119.8(3)
B1-Cl1	1.714(4)	N1-B1-Cl1	120.5(3)
B1-Cl2	1.730(4)	Cl1-B1-Cl2	119.7(2)
C1-N1	1.361(4)		
C5-N1	1.367(4)		
C4-C5	1.356(5)		
C1-C2	1.352(5)		
C2-C3	1.392(5)		
C3-C4	1.389(5)		

Synthesis of (py)BBr_3

In an oven dried Schlenk tube, pyridine (0.24 ml, 3.0 mmol, 1 equiv.) was dissolved in anhydrous hexane (5 ml). To this solution, which was cooled to 0 °C, BBr_3 (1 M in heptanes, 3.2 ml, 3.2 mmol, 1.07 equiv.) was added dropwise to form a colourless solid, and then warmed to room temperature. After stirring for 1 hour at room temperature the solution was removed using a filter cannula and the solid washed with anhydrous hexane (5 ml). The colourless solid was dried under vacuum to yield (py)BBr_3 (0.96 g, 98%).

NMR spectra were recorded in bromobenzene-d_5 using cyclohexane as internal standard. Cyclohexane peak referenced at 1.37 ppm in ^1H NMR and at 26.99 ppm in ^{13}C NMR
^1H NMR (400 MHz, C_6D_5Br): δ 6.94 (t, *J* = 7.1 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 1 H), 9.14-9.26 (m, 2 H).
$^{13}C\{^1H\}$ NMR (100 MHz, C_6D_5Br): δ 125.5 (q, *J* = 2.8 Hz), 143.2, 145.4 (q, *J* = 1.8 Hz).
^{11}B NMR (128 MHz, C_6D_5Br): δ -7.0.

Synthesis of (py)$AlBr_3$

In an oven dried J. Young NMR tube, under an inert atmosphere, $AlBr_3$ (100 mg, 0.37 mmol, 1 equiv.) was dissolved in anhydrous bromobenzene-d_5 (0.6 ml). To the solution pyridine (37 µl, 0.37 mmol, 1 equiv.) was added and the NMR tube was shaken for 5 minutes. After 12 hours the internal standard cyclohexane (5 µl) was added and NMR spectra were recorded.

^{27}Al NMR (104 MHz, C_6D_5Br): 101.0 ppm

Synthesis of $[(py)BBr_2][AlBr_4]$, Compound **4**:

In an oven dried Schlenk tube, under inert atmosphere, pyridine (0.24 ml, 3.0 mmol, 1 equiv.) was dissolved in anhydrous *ortho*-dichlorobenzene (3 ml). To the solution, which was cooled to 0 °C, BBr_3 (1 M in hexanes, 3 ml, 3.0 mmol, 1 equiv.) was added dropwise to form a white solid, and then warmed to room temperature. After stirring for 1 hour at room temperature $AlBr_3$ (800 mg, 3.0 mmol, 1 equiv.), dissolved in *ortho*-dichlorobenzene (8 ml), was added via cannula. The Schlenk tube containing $AlBr_3$ solution was washed with *ortho*-dichlorobenzene (5 ml). The reaction mixture was then stirred for 2 hours, layered with anhydrous pentane and placed in a fridge at 4 °C. Slow pentane diffusion yielded colourless crystals (1.71 g, 96 %).

Elemental Analysis: Expected for $C_5H_5AlBBr_6N$; C = 10.07, H = 0.85, N = 2.35. Found C = 10.06, H = 0.72, N = 2.29.

(Cyclohexane used as an internal reference, peak referenced at 1.37 ppm in ^1H NMR and at 26.99 ppm in ^{13}C NMR.)
^1H NMR (400 MHz, C_6D_5Br): δ 7.29 (mt, J = 6.94 Hz, 2 H), 7.80 (tq, J = 7.69, 1.43 Hz, 1 H), 8.99 (d, J=5.80 Hz, 2H).
$^{13}C\{^1H\}$ NMR (100 MHz, C_6D_5Br): δ 126.9, 146.0, 148.0 (br).
^{11}B NMR (128 MHz, C_6D_5Br): δ 18.9.
^{27}Al NMR (104 MHz, C_6D_5Br): δ 85.8.

Whilst the slow exchange regime could not be reached (CD_2Cl_2, to -70 °C) the assignment of **3** and **4** as borenium cations is supported by The addition of a further equivalent of $AlBr_3$ (to enhance the halide affinity of the aluminium Lewis acid) to **4**. This resulted in an ^{11}B NMR resonance of δ + 44.4 ppm, indicating that $[(py)BBr_2]^+$ now dominates in solution.

Variation in ^{11}B chemical shift (ppm) relative to the stoichiometry of $AlBr_3$

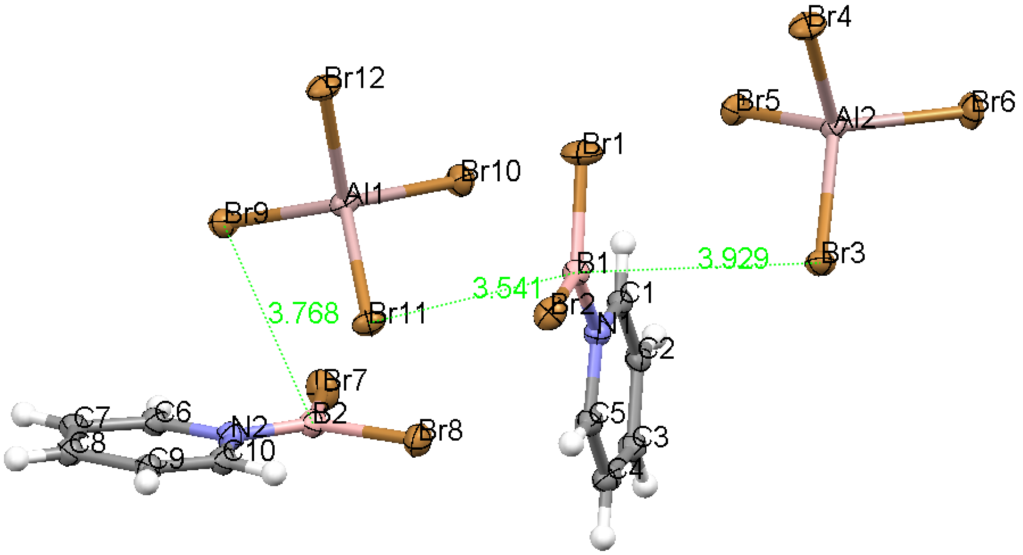
1Py + 1BBr_3 + 1 $AlBr_3$ in C_6D_5Br	^{11}B = 18.9	^{27}Al = 85.8	FWHH (^{27}Al) =2170 Hz
1Py + 1BBr_3 + 1.5 $AlBr_3$ in C_6D_5Br	^{11}B = 34.1	^{27}Al = 85.5	FWHH (^{27}Al) =2247 Hz
1Py + 1BBr_3 + 2 $AlBr_3$ in C_6D_5Br	^{11}B = 44.4	^{27}Al = 84.2	FWHH (^{27}Al) = 2838 Hz

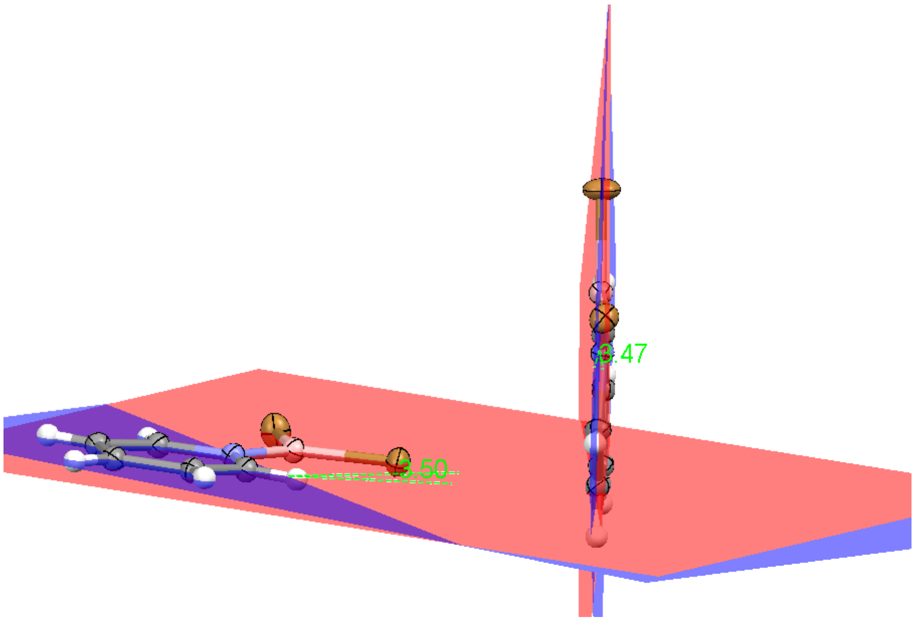
(FWHH=Full Width at Half Height)

Crystallographic Details of Compound **4**

$C_5H_5B_1Al_1Br_6N_1$,M = 596.29, monoclinic, a = 7.6227(3), b = 13.8546(6), c = 13.6784(5) b = 95.281(3)° Å, V = 1438.44(10) Å^3, T = 100(2) K , space group Pc, Z = 4, R_{int} = 0.0333 (for 3680 measured reflections), R_1 = 0.0474 [for 3169 unique reflections with >2s(I)], wR^2 = 0.1405 (for all 3680 unique reflections).

Below ORTEP diagrams of **4** (ellipsoids at 50 % probability level). Top showing the closest anion---cation contacts, bottom showing the interplane angles between the Br-B-Br plane and the pyridine rings, red plane = B_3O_3, blue = lutidine (atom colours: pink = boron and aluminium, dark grey = carbon, blue = nitrogen, orange = bromine)





Selected bond lengths (Å) and angles (º):

N1-B1	1.48(2)
B1-Br1	1.877(17)
B1-Br2	1.874(17)
B2-N2	1.46(2)
B2-Br7	1.851(18)
B2-Br8	1.918(19)

N1-B1-Br1	120.2(11)
N1-B1-Br2	120.9(11)
Br1-B1-Br2	118.7(9)
Br7-B2-Br8	117.7(9)
N2-B2-Br7	123.4(12)
N2-B2-Br8	118.8(12)

Reactivity of **4** towards additional pyridine and $AlBr_3$

In an oven dried J. Young NMR tube, under inert atmosphere, pyridine (16 µl, 0.2 mmol, 1 equiv.) was dissolved in anhydrous *ortho*-dichlorobenzene (0.6 ml). To the solution BBr_3 (1 M in heptanes, 0.2 ml, 0.2 mmol, 1 equiv.) and after 30 minutes $AlBr_3$ (53 mg, 0.2 mmol, 1 equiv.) were added. After 1 hour pyridine (16 µl, 0.2 mmol, 1 equiv.) was added to the resulting mixture and NMR spectra were recorded. ^{11}B and ^{27}Al NMR spectra were consistent with the formation of the two neutral adducts (py)BBr_3 and (py)$AlBr_3$ with *ca.* 15% of boronium [(py)$_2$$BBr_2$][$AlBr_4$].

^{11}B NMR (128 MHz, *ortho*-dichlorobenzene): δ 2.1, -8.0.
^{27}Al NMR (104 MHz, *ortho*-dichlorobenzene): δ 100, 80.7.

Synthesis of [(py)$_2$$BBr_2$][$AlBr_4$], Compound **5**

In an oven dried Schlenk tube fitted with a J. Young's tap, under inert atmosphere, pyridine (72 µl, 0.89 mmol, 1 equiv.) was added to a solution of [(py)BBr_2][$AlBr_4$] (531 mg, 0.89 mmol, 1 equiv.) in anhydrous *ortho*-dichlorobenzene (3 ml)and heated to 100 °C. After stirring the reaction mixture at 100 °C for 72 hours it was cooled at room temperature and filtered by filter cannula to remove the insoluble materials. The filtrate was layered with anhydrous pentane and placed in fridge at 4 °C. Slow pentane diffusion yielded colourless crystals (446 mg, 74 %).

Elemental Analysis: Expected for $C_{10}H_{10}AlBBr_6N_2$; C = 17.78, H = 1.49, N = 4.15. Found C = 17.89, H = 1.42, N = 4.09.

NMR spectra were recorded in bromobenzene-d_5 using cyclohexane as internal standard. Cyclohexane peak referenced at 1.37 ppm in ^1H NMR.
^1H NMR (400 MHz, C_6D_5Br): δ 7.46 (t, *J* = 6.9 Hz, 4 H), 7.80 (t, *J*=7.7 Hz, 2 H), 8.72 (br s, 4 H)
^{11}B NMR (128 MHz, C_6D_5Br): δ 3.2.
^{27}Al NMR (104 MHz, C_6D_5Br): δ 81.7.

Synthesis of $[(py)_4B_3O_3][AlBr_4]_2[Al_2Br_7]$, Compound **6**

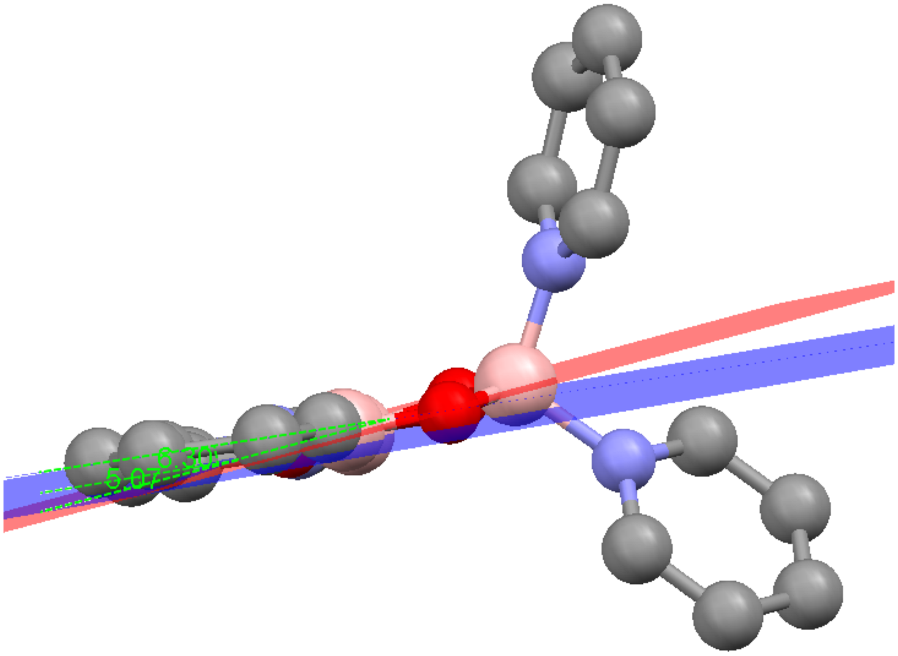
In an oven dried Schlenk tube fitted with a J. Young's tap, under inert atmosphere, $[(py)BBr_2][AlBr_4]$ (500 mg, 0.84 mmol, 1 equiv.) was suspended/partially dissolved in anhydrous *ortho*-dichlorobenzene (3 ml) and $AlBr_3$ (224 mg, 0.84 mmol, 1 equiv.) and pyridine (68 µl, 0.84 mmol, 1 equiv.) were added. Then the reaction mixture was heated to 150 °C. After 21 hours at 150 °C the reaction mixture was slowly cooled at 60 °C at which temperature a small quantity of colourless crystals suitable for X-ray analysis formed. The ^{11}B and NMR spectrum of the solution was consistent with the boronium cation $[(py)_2BBr_2]^+$ as the only boron containing species remained in solution.

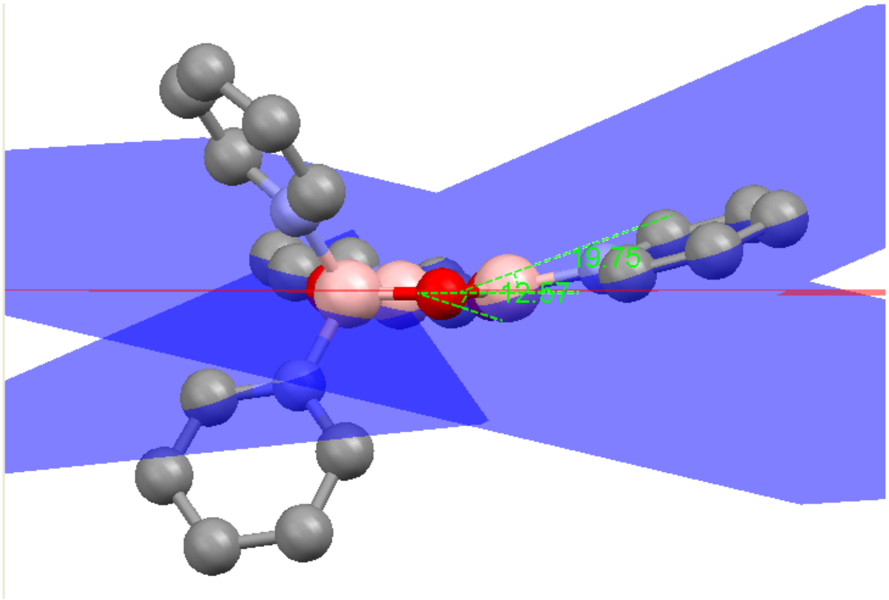
Elemental Analysis: Expected for $C_{20}H_{20}Al_4B_3Br_{15}N_4O_3$; C = 14.10, H = 1.18, N = 3.29. Found C = 14.26, H = 1.18, N = 3.20.

Crystallographic Details of Compound **6**

$C_{20}H_{20}B_3O_3Al_4Br_{15}N_4$,M = 1703.25, monoclinic, a = 10.3692(3), b = 11.1756(3), c = 41.7001(12) Å, α = 83.535(2)° β = 84.176(2)° γ = 75.954(3)° V = 4644.2(2) Å^3, T = 100(2) K , space group P-1, Z = 2, R_{int} = 0.0687 (for 16359 measured reflections), R_1 = 0.0670 [for 11913 unique reflections with >2s(I)], wR^2 = 0.1546 (for all 16359 reflections).

Below schematics of the two inequivalent tri-cations found in the asymmetric unit of **6** showing the interplane angles between the B_3O_3 (red plane) and pyridine rings (blue planes), (atom colours: pink = boron, dark grey = carbon, blue = nitrogen, red = oxygen)





Synthesis of **6** via addition of 0.5 equivalents of H_2O

Pyridine (61μl, 0.75mmol) was added to BBr_3 (0.75cm^3, 0.75mmol) in DCM (2cm^3) in a 20cm^3 Schlenk fitted with a J. Young's tap. The mixture was stirred for 5 minutes and then solvent removed in vacuo. $AlBr_3$ (400mg, 1.5mmol) and pyridine (61μl, 0.75mmol) were added and dissolved in o-DCB (7cm^3). Water (6.75μl, 0.375mmol) was added, the system was sealed and the vessel heated to 140°C for 16 hours. The mixture was slowly cooled over 8 hours to 40°C and maintained at 40°C for a further 16 hours, yielding a pale yellow solution and copious colourless crystalline material. The supernatant was removed and discarded. The crystalline material was suspended in o-DCB (7cm^3), the flask resealed and reheated to 140°C for three hours, until all was dissolved. The temperature was reduced to 100°C for three hours then slowly cooled to 50°C over two days, yielding a crop of colourless crystals. The supernatant was removed, the crystals washed with DCM (5cm^3) and dried in vacuo to give **6** (155mg, 0.09mmol, 72% based on water) as a colourless, microcrystalline solid.

Calculated (for $[C_{20}H_{20}N_4B_3O_3][AlBr_4]_2[Al_2Br_7]$: C14.1 H1.18 N 3.29 Found C: 14.17 H: 1.22 N: 3.29

Due to the insolubility of **6** in non-polar solvents and at ambient temperatures, NMR were recorded at elevated temperatures in o-DCB with a d_6-DMSO capillary used to supply a lock signal. Regrettably, the solvent peaks obscure the aromatic region of the ^{1}H spectrum.

^{11}B (o-DCB/d6-DMSO) : δ 28.5 (broad singlet, pwhh=2300Hz), -22.5 (broad singlet, pwhh=1500Hz). These resonances were observed in a 2 : 1 approximate ratio consistent with the structure of **6**.

A minor resonance at -5.25 (broad singlet, pwhh=600Hz) was also observed but we attribute this to a minor, more soluble impurity.

Synthesis of $[py_4B_3O_3][AlCl_4]_3$, compound **7**.

In a J. Youngs NMR tube, $[py\text{-}BCl_2][AlCl_4]$ (30mg, 0.091mmol) was dissolved in 0.5 mL of ortho-dichlorobenzene and C_6D_6 (16µL, 0.182mmol) was added. The solution was stirred for 20 minutes and hexamethyldisiloxane (19µL, 0.091mmol) added. The solution was left overnight and a colourless solid formed.

Weight: 4mg Yield: 44% (based on pyridine)

Elemental analysis:

Expected for $C_{20}H_{20}N_4B_3O_4Al_3Cl_{12}$: %C= 26.23 %H= 1.8% %N= 5.1

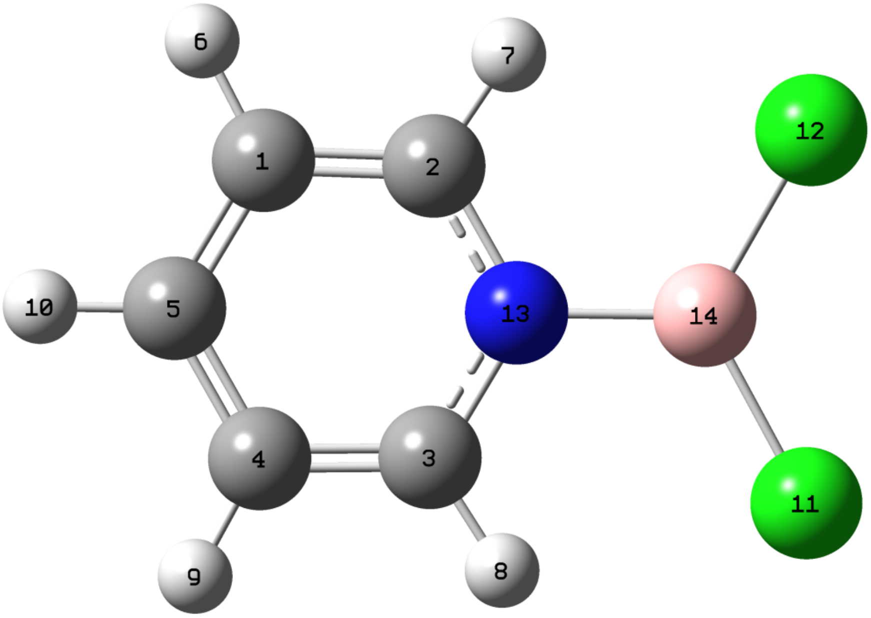
Found: %C= 26.51, 26.43 %H= 2.31, 2.37, %N= 6.13, 6.08

The lack of suitable crystalline material prevented characterisation by single crystal X-ray diffraction.

Computational Details:

Density functional calculations were carried out using the Gaussian09 suite of programs.[2] For direct comparison with previous computational work[3] on $[\mathrm{CatB(P^tBu_3)}]^+$ the MPW1K hybrid exchange-correlation functional[4] was employed (as described at Minnesota density functional website[5]) with the 6-311++G(d,p) basis set[6] for all calculations. The geometry was fully optimized and confirmed as a minimum through vibrational analysis. The optimized geometry was then used to perform natural bond order (NBO) analysis from which atomic charges were derived. Selected geometric parameters, full Cartesian coordinates and NBO charges for the borenium and boroxine systems discussed are given below.

[3]$^+$: $[\mathrm{pyBCl_2}]^+$



Selected Bond Length (Å)
N-B 1.511396
B-Cl 1.712993 and 1.712993

Selected Bond Angles (°)

N-B-Cl 119.168

Selected Bond Torsion Angles (°)

C(2)-N(13)-B(14)-Cl(12) 0.004

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Cartesian Coordinates
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -2.416831   -1.195635   -0.000045
      2          6           0       -1.049612   -1.168252    0.000031
      3          6           0       -1.049612    1.168252    0.000040
      4          6           0       -2.416831    1.195635   -0.000036
      5          6           0       -3.116377    0.000000   -0.000077
      6          1           0       -2.922801   -2.146306   -0.000078
      7          1           0       -0.458856   -2.066858    0.000058
      8          1           0       -0.458856    2.066858    0.000073
      9          1           0       -2.922801    2.146306   -0.000062
     10          1           0       -4.195415    0.000000   -0.000137
     11         17           0        1.977029    1.495771    0.000074
     12         17           0        1.977029   -1.495771    0.000070
     13          7           0       -0.369240    0.000000    0.000080
     14          5           0        1.142155    0.000000    0.000158
 ---------------------------------------------------------------------
NBO Charges:

Atom  No    Charge
 -----------------------------------------------------------------------
     C    1   -0.22562
     C    2    0.14574
     C    3    0.14574
     C    4   -0.22562
     C    5   -0.04072
     H    6    0.26065
     H    7    0.24898
     H    8    0.24898
     H    9    0.26065
     H   10    0.24921
    Cl   11   -0.04392
    Cl   12   -0.04392
     N   13   -0.61625
     B   14    0.63608


HOMO Energy: -14.0533eV
LUMO Energy:  -6.96802eV
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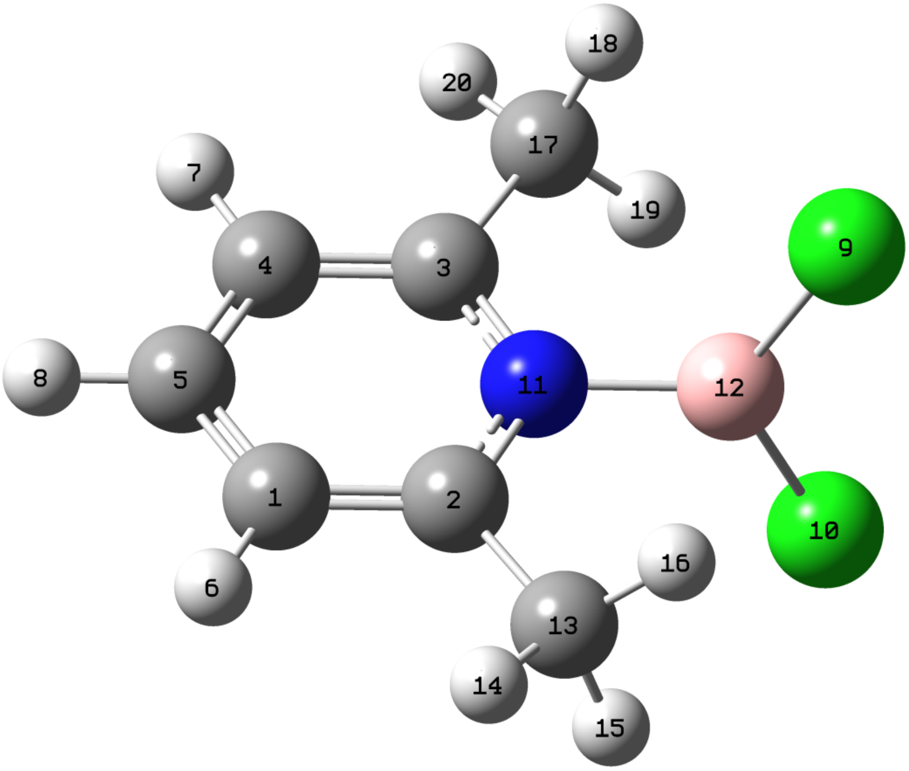
[1]$^+$: [lut-BCl2]+



Selected Bond Length (Å)
N-B 1.513207
B-Cl 1.714288 and 1.714308

Selected Bond Angles (°)

N-B-Cl 118.337 and 118.327

Selected Bond Torsion Angles (°)

C(3)-N(11)-B(12)-Cl(9) 85.383

Cartesian Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.336134	-1.098891	0.485160
2	6	0	-1.015162	-1.184617	0.113194
3	6	0	-1.083070	1.058408	-0.679345
4	6	0	-2.407285	1.150753	-0.320713
5	6	0	-3.037226	0.070710	0.265978
6	1	0	-2.806074	-1.953570	0.941493

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   7       1       0     -2.933679   2.072543  -0.501751
   8       1       0     -4.075006   0.140553   0.552574
   9      17       0      2.219483   0.351588   0.245264
  10      17       0      1.406926  -0.864058  -2.394741
  11       7       0     -0.424613  -0.105178  -0.455663
  12       5       0      1.030751  -0.203377  -0.858237
  13       6       0     -0.212507  -2.423900   0.288254
  14       1       0     -0.719792  -3.102501   0.963768
  15       1       0     -0.083049  -2.933564  -0.665346
  16       1       0      0.773071  -2.218797   0.702051
  17       6       0     -0.335421   2.193486  -1.282127
  18       1       0      0.324645   2.650272  -0.546231
  19       1       0      0.266741   1.881749  -2.133521
  20       1       0     -1.027510   2.952514  -1.627166
 ---------------------------------------------------------------------
NBO Charges:

   Atom  No    Charge
-----------------------------------------------------------------------
      C    1   -0.23439
      C    2    0.32184
      C    3    0.32185
      C    4   -0.23439
      C    5   -0.05541
      H    6    0.25061
      H    7    0.25061
      H    8    0.24442
     Cl    9   -0.03967
     Cl   10   -0.03969
      N   11   -0.65014
      B   12    0.64248
      C   13   -0.64399
      H   14    0.25487
      H   15    0.25643
      H   16    0.24361
      C   17   -0.64395
      H   18    0.25645
      H   19    0.24357
      H   20    0.25487
==================================================================

HOMO Energy: -13.0054eV
LUMO Energy:  -5.83276eV

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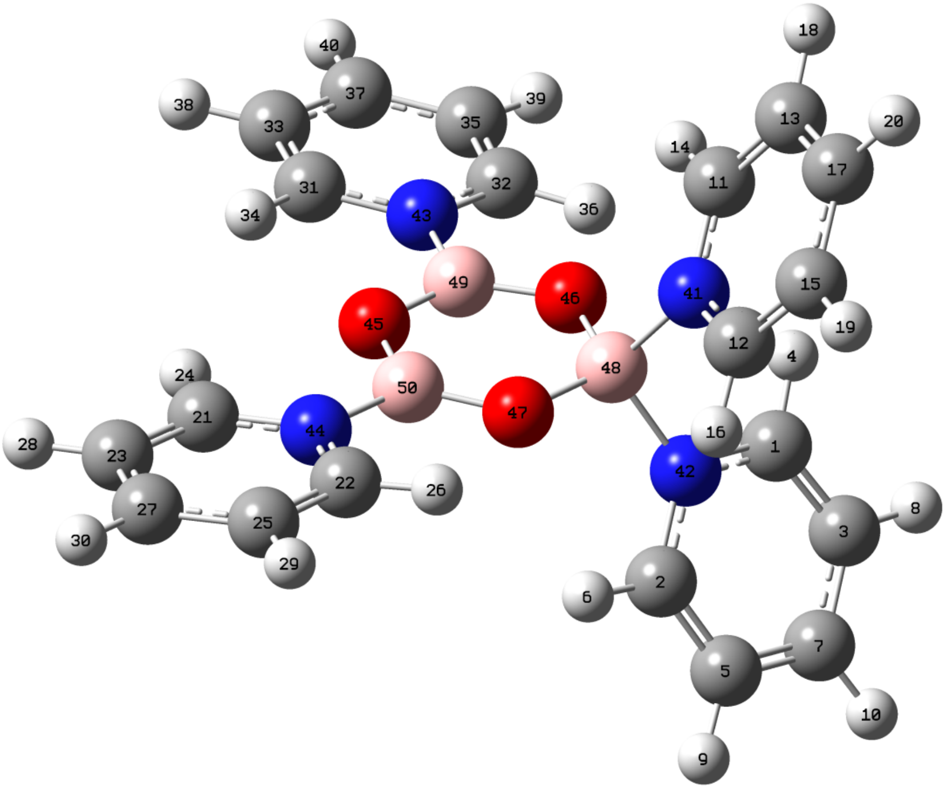
[6]$^{3+}$: [py-BO]$_3$py]$^+$



Selected Bond Length (Å)
N(43)-B(49) 1.49221
N(44)-B(50) 1.49221
N(41)-B(48) 1.57699
N(40)-B(48) 1.57699
B(49)-O(46) 1.32837
B(49)-O(45) 1.36602
B(50)-O(45) 1.36602
B(50)-O(47) 1.32837
B(48)-O(47) 1.44610
B(48)-O(46) 1.44610

Selected Bond Angles (°)
N(43)-B(49)-O(46) 119.754
N(43)-B(49)-O(45) 117.474
N(44)-B(50)-O(45) 117.474
N(44)-B(50)-O(47) 119.754
N(41)-B(48)-N(42) 107.251
N(41)-B(48)-O(46) 109.618
N(41)-B(48)-O(47) 108.900
N(42)-B(48)-O(46) 108.900
N(42)-B(48)-O(47) 109.618
O(45)-B(49)-O(46) 122.771
O(45)-B(50)-O(47) 122.771
O(46)-B(48)-O(47) 112.421

O(45)-B(48)-N(41) 126.374 – trans-annular
O(45)-B(48)-N(42) 126.374

Selected Bond Torsion Angles (°)
C(31)-N(43)-B(49)-O(45) 7.149
C(21)-N(44)-B(50)-O(45) 7.150

Cartesian Coordinates

```
-------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 -------------------------------------------------------------------
      1          6           0        2.769660    1.180992   -1.360234
      2          6           0        1.960593   -0.806718   -2.238359
      3          6           0        3.608419    1.356092   -2.429610
      4          1           0        2.731082    1.891171   -0.550844
      5          6           0        2.777966   -0.691666   -3.336140
      6          1           0        1.293220   -1.640559   -2.111029
      7          6           0        3.616863    0.404452   -3.437982
      8          1           0        4.247694    2.222661   -2.469880
      9          1           0        2.755140   -1.453533   -4.097826
     10          1           0        4.270064    0.516454   -4.289901
     11          6           0        1.960583    0.806722    2.238358
     12          6           0        2.769638   -1.181001    1.360251
     13          6           0        2.777947    0.691669    3.336146
     14          1           0        1.293219    1.640569    2.111018
     15          6           0        3.608388   -1.356102    2.429634
     16          1           0        2.731059   -1.891184    0.550865
     17          6           0        3.616833   -0.404457    3.438000
     18          1           0        2.755122    1.453540    4.097827
     19          1           0        4.247653   -2.222677    2.469914
     20          1           0        4.270026   -0.516460    4.289925
     21          6           0       -3.230228   -2.424876   -0.185236
     22          6           0       -1.227286   -3.621030    0.018508
     23          6           0       -3.953970   -3.585084   -0.205246
     24          1           0       -3.690159   -1.455642   -0.258827
     25          6           0       -1.902849   -4.809447    0.006229
     26          1           0       -0.156928   -3.560843    0.107956
     27          6           0       -3.286206   -4.797221   -0.107605
     28          1           0       -5.026740   -3.541224   -0.296494
     29          1           0       -1.355344   -5.733991    0.086904
     30          1           0       -3.838845   -5.724741   -0.119748
     31          6           0       -3.230227    2.424878    0.185226
     32          6           0       -1.227284    3.621033   -0.018515
     33          6           0       -3.953968    3.585086    0.205244
     34          1           0       -3.690157    1.455644    0.258813
     35          6           0       -1.902847    4.809450   -0.006228
     36          1           0       -0.156926    3.560845   -0.107965
     37          6           0       -3.286204    4.797224    0.107609
     38          1           0       -5.026738    3.541226    0.296495
     39          1           0       -1.355342    5.733995   -0.086899
     40          1           0       -3.838843    5.724743    0.119758
```

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   41         7           0        1.956551   -0.115232    1.264493
   42         7           0        1.956563    0.115231   -1.264488
   43         7           0       -1.882901    2.442093    0.075819
   44         7           0       -1.882902   -2.442091   -0.075832
   45         8           0       -1.820227    0.000000   -0.000010
   46         8           0        0.217069    1.197790    0.098481
   47         8           0        0.217069   -1.197788   -0.098493
   48         5           0        1.021311    0.000000   -0.000002
   49         5           0       -1.110219    1.165681    0.055551
   50         5           0       -1.110220   -1.165678   -0.055573
 ---------------------------------------------------------------------
```

NBO Charges:

```
  Atom  No    Charge
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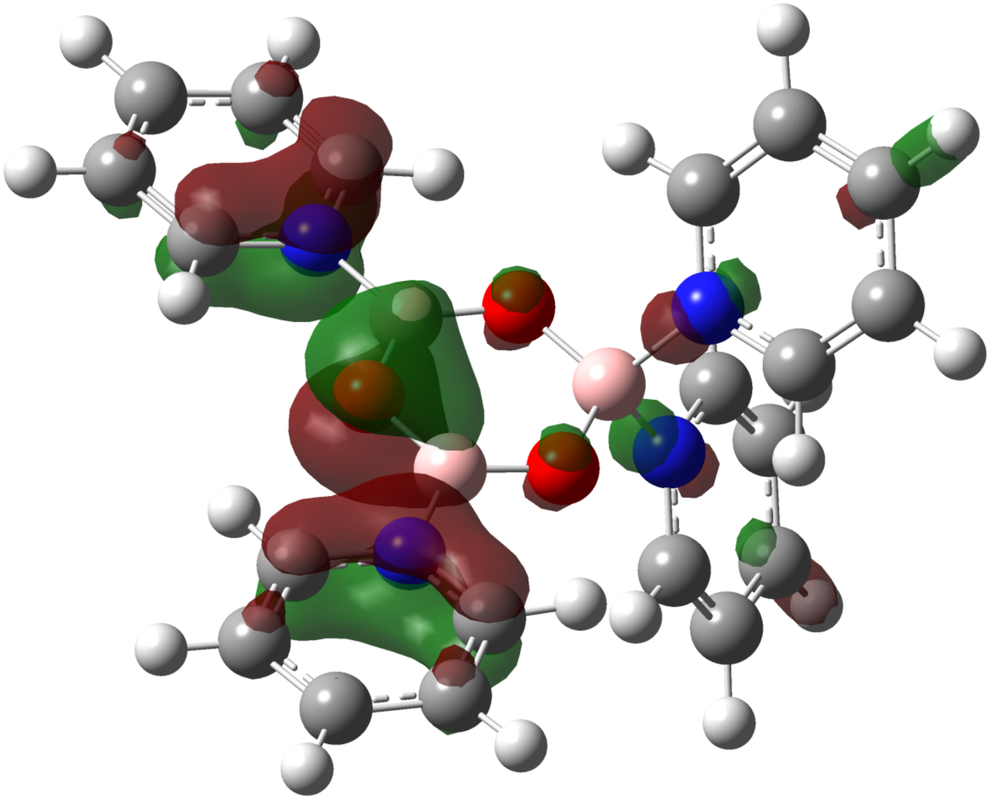
     C    1    0.11267
     C    2    0.11068
     C    3   -0.20983
     H    4    0.22487
     C    5   -0.21349
     H    6    0.22871
     C    7   -0.05704
     H    8    0.26428
     H    9    0.26336
     H   10    0.26000
     C   11    0.11068
     C   12    0.11267
     C   13   -0.21349
     H   14    0.22871
     C   15   -0.20983
     H   16    0.22487
     C   17   -0.05704
     H   18    0.26336
     H   19    0.26428
     H   20    0.26000
     C   21    0.13819
     C   22    0.13470
     C   23   -0.21679
     H   24    0.23708
     C   25   -0.21769
     H   26    0.23801
     C   27   -0.02498
     H   28    0.27029
     H   29    0.26927
     H   30    0.26302
     C   31    0.13819
     C   32    0.13470
     C   33   -0.21679
     H   34    0.23708
     C   35   -0.21769
     H   36    0.23801
     C   37   -0.02498
```

```
    H   38    0.27029
    H   39    0.26927
    H   40    0.26302
    N   41   -0.55542
    N   42   -0.55542
    N   43   -0.58722
    N   44   -0.58722
    O   45   -0.89455
    O   46   -0.90928
    O   47   -0.90928
    B   48    1.22358
    B   49    1.31210
    B   50    1.31210
 ==============================================================
```

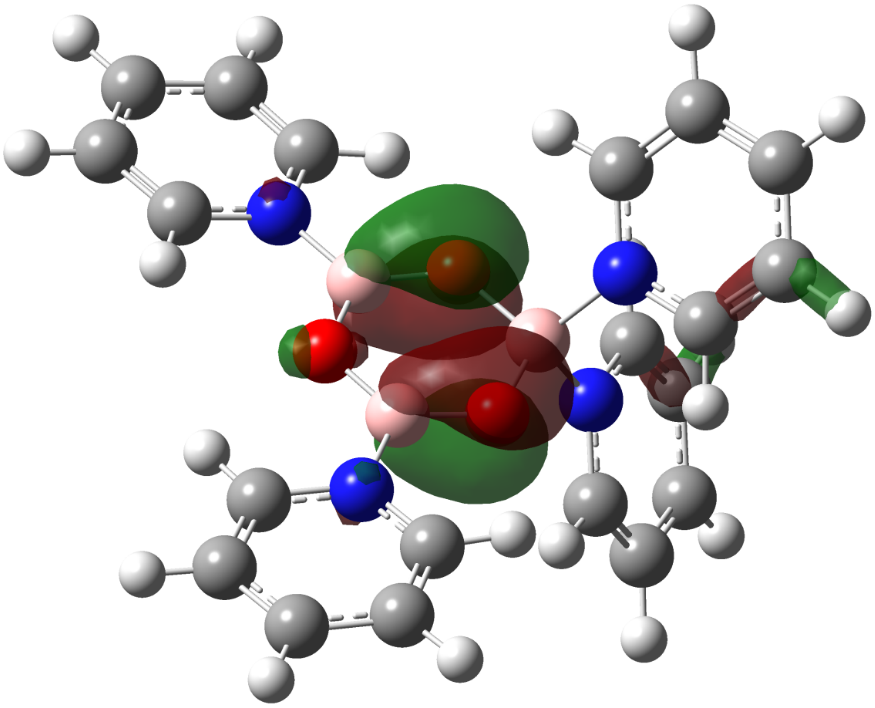
HOMO Energy: -17.4550eV
LUMO Energy: -10.5937eV

Calculated B-O π bonding orbitals of **[6]**$^{3+}$ (at the DFT MPW1K/6-311++G(d,p) level) at the 0.04 iso-surface. N = blue, O = red, C = grey, B =pink.

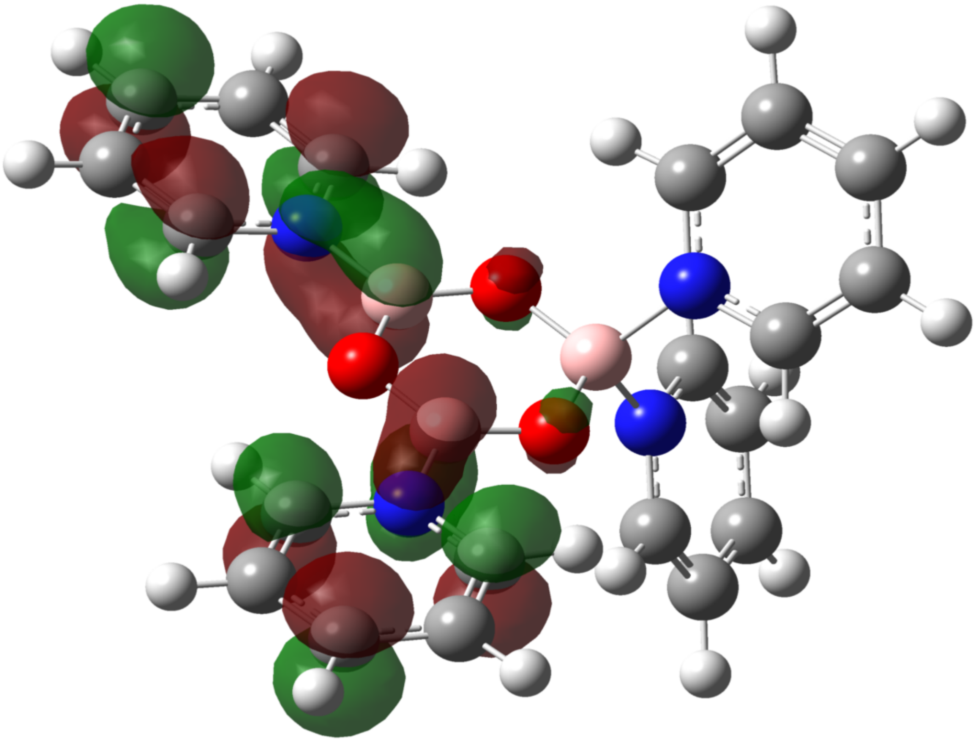
HOMO-21



HOMO-18



LUMO



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