Borenium Cations for the Direct Electrophilic Borylation of Arenes

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Abstract

Borenium Cations for the Direct Electrophilic Borylation of Arenes

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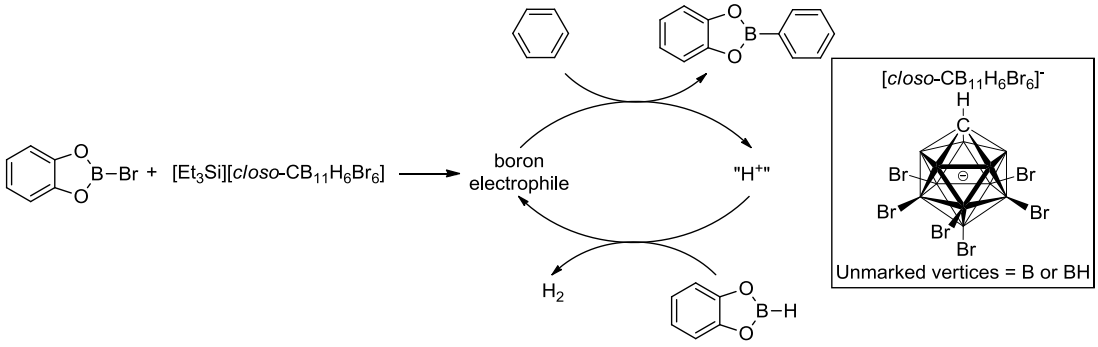
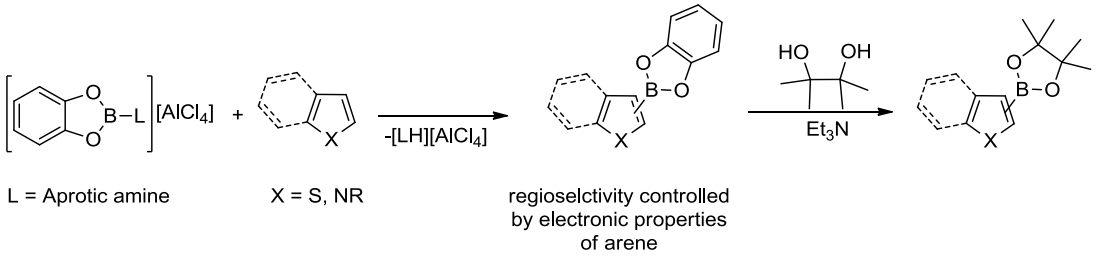
A catalytic (in Brønsted superacid) and a stoichiometric process were developed to synthesise aryl boronic esters with boron cations via electrophilic arene borylation.

The treatment of CatBX (Cat = catecholate; X = Cl, Br) with the triethyl salt $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ in arene solvent gave a transient boron electrophile that reacted as a synthetic equivalent of $[CatB]^+$ in intermolecular electrophilic aromatic borylation at 25 °C. The by-product of the reaction was a strong Brønsted acid that was able to catalyse arene borylation using CatBH at high temperature. This catalytic process furnished aryl boronic esters in high yield with H_2 as the only by-product. The use of the robust and weakly coordinating anion $[closo\text{-}CB_{11}H_6Br_6]^-$ and the electrophile-resistant catecholborane were crucial for the catalytic process.



The reaction mixture of R_2BCl (R_2 = Cat, Cl_4Cat, Cl_2), aprotic amine and $AlCl_3$ mainly gave a borenium salt $[R_2B(amine)][AlCl_4]$ which was in equilibrium with neutral species as revealed by NMR spectroscopy and reactivity studies. This reaction mixture was effective for the regioselective borylation, by electrophilic aromatic substitution, of a range of *N*-heterocycles, thiophenes and anilines at room temperature. The transterification *in situ* provided the synthetically useful and more stable pinacol boronate esters in excellent isolated yield. This process displayed remarkable functional-group tolerance for a boron based strong Lewis acid with weak bases (for example $-NMe_2$), ether, and halogen groups all compatible. This process represents a new and inexpensive one-pot direct arene borylation methodology for producing pinacol boronate esters.



DECLARATION

No portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

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List of abbreviations

9-BBN = 9-borabicyclo[3.3.1]nonane

bpy = 2,2´-bipyridine

Cat = catecholate

COD = 1,5-cyclooctadiene

Cp* = 1,2,3,4,5-pentamethycyclopenta-diene

Cy = cyclohexyl

dba = dibenzylideneacetone

DFT = density functional theory

DMA = *N*,*N*-dimethylaniline

DMAP = *p*-dimethylaminopyridine

DMTol = *N*,*N*-dimethyl-*p*-toluidine

dppf = 1,1'-bis(diphenylphosphino)ferrocene

dppp = 1,3-bis(diphenylphosphino)propane

dTBPy = 2,6-di-*tert*-butylpyridine

dtbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine

FLP = frustrated Lewis pair

Ind = η^5-indenyl

LDA = lithium diisopropylamide

LTMP = lithium 2,2,6,6-tetramethylpiperidide

NBO = natural bond order

Neop = neopentylglycolato

NHC = *N*-heterocyclic carbene

o-dCB = *ortho*-dichlorobenzene

Pin = pinacolate

Py = pyridine

THF = tetrahydrofuran

TIPS = triisopropylsilyl

TMSOTf = trimethylsilyl triflate

WCA = weakly coordinating anion

Chapter 1. Introduction

1.1 Background

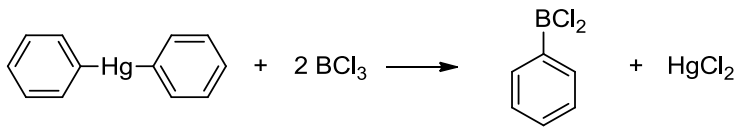
Aromatic and heteroaromatic boron species are useful compounds that are employed in organic synthesis, catalysis, materials science and medicine.[1] The interest in aromatic and heteroaromatic boronic acids and esters arises mainly from their general and efficient use in the Suzuki reaction as coupling agents to form biaryl sub-units.[2] Moreover, the boronic group can be converted efficiently into various functional groups such as alcohol,[3] amine,[4] sulfone,[5] nitro,[6] cyano [7] and halides.[8]

The growing applications of aromatic and heteroaromatic boronic acids and esters in academic research and industry led to improvements of old methods and to the development of new strategies for their preparation in last few decades. The main synthetic approaches are discussed individually below.

1.2 Preparation of aromatic boronic acids and esters

1.2.1 Transmetallation pathway

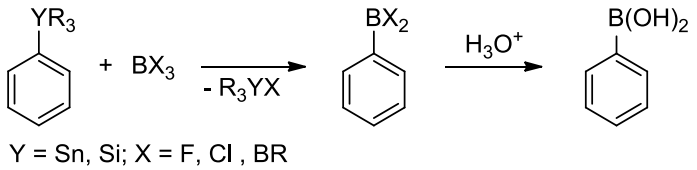
The first report on the synthesis of aryl boronic compounds dates back to 1880.[9] The treatment of diphenyl mercury with BCl_3 furnished phenyl boronic acid after aqueous acidic work-up (Eq. 1). This method remained unpopular due to safety and environmental reasons.



Eq. 1

Similar to diaryl mercury compounds, aryl silanes and stannanes underwent transmetallation with boron trihalide to give the corresponding aryl boronic acid

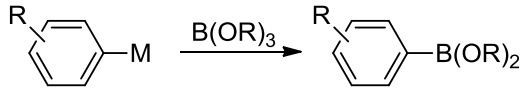
after an aqueous acidic work-up (Eq. 2).[10] The driving force for this reaction is the higher stability of the Si(Sn)-X (X = halogen) and/or B-C bonds of the products compared to the respective Si(Sn)-C and B-X bonds of the starting materials.



Y = Sn, Si; X = F, Cl , Br

Eq. 2

One of the cheapest and most common ways to synthesise aryl- and heteroaryl boronic compounds is the reaction of an aryl magnesium or lithium compound with a borate ester at low temperature (Eq. 3). The original procedure of addition of trimethyl borate to a phenylmagnesium compound at – 15 °C led after aqueous work-up to isolation of phenyl boronic acid in low yield, due to the formation of diphenyl borinic acid. The unwanted formation of the diphenyl borane species can be limited using a reverse order of addition[11] and sterically hindered boronates such as triisopropyl borate[12] and isopropyl pinacol borate (2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane).[13]

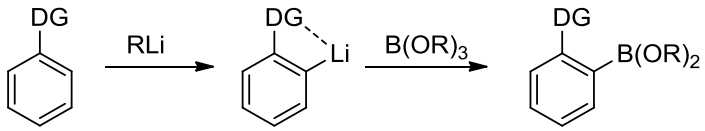


M = Li, MgX

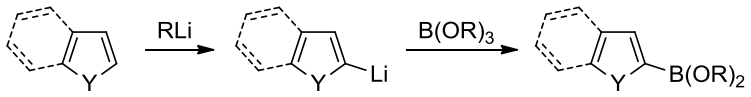
Eq. 3

Generally, aryl and heteroaryl magnesium or lithium compounds were prepared by metal-halogen exchange from the aryl halide and a Grignard or organolithium reagent. However, the direct metalation of arenes bearing *ortho*-directing groups such as amines,[14] ethers,[15] esters, and amides[16] was feasible (Eq. 4). The *ortho*-lithiation with esters as directing group was problematic due to the side reaction of the highly reactive organolithium intermediate with the benzoate substrate to give benzophenone. However, benzoate compounds can be efficiently borylated by

generation of the lithio benzoate intermediate with lithium diisopropylamide (LDA) or lithium 2,2,6,6-tetramethylpiperidide (LTMP) while the borate $B(O^iPr)_3$ was present *in situ*.[17,18] Moreover, the use of LTMP, allowed the *ortho*-borylation of benzonitrile, fluoro- and chlorobenzene.[18] The direct metalation was also applicable to certain heteroaryls such as pyrrole, furan, thiophene and their benzofused analogues. The metalation proceeds α to the heteroatom due to the increased acidity of protons in the α position (Eq. 5).[19]



Eq. 4



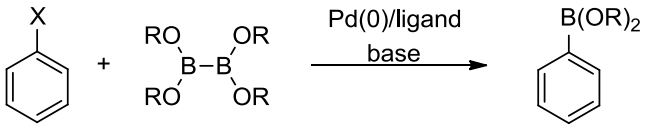
Eq. 5

Y = O, S, NR

The metalation methodology required low temperature, rigorous anhydrous conditions and was restricted to aryl compound having functional groups compatible with hard organometallic compounds. Therefore, new processes that used milder reaction conditions and were suitable to a larger number of substrates and functionalities were developed.

1.2.2 Metal catalysed pathway

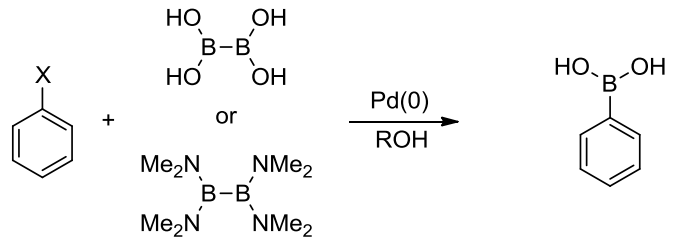
An efficient route to prepare aryl and heteroaryl boronate esters with good functional group compatibility was the cross-coupling reaction of diborons or dialkoxyboranes with aryl halides or triflates in presence of a base and a palladium catalyst (Eq. 6). In 1995, Miyaura and co-workers reported that catalytic quantities of $PdCl_2$(dppf) (dppf = 1,1'-bis(diphenylphosphino)ferrocene) in presence of KOAc promoted the cross-coupling reaction between bis(pinacolato)diboron (PinB-BPin) and aryl-iodides and bromides at 80 °C.[20]



Eq. 6

$PdCl_2$(dppf) was a valuable pre-catalyst for the cross-coupling borylation of aryl-iodides, bromides and triflates, however it was ineffective with less reactive aryl-chlorides.[20, 21] Improvements in substrate scope and in time of reaction were initially achieved using $Pd(dba)_2$ (dba = dibenzylideneacetone) with PCy_3 (Cy = cyclohexyl)[22] or $Pd(OAc)_2$ with the *N,N'*-bis(2,6-isopropylphenyl)-imidazolium chloride[23] which were also able to catalyse the borylation of cheaper and more commercially available aryl-chlorides at high temperature (80 - 110 °C). A further improvement was achieved by Buchwald and co-workers using $Pd(OAc)_2$ as pre-catalyst and the bulky 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl as ligand. This combination was effective to catalyse the borylation of aryl chlorides with PinB-BPin at room temperature.[24]

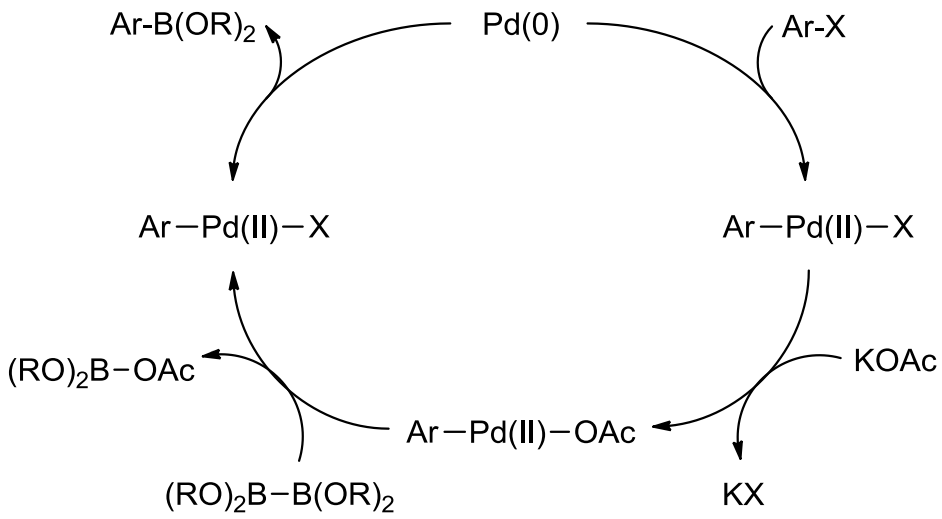
1,3-Diphenyl-1,3-propanediol and neopentylglycol boronic esters undergo hydrolysis to boronic acid more readily than related pinacol esters, therefore it is preferable to use bis(1,3-diphenyl-1,3-propanediolate)diboron and bis(neopentylglycolato)diboron (NeopB-BNeop) as boron source when the aryl boronic acid is the target.[25,26] Recently, Molander and co-workers reported the synthesis of aryl boronic acids in one step using as diboron source the bis-boronic acid[27] or tetrakis(dimethylamino)diboron[28] (synthetic precursors of tetralkoxy-diboron).[29]



Eq. 7

X = I, Br, Cl, OTf

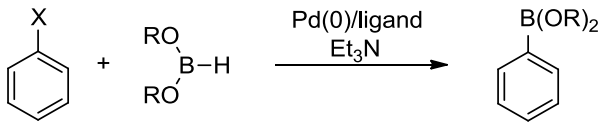
The use of a base in the cross-coupling reaction with diborons and arylhalides or triflates was crucial and KOAc was a suitable base since stronger bases such as K_3PO_4 and K_2CO_3 promoted the Suzuki coupling between the produced arylboronic ester and the starting arylhalide. It was postulated that the role of the base KOAc was to displace X (X = halide) from Ar-Pd-X to yield the Ar-Pd-OAc species which subsequently gave transmetallation with diborons (Scheme 1.1).[20]



Scheme 1.1 Proposed catalytic cycle for the borylation of aryl halides with tetralkoxydiborons.

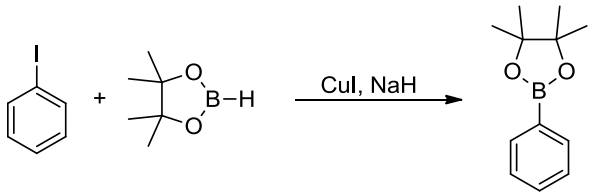
Diborons were excellent reagents in the cross-coupling reaction with aryl halides and triflates, however their use in the large scale synthesis was limited due to their price. In order to address this issue, the cross-coupling reaction of aryl halides with the more cost-effective dialkoxyboranes such as pinacolborane (PinBH),[30]

catecholborane (CatBH)[31] and 4,4,6-trimethyl-1,3,2-dioxaborinane[32] was developed.

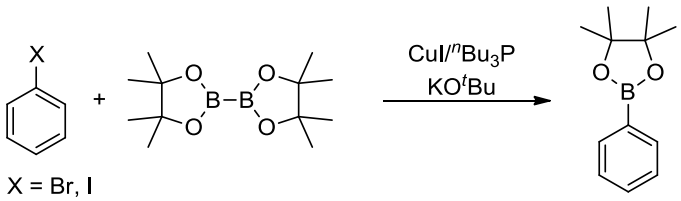


Eq. 8

Copper and nickel catalysts for the cross-coupling borylation of aryl halides and boranes have been recently developed as cheaper alternatives to the palladium catalysts. In 2006, Zhu and Ma reported the borylation of aryl iodides with PinBH in presence of the strong base NaH using CuI as catalyst (Eq. 9).[33] Subsequently, Marder and co-workers reported the copper catalysed coupling of aryl iodides and bromides with PinB-BPin or NeopB-BNeop using CuI and $^{n}Bu_3P$ in presence of the base KO^{t}Bu (Eq. 10).[34]



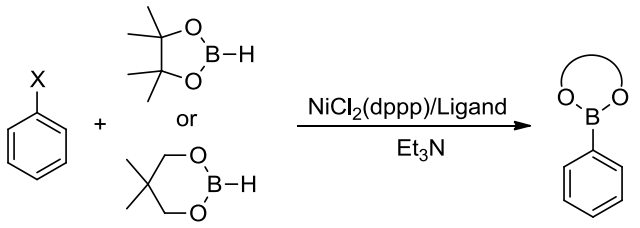
Eq. 9



Eq. 10

The copper catalysed cross-coupling borylation was limited to aryl bromides and iodides. Instead, the nickel catalysed cross-coupling borylation was effective also with aryl chlorides, mesylates and tosylates. Tour and co-workers reported the first nickel catalysed cross-coupling borylation using $NiCl_2$(dppp) (dppp = 1,3-bis(diphenylphosphino)propane) to borylate 1,4-dibromobenzene and 1,3,5-tribromobenzene with PinBH.[35] Subsequently, this process was developed by Percec and co-workers. Initially, they demonstrated that the use of $NiCl_2$(dppp) with a second equivalent of dppp as co-ligand was more effective than $NiCl_2$(dppp) alone to efficiently catalyse the cross-coupling borylation of aryl bromides and iodides with

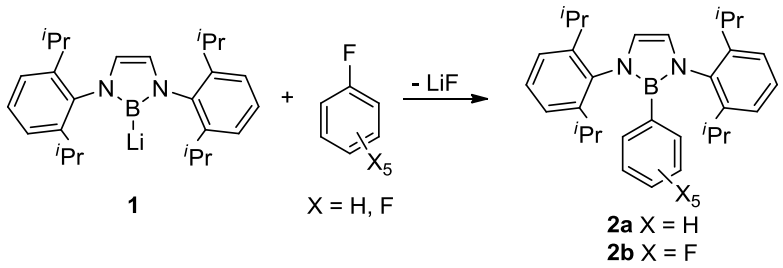
PinBH or NeopBH (Eq. 11).[36] Later, they extended this process to aryl chlorides, mesylates and tosylates using dppf as co-ligand.[37,38] Aryl mesylates and tosylates were borylated with low yield. However, the use of Zn as additive improved the yield and drastically reduced the time of reaction.[38]



Eq. 11

X = Cl, Br, I, TsO, MsO; Ligand = dppp, dppf

Nozaki and co-workers reported the preparation of aryl boronic compounds by reaction of the boryl lithium **1** with fluoroarenes (Eq. 12).[39] The reaction with fluorobenzene furnished phenylborane **2a** in low yield, while the reaction with hexafluorobenzene gave the pentafluorophenylborane **2b** in moderate yield. The improved yield with hexafluorobenzene was due to greater reactivity of this substrate toward the nucleophilic aromatic substitution than fluorobenzene.

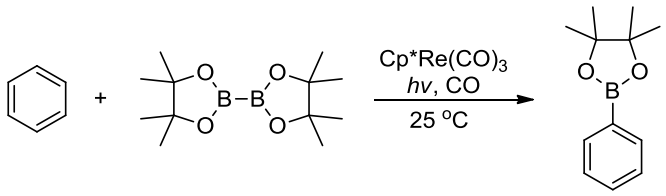


1 X = H, F **2a** X = H **2b** X = F

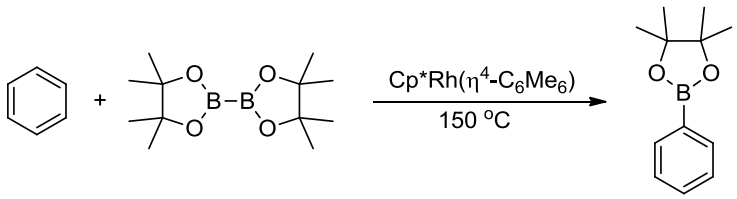
Eq. 12

An important advance in terms of atom-economy was the iridium or rhodium catalyzed borylation of arene C-H bonds. The first catalysed direct C-H borylation of arenes was the photochemical Cp*Re(CO)$_3$ (Cp* = 1,2,3,4,5-pentamethycyclopenta-diene) catalyzed borylation of benzene with PinB-BPin reported by Hartwig and Chen in 1999 (Eq. 13).[40] Later, Hartwig and co-workers reported the borylation of benzene with PinB-BPin catalysed by the rhodium complex Cp*Rh(η^4-C_6Me_6) at

high temperature (150 °C) (Eq. 14).[41]



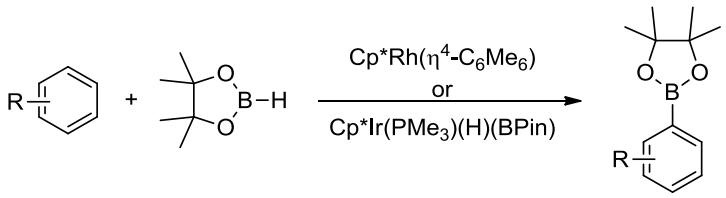
Eq. 13



Eq.14

Subsequently, Smith and co-worker reported the use of Hartwig's catalyst Cp*Rh(η^4-C_6Me_6) and the iridium catalyst Cp*Ir(PMe_3)(H)(Bpin) for the borylation of a range of arenes with PinBH (Eq. 15).[42] The rhodium catalyst provided higher turnover numbers than the iridium catalyst, but it was less selective toward alkyl and trihalomethyl substituted arenes because the rhodium catalyst also reacted at benzylic C-H and aliphatic C-halogen bonds.

Improvement in the iridium catalysed borylation was achieved using the more active pre-catalysts (Ind)Ir(COD) (Ind = η^5-indenyl, COD = 1,5-cyclooctadiene)[43] and $[Ir(OMe)(COD)]_2$[44] in the presence of a bipyridyl ligand such as 2,2'-bipyridine (bpy) and 4,4'-ditertbutyl-2,2'-bipyridine (dtbpy).

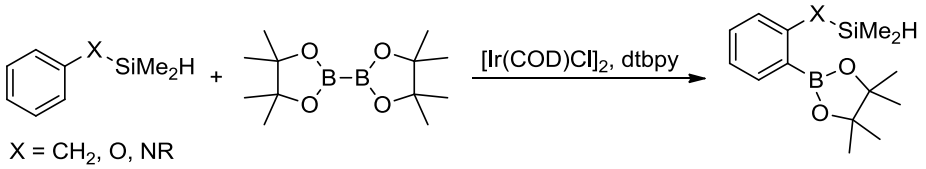


Eq. 15

The iridium and rhodium catalysed borylation of arenes with diborons or tetralkoxyborane generally proceeded regioselectively giving products determined by steric factors.[45] Monosubstituted benzenes gave an approximately statistical mixture of products deriving from *meta*- and *para*-borylation, while the 1,2- and 1,3-

disubstitued benzene gave 3,4- and 3,5-disubstitued phenyl boronic ester, respectively, as the only isomer. The five-membered heterocycles furan, pyrrole, thiophene and their benzo-fused derivatives were selectively borylated at the α-carbon.

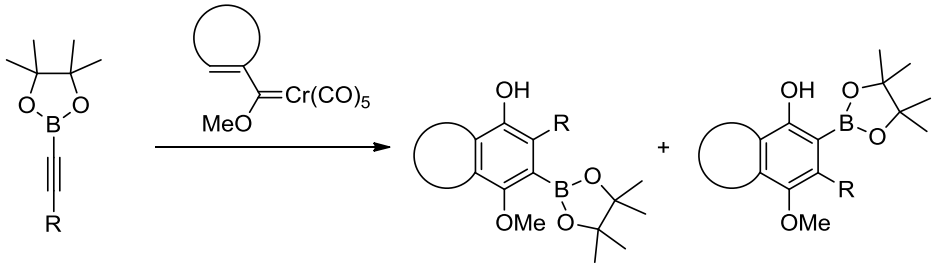
Recent advances in the iridium catalysed arene borylation led to development of o*rtho*-directed arene borylation. Arenes bearing an hydrosilyl substituent on the atom attached to the aromatic ring underwent borylation at the *ortho* position using the combination of $[Ir(COD)Cl]_2$ as catalyst and dtbpy as ligand (Eq. 16).[46] Instead, the *ortho*-borylation of benzoate esters was accomplished using the combination of $[Ir(OMe)(COD)]_2$ as catalyst and tris(3,5-bis(trifluoromethyl)phenyl)phosphine[47] or a silica-supported phosphine as ligand.[48]



Eq. 16

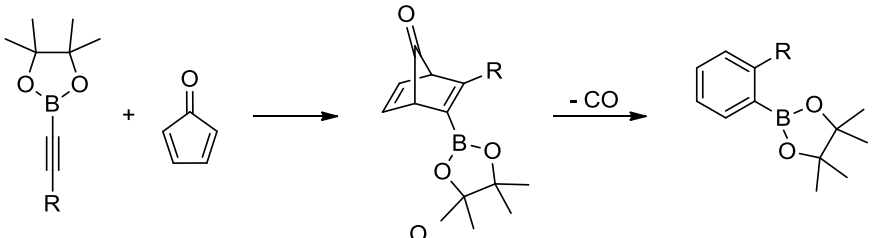
1.2.3 Cycloaddition pathway

A different approach to synthesise aromatic and heteroaromatic boronic compounds is the cycloaddition method developed by Harrity and co-workers. Initially, the Harrity group reported the synthesis of hydroquinone boronic ester derivatives by Dötz cycloaddition of Fisher chromium carbene complexes with alkynylboronic esters (Eq. 17).[49] Subsequently, they developed metal catalysed and metal free cycloaddition processes for the synthesis of aromatic and heteroaromatic boronic compounds.

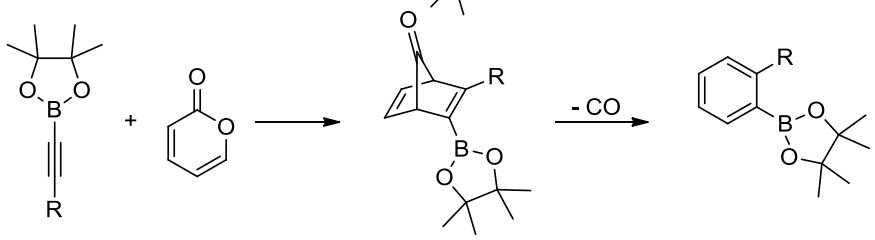


Eq. 17

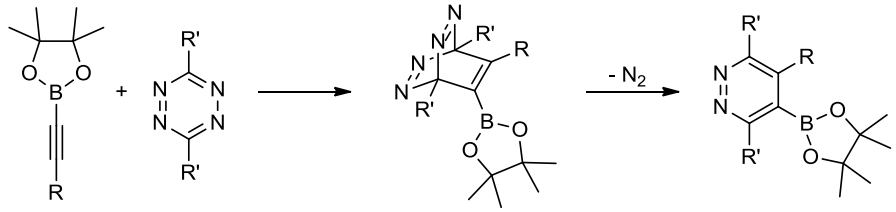
The reaction of alkynylboronates with dienes such as cyclopentadienones,[50] 2-pyrones[51] and 1,2,4,5-tetrazine[52] at high temperature (>140 °C) by a [4+2] cycloaddition gave six-membered aromatic boronic esters (Eq. 18-20). Instead, the reaction of alkynylboronates with nitrile oxides,[53] sydnones[54] and azides[55] at high temperature (>110 °C) by a [3+2] cycloaddition yielded isoxazole, pyrazole and triazole boronic esters respectively (Eq. 21-23).



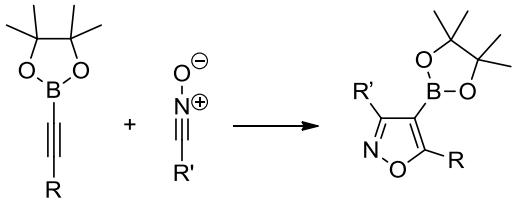
Eq. 18



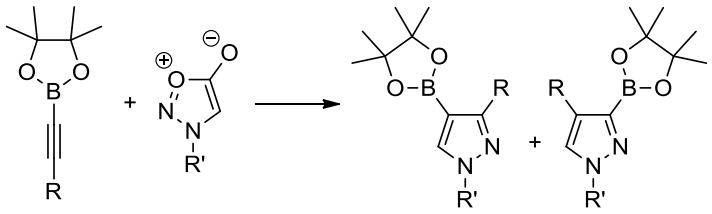
Eq. 19



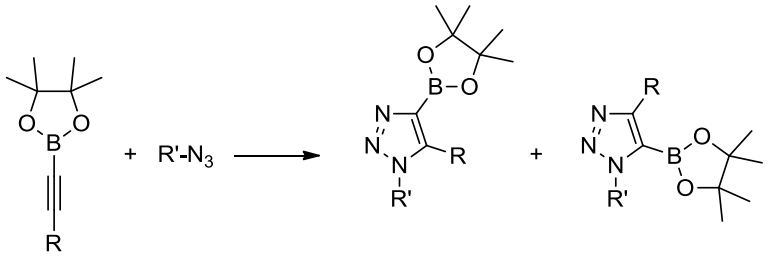
Eq. 20



Eq. 21

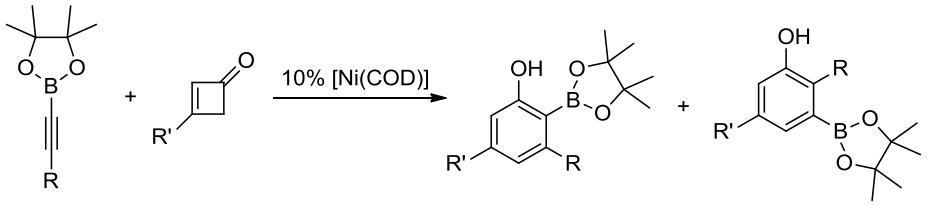


Eq. 22



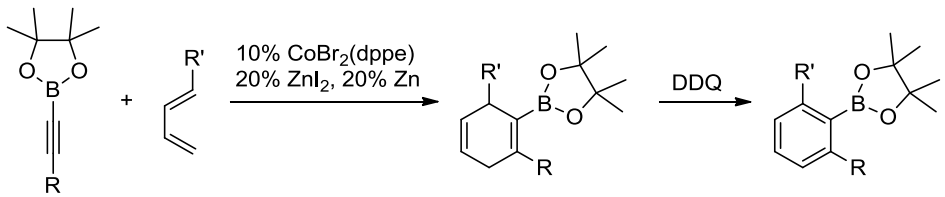
Eq. 23

Aryl boronic esters were also prepared at room temperature by nickel-catalysed benzannulation reaction of alkynylboronates with cyclobutenones (Eq. 24)[56] or by the cobalt-catalysed [4+2] cycloaddition of alkynylboronates with dienes via cycloaddition-elimination (Eq. 25) and cycloaddition-oxidation (Eq. 26) approaches.[57]



Eq. 24

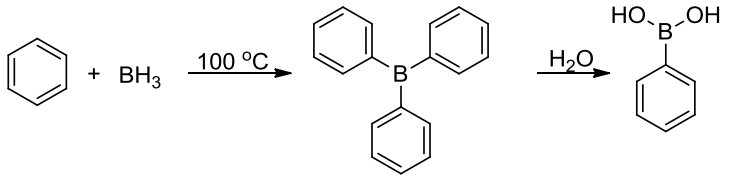
Eq. 25



Eq.26

1.2.4 Electrophilic aromatic substitution pathway

A method for the direct borylation of arene C-H bonds avoiding the use of expensive transition metals and providing complementary selectivity (electronic instead of steric) is the reaction of electrophilic boron compounds with arenes. In an early report, diborane reacted with benzene at 100 °C to form presumably triphenylborane which after aqueous work-up gave the phenylboronic acid (Eq. 27).[58]

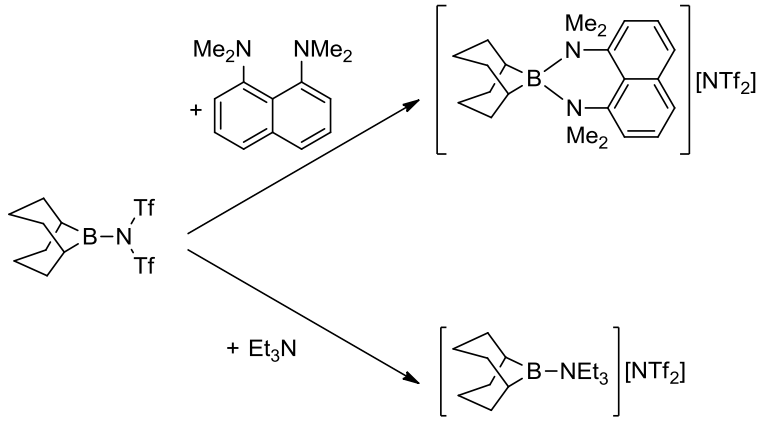


Eq. 27

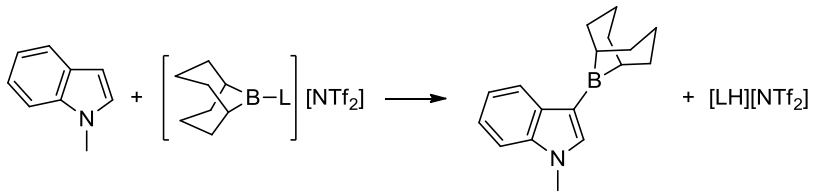
The boron trihalides were also reported to react with arenes giving aryl dihaloboranes ($ArBX_2$). BI_3 reacted with benzene at high temperature (119 °C) giving in low yield $C_6H_5BI_2$.[59] Instead, BCl_3 and BBr_3 borylated arenes at lower temperature and with good yield in the presence of AlX_3 (X = Cl, Br) or Al with catalytic quantities of AlX_3.[60] The success of arene borylation with BX_3 and AlX_3 relied on the removal of the HX by-product (either as gaseous HX in an open system or as H_2 by reaction of HX with Al) from the reaction media to prevent the reverse reaction of protodeboronation. This arene borylation possibly involved the formation of a highly electrophilic species deriving from the interaction of AlX_3 with BX_3. Muetterties proposed that BCl_3 with $AlCl_3$ in arene solvent forms the tricoordinate boron cation (borenium cation) $[(ArH)BCl_2]^+$,[60,61] while Olah proposed the coordination of the Lewis acid $AlCl_3$ to a chlorine atom of BCl_3 to form the chloride bridged species Cl_2B-(μ-Cl)-$AlCl_3$.[62] Although this system was effective to borylate arenes it had numerous drawbacks, including extensive isomerisation, functional group incompatibility and heterocycle decomposition, all attributable to the superacidic environment.

Recently, Vedejs and co-workers reported the intermolecular borylation of electron-rich arenes using the triflimide derivative of 9-borabicyclo[3.3.1]nonane (9-BBN-NTf_2) or a boron cation derived from it.[63] Treatment of 9-BBN-NTf_2 with Et_3N or 1,8-bis(dimethylamino)naphthalene gave a tricoordinate (borenium) or tetracoordinate (boronium) boron cation by displacement of the poor coordinating anion triflimide (Scheme 1.2). These boron cations were able to borylate electron

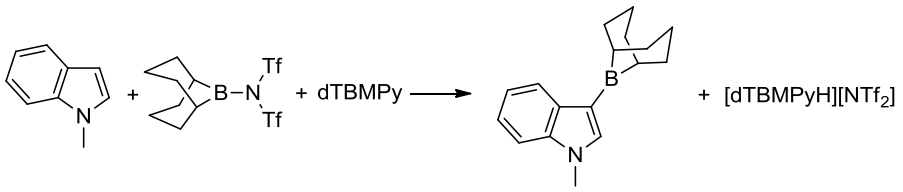
rich heteroarenes such as *N*-methyl pyrrole and indole (Eq. 28). Likewise, the combination of 9-BBN-NTf_2 with the bulky base 2,6-ditertbutyl-4-methylpyridine (dTBMPy) (to trap the protic by-product) borylated *N*-methylindole (Eq. 29).



Scheme 1.2 Reaction between 9-BBN-NTf_2 and 1,8-bis(dimethylamino)-naphthalene or Et_3N.

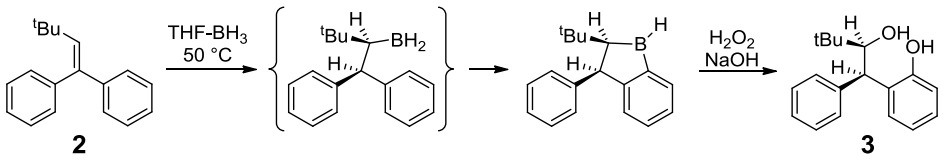


Eq. 28



Eq. 29

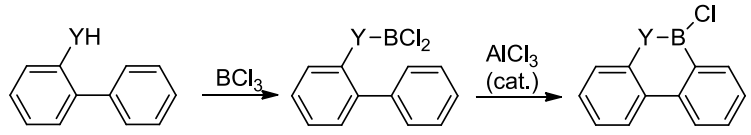
Other reported examples, of direct arene C-H borylation by boron species, are invariably intramolecular processes. For example, styrene derivative **2** gives arene borylation at 50 °C via the hydroboration product (Eq. 30).[64] The intramolecular arene borylation after the initial hydroboration occurred only for substrates having a bulky group on the carbon *ipso* to the boron. The bulky group allowed the arene borylation since forced the hydroboration product to place the boron atom close to the aromatic ring favouring the borylation of the aromatic ring.



2 **3**

Eq. 30

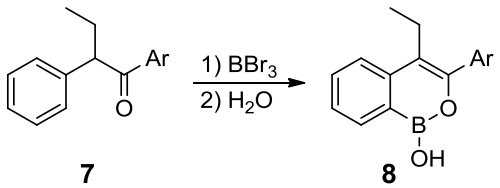
2-Amino-[65], 2-hydroxy-[66] and 2-mercaptobiphenyl[67] reacted with BCl_3 forming the dichloroborane intermediates **5** which underwent intramolecular borylation after exposure to catalytic aluminium chloride (Eq.31). The temperatures of reactions varied from 175 °C for the amino derivative to room temperature for the sulfur derivative, presumably due to increase boron electrophilicity controlled by heteroatom π donation (π donation: N > O > S).



4 **5** **6**

Eq. 31

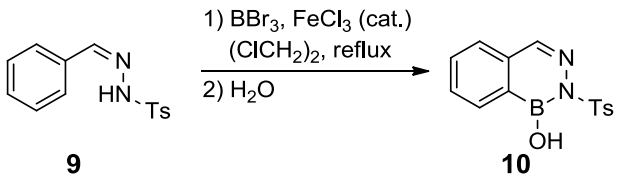
The benzylic ketone **7** also underwent arene borylation with excess of BBr_3 at room temperature.[68] The benzylic ketone **7** possibly formed a boron enolate and then the boron enolate underwent intramolecular borylation (Eq. 32).



7 **8**

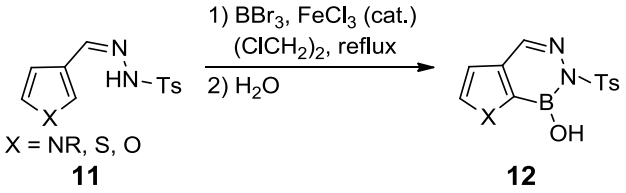
Eq. 32

Aryl tosylhydrazones **9** with excess of BBr_3 with or without catalytic quantities of $FeCl_3$ at moderate temperature (60-80 °C) gave the cyclic boron compound **10** after aqueous work-up (Eq. 33).[69] Likewise, the related tosylhydrazone of *N*-alkylated pyrrole, thiophene and furan underwent aromatic borylation (Eq. 34).[51]



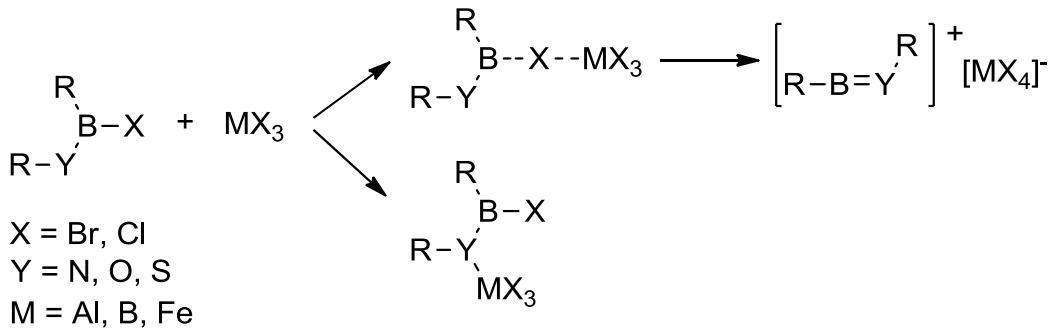
9 **10**

Eq. 33



Eq. 34

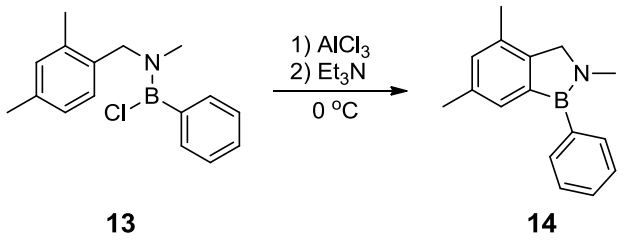
These direct borylations possibly proceed by the attack of a Lewis acid (the same boron halides, BX_3, are viable good Lewis acids) either on the heteroatom or on the halide directly bonded to boron (analogous to Friedel-Crafts reactions) (Scheme 1.3). Both lead to an increase of positive charge at the boron, enhancing electrophilicity and reactivity towards the aromatic ring. The formation of this species is never detected, possibly because it is highly reactive and rapidly forms the borylated arene product.



Scheme 1.3 Possible electrophilic species involved in the intramolecular borylation with haloboranes.

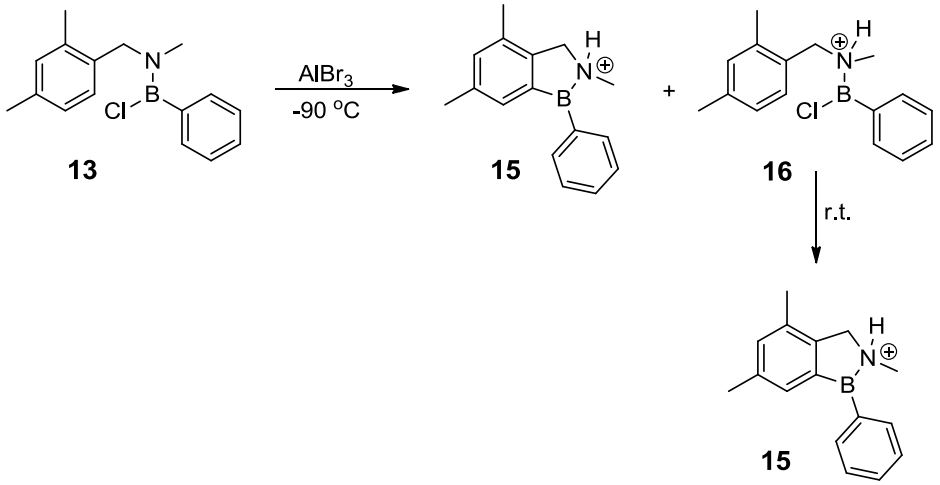
A different active boron species was observed by Shubin and co-workers in the synthesis of the cyclic boronic acid **14**. The reaction of **13** with unpurified $AlCl_3$ at 0 °C after treatment with Et_3N yielded the borylated product **14** (Eq. 35).[70] Low temperature NMR studies (-90 °C) of the reaction with the more soluble Lewis acid $AlBr_3$ revealed the formation of the protonated borylated product **15** along with the protonated starting material (borenium cation) **16** (Scheme 1.4). The latter rapidly converted into the protonated borylated product at room temperature suggesting that

the borenium cation **16** was an active electrophilic boron species. The protonation of **13** was attributed to protic contaminants present in the unpurified $AlBr_3$ used in the experiment.



13 **14**

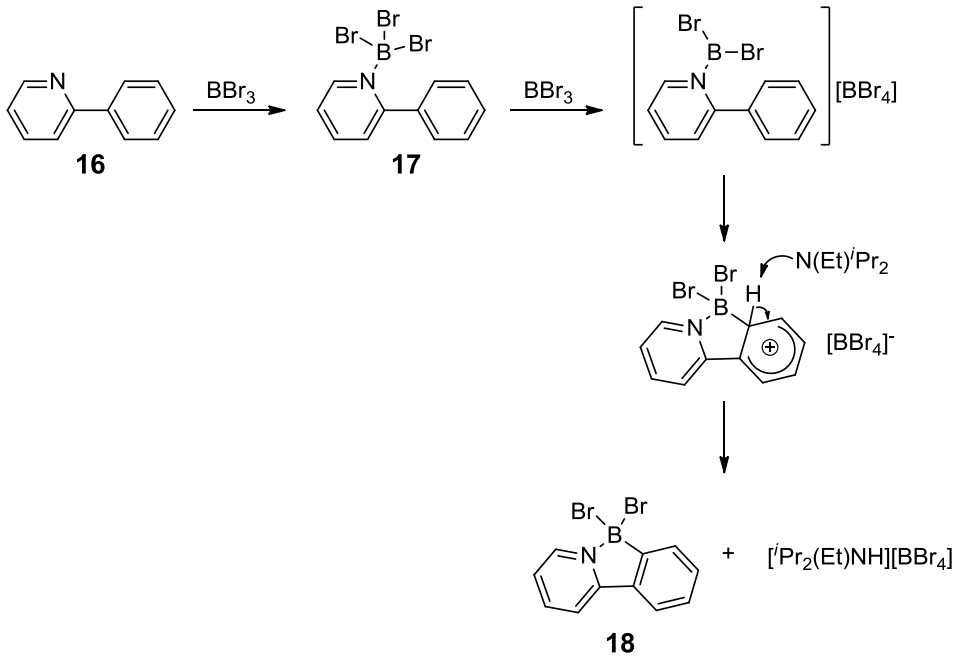
Eq. 35



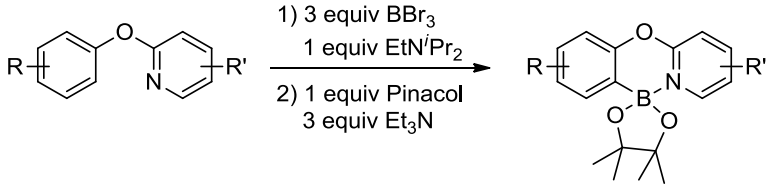
13 **15** **16** **15**

Scheme 1.4 Reaction between **13** and $AlBr_3$ at -90 °C.

The involvement of a borenium cation was also more recently postulated by Murakami and co-workers in the arene borylation of 2-phenylpyridines with 3 equivalents of BBr_3 in presence of an equivalent of $^{i}Pr_2NEt$.[71] The proposed mechanism of reaction proceeds by the initial coordination of the nitrogen atom of pyridine to BBr_3 to give the adduct **17**. Then a second molecule of BBr_3 abstracts a bromide from the adduct yielding a borenium cation which electrophilically attacks the aromatic ring. Subsequent loss of the proton from the arenium cation gives the pyridine-dibromoborane adduct **18** (scheme 1.5). A similar mechanism of reaction was possibly involved in the borylation of 2-phenoxypyridines with excess of BBr_3 in presence of $^{i}Pr_2NEt$ reported by Fu and co-workers (Eq. 36).[72]

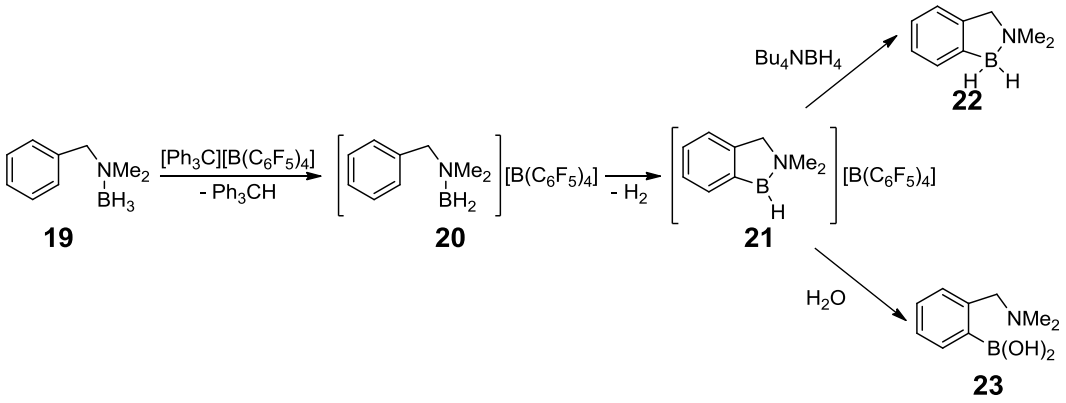


Scheme 1.5 Proposed mechanism of borylation of 2-phenylpyridine with BBr_3



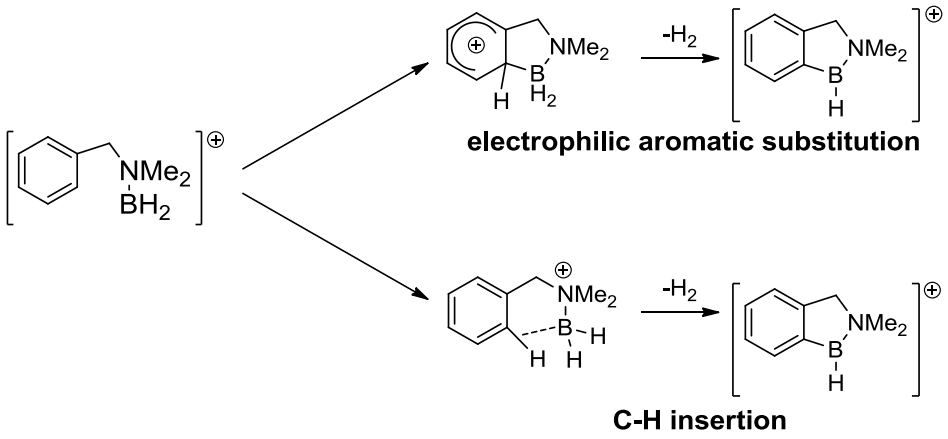
Eq. 36

Recently, Vedejs and co-workers reported the intramolecular borylation of benzyl amine borane derivatives by a transient boron cation at 20 °C.[73] Abstraction of hydride by trityl salt $[Ph_3C][B(C_6F_5)_4]$ from the benzyl amine-borane adduct **19** led to formation of the borocation **20**, which rapidly gave intramolecular borylation to the arene ring at room temperature (Scheme 1.6). Subsequent treatment with Bu_4NBH_4 or H_2O yielded the borane compound **22** or the arylboronic acid **23**, respectively.



Scheme 1.6 Intramolecular borylation of benzyl amine derivatives by a borenium cation.

It was noteworthy that *ortho*-deuterated benzylamine borane proceeded with a deuterium isotope effect of $K_H/K_D = 2.8$. This kinetic isotopic effect revealed that the C-H(D) bond cleavage was involved in the rate determining step. A possible explanation was that the rate limiting step was the slow proton abstraction from the Wheland intermediate because no good base was present in solution ($[B(C_6F_5)_4]^-$ is a very weak base).[74] However, computational calculations revealed that a C-H insertion process involving the three-center two-electron bonded intermediate was a viable alternative (Scheme 1.7).

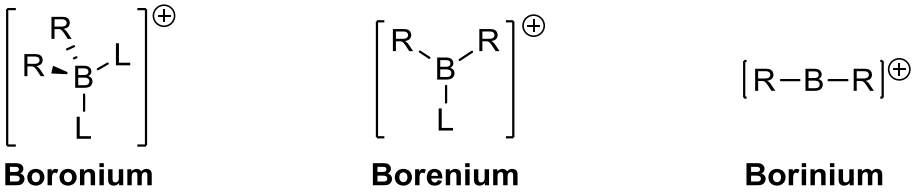


Scheme 1.7 Proposed mechanisms of intramolecular borylation of benzylamine-borane by borenium cation.

Boron cations with the enhanced electrophilicity at the boron centre are potentially useful species for the direct arene borylation. Hitherto, their use in such reaction is limited to arenes bearing a directing group that pre-coordinates boron. However, the synthesis of very reactive borenium cations is expected to expand the substrate scope towards intermolecular electrophilic borylation.

1.3 Boron monocations

Boron monocations can be classified into three distinct structural classes based on the coordination number at boron.[75] Dicoordinate, tricoordinate and tetracoordinate boron cations were named borinium, borenium and boronium cations, respectively, according to Nöth's terminology.

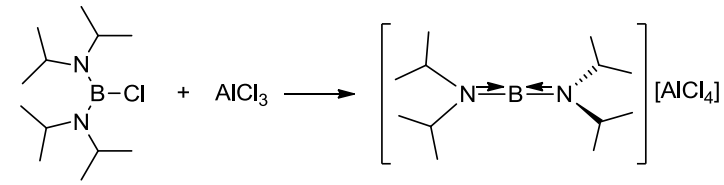


1.3.1 Borinium and boronium cations

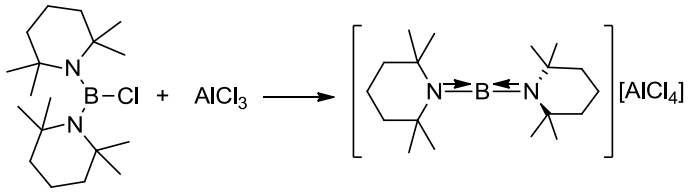
The generation of the less stabilised borinium cations in the condensed phase required bulky and good π-donating substituents to shield the boron centre from solvent and anion and relieve the electrophilicity on boron by π-donation.

Attempts to prepare the borinium cation from $(Me_2N)_2BCl$ by halide abstraction with $AlCl_3$ were unsuccessful, reportedly due to formation of the dimeric or trimeric cationic species $[(Me_2N)_2B]_2^{2+}$ and $[(Me_2N)_2B]_3^{3+}$ (Figure 1.1).[76] In contrast, haloboranes with bulky amino groups such as diisopropylamino and 2,2,6,6-tetramethylpiperidino reacted with halophilic Lewis acids such as BX_3, AlX_3 and GaX_3 (X = Cl, Br, I) to furnish the related borinium cations (Eq. 37, 38).[76, 77]

Figure 1.1 Proposed dimeric and trimeric cationic species formed from the reaction of $(Me_2N)_2BCl$ with $AlCl_3$.

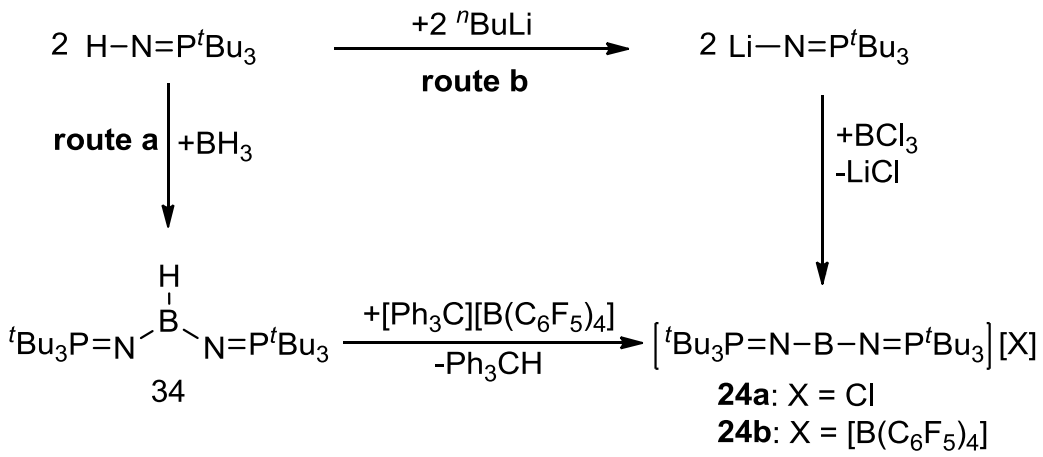


Eq. 37



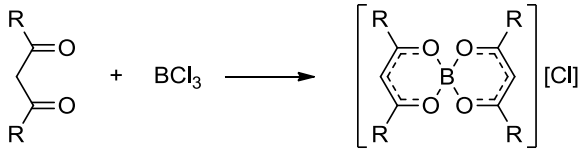
Eq. 38

A recent report by Stephan and co-workers reported the preparation of the borinium cation **22** which had an extended π-system.[78] This cation was prepared by two different pathways: (i) by the reaction of tri-*tert*-butylphosphinimide with $BH_3{\cdot}SMe_2$ followed by hydride abstraction with the trityl cation $[Ph_3C][B(C_6F_5)_4]$ (Scheme 1.8, route a), and (ii) by the reaction of the lithium salt of tri-*tert*-butylphosphinimide with BCl_3 (Scheme 1.8, route b). The use of the bulky phosphinimide prevented the formation of polymeric cationic species (for example $[(R_3P{=}N)_2B]_2^{2+}$ and $[(^tBu_3P{=}N)_2B]_3^{3+}$)[79] and the formation of the neutral trivalent borane ($(R_3P{=}N)_3B$).[80] Furthermore, the bulky phosphinimides made the boron atom sufficiently sterically congested to promote the spontaneous chloride dissociation in **24a**.



Scheme 1.8 Preparation of borinium cation **24**.

In opposition to borinium cations which are very reactive and required bulky and good π-donating substituents, the boronium cations are easily prepared. The first synthesis of a boronium cation can be dated 1905 and attributed to Singer and co-workers although they incorrectly formulated the product of the reaction between boron trichloride and 1,3-diketones as trialkoxyborane hydrochlorides $(RO)_3B•2HCl$. In 1968, Balaban and co-workers repeating the same experiments found that instead they were bis-(diketonato)boronium salts (Eq. 39).[81] Since then, many boronium cations have been reported,[82] however these cations were of scarce interest for synthetic application due to the filled coordination sphere which drastically reduced their reactivity.



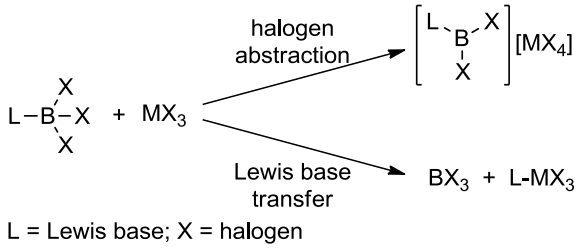
Eq. 39

Conversely, borenium cations with a formally vacant p orbital are more powerful electrophilic boron species.

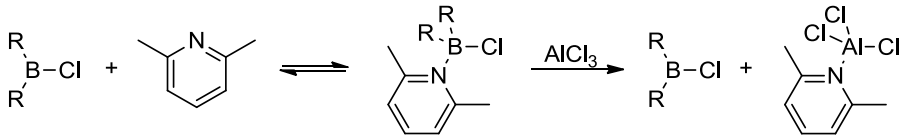
1.3.2 Borenium cations

1.3.2.1 Preparation of borenium cations by halide abstraction

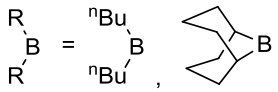
A common procedure to synthesise borenium cations is the halide abstraction from Lewis base-boron halide adducts with a halophilic Lewis acid such as AlX_3, GaX_3 and BX_3 (X = halogen). However, the reaction between the Lewis acid and the boron adduct does not necessarily give halide abstraction but it can also lead to transfer of the Lewis base from boron to the Lewis acid (Scheme 1.9). For example, the reaction of the 2,6-lutidine adduct of dibutyl boron chloride or 9-chloro-9-borabicyclo[3.3.1]nonane with $AlCl_3$ in CH_2Cl_2 yielded 2,6-lutidine•$AlCl_3$ (Eq. 40), while the reaction of the acridine adduct of 9-chloro-9-borafluorene with $AlCl_3$ in CH_2Cl_2 gave the borenium salt along with acridine•$AlCl_3$ (Eq. 41).[83] Instead, reaction of pyridine adduct of 9-chloro-9-borafluorene with $AlCl_3$ produced only the borenium salt (Eq. 42).[75a] The different reactivity of pyridine and 2,6-substituted pyridine can be attributed to the 2,6-substituents that can prevent the formation of a strong bond between boron and nitrogen in the adduct and disfavour a co-planar geometry between the pyridyl and $\{BR_2\}^+$ moieties in the borenium cation (a co-planar geometry between the pyridyl and $\{BR_2\}^+$ moieties is calculated to provide significant stabilization to the borenium cation by pyridyl→boron π donation).[84]

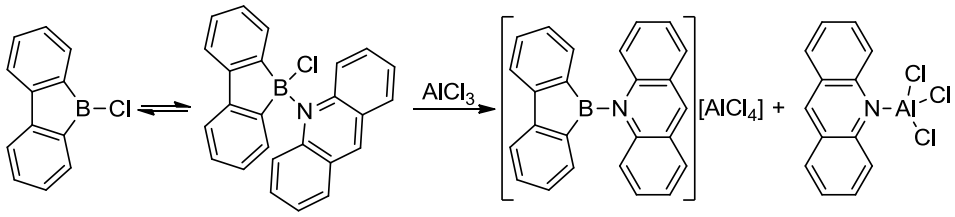


Scheme 1.9 Possible reactions between Lewis base-boron halide adducts with halophilic Lewis acid

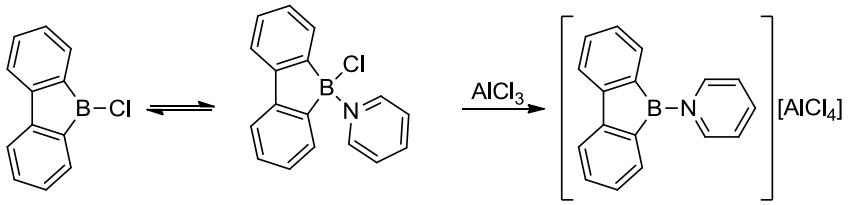


Eq. 40





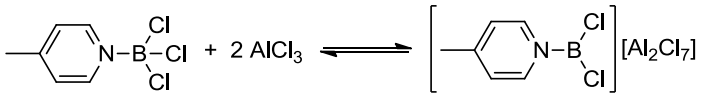
Eq. 41



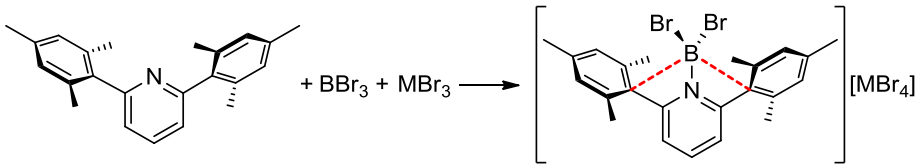
Eq. 42

The first borenium cation observed by ^{11}B NMR spectroscopy was synthesised by Ryschkewitsch and Wiggins via halide abstraction in 1970. The addition of two equivalents of $AlCl_3$ to Lewis base-acid adduct 4-picoline•BCl_3 in CH_2Cl_2 gave an equilibrium mixture containing mainly the borenium cation $[Cl_2B(4\text{-methylpyridine})]^+$ (K_{eq} ~ 20) (Eq. 43).[85] A similar pyridine stabilised borenium cation was prepared by Aldridge and co-workers using as ligand the bulky 2,6-dimesitylpyridine.[86] The reaction of two equivalents of BBr_3 with 2,6-dimesitylpyridine or the reaction of an equivalent of BBr_3 with 2,6-dimesityl pyridine followed by addition of an equivalent of $AlBr_3$ yielded the borenium cation $[(2,6\text{-dimesitylpyridine})BBr_2]^+$ cleanly (Eq. 44). The clean formation of the borenium cation was due to the steric shield of the mesityl groups in the 2,6-positions of pyridine. Likewise, the reaction of CatBBr with 2,6-dimesitylpyridine and $AlCl_3$ furnished the borenium cation (Eq. 45). It was noteworthy that the crystal structures of these borenium cations revealed close contacts between the boron centre and the *ipso* carbons of both the mesityl moieties consistent with an

interaction of the boron atom with aromatic mesityl moieties.



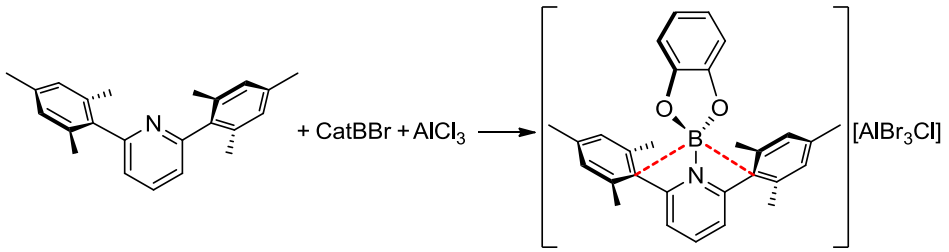
Eq. 43



Eq. 44

M = B, Al

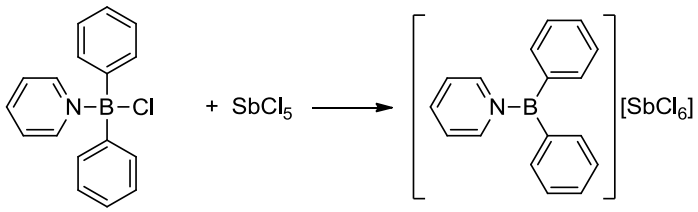
Red dashed line = closest contact between B and C



Eq. 45

Red dashed line = closest contact between B and C

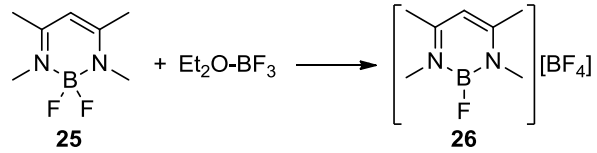
Fujio and co-workers reported the reaction of the pyridine adduct of chlorodiphenylborane in CH_2Cl_2 with an equivalent of $SbCl_5$ which furnished the pyridine stabilised diphenylborenium salt cleanly.[87] In this case the boron centre was not sterically shielded, and the clean formation of the borenium cation was possibly due to the formation of a less electrophilic and more π stabilised borenium cation than $[Cl_2B(4\text{-methylpyridine})]^+$ (Eq. 46).



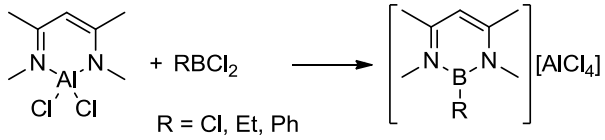
Eq. 46

A series of borenium cations isoelectronic with benzene were also prepared by Khun and co-workers.[88] Treatment of the β-diketiminato boron complex **25** with BF_3•OEt_2 yielded the aromatic borenium cation **26** (Eq. 47). Alternatively, this type of aromatic borenium cation can be prepared by metathesis reaction of the β-

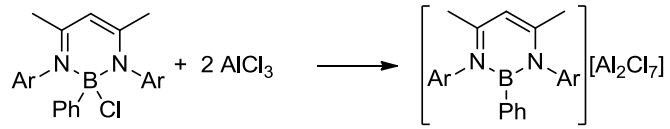
diketiminato aluminium complex **27** with $RBCl_2$ (R = Ph, Et, Cl) (Eq 48). An analogous aromatic borenium cation having the bulky diisopropylphenyl substituents at the nitrogen was synthesised and crystallographically characterised by Cowley and co-workers (Eq. 49).[89]



25 **26** Eq. 47



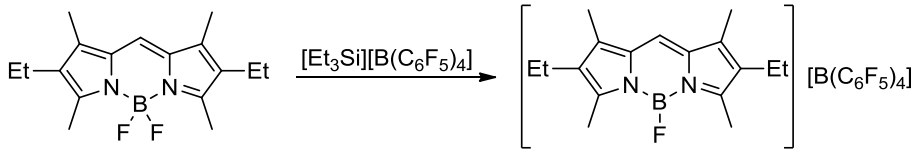
27 **28** Eq. 48



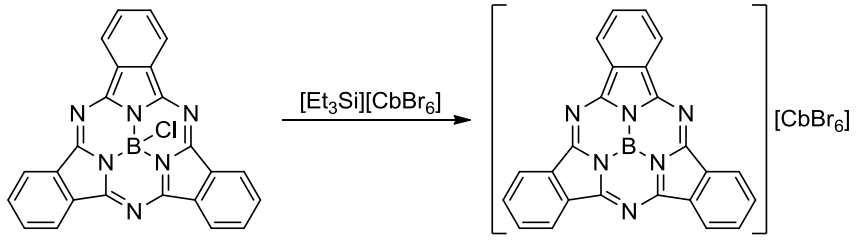
Ar = 2,6-diisopropylphenyl

29 **30** Eq. 49

Recently, the potent halophile triethylsilyl salts $[Et_3Si][B(C_6F_5)_4]$ and $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ were used as halogen abstractor for the preparation of the borenium cation **32** and **34** (Eq 50, 51).[90,91] In addition to their high halophilicity these silyl salts are source of weakly coordinating anions that are crucial for the synthesis of highly electrophilic boron cations.[92]

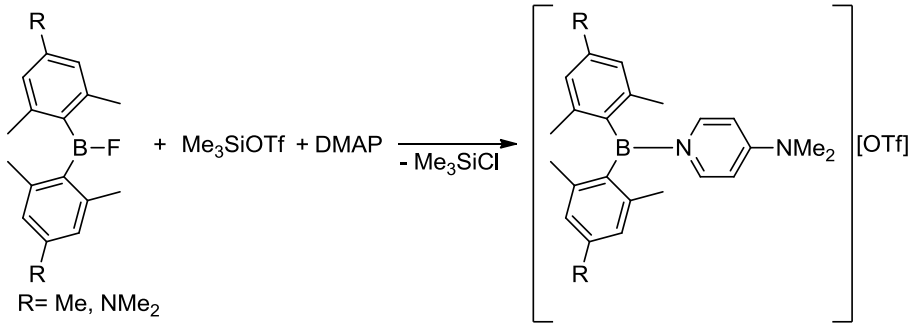


31 **32** Eq. 50

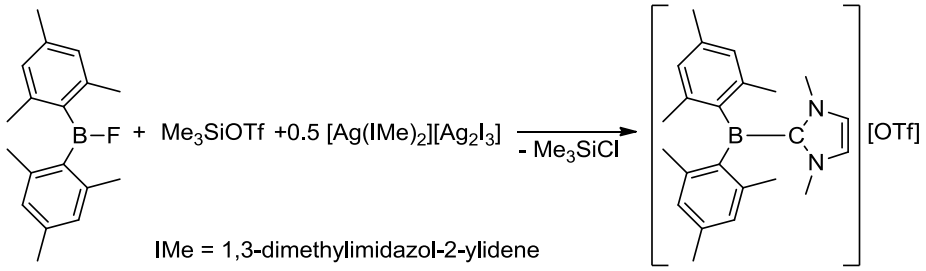


33 [CbBr6] = [*closo*-$CB_{11}H_6Br_6$] **34** Eq. 51

Another silyl species used in the preparation of borenium cation was trimethylsilyl triflate (TMSOTf). Treatment of Ar_2BF (Ar = 2,4,6-trimethylphenyl, 4-(*N*,*N*-dimethylamino)-2,6-dimethylphenyl) with TMSOTf in presence of the Lewis base *p*-dimethylaminopyridine (DMAP) furnished sterically protected borenium cations (Eq. 52).[93] In a similar way was also prepared the related *N*-heterocyclic carbene (NHC) stabilised borenium cation (Eq. 53).[94]

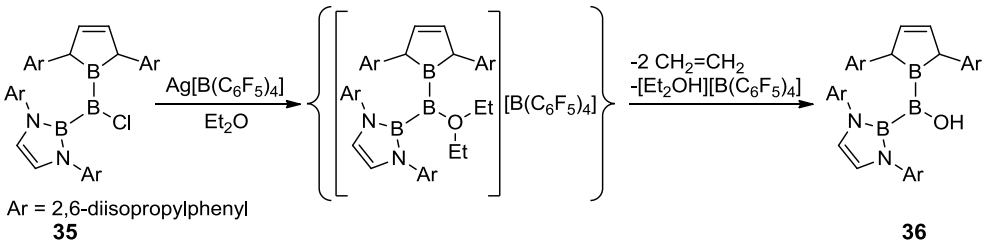


Eq. 52



Eq. 53

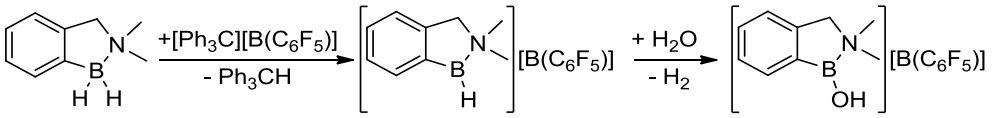
Recently, Nozaki and co-workers reported that the silver salt metathesis reaction of $Ag[B(C_6F_5)_4]$ with the chlorotriborane **35** in Et_2O gave a transient ether coordinated borenium cation. This borenium cation reacted further by spontaneous elimination of two molecules of ethylene and a proton to furnish the hydroxyborane **36** (Eq. 54).[95]



Eq. 54

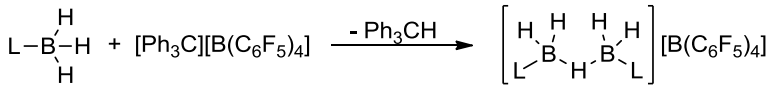
1.3.2.2 Preparation of borenium cations by hydride abstraction

Another valuable methodology to prepare borenium cations was the hydride abstraction. As described previously in the preparation of aromatic boronic acid and esters section, Vedejs and co-workers used this strategy to prepare a transient borenium cation which gave intramolecular borylation yielding the cyclic borenium cation **21** (Scheme 1.6, section 1.2.4). This cyclic borenium cation was initially prepared by the Vedejs group by treating the benzylamine-borane **37** with $[Ph_3C][B(C_6F_5)_4]$.[96] However, they erroneously attributed an ^{11}B NMR chemical shift of 38.7 ppm in CD_2Cl_2 to the compound **21** in the first report. Subsequently, repeating the reaction in strictly anhydrous condition they found that the borenium salt **21** had an ^{11}B NMR chemical shift of 58.9 ppm in CD_2Cl_2 and the compound with the ^{11}B NMR chemical shift at 38.7 ppm was the borenium cation **38** deriving from the reaction of **21** with adventitious H_2O.[73]



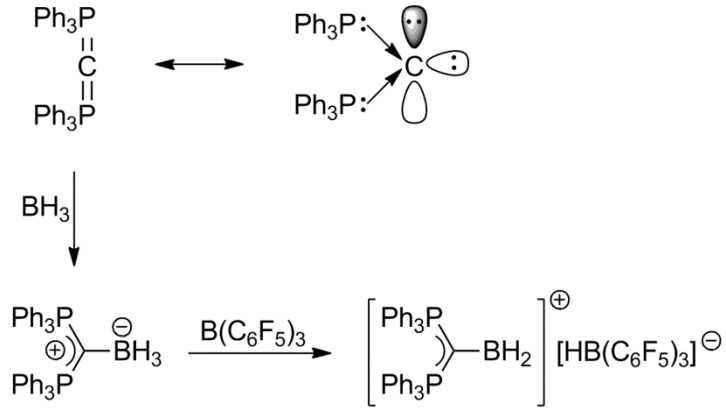
Eq.55

Attempts to produce dihydro-borenium salts by hydride abstraction from $L{\bullet}BH_3$ (L = tertiary amines, tertiary phosphines) with $[Ph_3C][B(C_6F_5)_4]$ furnished a cationic hydride-bridged dimer (Eq. 56). The abstraction of hydride from the borane adduct generated a high electrophilic dihydroborenium cation that coordinates to a hydride of the neutral borane adduct producing a cationic hydride-bridged dimer that resisted to the abstraction of a second hydride.[97] This species was identified at low temperature (-20 °C) and decomposed at room temperature reacting with the CH_2Cl_2 solvent as suggested by the formation of $[PyBCl_2][B(C_6F_5)_4]$ (Py = pyridine) when L was pyridine.



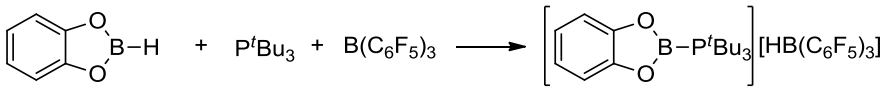
Eq. 56

A stable dihydroborenium cation was prepared by Alcarazo and co-workers using hexaphenylcarbodiphosphorane as ligand (Scheme 1.10).[98] The feature of this ligand is to have two lone electron pairs at the carbon with σ and π symmetry, respectively, that can stabilise the borenium cation by strong σ and π donation.[99]

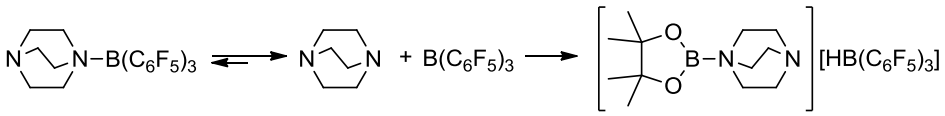


Scheme 1.10 Preparation of hexaphenylcarbodiphosphorane stabilised dihydroborenim cation.

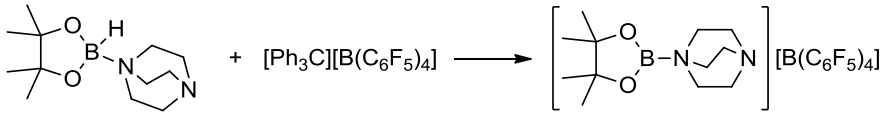
Stephan and co-workers synthesised and isolated the borenium salt $[CatB(P^tBu_3)][HB(C_6F_5)_3]$ (Cat = catecholate) by the reaction of the frustrated Lewis pair (FLP) $B(C_6F_5)_3$ and $^tBu_3P$ with CatBH (Eq. 57).[100] Likewise, Crudden and co-workers prepared the pinacolborenium salt $[PinB(DABCO)][HB(C_6F_5)_3]$ (DABCO = 1,4-diazabicyclo[2.2.2]octane, Pin = pinacolate) by treatment of the adduct DABCO•$B(C_6F_5)_3$, which is in equilibrium with the free species, with PinBH (Eq. 58).[101] The same borenium cation was also prepared by hydride abstraction from PinBH•DABCO with the trityl salt $[Ph_3C][B(C_6F_5)_4]$ (Eq. 59).



Eq.57

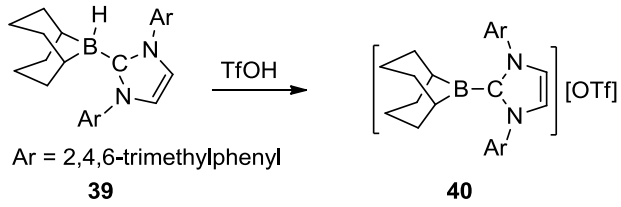


Eq. 58

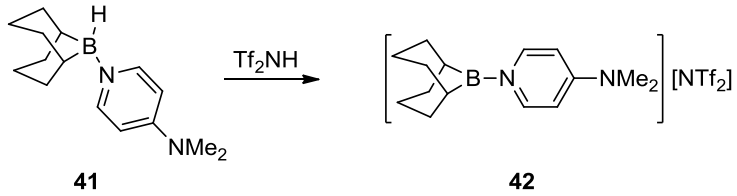


Eq. 59

The removal of the hydridic hydrogen from a borane adduct was recently accomplished by reaction with the strong Brønsted acids TfOH and Tf_2NH. The first borenium cation prepared by this methodology was reported by Lindsay and co-workers. Treatment of the 9-BBN adduct **39** with TfOH furnished the borenium cation **40** (Eq. 60).[102] Likewise, the borenium cation **42** was prepared by Vedejs and co-workers (Eq. 61).[63]



Eq. 60

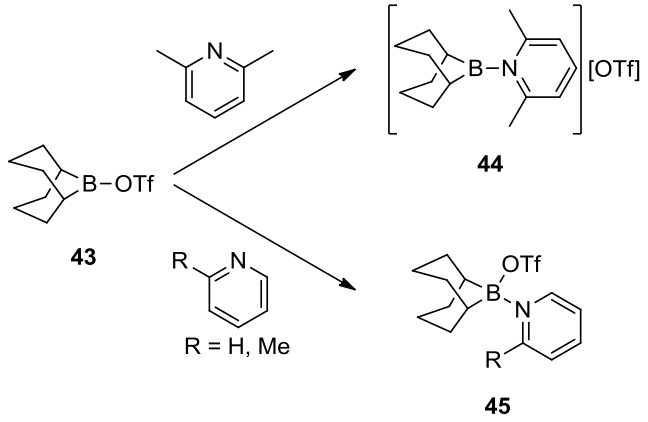


Eq. 61

1.3.2.3 Preparation of borenium cations by nucleophilic displacement

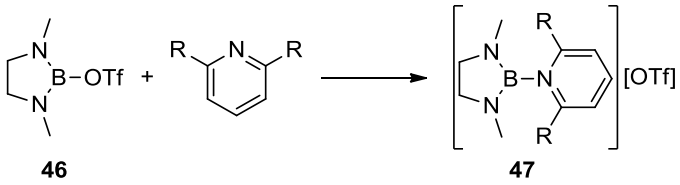
Another general method to prepare borenium cations was the nucleophilic displacement. The reaction of a borane derivative and a Lewis base generally gives a Lewis acid-base adduct, however if a good anionic leaving group and steric congestion at the boron are present the displacement of the anion can occur. For example, 2,6-lutidine displaces the triflato group when reacting with the triflate derivative of 9-BBN **43**. Instead, pyridine and 2,4-dimethyl-pyridine with **43**

furnished the Lewis acid-base adduct (scheme 1.11).[83]

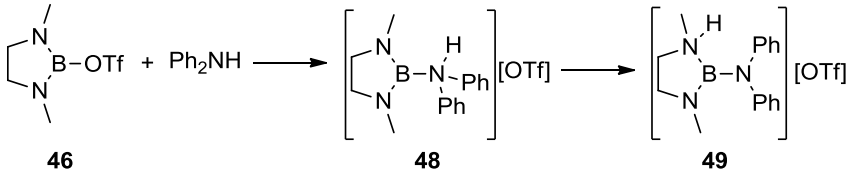


Scheme 1.11 Reaction of **43** with pyridine and *ortho*-substitued pyridines

The nucleophilic displacement methodology was also employed in the preparation of cyclic diazaborenium cations. The reaction of the triflate derivative of 1,3-dimethyl-1,3,2-diazaborolidine **46** with pyridine or 2,6-lutidine gave the related borenium cations (Eq. 62). Similar nucleophilic displacement was observed in the reaction of **46** with diphenylamine that then underwent a subsequent internal proton shift to furnish the borenium salt **49** (Eq. 63).[103]



Eq. 62

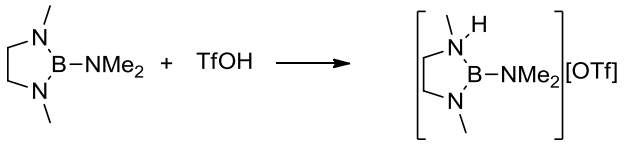


Eq.63

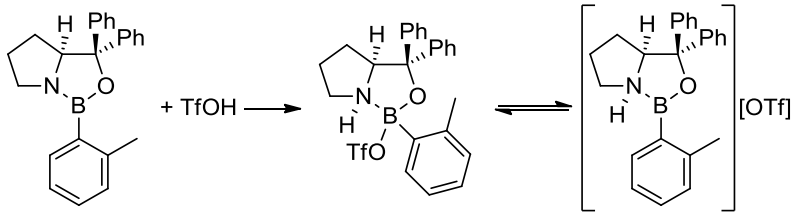
1.3.2.4 Preparation of borenium cations by electrophilic attack

The reaction of aminoboranes with strong acids can lead to formation of a borenium cation. For example **50** with TfOH furnished the cyclic borenium cation **51** (Eq. 64).[103] The protonation pathway was also used by Corey and co-workers to

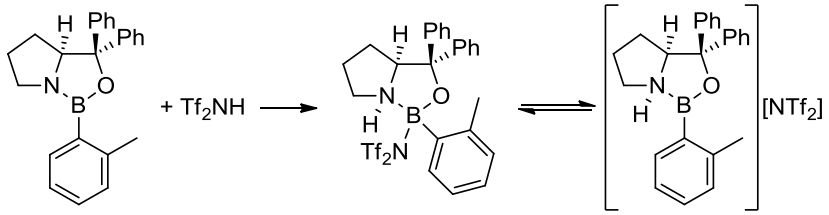
synthesise a chiral borenium cation. The addition of TfOH or Tf_2NH to the oxazaborolidine **52** furnished the related borenium cation in equilibrium with the neutral tetracoordinate boron species (Eq. 65, 66).[104] This methodology differs from previous techniques since it forms the borenium cation by electrophilic attack of a proton to the nitrogen centre bonded to boron without directly breaking a boron-substituent bond.



50 **51** Eq. 64

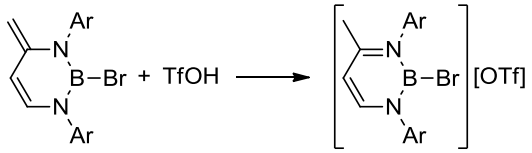


52 **53** **54** Eq. 65



52 **55** **56** Eq. 66

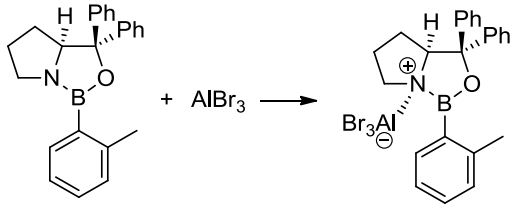
A different approach to form a borenium cation by the protonation pathway was reported by Driess and co-workers.[105] The reaction of TfOH with the unsaturated diaminoborane **57** furnished the borenium cation **58** by protonation at the exocyclic unsaturated carbon (Eq. 67).



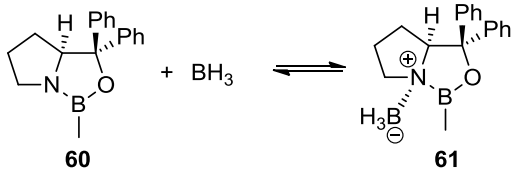
57 **58** Eq. 67

The reaction of a strong Lewis acid with aminoboranes can give a neutral Lewis acid-base adduct deriving from the coordination of the Lewis acid to the nitrogen

atom. Although this reaction does not furnish a cationic species, the compound contains a borenium subunit since the nitrogen has a formal positive charge. Important examples of such compounds are the oxazaborolidine derivative **59** and **61** which are useful in enantioselective catalysis as discussed in the next section. Whilst the nitrogen has the formal positive charge boron is significantly more electropositive thus will possess a significant degree of positive charge in **59** and **61**.



Eq. 68



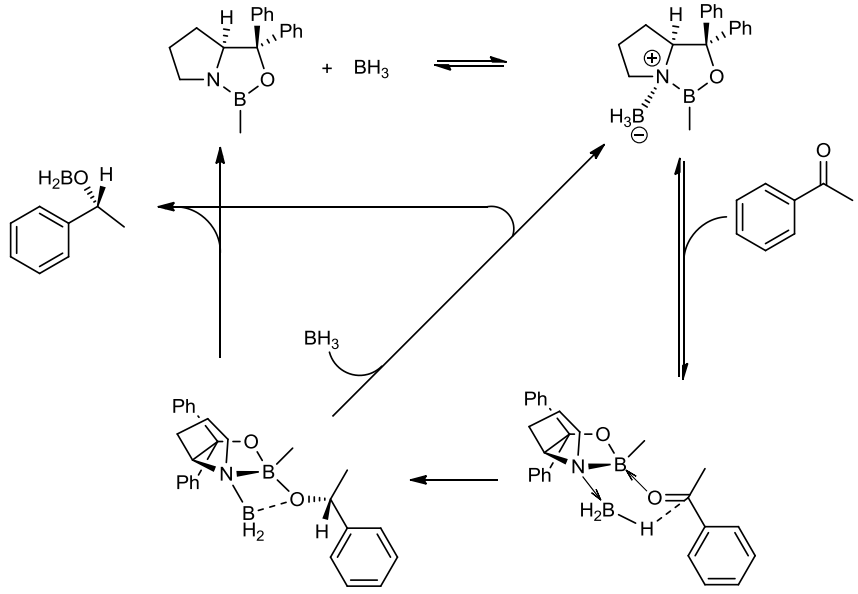
Eq. 69

1.4 Borenium cations in organic synthesis

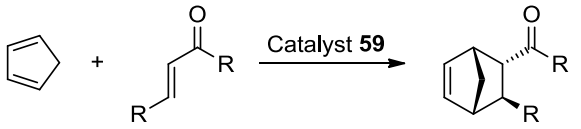
The enantioselective reduction of ketones with BH_3 catalysed by a chiral oxazaborolidine derivative is one of the widest applications where a borenium cation can be invoked.[106] The reaction initially proceeds by the coordination of BH_3 to the oxazaborolidine derivative giving a borenium subunit. The increased Lewis acidity of the endocyclic boron atom allows the facile complexation of a ketone which undergoes enantioselective reduction by intramolecular hydride transfer from the exocyclic borane to the carboxylic carbon (Scheme 1.12).

Another boron species containing a borenium subunit used in organic synthesis is the $AlBr_3$-oxaborolidine adduct **59** (Eq. 68) which is an efficient catalyst for the enantioselective Diels-Alder reaction of various dienes with α,β-unsaturated carbonyl dienophiles (Eq. 70).[107] This reaction was also efficiently catalysed by the

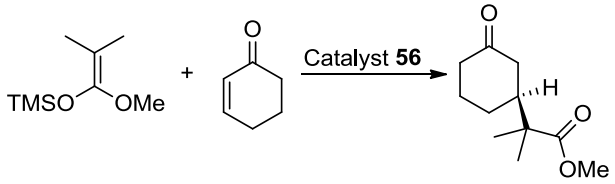
related borenium cations **54** and **56** deriving from the protonation of oxaborolidine **52** with TfOH and Tf_2NH, respectively (Eq. 65, 66).[104,108] Both these borenium cations are highly enantioselective catalysts, but the borenium cation **56** showed a broader substrate scope. Furthermore, **56** was also used as catalyst in the enantioselective Michael reaction of a ketene-silyl acetal with an enone giving the 1,4-product with excellent regio- and enantioselectivity (Eq. 71).[109]



Scheme 1.12 Proposed mechanism of the enantioselective reduction of ketones with BH_3 catalysed by oxazaborolidines.



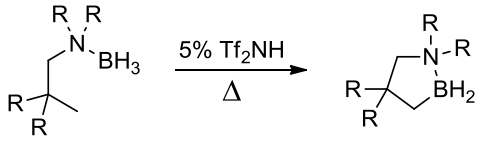
Eq. 70



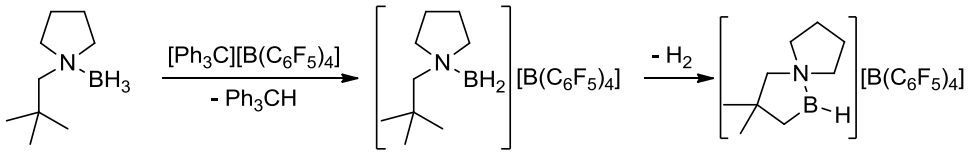
Eq. 71

Recently, a borenium cation was proposed to be involved in the intramolecular borylation of aliphatic C-H bonds of amine-borane adducts in presence of catalytic quantities of Tf_2NH at temperatures above 120 °C (Eq. 72).[110] Although in this catalytic process the nature of the borylating species was not clear, the related

stoichiometric *N*-directed borylation with $[Ph_3C][B(C_6F_5)_4]$ at room temperature suggested that the borenium cation **63** was a plausible intermediate of the reaction (Eq. 73).



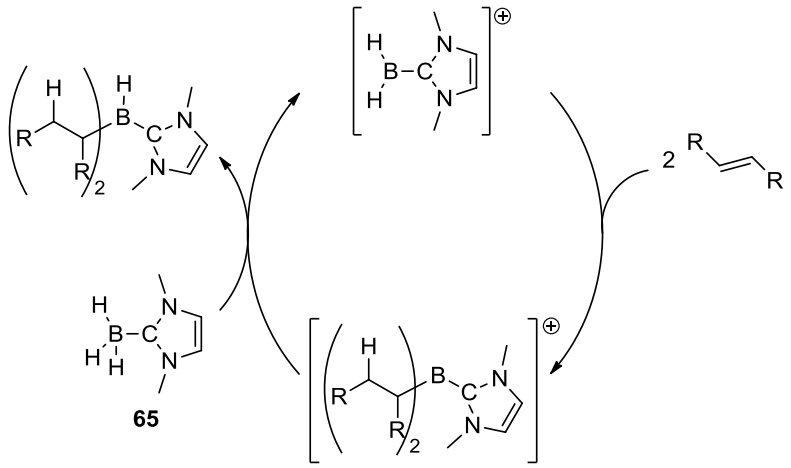
Eq. 72



62 **63** **64**

Eq. 73

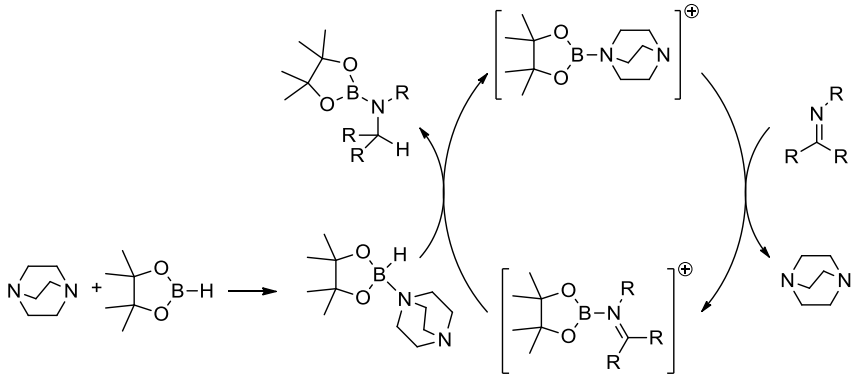
A similar borenium cation was also a possible species involved in the hydroboration of alkenes with the NHC•BH_3 adduct **65**.[111] Treatment of an alkene with **65** and catalytic quantities of Tf_2NH or $[Ph_3C][B(C_6F_5)_4]$ gave a hydroboration product at room temperature (Scheme 1.13). In the absence of catalysts the carbene borane adduct, **65**, does not hydroborate alkenes at room temperature.



Scheme 1.13 Proposed mechanism of alkene hydroboration.

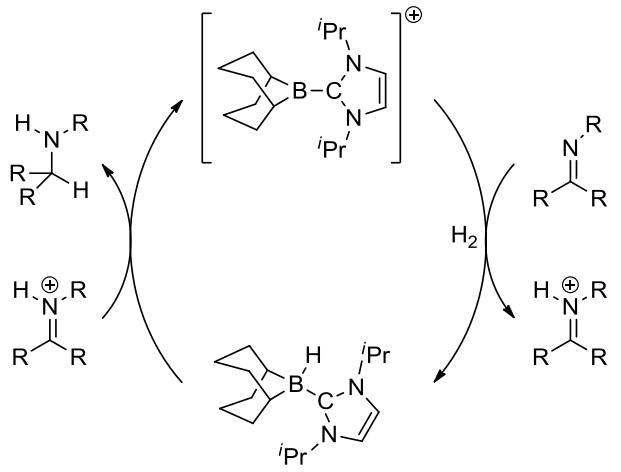
Another recent application of borenium cations in synthesis was the reduction of imines. The DABCO stabilised pinacolborenium cation was an effective catalyst for the reduction of a range of imines with PinBH.[101] The reaction of the

pinacolborenium cation with an imine gave a boron-activated iminium cation. The subsequent hydride transfer from PinBH•DABCO adduct to iminium gave an amine regenerating the borenium cation (Scheme 1.14).



Scheme 1.14 Proposed mechanism of imines reduction with PinBH catalysed by DABCO stabilised pinacolborenium cation.

An elegant alternative process for the reduction of imines with H_2 using a borenium cation as catalyst was developed by Stephan and co-workers. This process was based on the formation of FLPs between a 9-BBN-based borenium cation and an imine. Treatment of such FLPs with H_2 resulted in heterolytic hydrogen activation generating an iminium cation and a neutral NHC-borane adduct. Subsequent hydride transfer from the neutral NHC-borane adduct to iminium cation furnished the amine and regenerated the borenium cation (Scheme 1.15).[112]



Scheme 1.15 Proposed mechanism of imines reduction with H_2 catalysed by NHC stabilised 9-BBN cation.

Borenium cations were also used in intramolecular and intermolecular borylation of arenes (Scheme 1.6, Eq. 28). However, the intermolecular borylation was limited to arenes bearing a directing group, and the intermolecular borylation with defined borocations was not reported when this research programme was commenced.

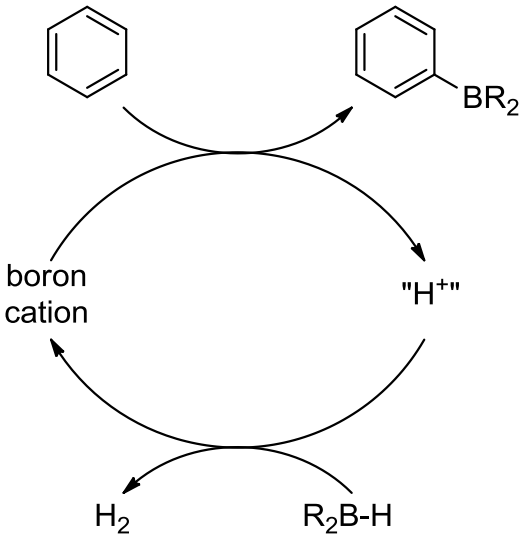
1.5 Summary and scope of thesis

Aryl boronic acids and esters are useful intermediates in synthesis. Several methodologies are well developed for their preparation, but each has its own limitations. However, reports on the intermolecular direct C-H borylation via electrophilic aromatic substitution were limited despite the intrinsic electrophilic nature of boron compounds. In order to achieve the electrophilic aromatic borylation, the increase of electrophilicity at boron is required relative to BX_3. A method to enhance the reactivity of boron compounds is to generate cationic boron species.

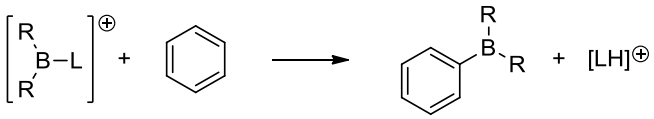
The target of the project discussed herein was to design, synthesise and isolate boron cations to employ as electrophilic reagents for the direct C-H borylation of arenes. The requirements for successful arene borylation by boron cations are a sufficiently electrophilic boron centre and the removal of the strong protic by-product deriving from the aromatic electrophilic borylation (to prevent the reverse reaction of protodeboronation and heterocycle decomposition).

Two different approaches are considered to remove the protic by-product. The first is the reaction of the proton with a hydridic borane R_2B-H to produce H_2 and regenerate an active borylating electrophile. In this way, it is possible to achieve a catalytic process (Scheme 1.16). The second method is to remove the proton by trapping with a Lewis base that did not irreversibly deactivate the boron electrophile.

Borenium cations are envisaged as suitable reagent for this methodology since they contain a Lewis base. This Lewis base would be released during arene borylation to irreversibly trap the proton by-product (Eq. 70).



Scheme 1.16 Proposed catalytic cycle for arene borylation.



L = Lewis base

Eq.70

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Chapter 2. Catalytic (in Brønsted super-acid) arene borylation

2.1 Introduction

Neutral tricoordinate boron compounds have Lewis acid character due to the formally vacant p orbital on the boron centre. Borenium and borinium cations should be more Lewis acidic and reactive than their neutral counterparts since in addition to one or two formally vacant p orbitals they possess a formal positive charge on the boron atom. However, their reactivity is related to the degree of electronic stabilisation and to the bulkiness of substituents on the boron.[1,2]

In the condensed-phase, the synthesis and the isolation of borinium cations, which are the most reactive boron monocations, is achieved using bulky and good π donating substituents on boron. These substituents allow the isolation of dicoordinated borocations but they generally hamper the reactivity of the borocation. Synthesis of a borinium cation, using a bidentate substituent on the boron atom, would result in a sp^2 hybridised boron centre. Such a hypothetical chelate restrained borinium cation would have a formally vacant sp^2 orbital not stabilized by π-donation from the ligand. Moreover, the chelate restrained borinium cation would have reduced steric shielding around the boron atom compared to a related linear borinium cation (Figure 2.1).

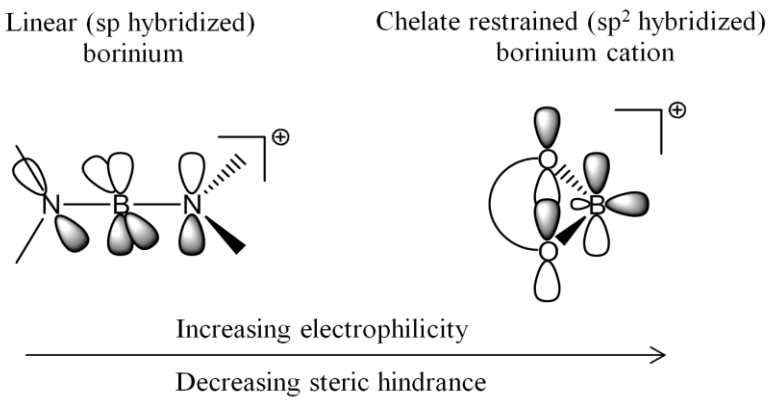


Figure 2.1 Linear borinium cation versus chelate restrained borinium cation

In the condensed-phase, the isolation of such a borinium cation, which lacks electronic stabilization and steric shielding, is not feasible because the borocation is expected to interact with anion or solvent (like silylium cations)[3] generating a borenium cation. Nevertheless, the use of an anion, which does not form a strong covalent bond and is easily displaced by weak nucleophiles, would lead to a highly reactive boron species.

Halogenated carborane derivatives (for example [*closo*-$CB_{11}H_6X_6$]) are considered among the least nucleophilic and the most robust anions presently known.[4] Their robustness is exemplified by their use in the isolation of strong electrophiles such as H^+,[5] $Alkyl^+$,[6] R_3Si^+ [7] and R_2Al^+.[8] Chemical inertness combined with a nucleophilicity comparable to toluene makes these anions suitable candidates as counterions for a strong electrophilic boron cation to use in arene borylation.

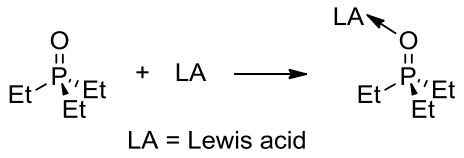
Because our target is the synthesis of arylboronic esters, which are extensively used in Suzuki cross-coupling, dioxo-ligated catecholboranes are chosen as borocation precursors. In addition to having a bidentate substituent, catecholboranes have reduced O-B π donation since the lone pair of the oxygen atom is partially delocalised in the aromatic ring.[9] In order to probe the potential electrophilicity of catecholboron cations, studies into their Lewis acidity are conducted.

2.2 Lewis acidity

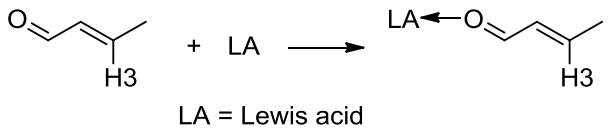
A preliminary investigation of borocation electrophilicity was accomplished assessing the Lewis acidity by two NMR techniques: the Gutmann-Beckett method[10] and the Childs method.[11]

The Gutmann-Beckett method is based on the phosphorus chemical shift of triethylphospine oxide ($Et_3P{=}O$) complexed with a Lewis acid (Eq. 1). Initially, this

method was introduced by Gutmann to describe quantitatively the electrophilic character of solvents and subsequently was extended to include Lewis acids by Beckett and co-workers. While, the Childs method is based on the difference in ^{1}H NMR chemical shift of the H3 proton between free crotonaldehyde and crotonaldehyde complexed to Lewis acid (Eq. 2).



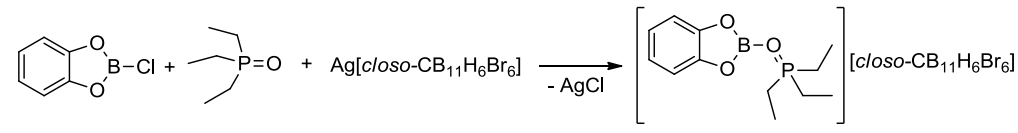
Eq. 1



Eq. 2

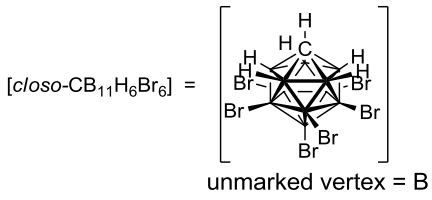
2.2.1 Assessment of the Lewis Acidity by the Gutmann-Beckett method

In presence of 0.9 equivalents of $Et_3P{=}O$, the metathesis reaction between equimolar amounts of Ag[*closo*-$CB_{11}H_6Br_6$] and B-bromocatecholborane (CatBBr) yielded the triethylphosphine oxide adduct [CatB(O=PEt_3)][*closo*-$CB_{11}H_6Br_6$] **1** (Eq. 3), which was purified by crystallisation (slow diffusion of hexane into CH_2Cl_2).



Eq. 3

1

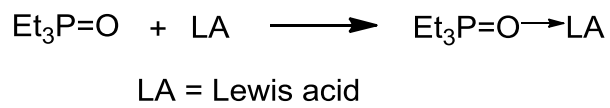


The phosphorus chemical shift of **1** at 106.9 ppm, which is considerably downfield compared to the reported phosphorus chemical shift of other Lewis acid/O=PEt_3 adducts (Table 2.1), suggests exceptional Lewis acidity for the $[CatB]^+$

moiety. A similar phosphorous chemical shift was observed by Ingleson in the analogous borate adduct $[CatB(O{=}PEt_3)][B(C_6F_5)_4]$.[12]

Instead, the phosphorous chemical shift of the analogous triflate, $CatB(O{=}PEt_3)(OTf)$, at 85.4 ppm was significantly upfield compared to $[CatB(O{=}PEt_3)][A]$ ([A] = [*closo*-$CB_{11}H_6Br_6]^-$, $[B(C_6F_5)_4]^-$). The disparity of phosphorous chemical shifts is due to the different interaction of each anion with the $[CatB(O{=}PEt_3)]^+$ moiety as indicated by ^{11}B NMR spectroscopy as well. The boron chemical shift for $CatB(O{=}PEt_3)(OTf)$ at 7.9 ppm in the characteristic region of tetracoordinated boron suggests a strong coordination of TfO^- to boron. Conversely, the boron chemical shift of **1** at 21.9 ppm for the $[CatB(O{=}PEt_3)]^+$ moiety, consistent with a tricoordinated boron atom, suggests no or a very weak interaction with the carborane anion [*closo*-$CB_{11}H_6Br_6]^-$.

Table 2.1 $^{31}P\{^1H\}$ chemical shift of $Et_3P{=}O$ adducts of a range of Lewis acids.



LA = Lewis acid

Lewis Acid	**$Et_3P{=}O$ adduct δ $^{31}P\{^1H\}$ (ppm)[a]**
$B(C_6F_5)_3$	76.6[b]
$AlCl_3$	80.3[b]
$F_2B(OTf)$	84.6[c]
$CatB(OTf)$	85.4[d]
BBr_3	90.3[b]
"$[CatB][B(C_6F_5)_4]$"	106.9[d]
"[CatB][*closo*-$CB_{11}H_6Br_6$]"	106.9[e]

[a] NMR spectra recorded in $CDCl_3$ unless otherwise stated. [b] Reference 13. [c] Reference 14. [d] Reference 12 [e] This work. NMR spectra recorded in CD_2Cl_2.

The crystal structure of **1** (Figure 2.2) corroborates the formation of a tricoordinated boron centre. The sum of the bond angles around the boron atom of 359.9º and the nearest anion-boron interaction at 3.411 Å indicate a very weak anion-cation interaction. The P1-O1 distance (1.595(5) Å) is longer than the P-O distance in the $Et_3P{=}O/B(C_6F_5)_3$ adduct (1.4973(17) Å) and is close to P-O bonds in phosphonium cations (for example in $[Ph_2(Me)P\text{-}O\text{-}CH_2{}^tBu]^+$ the P-O distance is 1.568(4) Å).[15] Furthermore, the B1-O1 distance at 1.374(9) Å is comparable to B1-O2 and B1-O3 bond lengths (1.372(7) and 1.381(7) Å, respectively). Although, the cation **1** can be viewed as a borenium cation it is best represented as a phosphonium cation as suggested by P1-O1 and B1-O1 distances.

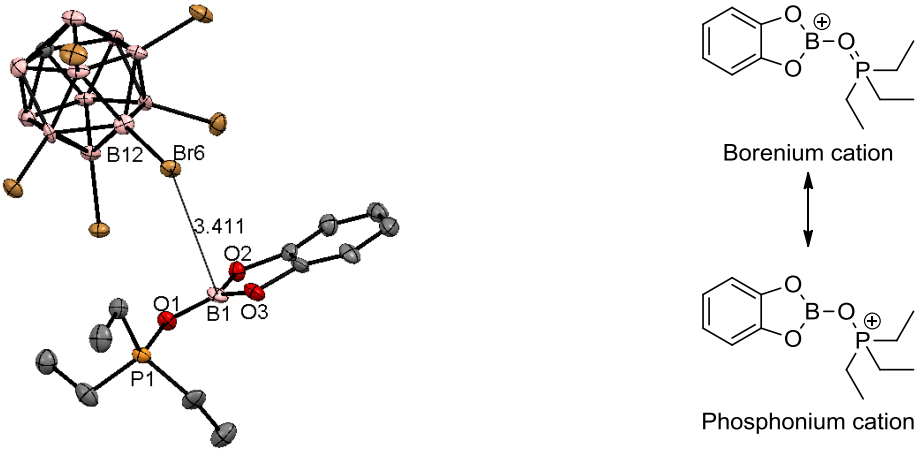


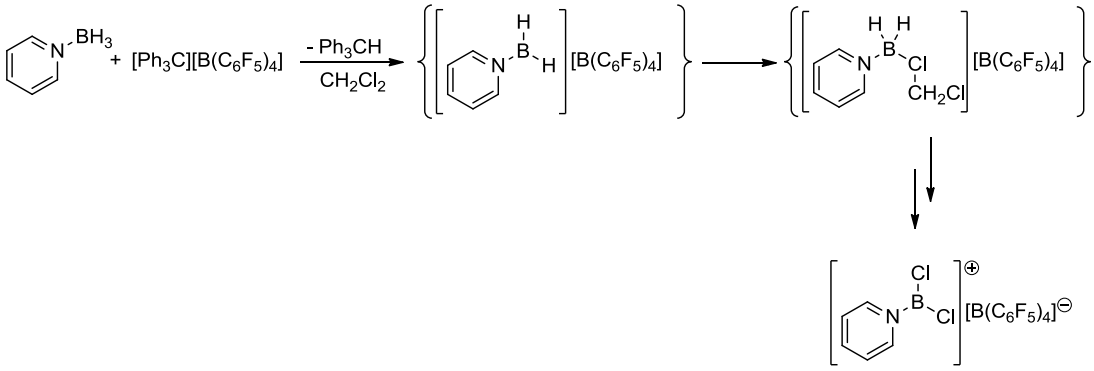
Figure 2.2 (*Left*) Molecular structure of **1**, hydrogens omitted for clarity and thermal ellipsoids at 50 % probability. Selected bond lengths (Å): P(1)-O(1) = 1.595(5), B(1)-O(1) = 1.374(9), B(1)-O(2) = 1.372(7), B(1)-O(3) = 1.381(7). Closest anion-cation contact Br(6)···B(1) = 3.411 Å. Angles at B Σ = 359.9°. (*Right*) Phosphonium and borenium resonance structures.

2.2.2 Assessment of the Lewis Acidity by the Child method

Initial attempts to assess the Lewis acidity using the second NMR method were unsuccessful. The addition of a mixture of crotonaldehyde and CatBBr in CH_2Cl_2 to Ag[*closo*-$CB_{11}H_6Br_6$] gave a mix of unidentified products possibly deriving from the

side reaction of the $[CatB(crotonaldehyde)]^+$ cation with the solvent.

The instability of strong electrophilic boron cations in CH_2Cl_2 is exemplified by the attempt of Vedejs and co-workers to synthesise the borenium cation $[PyBH_2]^+$ (Py = pyridine) partnered with $[B(C_6F_5)_4]^-$ in CH_2Cl_2.[16] The hydride abstraction from $Py{\cdot}BH_3$ with $[Ph_3C][B(C_6F_5)_4]$ gives a transient borenium cation "$[PyBH_2]^+$" that reacts with the chlorinated solvent leading to $[PyBCl_2][B(C_6F_5)_4]$ (Scheme 2.1).

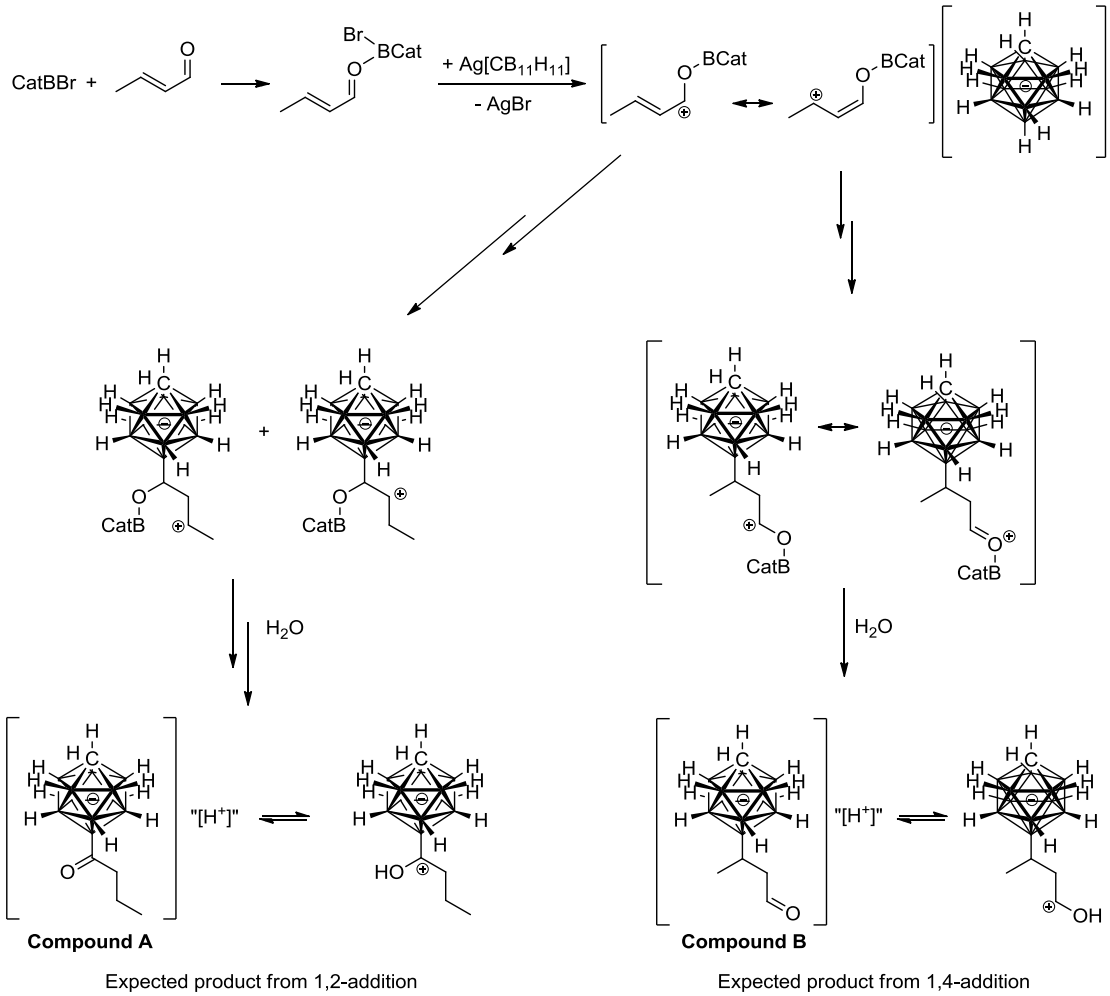


Scheme 2.1 Proposed mechanism of formation $[(Py)BCl_2][B(C_6F_5)_4]$ by solvent activation.

It is worthwhile to report that the reaction of crotonaldehyde, CatBBr and $Ag[closo\text{-}CB_{11}H_{12}]$ in toluene gave a substitution reaction on the carborane cage. *In situ* ^{11}B NMR spectrum mainly showed four new boron environments: one broad singlet at 22.4 ppm, one singlet at -5.4 ppm and two doublets at -13.3 ppm and at -15.5 ppm. The peak at 22.4 ppm can be attributed to CatBOR, while the other three peaks can be assigned to a B12 substituted carborane. The ^{11}B NMR chemical shift of the B12 at -5.4 ppm is closer to the related [*closo*-12-(Alkyl)-$CB_{11}H_{11}$] (for example [12-(Me)-$CB_{11}H_{11}$] +1.7 ppm)[17] than the related [*closo*-12-(OH)-$CB_{11}H_{11}$] (+10.7 ppm),[18] suggesting that the B12 is bounded to a carbon. Possibly, the product of the reaction occurred from an electrophilic reaction between a borenium/carbenium cation generated by silver metathesis and the carborane cage

(Scheme 2.2) ([closo-$CB_{11}H_{12}]^-$ is well documented to be susceptible to electrophilic alkylation, and can be regarded as a 3D analogue of benzene).[4c] The product or products are postulated to be a zwitterion compound arising from a 1,2 and/or 1,4 addition to crotonaldehyde.

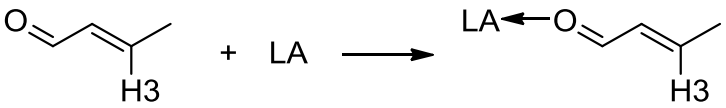
Attempts to isolate the zwitterionic species or the product derived from its hydrolysis were unsuccessful. However, negative ion electrospray mass spectra of the product or products after aqueous acid workup was consistent with the anion formulation of **A** and **B** (Scheme 2.2) (calculated mass for $C_5H_{18}B_{11}O$ = 213.2, found = 213.1).



Scheme 2.2 Proposed mechanism of reaction between CatBBr, crotonaldehyde and Ag[*closo*-$CB_{11}H_{11}$] in toluene.

At the end [CatB(crotonaldehyde)][*closo*-$CB_{11}H_6Br_6$] has been synthesised by Ingleson using C_6D_6 as solvent.[12] The $[CatB(crotonaldehyde)]^+$ moiety has a boron chemical shift of 23.8 ppm consistent with a tricoordinated boron centre. In the ^1H NMR spectrum the resonance of the H3 is shifted downfield by 1.28 ppm compared to free crotonaldehyde in C_6D_6. From comparison with the reported H3 chemical shift induced by other Lewis acids $[CatB]^+$ moiety is less acidic than the neutral BBr_3 and slightly more acidic than $AlCl_3$ (Table 2.2), although these were recorded in different solvent (CD_2Cl_2).

Table 2.2 ^1H chemical shift differences ($\Delta\delta$) of crotonaldehyde on complexation with various Lewis acids (in CD_2Cl_2 unless otherwise stated).



LA = Lewis acid

Lewis Acid	Δδ of the H3 proton of crotonaldehyde
$Me_3Si(OSO_2CF_3)$	0.7[a]
$B(C_6F_5)_3$	1.05[b]
$AlCl_3$	1.23[c]
"[CatB][*closo*-$CB_{11}H_6Br_6$]"	1.28[d]
$F_2B(OSO_2CF_3)$	1.46[a]
BBr_3	1.49[c]

[a] Reference 13. [b] Reference 19. [c] Reference 11. [d] Reference 12, the ^1H NMR of [CatB(crotonaldehyde)][*closo*-$CB_{11}H_6Br_6$] was recorded in C_6D_6.

The evaluation of the Lewis acidity of $[CatB]^+$ moiety by Gutmann-Beckett and Childs method shows that the $[CatB]^+$ moiety is a powerful Lewis acid. However, the $[CatB]^+$ moiety is the strongest Lewis acid with the Gutmann-Beckett method, while the $[CatB]^+$ moiety is less Lewis acidic than the neutral boron BBr_3 with the

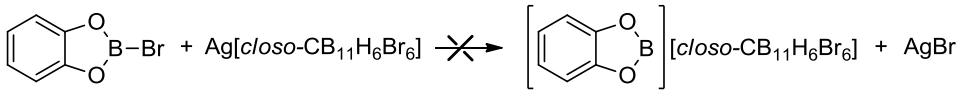
Childs method. The discrepancy in Lewis acidity when using different reference bases is not unusual and has been reported in several cases.[20] Different orders can be explained by Pearson's Hard Soft Acid Base (HSAB) theory.[21] In crotonaldehyde the C=O double bond is a pπ-pπ bond resulting predominately in a covalent bond. Instead, in the phosphine oxide the P=O double bond is predominately an ionic bond.[22] Consequently, the harder Lewis base phosphine oxide matches better than crotonaldehyde with the hard Lewis acidic boron centre of the $[CatB]^+$ moiety.

After initial studies on the catecholboron cation Lewis acidity, its potential in arene borylation was investigated.

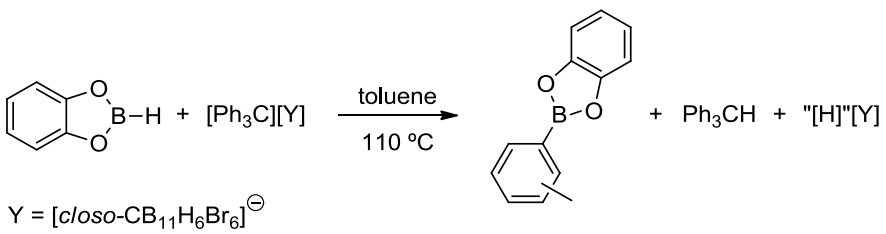
2.3 Arene Borylation

2.3.1 Stoichiometric Arene Borylation

Initial attempts to generate a catecholboron cation species by silver metathesis between Ag[*closo*-$CB_{11}H_6Br_6$] and CatBX (X = Cl, Br) in the absence of a good base were unsuccessful with starting materials returned unchanged. Instead, the reaction of CatBH with [Ph_3C][*closo*-$CB_{11}H_6Br_6$] in toluene proceeded, although at raised temperature (110 ºC) and slowly (4 days), to yield borylated toluene without any detectable intermediate by ^{11}B NMR.



Eq. 4

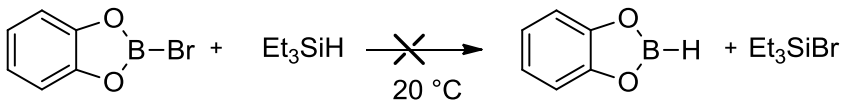


Eq. 5

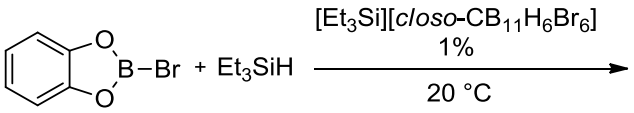
Arene borylation under milder conditions was achieved using the combination of CatBX (X = Cl, Br) and $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ in arene solvent (herein $[Et_3Si]^+$ moiety refers to $[Et_3Si(arene)]^+$ since the naked triethyl-silylium cation does not exist in condensed phase).[23] $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ was prepared, following the Reed procedure, [24] from $[Ph_3C][closo\text{-}CB_{11}H_6Br_6]$ and Et_3SiH and used *in situ* because the isolation of the extremely sensitive silylium species proved difficult.[25]

Reaction of CatBX with $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ in benzene at 20 °C resulted in a rapid formation of CatBPh along with small quantities of CatBH, and CatBOH as the only new boron-containing products (by ^{11}B NMR spectroscopy). CatBPh is the expected product from the reaction of an electrophilic boron species with benzene. CatBOH, constantly present in all reactions, is the product of reactions involving CatBX or a borocation species with adventitious water in the solvent or from the glass surface.

The last boron-containing species, CatBH, is possibly the product of reaction between an electrophilic boron species and trace of Et_3SiH. The indirect confirmation, that an electrophilic boron species is involved in the conversion of CatBBr to CatBH, was given by absence of reaction between CatBBr and Et_3SiH at 20 °C (Eq. 6) (in contrast the reaction of halogen/hydrogen exchange between the more Lewis acidic BCl_3 and Et_3SiH occurs at this temperature).[26] Conversely, the reaction between CatBBr and Et_3SiH in presence of catalytic quantities of $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ resulted in quantitative conversion of CatBBr in CatBH at 20 °C (by ^{11}B NMR spectroscopy) (Eq. 7).



Eq. 6



Eq. 7

An expected by-product from the stoichiometric benzene borylation with $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ and CatBX is a protic species (Eq. 5). This species in weakly nucleophilic environment is a Brønsted superacid which is expected to react with the hydridic CatBH to generate a new equivalent of boron electrophile. The reaction of this boron electrophile with arene will give arene borylation and will regenerate the Brønsted superacid making possible a catalytic arene borylation process.

2.3.2 Catalytic Arene Borylation

The addition of twenty equivalents of CatBH to the reaction mixture generated from $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ and CatBBr in benzene at 20 °C resulted in no reaction. In contrast, at raised temperature (80 °C) all CatBH was fully converted to CatBPh after 15 hours.

Evidence that a protic species is involved in the catalytic arene borylation with CatBH is given by: (i) the addition of the bulky basic amine 2,6-di-*tert*-butylpyridine as proton scavenger[27] halts the catalytic reaction and (ii) the pervasive H/D exchange of aromatics and the formation of HD when reactions are performed in d_6-benzene (Figure 2.3).

The Brønsted superacid at high temperature is hence able to catalyse the reaction between CatBH and arene. This catalytic process enables the synthesis of aryl boronic esters in one step producing H_2 as the only by-product (Scheme 2.3)

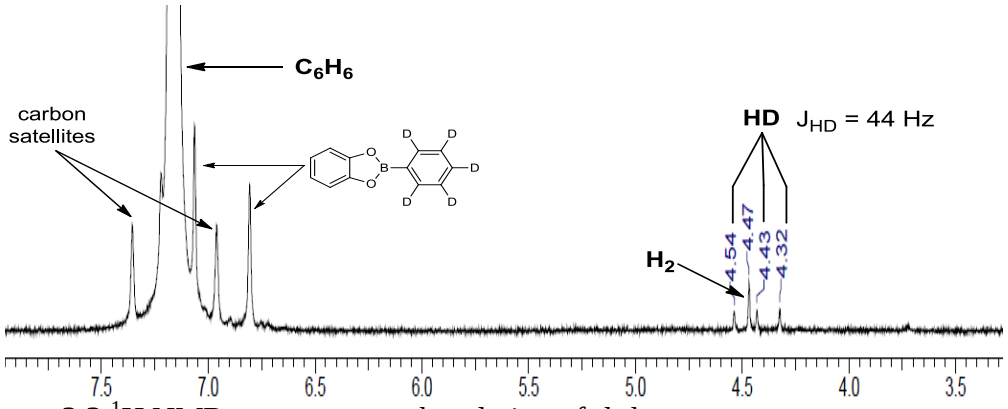
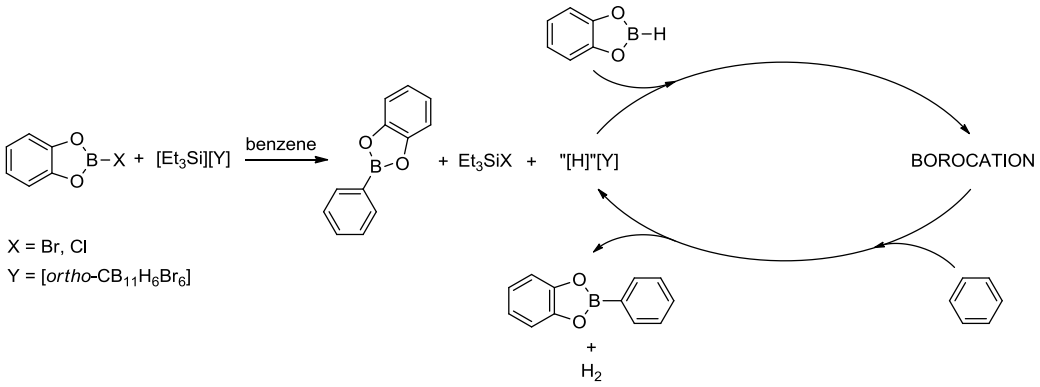


Figure 2.3 ^{1}H NMR spectrum post borylation of d_6-benzene.



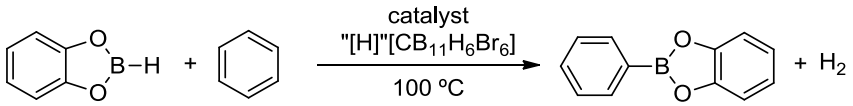
Scheme 2.3 Proposed catalytic cycle of arene borylation.

Investigation of the substrate scope of the catalytic (in Brønsted superacid) arene borylation was conducted using the reagent arene as solvent. Alkylated benzene and deactivated 1,2-chlorobenzene were efficiently borylated at the aromatic ring. Instead, anisole underwent C-O bond cleavage leading to formation of CatBOPh (by ^{11}B NMR spectroscopy).

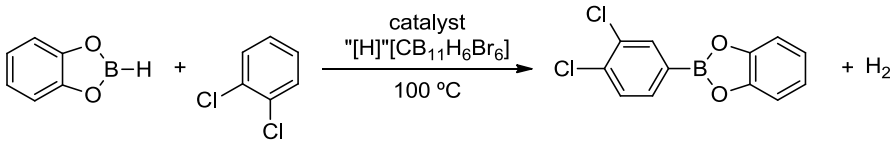
Fluorobenzene was stoichiometrically borylated at 20 °C by equimolar combination of [Et_3Si][*closo*-$CB_{11}H_6Br_6$] and CatBBr. However, attempts to carry out the catalytic (in Brønsted superacid) borylation with CatBH at 100 °C did not give arene borylation. Instead, anion decomposition was observed (by ^{11}B NMR spectroscopy). The anion decomposition is presumably caused by a phenyl or an incipient phenyl cation deriving from sp^2 C-F activation by a strongly Lewis acidic

and fluorophilic borocation species present in solution.[28]

Benzene and *ortho*-dichlorobenzene borylation yielded selectively the monoborylated product CatBPh (Eq. 8) and 2-(3,4-dichlorophenyl)-1,3,2-benzodioxaborole, respectively (Eq. 9). While, toluene gave a mixture of *meta*- and *para*-borylated toluene along with trace amounts of CatBPh (Table 2.3) (similar selectivity has been reported for the borylation of toluene with $BCl_3/AlCl_3/Al$).[29]

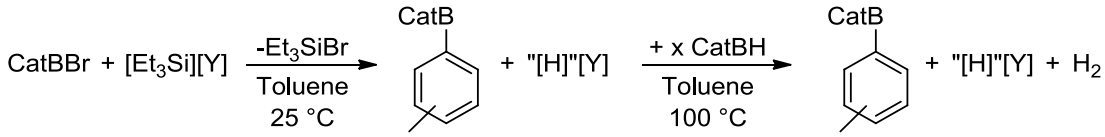


Eq. 8

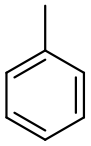


Eq. 9

Table 2.3 Catalytic (in Brønsted acid) borylation of toluene at 100 °C.



Y = [*ortho*-$CB_{11}H_6Br_6$]

Entry	Substrate	Equivalents of CatBH[a]	Time[b] (h)	Product Distribution[c]			
				CatBOH	CatB	CatB	CatB
1		10	15	0.4	0.4	53.0	46.2
2		20	36	0.4	0.6	53.0	46.0
3		50	84	8.9	0.7	32.4	58

[a] Number of equivalents of CatBH with respect to [Et_3Si][*closo*-$CB_{11}H_6Br_6$]. [b] Time for full conversion of CatBH. [c] Product distribution determined by GC and GC/MS

Meta- and *para*-xylene underwent arene borylation along with intra- and inter-molecular methyl migration leading to a mixture of phenyl-, tolyl-, xylyl- and mesityl-boronic esters (by GC/MS analysis). The reaction time and product

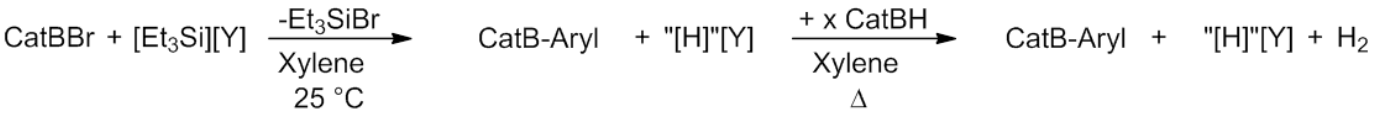
distribution were related to the temperature of reaction. Higher temperature reduced the reaction time, but led to an increase of products deriving from the methyl rearrangement (Table 2.4). It was noteworthy that both *meta*- and *para*-xylene gave as major product the 2-(3,5-dimethylphenyl)-1,3,2-benzodioxaborole boronic ester. This suggested that 2-(3,5-dimethylphenyl)-1,3,2-benzodioxaborole boronic ester was the more thermodynamically stable product. Furthermore, the predominant formation of borylated xylenes (> 80%) suggested that methyl migration was prevalently an intramolecular process as previously reported in studies of methyl rearrangement of xylenes by Brønsted acid.[30, 31]

The alkyl rearrangement was observed also in the borylation of ethylbenzene (Table 2.5). Ethylbenzene underwent a more extensive intermolecular alkyl migration than xylenes due to the formation of the secondary ethyl carbocation ($CH_3CH_2^+$) which was much more stable than the primary methyl carbocation (CH_3^+).

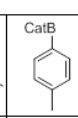
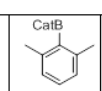
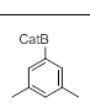
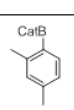
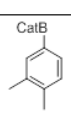
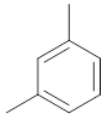
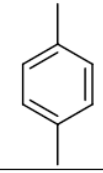
The different susceptibility of ethylbenzene and xylene to undergo intramolecular migration was also reported by Roberts and co-worker in the kinetic studies of alkyl rearrangement catalysed by triflic acid. At 25 °C, *ortho*- and *para*-xylene slowly isomerised to *meta*-xylene,[31] while ethyl benzene rapidly gave benzene and diethylbenzene.[32]

In the ethylbenzene borylation a compound with mass of 224.1 similar to CatB(PhEt) (PhEt = ethylphenyl), but with retention time not consistent with any of the products deriving from borylation on the aromatic ring, was revealed by GC/MS. Tentatively this product was assigned to CatB-CH_2CH_2-Ph. A plausible mechanism of its formation could involve the hydride abstraction on the ethyl group by a borocation, analogously to the reaction between *N*,*N*-diethylaniline and $B(C_6F_5)_3$.[33]

Table 2.4 Catalytic (in Brønsted acid) borylation of *para*- and *meta*-xylene.

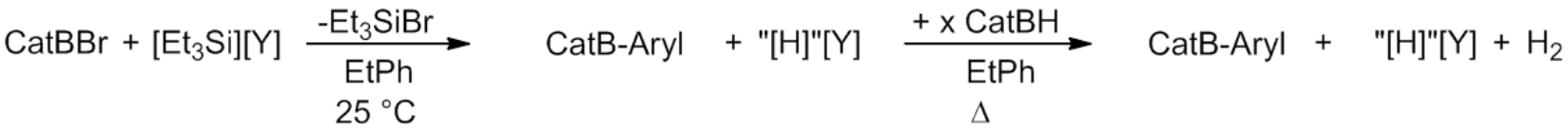


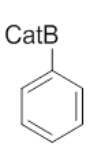
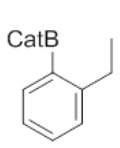
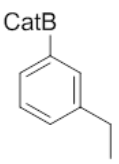
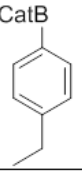
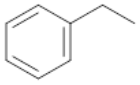
Y = [*ortho*-$CB_{11}H_6Br_6$]

Entry	Substrate	Equivalents of CatBH[a]	Temperature (°C)	Time[b] (h)	Product Distribution[c]										
					CatBOH					CatB(xylyl)	CatB(xylyl)				CatB(mesityl)[d]
1		10	100	96			0.7	0.5	19.7	0.4	0.3	67.9	0.9	9.1	0.7
2		10	145	24	0.2		4.2	2.8	17.8	1.3	2.3	41.7	5.2	20.7	3.8
3		20	145	14	1.2		4.1	2.4	13.3		0.7	42.5	1.0	26.1	8.8
4		10	100	120	4	1.2	15.7	11.5	10	0.7	0.7	39.1	3.6	6.3	7.2
5		20	145	40	0.7	0.6	17.6	12.5	8.6	0.5	0.7	30.1	0.1	16.9	11.7

[a] Number of equivalents of CatBH with respect to [Et_3Si][*closo*-$CB_{11}H_6Br_6$]. [b] Time for full conversion of CatBH. [c] Product distribution determined by GC and GC/MS. [d] Sum of products having molecular mass of 238.1 g mol^{-1}

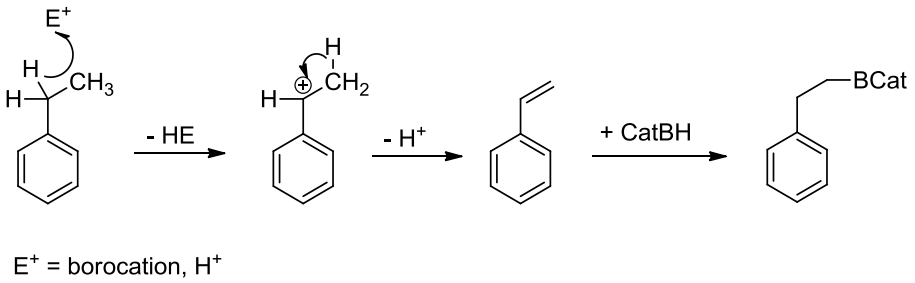
Table 2.5 Catalytic (in Brønsted acid) borylation of ethylbenzene.



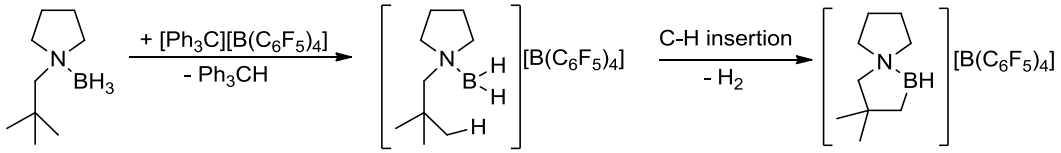
Substrate	Equivalents of CatBH[a]	Temperature (°C)	Time[b] (h)	Product Distribution[c]						
							CatB-Et-Ph		$CatB(Et_2Ph)$[d]	$CatB(Et_3Ph)$[e]
	20	100	120	9.6	16.6	8.7	6.8	4.6	36.4	17.1

[a] Number of equivalents of CatBH with respect to $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$. [b] Time for full conversion of CatBH. [c] Product distribution determined by GC and GC/MS. [d] Sum of products having molecular mass of 252.1 g mol^{-1}. [e] Sum of products having molecular mass of 280.2 g mol^{-1}.

Subsequently, the benzylic cation loses a proton giving styrene which undergoes hydroboration with CatBH (Scheme 2.4). An alternative mechanism to take in consideration is the direct aliphatic C-H insertion by a borocation, as recently reported by Vedejs in the nitrogen-directed aliphatic C-H borylation by borenium cation (Scheme 2.5).[34]



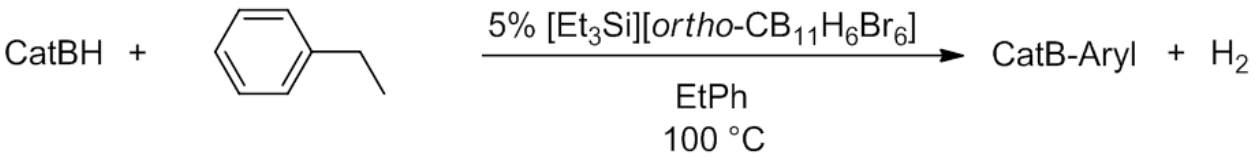
Scheme 2.4 Proposed mechanism of the formation of CatB-CH_2CH_2Ph via hydride abstraction.

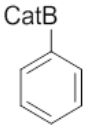
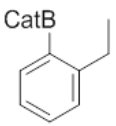
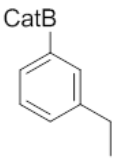
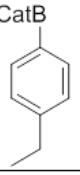
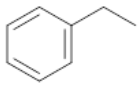


Scheme 2.5 Proposed mechanism of aliphatic C-H borylation via C-H insertion.

Ethylbenzene can also be borylated by the combination of [Et_3Si][*closo*-$CB_{11}H_6Br_6$] and CatBH without using CatBBr. Reaction between CatBH and catalytic quantities (5%) of [Et_3Si][*closo*-$CB_{11}H_6Br_6$] at 100 °C led to arene borylation with limited intermolecular ethyl rearrangement. The boron-containing products were mainly comprised of *meta*- and *para*-substituted ethylbenzene (Table 2.6). [Et_3Si][*closo*-$CB_{11}H_6Br_6$] was recovered at the end of the reaction (by recrystallisation) confirming that the silyl cation was the catalyst.

Table 2.6 Catalytic (in $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$) borylation of ethylbenzene.



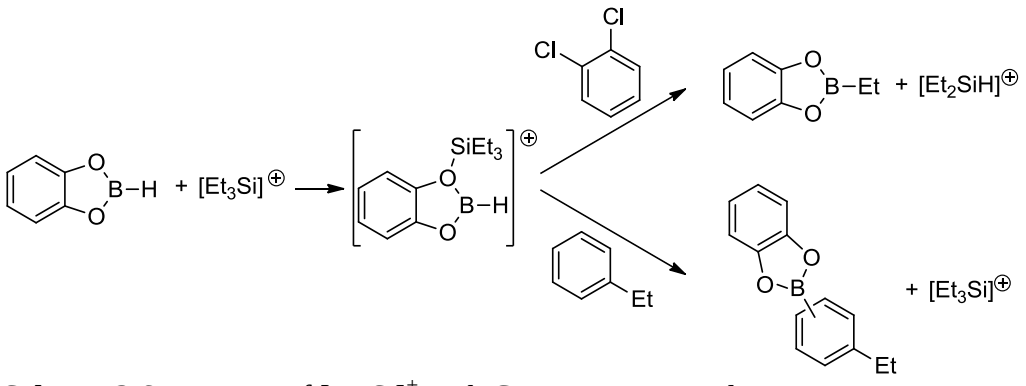
Substrate	Equivalents of CatBH[a]	Temperature (°C)	Time[b] (h)	Product Distribution[c]						
							CatB-Et-Ph		$CatB(Et_2Ph)^d$	$CatB(Et_3Ph)^e$
	20	100	44	1.9	2.4	47.4	0.5	39.1	5.9	3.0

[a] Number of equivalents of CatBH with respect to $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$. [b] Time for full conversion of CatBH. [c] Product distribution determined by GC and GC/MS. [d] Sum of products having molecular mass of 252.1 g mol^{-1}. [e] Sum of products having molecular mass of 280.2 g mol^{-1}.

Ingleson performing the reaction between $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ and CatBH in *ortho*-dichlorobenzene observed only a ligand redistribution reaction which generated CatBEt as the only new boron containing product.[12] The same reagent combination in toluene gave a mixture of boron-containing products arising from arene borylation (CatB(tolyl)) and ligand redistribution (CatBEt).

The reaction between $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$, CatBH and arene was thus sensitive to the nucleophilicity of the arene. The arene borylation reaction became favoured over ligand redistribution on increasing the nucleophilicity of the arene (*ortho*-dichlorobenzene < toluene < ethylbenzene).

The reaction of the silyl cation with CatBH possibly involves the coordination of the silyl cation to an oxygen of the catechol moiety increasing the electrophilicity of the boron centre. Then in the absence of a good nucleophilic arene this gives ligand redistribution, while in presence of ethylbenzene this leads to arene borylation (Scheme 2.6).



Scheme 2.6 Reaction of $[Et_3Si]^+$ with CatBH in arene solvent.

The $[Et_3Si]^+$ cation partnered with the $[closo\text{-}CB_{11}H_6Br_6]^-$ anion was able to generate a boron active species that borylates arenes. However, it is desirable from a cost perspective to seek a more economical anion than the carborane derivative.

2.4 Use of other Anions

TfO^-, which is a good leaving group and was considered a weakly coordinating anion (WCA) in the past,[35] was unsuccessfully tested by Ingleson as a counterion for the $[CatB]^+$ moiety in the arene borylation.[12] The absence of any arene borylation by CatB(OTf) with benzene was attributed to insufficient electrophilicity of the boron centre, as supported by the Lewis acidity studies. Hence, the use of a super-WCAs to achieve direct C-H arene borylation was essential.

Due to the importance of super-WCAs to achieve direct C-H arene borylation, the $[B(C_6F_5)_4]^-$ anion was tested. Combination of CatBBr and $[Et_3Si][B(C_6F_5)_4]$ (generated *in situ* from $[Ph_3C][B(C_6F_5)_4]$ and Et_3SiH)[36] in C_6D_6 at 20 °C yielded mainly borylated benzene along with small quantities of $B(C_6F_5)_3$ and $CatB(C_6F_5)$ (by independent synthesis) as the only boron-containing products (by ^{11}B NMR spectroscopy).

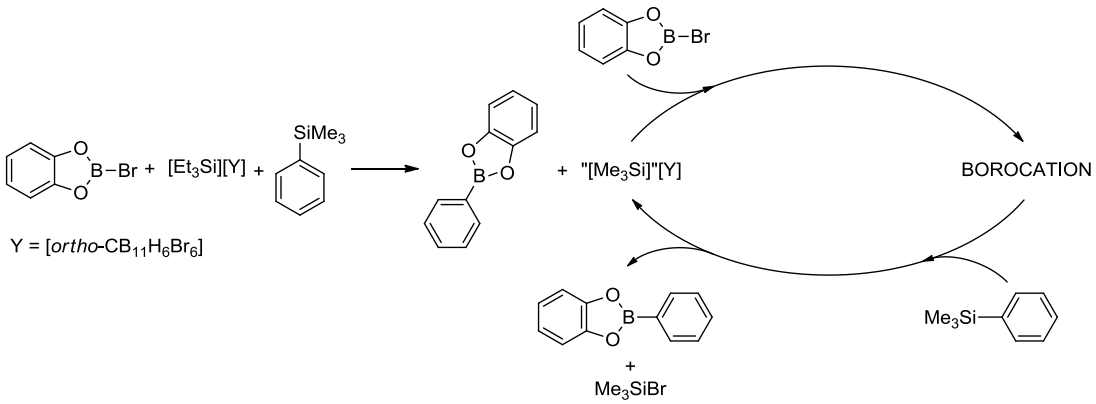
In order to determine the feasibility of the catalytic (in Brønsted acid) borylation ten equivalents of CatBH was added to this reaction mixture. After heating at 80 °C for 5 days the anion peak disappeared in ^{11}B NMR spectra, and the ^{19}F NMR spectra revealed mainly one C_6F_5 species consistent with $CatB(C_6F_5)$. Anion decomposition and $CatB(C_6F_5)$ formation can proceed similarly to the reported degradation of $[B(C_6F_5)_4]^-$ by a transient "$[R_2Al]^+$" cation.[37] Initial attack of a transient catecholboron cation to the borate anion leads to $CatB(C_6F_5)$ and $B(C_6F_5)_3$ (both species were observed in the stoichiometric arene borylation at 20 ^oC). Subsequently, $B(C_6F_5)_3$ degradation can involve either a transient catecholboron cation or the neutral CatBH (reaction of 2 equivalents of CatBH with 1 equivalent of $B(C_6F_5)_3$ in toluene at 110 °C yielded $CatB(C_6F_5)$ and $H_2B(C_6F_5)$).[12]

Altough the $[B(C_6F_5)_4]^-$ anion was weakly coordinating and enabled the

stoichiometric borylation of benzene with CatBBr, it was unstable at the high temperature required for the catalytic process. Therefore, the carborane anion [*closo*-$CB_{11}H_6Br_6]^-$ was the only anion possessing the necessary characteristics of robustness and stability to achieve the catalytic (in Brønsted acid) arene borylation.

2.5 Use of other boranes

In the reaction between CatBH and the Brønsted superacid by-product the limiting step was the formation of the active electrophile which required high temperature. This was indirectly confirmed by using ipso-directing[38] $PhSiMe_3$ as the arene reagent and CatBBr in place of CatBH. Catalytic borylation proceeded at 25 °C with a $[Me_3Si]^+$ leaving group (ligated by a weak nucleophile or anion coordinated), completing the cycle by reaction with CatBBr (Scheme 2.7). In control reactions CatBBr did not react with $PhSiMe_3$, in contrast to the more Lewis acidic BBr_3.[39]



Scheme 2.7 Proposed catalytic borylation of $PhSiMe_3$.

If the borylating species is a coordinated catecholborocation, solvent or anion coordinated, the substitution of the catecholboryl group with a better π donating groups will reduce the energy required for the hydride abstraction. This would allow the catalytic process to operate at lower temperature than with catecholborane.

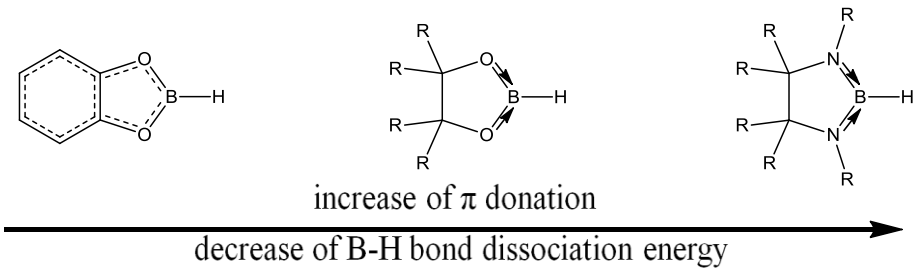


Figure 2.4

In pinacolborane (PinBH) the lone pair of the two oxygen atoms is delocalized only on the vacant p orbital of the boron atom, while in CatBH the lone pair of the oxygen atoms is partially delocalised into the aromatic ring as well (Figure 2.4).[9]

Attempts to carry out the Brønsted acid catalysed borylation by adding PinBH to the resulting mixture of stoichiometric borylation of toluene with CatBBr and $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ resulted in no borylation. After 2 hours the ^{11}B NMR spectrum revealed a significant quantity of a new product at 21.8 ppm consistent with a three coordinate boron centre bonded to three alkoxy ligands. Leaving the reaction for longer resulted in the decrease in intensity of all peaks, and a concomitant formation of insoluble materials. All PinBH was consumed after 12 hours at 20 °C, and the boron NMR spectrum showed only a very weak signal at 21.8 ppm.

The insoluble product was postulated to be polymeric materials arising from cationic initiated ring opening of pinacolborane, analogous to Lewis acid initiated THF ring opening.[40] To support a cationic ring opening mechanism a product deriving from pinacolborane ring opening was trapped by SMe_2. The reaction carried out with 1 equivalent of PinBH, prepared from pinacol and $BH_3{\cdot}SMe_2$, and 0.2 equivalents of $[Ph_3C][closo\text{-}CB_{11}H_6Br_6]$ in toluene at 100 °C resulted in formation of an orange oil and a small quantity of a colourless crystalline solid. X-ray crystallographic analysis of the crystalline solid revealed the formation of a (2,3-dimethylbutan-2-yl)dimethylsulfonium species ($[Me_2C(H)C(Me_2)SMe_2]^+$) (Figure

2.5).

A mechanism of $[Me_2C(H)C(Me_2)SMe_2]^+$ formation can be proposed involving a cationic attack on the oxo group of the pinacolyl moiety by either $[Ph_3C]^+$ or the borenium cation $[PinB•SMe_2]^+$ (deriving from the hydride abstraction reaction of $[Ph_3C][closo\text{-}CB_{11}H_6Br_6]$ with the adduct $PinBH·SMe_2$). Subsequent ring opening yields a tertiary carbocation which abstracts a hydride from Ph_3CH or $PinBH·SMe_2$ or pinacolborane. Successive cationic attack on the second oxo group and C-O bond cleavage leads to the 2,3-dimethylbutane-2-ylium cation which coordinates to SMe_2 yielding the product $[Me_2C(H)C(Me_2)SMe_2][closo\text{-}CB_{11}H_6Br_6]$ (Scheme 2.8).

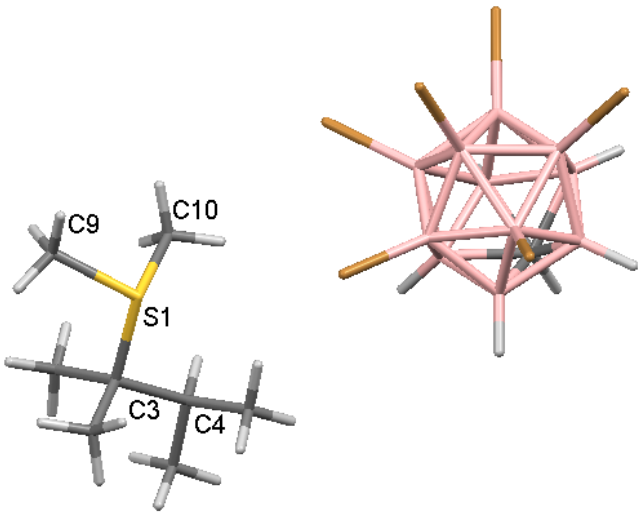
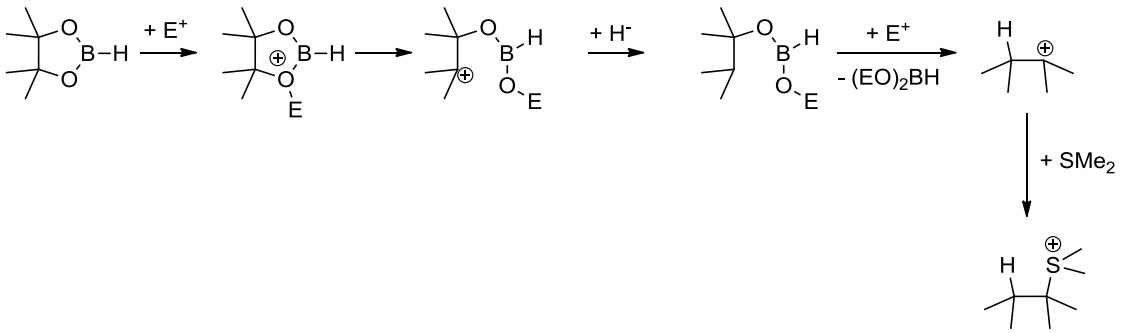


Figure 2.5 Crystal structure of $[Me_2C(H)C(Me_2)SMe_2][closo\text{-}CB_{11}H_6Br_6]$. Selected bond lengths (Å): C(3)-S(1) = 1.86(1), C(9)-S(1) = 1.83(1), C(10)-S(1) = 1.75(1).

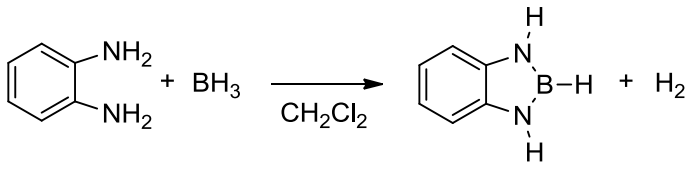


Scheme 2.8 Proposed mechanism of the formation of 2,3-dimethylbutane-2-ylium cation.

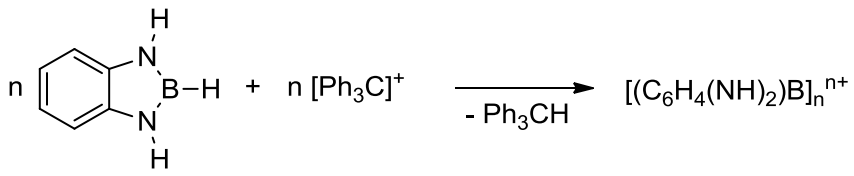
Analogous to pinacolborane, addition of 5,5-diethyl-1,3,2-dioxaborinane to the mixture resulting from the stoichiometric reaction between CatBBr and $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ yielded insoluble materials.

Failure to borylate arenes with pinacolborane and 5,5-diethyl-1,3,2-dioxaborinane can be ascribed to the susceptibility of the intermediate borenium cation to rearrange to a tertiary or primary carbocation. Consequently, to prevent the ring opening side reaction substituents such as phenylic and vinylic groups, which do not give stable carbocations, are required on the atom directly bonded to boron.

The diaza analogue of catecholborane, $(C_6H_4(NH)_2)BH$ **2**, was synthesised from *ortho*-diaminobenzene and BH_3 following the reported procedure (Eq. 10).[41] The diazaborole **2** in combination with $[Ph_3C][closo\text{-}CB_{11}H_6Br_6]$ gave insoluble materials. The formation of Ph_3CH suggested hydride abstraction and borocation formation, but no arene borylation was observed. The lack of borylation by any generated borocation may be due to rapid formation of insoluble oligomeric amine-bridged cationic species $[(C_6H_4(NH)_2)B]_n^{n+}$ (Eq. 11), as previously proposed by Parry and co-worker for the diaminoboron cation $[(R_2N)B]^+$ (Figure 2.6).[42]



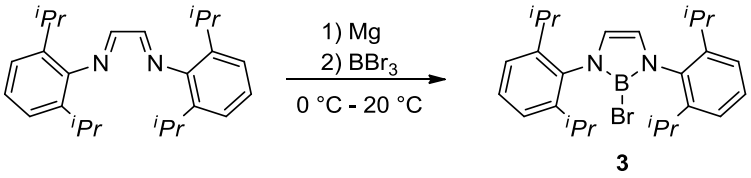
Eq. 10



Eq. 11

Figure 2.6 Proposed amine-bridged borocations.

To preclude the formation of amide bridged borocation oligomers *N,N'*-(2,6-diisopropylphenyl)-1-bromo-1,3,2-diazaborolane **3** was synthesised following the procedure of Nozaki and co-workers (Eq. 12).[43] Isopropyl groups on the aromatic ring create steric hindrance around the nitrogen atom precluding the approach of cationic species to the nitrogen atom (Figure 2.7).[44]



Eq. 12

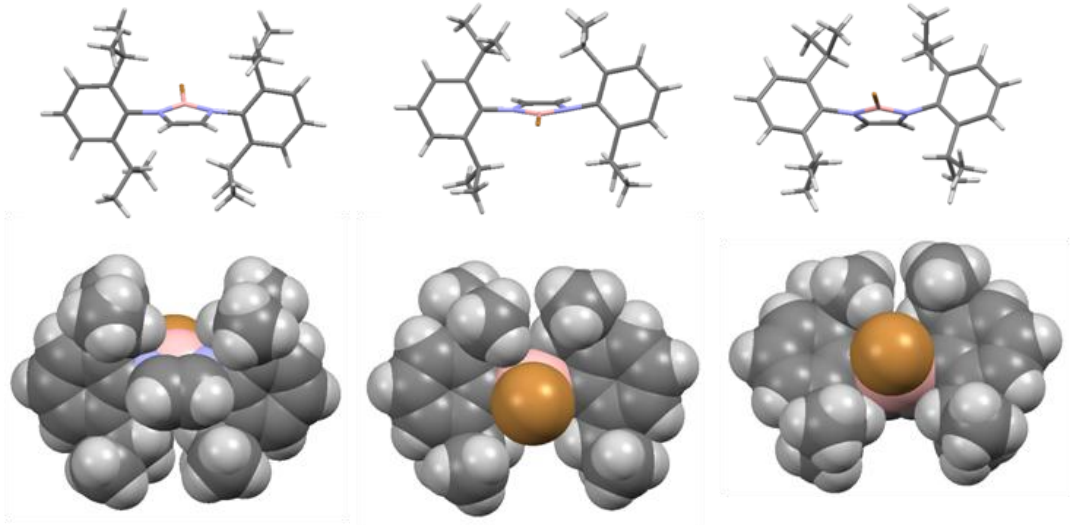
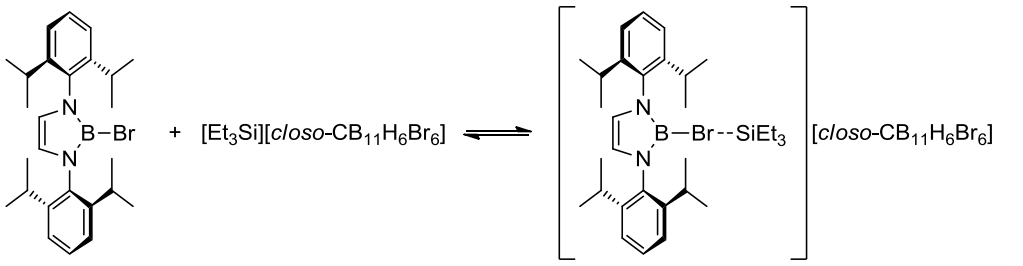


Figure 2.7 (Top) Capped-stick representation of the crystal structure of **3**. (Bottom) Van Der Waals representation of the crystal structure of **3**.

3 in presence of $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ led to a broadening of the ^1H NMR resonances of the borane compound, suggesting a fluxional process (Eq. 13).

However, attempts to reach the slow-exchange regime failed to -40 °C in 1/1 d_8-toluene/*ortho*-dichlorobenzene (*ortho*-dichlorobenzene was used to enhance the solubility of the ionic species at low temperature). The broadening of proton resonances was attributed to an interaction between the bromine atom and the silyl cation analogous to that observed for halide-bridge $R_3Si\text{-}X\text{-}SiR_3$ cations.[44] Attempts to borylate toluene and benzene with the combination of **3** and $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ were unsuccessful even at raised temperature.



Eq. 13

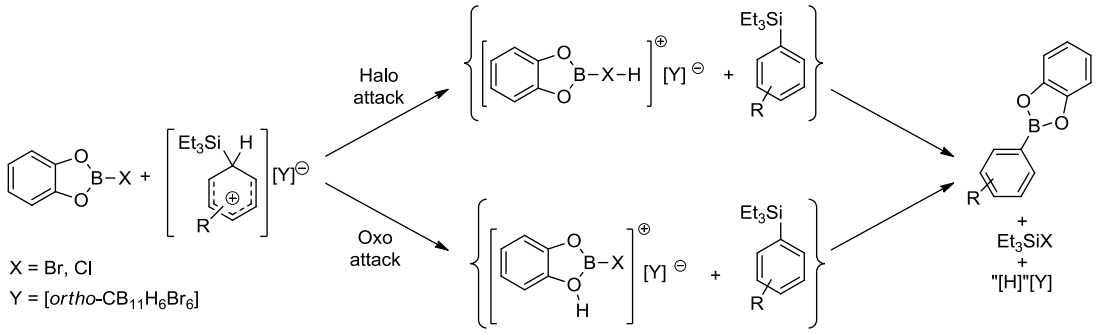
This last result revealed that $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ was unable to abstract halide to form a boron cation when the boron centre was shielded. Consequently, in the arene borylation with CatBBr and $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ the formation of a dicoordinated boron cation anion-coordinated can be ruled out. This leads us to postulate different electrophilic boron species and an alternative mechanism of reaction as discussed below.

2.6 Mechanistic consideration

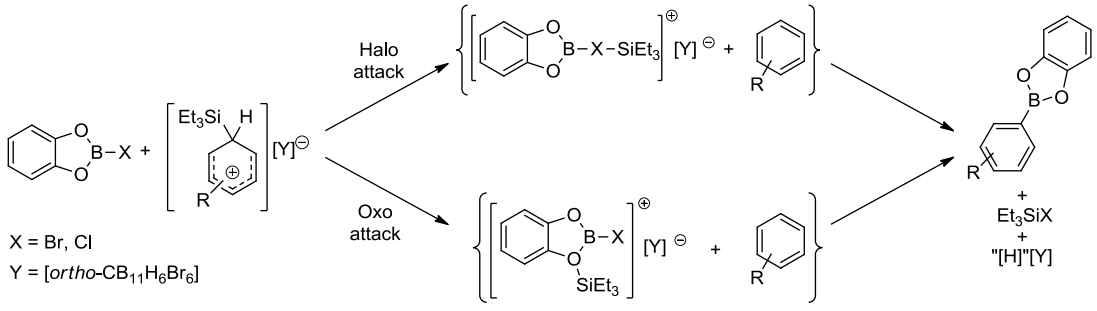
In arene solvent $[Et_3Si]^+$ when partnered with WCAs as $[closo\text{-}CB_{11}H_6Br_6]^-$ and $[B(C_6F_5)_4]^-$ exists as solvent coordinated $[Et_3Si(arene)]^+$.[23] Addition of CatBX (X = Br, Cl), which bears weakly basic/nucleophilic oxygen and halogen centres, to $[Et_3Si(arene)]^+$ can give proton abstraction (from the arene) or nucleophilic attack to silicon centre.

Proton abstraction from $[Et_3Si(arene)]^+$ by CatBX would give an oxo- or halo-

protonated CatBX and Aryl-$SiEt_3$. Subsequent transmetallation of silyl-arene by the borenium species (oxo- or halo-protonated CatBX) would give the catecholboryl-arene product (Scheme 2.9 top). Instead, nucleophilic attack to silicon centre would lead to arene displacement and formation of a silyl cation complex with CatBX. Coordination of $[Et_3Si]^+$ either to halogen (to form a halide-bridged species analogous to the reported species $[Et_3Si\text{-}X\text{-}SiEt_3]^+$)[45] or to the oxygen atom would lead to a borenium cation (Scheme 2.9 bottom). This borenium cation has enhanced electrophilicity on the boron centre and it would be able to react with arenes.



a) deprotonation pathway



a) desilylation pathway

Scheme 2.9 Proposed mechanisms of reaction of CatBX with $[Et_3Si\bullet arene][closo\text{-}CB_{11}H_6Br_6]$. (*Top*) Deprotonation pathway. (*Bottom*) Desilylation pathway.

The proton abstraction from $[Et_3Si(arene)]^+$ was rare and it was reported only in presence of a suitable amine as base.[46,47] Nucleophile attack at silicon (desilylation

reaction) was the preferred pathway of reaction of $[Et_3Si(arene)]^+$ with nucleophiles specially with oxygen or halogen-containing nucleophiles.[47] Therefore, it was more plausible that the arene borylation proceeds via desilylation by CatBX and formation of a borenium cation $[Et_3Si{\bullet}CatBX]^+$.

In an attempt to detect the active electrophilic species and/or any intermediate, low temperature NMR studies were carried out. Following, by ^{11}B NMR, the reaction of CatBBr with $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ in d_8-toluene from -40 ºC to 0 ºC no reaction was observed until -10 ºC. At this temperature the reaction mixture yielded CatB(d_7-tolyl) without any detectable intermediate (Figure 2.8).

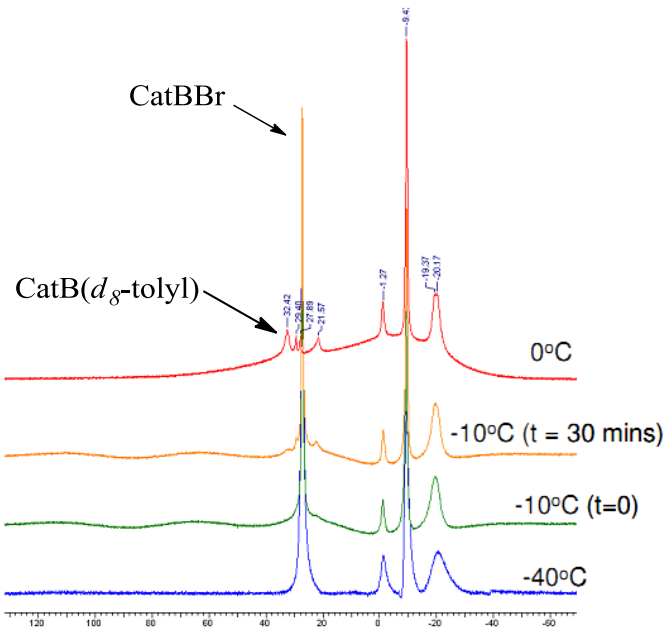
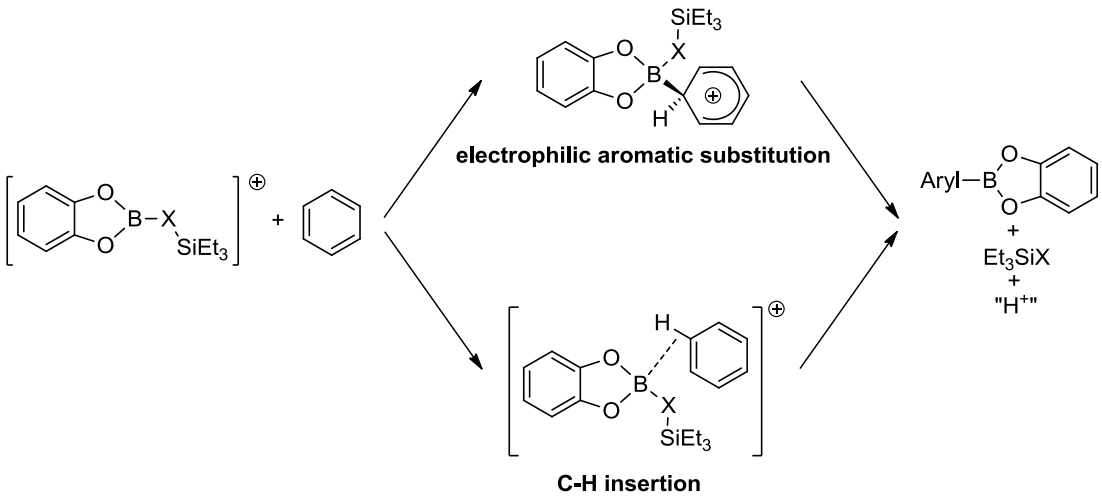


Figure 2.8 ^{11}B NMR of the reaction between CatBBr and $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ in d_8-toluene at different temperature. Resonances between 0 and -25 ppm are due to the anion.

The absence of any detectable intermediates did not permit any definitive conclusion. However, the lack of arene borylation at 20 °C with CatBH and $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ contradicted the idea that the borenium cation formed by coordination of the silylium cation to oxygen of the catechol moiety was the active

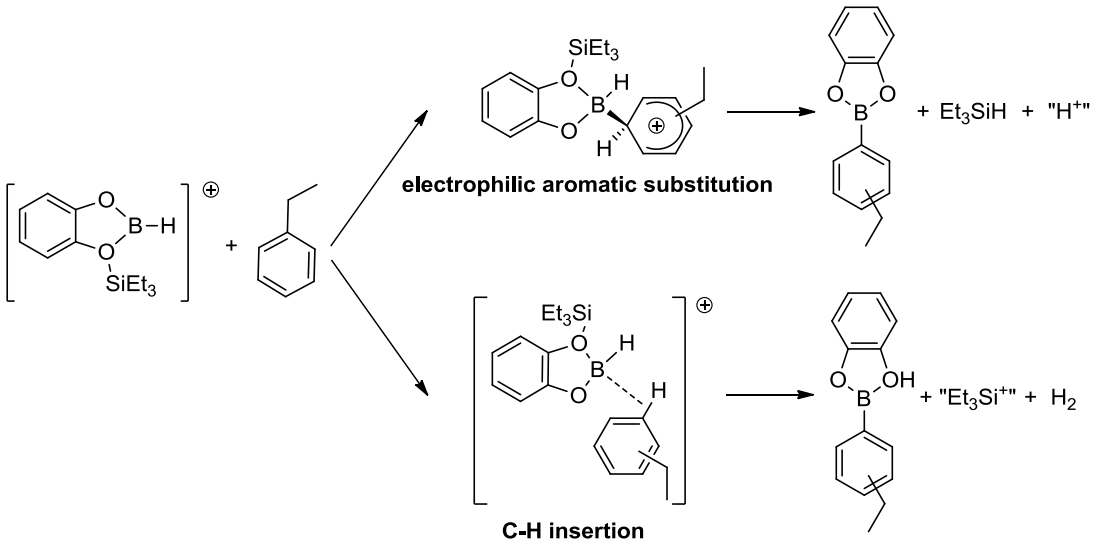
borylating species in the stoichiometric arene borylation with CatBX (coordination of Et_3Si^+ to oxygen in CatBH would be expected to produce a stronger boron electrophile than the respective Et_3Si^+ adduct of CatBX, due to the stabilizing effect of halide π-donation to boron in the latter). Hence, a feasible pathway of arene borylation with the combination of CatBX and [Et_3Si][*closo*-$CB_{11}H_6Br_6$] would be via initial formation of the cationic halide-bridge species [CatB-X-$SiEt_3$]$^+$.

The reaction of the transient borenium cation, generated by cationic attack on CatBX, with arene can proceed via electrophilic aromatic substitution or via C-H insertion (Scheme 2.10). The latter mechanism has been proposed by Vedejs and co-worker in the intramolecular borylation of benzylamine derivatives by a borenium cation. Calculations have shown that electrophilic aromatic borylation, in absence of a good base for proton abstraction from the Wheland intermediate (σ-complex), is a very slow process. Consequently, the C-H insertion pathway becomes a feasible mechanism of reaction.



Scheme 2.10 Proposed mechanism of reaction between borenium cation and arene.

In the direct C-H arene borylation with CatBX and $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ at 20 °C it is not possible to distinguish between electrophilic aromatic substitution and C-H insertion patway since in both the cases the expected reaction by-products are Et_3SiX and "H^+" (Scheme 2.10). Instead, in the ethylbenzene borylation with CatBH and $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ at 100 °C the two different mechanisms of reaction would produce different by-products. The arene borylation via electrophilic aromatic substitution would produce Et_3SiX and "H^+" as by-products while the arene borylation via C-H insertion would produce H_2 (Scheme 2.11). The lack of pervasive alkyl migration in the ethylbenzene borylation with CatBH and $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ at 100 °C (Table 2.6) suggests that "H^+" is not produced. Therefore, this rection possibly proceeds by a C-H insertion mechanism.



Scheme 2.11 Possible reaction pathways for the ethylbenzene borylation with CatBH and $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$.

2.7 Conclusions

The $[CatB]^+$ moiety partnered with the super-WCAs $[closo\text{-}CB_{11}H_6Br_6]^-$ and $[B(C_6F_5)_4]^-$ was shown to be strongly Lewis acidic on the basis of ^1H and $^{31}P\{^1H\}$ NMR spectroscopy of the crotonaldehyde and triethylphosphine oxide adducts,

respectively. CatBX (X = Cl, Br) in the presence of $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$ gave a transient borenium cation able to borylate arenes at low temperature. A by-product of the reaction was a Brønsted superacid that at high temperature was effective to catalyse the reaction between CatBH and arenes. This new catalytic route to aryl boronic esters proceeds in one step, from the arene and CatBH, atom efficiently with H_2 as the only by-product. Successful catalysis was dependent on the robust $[closo\text{-}CB_{11}H_6Br_6]^-$ anion and the use of the electrophile-resistant borane sources.

Experimental section

General Methods: 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 before use. Benzene and d_6-benzene were dried over Na/benzophenone and distilled under vacuum. Toluene, xylenes, mesitilene, d_2-dichloromethane were dried over calcium hydride and distilled under vacuum. All solvents are degassed and stored over molecular sieves (3Å) under inert atmosphere or in the glovebox. Catecholborane was distilled under reduced pressure. Trialkylsilanes were dried over CaH_2 and distilled under vacuum. $Et_3P{=}O$ was purified by sublimation and stored in the glovebox. All other materials were purchased from commercial vendors and used as received. $[Ph_3C][$*closo*-$CB_{11}H_6Br_6]$ and $Ag[$*closo*-$CB_{11}H_6Br_6]$ were prepared according to the literature procedures.[48, 49] NMR spectra were recorded with a Bruker AV-400 spectrometer (400 MHz ^1H; 100 MHZ ^{13}C; 128 MHz ^{11}B; 162 MHz ^{31}P; 62 MHz, ^{19}F 376.5 MHz, ^{27}Al 104.3 MHz, ^{29}Si 79.5 MHz). ^1H NMR chemical shifts are reported in ppm relative to protio impurities in the deuterated solvents and ^{13}C NMR using the centre line of C_6D_6 (or other solvent as appropriate) triplet as internal standard. ^{11}B NMR spectra were referenced to external $BF_3{:}Et_2O$, ^{31}P to H_3PO_4, ^{19}F to Cl_3CF, ^{29}Si to TMS and ^{27}Al to $Al(NO_3)_2$ in D_2O ($Al(H_2O)_6^{3+}$). GC spectra were recorded on a Dani master GC with Flame Ionisation Detector. Helium was used as a carrier gas. The following was the typical temperature program for analyzing the products using the VF-1MS column: Initial temperature: 70 °C, hold temperature for 2 min, increase temperature at a rate: 10 °C/min until temperature: 150 °C, then increase temperature at a rate: 5 °C/min until final temperature: 250 °C

In the $^{13}C\{^1H\}$ NMR the ipso carbon of aryl boronic esters (C directly bound to

quadrupolar B) is consistently not observed.

Synthesis of [CatB(O=PEt$_3$)][*closo*-CB$_{11}$H$_6$Br$_6$]:

In a J. Youngs tube, under inert atmosphere, CatBBr (8 mg, 0.040 mmol) was added to a solution of Et$_3$P=O (5 mg, 0.037 mmol) in CD_2Cl_2 (0.8 ml) and the solution was shaken. Then Ag[*closo*-CB$_{11}$H$_6$Br$_6$] (30 mg, 0.041 µmol) was added as a solid to this solution that was shaken in the dark resulting in the rapid precipitation of a white solid. Filtration and subsequent crystallization from dichloromethane/hexane layer by slow diffusion yielded colourless crystal suitable for X-ray analysis.

^{1}H NMR (CD_2Cl_2): δ 7.15-7.08 (m, 2H), 7.07-7.00 (m, 2H), 2.61 (dq, J_{HP}=10.85 Hz, J_{HH}= 7.57 Hz, 6H), 1.26 (dt, J_{HP}=20.18 Hz, J_{HH}= 7.57 Hz, 9H).

^{11}B NMR (CD_2Cl_2): δ 21.9 (br s), -1.8 (s, 1B), -9.9 (s, 5B), 20.3 (d, J_{BH}= 162.0 Hz, 5B).

^{31}P NMR (CD_2Cl_2): δ 106.89

Mass spectrometry: Attempts to observe the molecular ion [CatB(OPEt$_3$)]$^+$ failed. Instead what was continually observed was the product from addition of H_2O to this species (presumably forming a B-OH species);

Expected for [CatB(OH)(OPEt$_3$)]-H$^+$: 271.13, Found 271.1 m/z.

Synthesis of [CatB(O=PEt$_3$)$_2$][*closo*-CB$_{11}$H$_6$Br$_6$]:

In a J. Young's NMR tube, under inert atmosphere, CatBBr (8 mg, 0.040 mmol) was added to a solution of Et$_3$P=O (17 mgs, 0.126 mmol) in CD_2Cl_2 (1 ml) and the solution was shaken for 45 min. Then Ag[*closo*-CB$_{11}$H$_6$Br$_6$] (30 mg, 41 µmol) was added to this solution resulting in a rapid precipitation of a white solid.

^{1}H NMR (CD_2Cl_2): δ 6.75 (s, 4H), 2.08 (dq, J_{HP}=12.11 Hz J_{HH}= 7.57 Hz, 12H), 1.26

(dt, J_{HP}=18.66 Hz J_{HH}= 7.57 Hz, 18H).

^{11}B NMR (CD_2Cl_2): δ 7.0 (s, 1B), -1.8 (s, 1B), -9.9 (s, 5B), 20.3 (d, J_{BH}= 162.0 Hz, 5B).

^{31}P NMR (CD_2Cl_2): δ 83.89.

Direct reaction between [Ph_3C][*closo*-$CB_{11}H_6Br_6$] with catecholborane:

In a J. Youngs NMR tube, under inert atmosphere, [Ph_3C][*closo*-$CB_{11}H_6Br_6$] (20 mg, 0.023 mmol) was suspended in toluene (1 ml) and CatBH (2.5 µl, 23 µmol) was added. The NMR tube was sealed and heated at 100 °C. The reaction was monitored periodically by ^{11}B NMR. Time for complete consumption of CatBH: 4 days yielding predominantly PhBCat, with a small impurity of CatBOH.

Stoichiometric Borylation of Benzene [Ph_3C][*closo*-$CB_{11}H_6Br_6$]/Et_3SiH/CatBBr 1:1:1:

In a J. Youngs NMR tube, under inert atmosphere, [Ph_3C][*closo*-$CB_{11}H_6Br_6$] (25 mg, 0.029 mmol) was suspended in C_6D_6 (0.8 ml), triethylsilane (4.5 µl, 0.029 mmol) was added and the reaction mixture was shaken until the yellow solution became colorless and homogeneous. Then CatBBr (6 mg, 0.029 mmol) was added as a solid and the reaction mixture was shaken resulting in a rapid colour change to orange.

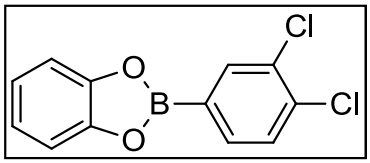
^{11}B NMR (C_6D_6): 32.7 (s), 28.9 (d), 22.6 (s), -0.91 (s), -9.14 (s), -19.64 (d).

General Procedure for Catalytic Borylation of Arenes:

In a Schlenk tube fitted with a J. Youngs tap, [Ph_3C][*closo*-$CB_{11}H_6Br_6$] (25 mg, 0.029 mmol) was suspended/partially dissolved in arene solvent (1 ml), Et_3SiH (4.5 µl, 0.029 mmol) was added and the mixture was stirred for 30 minutes. Then CatBBr

(6 mg, 0.029 mmol) was added and stirred for 5 minutes before to add CatBH (31µl, 0.29 mmol). The Schlenk tube was sealed and heated with stirring. When the reaction was finished (judged by full consumption of CatBH by ^{11}B NMR) the mixture was cooled at room temperature and anhydrous hexane (20 ml) was added. The solution was filtered and dried *in vacuo* yielding a white solid. The products were identified by NMR and/or GC or GC/MS.

2-(3,4-Dichlorophenyl)benzo[1,3,2]dioxaborole:



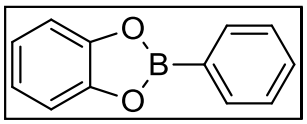
^{1}H NMR ($CDCl_3$): δ 8.15 (d, *J* = 1.5 Hz, 1H), 7.90 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.30-7.35 (m, 2H), 7.14-7.19 (m, 2H).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.2, 136.9, 136.6, 133.8, 132.9, 130.6, 123.1, 112.7.

^{11}B NMR ($CDCl_3$): δ 31.5.

Independent preparation of 2-Aryl-1,3,2-benzodioxaborole for GC comparison: Following a published procedure,[50] catechol (1 equivalent) and $MgSO_4$ were added to a stirred suspension of the respective arylboronic acid ($ArB(OH)_2$) in toluene. The mixture was stirred for 24 h at 20 °C and filtered. The solution was dried *in-vacuo* to afford the product as white solid. These were analytically pure, by microanalysis, NMR spectroscopy and GC analysis.

2-Phenyl-1,3,2-benzodioxaborole:



^{1}H NMR spectrum agrees with those previously published.[49]

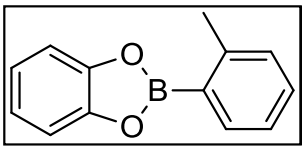
^{1}H NMR ($CDCl_3$): δ 7.14 (dd, *J* = 4.3, 7.7 Hz, 2 H), 7.32 (dd, *J* = 4.3, 7.7 Hz, 2 H), 7.46-7.62 (m, 3H), 8.09 (d, *J* = 8.3 Hz, 2 H).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.5, 135.0, 132.3, 128.2, 122.7, 112.5.

^{11}B NMR ($CDCl_3$): δ 32.6.

Anal. Calcd for $C_{12}H_9BO_2$: C, 73.53; H, 4.63. Found: C, 73.53, H, 4.57.

2-(2-Methylphenyl)-1,3,2-benzodioxaborole:



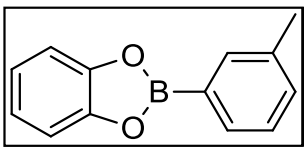
^{1}H NMR ($CDCl_3$): δ 8.90 (d, *J* = 7.3 Hz, 1H), 7.42 (m, 1H), 7.33-7.23 (m, 4H), 7.13-7.80 (m, 2H), 2.72 (s, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.4, 145.5 136.6, 132.1, 130.3, 125.2, 122.7, 112.5, 22.4.

^{11}B NMR ($CDCl_3$): δ 32.4.

Anal. Calcd for $C_{13}H_{11}BO_2$: C, 74.34; H, 5.28. Found: C, 74.28, H, 5.23.

2-(3-Methylphenyl)-1,3,2-benzodioxaborole:



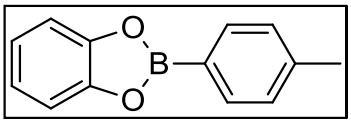
^{1}H NMR ($CDCl_3$): δ 7.84-7.98 (m, 2H) 7.37-7.46 (m, 2H), 7.28-7.36 (m, 2H), 7.06-7.19 (m, 2H), 2.45 (s, 3H).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 148.5, 137.7, 135.6, 133.2, 128.2, 122.7, 112.5, 21.3.

^{11}B NMR ($CDCl_3$): δ 32.2.

Anal. Calcd for $C_{13}H_{11}BO_2$: C, 74.34; H, 5.28. Found: C, 74.28, H, 5.23.

2-(4-Methylphenyl)-1,3,2-benzodioxaborole:



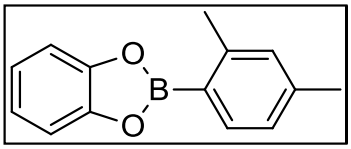
^{1}H NMR ($CDCl_3$): δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 4H), 7.12-7.05 (m, 2H) 2,39 (s, 3H)

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 148.5, 142.7, 135.0, 129.0, 122.6, 112.4, 21.9.

^{11}B NMR ($CDCl_3$): δ 32.2.

Anal. Calcd for $C_{13}H_{11}BO_2$: C, 74.34; H, 5.28. Found: C, 74.14; H, 5.21.

2-(2,4-dimethylphenyl)-1,3,2-benzodioxaborole:



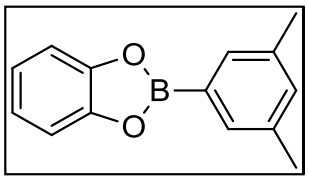
^{1}H NMR ($CDCl_3$): δ 7.98 (d, *J* = 7.82 Hz, 1H), 7.26-7.31 (m, 2H), 7.06-7.11 (m, 4H), 2.67 (s, 3H), 2.36 (s, 3H).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 148.4, 145.5, 136.7, 131.2, 126.0, 125.2, 122.6, 112.4, 22.3, 21.6.

^{1}B NMR ($CDCl_3$): δ 32,3.

Anal. Calcd. $C_{14}H_{13}BO_2$ C: 75.04 H: 5.85 Found C: 74.81 H: 5.87.

2-(3,5-dimethylphenyl)-1,3,2-benzodioxaborole:



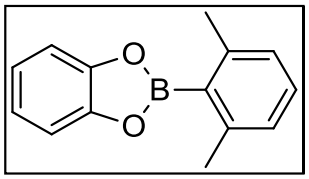
^{1}H NMR ($CDCl_3$): δ 7.68 (s, 2H), 7.25-7.31 (m, 2H), 7.18 (s, 1H), 7.06-7.12 (m, 2H), 2.36 (s, 6H).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.4, 145.5 137.6, 132.6, 122.7, 112.5, 21.2.

^{11}B NMR ($CDCl_3$): δ 32.3.

Anal. Calcd for $C_{14}H_{13}BO_2$ C: 75.04, H 5.85. Found C = 74.7, H = 6.00.

2-(2,6-dimethylphenyl)-1,3,2-benzodioxaborole:



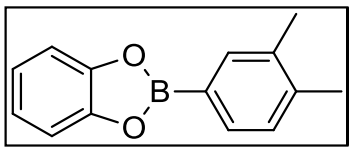
^{1}H NMR ($CDCl_3$): δ 7.30-7.35 (m, 2H), 7.23-7.29 (m, 1H), 7.11-7.17 (m, 2H), 7.08 (d, *J* =7.57 Hz, 2H), 2.53 (s, 6H).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.1, 144.2, 130.7, 127.2, 122.7, 112.6, 23.0.

^{11}B NMR ($CDCl_3$): δ 33.1.

Anal Calcd. For $C_{14}H_{13}BO_2$ C: 75.04, H: 5.85. Found C = 74.3, H = 5.99.

2-(3,4-dimethylphenyl)-1,3,2-benzodioxaborole:



^{1}H NMR ($CDCl_3$): δ 7.82 (s, 1H), 7.79 (d, *J* = 7.57 Hz, 1H), 7.24-7.29 (m, 2H), 7.22 (d, *J* = 7.57 Hz, 1H), 7.05-7.10 (m, 2H), 2.30 (s, 3H), 2.29 (s, 3H).

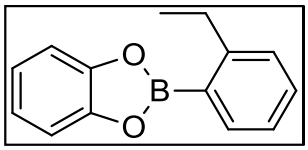
^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.5, 141.5, 136.4, 136.1, 132.6, 129.6, 122.6, 112.4,

20.1, 19.6.

^{11}B NMR ($CDCl_3$): δ 32.2.

Anal Calcd. For $C_{14}H_{13}BO_2$ C: 75.04, H: 5.85. Found C: 74.50, H: 5.97.

2-(2-ethylphenyl)-1,3,2-benzodioxaborole:



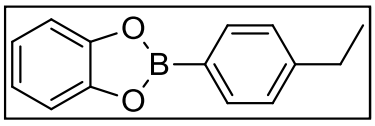
^{1}H NMR ($CDCl_3$): δ 8.12 (dd *J* = 7.6, 1.3 Hz, 1H), 7.49 (ddd, *J* = 7.6, 7.3, 1.5 Hz, 1H), 7.35-7.29 (m, 4H), 7.17 – 7.10 (m, 2H), 3.11 (q, 2H, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.1, 148.4, 136.8, 132.3, 128.9, 125.3, 122.7, 112.5, 29.0, 16.9.

^{11}B NMR ($CDCl_3$): δ 32.5.

Anal Calcd. For $C_{14}H_{13}BO_2$ C: 75.05, H 5.85. Found C: 74.02, H: 5.95.

2-(4-ethylphenyl)-1,3,2-benzodioxaborole:



^{1}H NMR ($CDCl_3$): δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.36-7.28 (m, 4H), 7.14 – 7.09 (m, 2H), 2.72 (q, *J* = 7.57 Hz, 2H), 1.28 (t, *J* = 7.57 Hz, 3H) .

^{13}C{^{1}H} NMR ($CDCl_3$): δ 149.0, 148.5, 135.1, 127.9, 122.7, 112.5, 29.2, 15.3.

^{11}B NMR ($CDCl_3$): δ 32.2.

Anal Calcd. For $C_{14}H_{13}BO_2$ C: 75.05, H 5.85. Found C: 73.84 H: 5.85.

Borylation of ethylbenzene with CatBH catalysed by [Et_3Si][*closo*-$CB_{11}H_6Br_6$]:

In a Schlenk tube fitted with a J. Youngs tap, under inert atmosphere, [Ph_3C][*closo*-$CB_{11}H_6Br_6$] (25 mg, 0.029 mmol) was suspended/partially dissolved in ethylbenzene (1 ml), Et_3SiH (4.5 µl, 0.029 mmol) was added and the mixture was stirred for 30 minutes. Then, CatBH (60 µl, 0.58 mmol) was added. The Schlenk tube was sealed and heated at 100 °C with stirring. When the reaction was finished (judged by full consumption of CatBH by ^{11}B NMR) the mixture was cooled at room temperature and anhydrous hexane (20 ml) was added. The solution was filtered and dried *in vacuo* yielding a white solid. The products were identified by GC/MS.

Attempted Catalytic Borylation of Toluene in presence of 2,6-di-*tert*-butylpyridine:

In a J. Youngs NMR tube, under inert atmosphere, [Ph_3C][*closo*-$CB_{11}H_6Br_6$] (20 mg, 0.023 mmol) was suspended in toluene, triethylsilane (4 µl, 0.023 mmol) was added and the reaction mixture was shaken until the yellow suspension/solution became colorless and homogeneous. Then, CatBBr (6 mg, 0.029 mmol) followed by shaking for 1 minute prior the addition of CatBH (31µl, 0.029 mmol) and 2,6-di-*tert*-butylpyridine (5 µl, 0.023 mmol) were added and the reaction mixture was heated at 100 ºC. The reaction was monitored by ^{11}B NMR. After 48 h no catalysis was observed.

Attempts to isolate [Et_3Si][*closo*-$CB_{11}H_6Br_6$]:

Into to glovebox in a vial [Ph_3C][*closo*-$CB_{11}H_6Br_6$] (25 mg, 29 µmol) was suspended/partially dissolved in toluene (1 ml), Et_3SiH (4.5 µl, 29 µmol) was added and the mixture was stirred until all the [Ph_3C][*closo*-$CB_{11}H_6Br_6$] dissolved. Hexane

(5 ml) was added resulting in the precipitation of a white solid. The solution was removed by Pasteur pipette and the white solid turned orange. The attempt to conduct the reaction of borylation dissolving the orange solid in toluene (1 ml) and adding CatBBr (6 mgs, 29 μmol) was unsuccessful.

Stoichiometric reaction between $[Ph_3C][B(C_6F_5)_4]$, Et_3SiH and CatBBr:

In a J. Youngs NMR tube, under inert atmosphere, $[Ph_3C][B(C_6F_5)_4]$ (30 mg, 0.032 mmol) was suspended in C_6D_6 (0.7 ml). Then Et_3SiH (5μl, 0.031 mmol) was added by microlitre syringe, the tube was sealed and the mixture was shaken until all $[Ph_3C][B(C_6F_5)_4]$ was dissolved. To the colourless solution with a colourless oil CatBBr (6.5 mg, 0.032 mmol) was added resulting in an immediate colour change of the solution to orange and the formation of an orange oil. ^{11}B NMR spectroscopy showed the formation of CatB(Ph) with small quantities of CatBOH, of anion decomposition products and an unidentified product at 43.3 ppm.

^{11}B NMR (C_6D_6): δ 61.2, 43.3, 32.8, 22.4, -16.0.

Attempt of the Catalytic Borylation with $[B(C_6F_5)_4]^-$ as anion:

To $[Ph_3C][B(C_6F_5)_4]/Et_3SiH$/CatBBr mixture in C_6D_6 was added 10 equivalents of CatBH and the solution was heated at reflux. ^{11}B NMR spectrum after 5 days at reflux showed no significant quantities of Ph-BCat produced and nearly complete consumption of $[B(C_6F_5)_4]^-$. $^{19}F\{^1H\}$ NMR spectrum showed one major C_6F_5 containing species which is assignable as $CatB(C_6F_5)$.

Synthesis of $CatB(C_6F_5)$:

$B(C_6F_5)_3$ (50 mg, 0.06 mmol) was loaded into a Schlenk tube fitted with a J.Youngs

tap, 5 ml of toluene and 2 equivalents of CatBH (20 µl, 0.12 mmol) were added. The Schlenk tube was sealed and refluxed for 5 hours. The volatile products were removed *in-vacuo* yielding a white solid. Yield (based on CatB-H) = 75 %.

^{1}H NMR (C_6D_6): δ 7.04 (m, 2H), 6.80 (m. 2H).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 150.7 (br d, J_{C-F} = 256 Hz), 148.3 (s), 144.3 (br d, J_{C-F} = 265 Hz), 137.9 (br d, J_{C-F} 257 Hz), 124.1 (s), 113.5 (s).

^{11}B NMR (C_6D_6): δ 29.5 (br s, pwhh = 205 Hz),

$^{19}F\{^{1}H\}$ NMR (C_6D_6): δ -128.3 (m), -147.3 (m), -161.5 (m).

Anal Calcd. For $C_{12}H_4O_2B_1F_{15}$ C = 50.35, H = 1.41. Found C = 48.81, H = 1.25.

Sample preparation for low temperature NMR study:

In a J. Youngs NMR tube, under inert atmosphere, $[Ph_3C][closo\text{-}CB_{11}H_6Br_6]$ (30 mg, 0.035 mmol) was suspended/partially dissolved in d_8-toluene (0.4 ml). Then Et_3SiH (5.5 µl, 0.035 mmol) was added by microlitre syringe and the mixture was agitated until dissolution of all solids, which resulted in a homogeneous colourless solution. The mixture was cooled to -78°C (some precipitation of a white solid was observed). In a Schlenk tube CatBBr (6 mg, 0.030 mmol) was dissolved in d_8-toluene (0.2), this was slowly added by cannula to the cooled solution of $[Et_3Si][closo\text{-}CB_{11}H_6Br_6]$. Without warming the NMR tube was inserted into a probe pre-cooled to -40°C. NMR spectra were then recorded at incremental steps.

Reaction between CatBBr/crotonaldehyde/Ag[*closo*-$CB_{11}H_{12}$].

In a Schlenk tube wrapped with the foil, under inert atmosphere, $Ag[closo\text{-}CB_{11}H_{11}]$ (30 mg, 0.12 mmol) was suspended/partially dissolved in toluene (3 ml) and the mixture was cooled to -78 °C). In another Schlenk tube CatBBr (24 mg, 0.12 mmol)

was dissolved in toluene (2 ml), crotonaldehyde (10 µl, 0.12 mmol) and stirred for 5 minutes. This reaction mixture was slowly added by cannula to the cooled solution of Ag[*closo*-$CB_{11}H_{11}$]. Then the reaction mixture was stirred for 30 minutes at -78 °C and allowed to warm at room temperature. After 3 h, an aliquot was transferred by cannula in a a J. Youngs NMR tube and ^{11}B NMR spectra was recorded.

^{11}B NMR (toluene): δ 5.4 (s, 1B), -13.3 (d, J_{BH} = 138 Hz, 5B), -15.5 (d, J_{BH} = 154 Hz, 5B).

Reaction with Pinacol borane:

In a J. Youngs NMR tube, under inert atmosphere, [Ph_3C][*closo*-$CB_{11}H_6Br_6$] (20 mg, 0.035 mmol) was suspended/partially dissolved in toluene (1 ml). Then Et_3SiH (5.5µl, 0.035 mmol) was added by microlitre syringe and the mixture was shaken for 20 minutes. CatBBr (6 mg, 0.035 mmol) was added and the reaction shaken for 2 minutes. Then PinBH (37 µl, 0.035 mmol) were added by microlitre syringe. After 12 hours at room temperature all pinacol borane was consumed with the formation of a gelatinous solid.

Synthesis of PinBH from pinacol and BH_3·SMe_2:

BH_3·SMe_2 (2M in toluene, 4.2 ml, $8.4x10^{-4}$ mol) was added dropwise to a solution of Pinacol (1 g, $8.4x10^{-4}$ mol) in toluene (8 ml) cooled to 0°C The solution was warmed to room temperature and stirred until gas evolution ceased. The concentration of PinBH was assessed by ^{1}H NMR comparing the hydrogen of B-H with the hydrogens of the CH_3 of the toluene.

^{11}B NMR (toluene): δ 28.9 (d, J_{B-H} = 175 Hz)

Isolation of [$Me_2C(H)C(Me_2)SMe_2$][*closo*-$CB_{11}H_6Br_6$]:

A J. Young's tube was charged with a solution of PinBH (0.87 M in toluene, 0.2 ml, 0.017 mmol) (synthesised from pinacol and $BH_3{\cdot}SMe_2$) and toluene was added (1 ml). Then [Ph_3C][*closo*-$CB_{11}H_6Br_6$] (30 mg, 0.034) was added as a solid. The solution was heated at 100°C for 15 hours. This resulted in the formation of an orange solution, orange oil and a small quantity of a colourless crystalline solid. The solution and oil was removed, and the crystals dried *in-vacuo*.

NMR of the crystals:

^{1}H NMR (CD_2Cl_2): δ 2.78 (s, 6H), 2.63 (br, 1H) 2.05 (septet, J = 8 Hz, 1H), 1.48 (s, 6H,), 1.13 (d, J = 8 Hz, 6H).

^{1}H{^{11}B} NMR (CD_2Cl_2): As above but with anion B-H visible as singlet at 2.39.

^{11}B NMR (CD_2Cl_2): δ -1.7 (s), -9.8 (s), -20.1 (d, J_{BH} = 167 Hz).

Synthesis of 2,2-diethyl-1,3-propandiolborane:

2,2-diethyl-1,3-propandiol was dissolved in toluene (5 ml) and then was added one equivalent of catecholborane. The solution was stirred for 30 min then was added hexane, filtered and the solution of hexane was dried. After distillation under vacuum gave colourless oil contaminated with 43 % of probable trialkoxyborane (by ^{11}B NMR).

Synthesis of 1,3,2-benzodiazaborole:

To solution of *ortho*-diaminobenzene (1 g, 9.25 mmol) in CH_2Cl_2 was added dropwise one equivalent of $BH_3{\cdot}$ SMe_2 and heated at reflux. After 4 hours it was warmed at room temperature and the solvent was removed under vacuum. The product was purified by sublimation giving white solid.

^{1}H NMR (C_6D_6): δ 7.05-6.98 (m, 2H), 6.83-6.67 (m, 2H), 5.83 (br s, 2H).

^{1}H{^{11}B} NMR (CD_2Cl_2): As above but with anion B-H visible as singlet at 4.59.

^{13}C{^{1}H} NMR ($CDCl_3$): δ 136.6, 120.2, 112.1.

^{11}B NMR (C_6D_6): δ 23.95 (d, J_{BH} = 153.76).

Synthesis of *N,N'*-(2,6-diisopropylphenyl)-1-bromo-1,3,2-diazaborolane 3:

Following the reported procedure,[43] in a J. Young's tube Mg (300 mg, 12.3 mmol) was suspended in ether (20 mL) and (2,6-^{i}Pr$_2$C$_6$H$_3$)N=CHCH=N(2,6-^{i}Pr$_2$C$_6$H$_3$) (968 mg, 2.57 mmol) was added. The mixture of reaction was heated to reflux for 24 hours. After cooling the solution to 0 ºC, a solution of BBr_3 (1 M in hexane, 2.6 ml, 2.6 mmol) was added to the mixture at 0 ºC. The resulting mixture was stirred for 12 hours at 0 ºC to afford a cream-green suspension. After solvents were removed under reduced pressure, hexane (20 ml) was added. The resulting suspension was filtered by filter cannula and the solid was washed with hexane (20 ml). Volatiles were removed from the filtrate to give a white solid (612 mg, 51%).

^{1}H NMR (C_6D_6) δ 1.20 (d, *J* = 7 Hz, 12H), 1.31 (d, *J* = 7 Hz, 12H), 3.16 (sep, *J* = 7 Hz, 4H), 6.12 (s, 2H), 7.14 (d, *J* = 9 Hz, 4H), 7.22 (dd, *J* = 8 Hz, 9 Hz, 2H);

^{13}C NMR (C_6D_6) δ 24.2, 24.5, 28.9, 120.2, 123.9, 128.5, 137.5, 146.4;

^{11}B NMR (C_6D_6) δ 20.2 (s).

Crystallographic Details

Crystal Data for [CatB(O=PEt$_3$)][*closo*-CB$_{11}$H$_6$Br$_6$]

Formula	$C_{13}H_{25}B_{12}Br_6O_3P$
M	869.47
Crystal system	Triclinic
Space group	P-1
a/Å	11.1776(2)
b/Å	11.7231(3)
c/Å	13.2003(3)
α/°	94.7950(10)
β/°	95.1870(10)
γ/°	115.5510(10)
Volume/Å	1539.63(6)
Z	2
Dcalcd g/cm^3	1.967
F(000)	866
T/K	100(2)
Absorption coefficient (μ)/mm^{-1}	7.981
Crystal size/mm	0.15 x 0.12 x 0.06
Reflections measured	6865
Reflections collected	5334
Goodness-of-fit on F2	1.046
Final R1 [I > 2σ(I)]	0.0649
(all data)	0.0927

Crystal Data for $[Me_2C(H)C(Me_2)SMe_2][closo\text{-}CB_{11}H_6Br_6]$

Formula	$C_{27}H_{43}B_{11}Br_6S$
M	998.04
Crystal system	Monoclinic
Space group	P2(1)
a/Å	15.3111(9)
b/Å	13.1454(8)
c/Å	19.6927(11)
α/°	90.00
β/°	90.657(6)
γ/°	90.00
Volume/Å	3963.3(4)
Z	4
D_{calcd} g/cm^3	1.67
F(000)	1944
T/K	100(2)
Absorption coefficient (μ)/mm^{-1}	6.151
Crystal size/mm	0.30 x 0.20 x 0.03
Reflections measured	13691
Reflections collected	8651
Goodness-of-fit on F^2	0.968
Final R1 [I > 2σ(I)]	0.0547
(all data)	0.0878

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Chapter 3. Arene borylation with catecholborenium cations

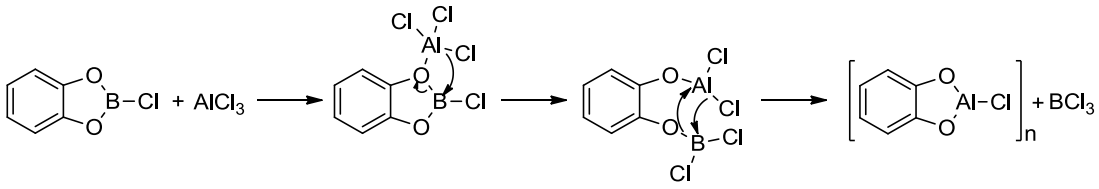
3.1 Introduction

In the catalytic electrophilic borylation process, using CatBH in combination with the Brønsted superacid deriving from the stoichiometric arene borylation by $[Et_3Si][closo\text{-}CB_{11}Br_6H_6]$ and CatBX (X = Cl, Br), it was crucial to use the chemically robust and weakly coordinating carborane anion. The requirement of the expensive carborane anion and high temperature combined with the side reaction of alkyl scrambling and poor functional group tolerance make this methodology unattractive. Nevertheless, this methodology showed that a borocation can be a suitable borylating reagent for arenes, presumably due to enhanced electrophilicity on the boron centre.

A simple and inexpensive route to generate borenium cations is the halide abstraction by a MX_3 (M = Al, Ga, Fe; X = halide) Lewis acid from a Lewis base-boron halide adduct.

3.2 Synthesis of catecholborenium cations

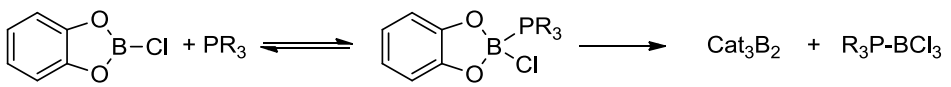
Attempts to generate a borocation by halide abstraction from CatBCl with $AlCl_3$ were unsuccessful. The addition of $AlCl_3$ to CatBCl resulted in a slow reaction of ligand redistribution between aluminium and boron. The ^{11}B NMR spectrum of an equimolar mixture of $AlCl_3$ and CatBCl in CD_2Cl_2 showed the formation of small quantities of BCl_3 while the chemical shift of CatBCl remained unchanged. The proposed mechanism of the formation of BCl_3 involves the initial coordination of $AlCl_3$ to the oxygen of CatBCl and subsequent chloride transfer (Scheme 3.1).



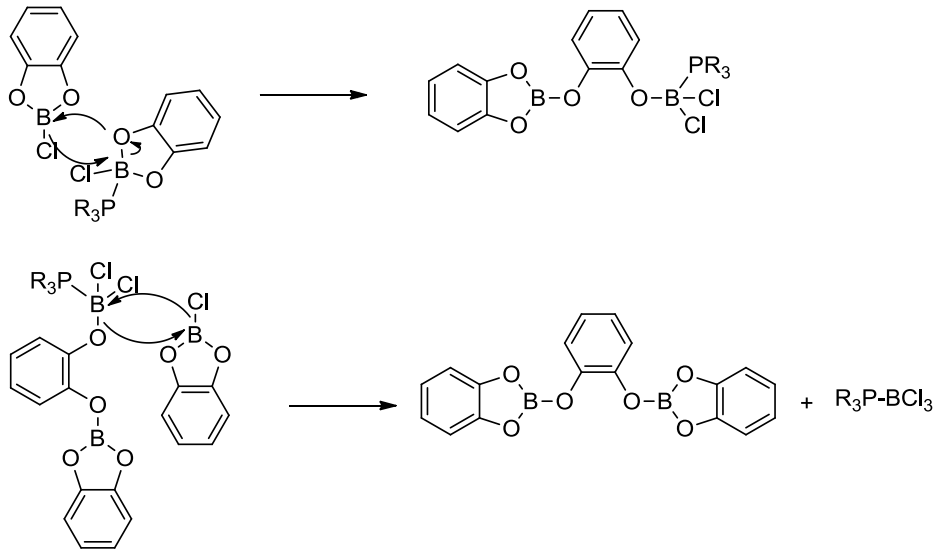
Scheme 3.1 Proposed mechanism of BCl_3 formation.

Therefore, the formation of the Lewis acid-base adduct CatBCl•L (L = aprotic amines or phosphines) is essential to synthesise catecholborenium cations. The coordination of the Lewis base to the boron centre will labilise the boron-halogen bond facilitating the halogen abstraction by a MX_3 Lewis acid.

As reported by Marder and co-workers, the formation of an adduct between CatBCl and basic tertiary phosphines suffers from boron substituent redistribution yielding Cat_3B_2 and $Cl_3B•PR_3$ (Eq. 1).[1] As proposed by Marder and co-workers, the substituent redistribution reaction is due to the presence of an equilibrium between $CatBCl•PR_3$ and starting materials. The coordination of the Lewis base to the boron centre causes the loss of the π-bond character between oxygen and boron increasing the nucleophilicity of the oxygens. Consequently, oxygen atoms in the adduct are nucleophilic enough to attack the boron centre of free CatBCl, leading to the ring opening of the dioxaborole and to the subsequent ligand redistribution between the two boron centres (Scheme 3.2).

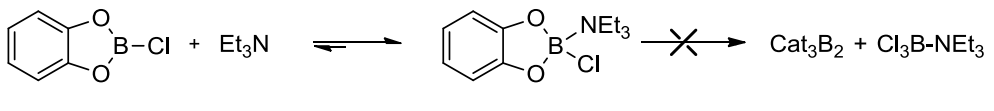


Eq. 1

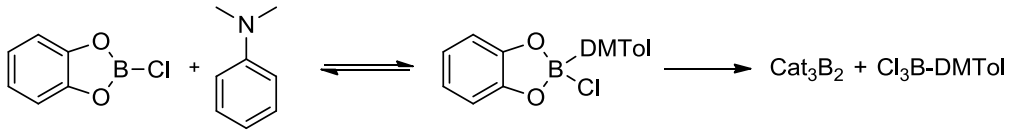


Scheme 3.2 Proposed mechanism of boron substituent redistribution of CatBCl with tertiary phosphines.

Marder and co-worker also reported that in contrast to PR_3 triethylamine (Et_3N) and pyridine led to the formation of stable adducts with CatBCl with the ^{11}B NMR chemical shifts of 13.3 and 11.8 ppm, respectively. The absence of the substituent redistribution reaction with the aforementioned amines is attributed to the stronger binding of these amines to CatBCl which shifts the reaction equilibrium toward the adduct formation. Indeed, the boron substituent redistribution takes place with the poorly Lewis basic amine *N*,*N*-dimethyl-*p*-toluidine (DMTol) which binds less strongly to CatBCl and consequently the equilibrium of CatBCl•DMTol formation is more shifted toward the free species compared to CatBCl•NEt_3.



Eq. 2



Eq. 3

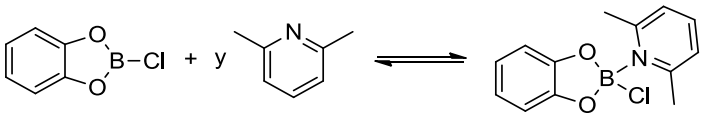
DMTol = *N*,*N*-Dimethyl-p-toluidine

The equilibrium between DMTol and CatBCl was previously studied in our

laboratory by Paul Singleton. The ^{11}B NMR spectrum of a CatBCl and DMTol mixture in a 2 : 1 ratio showed three peaks at 22.8, 20.4 and 10.4 ppm. The peaks at 22.8 and 10.4 ppm were attributed to Cat_3B_2[2] and Cl_3B•DMTol,[3] respectively, which were the products of the substituent redistribution reaction. The peak at 20.4 ppm was attributed to the fast (on the NMR timescale) transfer of the Lewis base between the adduct CatBCl(DMTol) and CatBCl at 20 °C. Low temperature NMR experiments showed that the resonance at 20.4 ppm split into two peaks at -40 °C, one at 28.8 ppm, which was attributable to CatBCl, and the other at 12.7 ppm, which was attributable to the neutral tetracoordinated boron compound CatBCl(DMTol).

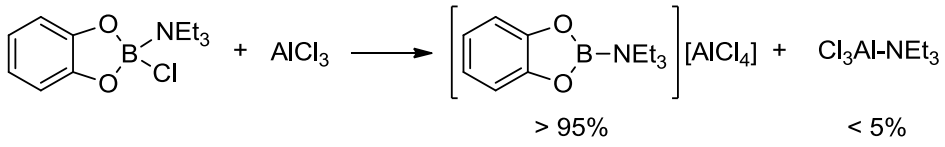
The equilibrium in the reaction of adduct formation was also observed between CatBCl and 2,6-lutidine in CD_2Cl_2. A mixture of CatBCl and 2,6-lutidine in 2 : 1 ratio showed only one peak in the ^{11}B NMR spectrum at 22.1 ppm, indicating a rapid base exchange at 20 °C on the NMR time scale. Moreover, an equimolar mixture of CatBCl and 2,6-lutidine displayed a ^{11}B NMR chemical shift at 16.7 ppm that was shifted upfield on addition of further 2,6-lutidine (Table 3.1).

Table 3.1 ^{11}B NMR chemical shift of the reaction of CatBCl with different amounts of 2,6-lutidine in CD_2Cl_2.



Number of equivalents of CatBCl	Number of equivalents of 2,6-lutidine	^{11}B NMR chemical shift (ppm)
1	0	28.4
1	0.5	22.1
1	1	16.7
1	1.5	14.5
1	2	13.5
1	3	13.0

The addition of $AlCl_3$ to the equimolar mixture of CatBCl and Et_3N resulted in a rapid reaction, producing the borenium salt $[CatB(NEt_3)][AlCl_4]$ as the major product along with trace amounts of the Lewis acid-base adduct $Cl_3Al{\bullet}NEt_3$, the ammonium salt $[Et_3NH][AlCl_4]$ and CatBOH. The latter two products are possibly due to adventitious water. The formation of small quantities of $AlCl_3{\bullet}NEt_3$ adduct is due to the side reaction of $AlCl_3$ with the free Lewis base present in solution since $CatBCl{\bullet}NEt_3$ formation is a reversible reaction, although it is shifted predominately towards $CatBCl{\bullet}NEt_3$.



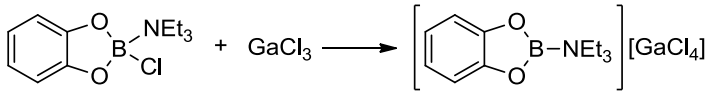
Eq. 4

The formation of the borenium salt $[CatB(NEt_3)][AlCl_4]$ was suggested by multinuclear NMR spectroscopy. The ^{11}B NMR spectrum showed a peak at 27.9 ppm in the characteristic region of tricoordinate dioxaboron compounds and it was comparable to the related borenium cations $[PinB(DMA)][HB(C_6F_5)_3]$ (DMA = *N*, *N*-dimethylaniline) and $[CatB(P^tBu_3)][HB(C_6F_5)_3]$ (26.4 and 29.9 ppm, respectively).[4,5] The ^{27}Al NMR spectrum showed the characteristic sharp peak of $[AlCl_4]^-$ at 104 ppm along with a small peak at 110 ppm attributable to $AlCl_3{\bullet}NEt_3$ (< 5%). Furthermore, the proton resonances of amine substituents in $[CatB(NEt_3)]^+$ were significantly shifted downfield compared to the free amine and the amine coordinated to the neutral Lewis acids $AlCl_3$ and CatBCl (Table 3.2).

Table 3.2 ^{1}H NMR chemical shift of free and Lewis acid coordinated Et_3N in CD_2Cl_2 at 20 °C.

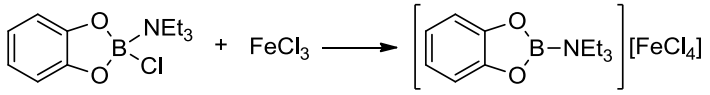
Compound	^{1}H NMR chemical shift of CH_2 in Et_3N moiety (ppm)	^{1}H NMR chemical shift of CH_3 in Et_3N moiety (ppm)
Et_3N	2.46 (q, *J* = 7.1 Hz)	0.97 (t, *J* = 7.1 Hz)
CatBCl•NEt_3	3.18 (q, *J* = 7.3 Hz)	1.26 (t, *J* = 7.3 Hz)
Et_3N•$AlCl_3$	3.13 (br. s)	1.34 (t, *J* = 7.4 Hz)
[CatB(NEt_3)][$AlCl_4$]	3.74 (q, *J* = 7.3 Hz)	1.43 (t, *J* = 7.3 Hz)

The substitution of the halophilic $AlCl_3$ with $GaCl_3$ and $FeCl_3$ also resulted in the formation of the borenium cation [CatB(NEt_3)]$^+$ (Eq. 5). *In situ* multinuclear NMR spectroscopy of the reaction between CatBCl•NEt_3 and $GaCl_3$ in CD_2Cl_2 clearly confirmed the formation of the borenium salt [CatB(NEt_3)][$GaCl_4$]. The ^{71}Ga NMR spectrum showed a sharp peak at 250.4 ppm which was consistent with $[GaCl_4]^-$,[6] while the ^{11}B NMR resonance at 28.0 ppm was similar to the related aluminate borenium cation.



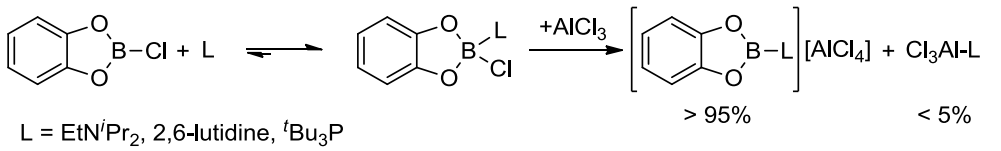
Eq. 5

The reaction carried out in a J. Young's NMR tube between CatBCl•NEt_3 and $FeCl_3$ in CD_2Cl_2 gave a pale yellow solution and the formation of microcrystalline solids, possibly [CatB(NEt_3)][$FeCl_4$]. The NMR machine had problem to lock the deuterated solvent signal, hence the ^{11}B NMR spectrum was recorded in no-lock mode and the minor CatBOH impurity was used as internal reference. The ^{11}B NMR chemical shift at 29.0 ppm was consistent with the formation of the borenium salt [CatB(NEt_3)][$FeCl_4$].



Eq. 6

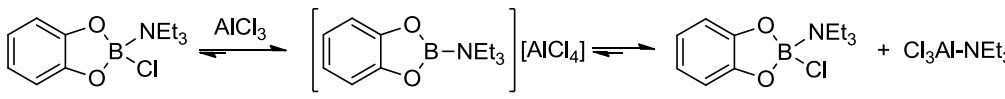
The synthesis of catecholborenium cations was also accomplished using different Lewis bases. Analogous to the reaction of CatBCl•Et_3N with $AlCl_3$, the treatment of the adduct of CatBCl with the strong bases EtN^iPr_2, 2,6-lutidine and $^tBu_3P$ with $AlCl_3$ yielded the borenium salts [CatB(L)][$AlCl_4$] along with trace amounts of Lewis acid-base adduct Cl_3Al•L, protonated Lewis base [LH][$AlCl_4$] and CatBOH.



Eq. 7

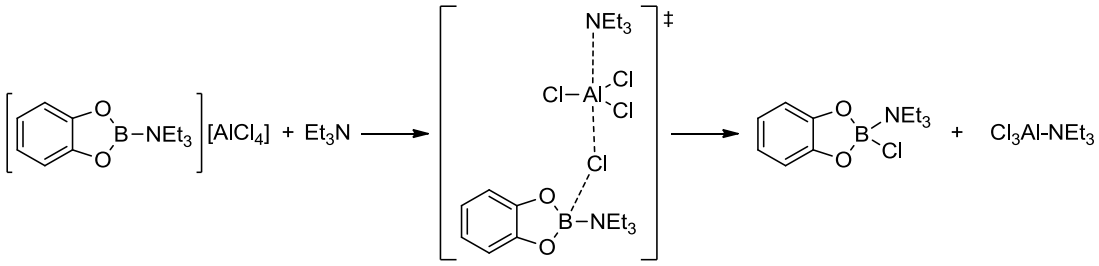
Instead, the use of poorly Lewis basic DMTol ($pK_a = 5.12$)[7] produced significant quantities of Cl_3Al•DMTol due to the fact that the equilibrium lies more towards the free starting materials, CatBCl and DMTol, compared to more basic amines Et_3N (pKa = 10.67),[8] EtN^iPr_2 (pKa = 11.44)[7] and 2,6-lutidine (pKa = 6.77).[9] It is noteworthy that NMR studies, conducted in our laboratory by Paul J. Singleton, revealed that the borenium salt [CatB(DMTol)][$AlCl_4$] was in rapid equilibrium with the neutral species at 20 °C.[10] This suggested that the halide abstraction from the neutral adduct CatBCl•amine by $AlCl_3$ was a reversible process.

The reversibility of the halide abstraction in the formation of [CatB(amine)][$AlCl_4$] was confirmed by the addition of an equivalent of Et_3N to [CatB(NEt_3)][$AlCl_4$] which led to formation of CatBCl•NEt_3 and Cl_3Al•NEt_3 (Eq. 8). The addition of Et_3N to [CatB(NEt_3)][$AlCl_4$] in absence of reversible halide transfer would give the boronium cation [CatB(NEt_3)$_2$][$AlCl_4$] or a frustrated Lewis pair (FLP)[11] (the borenium cation [9-BBN-NEt_3][Tf_2N] (9-BBN = 9-borabicyclo[3.3.1]nonane), as reported by Vedejs, upon addition of 1 equivalent of Et_3N formed a FLP).[12]

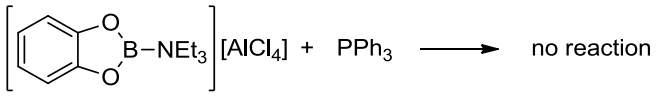


Eq.8

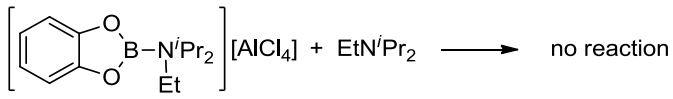
The formation of the two neutral Lewis acid-base adducts CatBCl(NEt_3) and Cl_3Al•NEt_3 on addition of a further equivalent of Et_3N proceeds, presumably, by a chloride transfer via a pentacoordinate aluminium (Scheme 3.3), as observed for bis-amine-$AlCl_3$.[13] This mechanism was indirectly supported by the absence of any reaction between [CatB(NEt_3)][$AlCl_4$] and PPh_3 and between [CatB(EtN^iPr_2)][$AlCl_4$] and EtN^iPr_2 which formed FLPs. The absence of halide transfer on addition of PPh_3 to [CatB(NEt_3)][$AlCl_4$] was attributed to the poorly basic nature of PPh_3 (pK_a = 2.73)[14] which was insufficiently nucleophilic to promote halide transfer. Instead, in the case of EtN^iPr_2, which is more basic and more bulky than Et_3N, the absence of reaction was attributable to steric bulkiness of EtN^iPr_2.



Scheme 3.3 Proposed mechanism of halide transfer in the reaction of Et_3N with [CatB(NEt_3)][$AlCl_4$]**.**



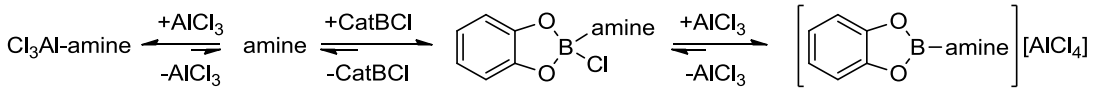
Eq. 9



Eq. 10

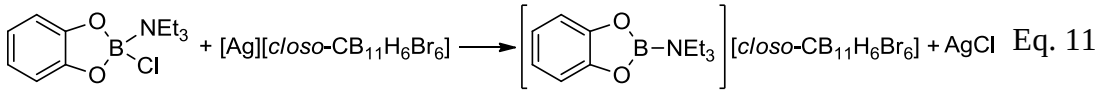
It is noteworthy to report that the addition of CatBCl to preformed $AlCl_3$•amine adducts also led to the generation of borenium salts. The addition of CatBCl to $AlCl_3$•(2,6-lutidine) in CH_2Cl_2 rapidly generated the borenium salt almost quantitatively. Instead, the addition of CatBCl to $AlCl_3$•NEt_3 yielded approximately 20% of borenium salt after 15 hours and no significant change in product distribution

was observed at 20 °C after 8 days. The formation of borenium cations starting from $AlCl_3$•amine also indicated that $AlCl_3$•amine formation was a reversible process (Scheme 3.4).



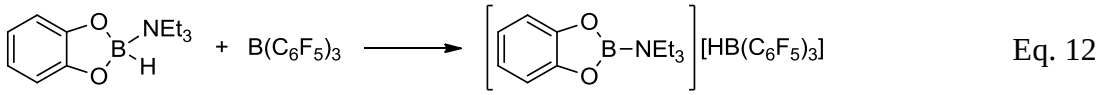
Scheme 3.4 Equilibria involved in the formation of catecholborenium salt by halide abstraction with $AlCl_3$.

The synthesis of the catecholborenium cation $[CatB(NEt_3)]^+$ was also achieved via the metathesis reaction between [Ag][*closo*-$CB_{11}H_6Br_6$] and CatBCl•NEt_3 and by the hydride abstraction from CatBH•NEt_3 with $B(C_6F_5)_3$. The metathesis reaction of the silver salt of [Ag][*closo*-$CB_{11}H_6Br_6$] with CatBCl•NEt_3 gave the borenium salt [$CatB(NEt_3)$][*closo*-$CB_{11}H_6Br_6$] (Eq. 11), which in CD_2Cl_2 had an ^{11}B NMR chemical shift for the catecholboryl moiety of 27.8 ppm, similar to borenium cations partnered with the tetrachlorometallates ([$CatB(NEt_3)$][MCl_4], M = Al, Ga).



Eq. 11

Analogous to the reaction reported by Stephan and co-workers between CatBH•P^tBu_3 and $B(C_6F_5)_3$ which give [$CatB(P^tBu_3)$][$HB(C_6F_5)_3$],[5] the reaction of CatBH•NEt_3 with $B(C_6F_5)_3$ yielded the borenium cation [$CatB(NEt_3)$][$HB(C_6F_5)_3$]. The ^{11}B NMR spectrum with a doublet centred at -25.2 ppm ($J_{B\text{-}H}$ = 90 Hz) characteristic of $[HB(C_6F_5)_3]^-$ and a broad singlet at 27.9 ppm for the catecholboryl moiety was consistent with the ionic formulation of this compound.



Eq. 12

Attempts to crystallise [CatB(NEt_3)][$AlCl_4$] and [CatB(2,6-lutidine)][$AlCl_4$] to have further confirmation of borenium cation formation by single crystal X-ray diffraction analysis were unsuccessful as these two borenium salts tend to form oils. However, crystals suitable for X-ray structural analysis were obtained by replacing the aromatic hydrogens of the catechol moiety with chlorine atoms.

The structures of [Cl_4CatB(NEt_3)][$AlCl_4$] (Figure 3.1) and [Cl_4CatB(2,6-lutidine)][$AlCl_4$] (Figure 3.2) have trigonal planar geometry at the boron atom (sum of the angles around the boron = 360.0°). The shortest distance between B and Cl of $[AlCl_4]^-$ at 3.444(3) and 3.381(4) Å, respectively, are consistent with borenium cation formulations. The B-O distances of 1.364(3) and 1.370(3) Å in [Cl_4CatB(NEt_3)][$AlCl_4$] and of 1.363(5) and 1.377(5) Å in [Cl_4CatB(2,6-lutidine)][$AlCl_4$] are shorter than in CatBCl (1.381(2) Å), indicating an increase in O→B π donation. The short B-N bond (1.505(3) and 1.499(6) Å in $[Cl_4CatB(NEt_3)]^+$ and $[Cl_4CatB(2,6\text{-lutidine})]^+$) are comparable to B-N bonds in the borenium cations $[(aryl)_2B(DMAP)]^+$ (1.480(3) and 1.501(4) Å).[15] In [Cl_4CatB(2,6-lutidine)][$AlCl_4$] the two aromatic rings are oriented at 37.79° to each other suggesting a partial π donation between pyridine ring and boron atom.

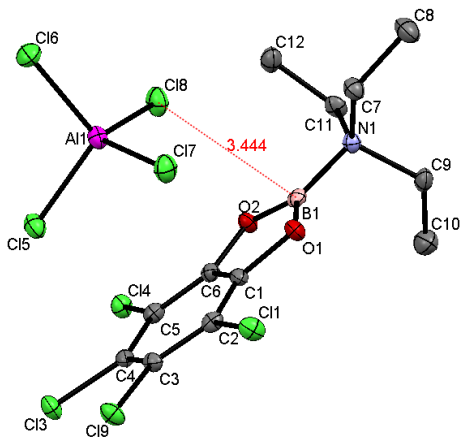


Figure 3.1 Crystal structure of compound [CatB(NEt_3)][$AlCl_4$], hydrogens omitted for clarity and thermal ellipsoids at 50 % probability. Selected bond lengths (Å): B(1)-N(1) = 1.5049(1), B(1)-O(1) = 1.3699(1), B(1)-O(2) = 1.3639(1), angles at B Σ = 360.0°.

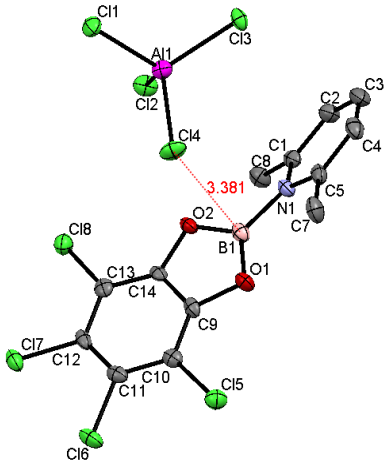


Figure 3.2 Crystal structure of compound $[Cl_4CatB(2,6\text{-lutidine})][AlCl_4]$, hydrogens omitted for clarity and thermal ellipsoids at 50 % probability. Selected bond lengths (Å): B(1)-N(1) = 1.499(6), B(1)-O(1) = 1.363(5), B(1)-O(2) = 1.377(5), angles at B Σ = 360.0°.

The crystal structure of $[CatB(NEt_3)]^+$ partnered with $[closo\text{-}CB_{11}H_6Br_6]^-$ was also obtained (Figure 3.3). The planar boron centre (sum of angles at boron = 360°) and the shortest distance between the positive boron centre and bromine atom of the carborane anion at 4.29 Å confirmed the formation of a borenium salt.

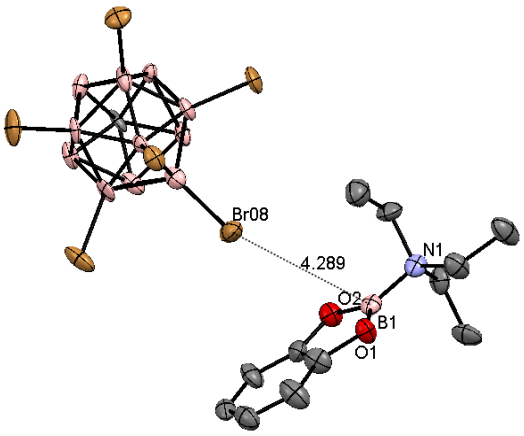


Figure 3.3 Crystal structure of compound $[CatB(NEt_3)][closo\text{-}CB_{11}H_6Br_6]$, hydrogens omitted for clarity and thermal ellipsoids at 50 % probability. Selected bond lengths (Å): B(1)-N(1) = 1.52(2), B(1)-O(1) = 1.34(2), B(1)-O(2) = 1.38(1), angles at B Σ = 360°.

In contrast to borenium salts $[CatB(amine)][AlCl_4]$, crystals suitable for X-ray structural analysis of the related P^tBu_3 ligated catecholborenium salt were obtained (Figure 3.4). In contrast to analogous amine-ligated borenium salts

[CatB(P^{t}Bu$_3$)][AlCl$_4$] showed a shorter anion-boron distance (3.270(3) Å) and a distorted planar geometry at the boron centre (angle between the B1-P1 bond and the plane passing through O1, B1 and O2 = 170.13°) indicating a cation-anion interaction. The bond lengths of the cationic part are identical within 3σ to that previously reported for [CatB(P^{t}Bu$_3$)][HB(C$_6$F$_5$)$_3$] where a related distortion from the trigonal planar geometry on the boron was also observed suggesting it is not a specific anion coordinating effect.[5]

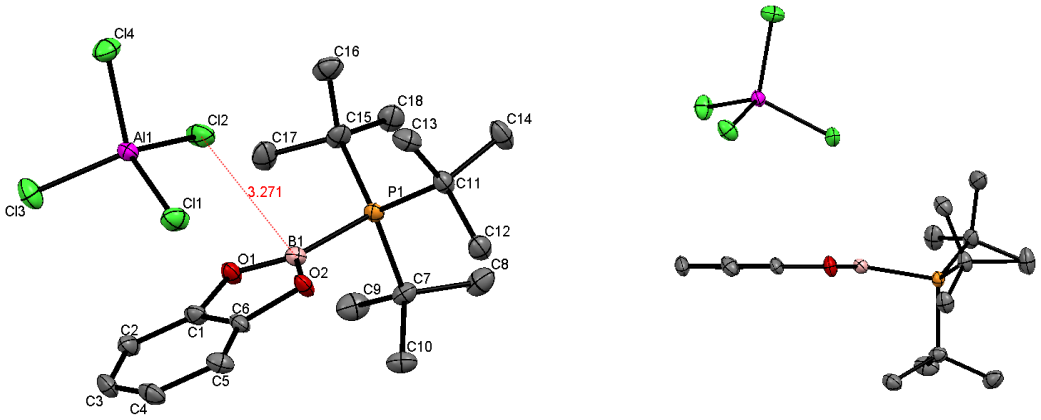


Figure 3.4 Two views of the crystal structure of compound [CatB(2,6-lutidine)][AlCl$_4$], hydrogens omitted for clarity and thermal ellipsoids at 50 % probability. Selected bond lengths (Å): B(1)-P(1) = 1.942(4), B(1)-O(1) = 1.364(4), B(1)-O(2) = 1.365(4), angles at B Σ = 358.9°

In addition to structural differences between amine and phosphine coordinated borenium cations, a different positive charge on boron was expected due to the significant difference in the Pauling electronegativity of nitrogen and phosphorus (χ_N = 3.0, χ_P = 2.2).

Calculations of natural bond order (NBO) charges for [CatB(NEt$_3$)]$^+$ and [Cl$_4$CatB(NEt$_3$)]$^+$ were performed at the DFT MPW1K/6-311++G(d,p) level (calculations performed by Dr. J. W. McDouall). This computational level is identical to that previously used by Stephan and co-workers for [CatB(PMe$_3$)]$^+$ to permit the direct comparison between borocations. At this level, the crystallographic

geometry of $[Cl_4CatB(NEt_3)]^+$ was in good agreement with that determined computationally. As expected, the amine ligated borenium cations possess considerably greater positive charge at boron compared to phosphine ligated borenium cation $[CatB(PMe_3)]^+$ (by *ca* 0.5 e^-) (Table 3.3). Furthermore, in $[CatB(PMe_3)]^+$ the major positive charge resides on the phosphorus centre. For this reason, Stephan found it more appropriate to name this cationic species a boryl-phosphonium cation rather than a borenium cation. Instead, in $[CatB(NEt_3)]^+$ and $[Cl_4CatB(NEt_3)]^+$ the borenium cation terminology is appropriate since the major positive charge resides on the boron centre while the nitrogen atom carries a negative charge.

Table 3.3 Calculated NBO charges at the DFT MPW1K/6-311 + + G(d,p) level.

Cation	**B**	**O**	**P or N**
$[CatB(NEt_3)]^+$	+1.338	-0.692	-0.609
$[Cl_4CatB(NEt_3)]^+$	+1.348	-0.675	-0.616
$[CatB(PMe_3)]^+$ [a]	+0.847	-0.650	+1.181
$[CatB]^+$ [a]	+1.530	-0.648	—

[a] Reference 5

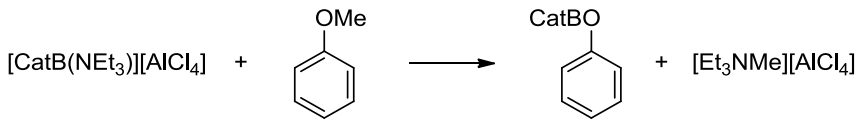
With catecholborenium cations easily synthesised from the combination of commercially available CatBCl, Lewis basic amines or phosphines and a MX_3 Lewis acid their reactivity was studied in direct C-H arene borylation.

3.3 Direct C-H Arene Borylation by borenium cation

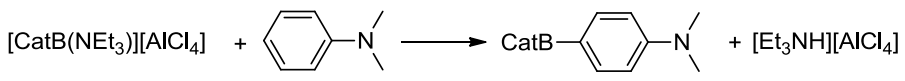
Initial reactivity studies on arene borylation with borenium compounds were accomplished with $[CatB(NEt_3)][AlCl_4]$ because the precursor $CatBCl{\bullet}NEt_3$ did not

undergo the unwanted boron substituent redistribution reaction. $[CatB(NEt_3)][AlCl_4]$ was generated *in situ* by mixing CatBCl, Et_3N and $AlCl_3$ (added last) in a 1 : 1.05 : 1.1 ratio.

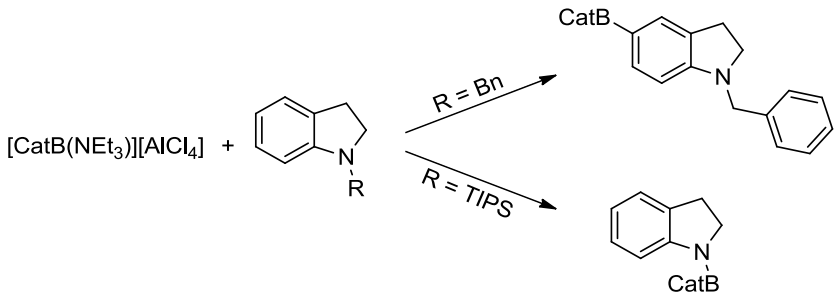
Attempts to react toluene with the borenium salt $[CatB(NEt_3)][AlCl_4]$ resulted in no arene borylation even at 140 °C in *ortho*-dichlorobenzene (o-dCB). Anisole also did not undergo arene borylation, instead slowly reacting with $[CatB(NEt_3)][AlCl_4]$ in CH_2Cl_2 at 20 °C to yield the product of ether cleavage (Eq. 13), analogous to the reaction of anisole with BBr_3.[16] The lack of reactivity of toluene towards $[CatB(NEt_3)][AlCl_4]$ was attributable to the insufficient nucleophilicity of the aromatic ring[17] combined with the limited electrophilicity of the boron electrophile in solution. Indeed, the addition of the strongly activated arene *N*,*N*-dimethylaniline (DMA) to $[CatB(NEt_3)][AlCl_4]$ in CH_2Cl_2 resulted in rapid (< 1 hour) arene borylation. The reaction proceeded with high regioselectivity giving arene borylation exclusively at the *para* position to the nitrogen atom (by ^1H NMR spectroscopy) (Eq. 14). Likewise, *N*-benzyl indoline was quantitatively and selectively borylated at the *para* position to the nitrogen atom (5-position) at 20 °C in 4 hours. The borylation occurred only at the 5-position of indoline with no benzyl borylation observed. This showed the high selectivity of $[CatB(NEt_3)][AlCl_4]$ in differentiating the activated aromatic ring of indoline moiety from the phenyl ring of the benzyl substituent on the nitrogen atom.



Eq. 13



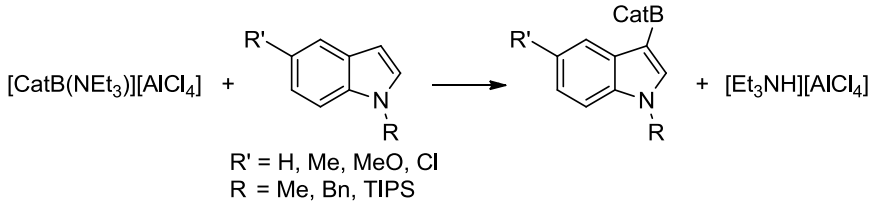
Eq. 14



Scheme 3.5 Reaction of $[CatB(NEt_3)][AlCl_4]$ with *N*-TIPS- and *N*-benzyl-indoline

A different chemoselectivity was observed by changing the substituent on the nitrogen atom of the indoline moiety from benzyl to triisopropylsilyl (TIPS). The *N*-TIPS-indoline slowly reacted with the borenium salt to give N-Si bond cleavage and only traces of borylation on the aromatic ring (by ^{11}B NMR spectroscopy)[18] after 7 days. This different chemoselectivity can be attributed to the deactivating effect of the silicon group on the nitrogen atom (the interaction of the lone pair of nitrogen with d orbitals of the silicon and/or the σ* orbitals of the Si–C bonds reduces the delocalisation of the lone pair into the phenyl ring with the consequence of a reduction in the aromatic ring nucleophilicity),[19] and/or to the steric effect of the TIPS group (the bulky TIPS group can prevent that the nitrogen centre acting as a base in the deprotonation step. See section 3.9)

In order to investigate the substrate scope of the borylation reaction by borenium salt, a range of electron rich heteroarenes were reacted with $[CatB(NEt_3)][AlCl_4]$. The reaction between $[CatB(NEt_3)][AlCl_4]$ and one equivalent of *N*-substituted indole derivatives readily gave the heteroarene borylated product in high yield. The reaction proceeded under electronic control yielding exclusively the 3-substituted indole derivative, consistent with an electrophilic aromatic substitution on indoles (Eq. 15).[20]



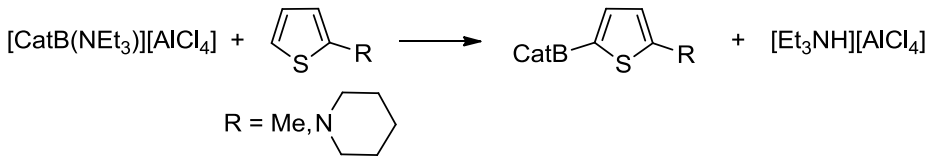
Eq. 15

As expected, the rate of reaction was related to substituents on indole. *N*-methyl- and *N*-benzylindole were borylated in 4 and 6 h, respectively, while *N*-TIPS-indole, which is less nucleophilic (and basic) than previous indole derivatives,[21] required 48 hours for complete borylation. Electron donating groups in the 5-position accelerated the reaction. 5-Methyl- and 5-methoxy-*N*-TIPS-indole yielded the respective borylated products in 24 and 30 hours (48 hours for unsubstituted *N*-TIPS-indole). The electron withdrawing chloride substituent on the phenyl ring of *N*-TIPS-indole drastically retarded or prevented the borylation reaction with $[CatB(NEt_3)][AlCl_4]$. The conversion of 5-Chloro-*N*-TIPS-indole was *ca.* 75 % (by ^1H NMR spectroscopy) after 10 days, while 6-chloro-*N*-TIPS-indole did not show any significant reaction after 3 days (by ^1H and ^{11}B NMR spectroscopy). The absence of reaction indicates greater deactivation when the chlorine atom was in the 6-position in line with the calculated proton affinity of the C3 position in the related fluoroindoles.[22]

It is noteworthy that the TIPS group on the nitrogen atom and the methoxy group in the phenyl ring of indole are well tolerated (by NMR analysis no evidence of N-Si bond cleavage and only traces of O-C bond cleavage) due to the arene borylation being kinetically favoured over N-Si and O-C bond cleavage (N-Si and O-C bond cleavage in *N*-TIPS-indoline and anisole, respectively, are slow reactions).

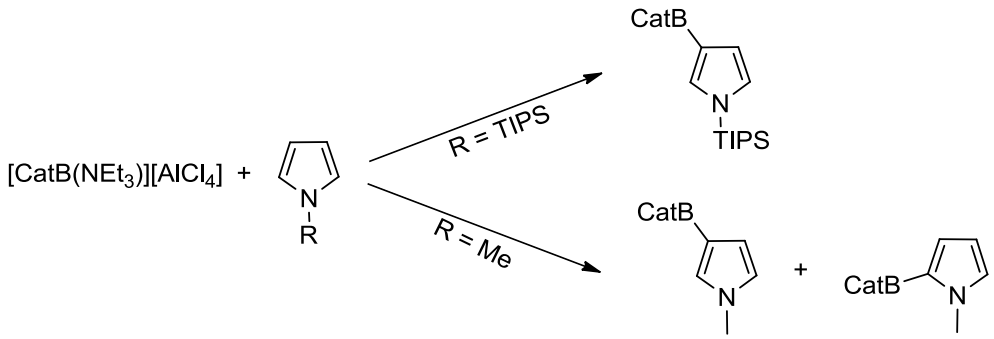
The less aromatic and less nucleophilic heterocycles benzofuran, furan and thiophene gave insoluble materials presumably deriving from polymerization initiated by acid.[23] In contrast, activated thiophenes undergo arene borylation. 2-piperidyl thiophene was rapidly (< 30 minutes) and selectively borylated in the 5-

position. While, 2-methyl thiophene reacted slowly (3 weeks) giving the 5-catecholboryl-2-methyl thiophene as the major product along with unidentified minor products.



Eq. 16

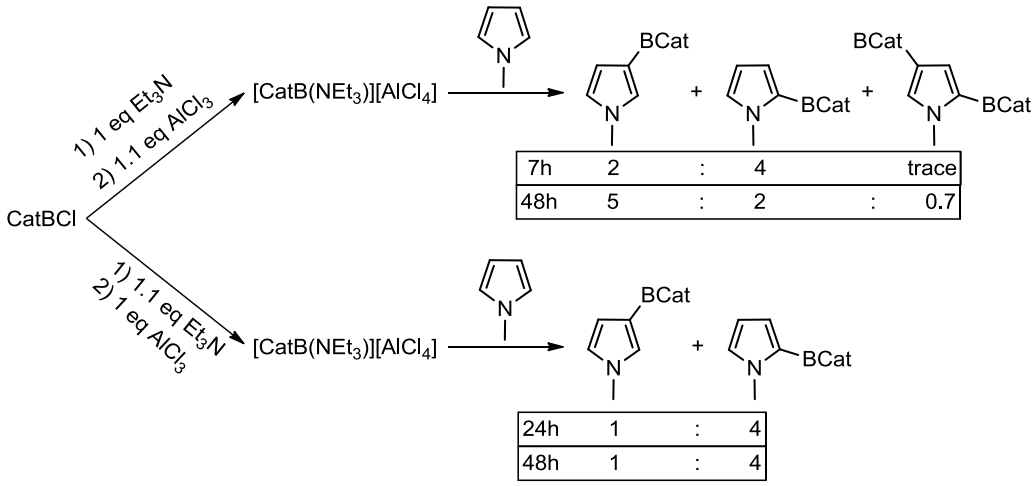
Analogous to indole derivatives, *N*-protected pyrrole was amenable to borylation. *N*-TIPS-pyrrole yielded exclusively the 3-borylated product since the sterically encumbered TIPS group obstructs attack at the 2-position.[24] In contrast, *N*-methyl-pyrrole was monoborylated to yield a mixture of the 2- and 3-substituted *N*-methyl-pyrrole using 1 equivalent of $[CatB(NEt_3)][AlCl_4]$ or diborylated selectively at the 2- and 4-position using 2.1 equivalents of $[CatB(NEt_3)][AlCl_4]$.



Scheme 3.6 Reaction of $[CatB(NEt_3)][AlCl_4]$ with *N*-TIPS- and *N*-methyl-pyrrole

The ratio distribution of products in the monoborylation of *N*-methyl-pyrrole was dependent on the ratio of CatBCl, Et_3N and $AlCl_3$ used to form the borenium salt and on the time of reaction (Scheme 3.7). The monoborylation of *N*-methylpyrrole in all cases initially proceeded with the formation of the 2-substituted product as major regioisomer, but isomerization took place in presence of excess Lewis acid. The reaction of the borenium cation, prepared by adding 1.1 equivalents of $AlCl_3$ to the

equimolar mixture of CatBCl and Et_3N, with *N*-methylpyrrole in CD_2Cl_2 at 20 °C was complete in 7 hours giving a 5 : 2 mixture of the 2- and 3-substituted products along with traces of diborylated product. The overall yield of borylated products did not significantly alter over the time (by NMR spectroscopy using the proteo impurity of the deuterated solvent as internal standard) while the ratio of the 2- and 3- isomers changed from 5 : 2 to 4 : 5 with an increase of diborylated product (~ 5%) after 24 hours, and to 2 : 5 with ~10% of diborylated product after 2 days. Longer reaction times resulted in negligible further changes in product distribution. Instead, borylation of *N*-methyl-pyrrole using an excess of amine (CatBCl, Et_3N and $AlCl_3$ in 1 : 1.1 : 1 ratio) was complete in 24 hours and the 2- and 3-catecholboryl-*N*-methylpyrrole ratio was 4 : 1. The product ratio did not alter with time. Therefore, the reaction in presence of excess of $AlCl_3$ (0.1 equivalents) promoted isomerisation of the 2-catecholboryl-*N*-methylpyrrole to the 3-isomer, while the reaction in presence of excess of amine (0.1 equivalents) prevented the isomerisation and retarded the borylation reaction (24 hours versus 7 hours) (Scheme 3.7).



Scheme 3.7 Borylation of *N*-methylpyrrole

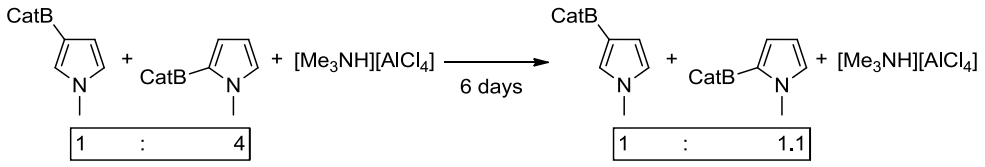
In literature, precedence for the isomerisation from 2-substituted to 3-substituted pyrroles has been reported in presence of strong Brønsted acids such as triflic acid.[25]

However, it has been also reported that in the gas phase the poorly acidic ammonium cation was able to protonate pyrrole.[26]

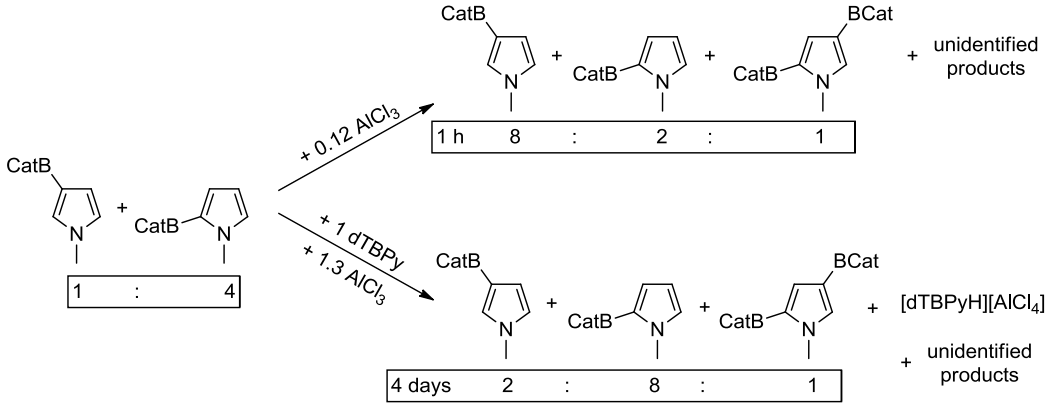
In order to study whether the rearrangement of the catecholboryl moiety is Brønsted or Lewis acid catalysed, the borylated mixture of 3- and 2-catecholboryl-*N*-methylpyrrole (1 : 4 ratio) was isolated by extraction with pentane and reacted with $AlCl_3$ and the Brønsted acid trimethylammonium tetrachloroaluminate ($[Me_3NH][AlCl_4]$).

3.4 Studies on catecholboryl migration

In order to test whether the poorly acidic ammonium salt $[R_3NH][AlCl_4]$, which was a by-product of heteroarene borylation, was able to promote the catecholboryl migration, $[Me_3NH][AlCl_4]$ was prepared by mixing $[Me_3NH][Cl]$ and $AlCl_3$ in CD_2Cl_2 in a 1 : 0.95 ratio (to ensure that free $AlCl_3$ was not present in solution). The addition of 1 equivalent of a 1 : 4 ratio mixture of 3- and 2-catecholboryl-*N*-methylpyrrole to $[Me_3NH][AlCl_4]$ in CD_2Cl_2 gave small quantities of *N*-methylpyrrole and $CatBCl(NMe_3)$ and no significant change in isomer distribution at 20 °C after 90 minutes (by ^1H NMR spectroscopy). *N*-methylpyrrole and $CatBCl(NMe_3)$ are presumably derived from the protodeboronation of catecholborylpyrrole, caused by the small amount of $[Me_3NH][Cl]$ present in solution, indicating that chloride coordination to boron is important for protodeboronation. Longer reaction times resulted in a very slow isomerisation and the 2-catecholboryl-*N*-methylpyrrole was still the major isomer present in solution after 6 days. The slowness of the isomerisation with $[Me_3NH][AlCl_4]$ suggested that isomerisation in the borylation of *N*-methylpyrrole with excess of $AlCl_3$ was due to a Brønsted acid stronger than $[Me_3NH][AlCl_4]$ or to the Lewis acid $AlCl_3$.



The addition of substoichiometric quantities of $AlCl_3$ (0.12 equivalents) to a 1 : 4 ratio mixture of 3- and 2-catecholboryl-*N*-methylpyrrole in CD_2Cl_2 resulted in a rapid isomerisation. After 1 hour, the 3-isomer was present as the major product and ~ 10% of 2,4-diborylated-*N*-methylpyrrole were formed. In contrast, the addition of 1.3 equivalents of $AlCl_3$ to a 1 : 4 ratio mixture of 3- and 2-catecholboryl-*N*-methylpyrrole in the presence of 1 equivalent of the sterically bulky base 2,6-di-*tert*-butylpyridine (dTBPy) as a proton scavenger gave no significant change in isomer ratio. After 45 minutes, the ^1H NMR revealed the formation of the diborylated pyrrole derivative (~ 10%), almost quantitative protonation of dTBPy and no significant change in isomer ratio of monoborylated isomers. Longer reaction times (4 days) resulted in negligible changes in the reaction mixture.



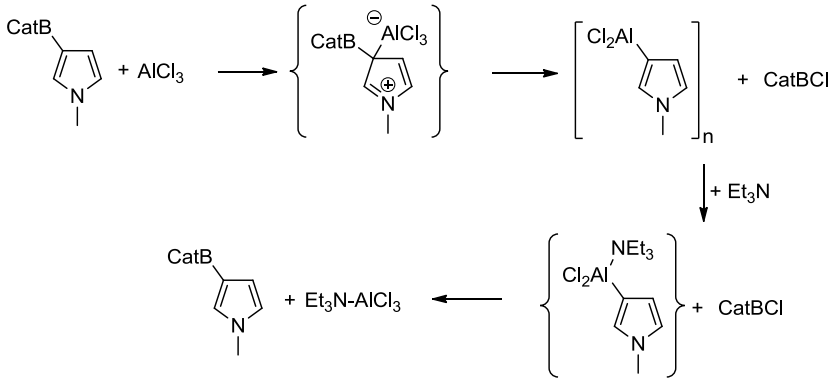
Scheme 3.8 Reaction between 3- and 2-catecholboryl-*N*-methylpyrrole and $AlCl_3$ with and without dTBPy.

The formation of protonated dTBPy indicates that the addition of $AlCl_3$ to catecholboryl-*N*-methylpyrrole in CH_2Cl_2 gives a Brønsted acid that in absence of a proton scavenger can promote catecholboryl migration. Hence, the proposed

mechanism of the catecholboryl rearrangement is the protonation of the ipso carbon of catecholboryl-*N*-methylpyrrole and subsequent catecholboryl migration. This migration can also be an intermolecular process as indicated by the formation of the diborylated pyrrole derivative.

The reaction of one or more equivalents of $AlCl_3$ with 3-catecholboryl-*N*-methylpyrrole (prepared by transmetallation of 3-trimethylsilyl-*N*-methylpyrrole with CatBCl) led to the rapid formation of CatBCl as the only boron containing product (by ^{11}B NMR spectroscopy). The addition of Et_3N to this mixture reaction produced 3-catecholboryl-*N*-methylpyrrole and $Cl_3Al{\bullet}NEt_3$ (by NMR spectroscopy) along with unidentified products.

The reaction of $AlCl_3$ with 3-catecholboryl-*N*-methylpyrrole possibly proceeds by the initial electrophilic attack of $AlCl_3$ to the *ipso* carbon of 3-catecholboryl-*N*-methylpyrrole which rapidly forms CatBCl and 3-Cl_2Al-*N*-methylpyrrole (presumably as an oligomer).[27] The subsequent addition of Et_3N forms an adduct with the organoaluminium compound which undergoes transmetallation with CatBCl (Scheme 3.9). This mechanism is indirectly supported by the regioselectivity of the reaction that re-forms 3-catecholboryl-*N*-methylpyrrole with no formation of 2-catecholboryl-*N*-methylpyrrole or diborylated product.



Scheme 3.9 Proposed mechanism of metallo-deboronation and subsequent transmetallation upon addition of Et_3N

Attempts to detect the intermediate species in the reaction of one equivalent of $AlCl_3$ with 3-catecholboryl-*N*-methylindole by NMR spectroscopy were unsuccessful because the transmetallation reaction was fast. In contrast, the metallation reaction was slow (complete in 5 days) using the less Lewis acidic $GaCl_3$. The ^1H NMR spectrum showed that all protons of 3-catecholboryl-*N*-methylindole were shifted downfield after the addition of one equivalent of $GaCl_3$. The resonance of the C2 proton was shifted downfield by 0.94 ppm suggesting the coordination of $GaCl_3$ to C3 of 3-catecholboryl-*N*-methylindole (Figure 3.5).

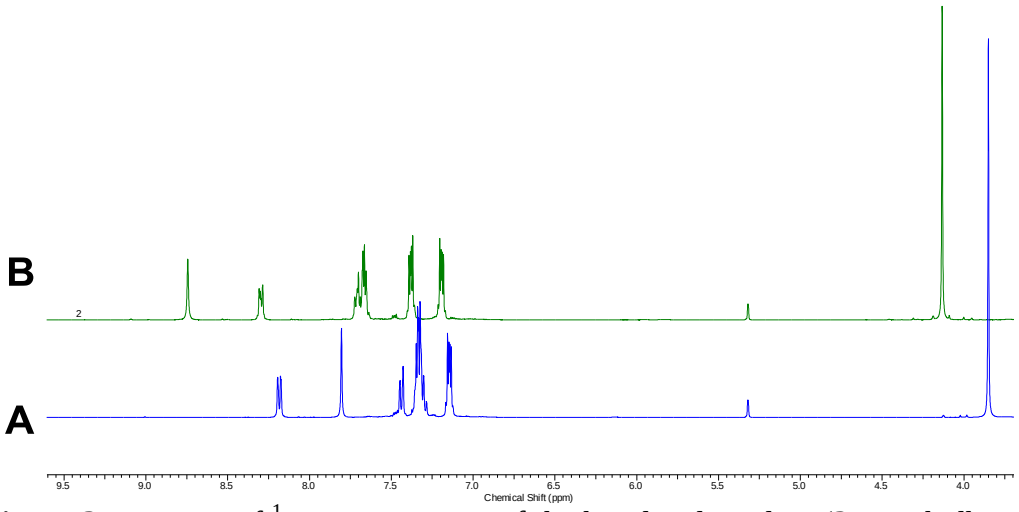


Figure 3.5 Portion of ^1H NMR spectra of the borylated product (3-catecholboryl-*N*-methylindole) from the reaction of 3-D-*N*-methylindole with $[CatB(NEt_3)][GaCl_4]$ in CD_2Cl_2 before (**A**) and after 5 minutes from the addition of 1 equivalent of $GaCl_3$ (**B**).

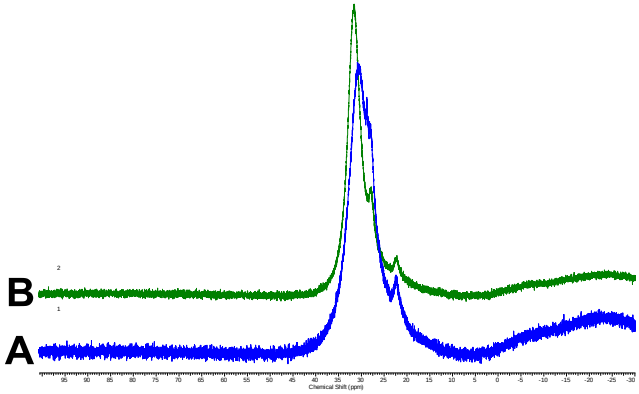
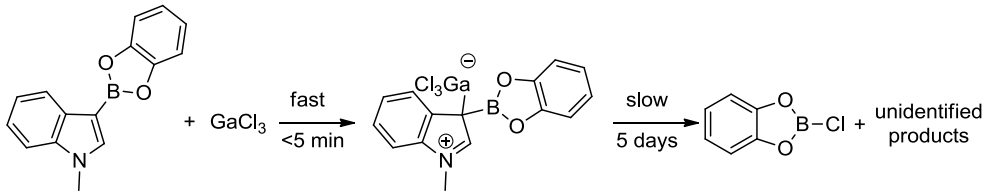


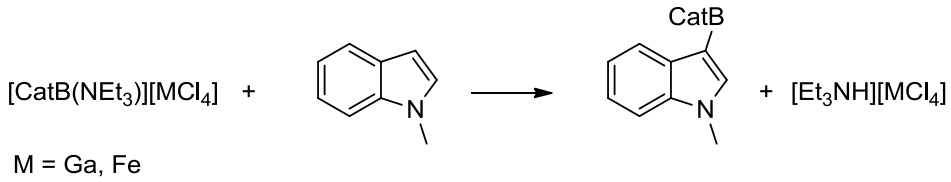
Figure 3.6 ^{11}B NMR spectra of the borylated product (3-catecholboryl-*N*-methylindole) from the reaction of 3-D-*N*-methylindole with $[CatB(NEt_3)][GaCl_4]$ in CD_2Cl_2 before (**A**) and after 5 minutes from the addition of 1 equivalent of $GaCl_3$ (**B**).



Eq. 18

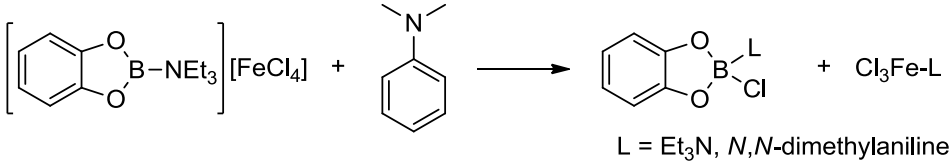
3.5 Direct C-H Arene borylation with [CatB(NEt$_3$)][GaCl$_4$] and [CatB(NEt$_3$)][FeCl$_4$].

Catecholborenium cations generated by halide abstraction from CatBCl•NEt$_3$ with GaCl$_3$ and FeCl$_3$, were also able to borylate *N*-methylindole in 20 and 90 minutes, respectively, analogous to the related catecholborenium cation [CatB(NEt$_3$)][AlCl$_4$].



Eq. 19

Attempts to use [CatB(NEt$_3$)][FeCl$_4$] in the borylation of *N*-methylpyrrole, furan and DMA were unsuccessful. *N*-methylpyrrole and furan led to the formation of insoluble materials, possibly due to oxidative polymerisation by FeCl$_3$.[28] Instead, combination of DMA with [CatB(NEt$_3$)][FeCl$_4$] led to the formation of the neutral adducts Cl$_3$Fe•L and CatBCl•L (L= Et$_3$N or DMA) (Eq. 20), as suggested by ^{11}B NMR spectrum which showed only a sharp peak at 13.2 ppm. The disparity of reactivity between [CatB(NEt$_3$)][AlCl$_4$] and [CatB(NEt$_3$)][FeCl$_4$] with DMA can be ascribed to more facile chloride transfer in [CatB(NEt$_3$)][FeCl$_4$] due to the lower Lewis acidity of FeCl$_3$ compared to AlCl$_3$.

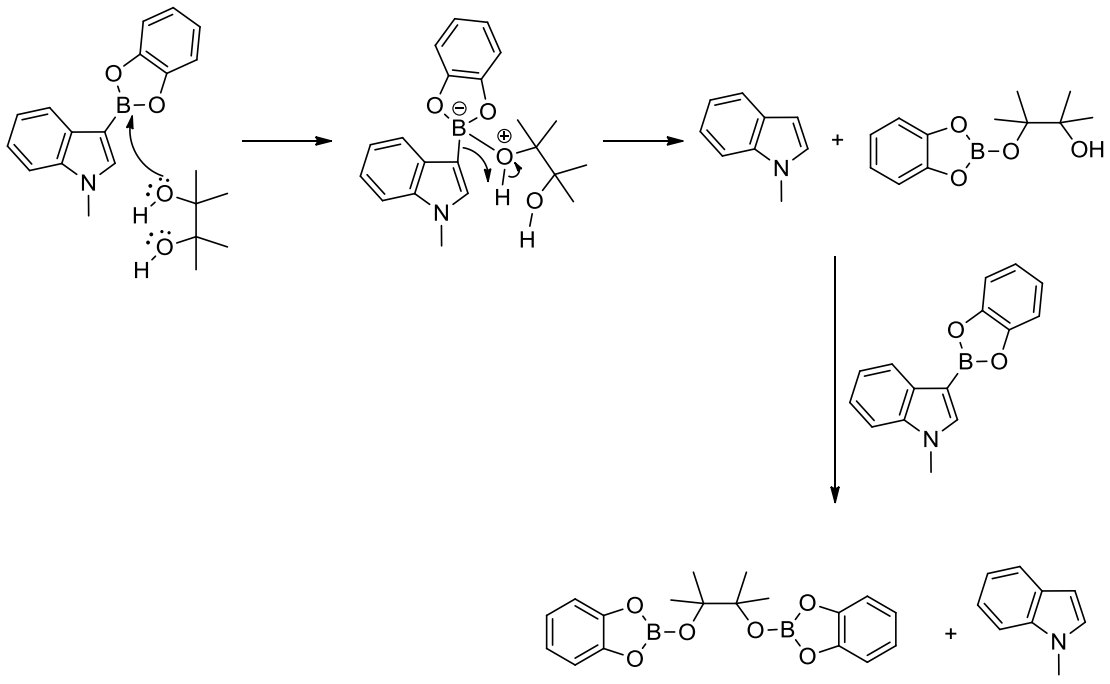


Eq. 20

The purification and isolation of catecholboryl-arenes obtained by borylation with catecholborenium cations proved difficult since they were sensitive to moisture and did not survive silica gel chromatography.[29] To overcome this drawback, the catechol moiety was replaced *in situ* with the pinacol group, which provided more stability towards hydrolysis and protodeborylation.

3.6 Transesterification reaction

Initial attempts to transesterify 3-catecholboryl-*N*-methylindole, following the procedure used for the arylboronate esters,[29, 30] were unsuccessful. The addition of one equivalent of pinacol to the isolated 3-catecholboryl-*N*-methylindole gave protodeborylation, yielding $(Pin)_{3-n}B_2(Cat)_n$ (n = 1-3) (Pin = pinacolate) and free heteroarene. A plausible mechanism of protodeboronation is the pre-coordination of the boron center with the oxygen atom of the pinacol and subsequent proton transfer (Scheme 3.10).



Scheme 3.10 Proposed mechanism of protodeboronation of 3-catecholboryl-*N*-methylindole with pinacol.

In order to prevent the proteodeboronation, the base Et_3N was used as proton scavenger. The equimolar reaction between pinacol and 3-catecholboryl-*N*-methylindole in presence of Et_3N (15 equivalents) resulted in quantitative transesterification to the pinacolboryl indole derivative. However, initial attempts to achieve borylation and transesterification in one pot were unsuccessful.

When the reaction of $[CatB(NEt_3)][AlCl_4]$ and *N*-methylpyrrole was complete, 15 equivalents of Et_3N and 1 or 1.5 equivalents of pinacol were added. The ^{1}H and ^{11}B NMR spectra revealed that protodeboronation occurred in addition to transesterification. Furthermore, products from protodeboronation increased with time (Figure 3.7). In contrast, quantitative transesterification was achieved using 2.1 or more equivalents of pinacol, and the resulting pinacolyl product was stable in the reaction mixture for 24 hours (by ^{11}B NMR) (Figure 3.8).

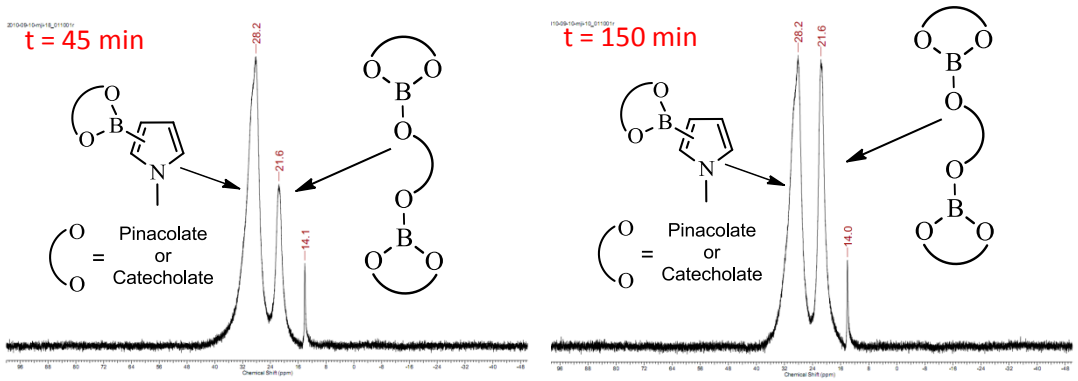


Figure 3.7 ^{11}B NMR of the transesterification reaction with 1.5 equivalents of pinacol in presence of Et_3N. *Left:* After 45 min. *Right:* After 150 min

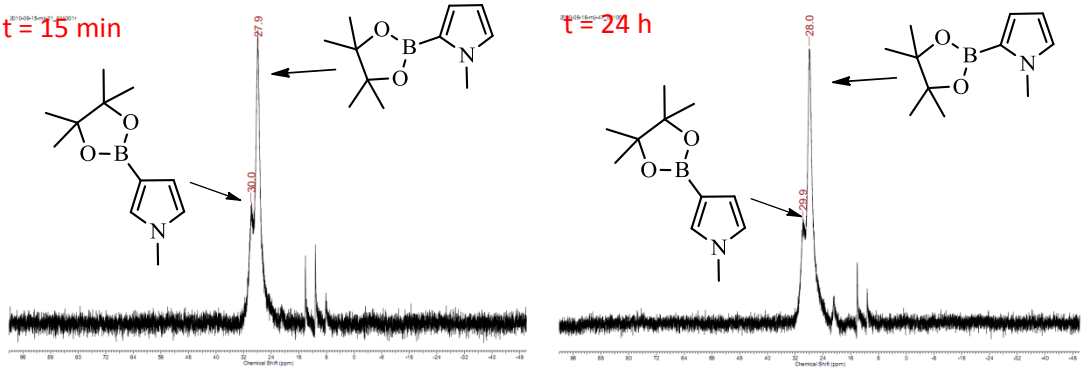


Figure 3.8 ^{11}B NMR of the transesterification reaction with 2.1 equivalents of pinacol in presence of Et_3N. *Left:* After 15 minutes *Right:* After 24 hours.

The requirement of at least 2 equivalents of pinacol was due to the side reaction between pinacol and $[AlCl_4]^-$, which formed an insoluble microcrystalline solid in CH_2Cl_2. The isolation of a crystal suitable for X-ray analysis revealed that the reaction of pinacol with $AlCl_3$ produced a dimeric species with formula $\{[\mu\text{-}OC(CH_3)_2C(CH_3)_2OH]AlCl_2\}_2$ (Figure 3.9). This dimer co-crystallised with two molecules of $[Et_3NH][Cl]$ where the chlorine atom formed H-bonds with the alkoxide and ammonium proton.

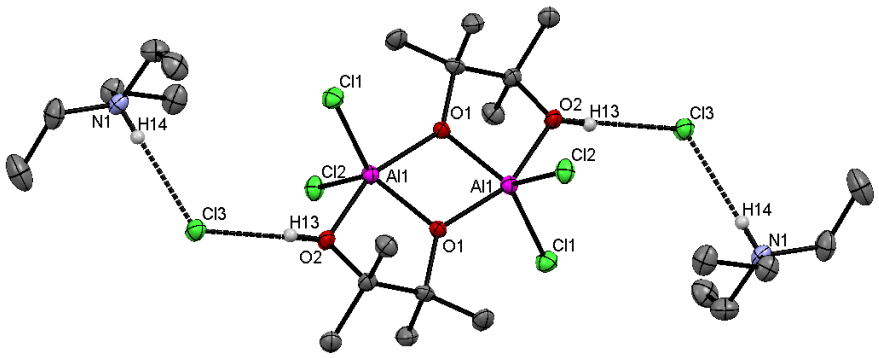
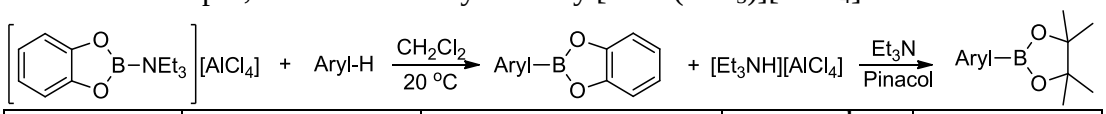


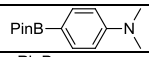
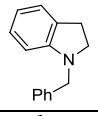
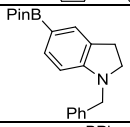
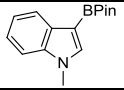
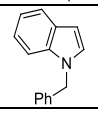
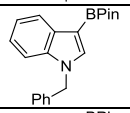
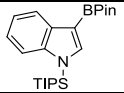
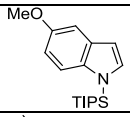
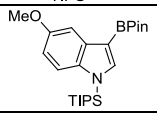
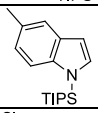
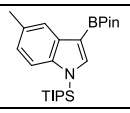
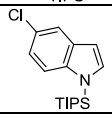
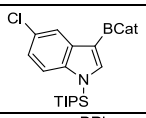
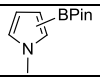
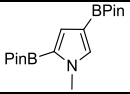
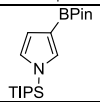
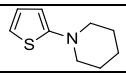
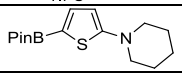
Figure 3.9 Crystal structure of $\{[\mu\text{-}OC(CH_3)_2C(CH_3)_2OH]AlCl_2\}_2$, aliphatic hydrogens omitted for clarity and thermal ellipsoids for non-hydrogen atoms draw at 50 % probability. Hydrogen bonds = dashed bonds. Selected bond lengths (Å): Al1-O1 = 1.835(2), Al1-O2 = 1.918(2), Al1-O1' = 1.878(1), Al1-Cl1 = 2.1762(9), Al1-Cl2 = 2.1569(9).

The $\{[\mu\text{-}OC(CH_3)_2C(CH_3)_2OH]AlCl_2\}_2$ structure presents two five-membered rings fused to a central planar four-membered ring consisting of approximately trigonal oxygens and trigonal-bipyramidal aluminums. Al-O distances (1.877(1), 1.918(1) and 1.835(1) Å) and Al-Cl bond lengths (2.1569(8) and 2.1763(7) Å) are comparable to those found in related four coordinated aluminum chloride alkoxides.[31]

In the end, various aromatic compounds were borylated by the catecholborenium salt $[CatB(NEt_3)][AlCl_4]$ with excellent yield and regioselectivity. The subsequent transesterification *in situ*, with 2 or more equivalents of pinacol, provided the more stable and robust pinacol boronate ester (Table 3.4).

Table 3.4 One-pot, direct arene borylation by $[CatB(NEt_3)][AlCl_4]$.[a]



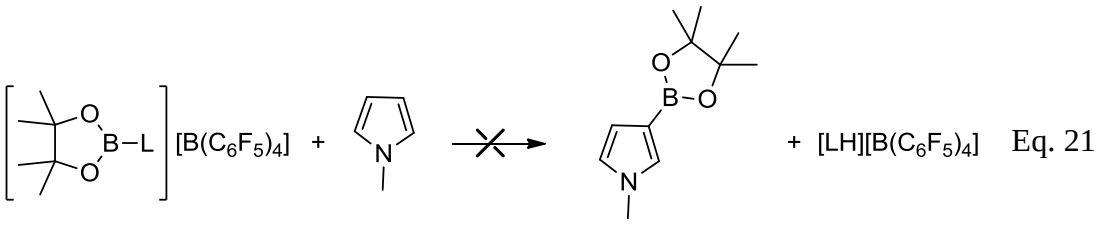
Entry	Substrate	Product	Time[b] (h)	Yield[c] (%)
1			< 0.5	85
2			4	96
3			4	92
4			6	95
5			48	78
7			30	88
8			24	86
9			504	~75[d]
10			4	91[e]
11			192	73
12			72	89
13			< 0.5	69

[a] Borenium cations prepared *in-situ* in CH_2Cl_2 from 1 equivalent of CatBCl, 1.05 equivalents of Et_3N, and 1.1equivalents of $AlCl_3$. 1 equivalent of arene substrate is then added. [b] Reaction time refers to consumption of all borenium cation (by multinuclear NMR spectroscopy). [c] Yield of isolated products unless otherwise stated. [d] Yield of 3-CatB-5-chloro-*N*-TIPS-indole by *in-situ* ^{1}H NMR spectroscopy. [e] This was a mixture of the 2- and 3-regioisomers, with individual yields at 39% and 52%, respectively. (e) 2.1 equivalents of borenium cation used.

Final products of direct C-H arene borylation by $[CatB(NEt_3)][AlCl_4]$ were pinacolboryl arenes. It would be suitable to start from the pinacolborenium cation for a more atom economical process (eliminating catechol). However, the preparation of

the pinacolborenium cation by halide abstraction from PinBCl was not a simple route, due to the instability of PinBCl.[32] On the other hand, PinBH is a stable and commercially available compound and pinacol borenium cations can be prepared by hydride abstraction.[33]

Ingleson, starting from PinBH(amine) (amine = 2,6-lutidine, *N*,*N*-dimethyl-aniline) and $[Ph_3C][B(C_6F_5)_4]$, achieved the synthesis of pinacol borenium salts $[PinB(amine)][B(C_6F_5)_4]$. However, attempts to borylate *N*-methylpyrrole with these pinacolborenium salts were unsuccessful. The absence of arene borylation with pinacolborenium cation is presumably due to the insufficient electrophilicity of the boron atom since the oxygens of pinacolyl group are better electron donors than the oxygens of catecholyl group.



Eq. 21

The electrophilicity of the boron atom was crucial for the direct C-H arene borylation. Therefore, in order to seek a more electrophilic species to expand the substrate scope, the related tetrachlorocatecholborenium cation was tested in arene borylation.

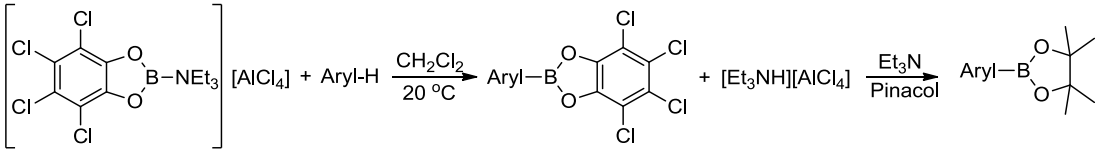
3.7 Direct C-H arene borylation with $[Cl_4CatB(NEt_3)][AlCl_4]$

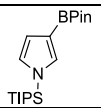
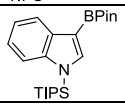
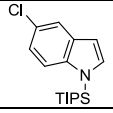
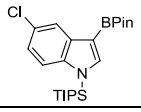
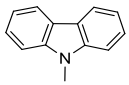
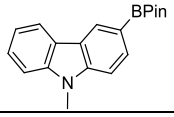
The substitution of the hydrogen atoms for the electron withdrawing chlorine atoms in the catecholboryl group is expected to increase the electrophilicity of the boron centre in the triethylamine-ligated catecholboron cation.

The initial proof of higher electrophilicity of $[Cl_4CatB(NEt_3)][AlCl_4]$ was given by borylation of *N*-TIPS-heterocycles. *N*-TIPS-pyrrole, *N*-TIPS-indole, 5-chloro-*N*-

TIPS-indole, which all required days for complete borylation with [CatB(NEt$_3$)][AlCl$_4$], were borylated with [Cl$_4$CatB(NEt$_3$)][AlCl$_4$] within hours (Table 3.5, entry 1-3). Furthermore, 9-methyl carbazole, which was unreactive towards [CatB(NEt$_3$)][AlCl$_4$], was efficiently borylated with the related tetrachloro-catecholborocation (table 3.5, entry 4).

Table 3.5 Direct arene borylation by [Cl$_4$CatB(NEt$_3$)][AlCl$_4$].[a]



Entry	Substrate	Product	Time[b] (h)	Yield[c] (%)
1			3	>95[d]
2			4	>95[d]
3			4	84
4			4	71

[a] Borenium cations prepared *in-situ* in CH_2Cl_2 from 1 equivalent of CatBCl, 1.05 equivalents of Et_3N, and 1.1equivalents of $AlCl_3$. 1 equivalent of arene substrate is then added. [b] Reaction time refers to consumption of all borenium cation by multinuclear NMR spectroscopy. [c] Yield of isolated products unless otherwise stated. [d] Yield by ^{1}H NMR spectroscopy.

Despite [Cl$_4$CatB(NEt$_3$)][AlCl$_4$] showing an increased substrate scope, it was still unable to borylate less activated arenes such as toluene. Hence, in order to seek a more reactive borylating mixture, Et$_3$N was replaced with different Lewis bases.

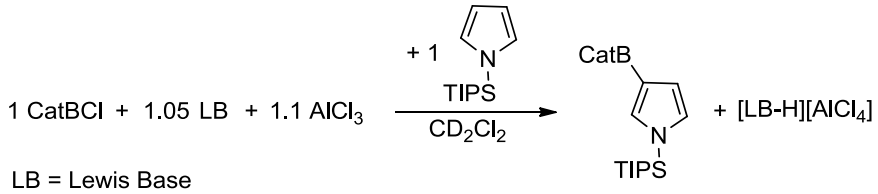
3.8 Effect of the Lewis base in the arene borylation

In order to study the influence of different Lewis bases, the borylation of *N*-TIPS-pyrrole was used as a benchmark. The borylating mixture was prepared by

premixing in a 1 : 1.05 ratio CatBCl and Lewis Base in CH_2Cl_2 and then adding 1.1 equivalents of $AlCl_3$.

Care has to be taken not to over-interpret these results as the reaction time was extremely sensitive to very minor (imperceptible by NMR) differences in the stoichiometry of the reaction (see section 3.11). However, the use of the Lewis base DMTol in combination with CatBCl and $AlCl_3$ clearly resulted in the most reactive mixture, borylating *N*-TIPS-pyrrole in less than 1 hour (Table 3.6, entry 5). Further confirmation of an enhanced borylating ability came from the borylation of 9-methylcarbazole which was complete at 20 °C in 48 hours (Eq. 22). In contrast, the borenium cation formed with 2,6-lutidine or Et_3N was unreactive towards 9-methylcarbazole at 20 °C after 24 hours.

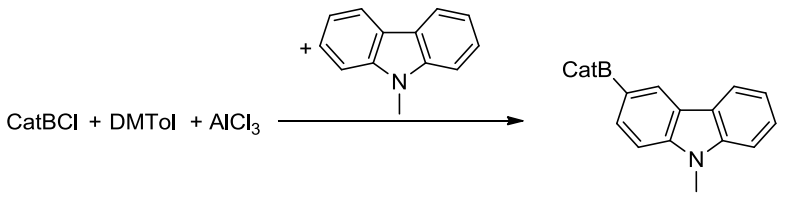
Table 3.6 Borylation of *N*-TIPS-pyrrole using various Lewis base.



LB = Lewis Base

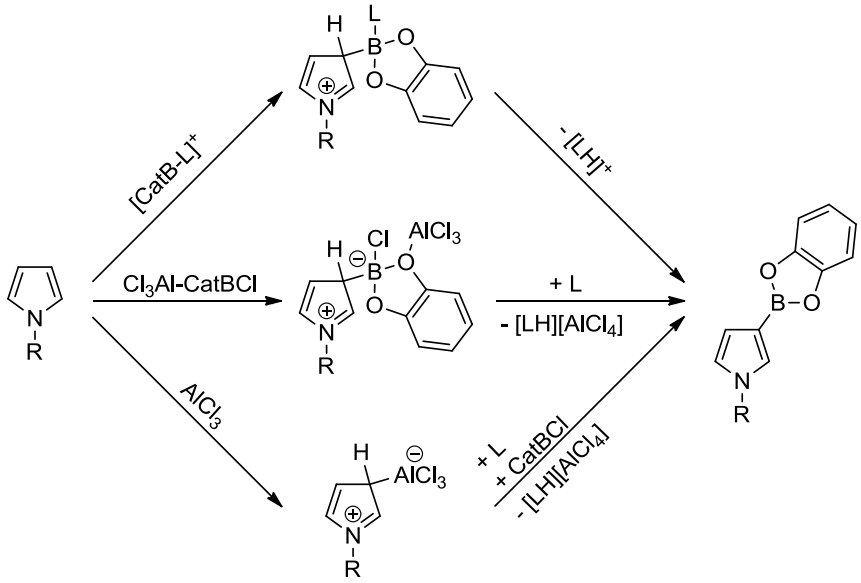
Entry	Lewis Base	pKa	Reaction Time (h)	Yield[a] (%)
1	EtN^iPr_2	11.44[b]	72	97
2	Et_3N	10.67[c]	72	89
3	PCy_3	9.7[d]	15	97[e]
4	2,6-Lutidine	6.7[f]	67	94
5	DMTol	5.24[b]	< 1	90

[a] isolated yield, unless otherwise stated. [b] reference 7. [c] reference 8. [d] reference 14. [e] by ^1H NMR spectroscopy. [f] reference 9.



Eq. 22

It is noteworthy to remark that the borenium cation was not the only electrophile present in solution since [CatB(L)][$AlCl_4$] was in equilibrium with $AlCl_3$ and CatBCl•L. The latter was further in equilibrium with CatBCl and L. Consequently, the electrophilic species $AlCl_3$ and CatBCl were also present in solution although at low (unobservable by NMR spectroscopy) concentrations. Therefore, it is possible to postulate that an electrophilic species deriving from the coordination of $AlCl_3$ to CatBCl (either on oxygen or on chlorine) or $AlCl_3$ itself can also be the active electrophile in the arene borylation (Scheme 3.11).



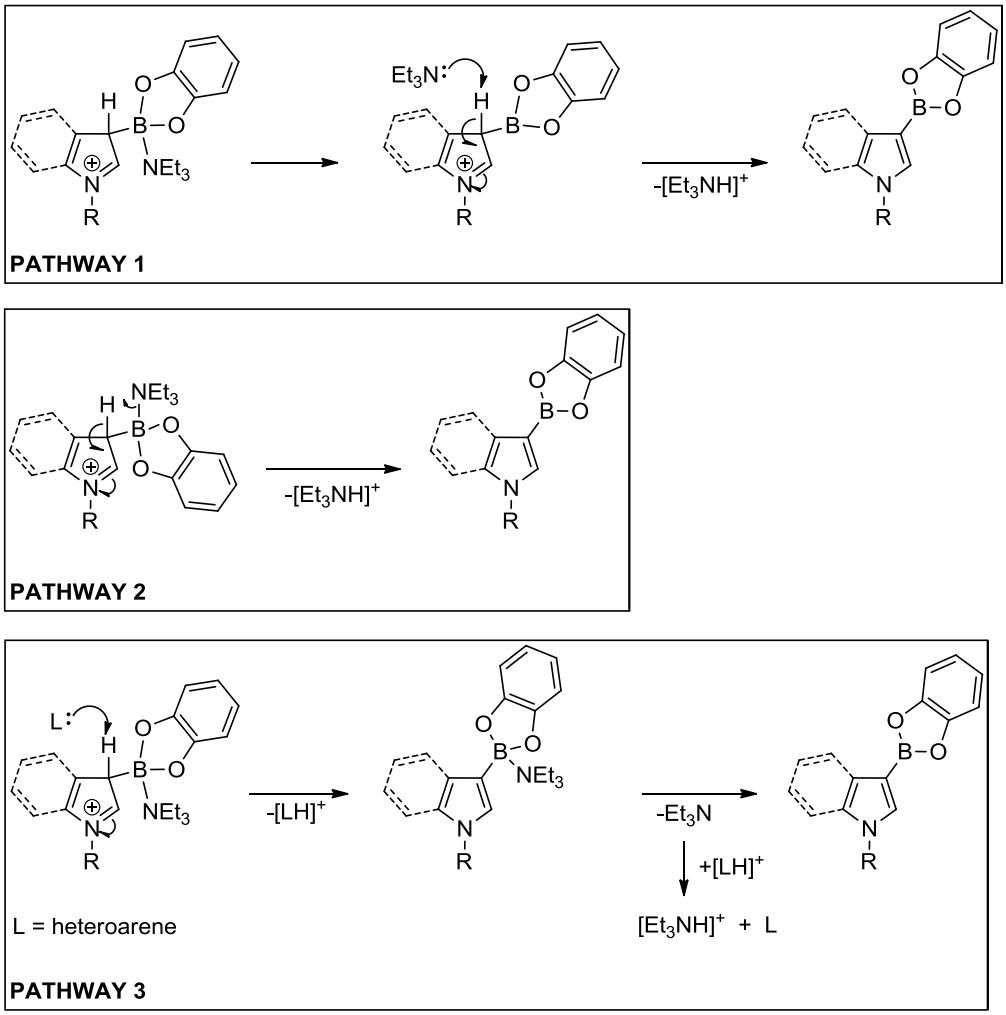
Scheme 3.11 Proposed reaction pathways.

In order to identify the active electrophile among the electrophilic species present in solution and the mechanism of reaction, reactions of arene with the borenium salt [CatB(NEt_3)][*closo*-$CB_{11}H_6Br_6$] and with the equimolar combination of CatBCl, dTBPy and $AlCl_3$ were carried out. The use of the anion [*closo*-$CB_{11}H_6Br_6$]$^-$ precludes the presence of electrophilic species other than [CatB(NEt_3)]$^+$ since the robust anion [*closo*-$CB_{11}H_6Br_6$]$^-$ does not undergo halide transfer observed with [$AlCl_4$]$^-$. While, with the mixture of CatBCl, dTBPy and $AlCl_3$ the formation of a

borenium cation is precluded since the nitrogen in the Lewis base dTBPy is sterically encumbered preventing coordination to boron.

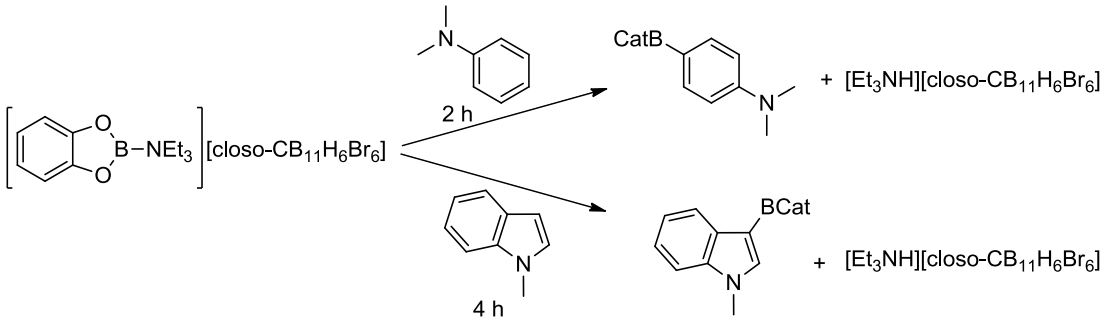
3.9 Arene borylation with [CatB(NEt$_3$)][*closo*-CB$_{11}$H$_6$Br$_6$].

The addition of one equivalent of DMA or *N*-methylindole to the borenium salt [CatB(NEt$_3$)][*closo*-CB$_{11}$H$_6$Br$_6$] (purified by crystallisation) in CD_2Cl_2 led to complete arene borylation in 2 and 4 hours, respectively. This indicated that the borenium cation [CatB(NEt$_3$)]$^+$ was an active borylating species since no other electrophiles were present in solution. Mechanistically arene borylation by this borenium cation must proceed by reversible formation of a σ-complex (arenium ion) and subsequent deprotonation. The deprotonation of the σ-complex can proceed through three different pathways: (1) decomplexation of the Lewis base and subsequent deprotonation by the decomplexed Lewis base, (2) Lewis base decomplexation and deprotonation in a concerted step and (3) deprotonation by a second equivalent of base (for example *N*-methylindole, DMA) and subsequent decomplexation of the Lewis base (Scheme 3.12). Involvement of the anion [*closo*-CB$_{11}$H$_6$Br$_6$]$^-$ in the deprotonation step is ruled out since the anion is an extremely weak base ([H][*closo*-CB$_{11}$H$_6$Br$_6$] is a Brønsted superacid able to protonate benzene).[34]

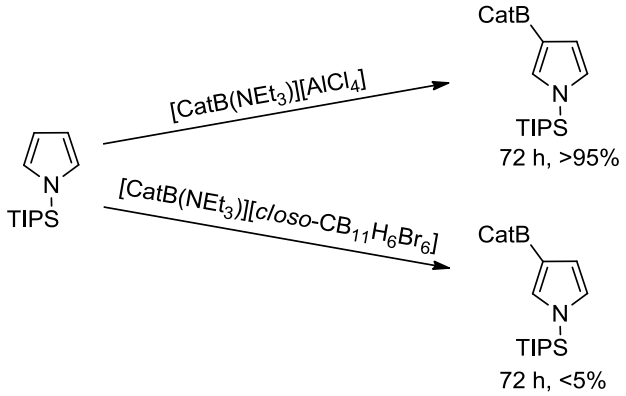


Scheme 3.12 Proposed mechanisms of deprotonation of the σ-complex.

Attempts to borylate *N*-TIPS-pyrrole with [CatB(NEt_3)][*closo*-$CB_{11}H_6Br_6$] resulted in an extremely slow reaction (< 5% in 72 hours by NMR spectroscopy). This was in contrast with *N*-TIPS-pyrrole borylation by [CatB(NEt_3)][$AlCl_4$] which was complete in 72 hours at 20 °C. The different reactivity of [CatB(NEt_3)][$AlCl_4$] and [CatB(NEt_3)][*closo*-$CB_{11}H_6Br_6$] toward *N*-TIPS-pyrrole suggests that equilibria present in solution with [CatB(NEt_3)][$AlCl_4$] enable another indispensable species for the borylation of *N*-TIPS-pyrrole to be present. This species can be either free Et_3N to deprotonate the arenium intermediate or a more electrophilic species than [CatB(NEt_3)]$^+$.



Scheme 3.13 Reaction of DMA and *N*-methylindole with [CatB(NEt$_3$)][*closo*-$CB_{11}H_6Br_6$]



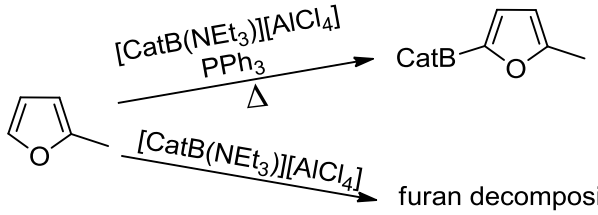
Scheme 3.14 Reaction of *N*-TIPS-pyrrole with [CatB(NEt$_3$)][$AlCl_4$] and [CatB(NEt$_3$)][*closo*-$CB_{11}H_6Br_6$].

In order to investigate whether the slow borylation of *N*-TIPS-pyrrole with [CatB(NEt$_3$)][*closo*-$CB_{11}H_6Br_6$] was due to the absence of a good base to deprotonate the arenium intermediate, the reaction was carried out in presence of the bulky base dTBPy. The coordination of dTBPy to the borenium cation was sterically precluded, hence the combination of [CatB(NEt$_3$)][*closo*-$CB_{11}H_6Br_6$] and dTBPy led to formation of a FLP (by NMR spectroscopy). Although the borenium cation and the free base dTBPy were both present in solution, the borylation of *N*-TIPS-pyrrole was still extremely slow (< 5 % in 24 hours by ^{1}H NMR spectroscopy). In contrast, Dr Michael J. Ingleson found that [CatB(NEt$_3$)][B(3,5-$C_6H_3Cl_2)_4$] borylated *N*-TIPS-

pyrrole at 20 °C in the presence of PPh_3 in less than 1 hour, with $[CatB(NEt_3)][B(3,5\text{-}C_6H_3Cl_2)_4]$ and PPh_3 representing a stable FLP. In the control reaction $[CatB(NEt_3)][B(3,5\text{-}C_6H_3Cl_2)_4]$ in the absence of PPh_3 was unable to borylate *N*-TIPS-pyrrole at 20 ^oC. These results indicated that the arene borylation with $[CatB(NEt_3)][closo\text{-}CB_{11}H_6Br_6]$ proceeded by formation of a σ-complex which requires an additional Brønsted base that is sufficiently basic and less bulky than dTBPy to effect deprotonation. Thus pathways 1 and 2 are not consistent with these observations.

The ability of $[CatB(NEt_3)][closo\text{-}CB_{11}H_6Br_6]$ to borylate *N*-methylindole and DMA in absence of additional base suggested that *N*-methylindole and DMA were the bases in the borylation of these substrates. In contrast, *N*-TIPS-pyrrole was not sufficiently basic to deprotonate the σ-complex.[35]

The crucial role of the Brønsted base in the arene borylation with the borenium cation $[CatB(NEt_3)]^+$ was further confirmed using the FLP $[CatB(NEt_3)][AlCl_4]$ / PPh_3 (see section 3.2). Catalytic quantities of PPh_3 (0.1 equivalents) drastically reduced the time of borylation of *N*-TIPS-pyrrole from 72 hours to less than 1 hour. Furthermore, subsequently James Lawson showed that the FLP $[CatB(NEt_3)][AlCl_4]/PPh_3$ enabled the regioselective C5 borylation of 2-methylfuran, which was previously not amenable to electrophilic borylation using catecholborenium cations due to rapid decomposition of the furan.



Scheme 3.15 Reaction between 2-methylfuran and $[CatB(NEt_3)][AlCl_4]$ with and without PPh_3.

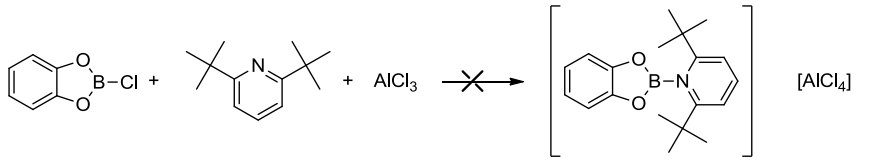
The successful use of [CatB(NEt_3)][*closo*-$CB_{11}H_6Br_6$] in arene borylation demonstrates that this borenium cation is an active electrophilic species. However, with [CatB(NEt_3)][$AlCl_4$] it is still possible that active electrophilic species other than the borenium cation are present in solution since all steps in the formation of [CatB(NEt_3)][$AlCl_4$] are reversible. Indeed, a species other than [CatB(NEt_3)]$^+$ has to be present to enable borylation of *N*-TIPS-pyrrole. While, this may be further Et_3N (from equilibrium) it may also be an additional electrophile.

In order to prevent the formation of a borenium cation and thus determine whether other electrophiles can also be involved in arene borylation, the bulky amine dTBPy was used in combination with CatBCl and $AlCl_3$.

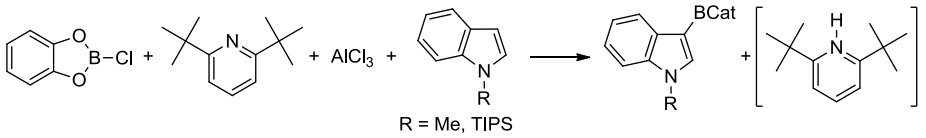
3.10 Borylation without borenium cation.

The non-nucleophilic mild base dTBPy is unable to give a B-N dative bond with CatBCl since the sterically bulky *tert*-butyl groups in the 2- and 6-positions creates a steric shield around the nitrogen centre. Consequently, the addition of $AlCl_3$ to the mixture of dTBPy and CatBCl in CH_2Cl_2 did not lead to formation of a borenium cation (by ^{11}B and ^{27}Al NMR spectroscopy). However, the combination of CatBCl, $AlCl_3$ and dTBPy in CH_2Cl_2 with *N*-methylindole or *N*-TIPS-indole or 9-methylcarbazole gave an extremely rapid reaction with the formation of the borylated product along with the protonated dTBPy (Eq. 24, 25). The reaction still proceeded regioselectively giving the expected product from electrophilic aromatic substitution. 9-Methylcarbazole was also diborylated efficiently in the 3 and 6 positions with good yield (73% after transesterification) in less than 1 hour (Eq. 26). Moreover, the combination of dTBPy, CatBCl and $AlCl_3$ in *ortho*-dichlorobenzene at 100 °C was able to borylate fluorene selectively at the 2 position although in low

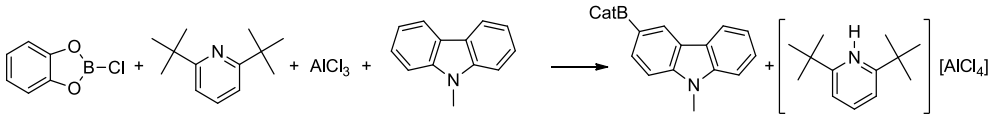
yield (37%) (Eq.27).



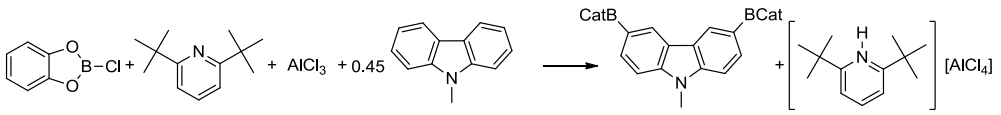
Eq. 23



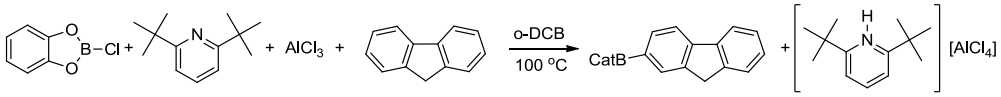
Eq. 24



Eq. 25



Eq. 26

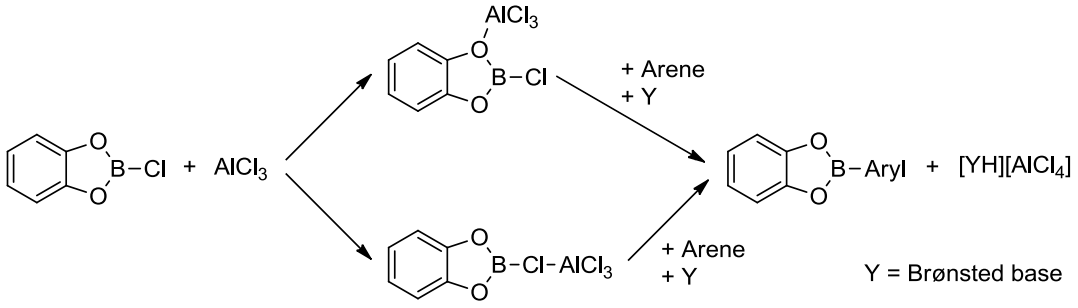


Eq. 27

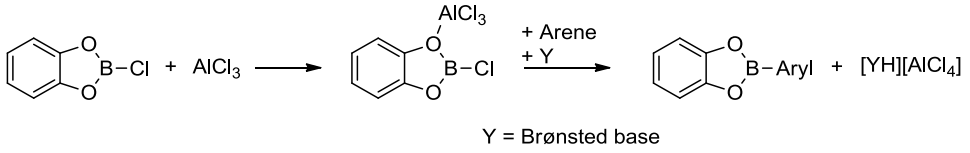
With the mixture CatBCl, dTBPy and $AlCl_3$ the formation of a borenium cation is ruled out, hence the electrophilic species CatBCl•$AlCl_3$ and $AlCl_3$ are postulated as alternative electrophiles.

In the absence of a good nucleophile the Lewis acid $AlCl_3$ can interact with CatBCl to give an halo- or oxo-coordinated CatBCl•$AlCl_3$ adduct. The formation of oxo-coordinated CatBCl•$AlCl_3$ was indirectly supported by the previous observation that $AlCl_3$ and CatBCl slowly led to the formation of BCl_3. Furthermore a similar intermediate was also proposed by Evans and co-workers in the Lewis acid catalysed hydroboration of alkenes with CatBH [36] and by Hall and co-workers in the Lewis

acid allylboration of aldehydes with allyl pinacolboronate esters.[37] The coordination of the Lewis acid $AlCl_3$ to CatBCl, which is itself intrinsically Lewis acidic, would generate a highly electrophilic boron species that in the presence of an arene and a Brønsted base would lead to arene borylation (Scheme 3.16).



Scheme 3.16 Arene borylation by halo- or oxo-coordinated $AlCl_3$ to CatBCl

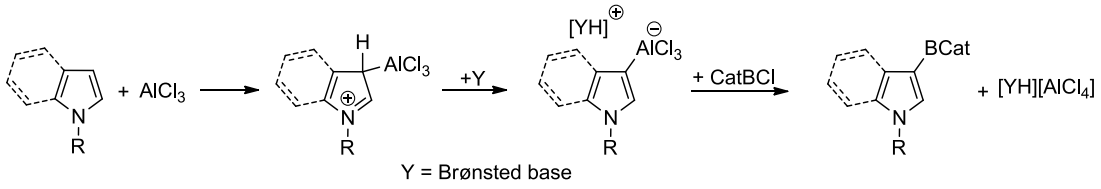


Eq. 28

An alternative mechanism of arene borylation to take into consideration is the initial electrophilic attack of $AlCl_3$ to the arene with subsequent deprotonation to $[ArylAlCl_3]^-$ and transmetallation with CatBCl yielding CatB-aryl (Scheme 3.17). This mechanism is indirectly supported by the previously observation that the organoaluminium compound, 3-(Cl_2Al)-*N*-methylndole upon addition of Et_3N underwent transmetallation by CatBCl (Scheme 3.9, section 3.4). Moreover, the involvement of an organometallic intermediate in the electrophilic aromatic substitution was previously postulated in several reactions such as the acylation of pyrrole[38] and indole[39] and the iodination of benzene with $Sc(OTf)_3$[40] and $Tl(OTf)_3$.[41]

The interaction of $AlCl_3$ with benzene to form a weak π-complex was computationally demonstrated[42] and the crystal structure of the related $(C_6F_5)_3Al$•arene (arene = toluene, benzene) π-complex was also reported.[43] Therefore, it is expected that electron rich arenes such as indole will form a stronger

complex with Lewis acids $AlCl_3$ and $GaCl_3$. This was corroborated by the isolation and the characterisation by X-ray diffraction of the complex *N*-methylindole•MCl_3 (M = Al, Ga).



Scheme 3.17 Proposed transmetallation route.

The main difference between *N*-methylindole•$AlCl_3$ (Figure 3.11) and *N*-methylindole•$GaCl_3$ (Figure 3.12) is that the former crystallises as a conglomerate, while the latter crystallises as a racemate. In both compounds the metals interacts with the most nucleophilic C3 site of the indole and have similar bond lengths and angles. The angle between the aromatic plane and the C3-M bond in *N*-methylindole•$AlCl_3$ and *N*-methylindole•$GaCl_3$ (110.17º and 107.9º, respectively) is between the π- and σ-complex extremes (defined as a π-complex at 90º and a σ-complex at 125°, Figure 3.10).[34] The C3-M distances (Al1-C3 = 2.083(8) and Ga1-C3 = 2.105(3) Å) are considerably shorter than (toluene)Al(C_6F_5)$_3$ (Al-C = 2.366(2) Å), indicating a strong interaction between the metal and the C3 of the *N*-methylindole. This highlights the key effect arene basicity has on increasing adduct strength, with M-C distances in *N*-methylindole•$AlCl_3$ and *N*-methylindole•$GaCl_3$ more closely approaching that of anionic [ArylMCl_3]$^-$ species (for example Ga-C = 1.944(8)Å in ([(Et_2O)Li][Cl_3Ga($C_6H_2{}^iPr_3$)])$_2$).[44]

Figure 3.10 Graphical representation π- and σ-complex.

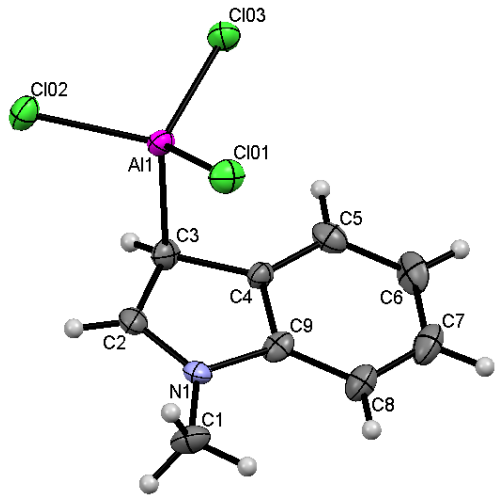


Figure 3.11 Crystal structure of *N*-methylindole•$AlCl_3$ (compound **A**), thermal ellipsoids for non-hydrogen atoms draw at 50 % probability. Selected bond lengths (Å) and angles (°): Al(1)-C(3) = 2.083(8), C(2)-N(1) = 1.33(1), N(1)-C(9) = 1.40(1); C(3)-Al(1)-Cl(1) 107.3 (3).

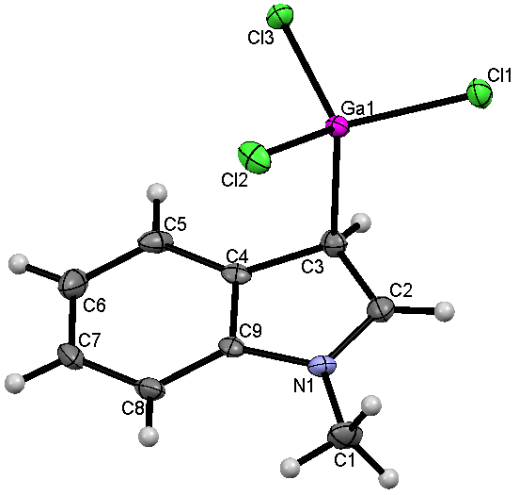


Figure 3.12 Crystal structure of one enantiomer of *N*-methylindole•$GaCl_3$ (compound **B**), thermal ellipsoids for non-hydrogen atoms draw at 50 % probability. Selected bond lengths (Å) and angles (°): Ga(1)-C(3) = 2.104(3), C(2)-N(1) = 1.322(5), N(1)-C(9) = 1.402(4); C(3)-Ga(1)-Cl(1) 109.61 (8).

The formation of *N*-methylindole•MCl_3 will significantly lower the pKa of *N*-methylindole favoring the deprotonation step in the transmetallation mechanism. However, attempts to deprotonate *N*-methylindole•$GaCl_3$ with dTBPy or Mes_3P (Mes = 2,4,6-trimethylphenyl) in CD_2Cl_2, resulted in the formation of insoluble

materials with the only identified species being [HY][$GaCl_4$] (Y = dTBPy, Mes_3P). Thus whilst deprotonation clearly took place [Aryl$GaCl_3$]$^-$ was reacting in the absence of a borane producing an intractable mixture. In contrast, the less bulky base PCy_3 does not deprotonate *N*-methylindole•$GaCl_3$ but immediately produces Cl_3Ga•PCy_3 and *N*-methylindole (by ^1H and ^{71}Ga NMR spectroscopy). These results indicate that a transmetallation mechanism is possible only when the base is sterically hindered (for example dTBPy).

In order to gain more information on the mechanism of reaction, kinetic studies on *N*-methylindole borylation by [CatB(NEt_3)][$AlCl_4$] and [CatB(NEt_3)][$GaCl_4$] were carry out by ^1H NMR spectroscopy.

3.11 Kinetic studies

The assessment of the rate constant for *N*-methylindole borylation by [CatB(NEt_3)][$AlCl_4$] and [CatB(NEt_3)][$GaCl_4$], prepared *in situ*, was complicated because the reaction rate was very sensitive to the imperceptible (by NMR spectroscopy) variation in reagent stoichiometry (with times for complete borylation varying from minutes to hours). This phenomenon, which persisted despite extensive purification of starting materials, also prevented a reliable assessment of kinetic isotope effect. However, it was possible to clearly determine the order of reaction which was independent of reaction duration.

All the reactions of [CatB(NEt_3)][$GaCl_4$], prepared *in situ*, with *N*-methylindole in CD_2Cl_2 at 0 °C were consistent with a global second order rate law (Figure 3.13). In contrast, the reaction between [CatB(NEt_3)][$AlCl_4$] and *N*-methylindole in CD_2Cl_2 at 20 °C followed an overall first order rate law (Figure 3.14). This suggested that the arene borylation proceeds by two different, anion dependent, mechanisms.

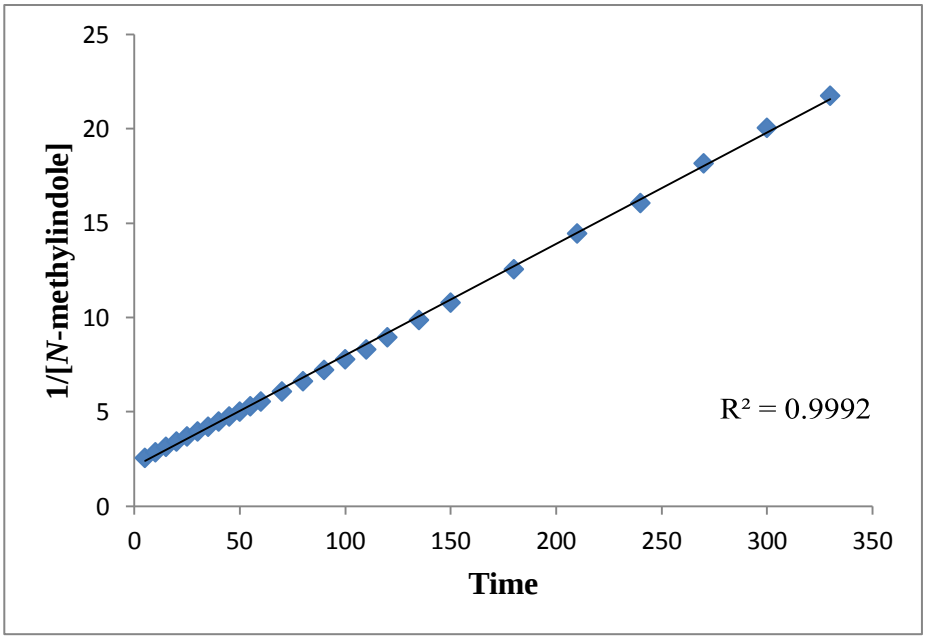


Figure 3.13 Second order kinetic plot for the borylation of *N*-methylindole with [CatB(NEt$_3$)][GaCl$_4$] in CD_2Cl_2 at 0 °C.

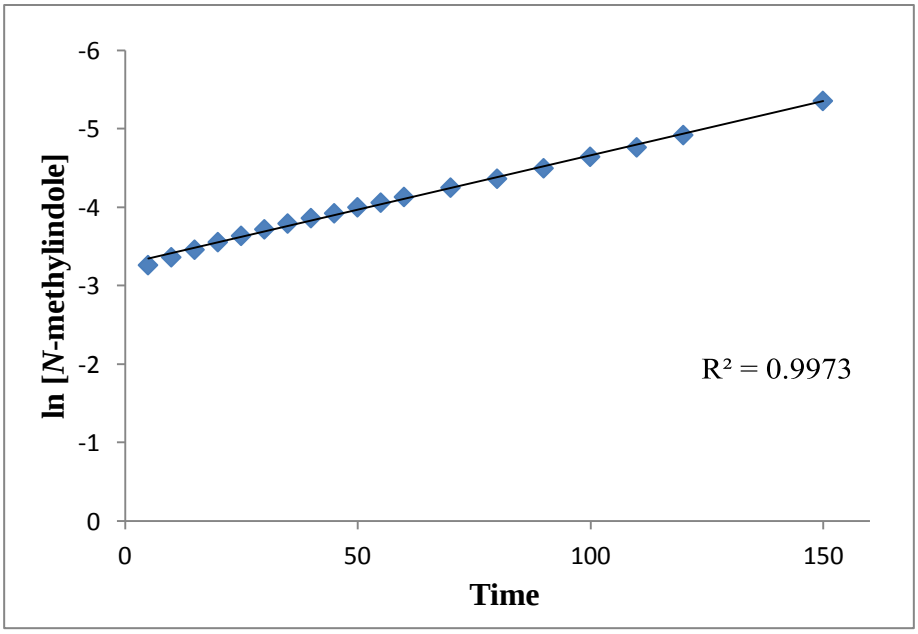


Figure 3.14 First order kinetic plot for the borylation of *N*-methylindole with [CatB(NEt$_3$)][AlCl$_4$] in CD_2Cl_2 at 20 °C.

The overall second order kinetic law for *N*-methylindole borylation by [CatB(NEt$_3$)][GaCl$_4$] is consistent with a classical electrophilic substitution mechanism where the limiting step is the formation of the arenium intermediate.

Therefore, the borylation of *N*-methylindole with [CatB(NEt_3)][$GaCl_4$] possibly involves the initial electrophilic attack of the borenium cation on the heterocycle. Instead, the *N*-methylindole borylation by [CatB(NEt_3)][$AlCl_4$] possibly proceeds either by a different mechanism (for example by the formation of the borylating species CatBCl•$AlCl_3$, or by the transmetallation route), or has a pre-equilibrium step via a rapidly and reversibly formed intermediate (possibly involving interaction of [CatB(NEt_3)][$AlCl_4$] and *N*-methylindole). Attempts to observe any intermediates in this reaction were unsuccessful, although addition of *N*-methylindole to [CatB(NEt_3)]$^+$ resulted in minor changes in the ^{1}H NMR spectrum, but these changes were observed for both [$AlCl_4$]$^-$ and [$GaCl_4$]$^-$ anions.

Attempts to gain more information about the mechanism of arene borylation with [CatB(NEt_3)][$AlCl_4$] by determining the rate order with respect to *N*-methylindole were unsuccessful. The reaction of [CatB(NEt_3)][$AlCl_4$] with more than 1 equivalent of *N*-methylindole led to complete consumption of *N*-methylindole possibly via acid catalysed oligomerisation of *N*-methylindole as suggested by ^{1}H NMR which showed a complicate aromatic region.

3.12 Conclusions

The reaction mixture CatBCl, Lewis base and $AlCl_3$ yielded a borenium cation which was in equilibrium with neutral species as revealed by NMR spectroscopy and reactivity studies. This mixture was able to borylate a series of arenes with excellent regioselectivity. Subsequent transesterification *in situ* provided the synthetically useful, and more stable to protodeboronation, pinacol boronate esters in good isolated yield. The arene borylation with [CatB(NEt_3)][*closo*-$CB_{11}H_6Br_6$] revealed that the borylation proceeded by initial borenium attack on arene followed by base

deprotonation of the arenium intermediate and Lewis base decomplexation. In the borylation of DMA and *N*-methylindole no additional base was required since they were sufficiently basic to abstract the proton on the arenium intermediate, while in the borylation of *N*-TIPS-pyrrole the use of an additional base was crucial. Although the borenium cation was clearly an active species, the arene borylation with the mixture of CatBCl, dTBPy and $AlCl_3$ (this mixture cannot form the borenium cation) suggested that different mechanisms can be involved in the arene borylation with [CatB(amine)][MCl_4] which was in equilibrium with the neutral species CatBCl and $AlCl_3$. The postulated alternative mechanisms involve either the coordination of a Lewis acid to CatBCl to generate a highly reactive boron electrophile followed by attack to arene or a transmetallation mechanism involving initial attack of aluminum Lewis acids on the activated arene nucleophile. The latter mechanism would proceed via heteroarene•$AlCl_3$ adducts, an example of which has been structurally characterized.

Experimental section

General Methods: 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. Benzene was distilled from Na/benzophenone under a N_2 atmosphere, hexane, *ortho*-dichlorobenzene, d_2-dichloromethane, d_3-chloroform, 2,6-lutidine and Et_3N were distilled from CaH_2 under an N_2 atmosphere, THF was distilled from potassium under an N_2 atmosphere, dichloromethane and pentane were dried by passing through a column of activated alumina. All the solvents were degassed prior to use and stored over molecular sieves. TIPS[24] and benzyl protected[45] N-heterocycles, 2-piperidinothiophene[46], 3-trimethylsilyl-*N*-methylpyrrole[47] and Ag[*closo*-$CB_{11}H_6Br_6$][48] were made by published procedures. All other materials were purchased from commercial vendors and used as received. NMR spectra were recorded with a Bruker AV-400 spectrometer (400 MHz ^1H; 100 MHZ ^{13}C; 128 MHz ^{11}B; 162 MHz ^{31}P; 62 MHz, ^{27}Al 104.3 MHz). ^1H NMR chemical shifts are reported in ppm relative to protio impurities in the deuterated solvents and ^{13}C NMR using the centre line of the deuterated solvent as internal standard. ^{11}B NMR spectra were referenced to external BF_3:Et_2O, ^{27}Al to $Al(NO_3)_3$ in D_2O and ^{71}Ga to $Ga(NO_3)_3$ in D_2O. 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 in borosilicate glass or in the spectrometer probe, whilst carbons directly bonded to boron are not observed in the $^{13}C\{^1H\}$ NMR spectra.

Synthesis of [CatB(NEt$_3$)][AlCl$_4$]:

In a J. Youngs valve NMR tube, under inert atmosphere, Et_3N (18 μl, 0.13 mmol) was dissolved in anhydrous CD_2Cl_2 (0.7 ml). To the solution CatBCl (20 mg, 0.13 mmol) was added and the reaction mixture was shaken for 5 minutes. Then powdered $AlCl_3$ (18 mg, 0.13 mmol) was added and the mixture was shaken until all $AlCl_3$ dissolved. Trace quantities of CatBOH, $[Et_3NH][AlCl_4]$ (combined < 5 %) and $(Et_3N)AlCl_3$ were present in the final product. All attempts to recrystallise this species led to oils.

NMR details of CatBCl(NEt$_3$):

^{1}H NMR (CD_2Cl_2): δ 6.70-6.82 (m, 4 H), 3.18 (q, *J* = 7.3 Hz, 6 H), 1.26 (t, *J* = 7.3 Hz, 9 H).

^{13}C NMR (CD_2Cl_2): δ 150.5, 120.4, 110.6, 49.7, 9.4.

^{11}B NMR (CD_2Cl_2): δ 12.9

NMR details of [CatB(NEt$_3$)][AlCl$_4$]:

^{1}H NMR (CD_2Cl_2): δ 7.43 - 7.54 (m, 2 H), 7.31 - 7.41 (m, 2 H), 3.74 (q, *J* = 7.3 Hz, 6 H), 1.43 (t, *J* = 7.3 Hz, 9 H).

^{13}C NMR (CD_2Cl_2): δ 146.9, 126.0, 114.6, 52.9, 9.4.

^{11}B NMR (CD_2Cl_2): δ 27.9.

^{27}Al NMR (CD_2Cl_2): δ 103.9.

Synthesis of [CatB(NEt$_3$)][GaCl$_4$]:

In an oven dried J. Young's NMR tube, under inert atmosphere, CatBCl (50 mg, 0.32 mmol) was dissolved in anhydrous CD_2Cl_2 (0.8 ml) and Et_3N (45 μl, 0.32 mmol) was added. After 10 minutes $GaCl_3$ (57 mg, 0.32 mmol) was added and the reaction mixture was rotated for 30 minutes.

^{1}H NMR (CD_2Cl_2): δ 7.45 - 7.52 (m, 2 H), 7.33 - 7.39 (m, 2 H), 3.74 (q, *J* = 7.3 Hz, 6 H), 1.43 (t, *J* = 7.3 Hz, 9 H).

^{13}C NMR (CD_2Cl_2): δ 146.8, 125.8, 114.5, 52.8, 9.3.

^{11}B NMR (CD_2Cl_2): δ 28.0.

^{71}Ga NMR (CD_2Cl_2): δ 250.3.

Synthesis of [CatB(NEt$_3$)][FeCl$_4$]:

In an oven dried J. Young's NMR tube, under inert atmosphere, CatBCl (22 mg, 0.14 mmol) was dissolved in anhydrous CD_2Cl_2 (0.7 ml) and Et_3N (21 µl, 0.15 mmol) was added. After 10 minutes $FeCl_3$ (25 mg, 0.15 mmol) was added and the reaction mixture was rotated for 30 minutes. The ^{11}B NMR spectrum was recorded in no-lock mode and the peak of the impurity CatBOH was referenced at 22.3 ppm.

^{11}B NMR (CD_2Cl_2): δ 29.0.

Synthesis of [CatB(NEt$_3$)][HB(C$_6$F$_5$)$_3$]:

In an oven dried J. Young's NMR tube, under inert atmosphere, CatBH (25 µl, 0.23 mmol) was dissolved in anhydrous CD_2Cl_2 (0.7 ml) followed by addition of Et_3N (32.5 µl, 0.23 mmol). After 10 minutes $B(C_6F_5)_3$ (120 mg, 0.23 mmol) was added. The reaction mixture was rotated for 2 hours and NMR spectra recorded.

^{1}H NMR (CD_2Cl_2) δ: 1.40 (t, *J* = 6.9 Hz, 9 H), 3.68 (quadruplet not resolved, 6 H), 7.28-7.37 (m, 2 H) 7.38 - 7.47 (m, 2 H).

^{11}B NMR (CD_2Cl_2) δ: -25.2 (d, *J* = 89 Hz, 1 B), 28.0 (s, 1 B).

Synthesis of [CatB(N(Et)^{i}Pr$_2$)][AlCl$_4$]:

In an oven dried J. Youngs valve NMR tube, under inert atmosphere, CatBCl (30

mg, 0.19 mmol) was dissolved in anhydrous CD_2Cl_2 (0.8 ml) and EtN^iPr_2 (33 µl, 0.19 mmol) was added. After 30 minutes $AlCl_3$ (26 mg, 0.19 mmol) was added and the reaction mixture was rotated for 30 minutes.

^{1}H NMR (CD_2Cl_2): δ 7.45 - 7.52 (m, 2 H), 7.33 - 7.38 (m, 2 H), 4.28 (sept, *J* = 6.6 Hz, 2 H), 3.87 (q, *J* = 7.3 Hz, 2 H), 1.62 (t, *J* = 7.3 Hz, 3 H), 1.56 (2 doublet overlapped, *J* = 6.6 Hz, 12 H)

^{13}C NMR (CD_2Cl_2): δ 146.5, 125.9, 114.6, 62.2, 49.5, 20.0, 18.9, 12.1.

^{11}B NMR (CD_2Cl_2): δ 27.8.

^{27}Al NMR (CD_2Cl_2): δ 103.8.

Synthesis of [CatB(2,6-lutidine)][$AlCl_4$]:

In a J. Youngs valve NMR tube, under inert atmosphere, 2,6-lutidine (38 µl, 0.32 mmol) was dissolved in anhydrous CD_2Cl_2 (0.7 ml). To the solution CatBCl (50 mg, 0.32 mmol) was added and the reaction mixture was shaken for 5 minutes. Then powdered $AlCl_3$ (43 mg, 0.32 mmol) was added and the mixture was shaken until all $AlCl_3$ dissolved.

^{1}H NMR (CD_2Cl_2): δ 8.57 (t, *J* = 8.1 Hz, 1 H), 7.92 (d, *J* = 8.1 Hz, 2 H), 7.51 - 7.61 (m, 2 H), 7.36 - 7.47 (m, 2 H), 2.87 (s, 3 H).

^{11}B NMR (CD_2Cl_2): δ 27.0.

^{27}Al NMR (CD_2Cl_2): δ 103.8.

Synthesis of [CatB(P^tBu_3)][$AlCl_4$]:

In an oven-dried Schlenk, under inert atmosphere, $^tBu_3P$ (183 mg, 0.90 mmol) was dissolved in anhydrous CH_2Cl_2 (1 ml) and CatBCl (140 mg, 0.90 mmol) was added. After 3 minutes $AlCl_3$ (120 mg, 0.90 mmol) was added to the mixture, which was

stirred for 1 hour and then layered with pentane. Slow diffusion of the layers yielded colourless crystals of [CatB(P^tBu_3)][$AlCl_4$] (406 mg, 92%) suitable for single-crystal X-ray diffraction analysis.

^{1}H NMR (CD_2Cl_2): δ 1.78 (d, $^3J_{H-P}$ = 15.4 Hz, 27H), 7.42 (m, 2H), 7.57 (m, 2H).

^{13}C NMR (CD_2Cl_2): δ 31.07, 40.50 (d, $^1J_{C-P}$ = 23.1 Hz), 114.48, 125.85, 147.12 (d, $^3J_{C-P}$ = 4.6 Hz).

^{11}B NMR (CD_2Cl_2): δ 29.88 (d, $^1J_{B-P}$ = 184 Hz).

^{27}Al NMR (CD_2Cl_2): δ 103.7.

^{31}P NMR (CD_2Cl_2): δ 26.8 (q, $^1J_{P-B}$ = 184 Hz).

Anal. Calcd. for $C_{18}H_{31}AlBCl_4O_2P$: C, 44.12; H, 6.38. Found: C, 44.23; H, 6.19.

Reaction of [CatB(NEt_3)][$AlCl_4$] with additional Et_3N:

To a CD_2Cl_2 solution of [CatB(NEt_3)][$AlCl_4$] (0.16 mmol in 0.5 ml) in a J. Young's NMR tube was added one equivalent of Et_3N (23 µl, 0.16 mmol) by microlitre syringe. The sample was shaken and NMR spectra were recorded within 10 minutes. These showed the only major boron containing product was CatBCl(NEt_3), whilst the ^{27}Al NMR spectra confirmed the consumption of the majority of $[AlCl_4]^-$ and formation of (Et_3N)$AlCl_3$.

Synthesis of Et_3N•$AlCl_3$:

In an oven dried Young's NMR tube, under inert atmosphere, Et_3N (45 µl, 0.32 mmol) was dissolved in anhydrous CD_2Cl_2 (0.8 ml) followed by addition of $AlCl_3$ (43 mg, 0.32 mmol). The reaction mixture was rotated for 1 hour and NMR spectra recorded.

^{1}H NMR (CD_2Cl_2): δ 3.13 (br. s., 6 H), 1.34 (t, *J* = 7.4 Hz, 9 H).

^{13}C NMR (CD_2Cl_2): δ 50.1, 9.9.

^{27}Al NMR (CD_2Cl_2): δ 110.1.

Reaction between Et_3N•$AlCl_3$ and CatBCl:

In an oven dried Young's NMR tube, under inert atmosphere, Et_3N (45 µl, 0.32 mmol) was dissolved in anhydrous CD_2Cl_2 (0.8 ml) followed by addition of $AlCl_3$ (43 mg, 0.32 mmol). The reaction mixture was shaken for 1 hour and CatBCl (50 mg, 0.32 mmol) was added. The reaction was shaken and allowed to stand for 12 hours. At this time the ratio of $[CatB(NEt_3)][AlCl_4]$ to free CatBCl was 1:4, confirming the reversibility of Et_3N binding to $AlCl_3$.

Synthesis of 2,6-lutidine•$AlCl_3$:

In an oven dried Young's NMR tube fitted with a sealed capillary containing d_6-DMSO, under inert atmosphere, 2,6-lutidine (22 µl, 0.19 mmol) was dissolved in anhydrous CH_2Cl_2 (0.7 ml) followed by addition of $AlCl_3$ (43 mg, 0.32 mmol). The reaction mixture was shaken for 1 hour and NMR spectra recorded.

^{1}H NMR (CH_2Cl_2): δ 7.97 (t, J = 7.8 Hz, 1 H), 7.41 (d, J = 7.8 Hz, 2 H), 3.07 (s, 6 H).

^{13}C NMR (CH_2Cl_2): δ 160.7, 143.3, 126.5, 26.7.

^{27}Al NMR (CH_2Cl_2): δ 99.7.

Reaction between 2,6-lutidine•$AlCl_3$ and CatBCl:

In an oven dried J. Young's NMR tube fitted with a sealed capillary containing d_6-DMSO, under inert atmosphere, 2,6-lutidine (22 µl, 0.19 mmol) was dissolved in anhydrous CH_2Cl_2 (0.7 ml) followed by addition of $AlCl_3$ (43 mg, 0.32 mmol). The

reaction mixture was shaken for 1 hour and CatBCl (50 mg, 0.32 mmol) was added. The NMR spectra showed the formation of [CatB(2,6-lutidine)][$AlCl_4$] as the only product after 10 minutes.

Synthesis of tetrachlorocatechol:

In an oven dried Schlenk tube equipped with a J. Young's tap and covered with foil, catechol (1 g, 9.1 mmol) was dissolved in ether (~10 mL) and cooled at -78 ºC. To the stirred solution was added, dropwise over a period of 90 minutes, sulphuryl chloride (3.7 mL, 45.6 mmol). Then the mixture was stirred at -78 ºC for 60 minutes, allowed to warm to room temperature and stirred overnight. The volatiles were removed under vacuum to give yellow solid (Yield = 1.61g, 71%).

^{1}H NMR ($CDCl_3$): δ 5.67.

^{13}C NMR ($CDCl_3$): δ 139.9, 123.8, 118.8.

Synthesis of *B*-chloro-3,4,5,6-tetrachlorocatecholborane (Cl_4CatBCl):

An oven dried Schlenk tube equipped with a Young's tap and covered with foil, was charged with a solution of BCl_3 (1 M in hexanes, 2.7 ml, 2.7 mmol) and cooled to -78 ºC. To the stirred solution was added, dropwise *via* cannula, a solution of 3,4,5,6-tetrachlorocatechol (481 mg, 1.9 mmol) in CH_2Cl_2 (~ 15 ml). The solution was stirred at -78 ºC for 30 minutes, then allowed to warm to room temperature and stirred overnight. The volatiles were removed under vacuum to give a white solid (496 mg) in which ~ 15 % of Cl_4CatBOH was present. The product of reaction was purified by washing with pentane (Yield = 300 mg, 53 %).

^{13}C NMR ($CDCl_3$): δ 144.1, 128.2, 116.9

^{11}B NMR ($CDCl_3$): δ 29.2.

Anal. Calc. for $C_6BCl_5O_2$ C 24.67. Found C 24.59.

Synthesis of $[Cl_4CatB(NEt_3)][AlCl_4]$:

In an oven dried Schlenk tube equipped with a Young's tap and covered with foil, Et_3N (24 μl, 0.17 mmol) was dissolved in CH_2Cl_2 (~ 6 ml). To the solution was added $Cl_4CatBCl$ (50 mg, 0.17 mmol) and the mixture stirred for 30 minutes, followed by addition of powdered $AlCl_3$ (23 mg, 0.17 mmol). The reaction mixture was stirred for 2 hours and filtered. The volume was reduced (to ~ 3 ml) and layered with pentane. Slow diffusion of the layers yielded colourless crystals of $[Cl_4CatB(NEt_3)][AlCl_4]$ (76 mg, 84 %), that were of good enough quality for single crystal X-ray diffraction analysis.

^{1}H NMR (CD_2Cl_2): δ 3.81 (q, *J* = 7.3 Hz, 6 H), 1.49 (t, *J* = 7.3 Hz, 9 H).

^{13}C NMR (CD_2Cl_2): δ 143.2, 131.1, 119.0, 48.6, 9.6

^{11}B NMR ($CDCl_3$): δ 28.1.

^{27}Al NMR (CD_2Cl_2): δ 103.9.

Anal. Calc. for $C_6H_{15}AlBCl_8NO_2$: C = 27.37, H = 2.87, N = 2.66. Found: C = 26.7, H = 3.32, N = 2.09.

Synthesis of $[Cl_4CatB(2,6\text{-lutidine})][AlCl_4]$:

In an oven dried Schlenk tube equipped with a Young's tap and covered with foil, 2,6-lutidine (40 μl, 0.34 mmol) was dissolved in CH_2Cl_2 (25 ml). To the solution was added $Cl_4CatBCl$ (100 mg, 0.34 mmol) and the mixture stirred for 1 h, followed by addition of powdered $AlCl_3$ (46 mg, 0.34 mmol). The reaction mixture was stirred for 2 h, filtered, and layered with pentane. Slow diffusion of the layers yielded colourless crystals of $[Cl_4CatB(2,6\text{-lutidine})][AlCl_4]$ (102 mg, 56 %), that were of

good enough quality for single crystal X-ray diffraction analysis.

NMR analysis was hampered by poor solubility of $[Cl_4CatB(2,6\text{-lutidine})][AlCl_4]$ in standard non-coordinating deuterated solvent.

Anal. Calc. for $C_{13}H_9AlBCl_8NO_2$: C = 29.31, H = 1.70, N = 2.63. Found: C = 29.46, H = 1.70, N = 2.53.

General Borylation Methodology:

Step 1:

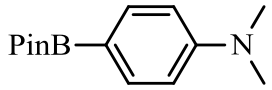
In an oven dried Schlenk tube equipped with a J. Young's tap under inert atmosphere Et_3N (1 equivalent) was dissolved in anhydrous CH_2Cl_2 followed by slow addition of CatBCl (or $Cl_4CatBCl$, 0.95 equivalents) as a solid (exothermic reaction). To the reaction mixture was added powdered $AlCl_3$ (1.05 equivalent) and it was stirred vigorously until all $AlCl_3$ had dissolved. To the mixture was then added the desired arene (1 equivalent) and stirring continued until the borylation reaction was complete. The order of addition of CatBCl (or $Cl_4CatBCl$) and $AlCl_3$ was irrelevant with identical borylated products and reaction times observed. Time of reaction was dependent on arene nucleophilicity and borenium cation electrophilicity

Step 2:

On completion of borylation excess Et_3N (~15 equivalents) followed by pinacol (3 equivalents, as a solid in one portion) were added to the reaction mixture and stirred for 1 hour. Caution this is a very exothermic process, on larger scales care must be taken (addition of the reaction mixture to a Et_3N solution of pinacol is recommended). Volatiles were removed under vacuum and the product extracted with 3x10 ml of hexane and filtered through a short plug of silica. Removal of the solvent yielded the desired product.

Due to poor solubility in pentane of a number of the pinacol boronate esters these had to be columned to remove aluminium and catechol containing by-products.

2-[4-(Dimethylamino)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



Step 1:

CatBCl 50 mg, 0.32 mmol

Et_3N 47 µl, 0.34 mmol

$AlCl_3$ 47 mg, 0.35 mmol

Dimethyl aniline 41 µl, 0.32 mmol

Time of reaction: 1 h

Step 2:

Pinacol 114 mg, 0.96 mol

Time of reaction: 1 h

Purified by flash column chromatography (CH_2Cl_2 : hexane 3 : 7 to CH_2Cl_2 : hexane 7 : 3) to furnish a white solid (68 mg, 85 %).

NMR data are identical to that previously reported.[49]

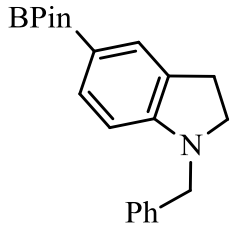
^{1}H NMR ($CDCl_3$) δ: 7.70 (d, *J* = 8.6 Hz, 2 H), 6.70 (d, *J* = 8.6 Hz, 2 H), 2.99 (s, 6 H), 1.33 (s, 12 H).

^{13}C {^{1}H}NMR ($CDCl_3$) δ: 152.5, 136.1, 111.2, 83.1, 40.1, 24.8.

^{11}B NMR ($CDCl_3$) δ: 30.7.

Anal. Calc. for $C_{14}H_{22}BNO_2$ C 68.04; H 8.97; N 5.67. Found C 67.37; H 9.67; N 5.64

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-benzyl-indoline:



Step 1:

CatBCl 50 mg, 0.32 mmol

Et_3N 47 µl, 0.34 mmol

$AlCl_3$ 47 mg, 0.35 mmol

1-benzyl indoline 89 mg, 0.32 mmol

Time of reaction: 1 h

Step 2:

Pinacol 114 mg, 0.96 mmol

Time of reaction: 1 h

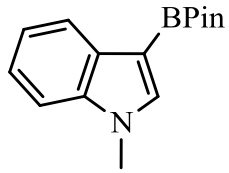
Purified by flash column chromatography (CH_2Cl_2 : hexane 3 : 7 to CH_2Cl_2 : hexane 7 : 3) to furnish a white solid. Yield 104 mg (96 %)

^{1}H NMR ($CDCl_3$) δ: 7.59 (d, *J* = 8.1 Hz, 1 H), 7.56 (s, 1 H), 7.36 - 7.32 (m, 4 H), 7.29 - (m, 1 H), 6.52 (d, *J* = 8.1 Hz, 1 H), 4.34 (s, 2 H), 3.40 (t, *J* = 8.7 Hz, 2 H), 3.00 (t, *J* = 8.7 Hz, 2 H), 1.34 (s, 12H).

^{13}C{^{1}H} ($CDCl_3$) δ: 154.6, 138.0, 135.3, 130.7, 129.0, 128.5, 127.7, 127.1, 105.7, 83.1, 52.8, 52.3, 27.9, 24.8.

^{11}B NMR ($CDCl_3$) δ: 30.6.

1-methyl-3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-indole:



Step 1:

CatBCl 100 mg, 0.65 mmol

Et_3N 95 µl, 0.68 mmol

$AlCl_3$ 95 mg, 0.71 mmol

1-methyl indole 81 µl, 0.65 mmol

Time of reaction: 4 h

Step 2:

Pinacol 230 mg, 1.9 mmol

Time of reaction: 1 h

Purified by flash column chromatography (CH_2Cl_2 : hexane 2 : 8 to CH_2Cl_2 : hexane 1 : 1) to furnish a colourless solid (154 mg, 92 %).

Product regioisomer determined by comparison to NMR data in reference 50.

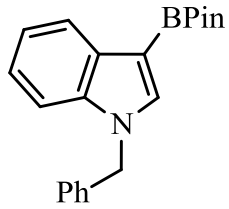
^{1}H NMR ($CDCl_3$) δ: 8.04 (d, *J* = 7.6 Hz, 1 H), 7.52 (s, 1 H), 7.29 - 7.35 (m, 1 H), 7.14 - 7.27 (m, 3 H), 3.79 (s, 3 H), 1.36 (s, 12 H).

^{13}C{^{1}H} NMR ($CDCl_3$) δ: 138.4, 137.8, 132.5, 122.6, 121.7, 120.2, 109.1, 82.7, 32.9, 24.9.

^{11}B NMR ($CDCl_3$) δ: 30.0.

Anal. Calc. for $C_{15}H_{20}BNO_2$ C 70.06; H 7.84; N 5.45. Found C 69.59; H 8.06; N 5.57

1-benzyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-indole



Step 1:

CatBCl 50 mg, 0.32 mmol

Et_3N 47 µl, 0.34 mmol

$AlCl_3$ 47 mg, 0.35 mmol

N-benzylindole 67 mg, 0.32 mol

Time of reaction: 7 h

Step 2:

Pinacol 114 mg, 0.96 mmol

Time of reaction: 1 h

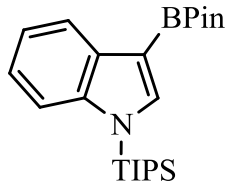
Purified by flash column chromatography (CH_2Cl_2 : hexane 3 : 7 to CH_2Cl_2 : hexane 1 : 1) to furnish a white solid. Yield 103 mg (95 %).

^{1}H NMR ($CDCl_3$) δ: 8.00 - 8.12 (m, 1 H), 7.60 (s, 1 H), 7.22 - 7.33 (m, 4 H), 7.09 - 7.21 (m, 4 H), 5.31 (s, 2 H), 1.36 (s, 12 H).

^{13}C NMR ($CDCl_3$) δ: 137.8, 137.3, 136.9, 132.7, 128.7, 127.7, 127.0, 122.7, 121.9, 120.4, 109.7, 82.8, 50.3, 24.9.

^{11}B NMR ($CDCl_3$) δ: 29.9.

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(triisopropylsilyl)-indole



Step 1:

CatBCl 50 mg, 0.32 mmol

Et_3N 47 µl, 0.34 mmol

$AlCl_3$ 47 mg, 0.35 mmol

1-(triisopropylsilyl)-indole 89 mg, 0.32 mmol

Time of reaction: 48 h

Step 2:

Pinacol 114 mg, 0.96 mmol

Time of reaction: 1 h

The product was extracted with 3x5 ml of hexane and the solution was filtered through a plug of silica, which was washed with additional 15 ml of hexane : CH_2Cl_2 1:4. The removal of solvent from combined solutions yielded a white solid. Yield 97 mg (78 %).

NMR data are identical to that previously reported.[51]

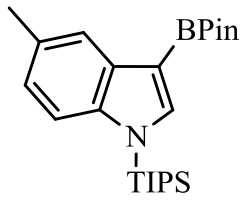
^{1}H NMR ($CDCl_3$) δ: 8.01 - 8.12 (m, 1 H), 7.69 (s, 1 H), 7.51 (dd, *J* = 2.1, 6.2 Hz, 1 H), 7.11 - 7.18 (m, 2 H), 1.75 (sept, *J* = 7.6 Hz, 3 H), 1.38 (s, 12 H), 1.15 (d, *J* = 7.6 Hz, 18 H).

^{13}C{^{1}H} NMR ($CDCl_3$) δ: 141.8, 141.2, 135.1, 122.3, 121.5, 120.4, 113.7, 82.6, 24.9, 18.1, 12.7.

^{11}B NMR ($CDCl_3$) δ: 30.6.

Anal. Calc. for $C_{23}H_{38}BSiNO_2$ C 69.16; H 9.59; N 3.51. Found C 67.41; H 9.99; N 3.24

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(triisopropylsilyl)-5-Methyl-Indole



Step 1:

CatBCl 30 mg, 0.19 mmol

Et_3N 28 µl, 0.20 mmol

$AlCl_3$ 28 mg, 0.21 mmol

1-(triisopropylsilyl)-5-Methyl-Indole 56 mg, 0.19 mmol

Time of reaction: 24 h

Step 2:

Pinacol 69 mg, 0.058 mmol

Time of reaction: 1 h

The product was extracted with 3x5 ml of hexane and the solution was filtered through a plug of silica, which was washed with additional 15 ml of hexane : CH_2Cl_2 1:4. The removal of solvent from combined solutions yielded a white solid. Yield 69 mg (86 %).

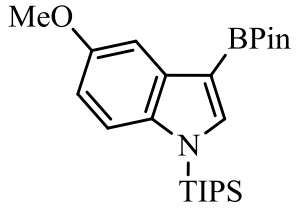
^{1}H NMR ($CDCl_3$) δ: 7.87 (s, 1 H), 7.67 (s, 1 H), 7.41 (d, *J* = 8.6 Hz, 1 H), 7.00 (d, *J* = 10.3 Hz, 1 H), 2.50 (s, 3 H), 1.75 (sept, *J* = 7.6 Hz, 3 H), 1.40 (s, 12 H), 1.16 (d, *J* = 7.6 Hz, 18 H).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ: 140.4, 139.0, 134.3, 128.7, 122.0, 121.0, 112.3, 81.6, 23.9, 20.4, 17.1, 11.7.

^{11}B NMR ($CDCl_3$) δ: 30.7.

Anal. Calcd. for $C_{24}H_{40}BNO_2Si$: C = 69.72, H = 9.75, N = 3.39. Found: C = 69.09; H = 10.31; N = 3.37

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(triisopropylsilyl)-5-Methoxy-Indole



Step 1:

CatBCl 50 mg, 0.32 mmol

Et_3N 47 μl, 0.34 mmol

$AlCl_3$ 47 mg, 0.35 mmol

1-(triisopropylsilyl)-5-methoxy-Indole 89 mg, 0.32 mmol

Time of reaction: 30 h

Step 2:

Pinacol 114 mg, 0.96 mol

Time of reaction: 1 h

The product was purified by flash column chromatography (CH_2Cl_2 : hexane 2 : 8 to CH_2Cl_2 : hexane 1 : 1) to furnish a white solid. Yield 122 mg (88 %).

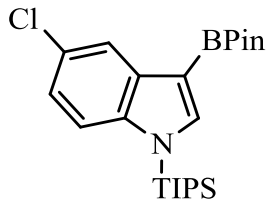
^{1}H NMR ($CDCl_3$) δ: 7.65 (s, 1 H), 7.57 (d, *J* = 2.8 Hz, 1 H), 7.38 (d, *J* = 9.2 Hz, 1 H), 6.80 (dd, *J* = 9.1 and 2.8 Hz, 1 H), 3.89 (s, 3H) 1.71 (sept, *J* = 7.6 Hz, 3 H), 1.37

(s, 12 H), 1.14 (d, *J* = 7.6 Hz, 18 H).

$^{13}C\{^{1}H\}$ ($CDCl_3$) δ: 154.5, 141.9, 136.7, 135.9, 114.2, 110.9, 104.5, 82.6, 55.7, 25.0, 18.1, 12.7.

^{11}B NMR ($CDCl_3$) δ: 30.6.

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(triisopropylsilyl)-5-chloro-Indole



Step 1:

$Cl_4CatBCl$: 52 mg, 0.17 mmol

Et_3N: 24 μl, 0.175 mmol

$AlCl_3$: 25 mg, 0.18 mmol

5-chloro-1-[triisopropylsilane]-indole: 53 mg 0.17 mmol)

Time of reaction: 4 h

Step 2:

Pinacol: 60 mg, 0.51 mmol

Time of Reaction 1h

The product was extracted with 3x5 ml of hexane and the solution was filtered through a plug of silica, which was washed with additional 15 ml of hexane : CH_2Cl_2 1:4. The removal of solvent from combined solutions yielded a white solid. Yield 62 mg, (84 %).

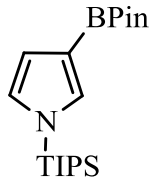
^{1}H NMR ($CDCl_3$) δ: 8.01 (s, 1 H), 7.66 (s, 1 H), 7.39 (d, *J* = 8 Hz, 1 H), 7.08 (d, J =

8 Hz, 1H) 1.69 (sept, *J* = 7.6 Hz, 3 H), 1.35 (s, 12H) 1.14 (d, *J* = 7.6 Hz, 18 H).

$^{13}C\{^{1}H\}$ ($CDCl_3$) δ: 142.3, 140.2, 136.4, 126.2, 121.8, 121.7, 114.5, 82.9, 24.9, 18.0, 12.6.

^{11}B NMR ($CDCl_3$) δ: 31.1.

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(triisopropylsilyl)-pyrrole



Step 1:

CatBCl 50 mg, 0.32 mmol

Et_3N 47 µl, 0.34 mmol

$AlCl_3$ 47 mg, 0.35 mmol

1-[triisopropylsilyl]-pyrrole 72 mg, 0.32 mmol

Time of reaction: 72 hours

Step 2:

Pinacol 114 mg, 0.96 mmol

Time of reaction: 1 h

The product was extracted with 3x5 ml of hexane and the solution was filtered through a plug of silica, which was washed with additional 15 ml of hexane : CH_2Cl_2 1:4. The removal of solvent from combined solutions yielded a white solid. Yield 101 mg (89 %).

NMR data are identical to that previously reported.[52]

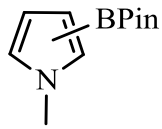
^{1}H NMR ($CDCl_3$) δ: 7.24 (dd, *J* = 2.0, 1.3 Hz, 1 H), 6.82 (dd, *J* = 2.5, 2.0 Hz, 1 H),

6.63 (dd, *J* = 2.5, 1.3 Hz, 1 H), 1.46 (t, *J* = 7.6 Hz, 3 H), 1.33 (s, 12 H), 1.09 (d, *J* = 7.6 Hz, 18 H).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ: 133.7, 125.0, 115.6, 82.7, 24.8, 17.8, 11.6.

^{11}B NMR ($CDCl_3$) δ: 30.1.

Regioisomers of 2 (or) 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-methyl-pyrrole



Step 1:

CatBCl 40 mg, 0.26 mmol

Et_3N 36 µl, 0.26 mmol

$AlCl_3$ 34 mg, 0.26 mmol

N-methylpyrrole 23 µl 0.26 mmol

Time of reaction: 20 hours

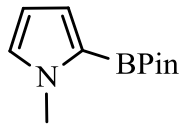
Step 2:

Pinacol 77 mg, 0.7 mmol

Time of reaction: 1 h

Purified and regioisomers separated by flash column chromatography (CH_2Cl_2 : hexane 1 : 1). Products isolated as white solids. Yield of the both regioisomers combined 49 mg (91 %).

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-methyl pyrrole



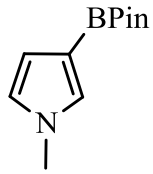
Yield = 21mg (39%)

^{1}H NMR ($CDCl_3$) δ: 6.77 - 6.87 (m, 2 H), 6.17 (dd, *J* = 2.5, 3.5 Hz, 1 H), 3.85 (s, 3 H), 1.32 (s, 12 H).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): 128.2, 121.8, 108.3, 83.0, 36.6, 24.8.

^{11}B NMR ($CDCl_3$) δ: 27.8.

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)- 1-methyl-pyrrole



Yield = 28 mg (52%)

NMR are identical to that previously reported.[53]

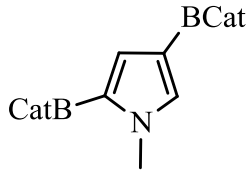
^{1}H NMR ($CDCl_3$) δ: 7.07 (t, *J* = 1.8 Hz, 1 H), 6.65 (t, *J* = 2.3 Hz, 1 H), 6.48 (dd, *J* = 1.8, 2.3 Hz, 1 H), 3.67 (s, 3 H), 1.32 (s, 12 H).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): 130.8, 122.8, 114.2, 82.7, 35.9, 24.7.

^{11}B NMR ($CDCl_3$) δ: 29.8 (br s)

Anal.Calc. for $C_{11}H_{18}BNO_2$ C 63.80; H 9.15; N 6.69. Found C 63.26; H 9.09; N 6.43

2,4-di(1,3,2-benzodioxaborolan-2-yl)- 1-methyl-pyrrole



Step 1:

CatBCl 100 mg, 0.64 mmol

Et_3N 95 µl, 0.68 mmol

$AlCl_3$ 95 mg, 0.71 mmol

1-Methyl pyrrole 27 µl, 0.30 mmol

Time of reaction: 120 h

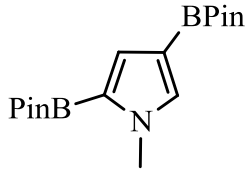
The product at this stage was purified by double crystallization (the product was dissolved in minimal amount of CH_2Cl_2 and cooled), to yield a white solid. Yield 51 mg (53 %).

^{1}H NMR ($CDCl_3$) δ: 7.71 (s, 1 H), 7.58 (s, 1 H), 7.21 - 7.34 (m, 4 H), 7.04 - 7.17 (m, 4 H), 4.10 (s, 3 H).

^{13}C NMR ($CDCl_3$) δ: 148.5, 148.2, 138.3, 130.9, 122.7, 122.4, 112.4, 112.2, 37.2.

^{11}B NMR ($CDCl_3$) δ: 31.1 (br s), 30.1 (br s).

2,4-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)- 1-methyl-pyrrole



Step 1:

CatBCl 30 mg, 0.19 mmol

Et_3N 95 µl, 0.20 mmol

$AlCl_3$ 95 mg, 0.21 mmol

1-Methyl pyrrole 8 µl, 0.09 mmol

Time of reaction: 192 h

Step 2:

Pinacol 69 mg, 0.58 mmol

Time of reaction: 1 h

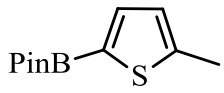
Purified by filtration through silica (CH_2Cl_2 : hexane 8 : 2) to furnish a white solid. Yield 22 mg (73 %).

^{1}H NMR ($CDCl_3$) δ: 7.20 (s, 2 H), 3.82 (s, 3 H), 1.29-1.28 (2 singlets overlapped, 24 H).

^{13}C NMR ($CDCl_3$) δ: 136.2, 129.0, 83.0, 82.7, 36.6, 24.7.

^{11}B NMR ($CDCl_3$) δ: 29.5, 28.6.

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methylthiophene



Step 1:

$Cl_4CatBCl$ 100 mg, 0.34 mmol

Et_3N 50 µl, 0.36 mol

$AlCl_3$ 50 mg, 0.37 mol

2-Methyl-thiophene 33 µl, 0.34 mmol

Time of reaction: 72 h

Step 2:

Pinacol 121 mg, 1.0 mmol

Time of reaction: 1 h

The product was extracted with 3x5 ml of hexane and the solution was filtered through a plug of silica, which was washed with additional 15 ml of CH_2Cl_2. The removal of solvent from combined solutions yielded a yellow oil. Yield 53 mg (69 %).

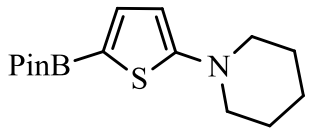
NMR spectra are similar to that previously reported.[54]

^{1}H NMR ($CDCl_3$) δ: 7.46 (d, *J* = 3.3 Hz, 1 H), 6.85 (dq, *J* = 3.3, 1.0 Hz ,1 H), 2.54 (d, *J* = 1.0 Hz, 3 H), 1.34 (s, 13 H).

^{13}C NMR ($CDCl_3$) δ: 147.5, 137.6, 127.0, 83.8, 24.7, 15.4.

^{11}B NMR ($CDCl_3$) δ: 28.7.

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-piperidinothiophene



Step 1:

CatBCl 50 mg, 0.32 mmol

Et_3N 47 μl, 0.34 mmol

$AlCl_3$ 47 mg, 0.35 mmol

2-piperidino-thiophene 41 μl, 0.32 mmol

Time of reaction: 0.5 h

Step 2:

Pinacol 114 mg, 0.96 mmol

Time of reaction: 0.5 h

The product was extracted with 2x15 ml of hexane and removed volatiles. Then the solid was quickly washed with 2x0.5 ml of MeOH (due to its extreme sensitivity to

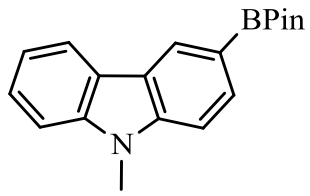
protodeboronation) to remove excess pinacol and dried. Yield 59 mg (62 %).

^{1}H NMR ($CDCl_3$) δ: 7.39 (d, *J* = 3.8 Hz, 1 H), 6.14 (d, *J* = 3.8 Hz, 1 H), 3.21 (t, *J* = 5.6 Hz 4 H), 1.66-1.74 (m, 4 H), 1.51 - 1.62 (m, 2 H), 1.26 - 1.38 (m, 12 H).

^{13}C NMR ($CDCl_3$) δ: 166.2, 138.2, 105.4, 83.5, 51.8, 25.1, 24.7, 23.8.

^{11}B NMR ($CDCl_3$) δ: 29.0 (br s).

9-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole:



Step 1:

Cl_4CatBCl 100 mg, 0.34 mmol

Et_3N 50 µl, 0.36 mmol

$AlCl_3$ 50 mg, 0.37 mmol

9-methyl-carbazole 62 mg, 0.34 mmol

Time of reaction: 24 h

Step 2:

Pinacol 121 mg, 1.0 mmol

Time of reaction: 1 h

Purified by flash column chromatography (CH_2Cl_2 : hexane 2 : 8 to CH_2Cl_2 : hexane 1 : 1). to furnish a white solid. Yield 75 mg (71 %).

The spectra are identical to that previously reported.[55]

^{1}H NMR ($CDCl_3$): 8.60 (s, 1 H), 8.13 (d, *J* = 7.6 Hz, 1 H), 7.94 (dd, *J* = 1.1, 8.2 Hz, 1 H), 7.47 (ddd, *J* = 1.1, 7.1, 8.2 Hz, 1 H), 7.39 (d, *J* = 8.1 Hz, 2 H), 7.25 (td, *J* = 1.0,

7.4 Hz, 1 H), 3.84 (s, 3 H), 1.40 (s, 12 H).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): 143.1, 141.0, 132.2, 127.7, 125.7, 123.0, 122.5, 120.5, 119.3, 108.4, 107.8, 83.6, 29.1, 24.9.

^{11}B NMR ($CDCl_3$): 31.1 (br s).

Anal.Calc. for $C_{19}H_{22}BNO_2$ C 74.24; H 7.22; N 4.56. Found C 73.42; H 7.17; N 4.40

Isolation of 2- and 3-catecholboryl-*N*-methylpyrrole:

In an oven-dried Schlenk, under inert atmosphere, CatBCl (300 mg, 1.94 mmol) was dissolved in anhydrous CH_2Cl_2 (2 ml) and Et_3N (0.3 ml, 2.15 mmol) was added dropwise. After 10 minutes $AlCl_3$ (259 mg, 1.94 mmol) was added and the reaction mixture was stirred for 24 hours. Volatiles were removed under vacuum and products were extracted with anhydrous hexane (25 ml). Then the solution was dried and products extracted for the second time with hexane (25 ml). Removal of the solvent yielded a colourless solid (269 mg, 67%). Product ratio was determined by ^{1}H NMR spectroscopy. 3-catecholboryl-*N*-methylpyrrole : 2-catecholboryl-*N*-methylpyrrole = 1 : 4.

Reaction of 2- and 3-catecholboryl-*N*-methylpyrrole in 1 : 4 ratio with $[Me_3NH][AlCl_4]$:

In an oven dried Young's NMR tube, under inert atmosphere, $AlCl_3$ (28 mg, 0.21 mmol) was dissolved/suspended in anhydrous CD_2Cl_2 (0.8 ml) followed by addition of $[Me_3NH][Cl]$ (21 mg, 0.22 mmol). The reaction mixture was rotated for 1 hour and the mixture of 2- and 3-catecholboryl-N-methylpyrrole (44 mg, 0.22 mmol) was added. Then the reaction mixture was monitored by NMR spectroscopy.

Reaction of 2- and 3-catecholboryl-*N*-methylpyrrole (1 : 4 ratio) with 0.12

equivalents of $AlCl_3$:

In an oven dried Young's NMR tube, under inert atmosphere, the mixture of 2- and 3-catecholboryl-N-methylpyrrole (50 mg, 0.25 mmol) was dissolved in anhydrous CD_2Cl_2 (0.8 ml). Then $AlCl_3$ (4 mg, 0.03 mmol) was added and the reaction mixture was monitored by NMR spectroscopy.

Reaction of 2- and 3-catecholboryl-*N*-methylpyrrole (1 : 4 ratio) with 1.3 equivalents of $AlCl_3$ in presence of 1 equivalent of dTBPy:

In an oven dried Young's NMR tube, under inert atmosphere, the mixture of 2- and 3-catecholboryl-N-methylpyrrole (35 mg, 0.18 mmol) was dissolved in anhydrous CD_2Cl_2 (0.8 ml) followed by addition of dTBPy (40 µl, 0.18 mmol) and $AlCl_3$ (30mg, 22 mmol). Then the reaction mixture was monitored by NMR spectroscopy.

Synthesis of 3-catecholboryl-*N*-methylpyrrole:

In an oven dried Schlenk tube, under inert atmosphere, 3-trimethylsilyl-*N*-methylpyrrole (59 mg, 0.38 mmol) was dissolved in anhydrous toluene (1 ml) and CatBCl (59 mg, 0.38 mmol) was added. After 1 hour volatiles were removed under vacuum. Then the product was extracted with anhydrous pentane (10 ml) and the solution was filtered by filter cannula. The solvent was removed and the product re-extracted with anhydrous pentane (5 ml). Removal of solvent yielded a colourless solid which was mainly 3-catecholboryl-*N*-methylpyrrole along with a minor amount of CatBOH.

NMR details of 3-catecholboryl-*N*-methylpyrrole:

^1H NMR (CD_2Cl_2): δ 7.30 (s, 1 H), 7.18 - 7.27 (m, 2 H), 7.03 - 7.11 (m, 2 H), 6.75 (s, 1 H), 6.63 (s, 1 H), 3.73 ppm (s, 3 H).

^{11}B NMR (CD_2Cl_2): δ 31.5.

Reaction of 3-catecholboryl-*N*-methylpyrrole with $AlCl_3$ and Et_3N:

In an oven dried Young's NMR tube, under inert atmosphere, 3-catecholboryl-*N*-methylpyrrole (14 mg, 0.07 mmol) was dissolved in anhydrous CD_2Cl_2 (0.7 ml) followed by addition of $AlCl_3$ (10 mg, 0.07 mmol). The reaction mixture was shaken and NMR spectra recorded. The ^{11}B NMR spectrum showed only a peak at 28.7 ppm consistent with CatBCl, while the ^{27}Al NMR spectrum showed a broad peak at 103 ppm tentatively assigned to oligomers of $\{(pyrrolyl)AlCl_2\}_n$. Then Et_3N (10 µl, 0.07 mmol) was added to the reaction mixture and NMR spectra were recorded. The ^{11}B NMR and ^{1}H NMR showed the formation of 3-catecholboryl-*N*-methylpyrrole along with unidentified products.

***In situ* reaction of 3-catecholboryl-*N*-methylindole with $AlCl_3$:**

In an oven dried Young's NMR tube, under inert atmosphere, CatBCl (50 mg, 0.32 mmol) was dissolved in anhydrous CD_2Cl_2 (0.8 ml) followed by addition of Et_3N (44 µl, 0.32 mmol). The reaction mixture was rotated for 30 minutes and $AlCl_3$ (43 mg, 0.32 mmol) was added. Then *N*-methylindole (40 µl, 0.32 mmol) was added. After 18 hours (in which time full borylation had occurred as determined by multinuclear NMR spectroscopy) $AlCl_3$ (43 mg, 0.32 mmol) was added and the NMR spectra were recorded. The ^{11}B NMR showed only a peak at 28.7 ppm.

***In situ* reaction of 3-catecholboryl-*N*-methylindole with $GaCl_3$:**

In an oven dried Young's NMR tube, under inert atmosphere, CatBCl (50 mg, 0.32 mmol) was dissolved in anhydrous CD_2Cl_2 (0.8 ml) followed by addition of Et_3N (44

µl, 0.32 mmol). The reaction mixture was shaken for 30 minutes and $GaCl_3$ (57 mg, 0.32 mmol) was added. Then 3-D-*N*-methylindole (40 µl, 0.32 mmol) was added. After 18 hours (in which time full borylation had occurred as determined by multinuclear NMR spectroscopy) $GaCl_3$ (57 mg, 0.32 mmol) was added and the reaction was monitored by NMR spectroscopy.

NMR details after 5 minutes:

^{1}H NMR (CD_2Cl_2): δ 8.74 (s, 1 H), 8.23 - 8.35 (m, 1 H), 7.61 - 7.78 (m, 3 H), 7.32 - 7.44 (m, 2 H), 7.09 - 7.28 (m, 2 H), 4.13 (s, 3 H), 3.23 (q, *J* = 7.31 Hz, 6 H), 1.34 (t, *J* = 7.31 Hz, 9 H).

^{11}B NMR (CD_2Cl_2): δ 30.9.

Borylation of *N*-methylindole with [CatB(NEt$_3$)][GaCl$_4$]:

In an oven dried J. Young's NMR tube, under inert atmosphere, CatBCl (50 mg, 0.32 mmol) was dissolved in anhydrous CD_2Cl_2 (0.8 ml) followed by addition of Et_3N (44 µl, 0.32 mmol). After 30 minutes $GaCl_3$ (57 mg, 0.32 mmol) was added and the reaction was rotated for 1 hour. *N*-methylindole (40 µl, 0.32 mmol) was added and the reaction mixture was rotated for 90 minutes. Then Et_3N (0.7 ml) followed by pinacol (113 mg, 0.96 mmol) were added to the reaction mixture and stirred for 1 hour. Volatiles were removed under vacuum and the product was purified by flash column chromatography on silica (eluent CH_2Cl_2 : hexane 3 : 7). Removal of the solvent yielded the desired product as white solid (73 mg, 89%).

Borylation of *N*-methylindole with [CatB(NEt$_3$)][FeCl$_4$]:

In an oven dried J. Young's NMR tube, under inert atmosphere, CatBCl (50 mg, 0.32 mmol) was dissolved in anhydrous CH_2Cl_2 (0.8 ml) and Et_3N (47 µl, 0.34

mmol) was added. After 30 minutes $FeCl_3$ (58 mg, 0.36 mmol) was added and the reaction mixture was rotated for 1 hour. *N*-methylindole (40 µl, 0.32 mmol) was added and the reaction mixture was rotated for 90 minutes. Then Et_3N (0.7 ml) followed by pinacol (113 mg, 0.96 mmol) were added to the reaction mixture and stirred for 1 hour. Volatiles were removed under vacuum and the product was purified by flash column chromatography on silica (eluent CH_2Cl_2 : hexane 3 : 7). Removal of the solvent yielded the desired product as white solid (76 mg, 92%).

Reaction of DMA with [CatB(NEt$_3$)][FeCl$_4$]:

In an oven dried J. Young's NMR tube, under inert atmosphere, CatBCl (20 mg, 0.13 mmol) was dissolved in anhydrous CD_2Cl_2 (0.8 ml) and Et_3N (18 µl, 0.13 mmol) was added. After 30 minutes $FeCl_3$ (21 mg, 0.13 mmol) was added and the reaction mixture was rotated for 24 hours. Then DMA (16 µl, 0.13 mmol) was added, the reaction mixture was shaken for 90 minutes and the ^{11}B NMR spectrum was recorded.

^{11}B NMR (CD_2Cl_2): 13.2.

Preparation of the sample for the kinetic study of *N*-methylindole borylation with [CatB(NEt$_3$)][AlCl$_4$]:

In an oven dried Young's NMR tube, under inert atmosphere, CatBCl (50 mg, 0.32 mmol) was dissolved in anhydrous CD_2Cl_2 (0.8 ml) followed by addition of Et_3N (44 µl, 0.32 mmol). After 30 minutes $AlCl_3$ (43 mg, 0.32 mmol) was added and the reaction was rotated for 16 hours. Then *N*-methylindole (40 µl, 0.32 mmol) was added and the reaction was monitored by ^1H NMR.

Preparation of the sample for the kinetic study of *N*-methylindole borylation

with [CatB(NEt$_3$)][GaCl$_4$]:

In an oven dried J. Young's NMR tube, under inert atmosphere, CatBCl (50 mg, 0.32 mmol) was dissolved in anhydrous CD_2Cl_2 (0.8 ml) followed by addition of Et_3N (44 µl, 0.32 mmol). After 30 minutes $GaCl_3$ (57 mg, 0.32 mmol) was added and the reaction was rotated for 16 hours. Then the reaction mixture was cooled to 0 °C and *N*-methylindole (40 µl, 0.32 mmol) was added. After vigorous shaking the NMR tube was inserted into a probe pre-cooled to 0 °C and and the reaction was monitored by ^{1}H NMR.

Borylation of DMA with [CatB(NEt$_3$)][*closo*-CB$_{11}$H$_6$Br$_6$]:

In an oven dried J. Young's NMR tube, under inert atmosphere, [CatB(NEt$_3$)][*closo*-$CB_{11}H_6Br_6$] (75 mg, 0.09 mmol) was dissolved in anhydrous CD_2Cl_2 (0.7 ml) followed by addition of DMA (12 µl, 0.09 mmol). The reaction mixture was rotated and monitored by multinuclear NMR spectroscopy. The borylation reaction was complete in 2 hours.

Borylation of *N*-methylindole with [CatB(NEt$_3$)][*closo*-CB$_{11}$H$_6$Br$_6$]:

In an oven dried J. Young's NMR tube, under inert atmosphere, [CatB(NEt$_3$)][*closo*-$CB_{11}H_6Br_6$] (29 mg, 0.035 mmol) was dissolved in anhydrous CD_2Cl_2 (0.7 ml) followed by addition of *N*-methylindole (4 µl, 0.035 mmol). The reaction mixture was rotated and monitored by NMR spectroscopy. The borylation reaction was complete in 4 hours.

Reaction between *N*-TIPS-pyrrole and [CatB(NEt$_3$)][*closo*-CB$_{11}$H$_6$Br$_6$]:

In an oven dried J. Young's NMR tube, under inert atmosphere, [CatB(NEt$_3$)][*closo*-CB$_{11}$H$_6$Br$_6$] (75 mg, 0.09 mmol) was dissolved in anhydrous CD_2Cl_2 (0.7 ml) followed by addition of *N*-TIPS-pyrrole (20 mg, 0.09 mmol). The reaction mixture was shaken and monitored by NMR spectroscopy. After 72 hours the borylated product was less than 5%.

Reaction between *N*-TIPS-pyrrole, dTBPy and [CatB(NEt$_3$)][*closo*-CB$_{11}$H$_6$Br$_6$]:

In an oven dried J. Young's NMR tube, under inert atmosphere, [CatB(NEt$_3$)][*closo*-CB$_{11}$H$_6$Br$_6$] (29 mg, 0.035 mmol) was dissolved in anhydrous CD_2Cl_2 (0.7 ml) followed by addition of *N*-TIPS-pyrrole (6 mg, 0.027 mmol). Then dTBPy (5 µl, 0.021 mmol) was added. The reaction mixture was shaken and monitored by NMR spectroscopy. After 72 hours the borylated product was less than 5%.

Borylation of *N*-TIPS-pyrrole with [CatB(NEt$_3$)][AlCl$_4$] in presence of PPh$_3$:

In an oven dried J. Young's NMR tube fitted with a sealed capillary containing d_6-DMSO, under inert atmosphere, CatBCl•NEt$_3$ (83 mg, 0.32 mmol) was dissolved in anhydrous CH_2Cl_2 (0.8 ml) followed by addition of $AlCl_3$ (43 mg, 0.32 mmol). The reaction mixture was rotated for 1 hour and PPh_3 (9 mg, 0.03 mmol) was added. Then *N*-TIPS-pyrrole (72 mg, 0.32 mmol) was added. The reaction was complete in less than 30 minutes (by NMR spectroscopy).

Borylation of *N*-methylindole with [CatB(NEt$_3$)][AlCl$_4$] in presence of PPh$_3$:

In an oven dried J. Young's NMR tube fitted with a sealed capillary containing d_6-DMSO, under inert atmosphere, CatBCl•NEt$_3$ (83 mg, 0.32 mmol) was dissolved in

anhydrous CH_2Cl_2 (0.8 ml) followed by addition of $AlCl_3$ (43 mg, 0.32 mmol). The reaction mixture was shaken for 1 hour and PPh_3 (4 mg, 0.015 mmol) was added. Then *N*-methylindole (40 µl, 0.32 mmol) was added. The reaction was complete in less than 10 minutes (by NMR spectroscopy).

Borylation of *N*-methylindole with the equimolar mixture of CatBCl, dTBPy and $AlCl_3$:

In an oven dried J. Young's NMR tube, under inert atmosphere, CatBCl (50 mg, 0.32 mmol) was dissolved in anhydrous CH_2Cl_2 (1 ml) followed by addition of 2,6-di-*tert*-butylpyridine (72 µl, 0.32 mmol), powdered $AlCl_3$ (43 mg, 0.32 mmol) and *N*-methylindole (40 µl, 0.32 mmol). The reaction mixture was stirred for 10 minutes. Then Et_3N (0.7 ml) and pinacol (115 mg, 0.97 mmol) were added to the reaction mixture and stirred for 1 h. Volatiles were removed under vacuum and the product was purified by flash column chromatography on silica (eluent CH_2Cl_2 : hexane 2 : 8 to CH_2Cl_2 : hexane 1 : 1). Removal of the solvent yielded the desired product as white solid (76 mg, 92%).

Monoborylation of 9-methylcarbazole with the equimolar mixture of CatBCl, dTBPy and $AlCl_3$:

In an oven dried J. Young's NMR tube, under inert atmosphere, CatBCl (25 mg, 0.16 mmol) was dissolved in anhydrous CH_2Cl_2 (1 ml) followed by addition of 2,6-di-*tert*-butylpyridine (36 µl, 0.16 mmol), powdered $AlCl_3$ (22 mg, 0.16 mmol) and 9-methylcarbazole (29 mg, 0.16 mmol). The reaction mixture was stirred for 30 minutes. Then Et_3N (0.4 ml) and pinacol (57 mg, 0.48 mmol) were added to the reaction mixture and stirred for 1 h. Volatiles were removed under vacuum and the

product was purified by flash column chromatography on silica (eluent CH_2Cl_2 : hexane 2 : 8 to CH_2Cl_2 : hexane 1 : 1). Removal of the solvent yielded the desired product as white solid (32 mg, 65%).

3,6-Di-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-methylcarbazole:

In an oven dried Schlenk tube, under inert atmosphere, CatBCl (30 mg, 0.19 mmol) was dissolved in anhydrous 1,2-dichlorobenzene (1 ml) followed by addition of 2,6-di-*tert*-butylpyridine (52 µl, 0.23 mmol), powdered $AlCl_3$ (33 mg, 0.25 mmol) and 9-methylcarbazole (16 mg, 0.88 mmol). The reaction mixture was stirred for 30 minutes. Then Et_3N (0.3 ml) and pinacol (69 mg, 0.58 mmol) (in one portion) were added to the reaction mixture and stirred for 1 h. Volatiles were removed under vacuum and the product was purified by flash column chromatography on silica (eluent CH_2Cl_2 : hexane = 3 : 1 to CH_2Cl_2). Removal of the solvent yielded the desired product as white solid (28 mg, 73%).

Product regioisomer determined by comparison to data in reference 56

^{1}H NMR ($CDCl_3$) δ: 8.7 (s, 2 H), 7.9 (dd, *J* = 8.3, 1.0 Hz, 2 H), 7.4 (d, *J* = 8.3 Hz, 2 H), 3.9 (s, 3 H), 1.4 (s, 24 H).

^{13}C NMR ($CDCl_3$) δ: 143.1, 132.1, 127.9, 122.7, 107.8, 83.5, 29.1, 24.9.

^{11}B NMR ($CDCl_3$) δ: 31.1.

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fluorine:

In an oven dried Schlenk tube equipped with a J. Young's tap under inert atmosphere CatBCl (30 mg, 0.19 mmol) was dissolved in 1 ml of anhydrous 1,2-dichlorobenzene followed by addition of 2,6-di-*tert*-butylpyridine (44 µl, 0.19 mmol), powdered $AlCl_3$ (26 mg, 0.19 mmol) and fluorene (31 mg, 0.19 mmol). The reaction mixture

was heated at 100 °C and stirred for 48h. Then Et_3N (0.3 ml) and pinacol (69 mg, 0.58 mmol) were added and the reaction mixture was stirred for 1 h. Volatiles were removed under vacuum and the product was purified by flash column chromatography on silica gel (eluent hexane to hexane : CH_2Cl_2 = 3 : 2). Removal of the solvent yielded the desired product as white solid (20 mg, 37%).

NMR data are identical to that previously reported.[57]

^{1}H NMR ($CDCl_3$) δ: 8.03 (s, 1 H), 7.68 - 7.95 (m, 3 H), 7.57 (d, *J* =7.3 Hz, 1 H), 7.29-7.44 (m, 2 H), 3.92 (s, 2 H), 1.39 (s, 12 H).

^{13}C NMR ($CDCl_3$) δ: 144.5, 143.9, 142.4, 141.5, 133.4, 131.2, 127.2, 126.7, 125.1, 120.4, 119.3, 83.7, 36.7, 24.9.

^{11}B NMR ($CDCl_3$) δ: 30.8.

General procedure for borylation with different Lewis Base:

In an oven dried J. Young's NMR tube under inert atmosphere CatBCl (50 mg, 0.32 mmol) was dissolved in 0.6 ml of anhydrous CH_2Cl_2 : CD_2Cl_2 (2 :1) followed by addition of Lewis Base (0.34 mmol). After 15 minutes powdered $AlCl_3$ (47 mg, 0.35 mmol) was added. The reaction mixture was shaken until all $AlCl_3$ dissolved and then *N*-TIPS-pyrrole (72 mg, 0.32 mmol) was added. The reaction was monitored by multinuclear NMR spectroscopy. On completion of borylation the reaction mixture was transferred via cannula under a positive pressure of Argon to a mixture of Et_3N (0.7 ml) and pinacol (114 mg, 0.96 mmol) in anhydrous CH_2Cl_2 (0.5 ml) contained in an oven dried Schlenk tube. After washing the J. Young's NMR tube with anhydrous CH_2Cl_2 (2 x 1 ml) the volatiles were removed under vacuum and the product was purified by flash column chromatography on silica gel (eluent CH_2Cl_2 : hexane = 3 : 1). Removal of the solvent yielded the desired product as a white solid.

Isolation of *N*-methylindole•$AlCl_3$:

In an oven dried J. Young's NMR tube, under inert atmosphere, $AlCl_3$ (50 mg, 0.37 mmol) was dissolved/suspended in anhydrous C_6D_6 (0.8 ml) and *N*-methylindole (47 µl, 0.37 mmol) was added. The reaction mixture was shaken (for 5 minutes) and heated at 80 °C until all solids were dissolved. Then the reaction mixture was slowly cooled to room temperature leading to formation of crystals suitable for x-ray diffraction analysis.

NMR analysis was hampered by the instability of the compound in solution.

Anal. Calcd. for $C_9H_9AlCl_3N$; C = 40.87, H = 3.43, N = 5.30. Found C = 40.78, H = 3.32, N = 5.29.

Synthesis of *N*-methylindole•$GaCl_3$:

In an oven dried Schlenk tube, under inert atmosphere, $GaCl_3$ (200 mg, 1.14 mmol) was dissolved in anhydrous CH_2Cl_2 and the solution was cooled to -78 °C. Then, under vigorous stirring, *N*-methylindole (142 µl, 1.14 mmol) was added and a colourless solid formed. The stirring was stopped and the reaction mixture allowed to warm to room temperature. Pink crystals suitable for single-crystal X-ray diffraction analysis were formed on standing overnight at room temperature. The solution was removed via filter cannula and the crystals were dried under vacuum yielding *N*-methylindole•$GaCl_3$ as pink crystals (257 mg, 74%).

^{13}C NMR analysis was hampered by low solubility of the compound.

Anal. Calcd. for $C_9H_9Cl_3GaN$; C = 35.15, H = 2.95, N = 4.56. Found C = 35.15, H = 3.00, N = 4.47.

^1H NMR ($CDCl_3$) δ: 8.49 (s, 1 H), 7.85 – 7.94 (m, 1 H), 7.57 – 7.72 (m, 3 H), 5.89

(br. s, 1 H), 4.11 (s, 3 H).

^{71}Ga NMR ($CDCl_3$) δ: 265.0.

Reaction of *N*-methylindole•$GaCl_3$ with dTBPy:

In an oven dried J. Young's NMR tube, under inert atmosphere, dTBPy (14.5 µl, 0.065 mmol) was dissolved in anhydrous CH_2Cl_2 (0.8 ml). Then *N*-methylindole•$GaCl_3$ (20 mg, 0.065 mmol) was added and the reaction mixture was sonicated until *N*-methylindole•$GaCl_3$ was full dissolved.

Crystallographic Details

Crystal Data for $[Cl_4CatB(NEt_3)][AlCl_4]$:

Molecular Formula	$C_{12}H_{15}Al_1B_1Cl_8N_1O_2$
Molecular Mass	526.64
Crystal system	Monoclinic
Space group	P21/c
a/Å	8.4606(3)
b/Å	5.8493(5)
c/Å	16.3531(5)
α/°	90.00
β/°	104.174(4)
γ/°	90.00
Volume/Å	2126.10(12)
Z	4
D_{calcd} g/cm^3	1.645
F(000)	1056
T/K	100(2)
Absorption coefficient (μ)/mm^{-1}	1.108
Crystal size/mm	0.70 x 0.10 x 0.10
Reflections measured	4352
Reflections collected	3180
Goodness-of-fit on F^2	0.925
Final R1 [I > 2σ(I)]	0.0317
(all data)	0.0511

Crystal Data for [Cl_4CatB(2,6-lutidine)][$AlCl_4$]:

Molecular Formula	$C_5H_5Al_1B_1Cl_6N_1$
Molecular Mass	329.59
Crystal system	Orthorhombic
Space group	Pbca
a/Å	9.1715(4)
b/Å	13.7626(9)
c/Å	32.5304(19)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å	4106.1(4)
Z	8
D_{calcd} g/cm^3	1.723
F(000)	2112
T/K	100(2)
Absorption coefficient (μ)/mm^{-1}	1.149
Crystal size/mm	0.70 x 0.10 x 0.10
Reflections measured	3573
Reflections collected	2674
Goodness-of-fit on F^2	1.053
Final R1 [I > 2σ(I)]	0.0449
(all data)	0.0648

Crystal Data for [CatB(NEt$_3$)][*closo*-CB$_{11}$H$_6$Br$_6$]:

Molecular Formula	$C_{13}H_{25}B_{12}Br_6N_1O_2$
Molecular Mass	836.52
Crystal system	Monoclinic
Space group	P21/n
a/Å	13.8192(8)
b/Å	25.5354(17)
c/Å	16.8644(9)
α/°	90.00
β/°	71.809(6)
γ/°	90.00
Volume/Å	5653.7(6)
Z	4
D_{calcd} g/cm^3	1.966
F(000)	3168
T/K	100(2)
Absorption coefficient (μ)/mm^{-1}	8.537
Crystal size/mm	0.40x0.10x0.10
Reflections measured	9961
Reflections collected	6783
Goodness-of-fit on F^2	1.018
Final R1 [I > 2σ(I)]	0.0852
(all data)	0.1188

Crystal Data for [CatB(P^{t}Bu$_3$][AlCl$_4$]:

Molecular Formula	$C_{18}H_{31}Al_1B_1Cl_4O_2P_1$
Molecular Mass	489.99
Crystal system	Monoclinic
Space group	P21/c
a/Å	12.3046(5)
b/Å	11.8986(5)
c/Å	16.7732(7)
α/°	90.00
β/°	102.448(4)
γ/°	90.00
Volume/Å	2397.99(17)
Z	4
D_{calcd} g/cm^3	1.357
F(000)	1024
T/K	100(2)
Absorption coefficient (μ)/mm^{-1}	0.609
Crystal size/mm	0.40x0.10x0.10
Reflections measured	4226
Reflections collected	2947
Goodness-of-fit on F^2	0.992
Final R1 [I > 2σ(I)]	0.0441
(all data)	0.0644

Crystal Data for {[μ-OC(CH$_3$)$_2$C(CH$_3$)$_2$OH]AlCl$_2$}$_2$:

Molecular Formula	$C_{24}H_{58}Al_2Cl_6N_2O_4$
Molecular Mass	705.38
Crystal system	Monoclinic
Space group	P21/c
a/Å	11.8521(4)
b/Å	11.4984(4)
c/Å	13.7899(5)
α/°	90.00
β/°	104.612(4)
γ/°	90.00
Volume/Å	1818.51(11)
Z	2
D_{calcd} g/cm^3	1.288
F(000)	752
T/K	100(2)
Absorption coefficient (μ)/mm^{-1}	0.0551
Crystal size/mm	0.60 x 0.20 x 0.10
Reflections measured	2327
Reflections collected	3206
Goodness-of-fit on F^2	0.901
Final R1 [I > 2σ(I)]	0.0320
(all data)	0.0705

Crystal Data for *N*-methylindole•$AlCl_3$:

Molecular Formula	$C_{12}H_{12}Al_1Cl_3N_1$
Molecular Mass	303.56
Crystal system	Monoclinic
Space group	P21/n
a/Å	9.358(2)
b/Å	12.215(3)
c/Å	12.764(3)
α/°	90.00
β/°	107.11(3)
γ/°	90.00
Volume/Å	1394.5(6)
Z	4
D_{calcd} g/cm^3	1.446
F(000)	620
T/K	100(2)
Absorption coefficient (μ)/mm^{-1}	0.696
Crystal size/mm	0.5x0.4x0.3
Reflections measured	2444
Reflections collected	1743
Goodness-of-fit on F^2	1.149
Final R1 [I > 2σ(I)]	0.1167
(all data)	0.1494

Crystal Data for *N*-methylindole•$GaCl_3$:

Molecular Formula	$C_9H_9Ga_1Cl_3N_1$
Molecular Mass	307.24
Crystal system	Monoclinic
Space group	P21/c
a/Å	13.3468(5)
b/Å	13.1469(5)
c/Å	13.1419(4)
α/°	90.00
β/°	90.046(3)
γ/°	90.00
Volume/Å	2306.00(14)
Z	8
D_{calcd} g/cm^3	1.770
F(000)	1216
T/K	100(2)
Absorption coefficient (μ)/mm^{-1}	1.770
Crystal size/mm	0.40x0.30x0.20
Reflections measured	3888
Reflections collected	3243
Goodness-of-fit on F^2	1.068
Final R1 [I > 2σ(I)]	0.0274
(all data)	0.0348

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Chapter 4. Arene borylation with dichloroborenium cations

4.1 Introduction

Catecholborenium salts [CatB(L)][$AlCl_4$] (L = aprotic amine or phosphine) have been readily prepared via halogen abstraction from CatBCl•L by $AlCl_3$. These borenium salts, or electrophiles derived from them, are able to borylate a range of arenes with good yield and regioselectivity. However, their ability to borylate arenes is limited to electron rich arenes. In order to find a cheaper and stronger electrophilic borylating mixture than CatBCl, amine and $AlCl_3$, CatBCl was replaced with the more electrophilic species BX_3 (X = Cl, Br).

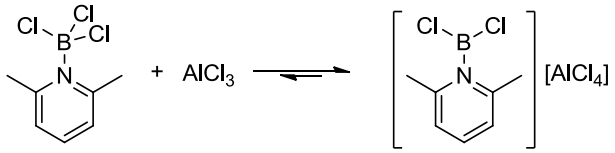
In 1959, Muetterties and Lappert reported in two independent works that BX_3 (X = Cl, Br) in combination with AlX_3 (or Al in presence of catalytic quantities of AlX_3) is able to borylate arenes.[1] The success of arene borylation with BX_3 and AlX_3 relies on the removal of HX by-product (either as gaseous HX in an open system or as H_2 by reaction of HX with Al) from the reaction media to prevent the reverse reaction of protodeboronation[2] and the formation of a stronger electrophilic species than BX_3. Even if the identity of the active electrophilic species was not clear, the formation of a borenium cation was postulated. Muetterties proposed that BCl_3 with $AlCl_3$ in arene solvent forms the borenium cation $[(ArH)BCl_2]^+$,[2,3] while Olah proposed the coordination of the Lewis acid $AlCl_3$ to a chlorine atom of BCl_3 to form the chloride bridged species Cl_2B-(μ-Cl)-$AlCl_3$.[4] Although one of these species is a sufficiently powerful electrophile to achieve the intermolecular C-H borylation of arenes, the formation of such a strong electrophilic species and/or the strong Brønsted acid HX leads to alkyl rearrangement in alkyl benzenes and precludes the borylation of arenes bearing substituents sensitive to strong acidic media and

heteroarenes such as thiophene. In order to address these issues, the use of a Lewis base in combination with BCl_3 and $AlCl_3$ was investigated. The Lewis base was envisaged to modulate electrophilicity at boron and act as a proton sponge sequestering HCl.

4.2 Synthesis and characterization of dihaloborenium cations

Dihaloborenium cations $[Cl_2B{\bullet}L]^+$ (L = aprotic amine) were readily prepared from the neutral adduct $X_3B{\bullet}L$ (X = Cl, Br) via halide abstraction by AlX_3 (X = Cl, Br).

The addition of an equivalent of $AlCl_3$ to a 1:1 mixture of BCl_3 and 2,6-lutidine in CH_2Cl_2 readily gave $[Cl_2B{\bullet}$2,6-lutidine$][AlCl_4]$ (Eq. 1). The formation of an ionic species was supported by multinuclear NMR spectroscopy (Figure 4.1). The ^{11}B NMR chemical shift at 46.9 ppm was comparable to the related borenium cations $[Cl_2B(Py)][B(C_6F_5)_4]$ (Py = pyridine) and $[Cl_2B{\bullet}$4-picoline$][Al_2Cl_7]$ (44.0 and 47.3 ppm, respectively),[5, 6] while the ^{27}Al NMR spectrum showed the characteristic sharp peak of $[AlCl_4]^-$ at 103.7 ppm.[7]



Eq.1

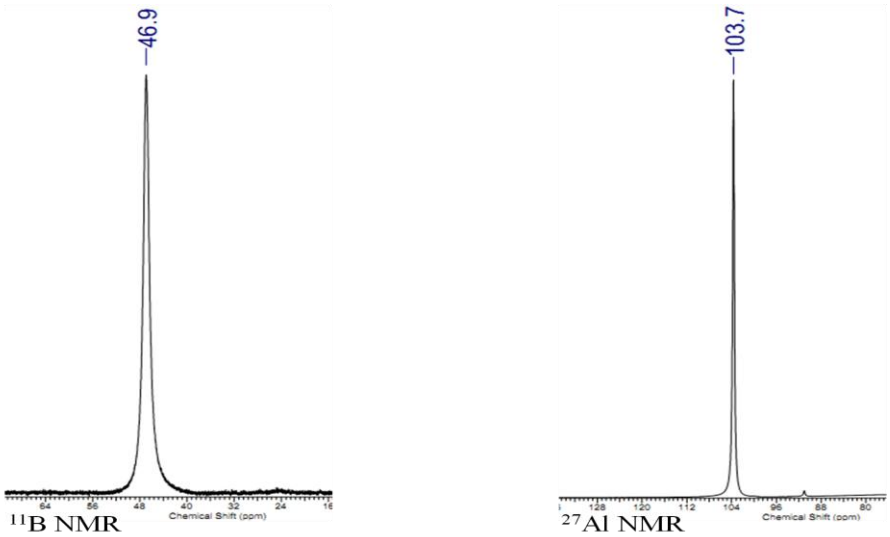


Figure 4.1 ^{11}B NMR (left) and ^{27}Al NMR spectra (right) of the reaction between BCl_3, 2,6-lutidine and $AlCl_3$ in CD_2Cl_2.

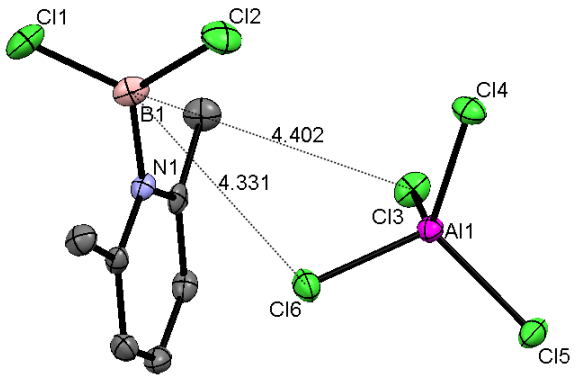
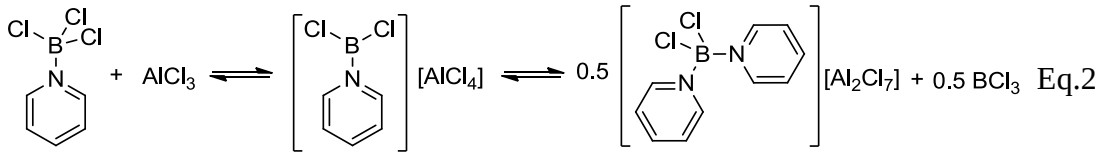


Figure 4.2 Crystal structure of $[Cl_2B(2,6\text{-lutidine})][AlCl_4]$, hydrogens omitted for clarity and thermal ellipsoids at 50 % probability. Selected bond lengths (Å): B1-Cl1 = 1.709(3), B1-Cl2 = 1.715(3), B1-N1 = 1.509(3). Angles at B Σ = 360.0°.

Definitive proof of $[Cl_2B\bullet 2,6\text{-lutidine}][AlCl_4]$ formation was given by single crystal X-ray diffraction (Figure 4.2). The crystal structure of $[Cl_2B(Py)][AlCl_4]$ with the sum of the angles around the boron atom at 360.0° is consistent with a tricoordinate boron centre. The pyridyl and Cl–B–Cl planes are almost orthogonal with an interplane angle of 84.8°, orientated to minimize repulsion between *ortho* methyls and chloride substituents. This precludes pyridyl to boron π donation which has been previously calculated to provide significant stabilization in the co-planar

pyridyl/$\{BX_2\}^+$ geometry.[8] The B-N bond at 1.509(3) is similar to the tetrachloro-catecholborenium cations $[Cl_4CatB(2,6\text{-lutidine})]^+$ and $[Cl_4CatB(NEt_3)]^+$ (1.499(6) Å and 1.505(3) Å, respectively).

The ^{11}B NMR spectrum of $[Cl_2B{\bullet}2,6\text{-lutidine}][AlCl_4]$ clearly showed the formation of a borenium salt, while the ^{11}B NMR spectrum of the reaction of a 1:1 mixture of $AlCl_3$ and $Cl_3B{\bullet}Py$ in CD_2Cl_2 showed a ^{11}B NMR chemical shift at 25.7 ppm (Figure 4.3). This resonance was significantly upfield from the expected ^{11}B NMR resonance of 44 ppm for the borenium $[Cl_2B(Py)][B(C_6F_5)_4]$ [6] and was attributed to fast multiple equilibriums on the NMR time scale (Figure 4.3). The borenium salt is possibly in equilibrium with neutral species and boronium salt (Eq. 2). An attempt to reach the slow exchange regime at -70 °C in CD_2Cl_2 was unsuccessful. However, the formation of the borenium salt $[Cl_2B(Py)][AlCl_4]$ was supported by single crystal X-ray diffraction.



Eq.2

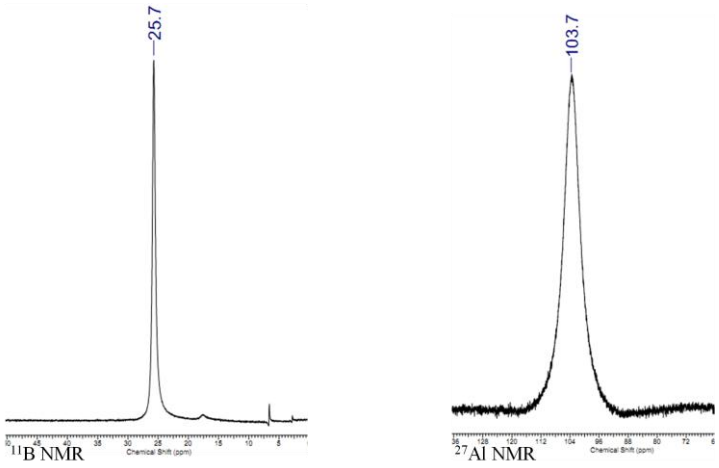


Figure 4.3 ^{11}B NMR (left) and ^{27}Al NMR spectra (right) of the reaction between BCl_3, pyridine and $AlCl_3$ in CD_2Cl_2.

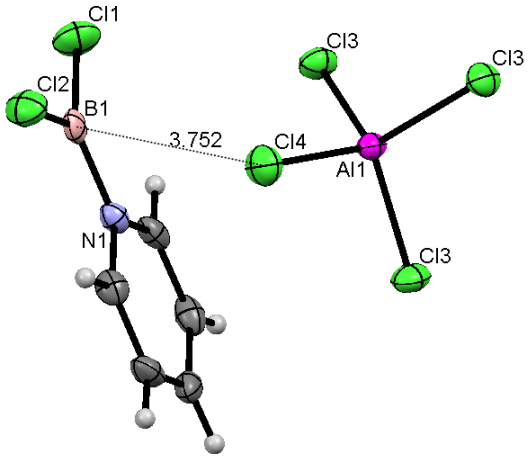


Figure 4.4 Crystal structure of $[Cl_2B(Py)][AlCl_4]$, thermal ellipsoids at 50 % probability. Selected bond lengths (Å): B1-Cl1 = 1.731(5), B1-Cl2 = 1.714(4), B1-N1 = 1.486(4). Angles at B Σ = 360.0°.

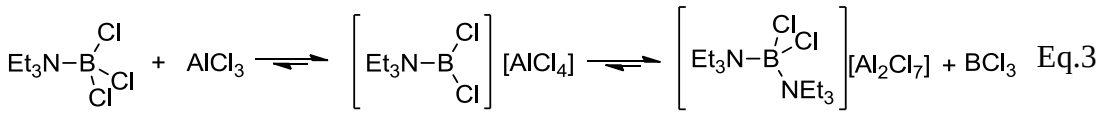
The crystal structure of $[Cl_2B(Py)][AlCl_4]$ (Figure 4.4) shows a trigonal planar geometry at the boron atom (the sum of the angles around boron is 360.0°) with a long anion-cation distance (the shortest distance between B and Cl of $[AlCl_4]^-$ is at 3.695(5) Å). These features are consistent with a tricoordinate boron centre and with the ionic formulation. The pyridyl and BCl_2 moieties are coplanar to maximise pyridyl→B π donation (interplanar angle pyridyl/BCl_2 = 0.82°). The B-N bond at 1.486(4) Å is shorter than in the related borenium cation $[Cl_2B•2,6\text{-lutidine}]^+$ (1.509(3) Å).

From the comparison of the structures of $[Cl_2B(Py)][AlCl_4]$ and $[Cl_2B(2,6\text{-lutidine})][AlCl_4]$ it is clear that substituents in 2,6-position of the pyridine ring are the origin of the different equilibriums position. The two *ortho* methyls in 2,6-lutidine, in addition to generating steric pressure in $Cl_3B•2,6$-lutidine,[9] shield the boron cation centre from the anion and disfavour the formation of the boronium cation, $[Cl_2B(2,6\text{-lutidine})_2]^+$.

The steric bulk of the amine is not the only factor that influences equilibrium positions in the reaction between $AlCl_3$ and $Cl_3B•$amine. The amine basicity is also

important to determine equilibrium positions as suggested by the synthesis of the borenium cations $[Cl_2B(NEt_3)][AlCl_4]$ and $[Cl_2B(DMTol)][AlCl_4]$ (DMTol = *N*,*N*-dimethyl-*p*-toluidine).

The reaction between $AlCl_3$ and $Cl_3B{\bullet}NEt_3$ in CD_2Cl_2 gave the borenium salt $[Cl_2B{\bullet}NEt_3][AlCl_4]$ which has an ^{11}B NMR resonance at 42.3 ppm (Figure 4.5), close to the expected chemical shift for $[Cl_2B{\bullet}amine]^+$ borenium cations. This suggested that the equilibrium position lies more toward the borenium cation than in the reaction between $AlCl_3$ and $Cl_3B{\bullet}Py$. The shift of equilibriums toward the borenium salt was attributed to the greater basicity and greater steric bulkiness of Et_3N compared to pyridine. Hence, Et_3N gave a more stabilized borenium cation and possibly disfavoured the formation of the boronium cation compared to the pyridyl analogue.



Eq.3

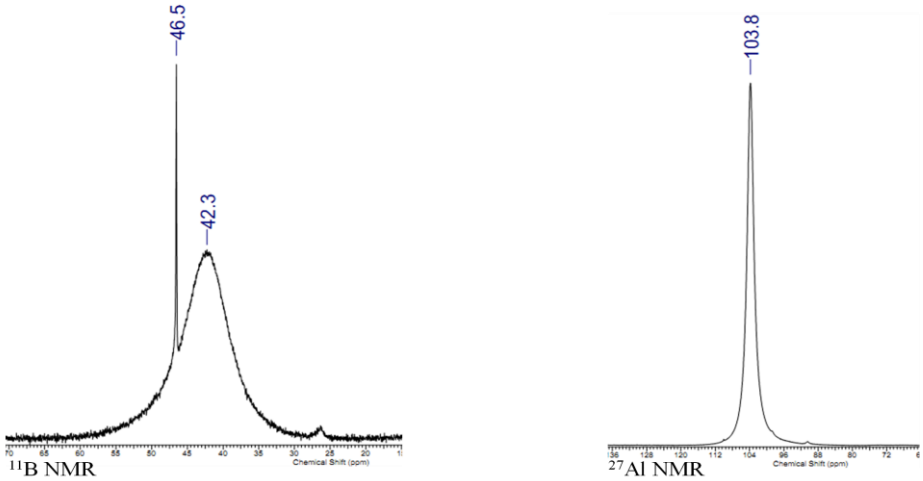
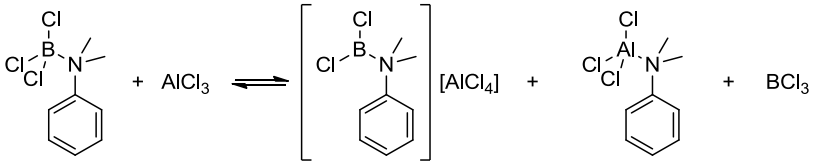


Figure 4.5 ^{11}B NMR (left) and ^{27}Al NMR spectra (right) of the reaction between BCl_3, Et_3N and $AlCl_3$ in CD_2Cl_2. The sharp resonance at 46.5 is BCl_3.

The use of DMTol, which is less basic and less bulky than Et_3N, gave the borenium cation as a minor product. The ^{11}B NMR spectrum of the reaction of $AlCl_3$

with the neutral adduct Cl_3B•DMTol in CD_2Cl_2 showed two peaks: a sharp peak at 46.5 ppm consistent with BCl_3 and a broad peak at 25.2 ppm that we attribute to the borenium cation $[Cl_2B$•DMTol$]^+$ in fast equilibrium with neutral species (DMTol•BCl_3) and possibly the boronium cation. The ^{27}Al NMR spectrum showed a broad peak at 103.1 ppm attributable to $[AlCl_4]^-$ in rapid equilibrium with $AlCl_3$ and a peak at 108.2 ppm consistent with Cl_3Al•DMTol. The attempt to reach the slow exchange regime cooling the reaction mixture to -70 °C was unsuccessful.



Eq. 4

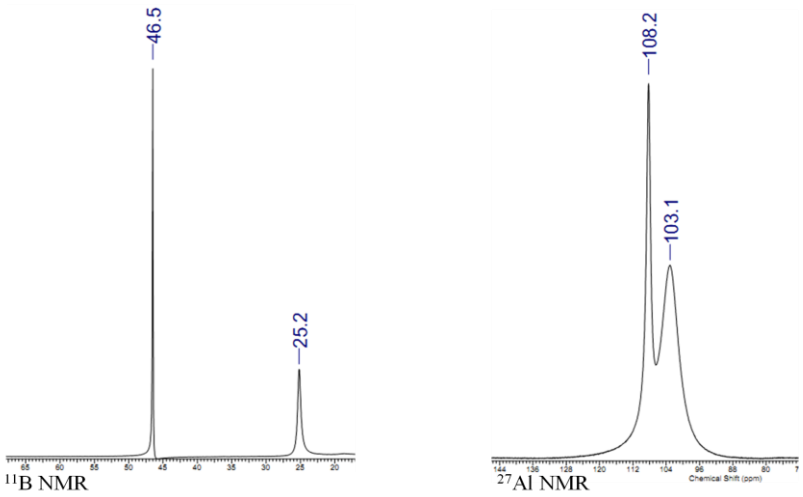
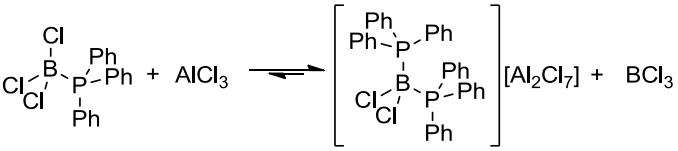


Figure 4.6 ^{11}B NMR (left) and ^{27}Al NMR spectra (right) of the reaction between DMTol•BCl_3 and $AlCl_3$ in CD_2Cl_2. The sharp resonance at 46.5 is BCl_3.

In contrast to chloride abstraction from amine•BCl_3 by $AlCl_3$ which yielded mainly borenium salts, the reaction of $AlCl_3$ with Cl_3B•PPh_3 led to the predominant formation of the boronium salt $[Cl_2B(PPh_3)_2][Al_2Cl_7]$ and BCl_3. The ^{11}B NMR spectrum mainly showed a sharp singlet at 46.6 ppm attributable to BCl_3 and a triplet centred at -0.3 ppm ($^1J_{PB}$ = 135 Hz) consistent with the boronium cation $[Cl_2B(PPh_3)_2]^+$.[10]



Eq. 5

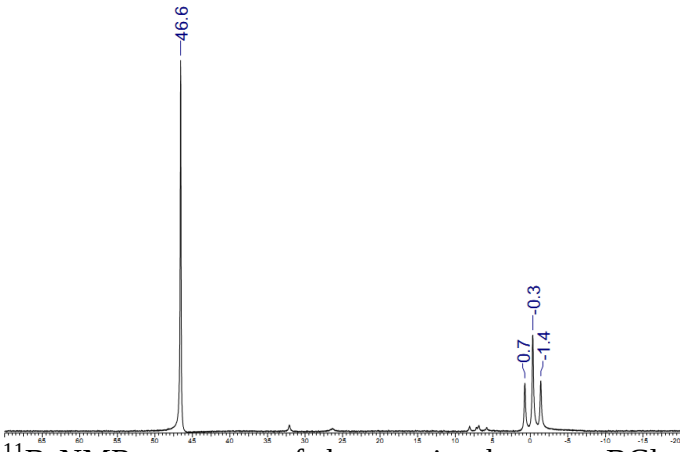


Figure 4.7 ^{11}B NMR spectrum of the reaction between BCl_3, PPh_3 and $AlCl_3$ in CD_2Cl_2.

In contrast to tricoordinate boron monocations, the related tricoordinate boron dications are elusive species in the condensed-phase due to their extreme electrophilicity. Instead, tetracoordinate boron dicationic species are invariably synthesised and several crystal structures reported.[11] A simple synthetic route to obtain tetracoordinate boron dications is the nucleophilic displacement of both bromine atoms from L•Br_2B-Y (L = pyridine derivatives; Y = Br, H) by pyridine or substituted pyridines.[11c-d]

In order to achieve the synthesis of a tricoordinate boron dication a less coordinating anion than Br^- and a different method are required. Our initial idea was to proceed via halogen abstraction by the Lewis acid AlX_3 (X = halogen) from a dihaloboronium cation. Since the B-Br bond is a weaker bond than an equivalent B-Cl bond, BBr_3 was chosen as starting material.

It is noteworthy that the addition of an equivalent of $AlBr_3$ to a 1 : 1 mixture of BBr_3 and 2,6-lutidine in 1,2-dichloroethane resulted in chloride abstraction from the solvent. The ^{11}B NMR spectrum of the reaction showed a sharp peak at 45.9 ppm

attributable to BCl_3 with a shoulder downfield consistent with the borenium cation $[Cl_2B(2,6\text{-Lutidine})]^+$ (Figure 4.8). The definitive proof of chloride abstraction from the solvent was given by the ^{27}Al NMR spectrum. The initial broad resonance at 89.5 ppm in the ^{27}Al NMR spectrum, attributed to the rapid exchange of halide atoms between aluminium and boron centres,[12] split into five peaks upon the addition of a second equivalent of 2,6-lutidine to the reaction mixture. These five peaks at 103.1, 99.4. 94.4, 88.0 and 80.2 ppm were consistent with $[AlCl_4]^-$, $[AlCl_3Br]^-$, $[AlCl_2Br_2]^-$, $[AlClBr_3]^-$ and $[AlBr_4]^-$, respectively (Figure 4.9).[13]

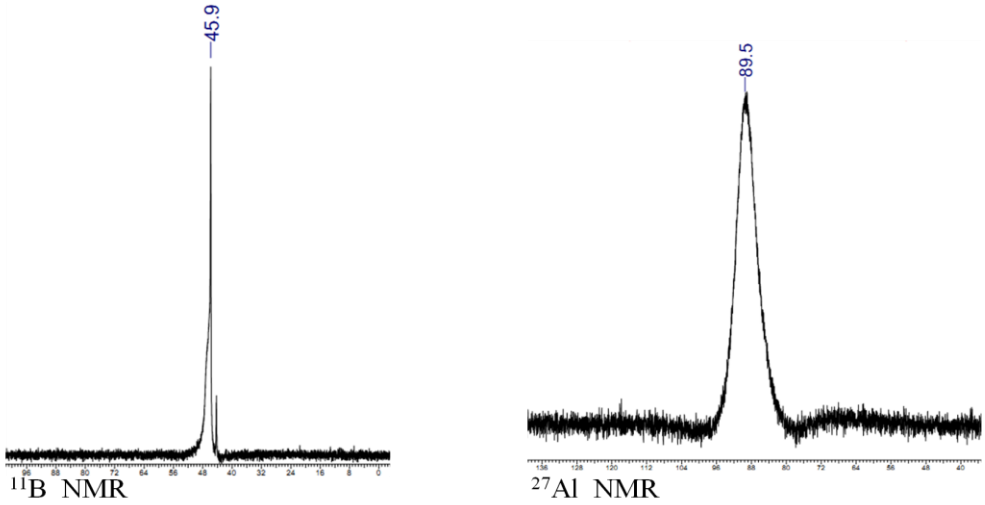


Figure 4.8 ^{11}B NMR (left) and ^{27}Al NMR spectra (right) of the reaction between BBr_3, 2,6-lutidine and $AlBr_3$ in 1,2-dichloroethane.

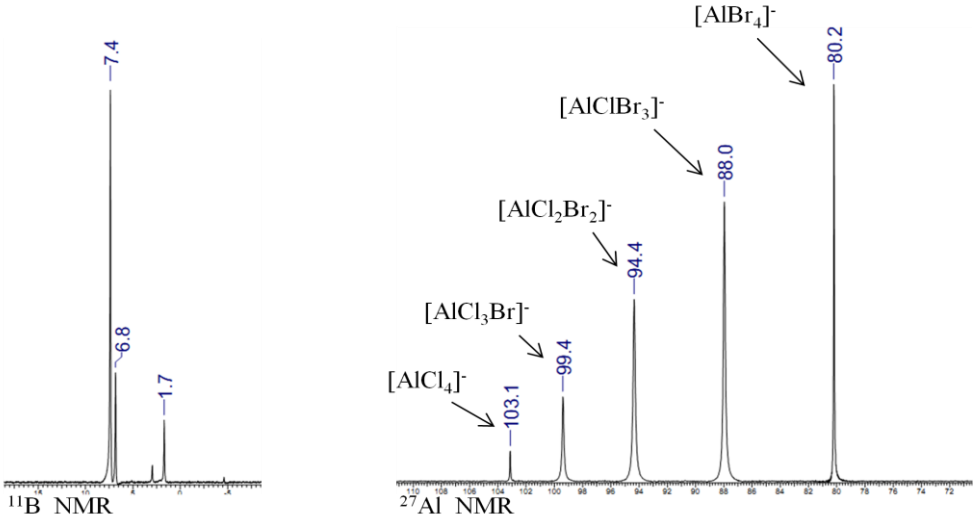
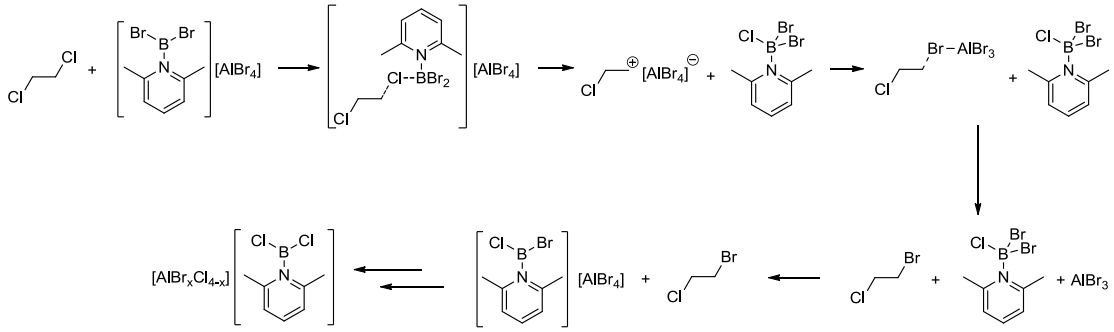


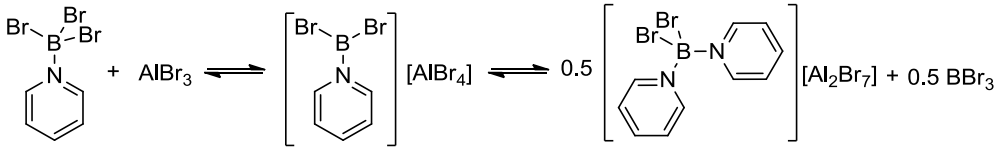
Figure 4.9 ^{11}B NMR (left) and ^{27}Al NMR spectra (right) of the reaction between BBr_3, 2,6-lutidine and $AlBr_3$ in 1,2-dichloroethane after the addition of a second equivalent of 2,6-lutidine.

Although it is not possible to exclude that 1,2-dichloroethane undergoes chloride abstraction with $AlBr_3$, the use of $AlBr_3$ in the chlorinated solvent CH_2Cl_2 for the synthesis of borinium salts [(tmp)B(R)][$AlBr_4$] (tmp = 2,2,6,6-tetramethylpiperidine, R = NMe_2, NEt_2, C_6H_5, CH_3)[13] and [(^{i}Pr$_2$N)$_2$B(R)][$AlBr_4$][14] along with the rapidity of the chloride abstraction suggest that the halide abstraction proceeds by an highly electrophilic species which is postulated to be the borenium cation (Scheme 4.1).



Scheme 4.1 Proposed mechanism of chloride abstraction.

The chloride abstraction from 1,2-dichloroethane by the mixture of $AlBr_3$, 2,6-lutidine and BBr_3 indicated that a more robust solvent than chlorinated aliphatic hydrocarbons has to be used for the synthesis of dibromoborenium cations. Indeed, the synthesis of the dibromoborenium cation was readily achieved using the robust halogenated benzenes *ortho*-dichlorobenzene (o-dCB) or d_5-bromobenzene as solvent.



Eq. 6

The ^{11}B NMR spectrum of the reaction of $AlBr_3$ with Br_3B•Py in d_5-bromobenzene showed only a peak at 18.9 ppm suggesting that the borenium salt [Br_2B(Py)][$AlBr_4$] was in equilibrium with the neutral species and possibly with the boronium salt, as previously observed for the chlorine congener. The formation of the borenium cation

was initially corroborated by further addition of $AlBr_3$ (to enhance the halide affinity of the aluminium Lewis acid)[15] which shifted the ^{11}B NMR resonance downfield into the expected region of the borenium cation (Table 4.1). The definitive proof of the formation of $[Br_2B(Py)][AlBr_4]$ was given by single crystal X-ray diffraction.

Table 4.1 ^{11}B and ^{27}Al NMR chemical shifts of the reaction between Br_3B•Py and x equivalents of $AlBr_3$ in d_5-bromobenzene. (FWHH=Full Width at Half Height)

Number of Equivalents of $AlBr_3$	^{11}B NMR chemical shift (ppm)	^{27}Al NMR chemical shift (ppm)
1	18.9	85.8 (FWHH = 2170 Hz)
1.5	34.1	85.5 (FWHH = 2247 Hz)
2	44.4	84.2 (FWHH = 2838 Hz)

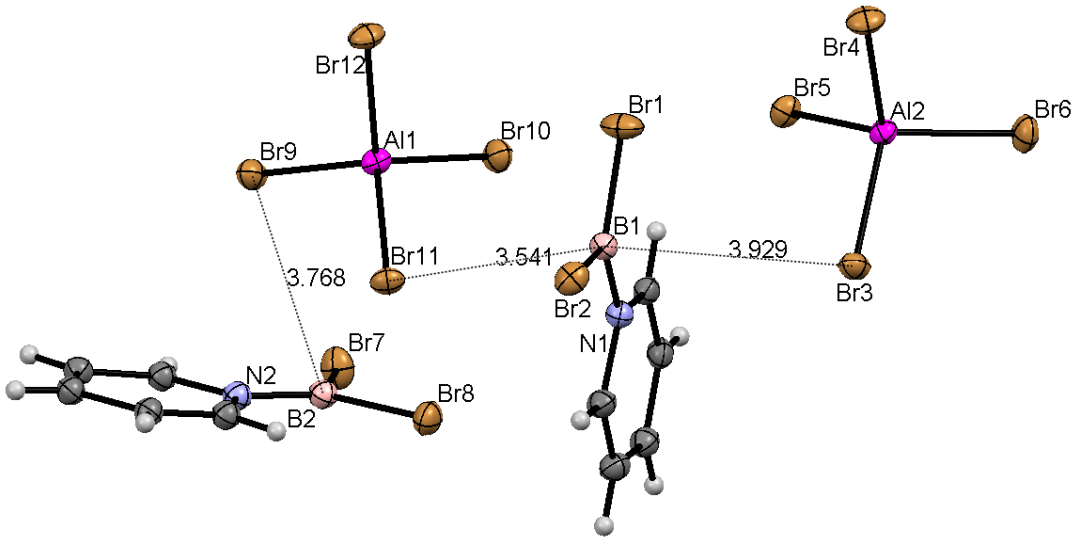
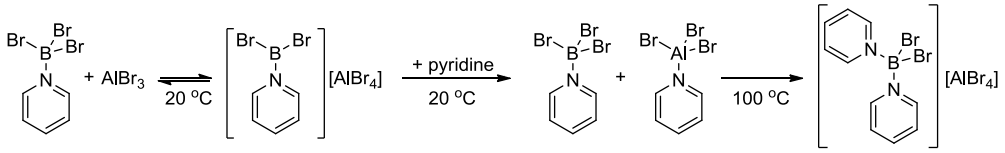


Figure 4.10 Crystal structure of $[Br_2B(Py)][AlBr_4]$, thermal ellipsoids at 50 % probability. Selected bond lengths (Å): B1-Br1 = 1.88(2), B1-Br2 = 1.87(2), B1-N1 = 1.48(2), B2-Br7 = 1.85(2), B2-Br8 = 1.92(2), B2-N2 = 1.46(2).

$[Br_2B(Py)][AlBr_4]$ crystallises with two molecules in the asymmetric unit with similar metrics. Analogous to the pyridine ligated dichloroborenium cation, $[Br_2B(Py)][AlBr_4]$ shows a trigonal planar boron centre (the sum of angles around boron are 359.8° and 359.7°) and long anion-cation distances (the shortest contact

between boron and a bromine of $[AlBr_4]^-$ is 3.541 Å). Again the pyridyl and the BBr_2 moieties are coplanar to maximise pyridyl→B π donation. The B-N distances (B1-N1 = 1.48(2) Å and B2-N2 = 1.46(2) Å are shorter than in the related dibromoborenium cation $[Br_2B(2,6\text{-dimesitylpyridine})]^+$ (1.530(7) Å) which is non planar due to steric factors.[16]

The addition of an equivalent of pyridine to the *in-situ* prepared borenium salt $[Br_2B(Py)][AlBr_4]$ in o-dCB gave the two neutral adducts, $Br_3B{\bullet}Py$ and $Br_3Al{\bullet}Py$ (by ^{11}B and ^{27}Al NMR spectroscopy). On heating the reaction mixture at 100 °C for 48 hours the boronium cation $[Br_2B(Py)_2][AlBr_4]$ was the major product as suggested by multinuclear NMR spectroscopy. The sharp peak in the ^{11}B NMR spectrum at 2.1 ppm and the sharp peak at 80.5 ppm in the ^{27}Al NMR spectrum were consistent with the formation of a tetracoordinate boron centre and $[AlBr_4]^-$.



Eq.7

In order to achieve a tricoordinate boron dication, the next step was the attempt to abstract a bromide from the dibromoboronium cation by $AlBr_3$. The addition of 2 equivalents of $AlBr_3$ to the boronium cation $[Br_2B(Py)_2][AlBr_4]$ in o-dCB resulted in no reaction even after 10 days at 150 °C (by ^{11}B and ^{27}Al NMR spectroscopy). Instead, the addition of an equivalent of pyridine and an equivalent of $AlBr_3$ to the borenium cation $[Br_2B(Py)][AlBr_4]$ in o-dCB led to the formation of colourless crystals after prolonged heating (21 hours at 150 °C). The ^{11}B NMR analysis of the solution revealed that the only boron species that remained in solution was the boronium cation $[Br_2B(Py)_2]^+$. Surprisingly the colourless crystals, which were insoluble in d_5-bromobenzene and CD_2Cl_2 at 20 °C, were identified by single crystal

X-ray diffraction analysis and by element analysis as the hexacyclic tricationic species $[(Py)_4B_3O_3][AlBr_4]_2[Al_2Br_7]$ (Figure 4.11).

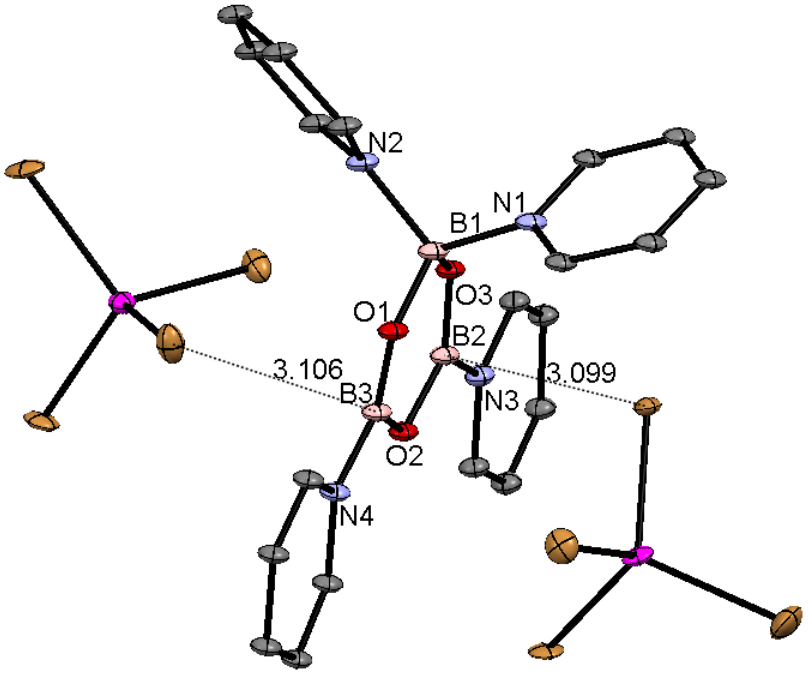


Figure 4.11 Crystal structure of $[(Py)_4B_3O_3][AlBr_4]_2[Al_2Br_7]$, thermal ellipsoids at 50 % probability and hydrogens and $[Al_2Br_7]^-$ omitted for clarity. Selected bond lengths (Å): B1-O1 = 1.44(2), B1-O3 = 1.46(1), B1-N1 = 1.56(2), B1-N2 = 1.58(2), B2-O3 = 1.28(2), B2-O2 = 1.39(2), B2-N3 = 1.49(2), B3-O2 = 1.36(1), B3-O1 = 1.32(1), B3-N4 = 1.48(2).

$[(Py)_4B_3O_3][AlBr_4]_2[Al_2Br_7]$ crystallises with two molecules in the asymmetric unit which are metrically similar, thus only one is discussed. The compound $[(Py)_4B_3O_3][AlBr_4]_2[Al_2Br_7]$ displays significantly closer anion-cation contacts (the shortest distances between the two tricoordinate boron and bromine of $[AlBr_4]^-$ are 3.106 and 3.099 Å) compared to that observed in $[Br_2B(Py)][AlBr_4]$ (3.499 Å), but the trigonal planar geometries at B2 and B3 (sum of the angles around the boron are 359.6° and 360.0°, respectively) and identical (within 3σ) Al–Br bond lengths in the $[AlBr_4]^-$ anions suggest that these close contacts are due to electrostatic forces and packing effects. The B_3O_3 ring in $[(Py)_4B_3O_3][AlBr_4]_2[Al_2Br_7]$ is almost planar (sum

of internal bond angles = 718.7°), and each pyridine coordinated to tricoordinate boron is almost coplanar (B_3O_3/pyridine inter-plane angles = 5.0 to 19.8°) indicating significant pyridyl→B π donation. The B_3O_3 ring has two extremely short B–O bonds (B2–O3 = 1.283(15), B3–O1 = 1.318(14) Å), less than the equivalent B–O bonds in neutral $(PhBO)_3$•pyridine (1.346(4) and 1.348(5) Å).[17] These shortest B-O distances, which involve the oxygen atoms bridging the tetra- and tri-coordinate boron centres and tricoordinate boron centre, indicate that a significant π bond character is present.

The formation of this tricationic species is presumably due to adventitious water, therefore in order to achieve a rational route for the synthesis of $[(Py)_4B_3O_3][AlBr_4]_2[Al_2Br_7]$, attempts to add known quantities of water were conducted. Initial attempts to prepare the trication species $[(Py)_4B_3O_3]^{3+}$ by controlled addition of an equivalent of H_2O were unsuccessful. The equimolar reaction of H_2O, $[Br_2B(Py)_2][AlBr_4]$ and $AlBr_3$ upon heating at 150 °C resulted in the formation of an intractable brown oil. An analogous result was obtained adding a premixed solution of equimolar pyridine and H_2O to the reaction mixture containing $[Br_2B(Py)][AlBr_4]$ and $AlBr_3$. In the end, in our laboratory, the synthesis of the tricationic boron species was achieved by Dr Ewan Clark by adding substoichiometric quantities (0.5 equivalents) of H_2O to the mixture of $[Br_2B(Py)][AlBr_4]$ and pyridine in o-dCB.[18]

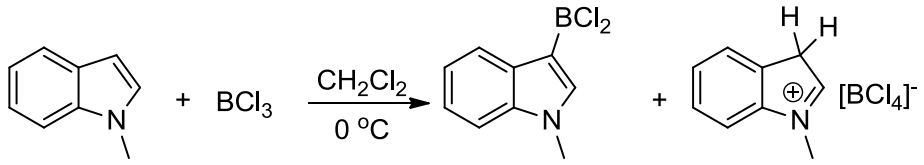
In order to test the reactivity of dihaloborenium salts, the direct C-H arene borylation was investigated with $[Cl_2B(amine)]^+$.

4.3 Arene borylation

The addition of *N*-methylindole to a solution of BCl_3 in CH_2Cl_2 at 20 °C gave a

mixture of unidentified products, possibly deriving from indole polymerisation promoted by acid.[19] In contrast, the addition of *N*-methylindole to a solution of BCl_3 in CH_2Cl_2 cooled at -78 °C yielded a white precipitate which was tentatively formulated as Cl_3B•*N*-methylindole adduct in analogy to the compounds formed between MCl_3 (M = Al, Ga) and *N*-methylindole. This heterogeneous reaction mixture yielded 3-Cl_2B-*N*-methylindole and protonated *N*-methylindole partnered with BCl_4 as major products after 10 days at 4 °C (Figure 4.12).

BCl_3 was sufficiently electrophilic to borylate the electron rich arene *N*-methylindole, however it was unable to borylate less nucleophilic arenes such as 2-methylthiophene with or without an additional base. Therefore, a more electrophilic species than BCl_3 was required for a broad arene substrate scope.



Eq. 8

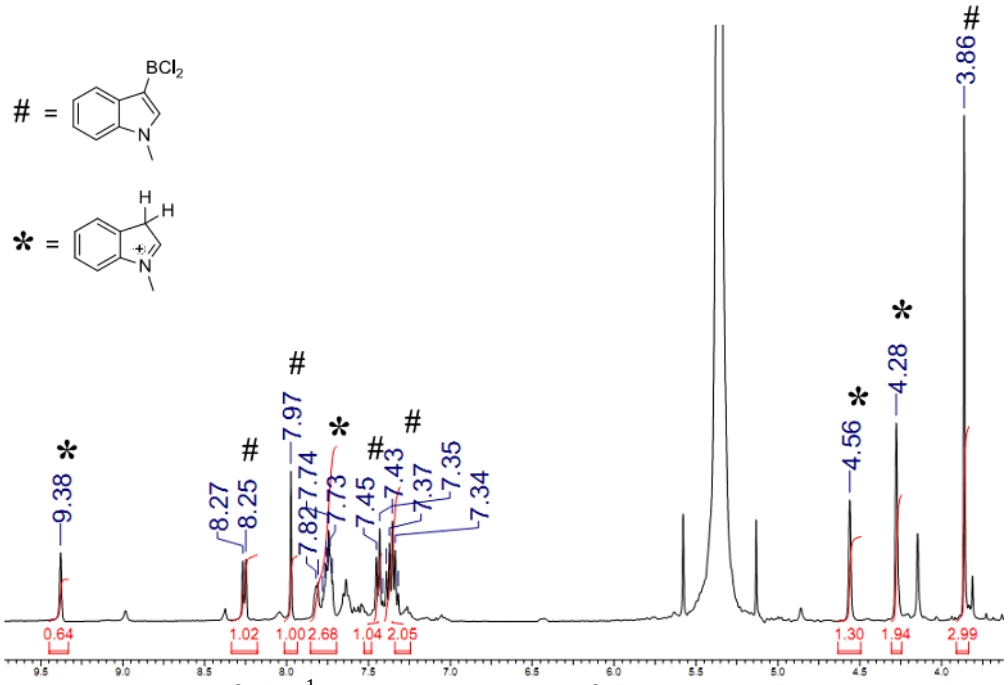
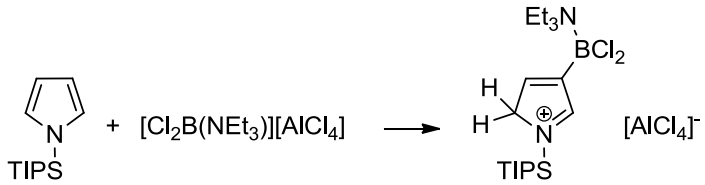


Figure 4.12 Part of the ^{1}H NMR spectrum of the reaction between BCl_3 and *N*-methylindole in CH_2Cl_2 at 0 °C after 10 days. d_6-DMSO in sealed capillary was used as lock solvent.

The amine ligated dichloroborenium cations are expected to have enhanced electrophilicity compared to neutral BCl_3 and initial studies on the reactivity of these borenium cations toward arenes were conducted with *N*-TIPS-pyrrole.

The borenium salt $[Cl_2B{\bullet}NEt_3][AlCl_4]$ rapidly reacted with *N*-TIPS-pyrrole in CD_2Cl_2 at 20 °C to give as major product the borylated arenium cation $[3\text{-}(Cl_2B{\bullet}NEt_3)\text{-}N\text{-TIPS-pyrrole}]^+$ (Eq. 9). The formation of the arenium cation was supported by multinuclear NMR spectroscopy. The ^{11}B NMR spectrum, recorded after 20 minutes from the addition of *N*-TIPS-pyrrole to $[Cl_2B{\bullet}NEt_3][AlCl_4]$ in CD_2Cl_2, showed a major peak at 6.0 ppm. This peak was assigned to the borylated arenium cation $[3\text{-}(Cl_2B{\bullet}NEt_3)\text{-}N\text{-TIPS-pyrrole}]^+$ (a similar chemical shift has been reported for the neutral analogue $(\eta^1\text{-}C_5Me_5)BCl_2(NMe_3)$ at 5.1 ppm).[20] The ^1H NMR spectrum showed a peak at 5.09 ppm attributable to the methylene group and two peaks at 7.46 and 8.92 ppm consistent with the vinylic protons. The borylated arenium cation slowly converted to form predominantly $3\text{-}(Cl_2B)\text{-}N$-TIPS-pyrrole and $[Et_3NH][AlCl_4]$ along with protonated *N*-TIPS-pyrrole as minor product.



Eq.9

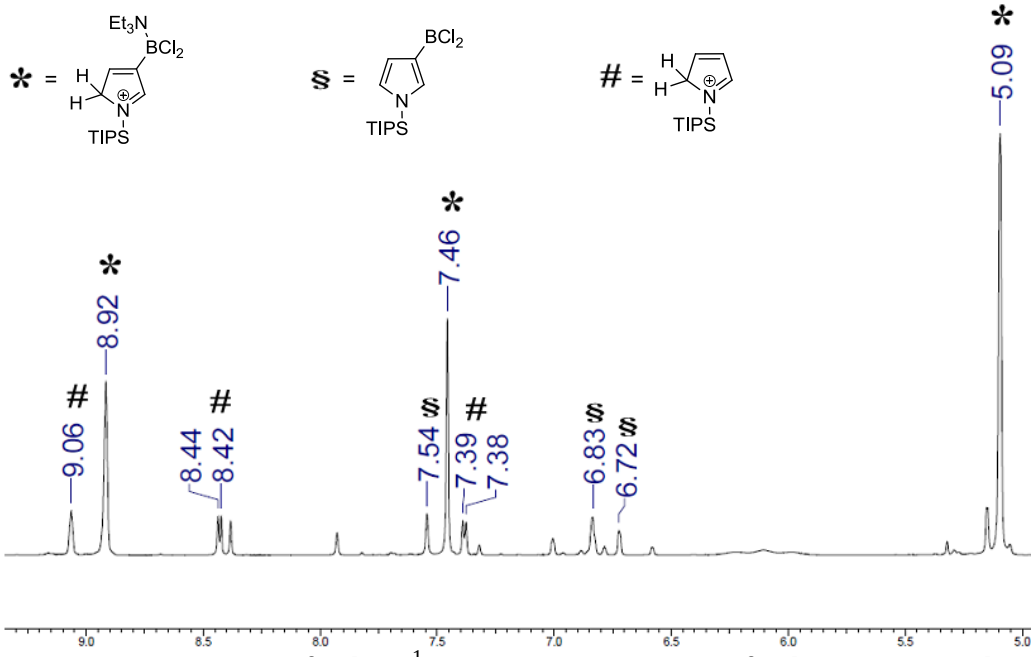


Figure 4.13 Part of the ^{1}H NMR spectrum of the reaction between $[Cl_2B(NEt_3)][AlCl_4]$ and *N*-TIPS-pyrrole in CD_2Cl_2 after 20 minutes.

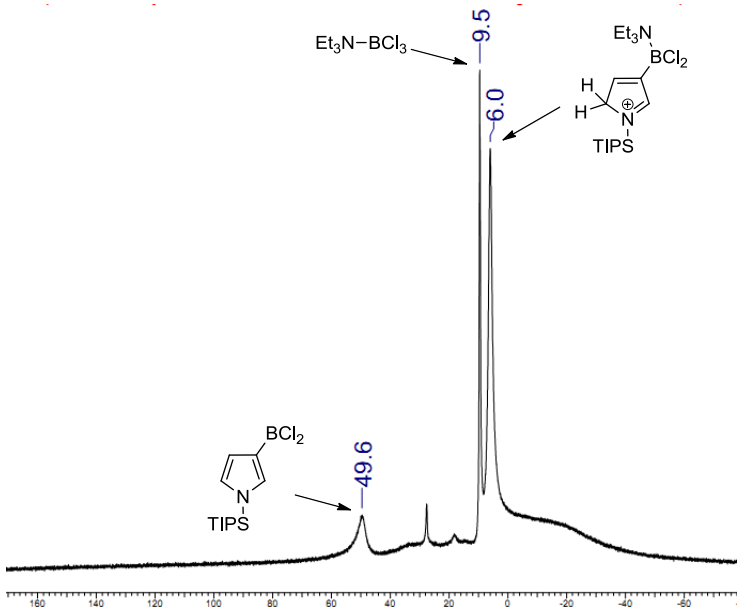
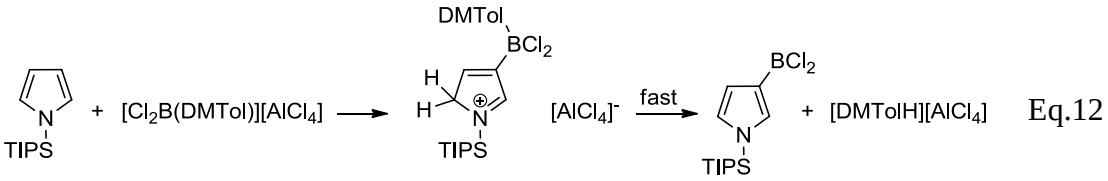


Figure 4.24 ^{11}B NMR spectrum of the reaction between $[Cl_2B(NEt_3)][AlCl_4]$ and *N*-TIPS-pyrrole in CD_2Cl_2 after 20 minutes.

In contrast to the borenium cation $[Cl_2B{\bullet}NEt_3][AlCl_4]$, $[Cl_2B{\bullet}$2,6-lutidine$][AlCl_4]$ rapidly borylated *N*-TIPS-pyrrole at 20 °C (< 30 minutes, by ^{1}H and ^{11}B NMR spectroscopy) without any borylated arenium cation intermediate observed. The disparity is ascribed to rapid dissociation of 2,6-lutidine from the borylated arenium

cation intermediate due to the *ortho* methyl substituents on the pyridine moiety which generated greater steric crowding at the four coordinate boron centre and consequently a rapid dissociation of the 2,6-lutidine. The presence of free 2,6-lutidine will then enable rapid deprotonation.

Analogous to the reaction of $[Cl_2B{\bullet}NEt_3][AlCl_4]$ with *N*-TIPS-pyrrole the intermediate borylated arenium cation was also observed in the reaction of stoichiometric BCl_3, Me_2NTol and $AlCl_3$ with *N*-TIPS-pyrrole, albeit as a minor initial product due to its rapid conversion to 3-(Cl_2B)-*N*-TIPS-pyrrole (Figure 4.15). The more rapid formation of the product of electrophilic aromatic substitution with DMTol compared to Et_3N was due to the more facile dissociation of the less basic DMTol in the borylated arenium intermediated.



Eq.12

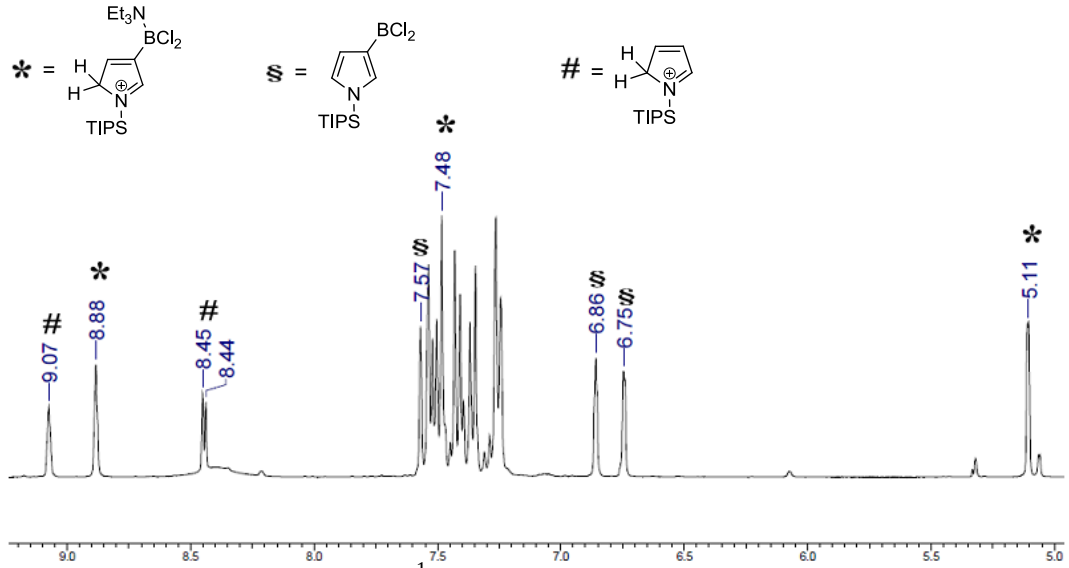
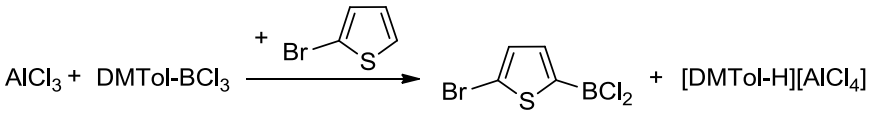


Figure 4.15 Part of the ^1H NMR spectrum of the reaction between $[Cl_2B(DMTol)][AlCl_4]$ and *N*-TIPS-pyrrole in CD_2Cl_2 after 90 minutes.

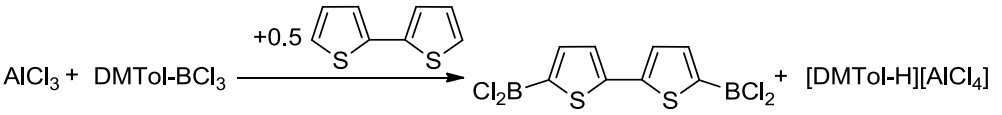
Subsequent arene borylation studies with the amine ligated dichloroborenium cation were accomplished using DMTol as amine, since this poorly basic amine is

expected to give a more reactive borylating species (in analogy to the catecholborenium cation) than Et_3N and 2,6-lutidine.

In contrast to the DMTol ligated catecholborenium cation, which was only able to borylate activated thiophenes, the equimolar combination of BCl_3, DMTol and $AlCl_3$ enabled the borylation of deactivated 2-bromothiophene giving exclusively the product of borylation at the 5 position (Eq. 11). Furthermore, the diborylation of 2,2'-bithiophene was also achieved (Eq. 12).

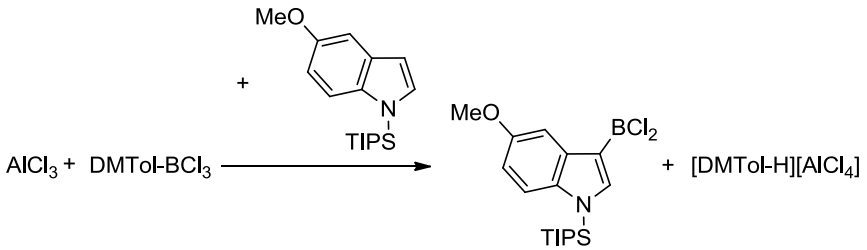


Eq.11



Eq.12

It is noteworthy that the borylating mixture of equimolar BCl_3, DMT and $AlCl_3$ reacted with 5-methoxy-*N*-methylindole to yield 3-Cl_2B-5-methoxy-*N*-methylindole without significant ether cleavage (by ^{11}B NMR spectroscopy). The compatibility of the methoxy group toward this strong boron Lewis acid is remarkable, and it is presumably due to the more rapid reaction of the boron Lewis acid at the nucleophilic C3 position of indole.

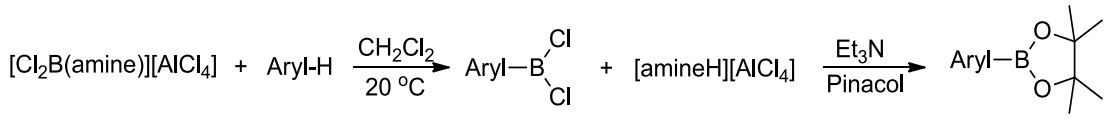


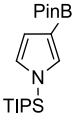
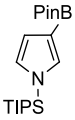
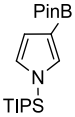
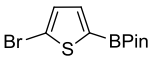
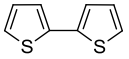
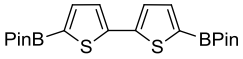
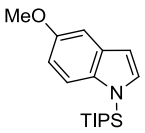
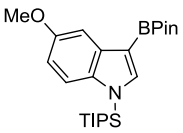
Eq.13

In order to facilitate the isolation of borylated products, dichloroboryl-heteroarenes were converted *in situ* to more stable pinacolboryl-heteroarenes. The esterification was accomplished following the procedure previously used for the transesterification of catecholboryl-heteroarenes. The esterification reaction

proceeded smoothly to give the desired product in good yield (Table 4.2). A full substrate scope study was subsequently performed by Dr Viktor Bagutski, Dr Sophia A. Solomon and Dr Dolores Caras-Quintero.

Table 4.4 One-pot, direct arene borylation by the equimolar mixture of Cl_3B•amine and $AlCl_3$.[a]



Entry	ArylH	Amine	Product	Yield[b] (%)	Time[c] (h)
1		Et_3N		71	18
2		2,6-lutidine		82	0.5
3		DMTol		69	3
4		DMTol		49	24
5		DMTol		81	24
6		DMTol		84	1.5

[a] For exact stoichiometries see experimental section. [b] Isolated yield. [c] Time before the addition of Et_3N and pinacol.

4.4 Conclusions

The reaction of the neutral adduct X_3B•amine with AlX_3 results in halide abstraction yielding mainly dihaloborenium salts $[X_2B(amine)][AlX_4]$. These borenium salts are in equilibrium with neutral species and possibly boronium salts in solution. Equilibrium positions are dependent on amine basicity and steric bulk. In contrast to the reaction of halide abstraction from X_3B•amine by AlX_3, which mainly

leads to formation of borenium cations, $Cl_3B{\bullet}PPh_3$ reacts with $AlCl_3$ to yield the tetracoordinate boronium salt $[Cl_2B(PPh_3)_2][Al_2Cl_7]$ and BCl_3. The addition of *N*-TIPS-pyrrole to the equimolar mixture of $Cl_3B{\bullet}$amine and $AlCl_3$ resulted in the regioselective borylation of the aromatic ring at the C3 position. The highly electrophilic mixture of $Cl_3B{\bullet}$DMTol and $AlCl_3$ was able to borylate deactivated thiophenes such as 2-bromothiophene whilst still being compatible with the methoxy group in 5-methoxy-*N*-TIPS-indole. Attempts to synthesise a tricoordinate boron dication were unsuccessful but in one of these attempts the first tricationic boroxine $[(Py)_4B_3O_3]^{3+}$ was isolated by serendipity and crystallographically characterised.

Experimental section

General methods: All manipulations of air and moisture sensitive species were performed under an atmosphere of argon or nitrogen using standard Schlenk and glovebox techniques. Glassware was dried in a hot oven overnight and heated before use. Hexane, *ortho* -dichlorobenzene, d_5-bromobenzene, d_1-chloroform, d_2-dichloromethane, pyridine, 2,6-lutidine, Et_3N and DMTol were dried over calcium hydride and distilled under vacuum. Pentane and dichloromethane were dried by passing through an alumina drying column incorporated into a MBraun SPS800 solvent purification system. All solvents were degassed and stored over molecular sieves (3Å) under inert atmosphere or in the glovebox. *N*-TIPS-pyrrole and 5-methoxy-*N*-TIPS-indole were prepared according to the literature procedures.[21,22] 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 ^{31}P; 62 MHz, ^{19}F 376.5 MHz, ^{27}Al 104 MHz). ^{1}H NMR chemical shifts are reported in ppm relative to protio impurities in the deuterated solvents and ^{13}C NMR using the solvent resonances unless otherwise stated. ^{11}B NMR spectra were referenced to external BF_3:Et_2O, ^{31}P to H_3PO_4, and ^{27}Al to $Al(NO_3)_2$ in D_2O ($Al(D_2O)_6^{3+}$). Resonances for the carbon directly bonded to boron are not observed in the $^{13}C\{^{1}H\}$ NMR spectra. Elemental analysis of air sensitive compounds were performed by London Metropolitan University service. BCl_3 purchased as a 1M solution in CH_2Cl_2 or heptanes or hexane was found to be of variable molarity. Therefore, BCl_3 molarity was approximately quantified by titration with PPh_3 (using ^{11}B and $^{31}P\{^{1}H\}$ NMR spectroscopy) prior to use.

Synthesis of Cl_3B•2,6-lutidine:

In an oven dried Schlenk tube, under inert atmosphere, 2,6-lutidine (0.34 ml, 3.0 mmol) was dissolved in anhydrous pentane (5 ml). The solution was cooled to 0 °C. Then, BCl_3 (0.8 M in hexane, 4 ml, 3.2 mmol) was added dropwise and a white solid formed. The heterogeneous reaction mixture was warmed to room temperature and vigorously stirred for 1 hour. Then, the solution was removed by filter cannula and the solid was washed with anhydrous pentane (2x5 ml). The colourless solid was dried under vacuum to yield Cl_3B•2,6-lutidine (567 mg, 84%).

Elemental Analysis: Expected for $C_7H_9BCl_3N$; C = 37.48, H = 4.04, N = 6.24. Found C = 37.39, H = 4.16, N = 6.07.

^{1}H NMR ($CDCl_3$): δ 7.87 (t, *J*=7.7 Hz, 1 H), 7.37 (d, *J*=7.8 Hz, 2 H), 3.16 (br. s, 6 H).

^{11}B NMR ($CDCl_3$): δ 7.9.

Synthesis [Cl_2B(2,6-lutidine)][$AlCl_4$]:

a) An oven dried Schlenk tube, under inert atmosphere, was charged with a solution of BCl_3 (0.8 M in CH_2Cl_2, 3 ml, 2.4 mmol). Then, the solution was cooled at 0 °C and 2,6-lutidine (0.28 ml, 2.4 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 0.5 hours. Then, the reaction mixture was transferred over 5 minutes via cannula under a positive pressure of argon to an oven dried Schlenk tube charged with $AlCl_3$ (320 mg, 2.4 mmol). The former Schlenk tube was washed with anhydrous CH_2Cl_2 (2x2 ml) and the washings were transferred to the Schlenk tube containing the reaction mixture. After stirring the reaction mixture for 2 hours the volume was reduced to ~4 ml. Then the reaction mixture was layered with anhydrous pentane and put in a freezer at -20 °C.

Colourless crystals were formed after diffusion was complete. The solution was removed by cannula and the crystals were washed with pentane (1 ml). The crystals were dried under vacuum yielding [Cl_2B(2,6-lutidine)][$AlCl_4$] (718 mg, 84 %) as pale yellow solid.

Elemental Analysis for $C_7H_9AlBCl_6N$: Calculated C = 23.51, H = 2.54, N = 3.86; Found C = 23.42, H = 2.64, N = 3.86.

^{1}H NMR (CH_2Cl_2/CD_2Cl_2) δ: 8.50 (t, *J* = 8.1 Hz, 1 H), 7.88 (d, *J* = 7.8 Hz, 2 H), 2.93 (s, 6 H).

$^{13}C\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2) δ: 153.0, 149.0, 127.8, 22.5.

^{11}B NMR (CH_2Cl_2/CD_2Cl_2) δ: 46.9.

b) In an oven dried Schlenk tube fitted with a J. Young's tap 2,6-lutidine (58 µl, 0.50 mmol) was dissolved in *ortho*-dichlorobenzene (1 ml) and BCl_3 (1.0 M in heptane, 0.5 ml, 0.50 mmol) was slowly added. Then to this mixture $AlCl_3$ (67 mg, 0.50 mmol) was added. The reaction mixture was heated at 90 ºC for 10 min. On slow cooling single crystals suitable for X-ray diffraction studies were grown.

Synthesis of [Cl_2B(Py)][$AlCl_4$]:

In an oven dried Schlenk tube fitted with a J. Young's tap, under inert atmosphere, pyridine (32 µl, 0.4 mmol) was dissolved in anhydrous CH_2Cl_2 (3 ml). The solution was cooled to 0 °C and BCl_3 (0.8 M in dichloromethane, 0.5 ml, 0.4 mmol) was added dropwise. Then the reaction mixture was warmed to room temperature. After stirring the reaction mixture for 1 hour $AlCl_3$ (53 mg, 0.4 mmol) 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 for $C_5H_5AlBCl_6N$: Calculated C = 18.22, H = 1.53, N = 4.25. Found C = 18.25, H = 1.58, N = 4.09.

The NMR of the isolated crystals were:

^{1}H NMR (CD_2Cl_2): δ 8.10 (t, *J* = 7.2 Hz, 2H), 8.63 (tt, *J* = 7.7, 1.5 Hz, 1 H), 9.34 (d, *J* = 5.8 Hz, 2 H).

$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 128.2, 146.0, 149.6.

^{11}B NMR (CD_2Cl_2): δ 25.7.

^{27}Al NMR (CD_2Cl_2): δ 103.6.

Synthesis of $Cl_3B•NEt_3$:

In an oven dried Schlenk tube, under inert atmosphere, Et_3N (1 ml, 7.2 mmol) was dissolved in dry pentane (5 ml). To the solution cooled at 0 °C, a solution of BCl_3 (0.8M in heptanes, 9 ml, 7.2 mmol) was added dropwise to form a white solid, and then the reaction mixture was warmed to room temperature. After stirring for 1 hour the solution was removed by filter cannula and the solid washed with dry pentane (2 x 20 ml). The white solid was dried under vacuum to give the desired product (1.46 g, 93%)..

^{1}H NMR (CD_2Cl_2): δ 3.19 - 3.43 (m, 6 H), 1.36 (t, *J* = 7.4 Hz, 9 H).

$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 53.0, 10.6.

^{11}B NMR (CD_2Cl_2): δ 9.5.

Synthesis of $[Cl_2B(NEt_3)][AlCl_4]$:

In an oven dried J. Young's NMR tube, under inert atmosphere, $Cl_3B•NEt_3$ (100 mg, 4.6 mmol) was dissolved in CD_2Cl_2 (0.7 ml) and $AlCl_3$ (61 mg, 4.6 mmol) was

added. The reaction mixture was shaken until $AlCl_3$ dissolved and NMR spectra were recorded. Analytically pure solid was not obtainable frustrating elemental analysis.

^{1}H NMR (CD_2Cl_2): δ 3.62 (q, *J* = 7.2 Hz, 6H), 1.41 (t, *J* = 7.4, 9 H).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 54.0, 9.9.

^{11}B NMR (CD_2Cl_2): δ 42.3.

^{27}Al NMR (CD_2Cl_2): δ 103.8.

Synthesis of Cl_3B•DMTol:

In an oven dried Schlenk tube, under inert atmosphere, DMTol (3 ml, 20.8 mmol) was dissolved in dry pentane (15 ml). To the solution cooled at 0 °C, a solution of BCl_3 (1M in heptanes, 16 ml, 16 mmol) was added dropwise to form a white solid, and then the reaction mixture was warmed to room temperature. After stirring for 1 hour the solution was removed by filter cannula and the solid washed with dry pentane (2 x 50 ml). The white solid was dried under vacuum to give the desired product (3.90 g, 97%).

Elemental Analysis for $C_9H_{13}BCl_3N$: Calculated C = 42.83, H = 5.19, N = 4.55. Found C = 41.95, H = 5.02, N = 4.41.

^{1}H NMR ($CDCl_3$): δ 7.52 (2 H, d, *J* = 8.8 Hz), 7.23 (2 H, d, *J* = 8.6 Hz), 3.50 (6 H, q), 2.38 (3H, s).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.5, 138.6 128.9, 123.5, 50.1, 20.7.

^{11}B NMR ($CDCl_3$): δ 10.4.

Equimolar reaction between $AlCl_3$ and Cl_3B•DMTol:

In an oven dried J. Young's NMR tube, under inert atmosphere, Cl_3B•DMTol (76

mg, 0.30 mmol) was dissolved in CD_2Cl_2 (0.7 ml) and $AlCl_3$ (40 mg, 0.30 mmol) was added. The reaction mixture was shaken until $AlCl_3$ dissolved and NMR spectra were recorded.

^{11}B NMR (CD_2Cl_2): δ 45.9, 24.5.

^{27}Al NMR (CD_2Cl_2): δ 108.2, 103.1.

Equimolar reaction between $Cl_3B{\bullet}PPh_3$ and $AlCl_3$:

In an oven dried J. Young's NMR tube, under inert atmosphere, $Cl_3B{\bullet}PPh_3$ (50 mg, 0.13 mmol) was dissolved in CD_2Cl_2 (0.7 ml) and $AlCl_3$ (18 mg, 0.13 mmol) was added. The reaction mixture was shaken until $AlCl_3$ dissolved and NMR spectra were recorded.

^{1}H NMR (CD_2Cl_2): δ 7.60 - 7.69 (m, 3 H), 7.46 - 7.55 (m, 6 H), 7.36 - 7.46 (m, 6 H).

^{11}B NMR (CD_2Cl_2): δ 46.6 (s), -0.3 (t, *J* = 135 Hz).

^{31}P NMR (CD_2Cl_2): δ -1.5 (q, *J* = 135 Hz).

^{27}Al NMR (C_6D_5Br): δ 103.3.

Reaction between BBr_3, Lutidine and $AlBr_3$ in 1,2-dichloroethane:

In a J. Young's NMR tube containing a sealed capillary filled with $(CD_3)_2SO$, BBr_3 (1.0 M in hexanes, 0.1 ml, 0.10 mmol) was slowly added to a solution of 2,6-lutidine (11.5 μl, 0.10 mmol) in 1,2-dichloroethane (0.8 ml). Then $AlBr_3$ (27 mg, 0.10 mmol) was added and shaken until all $AlBr_3$ dissolved at which point the NMR spectra were recorded.

^{11}B NMR (1,2-dichloroethane): δ 45.9 with a broad shoulder downfield.

^{27}Al NMR (1,2-dichloroethane): δ 89.5.

To the reaction mixture 2,6-lutidine (11.5 μl, 0.10 mmol) was added and NMR

spectra were recorded.

^{11}B NMR (1,2-dichloroethane): δ 7.4, 6.8, 2.9, 1.7.

^{27}Al NMR (1,2-dichloroethane): δ 103.1, 99.4. 94.4, 88.0, 80.2.

Synthesis of Br_3B•pyridine:

In an oven dried Schlenk tube, under inert atmosphere, pyridine (0.24 ml, 3.0 mmol) was dissolved in anhydrous hexane (5 ml). To the solution, which was cooled to 0 °C, BBr_3 (1 M in heptanes, 3.2 ml, 3.2 mmol) was added dropwise to form a colourless solid, and the reaction mixture was then warmed to room temperature. After stirring for 1 hour at room temperature the solution was removed by filter cannula and the solid washed with anhydrous hexane (5 ml). The colourless solid was dried under vacuum to yield Br_3B•pyridine (0.96 g, 98%).

NMR spectra were recorded in bromobenzene-d_5 using cyclohexane as internal standard. Cyclohexane was referenced at 1.37 ppm in ^{1}H NMR and at 26.99 ppm in ^{13}C NMR.

^{1}H NMR (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{^{1}H} NMR (C_6D_5Br): δ 125.5 (q, J = 2.8 Hz), 143.2, 145.4 (q, J = 1.8 Hz).

^{11}B NMR (C_6D_5Br): δ -7.0.

Synthesis of Br_3Al•pyridine:

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, the NMR tube was shaken for 5 minutes and NMR spectra were recorded.

^{27}Al NMR (C_6D_5Br): δ 101.0.

Synthesis of [$Br_2B(Py)$][$AlBr_4$]:

In an oven dried Schlenk tube, under inert atmosphere, pyridine (0.24 ml, 3.0 mmol) 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) was added dropwise to form a white solid, and the reaction mixture was then warmed to room temperature. After stirring for 1 hour at room temperature $AlBr_3$ (800 mg, 3.0 mmol), dissolved in *ortho*-dichlorobenzene (8 ml), was added via cannula. The reaction mixture was stirred for 2 hours, layered with anhydrous pentane and placed in a fridge at 4 °C. Slow pentane diffusion yielded colourless crystals suitable for X-ray analysis (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.

In a J. Young NMR tube (Py)BBr_3 (50 mg, 0.15 mmol) was dissolved in bromobenzene-d_5 (0.7 ml). To this solution $AlBr_3$ (40 mg, 0.15 mmol) and cyclohexane (5 µl) were added. After 14 hours NMR spectra were recorded.

Cyclohexane referenced at 1.37 ppm in ^{1}H NMR and at 26.99 ppm in ^{13}C NMR.

^{1}H NMR (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{^{1}H} NMR (C_6D_5Br): δ 126.9, 146.0, 148.0 (br).

^{11}B NMR (C_6D_5Br): δ 18.9.

^{27}Al NMR (C_6D_5Br): δ 85.8.

Reactivity of $[Br_2B(Py)][AlBr_4]$ towards additional pyridine at room temperature:

In an oven dried J. Young NMR tube, under inert atmosphere, pyridine (16 µl, 0.2 mmol) was dissolved in anhydrous *ortho*-dichlorobenzene (0.6 ml). To the solution BBr_3 (1 M in heptanes, 0.2 ml, 0.2 mmol) and after 30 minutes $AlBr_3$ (53 mg, 0.2 mmol) were added. After 1 hour pyridine (16 µl, 0.2 mmol) was added and NMR spectra were recorded. ^{11}B and ^{27}Al NMR spectra were consistent with the formation of the two neutral adduct Br_3B•pyridine and Br_3Al•pyridine with ca. 15% of boronium $[Br_2B(Py)_2][AlBr_4]$.

^{11}B NMR (*ortho*-dichlorobenzene): δ 2.1, -8.0.

^{27}Al NMR (*ortho*-dichlorobenzene): δ 100, 80.7.

Synthesis of $[Br_2B(Py)_2][AlBr_4]$:

In an oven dried Schlenk tube fitted with a J. Young's tap, under inert atmosphere, pyridine (72 µl, 0.89 mmol) was added to a solution of $[(Py)BBr_2][AlBr_4]$ (531 mg, 0.89 mmol) 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 suitable for X-ray analysis (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 referenced at 1.37 ppm in ^{1}H NMR

^{1}H NMR (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 (C_6D_5Br): δ 3.2.

^{27}Al NMR (C_6D_5Br): δ 81.7.

Reaction of $[Br_2B(Py)_2][AlBr_4]$ with 2 equivalents of $AlBr_3$:

In an oven dried J. Young's NMR tube, under inert atmosphere and containing a sealed capillary filled with $(CD_3)_2SO$, $[Br_2B(Py)_2][AlBr_4]$ (206 mg, 0.30 mmol) was dissolved in anhydrous *ortho*-dichlorobenzene (2 ml) and $AlBr_3$ (163 mg, 0.61 mmol) was added. The mixture was heated at 150 °C and the mixture was periodically monitored by NMR.

Synthesis of $[(Py)_4B_3O_3][AlBr_4]_2[Al_2Br_7]$:

In an oven dried Schlenk tube fitted with a J. Young's tap, under inert atmosphere, $[Br_2B(Py)][AlBr_4]$ (500 mg, 0.84 mmol) was suspended/partially dissolved in anhydrous *ortho*-dichlorobenzene (3 ml) and $AlBr_3$ (224 mg, 0.84 mmol) and pyridine (68 µl, 0.84 mmol) were added. Then the reaction mixture was heated to 150 °C. After 21 hours at 150 °C the reaction mixture was slowly cooled to 60 °C at which temperature colourless crystals suitable for X-ray analysis formed. ^{11}B NMR spectra of the solution were consistent with the boronium cation $[(py)_2BBr_2][AlBr_4]$ as the only boron containing species remaining in solution.

NMR of the solution:

^{11}B NMR (*ortho*-dichlorobenzene): δ 1.9.

Elemental Analysis of crystalline material: 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.

Attempt to synthesis $[(Py)_4B_3O_3][AlBr_4]_2[Al_2Br_7]$ by addition of 1 equivalent of H_2O:

In an oven dried J. Young's NMR tube, under inert atmosphere and containing a sealed capillary filled with $(CD_3)_2SO$, $[Br_2B(Py)_2][AlBr_4]$ (200 mg, 0.30 mmol) was dissolved in anhydrous *ortho*-dichlorobenzene (2 ml). H_2O (5 µl, 0.28 mmol) followed by $AlBr_3$ (10 mg, 0.37 mmol) were added. Then the mixture was heated at 150 °C and formed an immiscible brown oil.

Reaction of BCl_3 with *N*-methylindole at 4 °C:

An oven dried Schlenk tube, under inert atmosphere, was charged with BCl_3 (0.8 M in CH_2Cl_2, 1 ml, 0.8 mmol) and the solution was cooled at – 78 °C. Then, *N*-methylindole (112 µl, 0.8 mmol) was added and a colourless solid crashed out. The mixture was put in a fridge at 4 °C. After 10 days an aliquot was transferred in an oven dried J. Young's NMR tube containing a sealed capillary filled with $(CD_3)_2SO$ and NMR spectra were recorded.

Borylation of *N*-TIPS-pyrrole with the equimolar mixture of $Cl_3B{\bullet}NEt_3$ and $AlCl_3$:

In an oven dried J. Young's NMR tube, under inert atmosphere, $Cl_3B{\bullet}NEt_3$ (100 mg, 0.46 mmol) was dissolved in CD_2Cl_2 (0.7 ml) and $AlCl_3$ (61 mg, 0.46 mmol) was added. The reaction mixture was shaken until $AlCl_3$ dissolved and *N*-TIPS-pyrrole (102 mg, 0.46 mmol) was added and the NMR tube was rotated for 18 hours. Then, Et_3N (1 ml) followed by pinacol (119 mg, 1.0 mmol) were added to the reaction mixture. The mixture was shaken for 1 hour and volatiles were removed under vacuum. The product was purified by flash column chromatography (CH_2Cl_2 :

hexane 2 : 8 to CH_2Cl_2 : hexane 1 : 1) yielding a colourless solid (114 mg, 71 %).

^{1}H NMR and $^{13}C\{^1H\}$ NMR data are identical to that previously reported.[23]

^{1}H NMR ($CDCl_3$): δ 7.24 (t, *J* = 1.5 Hz, 1 H), 6.82 (dd, *J* = 2.0, 2.5 Hz, 1 H), 6.63 (dd, *J* = 1.3, 2.5 Hz, 1 H), 1.46 (sept, *J* = 7.6 Hz, 3 H), 1.33 (s, 12 H), 1.09 (d, *J* = 7.6 Hz, 18 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 133.7, 125.0, 115.6, 82.7, 24.8, 17.8, 11.6.

^{11}B NMR ($CDCl_3$): δ 30.1.

Borylation of *N*-TIPS-pyrrole with [Cl_2B(2,6-lutidine)][$AlCl_4$]:

In an oven dried J. Young's NMR tube, under inert atmosphere and containing a sealed capillary filled with $(CD_3)_2SO$, [Cl_2B(2,6-lutidine)][$AlCl_4$] (75mg, 0.21 mmol) was dissolved in CH_2Cl_2 (0.7 ml). Then *N*-TIPS-pyrrole (47 mg, 0.21 mmol) was added and the NMR tube was rotated for 0.5 hours. Then Et_3N (0.5 ml) followed by pinacol (52 mg, 0.44 mmol) were added to the reaction mixture. The mixture was shaken for 1 hour and volatiles were removed under vacuum. The product was purified by flash column chromatography (CH_2Cl_2 : hexane 2 : 8 to CH_2Cl_2 : hexane 1 : 1) yielding a colourless solid (62 mg, 82 %).

Borylation of *N*-TIPS-pyrrole with the equimolar mixture of Cl_3B•DMTol and $AlCl_3$:

In an oven dried J. Young's NMR tube, under inert atmosphere, Cl_3B•DMTol (100 mg, 0.40 mmol) was dissolved in CD_2Cl_2 (0.7 ml). $AlCl_3$ (53 mg, 0.40 mmol) was added and the reaction mixture was shaken until all $AlCl_3$ dissolved. Then *N*-TIPS-pyrrole (88 mg, 0.39 mmol) was added and the NMR tube was rotated for 0.5 hours. Then Et_3N (1 ml) followed by pinacol (97 mg, 0.82 mmol) were added to the

reaction mixture. The mixture was shaken for 1 hour and volatiles were removed under vacuum. The product was purified by flash column chromatography (CH_2Cl_2 : hexane 2 : 8 to CH_2Cl_2 : hexane 1 : 1) yielding a colourless solid (94 mg, 69 %).

Borylation of 2-bromothiophene with the equimolar mixture of Cl_3B•DMTol and $AlCl_3$:

In an oven dried J. Young's NMR tube, under inert atmosphere, Cl_3B•DMTol (100 mg, 40 mmol) was dissolved in CH_2Cl_2 (0.7 ml). $AlCl_3$ (53 mg, 0.40 mmol) was added and the reaction mixture was shaken until $AlCl_3$ dissolved. Then 2-bromothiophene (35 µl, 0.36 mmol) was added. After 24 hours Et_3N (0.5 ml) followed by pinacol (98 mg, 0.83 mmol) were added to the reaction mixture. The resulting mixture was shaken for 1 hour and volatiles were removed under vacuum. The product was extracted with hexane and filtered over a plug of silica pre-treated with hexane : Et_3N 9 :1. Removal of volatiles yielded a yellow oil (51 mg, 49 %).

^1H NMR and $^{13}C\{^1H\}$ NMR data are identical to that previously reported.[24]

^1H NMR ($CDCl_3$): δ 7.38 (d, *J* = 3.5 Hz, 1 H), 7.11 (d, *J* = 3.5 Hz, 1 H), 1.34 (s, 12 H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.5, 131.3, 119.4, 84.3, 24.7.

^{11}B NMR ($CDCl_3$): δ 28.4.

Borylation of 2,2'-bithiophene with the equimolar mixture of Cl_3B•DMTol and $AlCl_3$:

In an oven dried J. Young's NMR tube, under inert atmosphere, DMTol (58 µl, 0.40 mmol) was dissolved in anhydrous CH_2Cl_2 (0.4 ml) and BCl_3 (1.0 M in CH_2Cl_2, 0.38 ml, 0.38 mmol). $AlCl_3$ (56 mg, 0.42 mmol) was added to the reaction mixture and

the mixture was shaken until $AlCl_3$ dissolved. Then 2,2'-bithiophene (21 mg, 0.13 mmol) was added. After 24 hours Et_3N (0.54 ml, 3.84 mmol) followed by pinacol (110 mg, 0.93 mmol) were added to the reaction mixture. The resulting mixture was shaken for 1 hour and volatiles were removed under vacuum. The product was extracted with hexane (3x10 ml) and volatiles were removed under vacuum. The solid was washed with methanol (3 × 2 ml) and dried under vacuum to give a yellow solid (44 mg, 83%).

^1H NMR and $^{13}C\{^1H\}$ NMR data are identical to that previously reported.[25]

^1H NMR ($CDCl_3$): δ 7.53 (d, *J* = 3.5 Hz, 2H), 7.30 (d, *J* = 3.5 Hz, 2H), 1.35 (s, 24H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.1, 138.3, 129.1, 84.5, 25.0.

^{11}B NMR ($CDCl_3$): δ 29.7.

Borylation of 5-methoxy-*N*-TIPS-indole with the equimolar mixture of Cl_3B•DMTol and $AlCl_3$:

In an oven dried J. Young's NMR tube, under inert atmosphere, Cl_3B•DMTol (50 mg, 0.20 mmol) was dissolved in CH_2Cl_2 (0.7 ml). $AlCl_3$ (27 mg, 0.20 mmol) was added and the reaction mixture was shaken until $AlCl_3$ dissolved. Then 5-methoxy-*N*-TIPS-indole (54 mg, 0.18 mmol) was added and the NMR tube was rotated for 1.5 hours. Then Et_3N (0.4 ml) followed by pinacol (49 mg, 0.41 mmol) were added to the reaction mixture. The mixture was shaken for 1 hour and volatiles were removed under vacuum. The product was extracted with hexane (2x15 ml). Removal of volatiles yielded a colourless solid (53 mg, 84 %)

^1H NMR ($CDCl_3$): δ 7.65 (s, 1 H), 7.57 (d, *J* = 2.8 Hz, 1 H), 7.38 (d, *J* = 9.2 Hz, 1 H), 6.80 (dd, *J* = 9.1, 2.8 Hz, 1 H), 3.89 (s, 3H) 1.71 (sept, *J* = 7.6 Hz, 3 H), 1.37 (s, 12 H), 1.14 (d, *J* = 7.6 Hz, 18H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 154.5, 141.9, 136.7, 135.9, 114.2, 110.9, 104.5, 82.6, 55.7, 25.0, 18.1, 12.7.

^{11}B NMR ($CDCl_3$): δ 30.6.

Crystallographic Details

Crystal Data for $[Cl_2B(2,6\text{-lutidine})][AlCl_4]$:

Molecular Formula	$C_7H_9Al_1B_1Cl_6N_1$
Molecular Mass	357.64
Crystal system	Monoclinic
Space group	P21/n
a/Å	7.345(5)
b/Å	13.689(5)
c/Å	14.699(5)
α/°	90.000(5)
β/°	99.057(5)
γ/°	90.000(5)
Volume/Å	1459.5(12)
Z	4
D_{calcd} g/cm^3	1.628
F(000)	712
T/K	100(2)
Absorption coefficient (μ)/mm^{-1}	1.208
Crystal size/mm	0.20 x 0.11 x 0.10
Reflections measured	2576
Reflections collected	1937
Goodness-of-fit on F^2	0.897
Final R1 [I > 2σ(I)]	0.0288
(all data)	0.0433

Crystal Data for $[Cl_2B(Py)][AlCl_4]$:

Molecular Formula	$C_5H_5Al_1B_1Cl_6N_1$
Molecular Mass	329.59
Crystal system	Trigonal
Space group	P3c1
a/Å	12.708(5)
b/Å	12.708(5)
c/Å	13.720(5)
α/°	90.000(5)
β/°	90.000(5)
γ/°	120.000(5)
Volume/Å	1918.8(13)
Z	6
D_{calcd} g/cm^3	1.711
F(000)	972
T/K	100(2)
Absorption coefficient (μ)/mm^{-1}	1.371
Crystal size/mm	0.4 x 0.1 x 0.1
Reflections measured	2621
Reflections collected	2187
Goodness-of-fit on F^2	0.971
Final R1 [I > 2σ(I)]	0.0327
(all data)	0.0453

Crystal Data for $[Br_2B(Py)][AlBr_4]$:

Molecular Formula	$C_5H_5Al_1B_1Br_6N_1$
Molecular Mass	596.29
Crystal system	Monoclinic
Space group	Pc
a/Å	7.6227(3)
b/Å	13.8546(6)
c/Å	13.6784(5)
α/°	90.0
β/°	95.281(3)
γ/°	90.0
Volume/Å	1438.43(10)
Z	4
D_{calcd} g/cm^3	2.754
F(000)	1080
T/K	100(2)
Absorption coefficient (μ)/mm^{-1}	16.772
Crystal size/mm	0.7 x 0.1 x 0.1
Reflections measured	3680
Reflections collected	3169
Goodness-of-fit on F^2	1.087
Final R1 [I > 2σ(I)]	0.0474
(all data)	0.0603

Crystal Data for $[(Py)_4B_3O_3][AlBr_4]_2[Al_2Br_7]$:

Molecular Formula	$C_{40}H_{40}Al_8B_6Br_{30}N_8O_6$
Molecular Mass	3406.80
Crystal system	Triclinic
Space group	P-1
a/Å	10.3692(3)
b/Å	11.1756(3)
c/Å	41.7001(12)
α/°	83.535(2)
β/°	84.176(2)
γ/°	75.954(3)
Volume/Å	4644.2(2)
Z	2
D_{calcd} g/cm^3	2.436
F(000)	3136
T/K	100(2)
Absorption coefficient (μ)/mm^{-1}	13.036
Crystal size/mm	0.7 x 0.6 x0.3
Reflections measured	16359
Reflections collected	11913
Goodness-of-fit on F^2	1.105
Final R1 [I > 2σ(I)]	0.0670
(all data)	0.0972

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