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Review

Complexes of tris(pentafluorophenyl)boron with nitrogen-containing compounds: Synthesis, reactivity and metallocene activation

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Contents

Abstract

The strong Lewis acid tris(pentafluorophenyl)boron, $B(C_6F_5)_3$, reacts with several nitrogen-containing Lewis bases (nitriles, amines, imines, pyridines, etc.) and also with non-basic substrates (such as pyrroles and indoles) producing in both cases the B─N coordination adduct. With particular substrates (some tertiary amines, the imine ^{t}Bu(Me)C=NBn, *N*-methyl-pyrrole and -indole,) the 1:1 borane/*N*-compound reaction produces zwitterions where a new B─C bond is generated. Some of the borane–*N*-compound adducts present Brønsted acidity and can be reacted with di-methyl group 4 complexes with generation of weakly associated ion pairs, which are active catalysts for the polymerization of olefins.

Keywords: Perfluoroarylboranes; Boron–nitrogen complexes; Lewis acid–Lewis base adducts; Metallocenes; Ion pairs

1. Introduction

The development of homogeneous transition metal complexes as catalysts for olefin polymerization, such as group 4 metallocenes and other group 4–10 organometallics, has triggered a parallel quest for more and more efficient activators, or cocatalysts [1]. The industrially most widely used cocatalyst is methylalumoxane (MAO). MAO, an ill-defined mixture of the partial hydrolysis of trimethylaluminum, is commercially available, generally as toluene solutions. This material requires special handling and storage conditions, being both pyrophoric and chemically unstable, and a large excess of it (100–10,000 eq per eq of transition metal) is often required in order to reach optimum catalyst activity. The search for alternative, more stable

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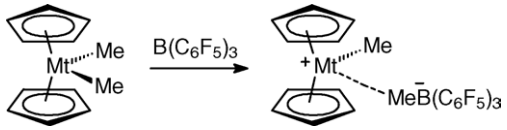


Scheme 1.

activators [2] generated a family of fluorinated aryl boron compounds, such as $B(C_6F_5)_3$, [3] or borate salts, e.g. $[Ph_3C][B(C_6F_5)_4]$ or $[PhNHMe_2][B(C_6F_5)_4]$. These Lewis or Brønsted acidic molecules are used as stoichiometric cocatalysts in olefin polymerization with a large number of alkylated organometallic complexes [4].

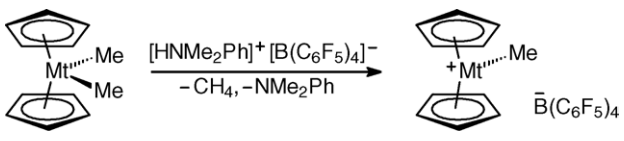
$B(C_6F_5)_3$ is among the strongest Lewis acids, [5] and in some instances it was found able to activate dialkylmetallocenes via a reversible dissociation of one alkyl ligand from the transition metal. The methylmetallocenium/methylborate ion pair formed in the case of the reaction with Cp_2MtMe_2 (Mt: Ti, Zr, Hf) is shown in Scheme 1 [6,7].

Due to the reversible nature of the above reaction, and the "tight ion-pair" obtained, $B(C_6F_5)_3$ is only seldom an efficient activator. $B(C_6F_5)_3$ is highly hygroscopic due to its high Lewis acidity and oxygen affinity, and, upon reaction with L_nMtMe_2, does not produce stable catalyst systems, possibly due to transfer of a C_6F_5 anion back to the transition metal center, with formation of neutral, inactive species $L_nMtCH_3(C_6F_5)$ and $CH_3B(C_6F_5)_2$ [8]. This decomposition pathway is obviously a problem when the catalyst/cocatalyst mixture cannot be prepared in situ in the presence of the monomer(s). A major improvement in activating performance is shown by the trihydrocarbylammonium perfluoroarylborates, which generates the alkylmetallocenium/borate catalyst systems by protonation of the Mt–CH_3 bond, with formation of the tertiary amine and methane. In this case, the perfluoroarylborates behave as weakly- or non-coordinating anions (Scheme 2) [9].

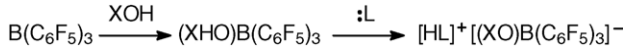
One potential drawback of ammonium perfluoroarylborates is the possible coordination of the tertiary amine to the metallocenium cation that could lead to catalyst deactivation.

In a similar way, but without the aforementioned downside, $[Ph_3C][B(C_6F_5)_4]$ generates the metal alkyl cation by abstracting a methyl group from the metal center, with formation of CH_3CPh_3 [10].

Despite the advantage of using a perfluoroborate salt as a stoichiometric activator, thus solving the major problem connected with the use of the MAO cocatalyst, there are some technical problems associated with the use of such borates, mainly the cost associated with the use of pentafluoroaryl groups: the tetrakis(perfluoroaryl)borates, being of



Scheme 2.



Scheme 3.

high molar mass and requiring an additional synthetic step compared to $B(C_6F_5)_3$, are more expensive on a molar base. In addition, the borate salts have limited solubility in the solvents used for olefin polymerization.

Besides use in the field of homogeneous polymerization catalysis, $B(C_6F_5)_3$ has also found several applications in organic chemistry as strong but selective Lewis acid. $B(C_6F_5)_3$, compared to other Lewis acids such as BF_3, $AlCl_3$ or $SnCl_4$, has the important advantage of being quite stable and air- and water-tolerant, and can be used to efficiently catalyze many organic transformations [11,17].

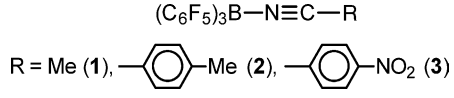
The Lewis acidity of $B(C_6F_5)_3$ has been used to convert it into a Brønsted acid, by complexation with water or alcohols (Scheme 3).

The water–$B(C_6F_5)_3$ system has been recently studied in detail by Norton and coworkers, [12] and Beringhelli and coworkers [13]. The acidity of boron-coordinated XOH has been demonstrated and applied to catalytic reactions in a number of instances, [11,14] but the borate $[(C_6F_5)_3BOR]^-$ (R=H, alkyl, aryl) is not expected to be a stable counterion for transition metal alkyl cations, due to the coordination ability of oxygen and irreversible transfer to the –OR group to the oxophylic Zr metal [15].

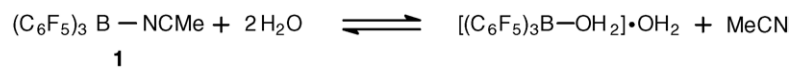
On the other side, the use of *N*-containing molecules to form complexes with $B(C_6F_5)_3$ has been the focus of some recent investigations, and provided a series of efficient and synthetically easily accessible activators for metallocene precatalysts. This review covers such recent developments.

2. Adducts with nitriles

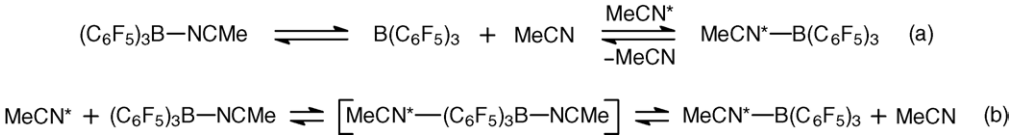
The acetonitrile–tris(pentafluorophenyl)borane complex, $(C_6F_5)_3B{\cdot}NCCH_3$ (**1**), was first synthesized by Erker and coworkers [5] together with two aromatic nitrilic derivatives **2** and **3**.



These complexes were easily obtained by adding at room temperature the nitrile in slight excess to the borane, both dissolved in pentane, and isolating the final compound by precipitation. The nitrile–$B(C_6F_5)_3$ adducts were analyzed with IR and X-ray diffraction analyses, focusing on the C≡N bond length which changes significantly on going from the free nitrile to the boron-coordinated nitrile. The C–N inter-atomic distance in the adduct is shorter than in the free nitrile, being, for instance, 1.124(3) Å in compound **1** versus 1.141(2) in acetonitrile. IR spectra gave additional support to this bond length modification, the IR $\nu_{C\equiv N}$ for the adducts are actually shifted to higher wavenumbers of about 95–99 cm^{-1} with respect to the free nitrile.



Scheme 4.

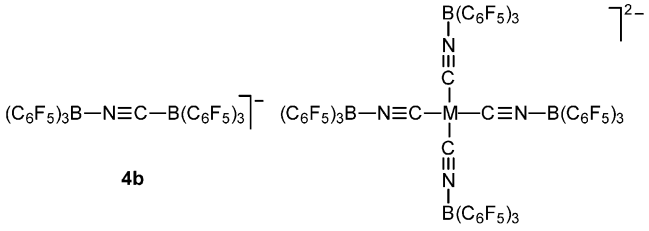


Scheme 5.

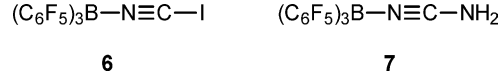
Although acetonitrile seems tightly coordinated to the borane, as indicated by the strong B–N bond (1.616(3) Å), Norton [12] and coworkers demonstrated that it can be easily displaced by water. The experiment was carried out by subsequent additions of H_2O to a solution of **1** in CD_3CN, the ligand exchange was monitored through ^{19}F NMR analysis at 300 K by observing the formation of $[(C_6F_5)_3B(OH_2)]\cdot H_2O$ versus **1** (Scheme 4).

The B–N bond lability in adduct **1** was also studied by dynamic ^1H NMR spectroscopy. Compound **1** can exchange acetonitrile with a S_N1 mechanism (equation a, Scheme 5), rather than an associative reaction involving a symmetric transition complex (equation b). This was deducted by observing the line broadening for the CH_3 signal in both complex and free acetonitrile, when an excess of MeCN or **1** is added. The kinetic constants of the dissociation process were calculated from ^1H NMR spectra registered in the range 280–330 K giving $\Delta H^{\ddagger} = 21.8(5)$ kcal mol^{-1} and $\Delta S^{\ddagger} = 23(2)$ eu.

In addition to adducts **1**–**3** deriving from organic nitriles, also some inorganic cyano-derivatives of $B(C_6F_5)_3$ are known. Anions **4b** [16] and **5** and **5′**, [16,17] for example, were obtained, respectively from KCN and $K_2[Ni(CN)_4]$ treated with $B(C_6F_5)_3$ at room temperature, and successively with Ph_3CCl to give the final salts $[Ph_3C]$ **4b** and $[Ph_3C]_2$**5**.



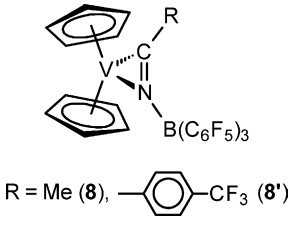
Complexes **6** and **7** are obtained in high yields simply combining bases ICN and $NCNH_2$, respectively, with the borane, at room temperature and in dichloromethane solution; they are stable compounds, in fact do not produce any visible decomposition after several days of exposition to air [18].



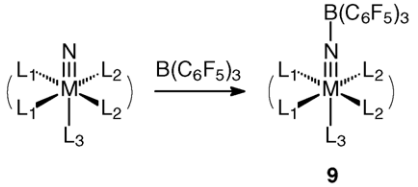
6 **7**

Adduct **7** failed to bond a second equivalent of $B(C_6F_5)_3$ via coordination at the aminic moiety of the cyanamide. All complexes **4b**–**7** were analyzed by X-ray diffraction.

$B(C_6F_5)_3$-activated nitriles in combination with dicyclopentadienyl vanadium yield to the formation of vanadaazirine complexes with generation of a η^2:C,N interaction to the vanadium center (complexes **8** and **8′**) [19]. The X-ray structure of these adducts evidences the presence of a cyclic VCN structure with two σ-type V–C and V–N bonds, and a significant change in the bond lengths of the nitrile moiety, in fact the C–N distance increases in the vanadaazirine complex with respect to the nitrile–borane adduct, while the N–B length is shorter in the metal complex than in the free B–N adduct (for the acetonitrile derivative: C–N = 1.236(3) Å in compound **8** versus 1.124(3) Å in adduct **1**, and N–B = 1.586(3) Å versus 1.616(3) Å in adduct **1**).



To conclude this section, we note another class of compounds, not including a cyano group. These compounds, pictured in Scheme 6, are transition-metal nitrido complexes containing a triple bond M≡N, where M can be Re, Mo, or Os, while $L_{1–3}$ can be phosphines, S_2CNR_2, tris(pyrazolyl)borate, halogen, etc. [20]. The nitrido group has the same electronic structure as the cyano group, being N involved in a triple bond with the metal, and having a free



Scheme 6.

nitrogen lone pair in an sp orbital, with basic character. The treatment of this adduct with $B(C_6F_5)_3$ produced in fact the nitridometal complex–Lewis acid adduct **9** in high yield.

The formation of the N–B dative bond caused a strengthening of the M≡N bond, as it happened in the case of the coordination of $B(C_6F_5)_3$ to nitriles, and the M≡N IR stretching frequencies are shifted to higher wavenumbers with respect to the nitrido-metal complex free of borane (in this case $\Delta\nu_{C\equiv N}$ ca. 30–40 cm^{-1}). According to Molecular Orbital Theory, the increased strength of the M–N bond in **9** is due to the σ-antibonding character of the nitrogen lone pair in the parent nitrido compound which, upon coordination of the Lewis acid, gains some N–B bonding character, and hence increases the M–N stretching frequency. The stability of the N–B bond was experimentally tested by adding different Lewis bases in excess to adducts **9**, and observing the reaction products through NMR. Tetrahydro-furan, triethylamine and triphenylphosphine were used as bases potentially able to displace the nitrido-metal complex from the coordination with $B(C_6F_5)_3$. As a result of 1 h stirring in dichloromethane solution of each adduct **9** with an excess of base, THF left unaltered all adducts **9**, whereas NEt_3 and PMe_3 gave different results depending on steric factors. In fact, the metal complexes with the bulkiest ligands had the borane still coordinated, whereas the other adducts had the borane totally or partially removed after the treatment, due to the formation of Et_3N– or Me_3P–$B(C_6F_5)_3$. However later investigations (see Section 3) revealed that direct reaction of NEt_3 with $B(C_6F_5)_3$ quickly evolves beyond the simple coordination product.

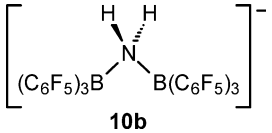
3. Reaction with amine- and aniline-like substrates

$B(C_6F_5)_3$ is expected to give stable adducts with the Lewis basic amines of type R_3N (with R = H, alkyl, or aryl). Compounds **10**, the coordination adduct of ammonia to the borane, is the simplest complex of this class and the first $B(C_6F_5)_3$ derivative to be reported [3a].

$H_3N{-}B(C_6F_5)_3$

10

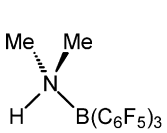
Another complex of $B(C_6F_5)_3$ with a simple aminic moiety is **10b**, a double coordination adduct to the NH_2^- group involving two borane molecules [21]. Anion **10b** was obtained as $[Na(OEt_2)_4]^+$ salt by reacting $NaNH_2$ with 2 equiv. of $B(C_6F_5)_3$ in a diethyl ether suspension, and was isolated in high yield from the reaction mixture as colorless crystals. The X-ray structure shows multiple intramolecular NH···F hydrogen bonds, which likely contribute to the remarkable stability of the anion; adduct **10b**, in fact, when treated with HCl, instead of producing the adducts **10** and Et_2O–$B(C_6F_5)_3$ as a consequence of the expected protolysis of one of the B–N bonds, afforded salt $[H(OEt_2)_4]$**10b**.



10b

An experimental procedure similar to the one used for synthesizing **10b** was applied to $LiNMe_2$, in order to get $[(C_6F_5)_3B{-}NMe_2{-}B(C_6F_5)_3]^-$, but in this case the reaction did not afford a clean product. The NMe_2–diborate complex could not be isolated even by deprotonation of adduct $Me_2HN{-}B(C_6F_5)_3$ (**11**) followed by excess $B(C_6F_5)_3$ [21].

While many adducts between secondary and tertiary amines are known, no adducts of $B(C_6F_5)_3$ with primary amines of type RH_2N have been reported so far. Five adducts of type $R_2HN{-}B(C_6F_5)_3$, **11**–**15**, where the coordination of the secondary basic amine to the electrophilic boron center causes the formation of a quaternarium ammonium salt, have been reported.



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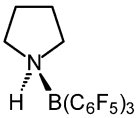

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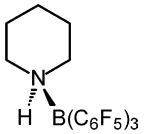

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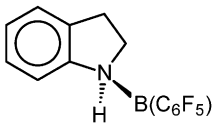

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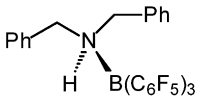
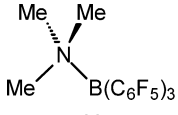


15

Compounds **12**, [22,23] **13** [22] and **14** [23] were studied in detail in both solution and solid state, where significant hydrogen bonding interactions of type N–H···F–C and C–H···F–C were observed. Complexes **12**, **14** and **15** [24] could not be deprotonated by 1 equiv. of NEt_3, indicating that borane coordination does not confer any Brønsted acidity to the quaternary nitrogen.

While with secondary amines (and very likely also with primary amines) the reaction of $B(C_6F_5)_3$ follows a predictable path giving the Lewis acid–base coordination adduct, the reaction takes an unexpected course in the case of tertiary amines. Except for trimethylamine, which in combination with $B(C_6F_5)_3$ produces the adduct $Me_3N{-}B(C_6F_5)_3$ (**16**), early reported by Massey and Park, [3a] with other tertiary amines the simple B–N coordination adduct is not the exclusive product.



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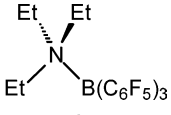
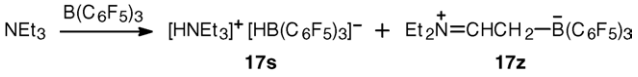


17

Massey and Park also described adduct **17**, obtained by mixing triethylamine and $B(C_6F_5)_3$ in pentane at room temperature [3b]. Triethylamine is actually known to give stable Lewis acid–Lewis base adducts; according to our experi-



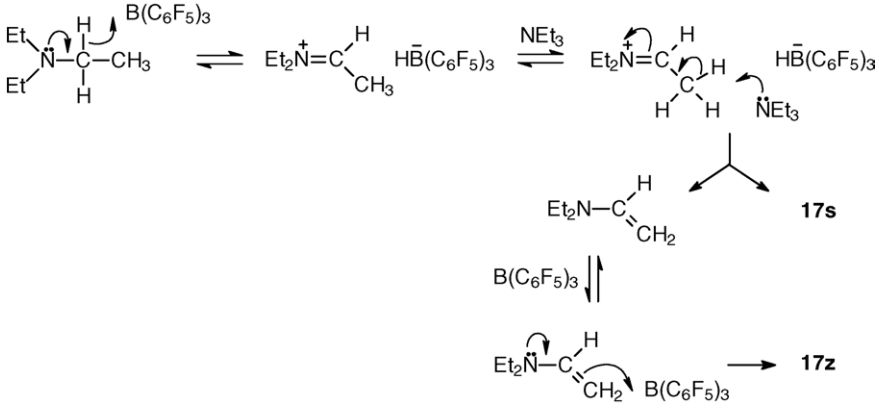
Scheme 7.

ence, however, when treated with 1 equiv. of $B(C_6F_5)_3$ in dichloromethane solution at room temperature, it does not give the expected B–N coordination adduct, but a mixture of salt $[HNEt_3]^+[HB(C_6F_5)_3]^-$ (**17s**) and zwitterion $Et_2N{=}CHCH_2{-}B(C_6F_5)_3$ (**17z**) is formed instead (Scheme 7) [25].

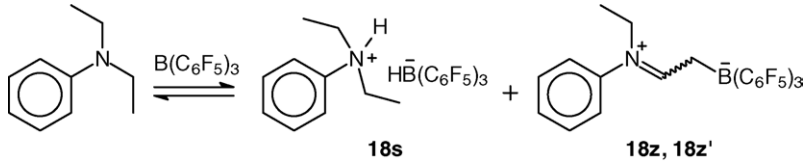
The reaction is quantitative, and yields compounds **17s** and **17z** in an equimolar ratio. The mechanism proposed for this reaction is illustrated in Scheme 8, and has been derived from a work [26] of the Basset group, which will be discussed next and which thoroughly describes the reaction between $B(C_6F_5)_3$ and two aniline derivatives. The unsaturation of the amine moiety in complex **17z** is due to the oxidative action of the electrophilic borane, which removes a hydride α to nitrogen, then the unreacted NEt_3 abstracts a β-proton from this intermediate to give the triethylammonium salt of the anion $[HB(C_6F_5)_3]^-$ (**17s**) and the enamine $Et_2N{-}CH{=}CH_2$, which is immediately trapped by the free borane to give zwitterion **17z**. Compounds **17s** and **17z** were identified and characterized from the reaction mixture by ^1H, ^{19}F, and ^{11}B NMR spectroscopy.

This rather complex mechanism is supported by many experimental evidences. The first reaction of this type to be studied in detail was the 1:1 reaction between Et_2NPh and $B(C_6F_5)_3$ in C_6D_6 solution [26]. The produced equilibrium was a mixture between the unreacted aniline and borane (40%), salt $[HNEt_2Ph]^+[HB(C_6F_5)_3]^-$ (**18s**) (30%), and zwitterion $PhEtN{=}CHCH_2{-}B(C_6F_5)_3$ (30%), which was present in the two stereoisomeric forms *E* (**18z**) and *Z* (**18z′**) in a 3:2 ratio (Scheme 9).

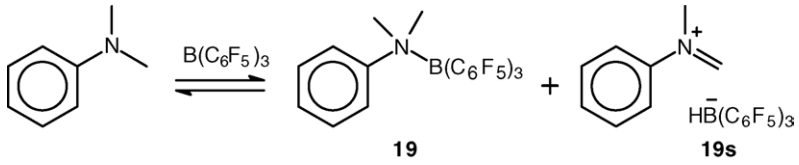
$B(C_6F_5)_3$ was already known to be able to remove hydride groups from organic substrates, [27] however, the evidence that the mechanism leading to zwitterions **17z** and **18z**, **z′** goes through the formation of the iminiums $[Et_2N{=}CHCH_2]^+$ and *E*,*Z*-$[PhEtN{=}CHCH_2]^+$ can be found in the reaction of $B(C_6F_5)_3$ with Me_2NPh, [26] whose iminium obviously cannot rearrange into the enamine. In this case in fact the reaction stops at the iminium salt, in the form of salt **19s** (Scheme 10). Together with the unreacted aniline and borane, also the coor-



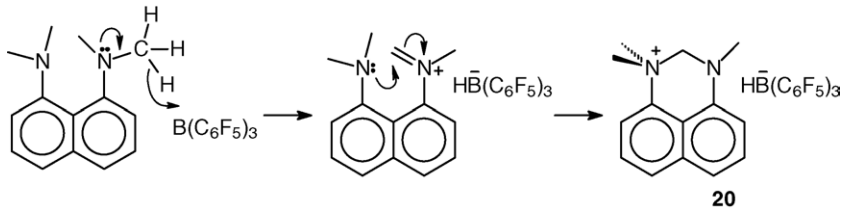
Scheme 8.



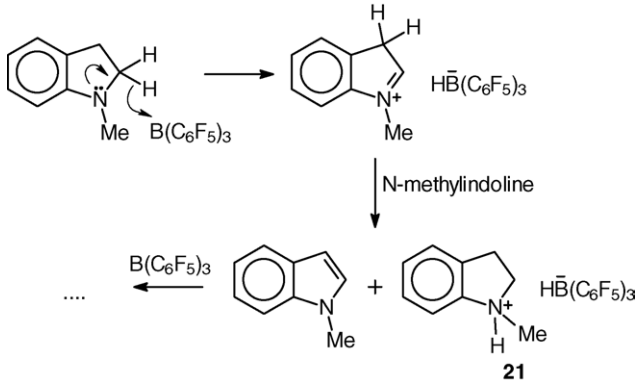
Scheme 9.



Scheme 10.



Scheme 11.



Scheme 12.

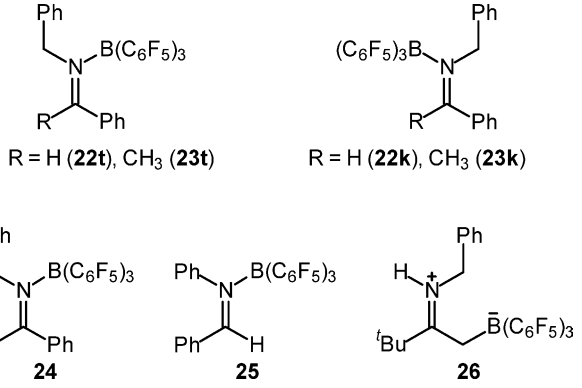
dination adduct $PhMe_2N{-}B(C_6F_5)_3$ (**19**) was detected in this equilibrium.

Two additional experiments of reaction involving $B(C_6F_5)_3$ and aniline derivatives further strengthened the hypothesis of formation of the iminium intermediate. The first evidence is the reaction with 1,8-bis(dimethylamino)naphthalene, commonly known as "proton sponge", which upon treatment with 1 equiv. of borane, yields compound **20** (Scheme 11) [25]. In this case the reactive iminium salt, formed after abstraction of the α-hydride by $B(C_6F_5)_3$, rearranges to the 1,1,3-trimethyl-2,3-dihydroperimidinium cation, where a methylene group is bridged between two nitrogen atoms. The reaction is quantitative and instantaneous in dichloromethane solution at room temperature.

The other evidence supporting the mechanism is the reaction between *N*-methylindoline and $B(C_6F_5)_3$, which among other products produces also *N*-methylindole as reaction intermediate, due to hydride abstraction and subsequent deprotonation (Scheme 12) [24]. The formation of the aromatic heterocycle was deduced through ^{1}H NMR by the detection of the unambiguous adduct between *N*-methylindole and $B(C_6F_5)_3$ (which will be discussed in Section 5), while the other product was identified as salt **21**.

4. Adducts with imines

Piers and coworkers synthesized the imine–$B(C_6F_5)_3$ adducts **22**–**26** [28].

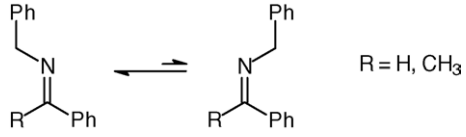


Asymmetric imines can exist in two isomers, and in standard conditions the most stable structure is the *E* isomer, where the most bulky groups are placed trans to the double bond N=C (Scheme 13). Both compounds **22** and **23** were obtained in two isomeric forms, which are the kinetic adduct (**-k**) and the thermodynamic adduct (**-t**), deriving, respectively from the *E* and *Z* isomers of the starting imine.

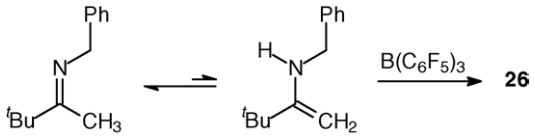
The adducts **22k** and **22t**, and **23k** and **23t** were isolated and fully characterized (NMR, IR, and X-ray) by varying the experimental conditions (reaction time, temperature, and imine/borane stoichiometry). The isomerization of the imine–$B(C_6F_5)_3$ adduct from the **-k** to the **-t** isomer goes through the $B(C_6F_5)_3$ dissociation and not through direct isomerization of the adduct.

Adducts **24** and **25**, deriving, respectively from imines $Ph_2C{=}NBn$ and $Ph(H)C{=}NPh$, were obtained in a single isomer being the first a symmetric imine, and presenting the second a big difference in terms of structure between the *E* and *Z* isomers.

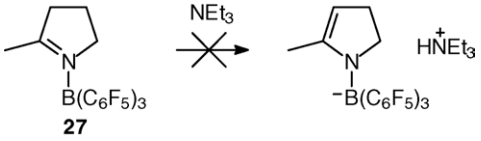
Reacting $B(C_6F_5)_3$ with imine ^{t}Bu(CH_3)C=NBn, zwitterion **26** was unexpectedly obtained, which is likely formed through the formation of enamine tautomer ^{t}Bu$(H_2C{=})$C–NBn and subsequent addition of the borane to the methylene group, which moves the equilibrium of Scheme 14 to the right. The formation of the expected B–N adduct presumably does not occur because of the strong steric



Scheme 13.



Scheme 14.



Scheme 15.

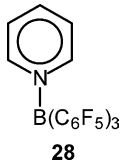
interactions that would be present between the bulky *tert*-butyl group and the benzyl or tris(pentafluorophenyl)borane groups in the final adduct in both possible *Z* and *E* isomers [28].

Piers and cowokers also evidenced the dynamic behavior of these congested *N*-bound imine–$B(C_6F_5)_3$ adducts due to restricted rotation about the B–N and the B–C bonds by using variable-temperature ^{19}F and ^{1}H NMR spectroscopy.

Complex **27** [23] was synthesized treating the imine 2-methyl-1-pyrroline with 1 equiv. of $B(C_6F_5)_3$ at room temperature [29]. Our interest around this adduct was to evaluate its acidity, to test if the reaction with NEt_3 could deprotonate the β-carbon and cause rearrangement of the double bond from C(2)=N to C(2)=C(3), therefore transform the imine moiety into enamine. However, treatment of **27** with NEt_3 at room temperature did not give the expected deprotonation and imine–enamine rearrangement reaction (Scheme 15).

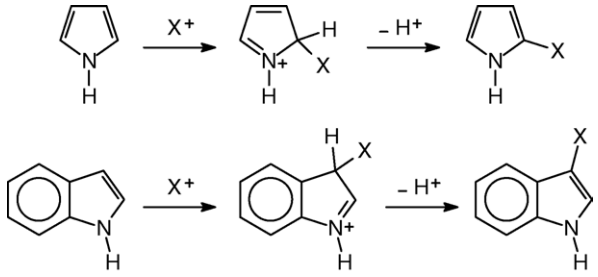
5. Reactivity with aromatic *N*-heterocycles

Pyridine has an unshared electron pair on the nitrogen, not involved in the aromatic π-electron sextet and located in a sp^2 orbital. Therefore pyridine favorably undergoes electrophilic additions involving donation of the nitrogen lone pair without losing aromaticity and yielding very stable Lewis acid–Lewis base adducts [30]. The coordination adduct of pyridine and $B(C_6F_5)_3$ (**28**) was first synthesized by Massey and Park right after their synthesis of $B(C_6F_5)_3$ itself, [3a] and applied more than 30 years later in a patent from Univation Technologies as activator of olefin polymerization catalysts [31]. The $B(C_6F_5)_3$ coordination adducts of pyridines and stilbazoles are highly polar chromophores [32].

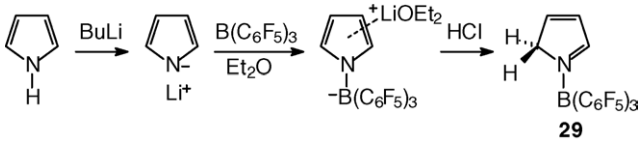


28

Going from six-membered to five-membered aromatic *N*-heterocycles, there is a substantial difference in the electronic



Scheme 16.



29

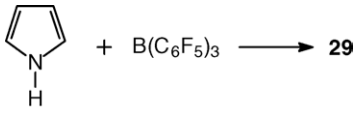
Scheme 17.

structure of the molecules. Pyrrole (or indole), in fact, has its nitrogen lone pair involved in the 6-π-electron aromatic system, therefore it normally does not partake in dative bonds with electrophiles [33]. Typical reactivity of pyrroles (or indoles) towards electrophiles goes through the attack of the acidic species generally to the α-carbon (or β- for indoles) and consequent loss of aromaticity, which can, however, be recovered by proton displacement (Scheme 16).

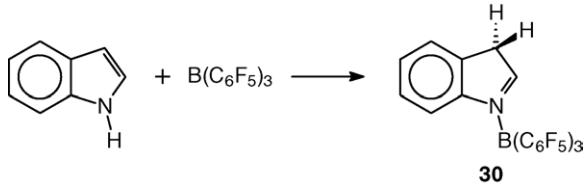
Nevertheless the B–N coordination adduct between $B(C_6F_5)_3$ and pyrrole is known from recent literature, [23,34] and was first synthesized through deprotonation of the *N*-heterocycle to give anion $[C_4H_4N]^-$, highly nucleophilic, subsequent treatment with borane, and final acidification to give the neutral compound **29** (Scheme 17) [34].

29 can be seen as the coordination adduct between the pyrrole tautomer, 2*H*-pyrrole, and the borane. The same adduct can be obtained by direct reaction of $B(C_6F_5)_3$ with pyrrole, without any need of deprotonation, as shown in Scheme 18 [23].

The same reaction occurs with indole (adduct **30**, Scheme 19) and with a series of 1*H*-pyrroles and 1*H*-indoles carrying various substituents (**31**–**40**) [23].



Scheme 18.

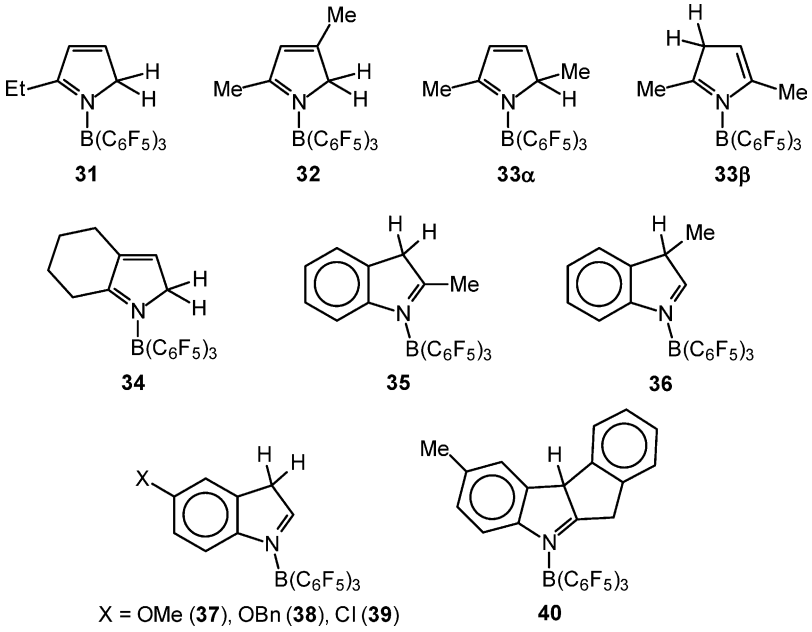


30

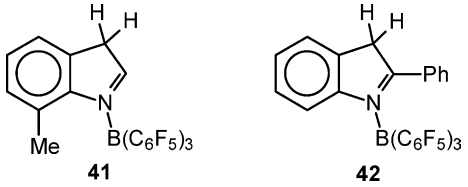
Scheme 19.

The borane causes a formal shift of the nitrogen-bound proton to the α-position for pyrrolic substrates, and to the β-position for indoles. The five-membered ring loses, in this way, the aromaticity due to the formation of the sp^3 carbon. An analogous reaction was observed before by Erker in the formation of $B(C_6F_5)_3$ keto-O-adducts of naphthols [35].

The reaction of formation of the B–N adducts is very easy and effective, it is in fact an instantaneous and quantitative reaction which can take place in different organic solvents, such as toluene, dichloromethane and diethyl ether. The final adduct can be isolated from the reaction mixture by simply removing the solvent at reduced pressure.



In the pyrrolic derivatives which carry an α-substituent (1-ethylpyrrole, 2,4-dimethylpyrrole and tetrahydroindole) the CH_2 group is formed in the α-position free of substituent, likely because this way the final adducts, (respectively **31**, **32** and **34**) achieve the structure with the most substituted N=C double bond. With 2,5-dimethylpyrrole both α-positions are hindered, and this led to the generation of 10% of β-isomer (**33**β) together with the main **33**α. Attempts were also carried out to synthesize the 7-methylindole and the 2-phenylindole adducts, but with the former a 1.4:1 mixture of the expected product **41** and starting material was obtained together with lower amounts of by-products, while 2-phenylindole yielded a 1:1 mixture of adduct **42** and starting material [23].

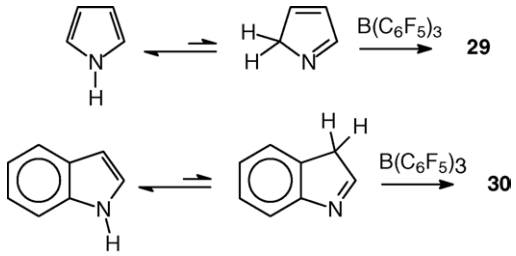


The reaction of $B(C_6F_5)_3$ with 5-methoxyindole and 5-benziloxyindole to yield the B–N complexes **37** and **38** revealed that alkoxy groups are not competing towards the aromatic nitrogen for the coordination of the borane, though $B(C_6F_5)_3$ is known to give very stable Lewis acid–base adducts with ether-like substrates; [36] compounds **37** and **38** are in fact formed in quantitative yield. This kind of reactivity could have been predicted also based on the synthesis of complex **30** itself in diethyl ether solution, in fact the adduct B–N was formed in quantitative yield despite the large excess of ether in the reaction mixture.

However when the heterocyle contains a carbonyl group as substituent, the borane strongly coordinates the oxygen [37,35] leaving the nitrogen unreacted [24].

With the exception of **29**, all pyrrole and indole–$B(C_6F_5)_3$ adducts (**30**–**40**) present an AB system for the CH_2 group, which becomes visible on their ^{1}H NMR spectra below a temperature value that depends on the steric encumbrance of the substituents next to the nitrogen atom. An accurate ^{19}F NMR study demonstrated that the adducts are asymmetric due to the spatial arrangement of the $-C_6F_5$ rings, whose rotation around the B–C axis can be slowed down below the NMR time-scale at lower temperatures, and which gives rise to the formation of two enantiomers. X-ray diffraction analysis on some adducts confirmed the chirality of these molecules due to the lack of a plane of symmetry because of the spatial arrangement of the perfluorophenyl rings. The interconversion of the two enantiomers was quantitatively studied for adduct **30** by line-shape simulation of the ^{1}H NMR spectra in $C_2D_2Cl_4$, the kinetic constant of the enantiomerization process were determined at each temperature, and the activation barrier ($\Delta G^{\neq}$) of enantiomerization was calculated to be 14.9 ± 0.2 kcal mol^{-1}.

The formation of the $(C_6F_5)_3$B–*N*-heterocyle adducts has been explained through two main mechanistic hypotheses. The pyrrolic (or indolic) substrate can be seen as a nucleophile



Scheme 20.

which reacts with the electrophilic borane, but following this assumption the expected product would be 2-[$B(C_6F_5)_3$]-2*H*-pyrrolium (or 3-[$B(C_6F_5)_3$]-3*H*-indolium in the case of indole), [33] which is hardly correlated to the final B–N adduct containing a CH_2 group in the α- (or β-) position. Also the possibility that the borane would attack the heterocycle directly at the nitrogen seems very unlikely [33a]. A possible, simple explanation of this reaction could be the existence of the tautomerization equilibrium between the heterocycle and its 2*H*- (or 3*H*-)isomer, and even if the tautomer is present in solution in very small amount, the favorable coordination with $B(C_6F_5)_3$ would drive the equilibrium to the right (Scheme 20).

The computed intramolecular isomerization barrier in the gas phase from 1-*H*-indole to 3-*H*-indole is very high, in the order of 50 kcal mol^{-1}, [38] however, it may be assumed that in solution and/or in the presence of some acidic catalytic species the tautomerization would have a much lower activation barrier [39]. A very possible explanation for the mechanism of formation of the $(C_6F_5)_3B$–*N*-heterocyle complexes can be in fact the involvement of the strong Brønsted acid H_2O–$B(C_6F_5)_3$, [12], which will act as nucleophile and protonate pyrrole (or indole) at the α- (or β-)carbon, according to the heterocycles behavior towards protic acid [33a]. The resulting protonated intermediate (**29h**, Scheme 21, exemplified for pyrrole) can evolve to the final adduct by intramolecular elimination of water (path *a*, Scheme 21) or, most probably, by attack of a free borane molecule and concomitant elimination of H_2O–$B(C_6F_5)_3$ (path *b*), which thus acts as catalyst of the reaction [23].

In addition to DFT calculations, which predict the hypothesized mechanism as very viable, [23] also some experimental evidences support this path. First of all, the coordination of water to $B(C_6F_5)_3$ is very strong, [12,14b] and even working in anhydrous conditions, it is practically impossible to have fully water-free $B(C_6F_5)_3$. The 1:1 reaction between indole and H_2O–$B(C_6F_5)_3$ showed the instantaneous formation of an intermediate species, identifiable with species **30h** according to NMR analysis, which over 3 days converted in high yield into adduct **30** by losing H_2O. The analogous reaction starting from 2,4-dimethylpyrrole, more nucleophilic than indole, yielded after a week a 1:4 mixture of **32** and **32h**. The latter has been isolated by crystallization and analyzed by X-ray diffraction [24,40].

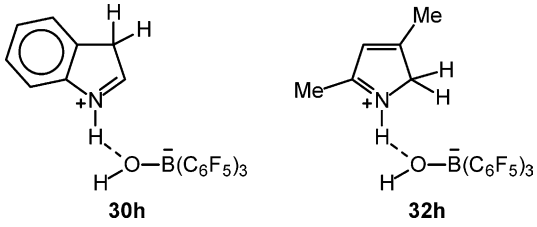
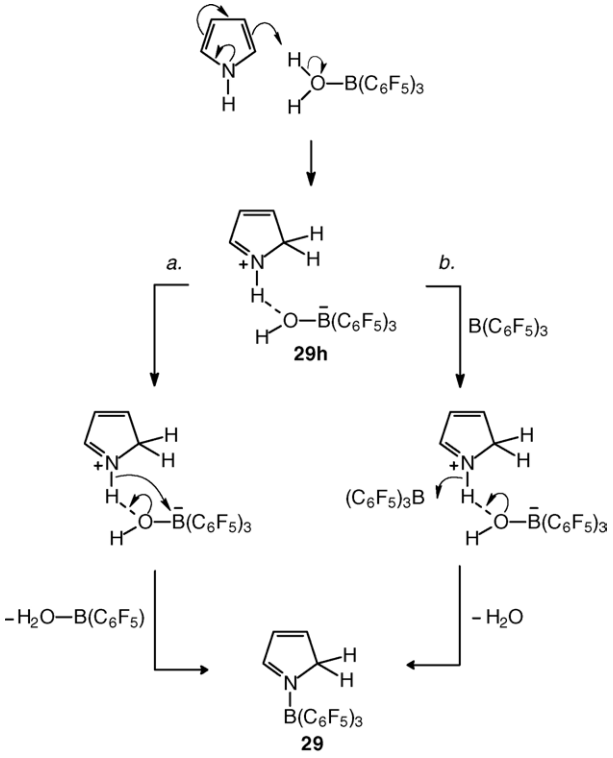


Fig. 1 shows the molecular structure of the hydrogen bonded species **32h**, in which a typical N–H···O interaction is present.

When 1 equiv. of $B(C_6F_5)_3$ is added to a 1:1 mixture of pyrrole and indole, the species instantaneously produced in higher yield is adduct **30**, which partially releases the borane to pyrrole. The equilibrium results in a 2:3 mixture of **29** and **30** after about 3 days (Scheme 22) [24]. The initial formation of **30** as kinetic adduct is in agreement with the values of basicity, slighty higher for indole than for pyrrole ($pK_a = -3.5$ [41a] and −3.8 [41b], respectively), indicating the initial protonation of the heterocycle as possible path of the mechanism.

The exchange reaction of borane between indole and pyrrole goes through a dissociative mechanism, as observed before for adduct **1**, which displaces MeCN in the presence of H_2O (Schemes 4 and 5).

In the case of *N*-methylpyrrole and *N*-methylindole the outcome of the reaction with $B(C_6F_5)_3$ is quite different. These two heterocycles give again formation of 1:1 adducts containing a methylene group in the five-membered ring, but the borane is now bonded to the carbon 2 in both deriva-



Scheme 21.

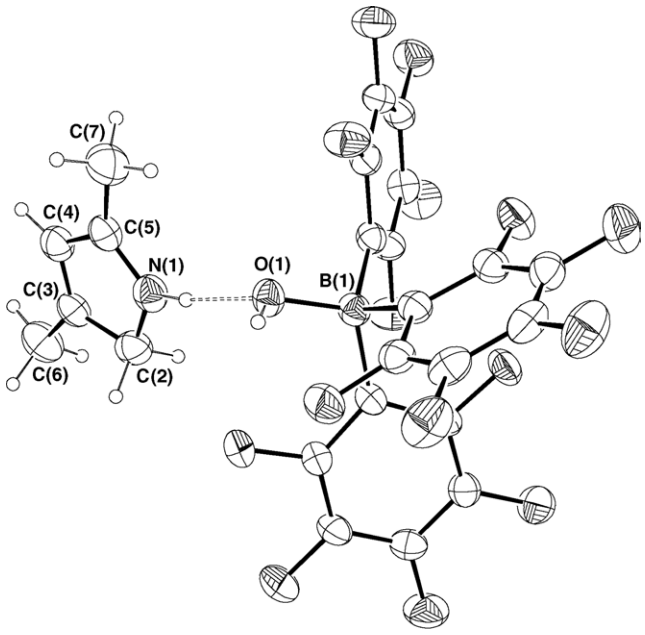
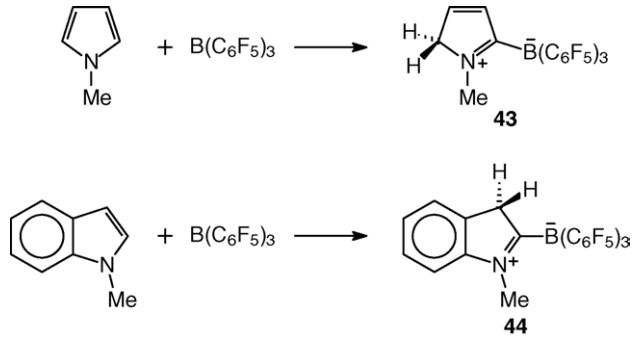


Fig. 1. Molecular structure of the hydrogen bonded species **32h**. [40] Selected bond lengths [Å] and angles [°]: B(1)—O(1) 1.485(3), N(1)—H 0.860, H···(O1) 1.789, N(1)···O(1) 2.641(4), N(1)—H···O(1) 171.0.



Scheme 23.

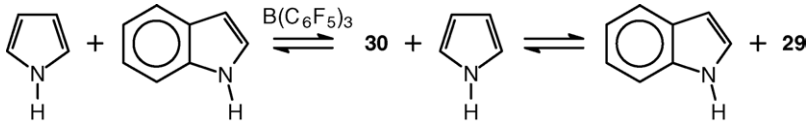
tives and the species are zwitterions (**43** and **44**, respectively, Scheme 23) [42]. The mechanisms of Schemes 20 and 21 proposed for the reaction of various pyrroles and indoles with $B(C_6F_5)_3$ cannot explain the reaction occurring with *N*-methylpyrrole and *N*-methylindole, which lack the potentially movable hydrogen at the 1-position.

The formation of **43** and **44** is rather slow (4–10 days at room temperature) compared to the instantaneous reaction of $B(C_6F_5)_3$ with pyrroles or indoles. In addition, adducts **43** and **44** are less stable in air and seem to be thermally labile (above 80 °C). The synthesis of **43** and **44** was monitored by ^1H and ^{13}C NMR, but no reaction intermediates could be detected, the only species visible in the reaction mixture being the starting heterocycle and the final borate complex. The proposed mechanism assumes that the first reaction step is a slow electrophilic attack of the borane to the heterocycle, following a second order kinetic (which is the global process rate). The resulting species 1-methyl-2-[$B(C_6F_5)_3$]-5*H*-pyrrole is probably unstable and prefers to rearrange to the final product by losing and recovering a proton, and the basic species which may allow this rearrangement is the free *N*-methylpyrrole itself (Scheme 24).

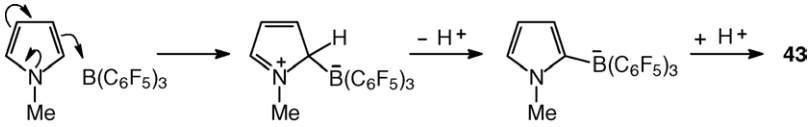
The mechanism with *N*-methylindole (Scheme 25) is more complicated because the borane is found bonded at the α-position, while it is known that electrophiles strongly prefer to attack indoles at their β-carbons. However it is possible that the borane attacks the indole at the β-position and migrates to the α to give a structure which can evolve to the final complex by a formal hydrogen migration, but a direct attack at the α-position can also occur. Intermediate 1-methyl-2-[$B(C_6F_5)_3$]-3*H*-indole can evolve to **44** likely by abstraction of the 2-proton by a base (probably free *N*-methylindole) followed by re-protonation at the nucleophilic β-position. Both heterocycles after the borane attack go through rearrangement in order to achieve the structures with more substituted double bonds and lower internal steric hindrance (the C–B bond goes in the same plane as the heterocycle).

In the pyrrole (**29**-like) and indole (**27**-like) borane adducts, and also for the *N*-methyl derivatives **43** and **44**, the presence of the N=C double bond combined with the effect of electron-withdrawing $B(C_6F_5)_3$ moiety generates a quite strong acidity of the proton(s) on the sp^3 C2 or C3 carbons: for example, they react with NEt_3 to give quantitatively the triethylammonium salts of the corresponding borate, as exemplified in Scheme 26 for adducts **29** and **43**, which give salts [$HNEt_3$]**29a** [23,43] and [$HNEt_3$]**43a**, [42] respectively. The reaction with the amine was used to probe the Brønsted acidity of the complexes, since their ability to lose a proton and to form a stable anion can be a preliminary indication of their potential co-catalytic nature (see Section 8).

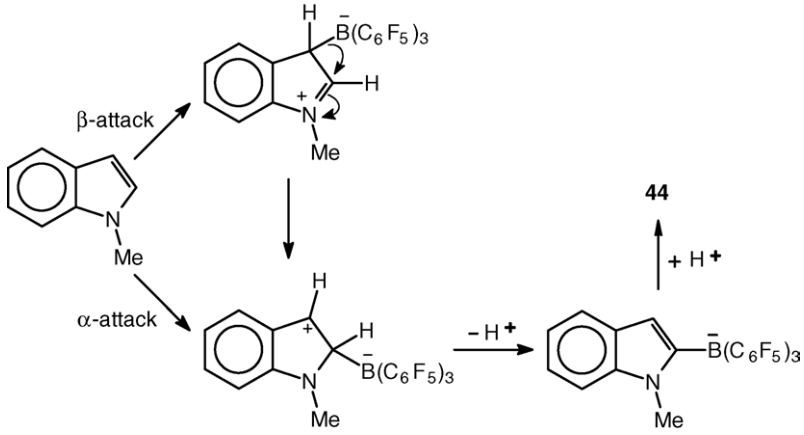
The deprotonation of the $(C_6F_5)_3B$–pyrroles or indoles adducts by NEt_3 was successfully carried out for most of them, and in all cases the driving force for this reaction is the restoration of aromaticity in the five-membered ring.Error! Bookmark not defined [42]. In the case of indole, the formation of the triethylammonium was successfully carried out also in a one step procedure starting from a mixture of indole and NEt_3 and by adding 1 equiv. of borane (Scheme 27). This reaction confirms the affinity of the borane to coordinate aromatic *N*-heterocycles: there is in fact no evidence of direct



Scheme 22.



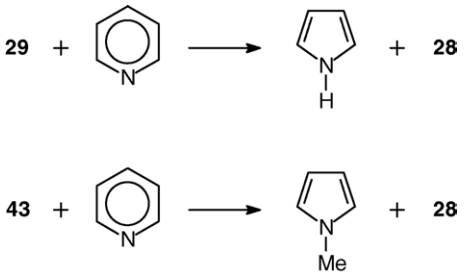
Scheme 24.



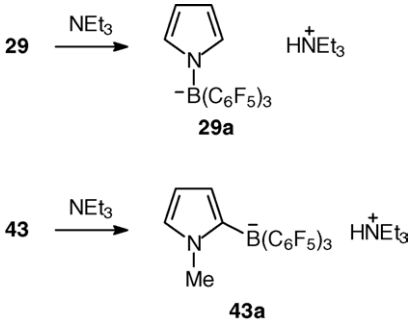
Scheme 25.

reaction between $B(C_6F_5)_3$ and NEt_3 and the formation of $[HNEt_3]$**30a** is quantitative [23].

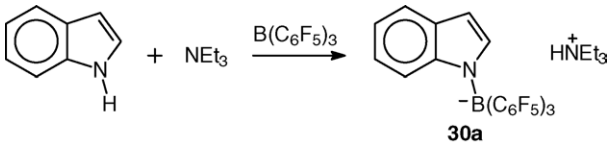
The reaction of deprotonation of the borane–*N*-heterocycle adducts was also attempted treating pyrrole–$B(C_6F_5)_3$ **29** and *N*-methylpyrrole–$B(C_6F_5)_3$ **43** with a different base such as pyridine, which has inferior Brønsted basicity, but higher nucleophilicity. However, pyridine displaces the pyrrolic moiety to give adduct **28** in both cases (Scheme 28) [24]. The crystal structure of $[NHEt_3]$**44a** has been solved [40] and a view of the borate anion **44a** is shown in Fig. 2.



Scheme 28.



Scheme 26.



Scheme 27.

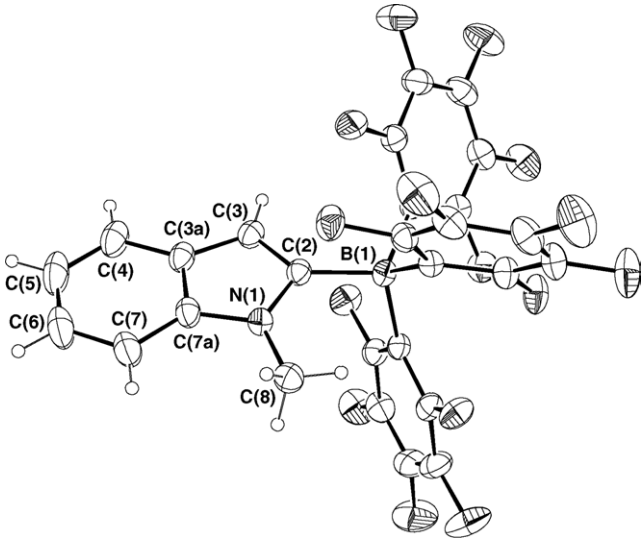
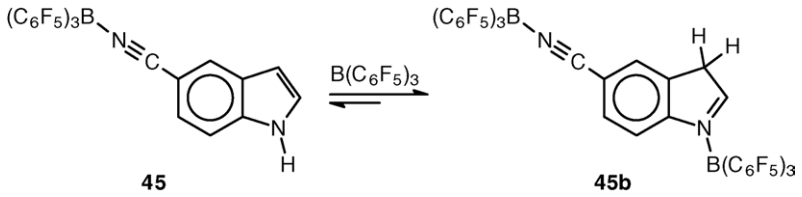


Fig. 2. Molecular structure of the anion **44a**. [40] The B—C bond lengths is 1.631(3) Å.



Scheme 29.

6. Adducts with heterocycles containing two or more nitrogen atoms

We reacted 5-cyanoindole with $B(C_6F_5)_3$ in order to investigate the competition between the nitrogen of the cyano group, noticeably nucleophilic, and the nitrogen involved in the aromatic five-membered ring, which, though lacking Lewis basic character, also reacts with $B(C_6F_5)_3$ to give stable B–N adducts (previous section). In this case however, $B(C_6F_5)_3$ strongly prefers the coordination with the cyano group to give adduct **45**, and partly coordinates to the indolic moiety to give the diborate **45b** only when a second equivalent is added (Scheme 29) [24]. The equilibrium between **45** and **45b** at room temperature in a dichloromethane solution results in a 3:2 ratio.

The molecular structure of **45** in the solid state is shown in Fig. 3; [40] the geometric parameters well reproduce the ones found for other adducts with nitriles.

As in Section 5, Scheme 27, it is shown that the borane prefers coordinating the aromatic nitrogen of indole rather than triethylamine, the reaction between tryptamine [3-(2-aminoethyl)indole] and $B(C_6F_5)_3$ was attempted with the purpose of obtaining the intramolecular ammonium salt in one step, but in this case the borane coordinates the NH_2 group to give adduct **46** (Scheme 30), leaving the pyrrolic ring unreacted [24]. This experiment points out the different behavior of $B(C_6F_5)_3$ towards primary or secondary amines with respect to tertiary amines, as already discussed in Section 3.

The competition between a pyridine- and a pyrrole-like substrate for the coordination with $B(C_6F_5)_3$ has been studied by observing the borane displacement by pyridine from adducts **29** (Scheme 28) and **30** [24]. The preference of the borane for the coordination to the azomethine nitrogen of pyridines can be directly observed in the reaction of $B(C_6F_5)_3$ with 7-azaindole, where $B(C_6F_5)_3$ coordinates exclusively the pyridinic moiety of the molecule to give adduct **47**, which does not react with a second equivalent of borane for both steric and electronic reasons (Scheme 31). Also the borane electrophilic attack to the β-carbon seems rather unlikely because of the positive charge on the pyridinic nitrogen, which reduces the nucleophilicity of the five-membered ring [24].

In addition, it has been observed that coordination of $B(C_6F_5)_3$ to pyridine is favored with respect to coordination with 7-azaindole, in fact the borane slowly displaces the latter from complex **47** to give the pyridine-complex **28**, which is more stable than **47** because of the reduced steric hindrance towards the $-C_6F_5$ groups (Scheme 32) [24].

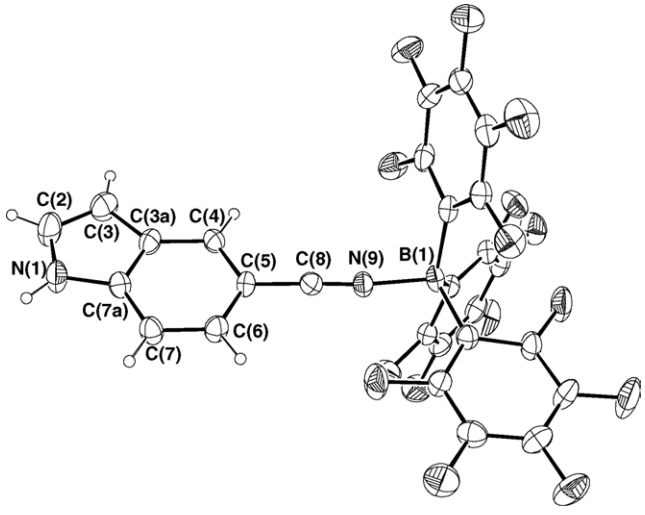
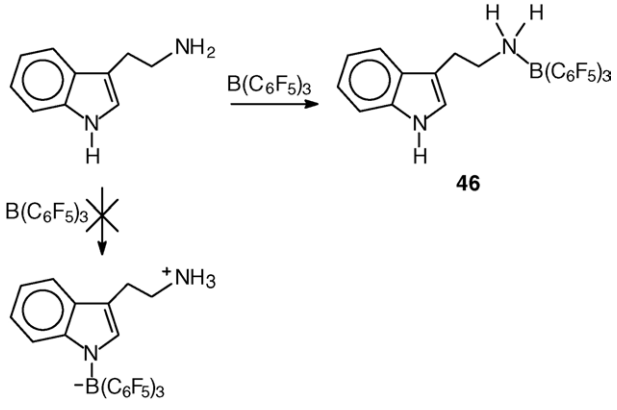
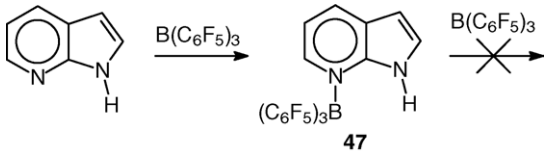


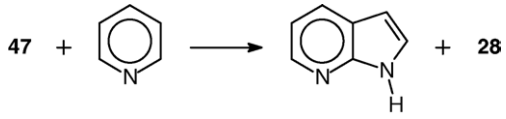
Fig. 3. Molecular structure of **45**. [40] Selected bond lengths [Å] and angles [°]: B(1)–N(9) 1.592(3), C(8)≡N(9) 1.133(3), C(5)–C(8)≡N(9) 177.0(2), C(8)≡N(9)–B(1) 174.6(2).



Scheme 30.

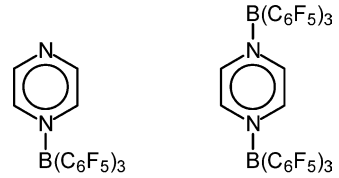


Scheme 31.



Scheme 32.

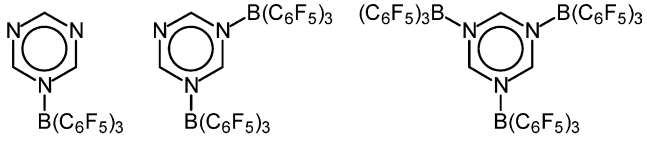
Pyrazine was successfully reacted with one and two molecules of $B(C_6F_5)_3$ yielding adducts **48** and **48b**, respectively [24].



48 **48b**

The molecular structure of **48b** in the solid state is compared to that of the pyridine adduct **28** in Fig. 4 [40]. As expected, the B–N bond distances in **48b** are longer that the one in **28**, due to the lower basicity of the diazine and to the presence of two $B(C_6F_5)_3$ moieties.

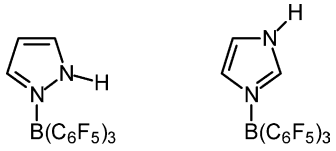
The mono-, bis- and tris-$B(C_6F_5)_3$ adducts of 1,3,5-triazine, (respectively **49**, **49b** and **49t**) were easily synthesized and well characterized by IR and NMR techniques [18].



49 **49b** **49t**

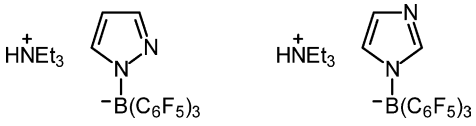
For adducts **49** and **49b** also the X-ray structure is available, while attempts to crystallize tris-borane **49t** resulted always in the isolation of bis-adduct **49b** and $B(C_6F_5)_3$. As evidenced from the X-ray analysis, there is a substantial extension of the B–N bond length going from **49** (1.644(3) Å) to **49b** (1.678(3) Å/1.687(3) Å); in the case of **49t** the B–N coordination interaction is expected to be even lower for both steric and electronic factors, and the complex is too labile to be isolated, but can be observed through solution NMR. The comparison between the ^{11}B and ^{19}F NMR spectra and the B–N bond lengths in adducts **6**, **7**, **49** and **49b** demonstrated that the highfield shift of the NMR signals is correlated with the increment of the B–N distances [18].

Pyrazole and imidazole carry two nitrogen atoms which are electronically different from each other, and when treated with $B(C_6F_5)_3$ they coordinate the borane only at the iminic nitrogen to give **50** [23] and **51** [23,44], respectively, while the NH moiety does not react even with an excess of borane.



50 **51**

Both pyrazolyl and imidazolyl derivatives **50** and **51** react with triethylamine by losing a proton and yielding salts $[HNEt_3]$**50a** and $[HNEt_3]$**51a**, respectively [23].



50a **51a**

Imidazole can bind 1 equiv. of $B(C_6F_5)_3$ when combined with a base able to activate also the second nitrogen (Scheme 33) [43]. Attempts to obtain the diborate derivative of pyrazole analogous to **51b** failed, likely because

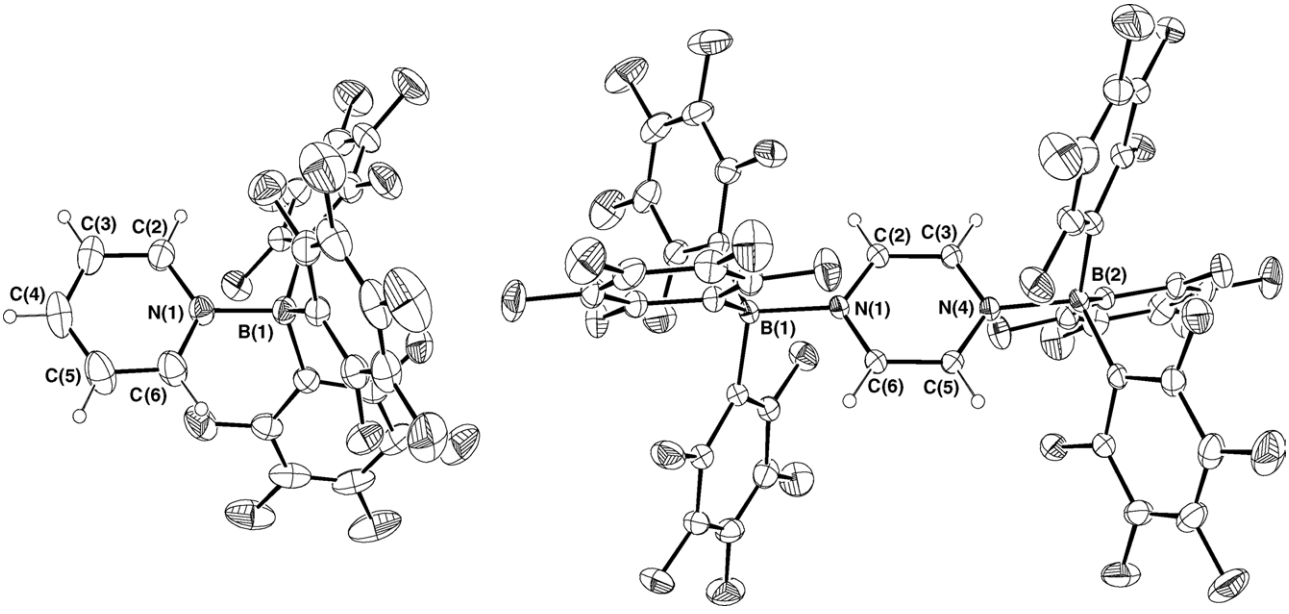
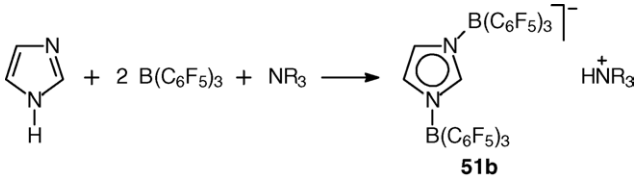
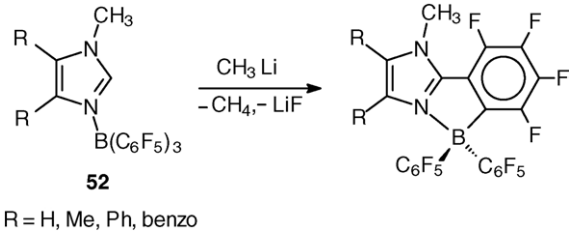


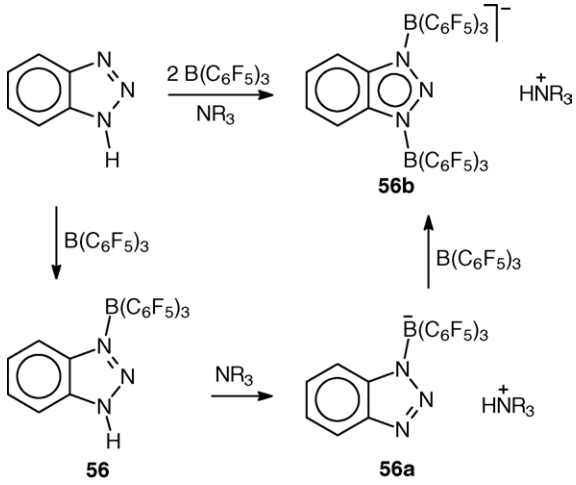
Fig. 4. Molecular structures of **28** [40] (left, B–N 1.628(2) Å) and **48b** [40] (right, B–N 1.645(2) and 1.652(2) Å). The pyrazine adduct shows an approximate C_i symmetry, with the two $B(C_6F_5)_3$ moieties arranged in a staggered conformation.



Scheme 33.



Scheme 34.

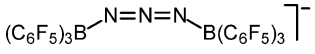


Scheme 35.

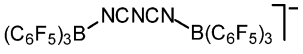
of the steric hindrance at the adjacent nitrogen atoms [24].

Some coordination adducts of $B(C_6F_5)_3$ with imidazole and benzimidazole derivatives of type **52** (Scheme 34) were synthesized and studied through dynamic ^{19}F NMR, where 15 separated signals for the borane moiety are detectable at low temperature, [45] confirming the tendency of the borane to assume asymmetric conformational arrangements, as already observed in the $B(C_6F_5)_3$ adducts of imines [28] and pyrroles and indoles [23]. Upon treatment with MeLi, these imidazolyl derivatives undergo deprotonation at the 2-carbon, but the anion is unstable and reacts intramolecularly to give a heterotricyclic molecule by nucleophilic aromatic substitution at one of the perfluoroaryl rings (Scheme 34).

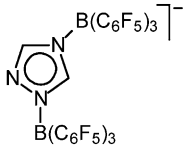
Most of the $B(C_6F_5)_3$ adducts with three-nitrogen-containing compounds are known from the patent literature; [46] here are reported the most representative complexes of this class, all of them are diborate anions, thus just two of the three nitrogens are involved.



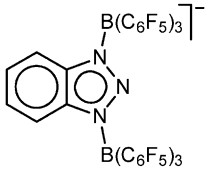
53b



54b



55b



56b

The mono-borate adduct of azide, $[(C_6F_5)_3BN_3]^-$ (**53**) was also synthesized [47].

Both benzotriazole derivatives with 1 equiv. of $B(C_6F_5)_3$ (neutral adduct **56** and the $[HNR_3^+]$ salt of anion **56a**) and with 2 equiv. (**56b**) were later studied also in our group [24]. Diborate **56b** is a very stable adduct, easily obtained in high yield by a one-step reaction of benzotriazole, borane and amine in 1:2:1 ratio (Scheme 35).

7. Crystal structures of adducts between $B(C_6F_5)_3$ and nitrogen-containing compounds

Table 1 collects some selected geometric parameters for the X-ray structurally characterized adducts between $B(C_6F_5)_3$ and some nitrogen containing compounds. Data have been retrieved from the Cambridge Crystallographic Data Centre [48] and the pertinent refcodes have been reported. The few entries lacking the CSD refcode refer to recently determined structures.

Bond lengths and angles within the $B(C_6F_5)_3$ moiety are unexceptional. The mean B–C_{ipso} bond distance is 1.643(12). In almost all the compounds the boron atom shows a distorted (*pseudo* D_{2d}) tetrahedral coordination geometry, in which four bond angles are larger – mean value 112(3)° – and two (opposite) are smaller – mean value 103(2)° – than the idealized tetrahedral value.

Boron–nitrogen bond distances show a sensible dependence on the electronic and steric environment, in particular bond distances are shorter in the presence of unhindered strong bases. This effect is notably evident in the series of azines pyridine, pyrazine, and 1,3,5-triazine: the B–N bond distance lengthens on lowering the basicity of the azine and on raising the number of coordinated borane moieties. The effect of a negative charge on the nitrogen atom can be seen comparing the pyrrole and indole derivatives (1.61 Å) to the pyrrolate and indolate ones (1.56 Å). In the case of imidazole, the effect is less pronounced (from 1.60 Å for imidazoles to 1.58 Å for imidazolates) since the negative charge is delocalized over two nitrogen atoms.

In all the aromatic heterocyclic derivatives, the aromatic ring is nearly perfectly planar and the N–B bond approximately lies in the plane of the ring.

Table 1
Selected bond distances [Å] and torsional angles [°] for adducts between $B(C_6F_5)_3$ and nitrogen containing compounds[a]

Compound	CSD Refcode	B–N	N–B–C–C			Reference
Nitriles						
MeC≡N–$B(C_6F_5)_3$ (**1**)	MANYOP01	1.610	−44.8	−45.1	−58.4	[12]
	MANYOP	1.616	44.3	45.5	58.4	[5]
4-$(NO_2)C_6H_4$C≡N–$B(C_6F_5)_3$ (**3**)	MANYUV	1.595	44.3	47.5	51.9	[5]
$[Ph_3C][(C_6F_5)_3B$–C≡N–$B(C_6F_5)_3]$ (**4b**)	BAQZIC	1.593	17.5	44.5	49.6	[16]
$[Ph_3C]_2[Ni\{C\equiv N–B(C_6F_5)_3\}_4]\cdot 2CH_2Cl_2$ (**5**)	BAQZEY[c]	1.574	−9.9	−52.4	−58.8	[16]
		1.574	26.0	45.4	61.3	
$[PhNHMe_2]_2[Ni\{C\equiv N–B(C_6F_5)_3\}_4]\cdot 2$ acetone (**5**)	YEQYOI[c]	1.578	3.5	−46.5	−67.7	[17]
		1.582	38.4	38.6	48.7	
$[Ph_3C]_2[Pd\{C\equiv N–B(C_6F_5)_3\}_4]\cdot 2CH_2Cl_2$ (**5′**)	YEQZAV[c]	1.571	−11.0	−50.2	−58.8	[17]
		1.578	27.9	44.3	61.5	
$IC\equiv N–B(C_6F_5)_3\cdot 1/2\ CH_2Cl_2$ (**6**)	XIPCAA	1.608	43.2	45.2	46.1	[18]
$H_2NC\equiv N–B(C_6F_5)_3$ (**7**)	XIPCOO[b]	1.572	−6.4	−54.0	−59.2	[18]
		1.573	6.8	54.4	56.2	
$[Cp_2V\{\eta^2\text{-}MeC\equiv N–B(C_6F_5)_3\}]$ (**8**)	IFUJOI	1.586	−51.8	−54.4	−54.7	[19]
$[Cp_2V\{\eta^2\text{-}4\text{-}(CF_3)C_6H_4C\equiv N–B(C_6F_5)_3\}]$ (**8′**)	IFUJUO	1.588	−37.4	−45.4	−64.6	[19]
Metal nitrides (**9**)						
$[(PPhMe_2)(Me_2dtc)_2Re\equiv N–B(C_6F_5)_3]$	GIWWOY	1.547	−15.4	52.4	69.1	[20a]
$[Tp(Ph)_2Os\equiv N–B(C_6F_5)_3]\cdot 2$ benzene	QOCSEG	1.592	22.0	−43.0	−81.4	[20b]
$[\{(Et_2dtc)_2Re\equiv N–B(C_6F_5)_3\}_2]$	BANQOW	1.573	−22.8	39.2	80.3	[20c]
		1.577	−8.8	43.1	72.4	
$[Cl(PPhMe_2)_2(HEt_2tcb)Re\equiv N–B(C_6F_5)_3]\cdot 1\ 1/2$ *n*-Hexane	BENVOF	1.593	8.7	−52.7	−69.7	[20d]
$[N(n\text{-}Bu)_4]\ [Cl_4(H_2O)Re\equiv N–B(C_6F_5)_3]$	GENPOE	1.589	−8.9	51.7	75.0	[20e]
Amines						
$[Na(OEt_2)_4][(C_6F_5)_3B–NH_2–B(C_6F_5)_3]$ (**10b**)	UDUJIM	1.628	−7.4	46.4	58.2	[21]
		1.637	−6.7	45.1	70.7	
dimethylamine–$B(C_6F_5)_3$ (**11**)	BAZRIE[b]	1.651	30.1	−31.6	−85.5	[21]
		1.653	31.9	−30.8	−89.4	
piperidine–$B(C_6F_5)_3$ (**12**)	EKUBUH[b]	1.629	23.8	−38.2	−86.1	[22]
		1.631	−20.6	40.6	78.6	
pyrrolidine–$B(C_6F_5)_3$ (**13**)	EKUBOB	1.628	−5.8	48.1	81.1	[22]
2,3-dihydroindole–$B(C_6F_5)_3$ (**14**)	IJOHIY	1.650	−15.9	47.2	77.0	[23]
Imines						
Z-Ph(H)C=N(Bz)–$B(C_6F_5)_3$ (**22t**)	MIVMEJ	1.627	20.0	−58.2	−68.5	[28]
E-Ph(Me)C=N(Bz)–$B(C_6F_5)_3\cdot 1/2$ toluene (**23k**)	MIVLUY[b]	1.629	17.3	−62.7	−71.0	[28]
		1.659	10.2	−64.7	−65.6	
Z-Ph(Me)C=N(Bz)–$B(C_6F_5)_3$ (**23t**)	MIVMAF	1.640	23.5	−55.7	−74.0	[28]
Ph_2C=N(Bz)–$B(C_6F_5)_3\cdot 1/2$ toluene (**24**)	MIVLOS	1.642	15.7	−66.0	−67.0	[28]
Z-Ph(H)C=N(Ph)–$B(C_6F_5)_3$ (**25**)	MIVMIN	1.648	−14.9	−49.6	−72.7	[28]
Heterocycles						
pyridine–$B(C_6F_5)_3$ (**28**)		1.628	10.8	−63.8	−64.1	[40]
4-(NMe_2)pyridine–$B(C_6F_5)_3\cdot$toluene	JUDMUQ	1.604	18.1	−54.2	−68.2	[32]
4-[4′-$(NMe_2)C_6H_4C\equiv C$]pyridine –$B(C_6F_5)_3$	JUDQEE	1.620	−21.3	49.0	73.8	[32]
2*H*-pyrrole–$B(C_6F_5)_3$ (**29**)	QEYSAO	1.608	−21.0	−43.1	−70.9	[34]
$[Li(OEt_2)][pyrrolate–B(C_6F_5)_3]$ (**29a**)	QEYRUH	1.576	11.3	−52.7	−68.7	[34]
3*H*-indole–$B(C_6F_5)_3$ (**30**)	IJOHAQ	1.613	−17.8	53.3	67.3	[23]
$[NHEt_3][indolate\ –B(C_6F_5)_3]$ (**30a**)	IJOHEU	1.565	−10.9	55.9	60.9	[23]
5-cyano-κ*N*-indole–$B(C_6F_5)_3$ (**45**)		1.591	−8.4	−50.3	−61.9	[40]
pyrazine–$[B(C_6F_5)_3]_2\cdot 2CH_2Cl_2$ (**48b**)		1.645	−14.6	60.6	63.4	[40]
		1.652	4.8	−56.8	−64.6	
1-Me-imidazole–$B(C_6F_5)_3$ (**52**)	XUCCIH[b]	1.597	3.4	−60.8	−68.6	[45a]
		1.605	3.1	−57.5	−64.9	
1,4,5-Me_3imidazole–$B(C_6F_5)_3$ (**52**)	GABQUW	1.588	8.4	−58.2	−62.0	[44]
1-Me-benzimidazole–$B(C_6F_5)_3$ (**52**)	GABRAD	1.600	15.0	−57.0	−63.2	[44]
$[H(OEt_2)_2][imidazolate–\{B(C_6F_5)_3\}_2]$ (**51b**)	FAGBAR	1.577	10.7	−53.7	−66.0	[52]
		1.588	13.2	−56.4	−59.5	
$[NHEt_3][imidazolate–\{B(C_6F_5)_3\}_2]\cdot$thf (**51b**)	XEDYOU[b]	1.579	−15.7	54.1	64.0	[43]
		1.584	−20.7	51.6	67.3	
		1.586	−11.4	54.2	62.4	
		1.587	−10.5	55.6	62.4	
$[Li(thf)_4][4,5\text{-}Me_2imidazolate–\{B(C_6F_5)_3\}_2]$	FAFZUI	1.581	9.2	−56.6	−63.5	[52]
		1.588	−7.3	55.9	65.3	
1,3,5-triazine–$B(C_6F_5)_3\cdot CH_2Cl_2$ (**49**)	XIPCEE	1.644	−9.5	61.1	63.9	[18]
1,3,5-triazine–$[B(C_6F_5)_3]_2\cdot 2CH_2Cl_2$ (**49b**)	XIPCII	1.678	−10.4	59.1	61.7	[18]
		1.686	−17.4	55.3	68.8	
$[NMe_4][N_3–B(C_6F_5)_3]$ (**53**)	WUSRAD	1.583	32.2	51.1	54.8	[47]

[a] Cp = η^5-cyclopentadienyl; Me_2dtc = *N*,*N*-dimethyldithiocarbamate; Et_2dtc = *N*,*N*-diethyldithiocarbamate; H_2Et_2tcb = *N*,*N*-diethylthiocarbamoylbenzamidine; Tp = hydridotris(pyrazolyl)borate.
[b] Two independent molecules.
[c] The dianion lies on an inversion center.

As can be seen from the torsional angles reported in Table 1, in almost all the adducts the $B(C_6F_5)_3$ moiety adopts a very similar conformation. In particular, one of the three phenyl ring eclipses the B–N bond while the other two exhibit a chiral two-bladed propeller-like conformation. Only few structures, mainly characterized by the absence of significant steric interactions between $B(C_6F_5)_3$ and the nitrogen ligand, show a *pseudo* C_3 three-bladed propeller-like conformation (see for instance compounds **1**, **3**, **6**, **53** and some of the metal coordinated nitriles).

From this evidence it can be inferred that the conformation of the $B(C_6F_5)_3$ molecular fragment is very rigid, so that the presence of a somehow high energy barrier to the enantiomerization process of the chiral propeller can be expected and indeed observed in solution for several adducts [28,23,45b].

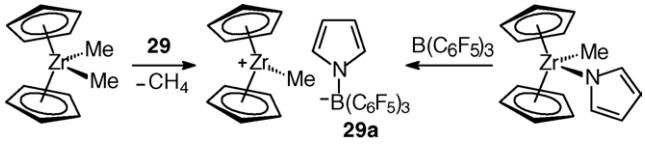
8. Reactivity with group 4 metal complexes and use as activators in olefin polymerization

In addition to a few fundamental studies, so far the investigation of the complexes of $B(C_6F_5)_3$ with nitrogen-containing molecules has been driven mostly by the interest in their potential as metallocene activators.

Compounds $[Ph_3C]$**4b** and $[Ph_3C]_2$**5** have been tested in reaction with metallocene complexes and studied by NMR spectroscopy, and their behavior was compared to that of $[Ph_3C][B(C_6F_5)_4]$ [17]. For all of them, the reaction with the zirconocene L_2ZrMe_2 ($L_2 = Cp_2$ or *rac*-$Me_2Si(Ind)_2$) generally gives rise to the initial formation of a binuclear metal species $[(L_2ZrMe)_2(\mu\text{-Me})]^+$ as cationic counterpart of anions **4b**, **5** or $[B(C_6F_5)_4]^-$. Though the specific results depend on the borate and experimental conditions (temperature, solvent, time), it is generally observed that after the initial and major formation of the binuclear zirconocene, also the mononuclear metal species $[(L_2ZrMe)^+\cdots X^-]$ is formed, which, in the case of X = **4b** and **5**, has short life and produces $L_2ZrMe(\mu\text{-Me})B(C_6F_5)_3$ among other decomposition products. $[Ph_3C]$**4b** resulted to be a more efficient cocatalyst than $[Ph_3C][B(C_6F_5)_4]$, and much more active than MAO (30–40 times) in the productivity of polyethylene in combination with the catalyst precursor *rac*-$Me_2Si(Ind)_2ZrMe_2$ [16,17].

The cocatalytic ability of $[Ph_3C]$**4b** and $[Ph_3C]$**10b** was tested in the polymerization of propylene using various C_2-symmetric *ansa*-zirconocenes. $[Ph_3C]$**4b** generally presents better behavior than $[Ph_3C]$**10b**, but the latter is more active in combination with high-activity metallocenes in tests carried out at 60 °C, due to the enhanced thermal stability of anion **10b**. The influence of the counteranions on polymer molecular weights and regio- and stereo-regularity was quite limited, except for one of the cases examined, $(2\text{-PhInd})_2ZrCl_2$, which is a conformationally fluxional complex [49].

Within the class of $(C_6F_5)_3B$–*N*-compound adducts, C_5H_5N–$B(C_6F_5)_3$ (**28**) is one of the most active, simple and stable cocatalysts of transition metal organometallic complexes; [31] however its mechanism of activation is not fully understood, being **28** neither a proton source nor an acidic species for the abstraction of an alkyl group from the metal center. According to the inventors, the activation process likely involves the trialkylaluminum compound (for example tri(isobutyl) aluminum) commonly employed as scavenger. The combination of adduct **28** with transition metal complexes is in fact inactive and does not initiate any polymerization; on the other hand the system becomes active when the alkyl aluminum is added. A possible explanation of this behavior is an exchange reaction of pyridine from **28** to aluminum, releasing the free borane, which then reacts with the alkylated transition metal complex to produce the catalytically active species.



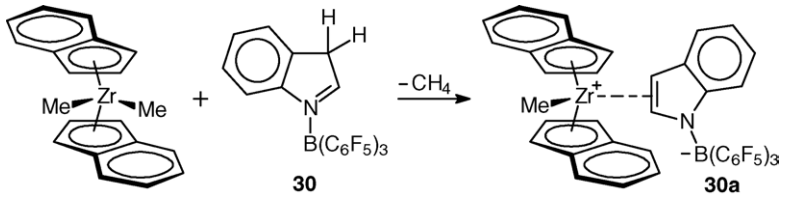
Scheme 36.

The adduct pyrrole–$B(C_6F_5)_3$ (**29**) was employed in the activation of a series of dimethyl or η^4-butadiene derivatives of *ansa*-zirconocene complexes for the polymerization of ethylene and propylene [34]. The left part of Scheme 36 shows the activation reaction of Cp_2ZrMe_2. The activation ability of **29** is due to its Brønsted acidity, being **29** a neutral proton source able to protonate a Zr–Me bond with loss of methane and generation of a reactive metallocenium cation having as counter anion $[(C_4H_4N)B(C_6F_5)_3]^-$ (**29a**), which is essentially a non-nucleophilic and quite stable species, unable to coordinatively saturate the metal center. Adduct **29** was compared to MAO and $B(C_6F_5)_3$, and resulted to have similar cocatalytic power and selectivity in both ethylene and propylene polymerization.

Scheme 36 (reaction on the right) also pictures the activation process of complex $Cp_2ZrMe(NC_4H_4)$, where a methyl ligand has been substituted by a pyrrolyl [50]. Treatment of this metallocene with $B(C_6F_5)_3$ produces the same ion pair as from the reaction between Cp_2ZrMe_2 and **29**, showing the strong affinity of the borane for the pyrrolyl moiety, preferred to the methyl group. The contact ion pair $[Cp_2ZrMe]$**29a** was analysed by NMR techniques, being too labile to be isolated by crystallization, and generated in situ for the polymerization tests.

Analogously to **29**, also adduct **30** indole–$B(C_6F_5)_3$ reacts with dimethyl metallocene complexes to give polymerization active ion pairs. In particular, the salt formed by treatment of Ind_2ZrMe_2 with 1 equiv. of **30** was isolated and characterized by NMR (Scheme 37) [51].

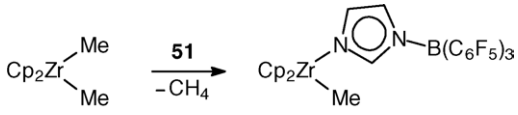
Salt of Scheme 37 and salt $[HNEt_3]^+[B(\text{indolyl})(C_6F_5)_3]^-$, obtained for treatment of **30** with NEt_3, contain the same counter anion, **30a**; however some noteworthy differences were observed in the respective proton spectra. This observation, together with a detailed 2D-NMR



Scheme 37.

study, led to the conclusion that there is coordination of the indole double bond to the zirconium atom, as evidenced in Scheme 37, in addition to weak, but detectable H–F interactions between one Cp ring and the $-B(C_6F_5)_3$ moiety [51].

Various pyrrole and indole–$B(C_6F_5)_3$ adducts were tested in ethylene polymerization and ethylene/propylene copolymerization employing Ind_2ZrMe_2 as precatalyst, and were compared to MAO and $B(C_6F_5)_3$. These borate derivatives are stoichiometric activators and generally present comparable or higher activity than MAO (used in a 500:1 ratio with the metallocene), and much higher activity than $B(C_6F_5)_3$. In addition, the Ind_2ZrMe_2/indole–$B(C_6F_5)_3$ and related catalyst systems require a lower amount of scavenger and are more stable compared to the $Ind_2ZrMe_2/B(C_6F_5)_3$ catalyst. Also the combination $Ind_2ZrCl_2/Al(i\text{-}Bu)_3$/indole-$B(C_6F_5)_3$ is an active catalyst system, thanks to the well known ability of alkylaluminum compouds in alkylating metallocene dichlorides by alkyl-halogen exchange. Also the triethylammonium salts generated by reaction between the pyrrole or indole–$B(C_6F_5)_3$ complexes and NEt_3 are active cocatalysts and show performance similar to that of the known $[PhNHMe_2]^+[B(C_6F_5)_4]^-$. In the case of the triethylammonium borate salts the proton source for the activation of the metal–methyl bond is the acidic $[HNEt_3]^+$, which generates methane, free triethylamine and the active ion pair as obtained on reactions of Schemes 36 and 37. The ammonium salts, however, generally shows slightly lower activity than the corresponding neutral B–N adducts, likely for the presence of triethylamine, which can compete with the olefin for coordination to the metal center [51].

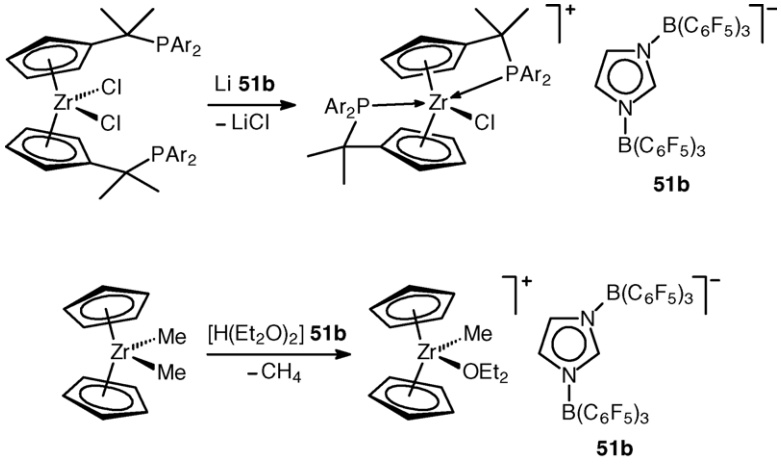


Scheme 38.

As expected, adduct 2-methylpyrroline–$B(C_6F_5)_3$ (**27**) and $B(C_6F_5)_3$ complexes of secondary amines (such as **12** and **14**) are not active, in agreement with their low Brønsted acidity, previously evidenced by the lack of NEt_3 deprotonation.

Imidazole–$B(C_6F_5)_3$ (**51**) is the most studied adduct among the borane derivatives of two-nitrogen containing heterocycles. Its cocatalytic activity resulted to be very low, almost nil, in combination with Ind_2ZrMe_2 in the copolyerization of ethylene/propylene [51]. **51** is enough acidic to protonate the metal–methyl bond in the metallocene precursor, however the basic nitrogen, free of borane, coordinates the metal center, and thus inhibits olefin coordination and polymer growth (Scheme 38) [44].

Differently, the diborate derivative **51b** is very active. It has been tested for the activation of $Me_2Si(\eta^5\text{-}Me_4C_5)(t\text{-}BuN)TiMe_2$ in the copolymerization of ethylene and 1-octene, revealing a much higher productivity in polymer than $B(C_6F_5)_3$. Compound **51b** has also the important advantage to be easy to synthesize, in addition to having good resistance towards hydrolysis and high temperatures [43].



Scheme 39.

Two metallocene-**51b** cation–anion pair derivatives were studied in solution by NMR techniques, the syntheses of these salts are report in Scheme 39. The metal cation is stabilized in both cases by neutral groups (intramolecularly by phosphine groups in the first reaction, and by a diethyl ether molecule in the second case) [52].

Diborate adducts of imidazole (**51b**), azide (**53b**), dicyanamide (**54b**), triazole (**55b**) and benzotriazole (**56b**) were described together with some other analogous derivatives in a patent of the Dow Chemical Company [46]. They all are monoanions, and are defined as "expanded anions" because of the delocalization of the anionic charge over a wide structure due to the electron-withdrawing effect of the perfluorinated rings, which, in fact, makes them weakly coordinating anions [53]. The counter cation is usually a tertiary ammonium having at least one long alkyl chain (such as dioctadecylmethylammonium), in order to improve the solubility of the activator in the reaction media. These cocatalysts can activate a suitable catalyst precursor analogously to $[PhNHMe_2]^+[B(C_6F_5)_4]^-$, [9] where it is the ammonium counter cation, a Brønsted acid, the responsible for the formation of the vacant site on the metal center. The diborate anion, which is a rather stable species, has the role to stabilize, but not to deactivate, the cationic metal during the polymerization process. These diborate derivatives have been successfully tested in propylene polymerization, ethylene/1-octene and ethylene/styrene copolymerization in combination with titanium or zirconium based catalysts [46].

9. Conclusions

Summing up, a new family of stable perfluoroarylborane–*N*-compound complexes has emerged in recent years, which have been proven useful as activators for olefin polymerization catalysts. Their stability and very simple synthesis and isolation make them attractive with respect to other activators, and certainly with respect to the parent borane itself, $B(C_6F_5)_3$. More basic studies are needed to evaluate, inter alia, the influence of the heterocycles on the thermal stability of the activated catalyst, its decay over time, and selectivity. Since the major limitation to the development of these activators is the high cost of $B(C_6F_5)_3$, other boranes with lower degree of fluorination, or other Lewis acids need also to be evaluated. One interesting development in this direction has been the recent disclosure of an alkylaluminum-bisindole complex that is also able to activate single-center catalysts [54].

Applications in other fields of homogeneous catalysis can be foreseen, but have still to be investigated.

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