

Formation and Characterization of Zwitterionic Stereoisomers from the Reaction of $B(C_6F_5)_3$ and NEt_2Ph : (*E*)- and (*Z*)-[$EtPhN^+ = CHCH_2 - B^-(C_6F_5)_3$]

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Keywords: Boranes / Aniline / Zwitterions / NMR spectroscopy

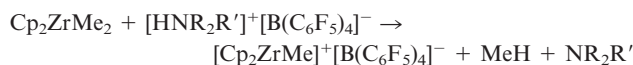
The stoichiometric reaction of $B(C_6F_5)_3$ and NEt_2Ph **I**, at room temperature, in an aromatic solvent, has been investigated by 1D and 2D NMR spectroscopy (1H , ^{11}B , ^{13}C , ^{15}N and ^{19}F). No $Et_2PhN \cdot B(C_6F_5)_3$ adduct was observed. An equilibrium between free $B(C_6F_5)_3$, NEt_2Ph , $[HB(C_6F_5)_3]^- [HNEt_2Ph]^+$ and two zwitterionic stereoisomers (*E*)- and (*Z*)-[$EtPhN^+ = CHCH_2 - B^-(C_6F_5)_3$] (30%) in an *E/Z* ratio of 3:2 was observed. Whatever the protic reagent $Z-OH$ [$Z = H, SiPh_3, (C-$

$C_5H_9)_7O_{12}Si_8$, or silanol group of silica], all the equilibria involved in solutions of **I** are quantitatively displaced towards the ionic form $[Z-O-B(C_6F_5)_3]^- [HNEt_2Ph]^+$. In the case of dimethylaniline, besides free $B(C_6F_5)_3$ and Me_2NPh , the 1:1 adduct $(C_6F_5)_3B \cdot NMe_2Ph$ and an iminium salt $[PhCH_3N = CH_2]^+ [HB(C_6F_5)_3]^-$ have been identified.

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Introduction

In homogeneous metallocene-based olefin polymerization catalysis, ammonium salts are known to activate neutral alkyl precursors into highly active metallocenium cations by irreversible protonolysis. These salts are generally composed of a tertiary ammonium cation $[HNR_2R']^+$ ($R = Me, Et$; $R' = Ph, Et$) and various non-coordinating anions such as metallocarboranes^[1] or borates.^[2–6] From the latter, the non-coordinating character of pentafluorophenylborates $\{[XB(C_6F_5)_3], X = -C_6F_5,^{[7]} -OH,^{[8]} -OR,^{[9]} (C-C_5H_9)_7O_{12}Si_8^{[10]}\}$, and their resistance towards anion decomposition, even though pentafluorophenylborates are far less stable towards decomposition when $X = OR$,^[11] have allowed the successful enhancement of the activity of metallocenium catalysts.^[12]



Interestingly, despite the fact that anilines are commonly used with tris(pentafluorophenyl)borane $[B(C_6F_5)_3]$ in the preparation of heterogeneous cocatalysts for olefin polymerization,^[13–16] no reports exist on the Lewis acid/base reactivity of such compounds in solution and the possible formation of aniline· $B(C_6F_5)_3$ adducts. Like boron trihalides,^[17,18] the strong Lewis acid $B(C_6F_5)_3$ is known to form stable adducts with amines or pyridines.^[19]

We report in this paper the results obtained by multinuclear 1D and 2D NMR spectroscopy (1H , ^{11}B , ^{13}C , ^{15}N , ^{19}F) on stoichiometric solutions of $B(C_6F_5)_3$ and NR_2Ph ($R = Et, Me$).

Results and Discussion

The addition of one equivalent of NEt_2Ph to $B(C_6F_5)_3$ in aromatic solvents led instantaneously to a pink coloration of the solution **I**. The ^{11}B NMR spectrum of **I** shows three resonance at $\delta = -13.7, -23.6$ and 60 ppm indicating the presence of at least three different species in the reaction mixture. In order to determine their structure, a study was performed using multinuclear 1H , ^{11}B , ^{13}C , ^{15}N and ^{19}F NMR spectroscopy.

In the 1H NMR spectrum of solution **I** (Figure 1), the major peaks at $\delta = 0.82$ (CH_3), 2.8 (CH_2) and $6.5–7$ ppm

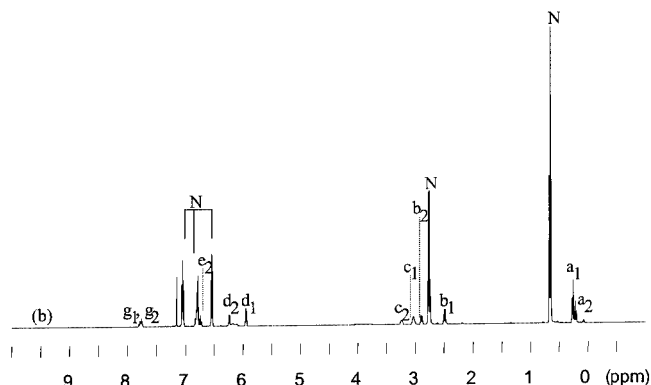


Figure 1. 1H NMR spectrum (500 MHz, 25 °C, C_6D_6) of solution **I**; N indicates peaks due to free Et_2NPh

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(aromatic protons) are characteristic of the free amine in solution. Additional peaks appear in the region of methyl (a_1 , a_2), methylene (b_1 , b_2 ; c_1 , c_2) and aromatic (d_1 , d_2 , e_2) protons. Two deshielded overlapping triplets (g_1 , g_2) and a very broad signal are also observed at $\delta = 7.8$ and 3.9 ppm, respectively. The intensities of these peaks, relative to those of the free amine, do not exceed 30%, and are sensitive to the concentration of the solution, suggesting the existence of an equilibrium or equilibria between NEt_2Ph and other species in solution. In all experiments, a ratio of 3:2 is observed for the areas of the peaks x_1/x_2 ($x = a-g$).

In the 2D-COSY NMR spectrum of **I** (Figure 2) the triplets a_1 and a_2 are correlated to the quadruplets b_1 and b_2 , respectively, supporting the fact that two different $-\text{CH}_2\text{-b-CH}_3\text{-a}$ fragments are present. A correlation is also detected between (c_1 , c_2) and (g_1 , g_2), indicating that the H_g protons are coupled to the $-\text{CH}_2\text{-c-X}$ fragments (Figure 2a). Analysis of the aromatic proton region of the spectrum (Figure 2b) shows the presence of two types of non-equivalent phenyl groups (in a d_1/d_2 ratio of 3:2). At lower levels, a weak correlation can be detected between the (b_1 , b_2) quadruplets and the (g_1 , g_2) triplets.

The solution ^{13}C NMR spectrum of **I** (Figure 3) shows the characteristic peaks for the methyl ($\delta = 11.4$ ppm), methylene ($\delta = 49.4$ ppm) and aromatic carbons ($\delta = 116\text{--}142$ ppm) of diethylaniline, as well as doublets representative of the pentafluorophenyl carbons ($\delta = 138\text{--}149$ ppm) of $\text{B}(\text{C}_6\text{F}_5)_3$. As in the ^1H NMR spectrum, two sets of additional peaks appear in the ^{13}C NMR spectrum of **I** for each methyl, methylene and aromatic carbon atom. Two new peaks are also present near $\delta = 190$ ppm that can be attributed to a $\text{C}=\text{Y}$ group, where Y is an electron-withdrawing center (O, N).

The upfield shift of the methyl and *ipso* carbons, as well as the downfield shifts of the methylene, *ortho* and *para* carbons of the diethylaniline (see Exp. Sect.) could indicate a protonation^[20,21] or a weakly coordinative interaction between NEt_2Ph and $\text{B}(\text{C}_6\text{F}_5)_3$, as described for other boron-aniline complexes.^[17]

More accurate structural information on the species present in **I** can be obtained by a ^1H - ^{13}C HSQC NMR experiment (Figure 4). The carbons of the methyl (a_1 , a_2) and methylene (b_1 , b_2) groups of the two $-\text{CH}_2\text{-b-CH}_3\text{-a}$ fragments can be assigned. The two broad methylene protons (c_1 , c_2) are correlated to a broad carbon resonance at $\delta = 34.5$ ppm, suggesting the proximity of a boron atom. The aromatic resonances associated with the *ortho* (d_1 , d_2), *meta* (e_1 , e_2) and *para* (f_1 , f_2) hydrogen atoms confirm the presence of two distinct phenyl groups in addition to the phenyl ring of the free aniline (Figure 4b). The two most deshielded carbons ($\delta = 190$ ppm) exhibit a correlation with the triplets (g_1 , g_2 , $\delta = 8$ ppm), supporting the presence of an $\text{H}_g\text{-C}=\text{Y}$ group ($\text{Y} = \text{O}, \text{N}$). In accordance with the results obtained by ^1H - ^1H COSY NMR experiments, the ^1H - ^{13}C HSQC NMR experiment confirms the existence of two different $-\text{CH}_2\text{-b-CH}_3\text{-a}$, phenyl and $\text{H}_g\text{-(C=Y)-CH}_2\text{-c-X}$ fragments.

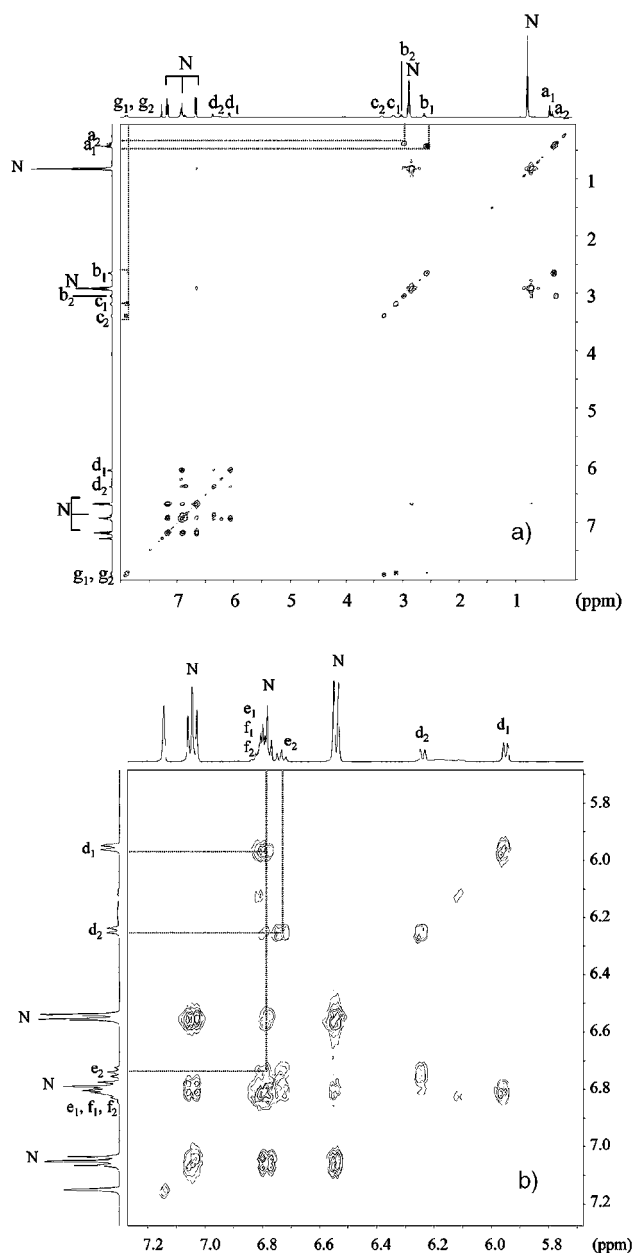


Figure 2. a) ^1H - ^1H COSY NMR spectrum (500 MHz, 25°C , C_6D_6) of solution **I**; b) expanded [$\delta = 7.2\text{--}5.7$ ppm] region

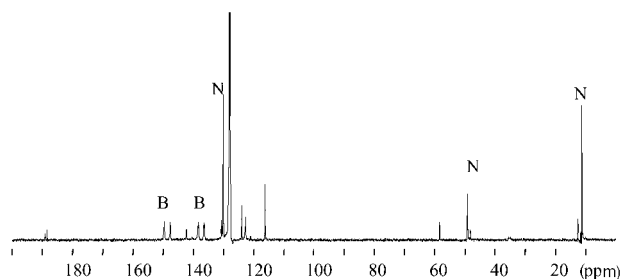


Figure 3. ^{13}C NMR spectrum (500 MHz, 25°C , C_6D_6) of solution **I**; N and B indicate peaks due to free Et_2NPh and $\text{B}(\text{C}_6\text{F}_5)_3$, respectively

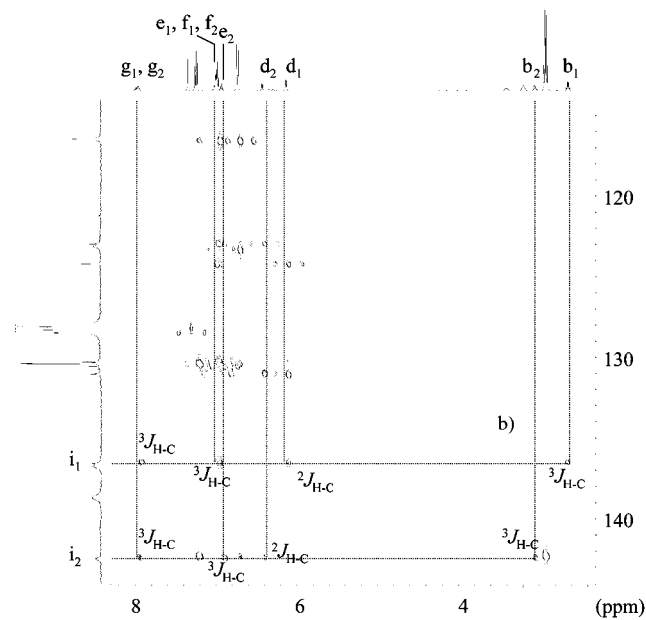
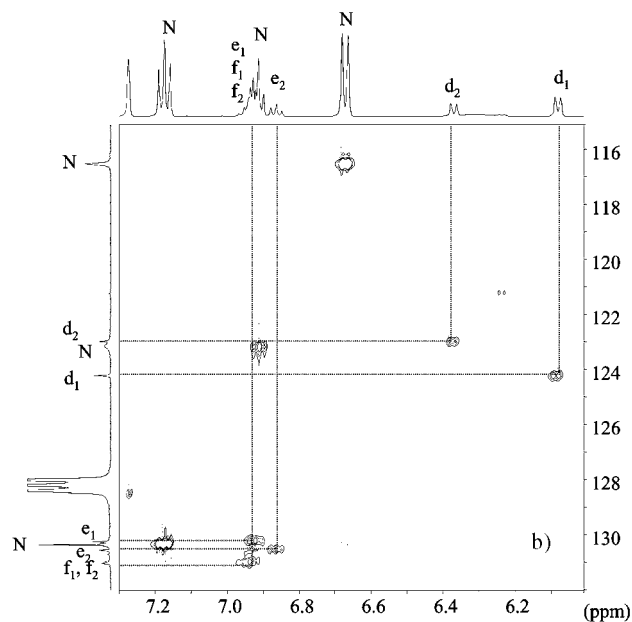
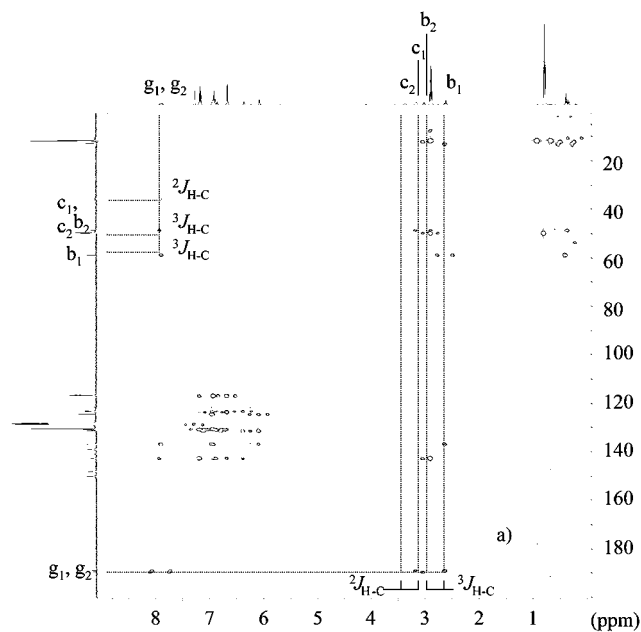
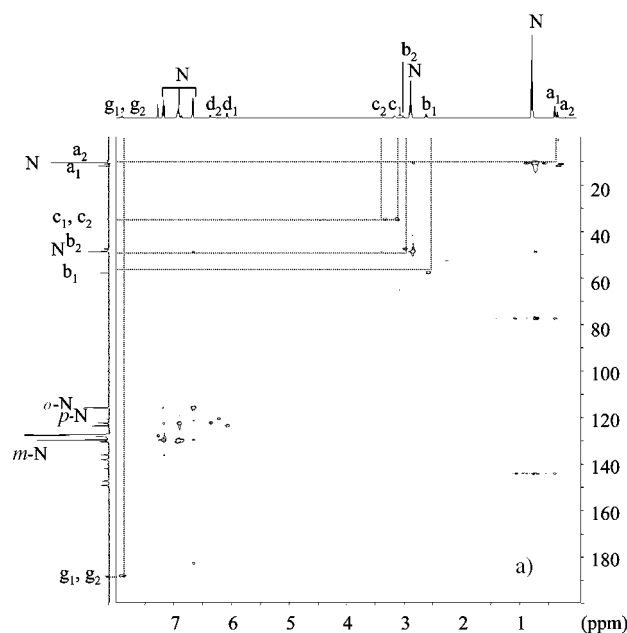


Figure 4. a) ^1H - ^{13}C HSQC NMR spectrum (500 MHz, 25 °C, C_6D_6) of solution **I**; b) expanded [$\delta = 7.3\text{--}6.0/\delta = 132\text{--}115$ ppm] region

Figure 5. a) ^1H - ^{13}C HMBC NMR spectrum (500 MHz, 25 °C, C_6D_6) of solution **I**; b) expanded [$\delta = 8.3\text{--}2.3/\delta = 144$ to -114 ppm] region

The ^1H - ^{13}C HMBC NMR experiments on **I** (Figure 5) allow the *ipso* carbons of the two distinct phenyl rings to be assigned (Figure 5b), and show their couplings with the methylene protons (b_1 , $b_2 - {}^3J_{\text{C-H}}$), with the deshielded triplets (g_1 , $g_2 - {}^3J_{\text{C-H}}$), and with aromatic *meta* (e_1 , $e_2 - {}^3J_{\text{C-H}}$) and *ortho* (d_1 , $d_2 - {}^2J_{\text{C-H}}$) hydrogens. The coupling between the deshielded triplets (g_1 , $g_2 - {}^3J_{\text{C-H}}$) and methylene protons (b_1 , $b_2 - {}^3J_{\text{C-H}}$) and, (c_1 , $c_2 - {}^2J_{\text{C-H}}$) is also evident (Figure 5a).

The ^{11}B NMR spectrum of **I** on a 300 MHz spectrometer shows two sharp peaks at $\delta = -13.7$ and -23.6 ppm, char-

acteristic of tetracoordinate anionic boron centers^[22] and a broad resonance at $\delta = 60$ ppm assigned to free $\text{B}(\text{C}_6\text{F}_5)_3$ ^[23–25] (Figure 6). No resonance characteristic of a $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{NET}_2\text{Ph}$ adduct is observed in the region between 0 and -5 ppm.^[22] The resonance at $\delta = -23.6$ ppm is unambiguously assigned to $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ due to the observed ^{11}B - ^1H coupling constant (${}^1J_{\text{B-H}} = 77.5$ Hz^[22,26]). This assignment is consistent with the presence of a broad signal at $\delta = 3.9$ ppm characteristic of the hydride^[27] in the ^1H NMR spectrum of **I**. The third resonance at $\delta = -13.7$ ppm is assigned by comparison to related

systems^[8,28–30] to a $[\text{R}-\text{B}(\text{C}_6\text{F}_5)_3]^-$ fragment (where R is an alkyl group with an sp^3 carbon bound to boron). The ^{11}B NMR spectrum of **I** on a 500 MHz spectrometer shows that there are two signals at $\delta = -13.1$ (B_2) and -13.5 ppm (B_1) in an approximate B_2/B_1 ratio of 2:5 (Figure 6). This indicates the presence of two types of anionic boron compound in which the boron atoms are located in very similar environments.

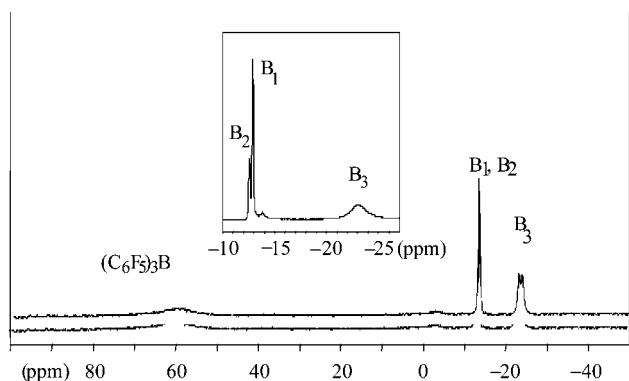


Figure 6. ^{11}B NMR spectrum (500 MHz, 25 °C, C_6D_6) of solution **I**

^1H - ^{11}B HMBC NMR experiments show a $^2J_{\text{B-H}}$ coupling between the $[\text{R}-\text{B}(\text{C}_6\text{F}_5)_3]^-$ boron atoms and the (c_1 , c_2) protons (Figure 7). In spite of the short T_2 of the quadrupolar ^{11}B nucleus, ^1H - ^{11}B HMBC experiments were attempted to confirm the linkage of the $-\text{CH}_2-\text{B}(\text{C}_6\text{F}_5)_3$. The quality of the 2D matrix was surprisingly good and allowed us to attribute the broad resonances c_1 and c_2 in the ^1H ($\delta_{\text{c}_1} = 3.15$, $\delta_{\text{c}_2} = 3.45$ ppm) and ^{13}C NMR spectra ($\delta_{\text{c}_1, \text{c}_2} = 34.5$ ppm) to be attributed to the $-\text{CH}_2-\text{B}(\text{C}_6\text{F}_5)_3$ moieties.^[30–32] A $^3J_{\text{B-H}}$ coupling of the $[-\text{CH}_2-\text{B}(\text{C}_6\text{F}_5)_3]^-$ boron atoms with the (g_1 , g_2) protons is an additional proof for the structure of $H-(\text{C}=\text{X})-\text{CH}_2-\text{B}(\text{C}_6\text{F}_5)_3$. Furthermore, a third coupling is observed between the major boron resonance B_1 and the methylene protons b_1 , while there is no correlation between B_2 and the methylene protons b_2 .

^1H - ^{15}N HMBC NMR experiments indicate that three different nitrogen resonances are present at $\delta = 74$, 209.5 and 210.2 ppm (Figure 8 and 9). The major peak at $\delta = 74$ ppm (N) corresponds to the nitrogen atom of NEt_2Ph . The resonances at $\delta = 209.5$ for (N_1) and $\delta = 210.2$ ppm (N_2) are characteristic of an sp^2 -hybridized nitrogen atom, such as an iminium center.^[22] Correlations are observed between these peaks and the methyl (a_1 , $\text{a}_2 - ^3J_{\text{N-H}}$), the methylene (b_1 , $\text{b}_2 - ^2J_{\text{N-H}}$; c_1 , $\text{c}_2 - ^3J_{\text{N-H}}$), the *ortho* (d_1 , $\text{d}_2 - ^3J_{\text{N-H}}$) and imino (g_1 , $\text{g}_2 - ^2J_{\text{N-H}}$) protons, indicating the existence of two types of iminium center in slightly different environments, as observed in the ^{11}B NMR spectrum.

The ^{19}F NMR spectrum of **I** reveals a complex pattern of non-equivalent pentafluorophenyl groups at ambient temperature, three types of pentafluorophenyl ligand (**a**, **b**, **c**) bound to anionic boron centers are present^[32] (Table 1). No pentafluorobenzene is formed in solution.

Thus, multinuclear NMR studies indicate that in solutions containing equimolar amounts of $\text{B}(\text{C}_6\text{F}_5)_3 + \text{NEt}_2\text{Ph}$

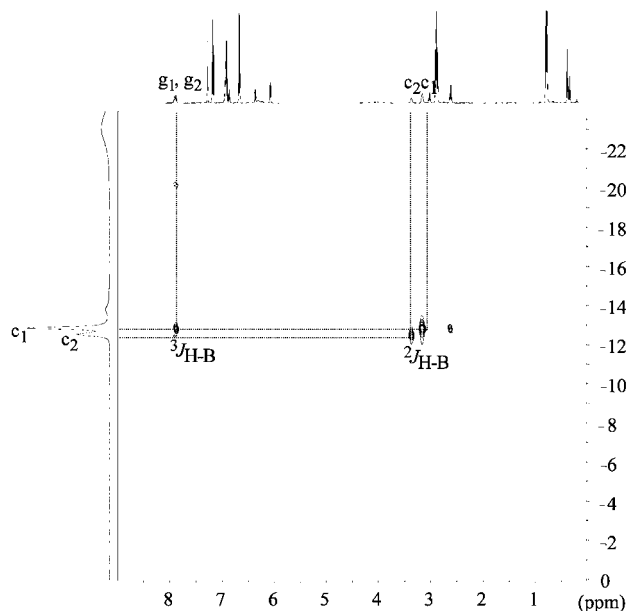


Figure 7. ^1H - ^{11}B NMR HMBC NMR spectrum (500 MHz, 25 °C, C_6D_6) of solution **I**

(**I**) at ambient temperature, several species are present: $\text{B}(\text{C}_6\text{F}_5)_3$, NEt_2Ph , $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ (HNEt_2Ph)⁺ and two new species (**A**₁, **A**₂ in Scheme 1) in a constant A_1/A_2 ratio of 3:2. In none of the experiments is formation of the $(\text{C}_6\text{F}_5)_3\text{B} \cdot \text{NEt}_2\text{Ph}$ adduct observed. The zwitterionic stereoisomeric species **A**₁ (*E* isomer) and **A**₂ (*Z* isomer) come closest to explaining the 2D NMR experimental data.

In the ^1H - ^{11}B HMBC NMR spectra, the long range coupling between the boron resonance B_1 and the methylene protons b_1 is only possible for the *trans*-isomer **A**₁ (*E* isomer) in a particular conformation. According to the relative intensities of the peaks associated with **A**₁ in the ^1H , ^{11}B and ^{15}N NMR spectra, this result definitively proves that **A**₁ (*E* isomer) is the major species, as expected on the basis of steric considerations.

Multinuclear NMR studies performed on **I** at ambient temperature enable the other boron species, besides unchanged $\text{B}(\text{C}_6\text{F}_5)_3$, to be identified as $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ and the two stereoisomers **A**₁ and **A**₂ of $[\text{RCH}_2-\text{B}(\text{C}_6\text{F}_5)_3]^-$. The formation of the $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ anion can be explained by a reversible abstraction of the α -hydrogen from NEt_2Ph by $\text{B}(\text{C}_6\text{F}_5)_3$ affording the iminium cations (**B**) (reaction 1 in Scheme 2). This hydride abstraction by $\text{B}(\text{C}_6\text{F}_5)_3$ could be facilitated by conjugation with the lone pair of the nitrogen atom, and has already been reported for organic substrates^[33] and for organometallic complexes.^[26,27] However, there is no evidence for the presence of the iminium cations (**B**) in solution. It is likely that, in the presence of NEt_2Ph , the iminium salt (**B**) initially formed is rapidly converted into enamine (**C**) and an anilinium salt (reaction 2, Scheme 2). The conversion of tertiary iminium salts into enamines in presence of a base is well documented.^[34] At this stage, an electrophilic addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to the enamine intermediate yields the zwitterions (**A**₁, **A**₂) (reaction

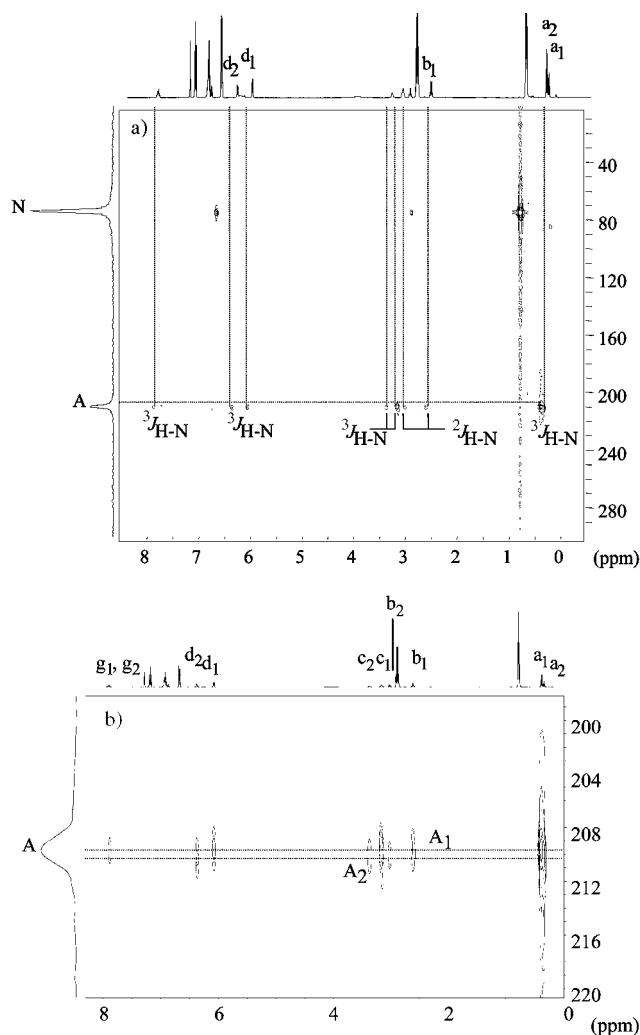


Figure 8. a) ^1H - ^{15}N NMR HMBC NMR spectrum (500 MHz, 25 °C, C_6D_6) of solution I; b) expanded $[\delta = 199\text{--}220\text{ ppm}]$ region

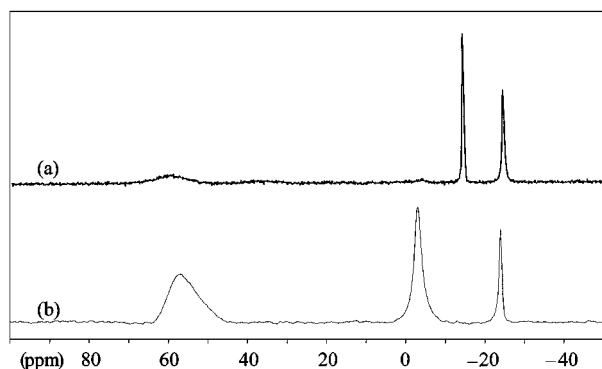


Figure 9. ^{11}B NMR spectrum (300 MHz, 25 °C, C_6D_6) of: a) solution I; b) solution I_{Me}

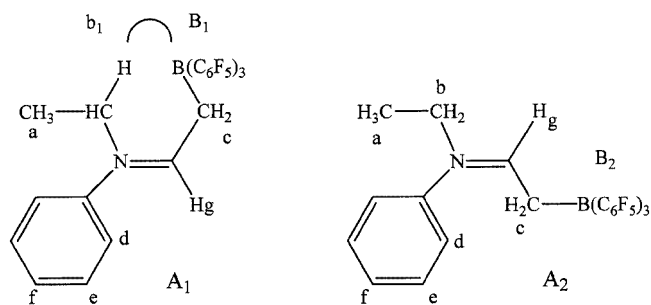
3, Scheme 2), as already reported for other Lewis acids such as GeCl_4 , SnCl_4 ,^[35] and TiCl_4 .^[36,37]

The involvement of the iminium ion (B) as an intermediate is demonstrated by using dimethylaniline as a base

Table 1. ^{19}F NMR chemical shifts of C_6F_5 ligands in I

Attribution	Chemical shifts ^[a]			$\Delta(\delta_{m,p})$
	<i>o</i> - C_6F_5	<i>p</i> - C_6F_5	<i>m</i> - C_6F_5	
$\text{B}(\text{C}_6\text{F}_5)_3$ ^[b]	-128.7	-141.7	-160.0	18.3
a ^[b]	-132.6	-158.6	-164.8	6.2
b ^[b]	-132.2	-159.5	-164.3	4.8
c ^[b]	-133.5	-161.2	-165.4	4.2

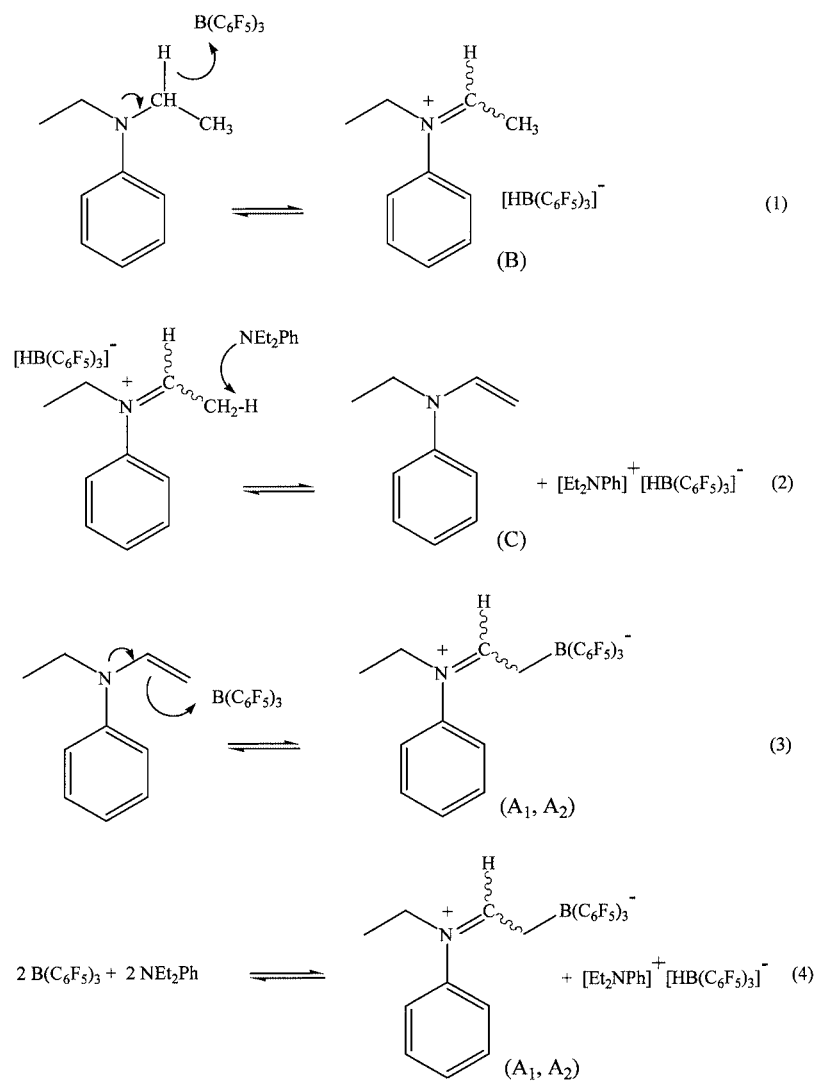
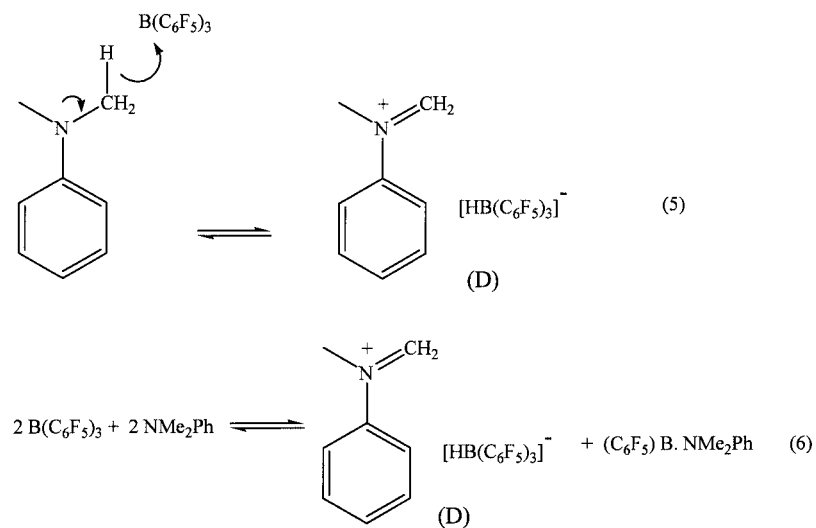
[a] δ in ppm. [b] At 25 °C in C_6D_6 .



Scheme 1. Structure of the two stereoisomers (A_1) and (A_2) present in solution I

instead of diethylaniline. The reaction of equimolar amounts of $\text{B}(\text{C}_6\text{F}_5)_3$ and NMe_2Ph in concentrated $[\text{D}_6]\text{benzene}$ solution was monitored by ^{11}B NMR spectroscopy at room temperature. The spectra of the pale pink solution of I_{Me} show the presence of a sharp peak at $\delta = -24\text{ ppm}$ characteristic of the $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ anion. This indicates the formation of the iminium (B_{Me}) by α -hydrogen abstraction with $\text{B}(\text{C}_6\text{F}_5)_3$ (reaction 5, Scheme 3). It should be noted that there is also a peak at $\delta = -3\text{ ppm}$ which is assigned to the Lewis acid-base complex $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{NMe}_2\text{Ph}$ (V). The fact that no peak characteristic of zwitterions A_1 and A_2 is present at $\delta = -13\text{ ppm}$ proves that electrophilic addition of $\text{B}(\text{C}_6\text{F}_5)_3$ does not proceed for dimethylaniline. This can be rationally explained by the fact that formation of an enamine intermediate is not possible in the case of dimethylaniline. Thus, the reaction pathway is stopped at the stage of the formation of the ternary iminium salt (B_{Me}).

The overall equilibria observed in solutions I and I_{Me} are summarized in reaction 4 (Scheme 2) and reaction 6 (Scheme 3) respectively. It should be noted that in the ^{11}B NMR spectrum of I (Figure 9) the intensity ratio of 1:0.9 between the two sharp peaks at $\delta = -13.7$ and -23.6 ppm , that is $[\text{CH}_2\text{-B}(\text{C}_6\text{F}_5)_3]^-/[\text{HB}(\text{C}_6\text{F}_5)_3]^-$, is in good agreement with the stoichiometry expected from reaction 4 in Scheme 2. However, in all cases, the reaction of R-OH compounds [$\text{R} = \text{H}$, Ph_3Si , $(\text{c-C}_5\text{H}_9)_7\text{O}_{12}\text{Si}$ or silanol group of silica] with $[\text{B}(\text{C}_6\text{F}_5)_3 + \text{NEt}_2\text{Ph}]$ solutions leads quantitatively to the formation of $[\text{RO-B}(\text{C}_6\text{F}_5)_3]^- (\text{HNEt}_2\text{Ph})^+$ confirming that all equilibria involved in solutions of I are displaced towards the ionic form $[\text{RO-B}(\text{C}_6\text{F}_5)_3]^- (\text{HNEt}_2\text{Ph})^+$ in the presence of protic compounds.^[39]

Scheme 2. Proposed mechanism to explain the formation of stereoisomers (A₁) and (A₂)Scheme 3. Structure of the compounds of the reaction of $B(C_6F_5)_3$ and Me_2NPh , solution **I_{Me}**

Conclusion

The presence of several species in equilibrium in a solution of $(\text{C}_6\text{F}_5)_3\text{B}$ and R_2NPh (1: 1) has been established by several NMR experiments. In the case of dimethylaniline, besides free $\text{B}(\text{C}_6\text{F}_5)_3$ and Me_2NPh , the 1:1 adduct $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{NMe}_2\text{Ph}$ and an iminium salt $[\text{PhCH}_3\text{N}=\text{CH}_2]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ have been identified. With diethylaniline, 40% of the products were unchanged $(\text{C}_6\text{F}_5)_3\text{B}$ and Et_2NPh , 30% were the iminium salt $[\text{HB}(\text{C}_6\text{F}_5)_3]^-[\text{HNEt}_2\text{Ph}]^+$, and the remaining 30% were converted into the zwitterionic stereoisomers (*E*)- and (*Z*)- $[\text{PhEtN}^+=\text{CH}-\text{CH}_2\text{B}^-(\text{C}_6\text{F}_5)_3]$ in a 3:2 ratio. In the presence of a protic compound this equilibrium is totally displaced towards the ionic form $[\text{RO}-\text{B}(\text{C}_6\text{F}_5)_3]^-[\text{HNEt}_2\text{Ph}]^+$.

Experimental Section

All operations were carried out under an argon atmosphere using glovebox (Jacomex or MBraun) or vacuum-line techniques. Toluene and pentane were distilled under argon from Na/K alloy, degassed and stored under argon over Na (toluene) or 3 Å molecular sieves (pentane). C_6D_6 (SDS – 99.6%) and CD_2Cl_2 (SDS – 99.6%) were degassed by three “freeze-pump-thaw” cycles and dried over freshly regenerated 3 Å molecular sieves. NEt_2Ph (Aldrich Chemicals, 98%) and NMe_2Ph (Aldrich Chemicals, 99%) were dried over KOH, distilled under vacuum and used immediately. $\text{B}(\text{C}_6\text{F}_5)_3$ (Merck Chemicals, > 97%) was dried using Me_3SiCl ,^[38] purified by vacuum sublimation and controlled by ^{19}F NMR spectroscopy before use. The NMR spectra were recorded with Bruker AC 200 MHz (^{19}F), AC 300 MHz (^1H , ^{13}C), DRX 300 MHz (^{11}B) and DRX 500 MHz (^1H , ^{13}C , ^{11}B , ^{15}N 2D NMR) spectrometers. Chemical shifts are reported in ppm and referenced to residual solvent resonances (C_6D_6 : $\delta = 7.15$ ppm for ^1H , $\delta = 128$ ppm for ^{13}C ; CD_2Cl_2 : $\delta = 5.32$ ppm for ^1H , $\delta = 53.8$ ppm for ^{13}C), or external standards (^{19}F : CFCl_3 ; ^{11}B : $\text{BF}_3\cdot\text{OEt}_2$; ^{15}N : *N,N*-dimethylformamide).

2D COSY experiments were acquired with the standard Bruker COSYgp experiment and processed in absolute mode. 2D HSQC experiment were acquired with the standard Bruker inviegt experiment and processed in phases mode. 2D HMBC experiment were acquired with the standard Bruker inv4gplnd and processed in absolute mode, as shown in Table 2.

Table 2. Standard parameters for the 2D NMR experiments

	$^1\text{H}-^{13}\text{C}$	$^1\text{H}-^{15}\text{N}$	$^1\text{H}-^{11}\text{B}$
D6	50ms	100 ms	25 ms
Gradients	20–20–10	70–30–50	60–20–6567
Row data size	4096×1024	4096×256	2048×512

Reactions of Equimolar Amounts of $[\text{B}(\text{C}_6\text{F}_5)_3+\text{NEt}_2\text{Ph}]$ (I) and $[\text{B}(\text{C}_6\text{F}_5)_3+\text{NMe}_2\text{Ph}]$ (I_{Me})

Preparation of I: In an NMR tube, $\text{B}(\text{C}_6\text{F}_5)_3$ (75 mg, 0.15 mmol) was dissolved in 0.4 mL of C_6D_6 . NEt_2Ph (23.3 μL , 0.15 mmol) was then added with a syringe to give a pink solution after agitation.

NEt_2Ph : ^1H NMR (C_6D_6): $\delta = 7.17$ (dd, $^3J_{\text{H-H}} = 7.9$ Hz, 2 H, *m*- C_6H_5), 6.9 (t, $^3J_{\text{H-H}} = 7.2$ Hz, 1 H, *p*- C_6H_5), 6.66 (d, $^3J_{\text{H-H}} =$

8.2 Hz, 2 H, *o*- C_6H_5), 2.80 (q, $^3J_{\text{H-H}} = 7.1$ Hz, 4 H, CH_2), 0.82 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 6 H, CH_3) ppm. ^{13}C NMR: $\delta = 142.4$ (s, *i*- C_6H_5), 130.3 (s, *m*- C_6H_5), 123.1 (br. s, *p*- C_6H_5), 116.4 (s, *o*- C_6H_5), 49.4 (s, CH_2), 11.4 (s, CH_3) ppm. ^{15}N NMR: $\delta = 71$ (s, NEt_2Ph) ppm.

$\text{B}(\text{C}_6\text{F}_5)_3$: ^{11}B NMR: $\delta = 59$ (br. s, $\text{B}(\text{C}_6\text{F}_5)_3$) ppm. ^{13}C NMR: $\delta = 148.8$ (d, $^1J_{\text{C-F}} = 243$ Hz, *o*- C_6F_5), 141.5 (d, $^1J_{\text{C-F}} = 230$ Hz, *p*- C_6F_5), 137.7 (d, $^1J_{\text{C-F}} = 247$ Hz, *m*- C_6F_5) ppm. ^{19}F NMR: $\delta = -128.6$ (br. s, 6 F, *o*- C_6F_5), -141.7 (br. s, 3 F, *p*- C_6F_5), -160.0 (br. s, 6 F, *m*- C_6F_5) ppm.

[A₁, (*E*)-isomer]: ^1H NMR (20%): $\delta = 7.88$ (t, $^3J_{\text{H-H}} = 7.9$ Hz, 1 H, $\text{H}-\text{C}=\text{N}$), 6.92 (m, *m*- and *p*- C_6H_5), 6.17 (d, $^3J_{\text{H-H}} = 7.2$ Hz, 2 H, *o*- C_6H_5), 3.15 (br. m, 2 H, $\text{CH}_2\text{-B}$), 2.60 (q, $^3J_{\text{H-H}} = 7.25$ Hz, 2 H, CH_2), 0.40 (t, $^3J_{\text{H-H}} = 7.2$ Hz, 3 H, CH_3) ppm. ^{11}B NMR: $\delta = -12.9$ (s, $[-\text{CH}_2\text{-B}(\text{C}_6\text{F}_5)_3]^-$) ppm. ^{13}C NMR: $\delta = 188.6$ (s, $\text{C}=\text{N}$), 136.5 (s, *i*- C_6H_5), 131 (s, *m*- C_6H_5), 130.2 (s, *p*- C_6H_5), 124.2 (s, *o*- C_6H_5), 58.5 (s, CH_2), 34.5 (br. $\text{CH}_2\text{-B}$), 12.7 (s, CH_3) ppm; C_6F_5 signals not resolved. ^{15}N NMR: $\delta = 209.5$ (s, $\text{EtPhN}^+=\text{CH}-$) ppm. ^{19}F NMR: $\delta = -132.6$ (d, $^3J_{\text{F-F}} = 19$ Hz, 6 F, *o*- C_6F_5), -158.6 (br. s, 3 F, *p*- C_6F_5), -164.8 (br. s, 6 F, *m*- C_6F_5) ppm.

[A₂, (*Z*)-isomer]: ^1H NMR (10%): $\delta = 7.91$ (t, $^3J_{\text{H-H}} = 8.5$ Hz, 1 H, $\text{H}-\text{C}=\text{N}$), 6.92 (m, *m*- C_6H_5), 6.85 (t, $^3J_{\text{H-H}} = 7.7$ Hz, 1 H, *p*- C_6H_5), 6.36 (d, $^3J_{\text{H-H}} = 7.9$ Hz, 2 H, *o*- C_6H_5), 3.45 (br. m, 2 H, $\text{CH}_2\text{-B}$), 3.10 (q, $^3J_{\text{H-H}} = 7.4$ Hz, 2 H, CH_2), 0.35 (t, $^3J_{\text{H-H}} = 7.2$ Hz, 3 H, CH_3) ppm. ^{11}B NMR: $\delta = -12.6$ (s, $[-\text{CH}_2\text{-B}(\text{C}_6\text{F}_5)_3]^-$) ppm. ^{13}C NMR: $\delta = 189.2$ (s, $\text{C}=\text{N}$), 142.4 (s, *i*- C_6H_5), 130.9 (s, *m*- C_6H_5), 130.5 (s, *p*- C_6H_5), 122.9 (s, *o*- C_6H_5), 48.3 (s, CH_2), 34.5 (br. $\text{CH}_2\text{-B}$), 11.8 (s, CH_3) ppm; C_6F_5 signals not resolved. ^{19}F NMR: $\delta = -132.6$ (d, $^3J_{\text{F-F}} = 19$ Hz, 6 F, *o*- C_6F_5), -158.6 (br. s, 3 F, *p*- C_6F_5), -164.8 (br. s, 6 F, *m*- C_6F_5) ppm. ^{15}N NMR: $\delta = 210.2$ (s, $\text{EtPhN}^+=\text{CH}-$) ppm.

$[\text{HB}(\text{C}_6\text{F}_5)_3]^-$: ^1H NMR: $\delta = 3.90$ (br, 1 H) ppm. ^{11}B NMR: $\delta = -23.6$ (d, $^1J_{\text{B-H}} = 77.5$ Hz) ppm. ^{19}F NMR: $\delta = -132.2$ (d, $^3J_{\text{F-F}} = 22$ Hz, 6 F, *o*- C_6F_5), -159.5 (t, $^3J_{\text{F-F}} = 22$ Hz, 3 F, *p*- C_6F_5), -164.3 (m, 6 F, *m*- C_6F_5) ppm; $\delta = -133.5$ (br. m, 6 F, *o*- C_6F_5), -161.2 (br. m, 3 F, *p*- C_6F_5), -165.4 (br. m, 6 F, *m*- C_6F_5) ppm.

Preparation of I_{Me}: In an NMR tube, $\text{B}(\text{C}_6\text{F}_5)_3$ (97 mg, 0.19 mmol) was dissolved in 0.4 mL of C_6D_6 . NMe_2Ph (24 μL , 0.19 mmol) was then added with a syringe to give a pale pink solution.

NMe_2Ph : ^1H NMR: $\delta = 7.31$ (dd, $^3J_{\text{H-H}} = 7.0$ Hz, 2 H, *m*- C_6H_5), 6.88 (t, $^3J_{\text{H-H}} = 7.0$ Hz, 1 H, *p*- C_6H_5), 6.72 (d, $^3J_{\text{H-H}} = 8.5$ Hz, 2 H, *o*- C_6H_5), 2.62 (s, 3 H, CH_3) ppm. ^{15}N NMR: $\delta = 43.7$ (s, NMe_2Ph) ppm.

$(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{NMe}_2\text{Ph}$: ^1H NMR: $\delta = 7.17$ (d, $^3J_{\text{H-H}} = 8.5$ Hz, 2 H, *o*- C_6H_5), 6.8 (t, $^3J_{\text{H-H}} = 8.2$ Hz, 1 H, *p*- C_6H_5), 6.67 (t, $^3J_{\text{H-H}} = 8.4$ Hz, 2 H, *m*- C_6H_5), 2.55 (s, 6 H, CH_3) ppm. ^{11}B NMR: $\delta = -2.9$ (s, $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{NMe}_2\text{Ph}$) ppm. ^{15}N NMR: $\delta = 52.3$ [s, $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{NMe}_2\text{Ph}$] ppm. ^{19}F NMR: $\delta = -132.7$ (d, $^3J_{\text{F-F}} = 20$ Hz, 6 F, *o*- C_6F_5), -159.1 (t, $^3J_{\text{F-F}} = 20$ Hz, 3 F, *p*- C_6F_5), -165.4 (m, 6 F, *m*- C_6F_5) ppm.

$[\text{PhMe}(\text{N}=\text{CH}_2)]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$: ^{11}B NMR: $\delta = -23.9$ (s, $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$) ppm. ^{19}F NMR: $\delta = -132.1$ (d, $^3J_{\text{F-F}} = 22$ Hz, 6 F, *o*- C_6F_5), -159.7 (t, $^3J_{\text{F-F}} = 22$ Hz, 3 F, *p*- C_6F_5), -164.4 (m, 6 F, *m*- C_6F_5); $\delta = -133.3$ (br. m, 6 F, *o*- C_6F_5), -161.6 (br. m, 3 F, *p*- C_6F_5), -165.4 (br. m, 6 F, *m*- C_6F_5) ppm.

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