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Synthesis and Reactivity of $(C_6F_5)_3B-N$-Heterocycle Complexes. 1. Generation of Highly Acidic sp^3 Carbons in Pyrroles and Indoles

Simona Guidotti,[†] Isabella Camurati,[†] Francesca Focante,[‡] Luca Angellini,[‡] Gilberto Moscardi,[†] Luigi Resconi,*[,†] Rino Leardini,[‡] Daniele Nanni,[‡] Pierluigi Mercandelli,[§] Angelo Sironi,[§] Tiziana Beringhelli,[#] and Daniela Maggioni[#]

Basell Polyolefins, Centro Ricerche G. Natta, I-44100 Ferrara, Italy; Dipartimento di Chimica Organica "A. Mangini", Università di Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy; and Dipartimento di Chimica Strutturale e Stereochimica Inorganica and Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Università di Milano, Via Venezian 21, I-20133 Milano, Italy

luigi.resconi@basell.com

Received October 14, 2002

The reaction of pyrroles and indoles with $B(C_6F_5)_3$ and BCl_3 produces 1:1 B−N complexes containing highly acidic sp^3 carbons, for example, *N*-[tris(pentafluorophenyl)borane]−5*H*-pyrrole (**1**) and *N*-[tris-(pentafluorophenyl)borane]−3*H*-indole (**2**), that are formed by a new formal N-to-C hydrogen shift, the mechanism of which is discussed. With some derivatives, restricted rotation around the B−N bond and/or the B−C bonds was observed by NMR techniques, and some rotational barriers were calculated from experimental data. The acidity of the sp^3 carbons in these complexes is shown by their ability to protonate NEt_3, with formation of pyrrolyl- and indolyl-borate ammonium salts. The driving force for this reaction is given by the restoration of the aromaticity of the heterocycle.

Introduction

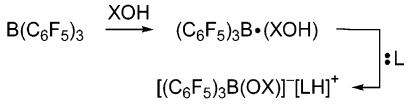
There has recently been a growing interest in the chemistry of perfluoroarylboranes, due to both their high Lewis acidity and chemical stability.[1−4]

The Lewis acidity of $B(C_6F_5)_3$ can be converted into Brønsted acidity by complexation with water or alcohols (Scheme 1). The complexity of the water−$B(C_6F_5)_3$ system has been recently investigated in detail.[5] The acidity of boron-coordinated XOH has been demonstrated and applied to catalytic reactions.[6,7]

On the other hand, there is little known about aryl borane/secondary amine complexes and of how the reactivity of the *N*-bound proton would be affected by coordination of the same nitrogen to a highly Lewis acidic borane such as $B(C_6F_5)_3$. Recently, Klosin and co-workers at Dow have reported the coordination of 2 equiv of $B(C_6F_5)_3$ to imidazole and the formation of delocalized, stable bis[$B(C_6F_5)_3$]−imidazolate complexes, by reaction with amines.[8] They also have shown that the pyrrole−$B(C_6F_5)_3$ complex, although neither isolated nor characterized, is able to protonate triethylamine, with formation of the [(pyrrolyl)$B(C_6F_5)_3$]$^-$[$HNEt_3$]$^+$ salt.

Erker has synthesized the 5*H*-pyrrole−$B(C_6F_5)_3$ complex, **1**, by protonation of the Li salt of the [B(1-pyrrolyl)-$(C_6F_5)_3$] borate (Scheme 2). The C5 methylene group of **1** is sufficiently acidic to protonate a CH_3 of the metallocene dimethyl catalyst with formation of methane, the [B(1-pyrrolyl)$(C_6F_5)_3$] borate anion, and the metallocenium methyl cation.[9]

SCHEME 1



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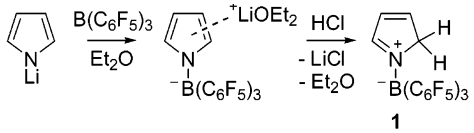

[†] Basell Polyolefins.
[‡] Università di Bologna.
[§] Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano.
[#] Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Università di Milano.

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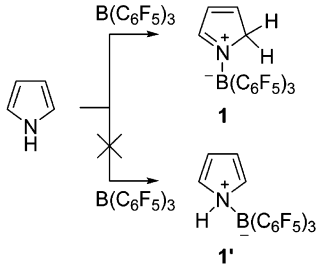
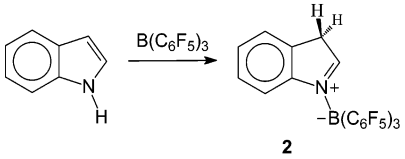
10.1021/jo020647x CCC: $25.00
Published on Web 06/18/2003

SCHEME 3



SCHEME 4



Piers and co-workers recently reported the synthesis and structural features of imine−$B(C_6F_5)_3$ complexes, notably the restricted rotation around the N−B bond.[10]

In an independent investigation, we have found that **1** and related B−N complexes can be obtained directly by complexation between $B(C_6F_5)_3$ and aromatic, five-membered *NH*-heterocycles, such as indole and pyrrole, by a new reaction that produces B−N complexes with highly acidic sp^3 CH.[11] In this paper we describe the synthesis, characterization, and origin of the high acidity of such complexes, which is unparalleled in known borane−imine complexes.

Results and Discussion

Synthesis and Characterization of Borane−Pyrrole and Borane−Indole Complexes. Reaction of pyrrole with 1 equiv of $B(C_6F_5)_3$ in pentane, toluene, Et_2O, or CH_2Cl_2 gives quantitative and instantaneous conversion to the 5*H*-pyrrole−$B(C_6F_5)_3$ complex, **1** (Scheme 3).

The fact that complexation of pyrrole with $B(C_6F_5)_3$ does not give the tetrahedral B−NHC_4H_4 complex **1′** is demonstrated by its ^{1}H NMR spectrum, which shows (in CD_2Cl_2) a diagnostic, broad singlet (2H) at 4.7 ppm for the C5 methylene and three peaks for the three vinylic protons at 8.6 (H2, m), 7.9 (H4, dq), and 6.9 (H3, dq) ppm. NOESY experiments and single-crystal X-ray diffraction confirmed the structure of complex **1** as being identical to that reported by Erker and ruled out the formation of the 3*H*-pyrrole−$B(C_6F_5)_3$ complex. Therefore **1** can be conveniently obtained by one-step direct complexation of pyrrole and $B(C_6F_5)_3$, thus avoiding both previous deprotonation of the heterocycle and final protonation of Erker's [(1-pyrrolyl)$B(C_6F_5)_3$]Li reagent.[9]

Analogously, indole reacts with $B(C_6F_5)_3$ in toluene, Et_2O, or CH_2Cl_2 to give quantitative and instantaneous conversion to the 3*H*-indole−$B(C_6F_5)_3$ complex **2** (Scheme 4).

Unlike **1**, the spectrum of which does not change even when the temperature is lowered to 173 K, the ^{1}H NMR spectrum of **2** shows significant changes in the range from 360 to 271 K. At the lowest temperature, the C3 methylene gives rise to a clean AB-type spectrum that clearly indicates restricted rotation around the B−N bond and/or the B−C bonds. This behavior will be discussed further on. The structure of **2** was confirmed by a single-crystal X-ray analysis (see Solid State Structure section).

Both **1** and **2** are formed quantitatively and instantaneously, irrespective of the solvent or the order of addition (see Experimental Section for details). It is worth noting that **2** is stable in air for several days.

CHART 1

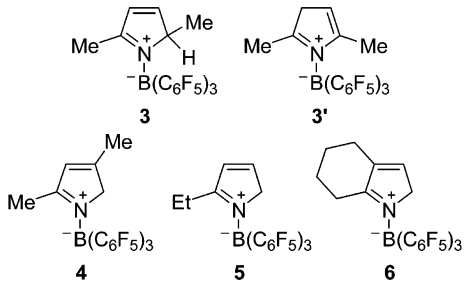
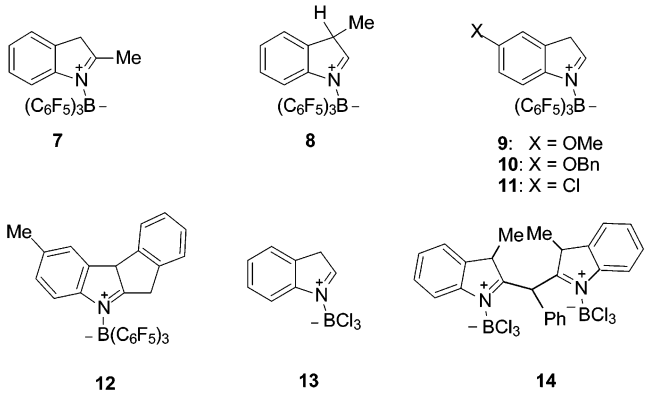


CHART 2



Several other pyrrole− (Chart 1) and indole−borane (Chart 2) complexes were synthesized in nearly quantitative yields. 2,5-Dimethylpyrrole−$B(C_6F_5)_3$ (**3**) also contained ∼10% of the 3*H*-isomer **3′**. The ^{1}H NMR spectra of the pyrrole−$B(C_6F_5)_3$ complexes **4**−**6**, contrary to the ^{1}H NMR spectrum of **1**, show a broad AB-system for the methylene group in the α-position to the nitrogen atom, indicating the presence of stereolabile conformational enantiomers.

The reaction between $B(C_6F_5)_3$ and 2-methyl- or 3-methylindole cleanly gave the related 2-methyl- (**7**) and 3-methyl-3*H*-indole−$B(C_6F_5)_3$ (**8**) complexes. Complex **7** is already "frozen" at room temperature, showing at 297 K a clear AB-type spectrum for the C3 methylene. At about the same temperature (291 K), complex **8** clearly shows two diastereoisomeric species. Other indole derivatives (**9**−**12**) behave analogously.

BCl_3, which has Lewis acidity comparable to that of $B(C_6F_5)_3$,[3,5,12] reacts with indole to give 3*H*-indole−BCl_3 (**13**), the structure of which was assigned by analogy with that of **2**, due to the presence of the diagnostic methylene signal, in this case a singlet at 4.3 ppm (CD_2Cl_2).

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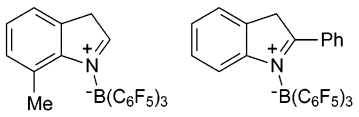
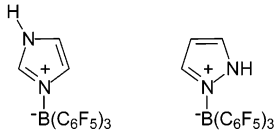
CHART 3



15 **16**

CHART 4



17 **18**

The reaction between $B(C_6H_5)_3$ and indole did not afford any adduct, due to the weak Lewis acidity of triphenylborane; on the contrary, BF_3 reacted with indole, but no characterizable products were obtained.

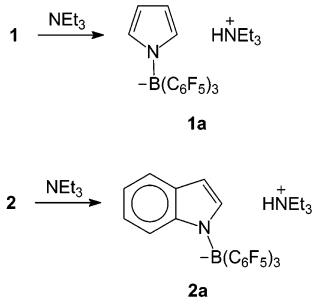
3,3′-Dimethyl-2,2′-diindolylphenylmethane was synthesized from 3-methylindole and benzaldehyde in nearly quantitative yield by acid catalysis.[13] Reaction of BCl_3 (2 equiv) with the bisindolylmethane gave in ∼87% yield compound **14**: its ^{1}H NMR spectrum ($CDCl_3$) shows a quartet at 4.2 ppm for the 3- and 3′-*H* protons and a doublet at 1.0 ppm for the methyl groups. Its ^{13}C NMR ($CDCl_3$) confirmed the occurrence of the N-to-C hydrogen shift showing a *C*H$_3$ signal at 16.0 ppm and a *C*H signal at 43.4 ppm for the C3 and C3′. On the contrary, the reaction between $B(C_6F_5)_3$ (2 equiv) and 3,3′-dimethyl-2,2′-diindolylphenylmethane did not afford any adduct, probably due to the steric hindrance of the phenyl group, which blocks the borane approach.

Attempts were also carried out to synthesize the 7-methylindole and the 2-phenylindole adducts (Chart 3). The reaction of the former with $B(C_6F_5)_3$ in dichloromethane is slow. After 5 min at room temperature, a 1.4:1 mixture of the expected product **15** and starting material was formed together with lower amounts of byproducts. The lower conversion rate observed is probably due to the steric hindrance of the methyl group on C7, which hinders $B(C_6F_5)_3$ coordination to nitrogen. Consumption of 7-methylindole proceeds together with the decomposition of the expected adduct to give many unidentified byproducts. Similarly, 2-phenylindole reacts with $B(C_6F_5)_3$, yielding a ca. 1:1 mixture of the 2-phenylindole−$B(C_6F_5)_3$ complex **16** and starting material. This product/reagent ratio does not change for 24 h, and attempts to shift the equilibrium to the product by adding excess borane failed.

A few experiments were carried out with heterocycles containing two nitrogen atoms (Chart 4). The reaction of $B(C_6F_5)_3$ with imidazole and pyrazole gave the known **17**[14] and the new **18**, respectively, as expected on the basis of the higher basicity of the iminic nitrogen with respect to the NH moiety.

In the pyrrole (**1**-like) and indole (**2**-like) adducts, the presence of the N=C double bond combined with that of the strong electron-withdrawing $B(C_6F_5)_3$ Lewis acid

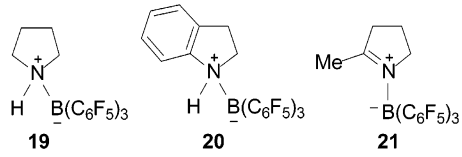
SCHEME 5



1a

2a

CHART 5



19 **20** **21**

generates a quite strong acidity of the proton(s) on the sp³ C5 or C3 carbon: for example, **1** and **2** react with NEt_3 to give quantitatively the known $[B(1\text{-pyrrolyl})(C_6F_5)_3]^-[HNEt_3]^+$ salt **1a**[8] and the $[B(1\text{-indolyl})(C_6F_5)_3]^-[HNEt_3]^+$ salt **2a**, respectively (Scheme 5). This reaction can be used to probe the acidity of the borane−imine complexes.

In addition to **1a** and **2a**, we obtained the salts $[B(2,5\text{-dimethyl-1-pyrrolyl})(C_6F_5)_3]^-[HNEt_3]^+$ (**3a**), $[B(2\text{-ethyl-1-pyrrolyl})(C_6F_5)_3]^-[HNEt_3]^+$ (**5a**), $[B(2\text{-methyl-1-indolyl})(C_6F_5)_3]^-[HNEt_3]^+$ (**7a**), $[B(3\text{-methyl-1-indolyl})(C_6F_5)_3]^-[HNEt_3]^+$ (**8a**), $[B(5\text{-methoxy-1-indolyl})(C_6F_5)_3]^-[HNEt_3]^+$ (**9a**), $[B(2\text{-methylindeno}[2,1\text{-}b]\text{indol-5-yl})(C_6F_5)_3]^-[HNEt_3]^+$ (**12a**), $[B(1\text{-indolyl})Cl_3]^-[HNEt_3]^+$ (**13a**), $[B(1\text{-imidazolyl})(C_6F_5)_3]^-[HNEt_3]^+$ (**17a**), and $[B(1\text{-pyrazolyl})(C_6F_5)_3]^-[HNEt_3]^+$ (**18a**).

The pyrrolidine− (**19**) and indoline−$B(C_6F_5)_3$ (**20**) complexes were originally prepared to check whether the H-shift is necessary to generate proton acidity in the aromatic *N*-heterocycle−$B(C_6F_5)_3$ complexes. As expected, neither **19** nor **20** is able to protonate Et_3N, indicating that, indeed, simple B−N coordination is not sufficient to impart acidity to the N−H bond. On the other hand, steric shielding by the borane cannot justify the lower acidity, because it is not likely to be sufficient to prevent deprotonation of the adduct by the small amine. In addition, also 2-methyl-1-pyrroline−$B(C_6F_5)_3$ **21** does not react with NEt_3: this shows that one double bond is not sufficient for inducing proton acidity (Chart 5).

The strong acidity of the sp³ CH group in **1**- and **2**-like adducts is therefore very likely induced by the rearomatization of the heterocyclic ring and localization of the negative charge on the boron atom, upon formation of the anion. As a consequence, the resulting borate anions are quite stable and are not expected to interact with a strong Lewis acid, such as a metallocene alkyl cation (other than, possibly, by a labile metal−F dipolar interaction). This is also confirmed by a previous investigation by Erker, who has shown that $Cp_2ZrMe(NC_4H_4)$ transfers the pyrrolyl anion to $B(C_6F_5)_3$, rather than the CH_3 group, and that the resulting methylzirconocenium cation is an active ethylene polymerization catalyst.[15]

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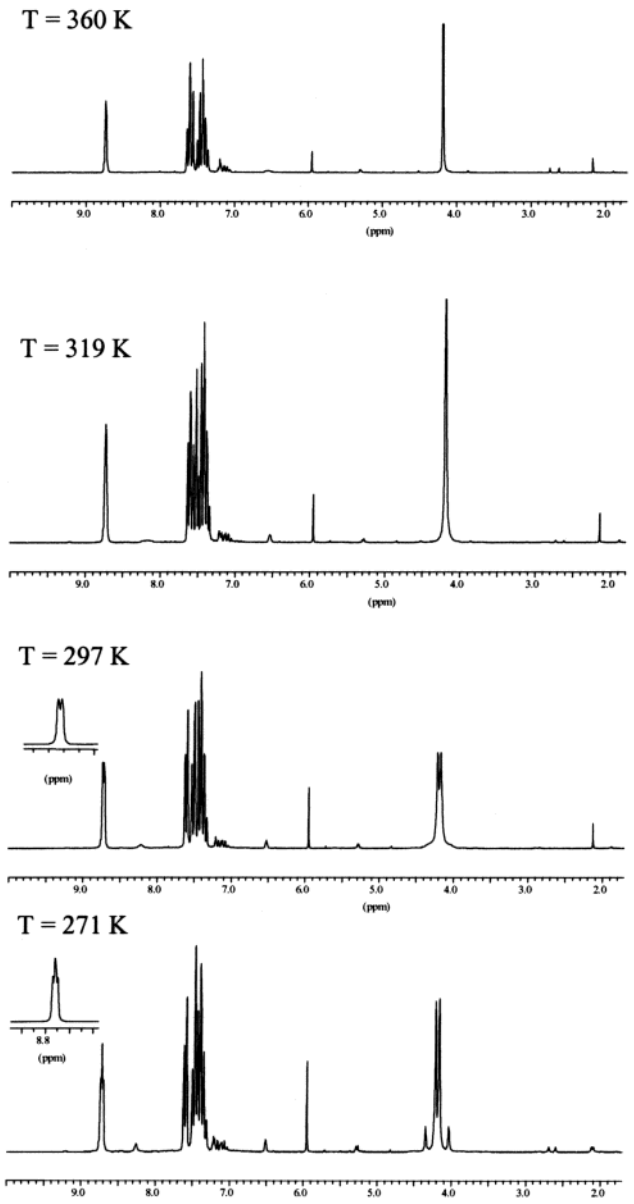

FIGURE 1. ^{1}H NMR spectra of compound **2** at 360, 319, 297, and 271 K in $C_2D_2Cl_4$.

Conformational Studies of Indole−B(C_6F_5)$_3$ and Pyrrole−B(C_6F_5)$_3$ Adducts by Dynamic NMR in $C_2D_2Cl_4$. Figure 1 shows the ^{1}H NMR spectra of adduct **2** recorded at various temperatures. For this compound, anisochronous methylene signals can be observed on cooling, so that the singlet recorded for the methylene protons at 319 K (4.19 ppm) decoalesces below 271 K into an AB-type spectrum. At the same time, the singlet due to H2 (8.73 ppm) changes first into a doublet and finally into a triplet when the temperature is lowered from 319 to 297 and 271 K, respectively. A COSY experiment carried out on compound **2** showed that there is no coupling between H2 and the two geminal H3 protons; therefore, the AB spectrum must be ascribed to the diastereotopicity of the methylene protons, whereas the multiplicity of H2 can be explained by spin−spin through-space couplings of H2 with one (297 K) or two (271 K) fluorine atoms of the borane moiety. Analogous features can be observed in the ^{1}H NMR spectra of adduct **7**, the methylene protons of which, even at room temperature, give rise to an unambiguous AB spectrum (2.59 ppm), which coalesces only above 381 K (see Supporting Information). In addition, at 239 K, the ^{1}H NMR spectrum of adduct **8** clearly shows the presence of two diastereomeric species in a 55:45 ratio, which are evidenced by the two overlapped quartets arising from the H3 proton (4.23 and 4.36 ppm) as well as the two doublets originated by the methyl group (1.53 and 1.65 ppm); these signals begin to coalesce above room temperature (see Supporting Information). As for compound **2**, a proton−fluorine through-space coupling gives rise at 297 K, for the H2 proton, to a doublet (8.68 ppm) that transforms into a triplet on cooling to 239 K.

As far as the pyrrole adducts are concerned, compounds **4** and **5** (see Supporting Information) behave like the indole analogues. Indeed, once again, anisochronous methylene signals can be observed on cooling, and decoalescence of the methylene singlet into an AB-type spectrum clearly occurs at 239 K for both adducts. Compound **5** additionally shows decoalescence of the ethyl signals into an ABX_3 spectrum (0.70−2.87 ppm), due to diastereotopicity of the methylenic protons of the ethyl group. It is worth noting that the ^{1}H NMR spectra of the parent compound **1** did not change at all when the temperature was varied in the range of 173−353 K.

The spectroscopic behavior of adducts **2**, **4**, **5**, **7**, and **8** can be explained by assuming that these compounds are chiral molecules: this hypothesis was confirmed by the X-ray structure of **2** (see Solid State Structures section), which clearly shows the lack of a plane of symmetry because of the spatial arrangement of the fluorinated rings of the borane moiety. Compound **2** and its analogues therefore exist as pairs of stereolabile conformational enantiomers (atropisomers) that can interconvert through rotation about the B−N and/or the B−C bonds. When the interconversion barriers are sufficiently large, that is, the bond rotations are slow enough, the two enantiomeric species can be detected by NMR techniques through the diastereotopicity of the methylene protons (**2**, **4**, **5**, and **7**). If the molecule contains a further asymmetry element, two stereolabile diastereoisomers are produced. In principle, they could form in nonequal amounts and should be spectroscopically detected as distinct species: indeed, due to its asymmetric C3 atom, this is exactly what was observed for adduct **8**.

The dynamic behavior of congested N-bound imine−B(C_6F_5)$_3$ adducts due to restricted rotation about the B−N and B−C bonds has been recently evidenced by Piers and cowokers using variable-temperature ^{19}F and ^{1}H NMR spectroscopy.[10]

The interconversion of the two enantiomers was quantitatively studied for adduct **2**. Simulation (Figure 2, right) of the ^{1}H NMR spectra in $C_2D_2Cl_4$ (Figure 2, left) of **2** at various temperatures allowed determination of the kinetic constant of bond rotation, and thence of the enantiomerization process, at each temperature. As one can see, at 360 K the rotation is practically free ($k > 10^5$ s^{-1}), whereas at 271 K the two enantiomeric conformers do not interconvert in the NMR time scale. In the cases of the two intermediate temperatures (319 and 297 K) values of 700 and 41 s^{-1} were found, respectively, from

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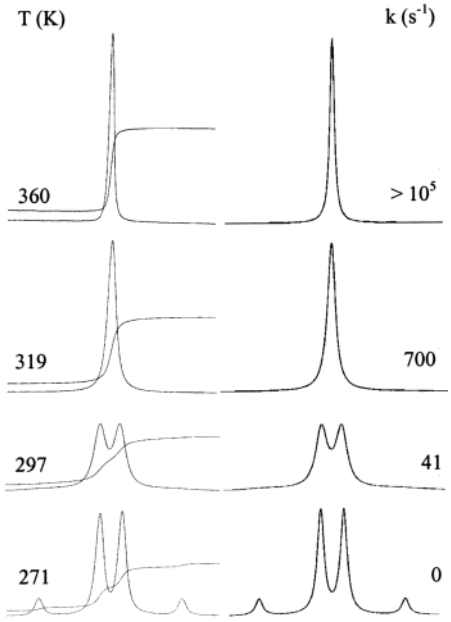


FIGURE 2. (Left) Experimental ^{1}H NMR signal of the methylene hydrogens of **2** as a function of temperature. (Right) Computer simulations obtained with the rate constants indicated.

which we calculated a value of 14.9 ± 0.2 kcal mol^{-1} for the activation barrier ($\Delta G^{\ddagger}$) of the enantiomerization.

The barrier is probably originated by the steric hindrance experienced by the 2- and, particularly, 7-hydrogen during transit of the fluorinated rings. In the case of **7**, the methyl group in the 2-position is an additional obstacle for rotation of the borane moiety and the enantiomerization barrier rises to a significant extent ($\Delta G^{\ddagger}$ = 18.4 ± 0.2 kcal mol^{-1}, calculated by line-shape simulation as above). The barrier was also likewise determined for the pyrrole adduct **4**. The calculated value ($\Delta G^{\ddagger}$ = 14.5 ± 0.2 kcal mol^{-1}) is more comparable to that of compound **2**: this let us conclude that the very high barrier observed for adduct **7** is the result of the overall steric hindrance due to the simultaneous presence of (C2)Me and H7.

Structure and Dynamics in Toluene Solution of Compound 2. In this solvent the ^{1}H spectrum is similar to the one in $C_2D_2Cl_4$, but a substantial low-field shift of hydrogen H7 of the six-membered ring has been observed (see Experimental Section and Supporting Information, Figures S22 and S23, for the assignments) (Figure 3).

At further variance with $C_2D_2Cl_4$, a significant temperature dependence of the chemical shifts was observed for H7, H2, and the two diastereotopic methylenic (H3/H3′) resonances. These latter signals, as in $C_2D_2Cl_4$, with rising temperature broaden and coalesce above 313 K (Figure 3). The proton NMR alone cannot discriminate among the many dynamic processes that could give rise to this behavior. A ^{19}F NMR study was therefore performed to obtain more detailed information.

At 300 K, the 1D ^{19}F NMR spectrum showed six resonances in the ortho region (some accidental overlaps occur in the para and meta regions), indicating a C_1 symmetry for compound **2**. The variable-temperature spectra (Figure 4) confirmed the occurrence of dynamic processes. However, the resonances were not homogeneously broadened (e.g., at 332 K in the ortho region two signals were still sharper than the others). This indicates that rotation around the B−N bond is not the dominant

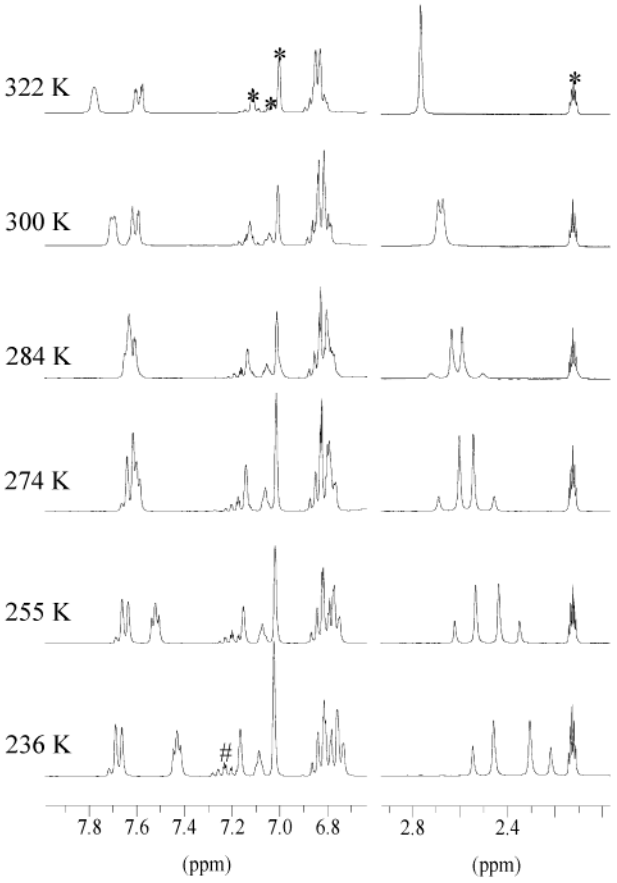


FIGURE 3. ^{1}H NMR spectra at variable temperature of **2** (C_7D_8, 7.1 T, ∗ = solvent signals, # = impurity).

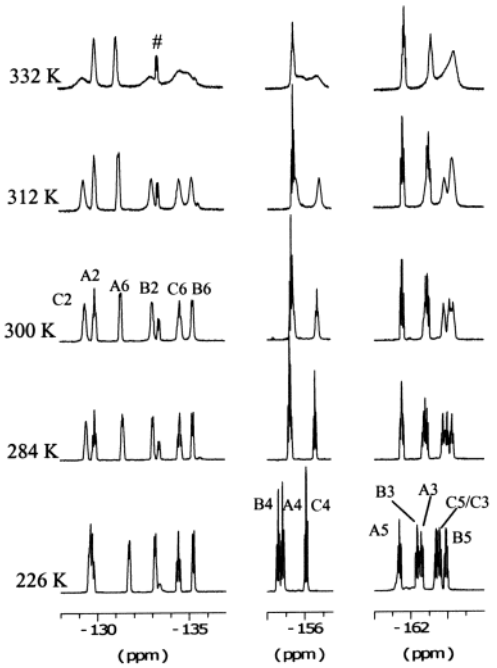


FIGURE 4. ^{19}F NMR spectra of **2** at variable temperature (C_7D_8, 7.1 T, # = impurity). The signals are labeled according to Figure 5.

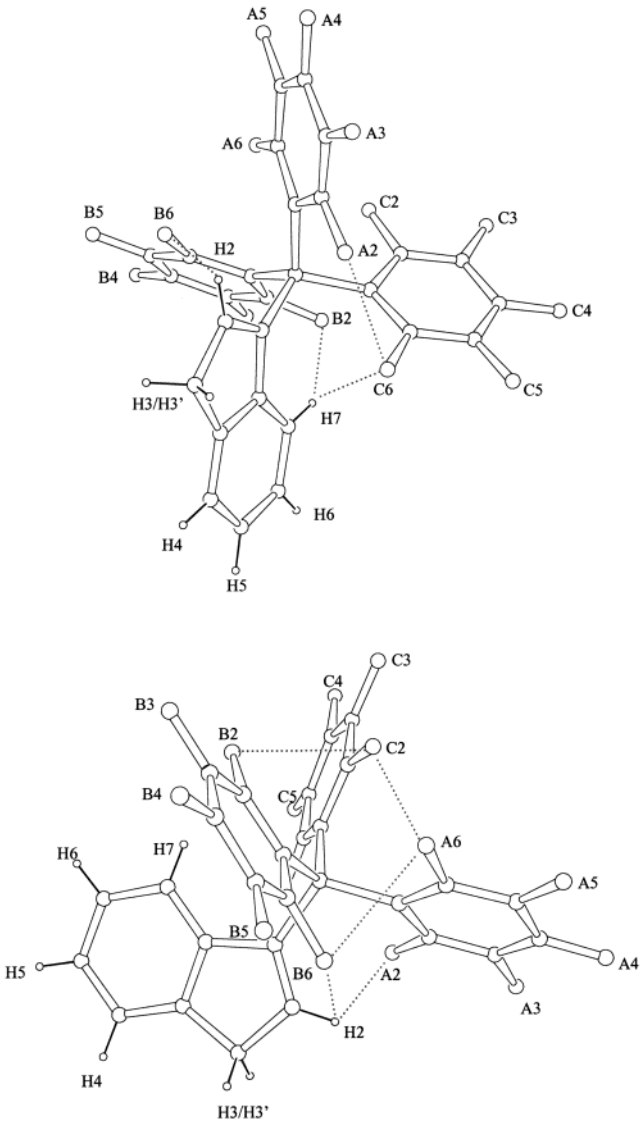


FIGURE 5. Solution structure of compound **2** as derived from 2D $^{19}F-^{19}F$ and $^{19}F-^{1}H$ correlation experiments. The experimental dipolar and scalar interactions are indicated with dotted lines.

TABLE 1. Assignments of the ^{19}F Resonances of Compound 2 at 233 K (δ)

ring	ortho	para	meta
A	−129.76(A2)	−154.84(A4)	−161.35(A5)
	−131.65(A6)		−162.59(A3)
B	−133.10(B2)	−154.63(B4)	−162.34(B3)
	−135.25(B6)		−163.95(B5)
C	−129.51(C2)	−156.10(C4)	−163.54(C3)
	−134.46(C6)		−163.46(C5)

dynamic process, because it would interconvert all three rings and therefore affect all of the resonances to the same extent.

The solution structure of compound **2**, as established through low-temperature 2D $^{19}F-^{19}F$ and $^{19}F-^{1}H$ scalar and dipolar correlation experiments (see Supporting Information Figures S24, S25, and S26), is shown in Figure 5, and the assignments of the fluorine resonances of the three rings are reported in Table 1. Clues to establish the orientation of the heterocyclic molecule with

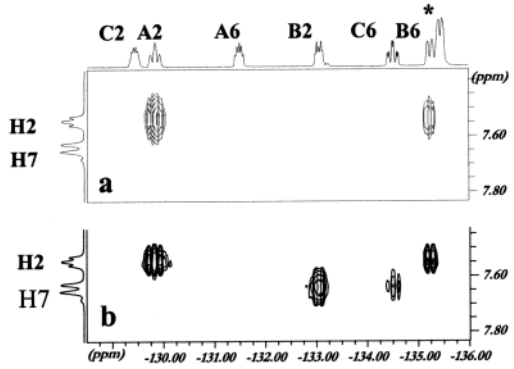


FIGURE 6. Selected regions of 2D $^{19}F-^{1}H$ correlated experiments on compound **2** (C_7D_8, 7.1 T, 265 K, $*$ = impurity): (a**)** scalar correlation experiment optimized for J_{HF} = 10 Hz (64 fid, SW 16560 Hz, TD 4K, D1 = 1.5 s, 128 experiments, zero-filled once in F1, weighting functions: squared shifted sine bell in F2 and sine in F1); (b**)** dipolar correlation experiment (τ_m = 0.55 s, 128 fid, SW 16560 Hz, TD 4K, D1 = 1.5 s, 128 experiments, zero-filled once in F1, weighting functions: squared shifted sine bell in F2 and sine in F1).

respect to the three phenylic rings came from the observed scalar and dipolar coupling between some of the ortho fluorines and the H2 or H7 hydrogen atoms (Figure 6), whereas the occurrence of through-space couplings[16] and dipolar correlations between ortho fluorines belonging to different rings probed the relative conformation of the aryl rings (Figure 7). All of the spatial relationships found from these experiments are indicated in Figure 5.

To take into account all of the experimental scalar and dipolar interactions, the three phenyl rings should have different tilts with respect to the heterocyclic moiety, as sketched in Figure 5. Such a conformation is similar to the one established in the solid state (see below) for compound **2** and related derivatives.

Two-dimensional $^{19}F-^{19}F$ EXSY experiments showed that the most relevant enantiomerization pathway of compound **2**, occurring already at 275 K, is the exchange of rings B and C, whereas ring A maintains its identity (Figure 8a). It is worth noting that in this process ring A does not flip: in fact, the 2D maps do not show direct exchange between the ortho fluorines atoms of A, and in the ^{1}H variable-temperature spectra H2 (that is, a triplet at low temperature for its interaction with A2 and B6 fluorine atoms) becomes a doublet, albeit broadened, up to 313 K, indicating the persistence of the scalar H−F correlation with A2. Likely, the B/C interconversion is accomplished through the libration of the heterocycle and of ring A with respect to the B−N and B−C bonds, respectively, whereas rings B and C rotate as and opposite to ring A, respectively.

At 278 K 2D $^{19}F-^{19}F$ EXSY experiments showed unambiguous much weaker exchange cross-peaks among the ortho signals of rings A and B (but no cross-peaks among ortho signals of A and C and between those of A)

(16) For other experimental examples of through-space $^{19}F-^{19}F$ couplings see, for instance: (a) Mallory, F. B.; Mallory, C. W.; Butler, K. E.; Lewis, M. B.; Xia, A. Q.; Luzik, E. D., Jr.; Fredenburg, L. E.; Ramanjulu, M. M.; Van, Q. N.; Francl, M. M.; Freed, D. A.; Wray, C. C.; Hann, C.; Nerz-Stormes, M.; Carroll, P. J.; Chirlian, L. E. *J. Am. Chem. Soc.* **2000**, *122*, 4108. (b) Ernst, L.; Ibrom, K.; Marat, K.; Mitchell, R. H.; Bodwell, G. J.; Bushnell, G. W. *Chem. Ber.* **1994**, *127*, 1119.

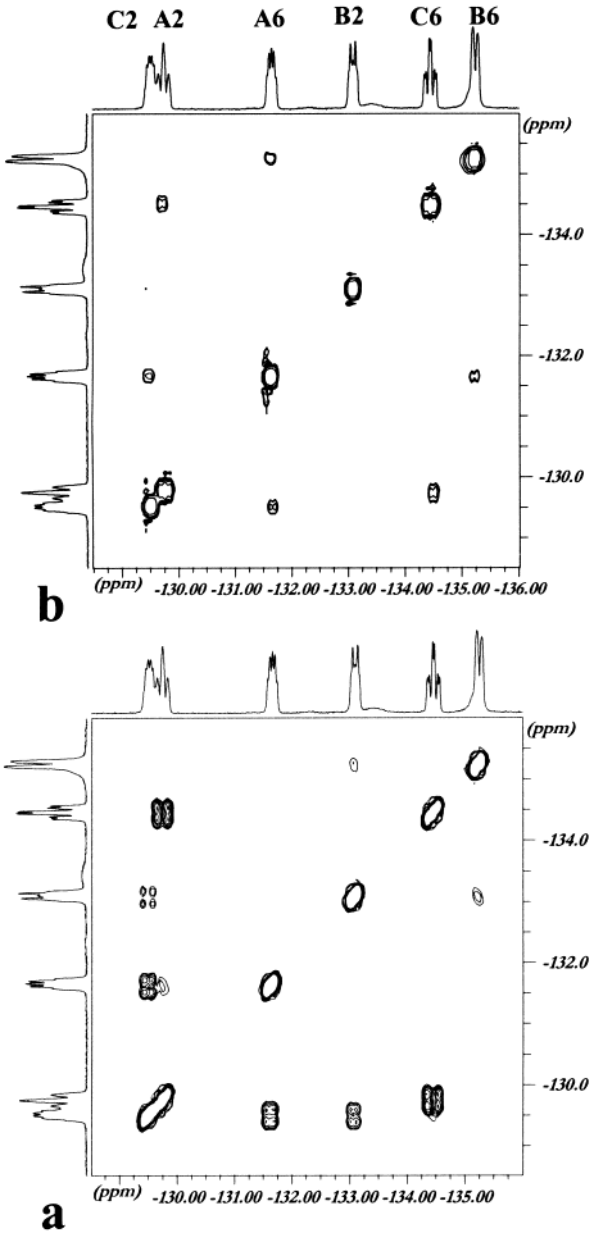


FIGURE 7. (a) Ortho region of a 2D ^{19}F COSY45 experiment (C_7D_8, 7.1 T, 233 K, 8 fid, SW 14120 Hz, TD 2K, D1 = 0.5 s, 512 experiments, zero-filled to 1 K in F1, weighting functions: squared shifted sine bell in F1 and sine in F2) showing "through-space" correlations between fluorines belonging to different rings (namely, C2 with A6 and B2; A2 with C6), and one "through-bond" cross-peak (B2 ↔ B6). (b) Ortho region of a 2D ^{19}F NOESY experiment (C_7D_8, 7.1 T, 233 K, τ_m = 300 ms, 16 fid, SW 14120 Hz, TD 2K, D1 = 0.5 s, 512 experiments, zero-filled to 1 K in F1, weighting functions: shifted sine bell in both dimensions) showing dipolar correlations between different rings (cross-peaks of opposite sign with respect to diagonal peaks).[17]

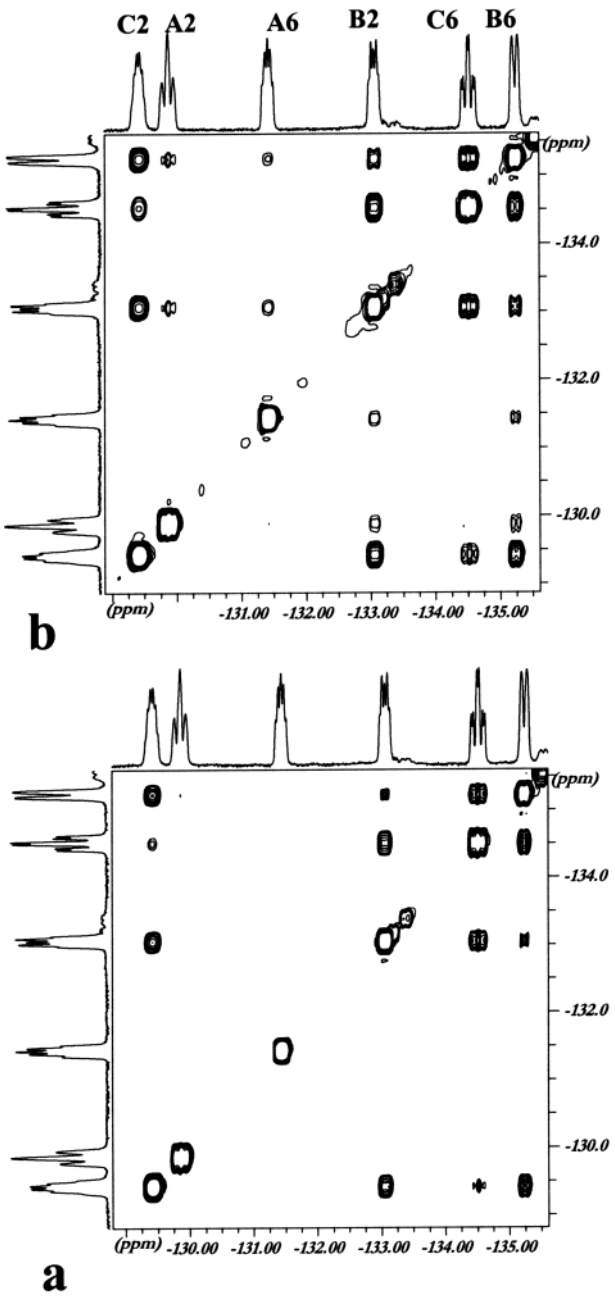


FIGURE 8. Ortho region of a 2D EXSY experiment performed on compound **2** (C_7D_8, 7.1 T, 16 fid, SW 12820 Hz, TD 2K, D1 = 1 s, 512 experiments, zero-filled to 2K in F1, weighting functions: shifted sine bell in both dimensions): (a) 275 K and τ_m = 100 ms, showing the exchange of ring C and B (C2/B2, C2/B6, B2/C6, C6/B6, and their symmetry-related cross-peaks are of the same sign as the diagonal peaks); (b) 278 K and τ_m = 100 ms, showing the exchange cross-peaks between rings A and B.

(Figure 8b). The occurrence of this second slower process involving ring A leads eventually to the overall exchange of all the ortho resonances as observed in a 2D experiment at 300 K and τ_m = 100 ms (Figure S27). At 300 K, the kinetic constants of these processes are 39 and 3 s^{-1}, respectively.

Simulation of the para region of the 1D ^{19}F spectra in the range from 283 to 350 K together with the analysis of various 2D EXSY experiments in the range of 275−300 K gave the rate constants for the low-energy and the high-energy processes (Table S3; Figure S28). The activation parameters calculated accordingly are E_a = 16.7(1) kcal mol^{-1}, $\Delta H^{\#}$ = 16.0(1) kcal mol^{-1}, and $\Delta S^{\#}$ = 2.2(1) cal mol^{-1} K^{-1} for B/C exchange and E_a = 18.0(2), $\Delta H^{\#}$ = 17.4(2) kcal mol^{-1}, and $\Delta S^{\#}$ = 1.7(1) cal mol^{-1} K^{-1} for A/B exchange. The rate constants obtained from the simulation of ^{1}H spectra account for both of the processes;

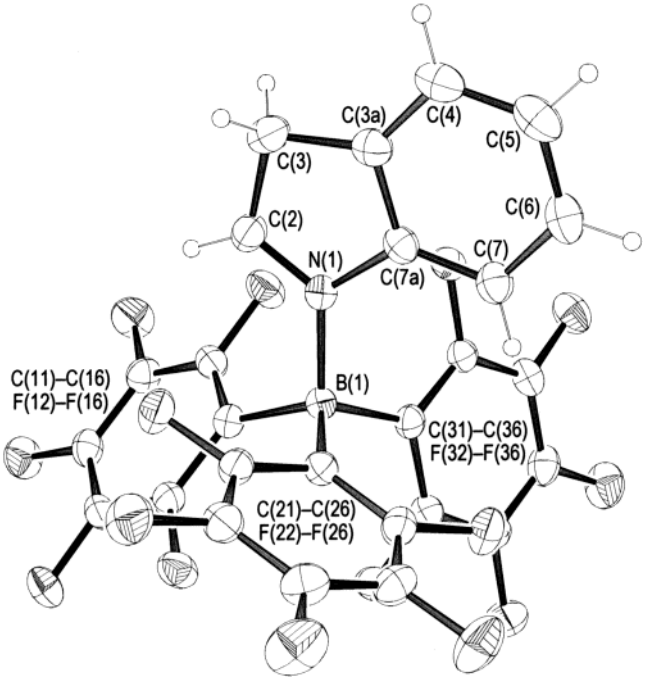


FIGURE 9. ORTEP view of the structure of (3*H*-indole)tris(pentafluorophenyl)boron (**2**) in the crystal. Thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms are given arbitrary radii.

however, the rate of the second process being 1 order of magnitude smaller, their values and the activation parameters are the same as those obtained from ^{19}F (Figure S28). The dynamic behavior of congested N-bound imine−$B(C_6F_5)_3$ adducts due to restricted rotation about the B−N and the B−C bonds has been recently evidenced by Piers and co-wokers using variable-temperature ^{19}F and ^1H NMR spectroscopy.[10] These imine adducts exhibit (at least in the solid state) conformations of the B-bound phenyl rings very similar to that observed in the present case (both in solution and in the solid state, see below). However, the enantiomerization activation parameters found for **2** are slightly larger than those reported by Piers et al. ($\Delta G^{\#} \sim 66$ vs 60 kJ mol^{-1}) despite the π stacking interactions between fluorinated and hydrogenated phenyl rings observed in their compounds. Likely in compound **2** the overall H−F interactions help in maintaining the preferred conformation of the perfluorinated rings and, indeed, the low-energy enantiomerization process in **2** implies the cleavage of most of these H···F interactions (all of those involving H7 and one of the two involving H2).

Solid State Structures of Complexes between Indoles and $B(C_6F_5)_3$. The molecular structures of **2**, **2a**, and **20** have been determined in the solid state by X-ray diffraction analysis. Figures 9, 10, and 11 show ORTEP views of **2**, the indolate anion of **2a**, and **20**, respectively. Tables 2 (distances) and 3 (angles) contain the most relevant bonding parameters for the three compounds.

The formulation of **2**, **2a**, and **20** as equimolecular adducts between the indoles and tris(pentafluorophenyl)-borane is confirmed. The borane and the heterocyclic moieties are connected by a strong B−N bond. In all three compounds the boron atom shows a distorted (*pseudo* D_{2d}) tetrahedral coordination geometry, in which four bond angles are larger and two (opposite) are smaller than the idealized value of 109.5°. The nitrogen atoms in both **2** and **2a** have a trigonal planar coordination geometry, as indicated by the sum of bond angles at N(1) (359.6 and 358.7° for **2** and **2a**, respectively), whereas in **20** the nitrogen atom is tetrahedrally coordinated.

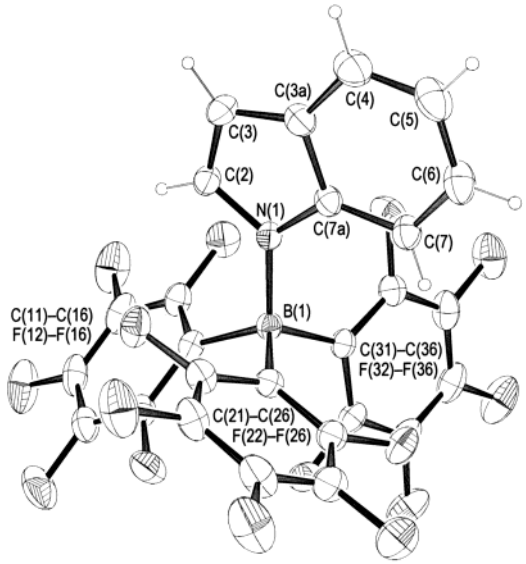


FIGURE 10. ORTEP view of the structure of the (1*H*-indol-1-yl)tris(pentafluorophenyl)borate anion of **2a** in the crystal of its triethylammonium salt. Thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms are given arbitrary radii.

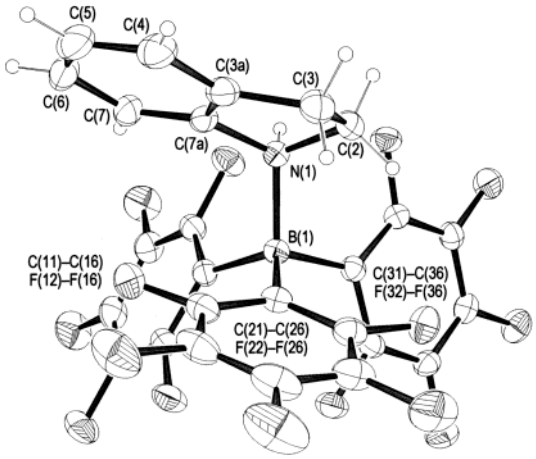


FIGURE 11. ORTEP view of the structure of (2,3-dihydro-1*H*-indole)tris(pentafluorophenyl)boron (**20**) in the crystal. Thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms are given arbitrary radii.

Compound **2** is a rare example of the 3*H*-indole tautomeric form.[18] As expected, the observed bond distances are in accordance with a localization of the double bond between N(1) and C(2) [1.284(3) Å] in the five-membered ring.[19]

In complex **2a** the bond distances within the heterocyclic moiety are very similar to that observed in the free indolate anion[20] and are consistent with an extensive delocalization of the π electrons in the rings.

TABLE 2. Selected Bond Distances (Å) for 2, 2a, and 20

	2	2a	20
N(1)−C(2)	1.284(3)	1.374(4)	1.530(2)
N(1)−C(7a)	1.447(3)	1.390(4)	1.478(2)
N(1)−B(1)	1.613(3)	1.565(4)	1.650(2)
C(2)−C(3)	1.471(3)	1.355(4)	1.525(3)
C(3)−C(3a)	1.489(3)	1.413(5)	1.495(3)
C(3a)−C(4)	1.376(3)	1.407(5)	1.387(3)
C(3a)−C(7a)	1.386(3)	1.421(4)	1.379(3)
C(4)−C(5)	1.372(4)	1.374(6)	1.378(4)
C(5)−C(6)	1.373(4)	1.403(6)	1.381(4)
C(6)−C(7)	1.390(3)	1.374(5)	1.386(3)
C(7)−C(7a)	1.374(3)	1.398(4)	1.376(3)
B(1)−C(11)	1.641(3)	1.663(4)	1.649(3)
B(1)−C(21)	1.647(3)	1.661(4)	1.642(3)
B(1)−C(31)	1.641(3)	1.662(4)	1.651(2)

TABLE 3. Selected Bond and Torsional Angles (Degrees) for 2, 2a, and 20

	2	2a	20
C(2)−N(1)−C(7a)	108.28(18)	106.3(2)	103.32(13)
C(2)−N(1)−B(1)	126.71(18)	128.0(2)	113.17(13)
C(7a)−N(1)−B(1)	124.61(16)	124.4(2)	117.72(13)
N(1)−C(2)−C(3)	113.4(2)	111.6(3)	106.28(15)
C(2)−C(3)−C(3a)	101.82(18)	107.3(3)	102.47(16)
C(3)−C(3a)−C(4)	132.9(2)	135.2(3)	129.4(2)
C(3)−C(3a)−C(7a)	107.71(19)	106.2(3)	111.30(16)
C(4)−C(3a)−C(7a)	119.4(2)	118.5(3)	119.2(2)
C(3a)−C(4)−C(5)	118.5(2)	119.6(4)	118.6(2)
C(4)−C(5)−C(6)	121.5(2)	120.7(3)	121.3(2)
C(5)−C(6)−C(7)	121.1(2)	121.7(4)	120.9(2)
C(6)−C(7)−C(7a)	116.4(2)	117.9(3)	116.9(2)
N(1)−C(7a)−C(3a)	108.77(18)	108.5(3)	110.67(16)
N(1)−C(7a)−C(7)	128.24(19)	129.9(3)	126.20(18)
C(3a)−C(7a)−C(7)	123.0(2)	121.6(3)	123.12(18)
N(1)−B(1)−C(11)	109.75(16)	112.0(2)	110.85(13)
N(1)−B(1)−C(21)	101.32(16)	103.1(2)	104.01(13)
N(1)−B(1)−C(31)	111.53(17)	112.9(2)	108.39(13)
C(11)−B(1)−C(21)	114.27(17)	111.5(2)	116.66(14)
C(11)−B(1)−C(31)	104.38(17)	103.0(2)	102.39(13)
C(21)−B(1)−C(31)	115.71(17)	114.5(2)	114.49(14)
B(1)−C(11)−C(12)	120.99(18)	120.2(3)	121.08(15)
B(1)−C(11)−C(16)	125.69(18)	126.1(3)	125.00(15)
C(12)−C(11)−C(16)	113.01(18)	113.3(3)	112.83(16)
B(1)−C(21)−C(22)	119.31(18)	118.4(3)	122.25(16)
B(1)−C(21)−C(26)	127.84(19)	128.8(3)	124.12(16)
C(22)−C(21)−C(26)	112.8(2)	112.6(3)	113.45(17)
B(1)−C(31)−C(32)	118.29(18)	119.0(3)	118.95(14)
B(1)−C(31)−C(36)	127.39(18)	127.5(3)	127.69(15)
C(32)−C(31)−C(36)	113.9(2)	113.2(3)	113.10(15)
N(1)−B(1)−C(11)−C(12)	53.3(3)	55.9(4)	47.2(2)
N(1)−B(1)−C(21)−C(22)	67.3(2)	60.9(3)	77.00(19)
N(1)−B(1)−C(31)−C(32)	169.98(18)	176.0(2)	170.43(14)

The heterocyclic moiety in the 2,3-dihydro-1*H*-indole complex **20** does not present any unusual feature. The pentagonal ring assumes an envelope conformation on C(2).

TABLE 4. Selected F···F and F···H Distances (Å) for 2[a]

	F(22)	F(26)	F(32)	F(36)	H(2)	H(7)
F(12)	4.650(3)	5.763(4)	4.719(3)	**2.796(2)**	**2.61**	4.98
F(16)	**2.850(2)**	4.429(3)	**2.940(2)**	5.947(4)	4.45	5.62
F(22)			4.748(3)	5.599(4)	**2.84**	4.85
F(26)			**2.784(3)**	4.629(3)	5.70	**2.48**
F(32)					5.48	4.38
F(36)					3.97	**3.10**

[a] Close contacts are indicated in bold (the sums of the van der Waals radii for the F···F and F···H contacts are 3.0 and 2.7 Å, respectively).

Boron−nitrogen bond distances show a sensible dependence on the electronic environment: the longer [1.650(2) Å] is, as expected, the one involving the sp³ hybridized nitrogen atom in **20**. In complexes **2** and **2a**, in which the nitrogen atoms are sp² hybridized, the B−N distances are 1.613(3) and 1.565(4) Å, the shorter one involving the negatively charged indolate moiety (which is a better Lewis base than the neutral 3*H*-indole tautomer). The same trend has been reported for the pyrrole derivatives 2*H*-pyrrole−$B(C_6F_5)_3$ (**1**) and [1*H*-pyrrol-1-yl-$B(C_6F_5)_3$]$^-$ (**1a**), in which the B−N distances are 1.608(2) and 1.576(4) Å, respectively.[9]

As can be seen from Figures 9−11 and from the torsional angles reported in Table 3, in the three complexes the $B(C_6F_5)_3$ moiety adopts a very similar conformation. In particular, one of the three phenyl rings [the one labeled C(31)−C(36)] eclipses the B−N bond, whereas the other two exhibit a chiral two-bladed propeller-like conformation. This very same conformation can be found in most of the crystal structures of tris(pentafluorphenyl)-borane derivatives collected in the Cambridge Structural Database:[21] from this evidence it can be inferred that this molecular fragment is a very rigid one, so that the presence of a somehow high-energy barrier to the enantiomerization process of the chiral propeller can be expected.

This conformation results in some short F···F nonbonded contacts between the *ortho*-fluoro substituents of the three phenyl rings and in some F···H contacts involving the hydrogen atoms bound to C(2) and C(7). A list of these interactions for compound **2** (in which they can also be evidenced in solution, at low temperature, by NMR spectroscopy—see previous section) is given in Table 4. Moreover, in compound **20** the hydrogen atom bound to nitrogen is involved in a bifurcated intramolecular hydrogen bond with the fluorine atoms F(12) and F(36) (the two NH···F distances are 2.15 Å).

Possible Mechanism of Formation of Borane−Pyrrole and Borane−Indole Complexes. The formation of the B−N adducts can be considered as the reaction

(17) In the ortho region, NOE cross-peaks among resonances of different rings supported the occurrence of the through-space couplings observed in the COSY spectrum. The correlation between A6 and B6, observable only in the NOESY spectrum, indicates that likely the closeness in the space of these two fluorine atoms does not give rise to an effective overlap of fluorine p orbitals, as required for through-space coupling.[16] On the other hand, the strongly scalar coupled C2/B2 signals do not show NOE cross-peaks, likely for the occurrence of double and zero quantum *J* modulation; see: Ernst, R. R.; Bodenhausen, G.; Wokaun, A. In *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Oxford Science Publications: Oxford, U.K., 1987; Chapter 9.

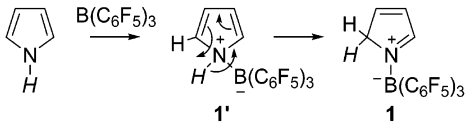
(18) To the best of our knowledge, the crystal structure of only another derivative of this tautomer has been reported, namely, the complex [$PdCl_2$(2-methyl-3*H*-indole)$_2$]. Yamauchi, O.; Takani, M.; Toyada, K.; Masuda, H. *Inorg. Chem.* **1990**, *29*, 1856.

(19) The observed bond distances fully agree with the ones predicted for the 3*H*-indole tautomer by density functional computation (B3LYP/cc-pVDZ): Dubnikova, F.; Lifshitz, A. *J. Phys. Chem. A* **2001**, *105*, 3605.

(20) Bond distances (Å) for the 7-methylindolate anion are as follows: N(1)−C(2), 1.383(4); N(1)−C(7a), 1.392(4); C(2)−C(3), 1.390(5); C(3)−C(3a), 1.420(5); C(3a)−C(4), 1.409(5); C(3a)−C(7a), 1.435(4); C(4)−C(5), 1.370(6); C(5)−C(6), 1.402(6); C(6)−C(7), 1.385(5); C(7)−C(7a), 1.406(5). Karl, M.; Harms, K.; Seybert, G.; Massa, W.; Fau, S.; Frenking, G.; Dehnicke; K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 2055.

(21) CSD version 5.22 (Oct 2001). Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, C. F.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187.

SCHEME 6



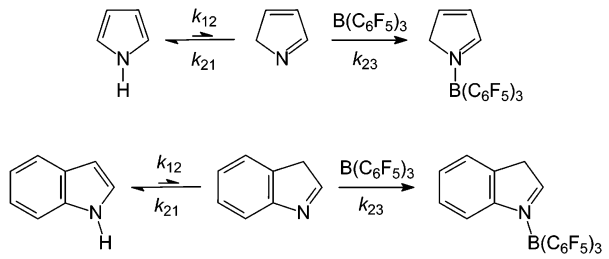
between a nucleophile (the heterocycle) and an electrophile (the borane). The attack of electrophiles on the 2- or 3-position of pyrrole and indole, respectively, is a well-known process.[22] Nevertheless, formation of our pyrrole and indole adducts cannot be accounted for simply by the intervention of the borane as an electrophile, because it would not be easy to explain the subsequent, concomitant migrations of the N−H bond and the borane moiety between nitrogen and carbon.

In the case of pyrrole, a simple explanation could be coordination of the borane to nitrogen followed by 1,2 intra-(or inter-)molecular translocation of the N−H hydrogen in the adduct **1′** (Scheme 6). The latter step can be promoted by a polarization of the N−H bond induced by the solvent or a fluorine atom. Supporting this hypothesis, the X-ray structure of the indoline−$B(C_6F_5)_3$ complex **20** shows two strong intramolecular $NH-F_{ortho}$ interactions (d_{H-F} = 2.15 Å) (see Solid State Structures section). However, this mechanism cannot effectively justify the formal 1,3-H shift observed with indole derivatives. Furthermore, direct coordination of $B(C_6F_5)_3$ to the nitrogen atom of pyrrole or indole is unlikely, given the aromaticity of the heterocyclic ring. Trying to answer these questions, we have carried out DFT calculations in the gas phase. They indicate that, taking the energy of the reactants at infinity as a reference, adduct **1′** is stabilized only by 0.9 kcal mol^{-1}, despite a rather low-energy barrier of 3.4 kcal mol^{-1} needed for its formation. Taking into account possible relatively large entropic effects, the formation of adduct **1′** can be reasonably thought to be unlikely.

Moreover, calculations aimed at evaluating the possible assistance of the *ortho*-F to the 1,2-H shift (step **1′**−**1** in Scheme 6) indicated that the fluorine atom should not play a role, at least in the early steps of this process. Indeed, only after the system has overcome an energy barrier of nearly 35 kcal mol^{-1} is a favorable H−F interaction observed. Finally, test calculations on the step **1′**−**1** performed on the simplified system BF_3−pyrrole and C_6F_6, aiming at evaluating the assistance of a F atom by a further incoming $B(C_6F_5)_3$ molecule, gave no results.

A simple explanation for the formation of **1** would be the presence of minor amounts of the 3*H*-indole and 5*H*-pyrrole tautomers at equilibrium in solution, which would be immediately trapped by the borane, thus driving the equilibrium to the right (Scheme 7). However, the computed intramolecular isomerization barrier in the gas phase from 1*H*-indole to 3*H*-indole is very high, on the order of 50 kcal mol^{-1}.[23,24] Because the complexation of $B(C_6F_5)_3$ to the 3*H*-indole can be assumed to be much faster than the 3*H*-indole → 1*H*-indole reaction (that is,

SCHEME 7



$k_{23} \gg k_{21}$), by assuming the steady state approximation on 3*H*-indole, we can estimate that d[**2**]/d$t = k_{12}$[indole], with $k_{12} \approx 10^{-24}$ s^{-1} at 25 °C. Although the inclusion of solvent effects may reduce the calculated barrier for indole tautomerization, we believe that an alternative mechanism may be involved. In particular, because the tautomerization reaction of both pyrrole and indole is catalyzed by acids,[25] we make the hypothesis that B−N adducts can be more conveniently accounted for through nucleophilic attack of boron-coordinated water to a pyrrole (or indole) double bond, followed by reorganization. The coordination of $B(C_6F_5)_3$ with water is very fast. Any experiment aimed at having water-free borane showed the presence of residual water in amounts depending on the purification process used (see Experimental Section for details). Because it is practically impossible to have fully water-free $B(C_6F_5)_3$, the water-catalyzed reaction would seem to be a likely possibility and is in accordance with the different structures of pyrrole (electrophilic attack on C_α) and indole (electrophilic attack on C_β) derivatives. After protonation of the heterocycle, the resulting species can evolve to the final adduct by intramolecular elimination of water (path *a* of Scheme 8, shown for indole) or by attack of a non-coordinated borane molecule and concomitant elimination of $H_2O-B(C_6F_5)_3$ (path *b* of Scheme 8), which hence acts as a catalyst.

DFT calculations showed that formation of species **22** could be a viable process. Indeed, both indole and pyrrole form a preliminary adduct with $H_2O-B(C_6F_5)_3$, stabilized by 2.5 and 6.4 kcal mol^{-1}, respectively, with respect to the reactants. The proton-transfer process has been investigated for pyrrole only. The transition state to species $\mathbf{22_{pyrr}}$ from the initial adduct is at 6.2 kcal mol^{-1}; $\mathbf{22_{pyrr}}$ and $\mathbf{22_{ind}}$ are at +0.14 and −11.4 kcal mol^{-1} with respect to the adducts, respectively. The optimized structures (Figure 12) display a bridging hydrogen atom between nitrogen and oxygen.

Both species $\mathbf{22_{pyrr}}$ and $\mathbf{22_{ind}}$ are nearly 23 kcal mol^{-1} more stable than the isolated $H_2O-B(C_6F_5)_3$ adduct and 5*H*-pyrrole and 3*H*-indole, respectively. Moreover, $\mathbf{22_{pyrr}}$ is 15.1 and 8 kcal mol^{-1} more stable than the two limit species in which the bridging H atom is at bond distance only with N or O, respectively. This may be related to a high activation energy, required for the completion of proton transfer to oxygen, if no other molecule takes part in the reaction. This step was actually found to be efficiently assisted by a free $B(C_6F_5)_3$ [or $H_2O-B(C_6F_5)_3$], which coordinates the nitrogen atom while simultaneously displacing $H_2O-B(C_6F_5)_3$. We simulated this process for $\mathbf{22_{pyrr}}$ by choosing a BF_3 molecule (for computa-

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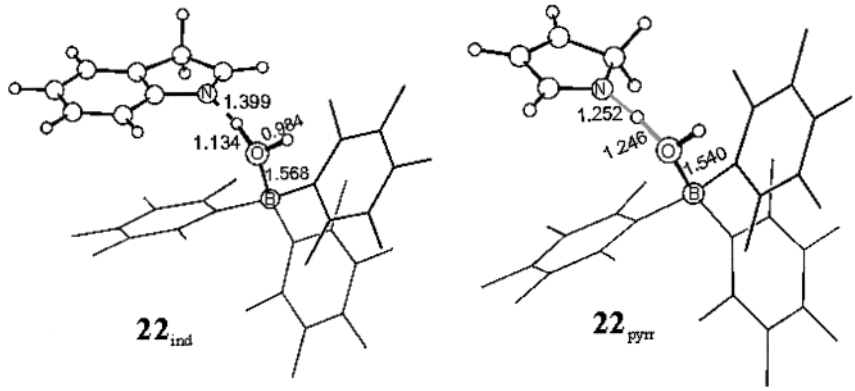
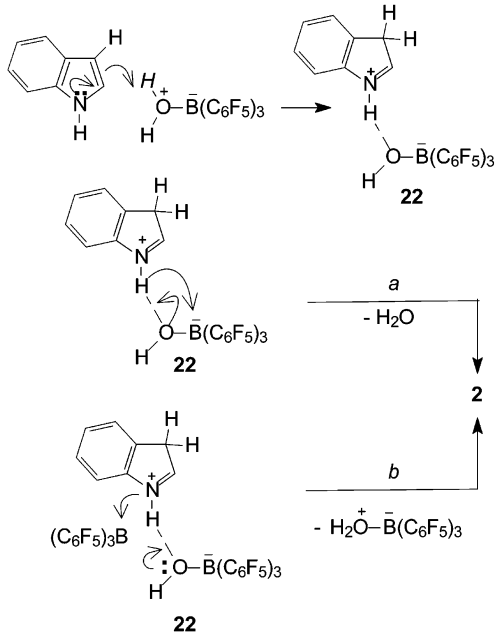


FIGURE 12. Optimized structures of species $\mathbf{22_{ind}}$ and $\mathbf{22_{pyrr}}$.

SCHEME 8



tional reasons): the energy barrier is only 0.5 kcal mol^{-1} with respect to the isolated $\mathbf{22_{pyrr}}$ and BF_3. Finally, **1** and **2** are 11.9 and 14.5 kcal mol^{-1} more stable than the starting $B(C_6F_5)_3$ and indole or pyrrole, respectively.

The occurrence of path *b* (Scheme 8) as the main product-forming mechanism was also suggested by experiments carried out on indole with variable amounts of preformed $H_2O-B(C_6F_5)_3$ 1:1 complex. In the presence of 1 equiv of $H_2O-B(C_6F_5)_3$, formation of adduct **2** was a very slow process that took 3 days to go to completion. In addition, formation of **2** was accompanied by an intermediate species (revealed by ^{1}H NMR) that gradually disappeared during the course of the reaction. Formation of **2** was instead almost as fast as usual by using 0.7 equiv of $H_2O-B(C_6F_5)_3$ together with 0.3 equiv of "free" borane.

These data are clearly consistent with a mechanism that entails preliminary formation of adduct $\mathbf{22_{ind}}$ followed by bimolecular elimination of $H_2O-B(C_6F_5)_3$ by a borane molecule (Scheme 8, path *b*). The unimolecular alternative (Scheme 8, path *a*) could operate to some extent but is probably a very minor process in the presence of free borane.

Conclusions

The reaction of pyrroles and indoles with tris(pentafluoroaryl)borane produces 1:1 B−N complexes that contain highly acidic sp^3 carbons, generated by a formal, nitrogen to carbon 1,3-H shift. A seemingly related process has been observed by Erker in the formation of $B(C_6F_5)_3$ keto-*O*-adducts of naphthols.[26] The $(C_6F_5)_3B-$N-heterocycle complexes are able to protonate Lewis bases such as trialkylamines. The mechanism of formation of these adducts probably entails protonation of the heterocycle by catalytic amounts of $H_2O-B(C_6F_5)_3$, followed by displacement of $H_2O-B(C_6F_5)_3$ from the resulting complex by a free borane molecule. Restricted rotation about the B−N and B−C bonds was observed in some derivatives, and the corresponding barriers were calculated by NMR line-shape simulation. The activating ability of these complexes in olefin polymerization[9,11] will be the subject of a future publication.

Experimental Section

General Procedures. All operations were performed under nitrogen by using conventional Schlenk-line techniques. Solvents were purified by degassing with N_2 and passing over activated (8 h, N_2 purge, 300 °C) Al_2O_3 and stored under nitrogen. Indole, 2-methylindole, 3-methylindole, 5-methoxyindole, 5-benzyloxyindole, 5-chloroindole, pyrrole, 2,5-dimethylpyrrole, 2,4-dimethylpyrrole, 2-ethylpyrrole, 4,5,6,7-tetrahydroindole, pyrrolidine, indoline, 2-methyl-1-pyrroline, imidazole, pyrazole, BPh_3, BCl_3 (1.0 M solution in heptane), $BF_3{\cdot}Et_2O$, benzaldehyde, and $B(C_6F_5)_3$ (Boulder Scientific Co.) were used as received. 2-Methyl-5,6-dihydroindeno[2,1-*b*]indole[27] was synthesized according to the literature. Triethylamine was dried over KOH pellets and stored under nitrogen over activated 4 Å molecular sieves before use.

The ^{1}H and ^{13}C NMR spectra of the compounds were obtained using a Bruker DPX 200 spectrometer operating in the Fourier transform mode at room temperature at 200.13 and 50.33 MHz, respectively. The samples were dissolved in $CDCl_3$, CD_2Cl_2, $C_2D_2Cl_4$, C_6D_6, or $C_6D_5CD_3$. As reference, the residual peak of $CHCl_3$, $CHDCl_2$, C_2HDCl_4, C_6HD_5, or C_6D_5-CHD_2 in the ^{1}H spectra (7.25, 5.35, 5.95, 7.15, or 2.10 ppm, respectively) and the peak of the solvent in the ^{13}C spectra (53.80 ppm for CD_2Cl_2 and 128.00 ppm for C_6D_6) were used.

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Proton spectra were acquired with a 15° pulse and 2 s of delay between pulses; 32 transients were stored for each spectrum. The carbon spectra were acquired with a 45° pulse and 6 s of delay between pulses; ~512 transients were stored for each spectrum. CD_2Cl_2 and $C_2D_2Cl_4$ were used as received, whereas $CDCl_3$, C_6D_6, and $C_6D_5CD_3$ were dried over activated 4 Å molecular sieves before use. Preparation of the samples was carried out under nitrogen by using standard inert atmosphere techniques.

The NMR spectra of the dynamics study in toluene solution of compound **2** were recorded on Bruker DRX 300 and AMX 500. Most of the ^{19}F spectra were acquired on the DRX300 spectrometer without proton decoupling, because the detuned proton channel was used for pulsing ($PW_{90°} = 26$ μs). The spectra were referenced to coaxial tube $CFCl_3$ ($\delta = 0.0$). The temperature was calibrated with standard CH_3OH/CD_3OD and ethylene glycol/DMSO solutions. All of the fluorine signals are complex multiplets due to *intra*-ring $^{19}F-^{19}F$ couplings and the occurrence also of through-space *inter*-ring $^{19}F-^{19}F$ coupling and of $^{1}H-^{19}F$ couplings, for some of the ortho resonances. Only in the para region do the signals appear as deceptively simple triplets of triplets.

GC-MS analyses were carried out on an HP 5890 series 2 gas cromatograph and an HP 5989B quadrupole mass spectrometer. MS analysis of *N*-[tris(pentafluorophenyl)borane]-3*H*-indole (**2**) was carried out on a WATERS micromass ZQ 4000, by using the electrospray ionization technique (ESI).

The melting points of the compounds were obtained by using a capillary electrothermal instrument.

For calculation of the barriers of the B−N bond torsion, total line-shape simulations were performed by means of a PC version of the DNMR-6 program (QCPE program 633, Indiana University, Bloomington, IN).

***N*-[Tris(pentafluorophenyl)borane]−5*H*-Pyrrole (1). (a) Experiment in CH_2Cl_2.** A yellow-orange solution of pyrrole (0.35 g, 5.11 mmol) in 10 mL of dichloromethane was added at room temperature under nitrogen atmosphere to a light yellow solution of tris(pentafluorophenyl)borane (2.64 g, 5.12 mmol) in 40 mL of dichloromethane in a 100 mL Schlenk flask. Exothermicity was not observed. The obtained yellow reaction mixture was stirred for 2 h at room temperature, and then the solvent was removed in vacuo to give a whitish powder as product (yield 100%): mp 181.1−183.6 °C; ^1H NMR (CD_2Cl_2) δ 4.71 (bs, 2H, *H*5,*H*5′), 6.94 (dq, 1H, $J = 5.48$ Hz, $J = 1.08$ Hz, *H*3), 7.90 (dq, 1H, $J = 5.48$ Hz, $J = 1.08$ Hz, *H*4), 8.58 (m, 1H, $J = 1.08$ Hz, *H*2); ^{13}C NMR (CD_2Cl_2) δ 66.72 (m, *C*5), 128.61 (*C*3), 156.98 (*C*4), 172.04 (*C*2); NOESY (CD_2Cl_2) δ^1H/δ^1H 4.71/7.90 (*H*5/*H*4), 7.90/6.94 (*H*4/*H*3), 6.94/8.58 (*H*3/*H*2); ^1H NMR (C_6D_6) δ 3.70 (bs, 2H, *H*5,*H*5′), 5.62 (dq, 1H, $J = 6.16$ Hz, $J = 1.08$ Hz, *H*3), 6.51 (dq, 1H, $J = 6.16$ Hz, $J = 1.08$ Hz, *H*4), 7.51 (m, 1H, $J = 1.08$ Hz, *H*2); ^{13}C NMR (C_6D_6) δ 65.76 (m, *C*5), 127.38 (*C*3), 155.67 (*C*4), 171.38 (*C*2); NOESY (C_6D_6) δ^1H/δ^1H 3.70/6.51 (*H*5/*H*4), 6.51/5.62 (*H*4/*H*3), 5.62/7.51 (*H*3/*H*2).

The ^1H NMR spectrum in C_6D_6 of complex **1** does not change when the temperature is varied from 173 to 353 K.

(b) Experiment in Toluene. A light yellow solution of tris(pentafluorophenyl)borane (1.182 g, 2.31 mmol) in 8 mL of toluene was added at room temperature to a yellow solution of pyrrole (0.158 g, 2.30 mmol) in 2 mL of toluene under nitrogen atmosphere in a 25 mL Schlenk flask. Exothermicity was not observed. The obtained yellow reaction mixture was stirred for 2 h at room temperature, and then the solvent was removed in vacuo to give a yellow powder as product (1.255 g, purity = 99.5%, yield = 93.8%).

(c) Experiment in Pentane. Pyrrole (0.270 g, 3.94 mmol) was added at room temperature to a light yellow suspension of tris(pentafluorophenyl)borane (2.03 g, 3.94 mmol) in 45 mL of pentane in a 50 mL Schlenk flask. Exothermicity was not observed. After 30 min of stirring at room temperature, a milky suspension was formed and analyzed by ^1H NMR. The pyrrole conversion was found to be quantitative. The solvent was then removed in vacuo to give a whitish powder as product (yield 100%). Traces of the *N*-[tris(pentafluorophenyl)borane]-3*H*-pyrrole isomer were noticed.

Triethylammonium [Tris(pentafluorophenyl)](1*H*-pyrrol-1-yl)borate (1a). A solution of triethylamine (0.1657 g, 1.63 mmol) in 5 mL of dichloromethane was added dropwise at room temperature under nitrogen atmosphere to a solution of **1** (0.9780 g, 1.69 mmol) in 12 mL of dichloromethane in a 25 mL Schlenk flask. Exothermicity was not observed. The light yellow solution was stirred for 1 h at room temperature, and then the solvent was removed in vacuo to give a whitish solid as product (1.14 g, 100%): mp 151.1−152.9 °C.

An aliquot of the product was dissolved into a few milliliters of CH_2Cl_2, and the resulting solution was stored at 5 °C for 20 h: crystals were isolated and analyzed by ^1H NMR: ^1H NMR (CD_2Cl_2) δ 1.27 [t, 9H, $J = 7.24$ Hz, $N(CH_2CH_3)_3$], 3.03 [q, 6H, $J = 7.24$ Hz, $N(CH_2CH_3)_3$], 4.85 (bs, 1H, N*H*), 5.95 (t, 2H, $J = 2.15$ Hz, *H*4, *H*3), 6.80 (m, 2H, *H*5, *H*2); ^{13}C NMR ($CDCl_3$) δ 8.46 [$N(CH_2CH_3)_3$], 46.79 [$N(CH_2CH_3)_3$], 104.13 (*C*4, *C*3), 127.03 (*C*5, *C*2).

***N*-[Tris(pentafluorophenyl)borane]−3*H*-Indole (2). (a) Experiment at Room Temperature in CH_2Cl_2 by Adding $B(C_6F_5)_3$ to Indole.** Indole (1.07 g, 9.0 mmol) was dissolved in 10 mL of CH_2Cl_2 and charged into a 50 mL Schlenk under nitrogen atmosphere. A solution of $B(C_6F_5)_3$ (4.61 g, 9.0 mmol) in 25 mL of CH_2Cl_2 was added at room temperature under stirring. During the addition, the color of the solution turned immediately from yellowish to amber yellow; exothermicity was not observed. The reaction mixture was stirred at room temperature for 1 h, and then the solvent was removed in vacuo to give a whitish solid as product (5.32 g, 94.4%): mp 203.9−206.7 °C; ^1H NMR (CD_2Cl_2) δ 4.30 (broad AB system, 2H, *H*3,*H*3′), 7.39−7.72 (m, 3H, Ar), 7.72 (d, 1H, $J = 7.6$ Hz, *H*4), 8.83 (d, 1H, $J_{HF} = 5.0$ Hz, *H*2); ^{13}C NMR (CD_2Cl_2) δ 42.18 (*C*3), 118.26 (*C*H), 125.35 (*C*H), 129.16 (*C*H), 129.20 (*C*H), 133.07 (*C*), 147.97 (*C*), 175.43 (*C*2) (peak assigned by a DEPT experiment); NOESY (CD_2Cl_2) δ^1H/δ^1H 4.30/7.72 (*H*3/*H*4), 8.83/4.30 (*H*2/*H*3).

^1H NMR analysis at variable temperatures: $T = 271$ K, ^1H NMR ($C_2D_2Cl_4$) δ 4.19 (AB system, 2H, $J = 26.2$ Hz, *H*3,*H*3′), 7.31−7.62 (m, 4H, Ar), 8.72 (t, 1H, $J_{HF} = 4.3$ Hz, *H*2); $T = 297$ K, ^1H NMR ($C_2D_2Cl_4$) δ 4.19 (broad AB system, 2H, *H*3,*H*3′), 7.32−7.62 (m, 4H, Ar), 8.72 (t, 1H, $J_{HF} = 4.9$ Hz, *H*2); $T = 319$ K, ^1H NMR ($C_2D_2Cl_4$) δ 4.19 (bs, 2H, *H*3,*H*3′), 7.34−7.63 (m, 4H, Ar), 8.73 (s, 1H, *H*2); $T = 360$ K, ^1H NMR ($C_2D_2Cl_4$) δ 4.18 (s, 2H, *H*3,*H*3′), 7.36−7.63 (m, 4H, Ar), 8.73 (s, 1H, *H*2).

ESI, m/z 628 [$M^+ - 1$].

(b) Experiment at 0 °C in CH_2Cl_2 by Adding Indole to $B(C_6F_5)_3$. A solution of indole (0.18 g, 1.56 mmol) in 2 mL of dichloromethane was added at 0 °C under nitrogen atmosphere to a solution of tris(pentafluorophenyl)borane (0.81 g, 1.59 mmol) in 6 mL of dichloromethane in a 25 mL Schlenk flask. Exothermicity was not observed. The reaction mixture was allowed to warm to room temperature and stirred for 20 h. A ^1H NMR analysis showed that the reaction was already complete after 1 h of stirring at room temperature. The solvent was evaporated in vacuo to give a whitish solid as product (yield = 95.0%).

(c) Experiment at Room Temperature in CH_2Cl_2 by Adding Indole to $B(C_6F_5)_3$. A solution of indole (0.41 g, 3.42 mmol) in 6 mL of dichloromethane was added at room temperature under nitrogen atmosphere to a solution of tris(pentafluorophenyl)borane (1.76 g, 3.43 mmol) in 9 mL of dichloromethane in a 25 mL Schlenk flask. Exothermicity was not observed. During the addition the color of the solution turned from light yellow to yellow. After 6 h of stirring at room temperature, the solvent was evaporated in vacuo to give a whitish solid as product (2.18 g, purity = 99%, yield = 100%). The ^1H NMR analysis showed the presence of 1 wt % of unreacted indole. ^1H NMR (CD_2Cl_2) δ 4.28 (broad AB system, 2H, *H*3,*H*3′), 7.39−7.72 (m, 4H, Ar), 8.81 (d, 1H, $J_{HF} = 4.9$ Hz, *H*2).

(d) Experiment at −20 °C in Diethyl Ether by Adding Indole to B(C_6F_5)$_3$. A solution of indole (0.72 g, 6.05 mmol) in 5 mL of diethyl ether was added at −20 °C under nitrogen atmosphere to a suspension of tris(pentafluorophenyl)borane (3.13 g, 6.07 mmol) in 20 mL of diethyl ether in a 50 mL Schlenk flask. During the addition the color of the suspension turned from whitish to yellow. The reaction mixture was then allowed to warm to room temperature and stirred for 2 h with final formation of a yellow solution. A ^{1}H NMR analysis showed that the reaction was already complete after 1 h of stirring at room temperature. The solvent was evaporated in vacuo to give a light yellow solid as product (yield 100%). ^{1}H NMR ($CDCl_3$) δ 4.22 (broad AB system, 2H, *H*3,*H*3′), 7.34−7.66 (m, 4H, Ar), 8.77 (d, 1H, J_{HF} = 5.0 Hz, *H*2).

(e) Experiment at Room Temperature in Toluene by Adding Indole to B(C_6F_5)$_3$. A solution of indole (0.65 g, 5.55 mmol) in 5 mL of toluene was added at room temperature under nitrogen atmosphere to a solution of tris(pentafluorophenyl)borane (2.82 g, 5.51 mmol) in 15 mL of toluene in a 50 mL Schlenk flask. Exothermicity was not observed. After 1 h of stirring at room temperature, a ^{1}H NMR analysis showed complete conversion of starting indole to the complex **2**. The solvent was evaporated in vacuo to give a whitish solid as product (yield = 100%): ^{1}H NMR (CD_2Cl_2) δ 4.29 (broad AB system, 2H, *H*3,*H*3′), 7.40−7.72 (m, 4H, Ar), 8.82 (d, 1H, J_{HF} = 5.1 Hz, *H*2).

(f) Experiment at 0 °C in Toluene by Adding B(C_6F_5)$_3$ to Indole. A solution of tris(pentafluorophenyl)borane (1.31 g, 2.56 mmol) in 8 mL of toluene was added at 0 °C under nitrogen atmosphere to a solution of indole (0.30 g, 2.54 mmol) in 2 mL of toluene in a 25 mL Schlenk flask. The reaction mixture was then allowed to warm to room temperature and stirred for 4 h with final formation of a yellow solution. The solvent was evaporated in vacuo to give a whitish solid as product (1.49 g, purity = 97%, yield = 90.4%). The ^{1}H NMR analysis showed the presence of 3 wt % of unreacted indole. ^{1}H NMR (CD_2Cl_2) δ 4.28 (broad AB system, 2H, *H*3,*H*3′), 7.38−7.72 (m, 4H, Ar), 8.81 (d, 1H, J_{HF} = 4.7 Hz, *H*2).

The stability in air of complex **2** was checked both in solution and in the solid state. The complex was found to be quite stable in air, more in the solid state than in solution. Indeed, after 9 days, a CD_2Cl_2 solution of a sample showed little decomposition to a 5 wt % of indole and to a few weight percent of a second compound not identified, whereas after the same time an analogous powdery sample showed <2 wt % of indole and traces of this unknown compound. After 15 days, the powdery sample became pink from white, but its ^{1}H NMR spectrum in CD_2Cl_2 did not change.

***N*-[Tris(pentafluorophenyl)borane]−3*H*-Indole (2) in Toluene-d_8.** *N*-[Tris(pentafluorophenyl)borane]−3*H*-indole (**2**) (30.9 mg) was directly dissolved in the NMR tube under nitrogen. The assigments of the resonances were performed through appropriate standard 2D experiments (Supporting Information): ^{1}H−^{1}H NOESY and COSYGS for ^{1}H; ^{1}H−^{13}C HMQC for ^{13}C; ^{19}F−^{19}F COSY45 and NOESY. ^{1}H NMR (C_7D_8, 290 K, 11 T) δ 2.60 (AB system, ^2J = 26.42 Hz, 1H, *H*3), 2.68 (AB system, 1H, *H*3′), 6.75 (m, 1H, *H*4), 6.79 (m, 1H, *H*6), 6.81 (m, 1H, *H*5), 7.58 (*pseudo*-d, 1H, *J* = 7.76 Hz, *H*7), 7.64 (*pseudo*-d, br, 1H, *H*2); ^{13}C NMR (C_7D_8, 300 K, 7.1 T) δ 40.3 ($1CH_2$, *C*3), 117.96 (1CH, *C*7), 124.6 (1CH, *C*4), 128.66, 128.59 (2CH, *C*5/*C*6), 132.5, 147.6 (2Cq, *C*3a/*C*7a), 174.8 (1CH, *C*2); ^{11}B NMR (C_7D_8, 300 K, 7.1 T) δ −3.47 (s, br); ^{19}F NMR (C_7D_8, 300 K, 7.1 T) ring A, δ −129.90 (m, *ortho*), −131.31 (m, *ortho*), −155.32 (*ps*-t, *para*), −161.55 (m, *meta*), −162.94 (m, *meta*); ring B, δ −133.04 (m, *ortho*), −135.23 (m, *ortho*), −155.44 (*ps*-t, *para*), −163.49 (m, *meta*), −164.32 (m, *meta*); ring C, δ −129.37 (m, *ortho*), −134.52 (m, *ortho*), −156.76 (*ps*-t, *para*), −163.81 (m, *meta*), −164.12 (m, *meta*).

The heteronuclear ^{19}F−^{1}H HETCOR and HOESY experiments were performed at 263 K on a DRX300 spectrometer equipped with a QNP probe ($PW_{90°}$ = 9.5 μs).

The ^{19}F spectrum at 233 K was simulated with the program WINDAISY to obtain the coupling constants reported in Tables S1 and S2 (Supporting Information). To the best of our knowledge, there are no programs that can handle the whole size of the exchange problem (exchange between three sites with five nonequivalent coupled spins each, or even more if also heteronuclear coupling is included), so the analysis was simplified to the exchange among three ABX sites (i.e., only the para and meta resonances for each ring were considered). In this assumption, computer simulations of the para region of the 1D ^{19}F variable temperature spectra were performed with WINDYNAMICS. The rate constants obtained accordingly and the Arrhenius plots are available in the Supporting Information (Table S3 and Figure S28).

Triethylammonium [Tris(pentafluorophenyl)](1*H*-indol-1-yl)borate (2a). Triethylamine (0.22 mL, 1.60 mmol) was added dropwise at room temperature under nitrogen atmosphere to a solution of **2** (1.01 g, 1.60 mmol) in 5 mL of dichloromethane in a 25 mL Schlenk flask. During the addition the solution turned from yellow to pink. Exothermicity was not observed. After 1 h of stirring at room temperature, the solvent was removed in vacuo to give a pinkish solid, which was determined to be the desired product by ^{1}H NMR analysis in CD_2Cl_2 (1.16 g, 99.3%): mp 178.6−181.2 °C; ^{1}H NMR (CD_2Cl_2) δ 1.03 [t, 9H, *J* = 7.3 Hz, $N(CH_2CH_3)_3$], 2.73 [q, 6H, *J* = 7.3 Hz, $N(CH_2CH_3)_3$], 4.70 (bs, 1H, N*H*), 6.33 (m, 1H, *H*3), 6.89−6.98 (m, 2H, Ar), 7.27−7.33 (m, 2H, *H*2 and Ar), 7.45−7.54 (m, 1H, Ar); ^{13}C NMR (CD_2Cl_2) δ 8.77 [$N(CH_2CH_3)_3$], 47.71 [$N(CH_2CH_3)_3$], 98.01 (*C*3), 114.38 (*C*2), 118.13, 119.20, 120.03 (*C*4, *C*5, *C*6), 130.48 (*C*3a), 135.26 (*C*7), 141.17 (*C*7a).

(a) Experiment in One Step. Indole (0.292 g, 2.47 mmol) and triethylamine (0.252 g, 2.48 mmol) were dissolved under nitrogen atmosphere into 2 mL of dichloromethane in a 25 mL Schlenk flask. A solution of tris(pentafluorophenyl)borane (1.26 g, 2.46 mmol) in 6 mL of dichloromethane was added at 0 °C under stirring. At the end of the addition the yellow solution was allowed to warm to room temperature and stirred for 17 h. A ^{1}H NMR analysis showed that the reaction was already complete after 1 h of stirring at room temperature. The solvent was then removed in vacuo to give a pink solid as product (1.54 g, 85.7%). The product was dissolved into 15 mL of CH_2Cl_2, and the resulting solution was stored at 5 °C for 4 h and then at −20 °C for 12 days. Crystals were isolated and analyzed by ^{1}H NMR in CD_2Cl_2 at variable temperatures: *T* = 298 K, ^{1}H NMR (CD_2Cl_2) δ 1.03 [t, 9H, *J* = 7.3 Hz, $N(CH_2CH_3)_3$], 2.73 [q, 6H, *J* = 7.3 Hz, $N(CH_2CH_3)_3$], 4.70 (bs, 1H, N*H*), 6.33 (m,1H, *H*3), 6.89−6.98 (m, 2H, Ar), 7.27−7.33 (m, 2H, *H*2 and Ar), 7.45−7.54 (m, 1H, Ar); *T* = 263 K, ^{1}H NMR (CD_2Cl_2) δ 0.99 [t, 9H, *J* = 7.24 Hz, $N(CH_2CH_3)_3$], 2.75 [q, 6H, *J* = 7.24 Hz, $N(CH_2CH_3)_3$], 4.84 (bs, 1H, N*H*), 6.33 (d, 1H, *J* = 2.84 Hz, *H*3), 6.89−6.98 (m, 2H, Ar), 7.24−7.34 (m, 2H, *H*2 and Ar), 7.45−7.54 (m, 1H, Ar); *T* = 248 K, ^{1}H NMR (CD_2Cl_2) δ 0.97 [t, 9H, *J* = 7.34 Hz, $N(CH_2CH_3)_3$], 2.74 [bq, 6H, *J* = 7.34 Hz, $N(CH_2CH_3)_3$], 4.88 (bs, 1H, N*H*), 6.33 (d, 1H, *J* = 2.84 Hz, *H*3), 6.89−6.97 (m, 2H, Ar), 7.24−7.36 (m, 2H, *H*2 and Ar), 7.45−7.53 (m, 1H, Ar); *T* = 238 K, ^{1}H NMR (CD_2Cl_2) δ 0.96 [t, 9H, *J* = 7.34 Hz, $N(CH_2CH_3)_3$], 2.73 [m, 6H, *J* = 7.34 Hz, $N(CH_2CH_3)_3$], 4.82 (bs, 1H, N*H*), 6.33 (d, 1H, *J* = 2.84 Hz, *H*3), 6.88−6.97 (m, 2H, Ar), 7.24−7.35 (m, 2H, *H*2 and Ar), 7.44−7.53 (m, 1H, Ar); *T* = 203 K, ^{1}H NMR (CD_2Cl_2) δ 0.90 [t, 9H, *J* = 7.34 Hz, $N(CH_2CH_3)_3$], 2.72 [m, 6H, *J* = 7.34 Hz, $N(CH_2CH_3)_3$], 4.86 (bs, 1H, N*H*), 6.32 (d, 1H, *J* = 2.93 Hz, *H*3), 6.87−6.96 (m, 2H, Ar), 7.23−7.34 (m, 2H, *H*2 and Ar), 7.43−7.52 (m, 1H, Ar). The CD_2Cl_2 solution of the crystals was stable for 1 day under nitrogen atmosphere.

***N*-[Tris(pentafluorophenyl)borane]−2,5-Dimethyl-5*H*-pyrrole (3).** A pink solution of 2,5-dimethylpyrrole (0.313 g, 3.22 mmol) in 8 mL of dichloromethane was added at room temperature under nitrogen atmosphere to a light yellow solution of tris(pentafluorophenyl)borane (1.659 g, 3.22 mmol) in 15 mL of dichloromethane in a 25 mL Schlenk flask.

Exothermicity was not observed. The reaction mixture was stirred for 5 h at room temperature and analyzed by ^{1}H NMR at different times. The final light-orange solution was dried in vacuo, giving a yellow powder as product (1.878 g, 96.1%): mp 145.8−146.9 °C.

The product was found to be, by NMR analysis, a mixture of *N*-[tris(pentafluorophenyl)borane]−2,5-dimethyl-5*H*-pyrrole (**3**, 90%) and *N*-[tris(pentafluorophenyl)borane]−2,5-dimethyl-3*H*-pyrrole (**3′**, 10%). *N*-[Tris(pentafluorophenyl)borane]−2,5-dimethyl-5*H*-pyrrole (**3**): ^{1}H NMR (CD_2Cl_2) δ 1.23 (bt, 3H, J = 7.14 Hz, CH_3 in 5), 2.20 (d, 3H, J = 2.84 Hz, CH_3 in 2), 5.41 (bs, 1H, *H*5), 6.62 (dd, 1H, J = 5.48 Hz, J = 1.17 Hz, *H*3), 7.67 (m, 1H, J = 5.48 Hz, *H*4); ^{1}H NMR (C_6D_6) δ 0.50 (m, 3H, CH_3 in 5), 1.29 (d, 3H, J = 2.74 Hz, CH_3 in 2), 4.70 (bs, 1H, *H*5), 5.27 (dd, 1H, J = 5.38 Hz, J = 1.17 Hz, *H*3), 6.21 (dm, 1H, J = 5.38 Hz, *H*4); ^{13}C NMR (CD_2Cl_2) δ 15.94 (d, J_{CF} = 15.3 Hz, *C*H$_3$ in 5), 19.36 (bs, *C*H$_3$ in 2), 77.02 (d, J_{CF} = 15.3 Hz, *C*H5), 130.31 (*C*3), 161.43 (*C*4), 185.86 (d, J_{CF} = 3.70 Hz, *C*2); NOESY (CD_2Cl_2) δ^1H/δ^1H 5.41/1.23 (*H*5/CH_3 in 5), 2.20/6.62 (CH_3 in 2/*H*3), 6.62/7.67 (*H*3/*H*4), 7.67/5.41 (*H*4/*H*5). *N*-[Tris(pentafluorophenyl)borane]−2,5-dimethyl-3*H*-pyrrole (**3′**): ^{1}H NMR (CD_2Cl_2) δ 2.03 (bs, 3H, CH_3), 2.44 (m, 3H, J = 2.05 Hz, CH_3), 3.71 (broad AB system, 2H, J = 26.8 Hz, *H*3,*H*3′), 6.10 (bs, 1H, *H*4); ^{1}H NMR (C_6D_6) δ 1.53 (m, 3H, CH_3), 1.61 (bs, 3H, CH_3), 2.09 (broad AB system, 2H, J = 27.1 Hz, *H*3,*H*3′), 4.98 (bs, 1H, *H*4).

The ^{1}H NMR analysis of **3** at variable temperatures in CD_2Cl_2 showed a significant change only in the signal of the methyl group in the 2-position, which resulted in a clear triplet at 238 K, with chemical shift of 1.18 ppm and J = 7.24 Hz.

Triethylammonium [Tris(pentafluorophenyl)](2,5-dimethyl-1*H*-pyrrol-1-yl)borate (3a). A solution of triethylamine (0.2209 g, 2.17 mmol) in 5 mL of dichloromethane was added dropwise at room temperature under nitrogen atmosphere to a solution of **3** (1.3080 g, 2.15 mmol) in 12 mL of dichloromethane in a 25 mL Schlenk flask. Exothermicity was not observed. The yellow solution was stirred for 1 h at room temperature, and then the solvent was removed in vacuo to give a yellow-light orange solid as product (yield 100%): mp 119.8−121.5 °C.

An aliquot of the product was dissolved into a few milliliters of CH_2Cl_2, and the resulting solution was stored at −20 °C for a few days: crystals were isolated and analyzed by ^{1}H NMR: ^{1}H NMR (CD_2Cl_2) δ 1.28 [t, 9H, J = 7.24 Hz, N(CH$_2$C*H*$_3$)$_3$], 1.96 (bs, 6H, CH_3), 3.06 [q, 6H, J = 7.24 Hz, N(C*H*$_2$CH$_3$)$_3$], 5.68 (bs, 3H, *H*3, *H*4, N*H*); ^{1}H NMR (C_6D_6) δ 0.38 [t, 9H, J = 7.24 Hz, N(CH$_2$C*H*$_3$)$_3$], 1.87 [q, 6H, J = 7.24 Hz, N(C*H*$_2$CH$_3$)$_3$], 2.13 (bs, 6H, CH_3), 5.55 (bs, 3H, *H*3, *H*4, N*H*); ^{13}C NMR (CD_2Cl_2) δ 8.84 [N(CH$_2$*C*H$_3$)$_3$], 16.63 (m, *C*H$_3$), 47.35 [N(*C*H$_2$CH$_3$)$_3$], 104.69 (*C*3, *C*4), 137.29 (*C*2, *C*5).

***N*-[Tris(pentafluorophenyl)borane]−2,4-Dimethyl-5*H*-pyrrole (4).** A yellow-orange solution of 2,4-dimethylpyrrole (0.564 g, 5.75 mmol) in 5 mL of dichloromethane was added at room temperature under nitrogen atmosphere to a light yellow solution of tris(pentafluorophenyl)borane (3.267 g, 6.34 mmol) in 20 mL of dichloromethane in a 50 mL Schlenk flask. Exothermicity was not observed. The yellow reaction mixture was stirred for 20 h at room temperature and analyzed by ^{1}H NMR at different times. The final yellow solution was dried in vacuo, giving a dark yellow powder as product (yield = 100%): mp 209.2−211.8 °C; ^{1}H NMR (CD_2Cl_2) δ 2.20 (t, 3H, J = 2.74 Hz, CH_3 in 2), 2.29 (d, 3H, J = 1.57 Hz, CH_3 in 4), 4.82 (broad AB system, 2H, *H*5,*H*5′), 6.41 (q, 1H, J = 1.57 Hz, *H*3); ^{1}H NMR (C_6D_6) δ 1.14 (d, 3H, J = 1.47 Hz, CH_3 in 4), 1.41 (t, 3H, J = 2.74 Hz, CH_3 in 2), 4.20 (bs, 2H, *H*5,*H*5′), 5.06 (bq, 1H, J = 1.47 Hz, *H*3); ^{13}C NMR (CD_2Cl_2) δ 14.56 (*C*H$_3$ in 4), 18.40 (*C*H$_3$ in 2), 70.32 (*C*5), 128.65 (*C*3), 169.60 (*C*4), 185.40 (*C*2); NOESY (CD_2Cl_2) δ^1H/δ^1H 4.82/2.29 (*H*5/CH_3 in 4), 2.29/6.41 (CH_3 in 4/*H*3), 6.41/2.20 (*H*3/CH_3 in 2).

NMR analyses at variable temperatures: T = 239 K, ^{1}H NMR (CD_2Cl_2) δ 2.16 (m, 3H, CH_3 in 2), 2.25 (d, 3H, J = 1.22 Hz, CH_3 in 4), 4.64 (AB system, 1H, J = 24.26 Hz, J = 2.54 Hz, *H*5), 4.90 (AB system, 1H, J = 24.26 Hz, *H*5′), 6.39 (bq, 1H, J = 1.22 Hz, *H*3). ^{13}C NMR (CD_2Cl_2) δ 14.52 (*C*H$_3$ in 4), 18.14 (d, J_{CF} = 3.12 Hz, *C*H$_3$ in 2), 69.83 (t, J_{CF} = 9.86 Hz, *C*5), 128.11 (*C*3), 169.16 (*C*4), 184.94 (d, J_{CF} = 3.12 Hz, *C*2). T = 313 K, ^{1}H NMR ($C_2D_2Cl_4$) δ 2.14 (m, 3H, CH_3 in 2), 2.23 (d, 3H, J = 1.33 Hz, CH_3 in 4), 4.72 (bs, 2H, *H*5, *H*5′), 6.32 (m, 1H, *H*3).

***N*-[Tris(pentafluorophenyl)borane]−5-ethyl-5*H*-pyrrole (5).** An orange solution of 2-ethylpyrrole (0.367 g, 3.47 mmol) in 5 mL of dichloromethane was added at room temperature under nitrogen atmosphere to a light yellow solution of tris(pentafluorophenyl)borane (1.800 g, 3.49 mmol) in 15 mL of dichloromethane in a 25 mL Schlenk flask. During the addition the color of the solution turned immediately from orange to dark orange; exothermicity was not observed. The reaction mixture was stirred overnight at room temperature: a ^{1}H NMR analysis showed the presence of ∼11 mol % of unreacted 2-ethylpyrrole. Then 0.21 g (0.41 mmol) of tris(pentafluorophenyl)borane was added to complete the reaction. After a few minutes of stirring, the solvent was removed in vacuo to give a dark yellow powder as product (yield = 100%): mp 185.4−186.8 °C; ^{1}H NMR (CD_2Cl_2) δ 0.88 (t, 3H, J = 7.43 Hz, CH_3), 2.67 (bm, 2H, CH_2), 4.99 (broad AB system, J = 25.24 Hz, 2H, *H*5,*H*5′), 6.88 (dt, 1H, J = 5.58 Hz, J = 1.27 Hz, *H*3), 7.77 (d, 1H, J = 5.58 Hz, *H*4); ^{1}H NMR (C_6D_6) δ 0.075 (t, 3H, J = 7.43 Hz, CH_3), 2.00 (m, 2H, J = 7.43 Hz, CH_2), 4.14 (broad AB system, J = 25.14 Hz, 2H, *H*5,*H*5′), 5.54 (dt, 1H, J = 5.48 Hz, J = 1.27 Hz, *H*3), 6.31 (d, 1H, J = 5.48 Hz, *H*4); NOESY (CD_2Cl_2) δ^1H/δ^1H 2.67/6.88 (C*H*$_2$/*H*3), 6.88/7.77 (*H*3/*H*4), 7.77/4.99 (*H*4/*H*5); ^{13}C NMR (CD_2Cl_2) δ 9.80 (*C*H$_3$), 25.48 (*C*H$_2$), 68.36 (m, *C*5), 130.30 (*C*3), 154.37 (*C*4), 189.38 (*C*2).

^{1}H NMR analysis at variable temperatures: T = 239 K, ^{1}H NMR (CD_2Cl_2) δ 0.79 (t, 3H, J = 7.34 Hz, CH_3), 2.34−2.87 (m, 2H, CH_2), 4.94 (AB system, 2H, J = 26.21 Hz, *H*5,*H*5′), 6.84 (d, 1H, J = 5.48 Hz, *H*3), 7.76 (d, 1H, J = 5.48 Hz, *H*4); T = 313 K, ^{1}H NMR ($C_2D_2Cl_4$) δ 0.80 (t, 3H, J = 7.52 Hz, CH_3), 2.42−2.90 (broad AB system, 2H, CH_2), 4.91 (broad AB system, 2H, *H*5,*H*5′), 6.78 (d, 1H, J = 5.55 Hz, *H*3), 7.69 (d, 1H, J = 5.55 Hz, *H*4); T = 320 K, ^{1}H NMR ($C_2D_2Cl_4$) δ 0.81 (t, 3H, J = 7.52 Hz, CH_3), 2.56 (bs, 2H, CH_2), 4.91 (bs, 2H, *H*5,*H*5′), 6.78 (d, 1H, J = 5.53 Hz, *H*3), 7.69 (d, 1H, J = 5.53 Hz, *H*4); T = 332 K, ^{1}H NMR ($C_2D_2Cl_4$) δ 0.83 (t, 3H, J = 7.51 Hz, CH_3), 2.58 (bs, 2H, CH_2), 4.92 (bs, 2H, *H*5,*H*5′), 6.78 (d, 1H, J = 5.51 Hz, *H*3), 7.69 (d, 1H, J = 5.51 Hz, *H*4).

Triethylammonium [Tris(pentafluorophenyl)](2-ethyl-1*H*-pyrrol-1-yl)borate (5a). A solution of triethylamine (0.2288 g, 2.25 mmol) in 6 mL of dichloromethane was added dropwise at room temperature under nitrogen atmosphere to a solution of **5** (1.3518 g, 2.23 mmol) in 10 mL of dichloromethane in a 25 mL Schlenk flask. Exothermicity was not observed. The orange solution was stirred for 4 h at room temperature, and then the solvent was removed in vacuo to give an orange powder as product (1.58 g, 100%): mp 79.7−81.6 °C; ^{1}H NMR (CD_2Cl_2) δ 0.94 (t, 3H, J = 8.02 Hz, CH_3), 1.28 [t, 9H, J = 7.24 Hz, N(CH$_2$C*H*$_3$)$_3$], 1.94−2.80 (bm, 2H, CH_2), 3.07 [q, 6H, J = 7.24 Hz, N(C*H*$_2$CH$_3$)$_3$], 5.89 (bs, 2H, *H*3, *H*4), 6.17 (bs, 1H, N*H*), 6.74 (bs, 1H, *H*5); ^{13}C NMR (CD_2Cl_2) δ 8.74 [N(CH$_2$*C*H$_3$)$_3$], 13.67 (*C*H$_3$), 21.24 (*C*H$_2$), 47.33 [N(*C*H$_2$CH$_3$)$_3$], 102.24 (*C*3 or *C*4), 103.74 (*C*4 or *C*3), 126.73 (*C*5), 142.91 (*C*2).

^{1}H NMR analysis at variable temperatures: T = 238 K, ^{1}H NMR (CD_2Cl_2) δ 0.94 (t, 3H, J = 7.27 Hz, CH_3), 1.25 [t, 9H, J = 7.24 Hz, N(CH$_2$C*H*$_3$)$_3$], 1.95−2.70 (m, 2H, CH_2), 3.05 [bm, 6H, N(C*H*$_2$CH$_3$)$_3$], 5.89 (bs, 1H, *H*3), 5.92 (m, 1H, *H*4), 6.75 (bs, 1H, *H*5), 6.86 (bs, 1H, N*H*).

***N*-[Tris(pentafluorophenyl)borane]−2*H*-4,5,6,7-Tetrahydroindole (6).** A solution of 4,5,6,7-tetrahydroindole (0.65 g, 5.25 mmol) in 3 mL of dichloromethane was added at room temperature under nitrogen atmosphere to a solution of tris(pentafluorophenyl)borane (2.69 g, 5.25 mmol) in 15 mL of dichloromethane in a 25 mL Schlenk flask. A light exothermicity was observed. The reaction mixture was stirred for 30

min at room temperature, and then the solvent was evaporated in vacuo to give a brick red powder as product (yield = 100%): mp 108.8−111.8 °C; ^{1}H NMR (CD_2Cl_2) δ 1.02−3.42 (bs, 8H, *H*4,*H*4′, *H*5,*H*5′, *H*6,*H*6′, *H*7,*H*7′), 4.85 (broad AB system, 2H, *H*2,*H*2′), 7.34 (bm, 1H, *H*3); ^{13}C NMR (CD_2Cl_2) δ 21.74 (*C*5 and *C*6), 23.87 (*C*4), 29.76 (*C*7), 66.39 (d, *C*2, J_{CF} = 10.4 Hz), 140.78 (*C*3a), 147.02 (*C*3), 186.25 (*C*7a).

^{1}H NMR analyses at variable temperatures: *T* = 238 K, ^{1}H NMR (CD_2Cl_2) δ 1.26−3.16 (bm, 8H, *H*4,*H*4′, *H*5,*H*5′, *H*6,*H*6′, *H*7,*H*7′), 4.80 (AB system, 2H, *J* = 26.02 Hz, *H*2,*H*2′), 7.34 (bs, 1H, *H*3).

***N*-[Tris(pentafluorophenyl)borane]−2-Methyl-3*H*-indole (7). (a) Experiment in CH_2Cl_2.** A solution of 2-methylindole (0.67 g, 5.01 mmol) in 10 mL of dichloromethane was added at room temperature under nitrogen atmosphere to a solution of tris(pentafluorophenyl)borane (2.60 g, 5.05 mmol) in 15 mL of dichloromethane in a 50 mL Schlenk flask. Exothermicity was not observed. During the addition the color of the solution turned from light orange to orange. A ^{1}H NMR analysis in CD_2Cl_2 showed quantitative conversion of the starting 2-methylindole after 1 h of stirring at room temperature. The reaction mixture became a light pink suspension after 4 h of stirring at room temperature. The stirring was continued overnight, and then the suspension was filtered on a G3 frit. The residue on the frit was a white solid and was determined to be the desired product by ^{1}H NMR analysis in C_6D_6 (2.16 g, 67.0%), mp 204.3−204.5 °C. The final complex is not fully soluble in CD_2Cl_2, whereas it is fully soluble in C_6D_6: ^{1}H NMR (C_6D_6) δ 1.70 (m, 3H, C*H*$_3$), 2.46 (AB system, 2H, *J* = 25.63 Hz, *H*3,*H*3′), 6.64−6.83 (m, 3H, Ar), 7.61−7.69 (m, 1H, Ar); ^{13}C NMR (C_6D_6) δ 18.77 (dd, J_{CF} = 9.20 Hz, J_{CF} = 2.50 Hz, *C*H$_3$), 46.88 (*C*3), 117.74 (dd, J_{CF} = 7.66 Hz, J_{CF} = 1.84 Hz, *C*7), 123.83 (Ar), 127.75 (Ar), 128.15 (Ar), 130.79 (*C*3a), 150.44 (d, J_{CF} = 3.98 Hz, *C*7a), 189.36 (*C*2); COSY (C_6D_6) δ^1H/δ^1H 2.46/1.70 (*H*3/C*H*$_3$).

^{1}H NMR analyses at variable temperatures: *T* = 297 K, ^{1}H NMR ($C_6D_5CD_3$) δ 1.84 (m, 3H, C*H*$_3$), 2.59 (AB system, 2H, *J* = 25.43 Hz, *H*3,*H*3′), 6.71−6.88 (m, 3H, Ar), 7.60−7.66 (m, 1H, Ar); *T* = 354 K, ^{1}H NMR ($C_6D_5CD_3$) δ 1.95 (bs, 3H, C*H*$_3$), 2.85 (broad AB system, 2H, *H*3,*H*3′), 6.80−6.91 (m, 3H, Ar), 7.53−7.61 (m, 1H, Ar); *T* = 381 K, ^{1}H NMR ($C_6D_5CD_3$) δ 1.98 (bs, 3H, C*H*$_3$), 2.93 (bs, 2H, *H*3,*H*3′), 6.86−6.98 (bm, 3H, Ar), 7.53−7.58 (bm, 1H, Ar).

(b) Experiment in Toluene. A pink solution of 2-methylindole (0.3104 g, 2.32 mmol) in 10 mL of toluene was added at room temperature under nitrogen atmosphere to a solution of tris(pentafluorophenyl)borane (1.2029 g, 2.34 mmol) in 15 mL of toluene in a 50 mL Schlenk flask. Exothermicity was not observed. A ^{1}H NMR analysis in toluene-d_8 showed quantitative conversion of the starting 2-methylindole after 10 min of stirring at room temperature. Then the orange solution was evaporated in vacuo to give a light pink powder, which was determined to be the desired product by ^{1}H NMR analysis in toluene-d_8 (1.44 g, 96.5%).

Triethylammonium [Tris(pentafluorophenyl)](2-methyl-1*H*-indol-1-yl)borate (7a). A solution of triethylamine (0.1339 g, 1.32 mmol) in 10 mL of dichloromethane was added dropwise at room temperature under nitrogen atmosphere to a white suspension of **7** (0.8476 g, 1.32 mmol) in 10 mL of dichloromethane in a 25 mL Schlenk flask. During the addition the white suspension became a light yellow solution. Exothermicity was not observed. A ^{1}H NMR analysis in C_6D_6 showed complete conversion after 1 h of stirring at room temperature. Then after 2 h, the solvent was removed in vacuo to give a white solid, which was determined to be the desired product by ^{1}H NMR analysis (0.858 g, 87.3%): mp 87.0−89.2 °C; ^{1}H NMR (C_6D_6) δ 0.20 [t, 9H, *J* = 7.24 Hz, N(CH$_2$C*H*$_3$)$_3$], 1.64 [q, 6H, *J* = 7.24 Hz, N(C*H*$_2$CH$_3$)$_3$], 2.39 (bs, 3H, C*H*$_3$), 6.61−6.78 (m, 2H, C*H*), 7.04−7.09 (m, 1H, C*H*), 7.14 (m, 1H, C*H*), 7.47−7.51 (m, 1H, C*H*); ^{1}H NMR (CD_2Cl_2) δ 0.99 [t, 9H, *J* = 7.24 Hz, N(CH$_2$C*H*$_3$)$_3$], 2.23 (bs, 3H, C*H*$_3$), 2.66 [q, 6H, *J* = 7.24 Hz, N(C*H*$_2$CH$_3$)$_3$], 4.20 (bs, 1H, N*H*), 6.17 (bs, 1H, *H*3), 6.76−6.93 (m, 2H, C*H*), 7.06−7.10 (m, 1H, C*H*), 7.36−7.41 (m, 1H, C*H*); ^{13}C NMR (CD_2Cl_2) δ 8.80 [N(CH$_2$*C*H$_3$)$_3$], 16.41 (dd, J_{CF} = 6.10 Hz, J_{CF} = 3.70 Hz, *C*H$_3$), 47.58 [N(*C*H$_2$CH$_3$)$_3$], 101.09 (*C*H), 114.87 (dd, J_{CF} = 6.10 Hz, J_{CF} = 1.20 Hz, *C*H), 117.46 (*C*H), 117.56 (*C*H), 118.83 (*C*H), 130.09 (*C*), 142.96 (*C*), 146.34 (*C*).

^{1}H NMR analyses at variable temperatures: *T* = 238 K, ^{1}H NMR (CD_2Cl_2) δ 0.92 [t, 9H, *J* = 7.24 Hz, N(CH$_2$C*H*$_3$)$_3$], 2.17 (bs, 3H, C*H*$_3$), 2.64 [q, 6H, *J* = 7.24 Hz, N(C*H*$_2$CH$_3$)$_3$], 4.20 (bs, 1H, N*H*), 6.15 (bs, 1H, *H*3), 6.74−6.91 (m, 2H, C*H*), 7.02 (d, 1H, *J* = 8.31 Hz, C*H*), 7.37 (dd, 1H, *J* = 7.34 Hz, *J* = 0.98 Hz, C*H*).

***N*-[Tris(pentafluorophenyl)borane]−3-Methyl-3*H*-indole (8).** A solution of 3-methylindole (0.92 g, 6.87 mmol) in 10 mL of dichloromethane was added at room temperature under nitrogen atmosphere to a solution of tris(pentafluorophenyl)borane (3.53 g, 6.85 mmol) in 15 mL of dichloromethane in a 50 mL Schlenk flask. Exothermicity was not observed. During the addition the color of the solution turned from light yellow to yellow. After 30 min of stirring at room temperature, a ^{1}H NMR analysis showed the presence of traces of unreacted 3-methylindole. Then 0.23 g (0.45 mmol) of tris(pentafluorophenyl)borane was added to complete the reaction. After overnight stirring, the solvent was removed in vacuo to give a white powder as product (yield = 100%): mp 114.2−117.5 °C; ^{1}H NMR (CD_2Cl_2) δ 1.61 (bs, 3H, C*H*$_3$), 4.31 (bs, 1H, *H*3), 7.35−7.67 (m, 4H, Ar), 8.69 (d, 1H, J_{HF} = 5.3 Hz, *H*2); ^{1}H NMR (C_6D_6) δ 0.65 (bs, 3H, C*H*$_3$), 2.74 (bs, 1H, *H*3), 6.62−6.84 (m, 3H, Ar), 7.53−7.62 (m, 1H, Ar), 7.91 (bs, 1H, *H*2, first diastereoisomer), 7.97 (bs, 1H, *H*2, second diastereoisomer); ^{13}C NMR (C_6D_6) δ 11.72 (*C*H$_3$), 46.97 (*C*3), 111.18 (*C*H), 117.99 (*C*7), 123.76 (*C*H), 128.97 (*C*H), 138.32 (*C*3a), 146.52 (*C*7a), 179.29 (*C*2). The complex **8** cleanly shows two diastereoisomers at 291 K in CD_2Cl_2. The ratio between the two diastereoisomers is 55(first):45(second) at 283 K in CD_2Cl_2 and does not change at lower temperature.

^{1}H NMR analyses at variable temperatures: *T* = 173 K, ^{1}H NMR (CD_2Cl_2) δ 1.49 (d, 3H, *J* = 6.85 Hz, C*H*$_3$, first diastereoisomer), 1.61 (d, 3H, *J* = 6.85 Hz, C*H*$_3$, second diastereoisomer), 4.24 (q, 1H, *J* = 6.85 Hz, *H*3, second diastereoisomer), 4.38 (q, 1H, *J* = 6.85 Hz, *H*3, first diastereoisomer), 7.31−7.64 (m, 4H, Ar), 8.38−8.73 (m, 1H, *H*2); *T* = 203 K, ^{1}H NMR (CD_2Cl_2) δ 1.50 (d, 3H, *J* = 7.9 Hz, C*H*$_3$, first diastereoisomer), 1.62 (d, 3H, *J* = 7.9 Hz, C*H*$_3$, second diastereoisomer), 4.24 (q, 1H, *J* = 7.9 Hz, *H*3, second diastereoisomer), 4.36 (q, 1H, *J* = 7.9 Hz, *H*3, first diastereoisomer), 7.32−7.64 (m, 4H, Ar), 8.64−8.71 (m, 1H, *H*2); *T* = 239 K, ^{1}H NMR (CD_2Cl_2) δ 1.53 (d, 3H, *J* = 8.02 Hz, C*H*$_3$, first diastereoisomer), 1.65 (d, 3H, *J* = 8.02 Hz, C*H*$_3$, second diastereoisomer), 4.23 (q, 1H, *J* = 8.02 Hz, *H*3, second diastereoisomer), 4.36 (q, 1H, *J* = 8.02 Hz, *H*3, first diastereoisomer), 7.34−7.65 (m, 4H, Ar), 8.66−8.71 (m, 1H, *H*2); *T* = 239 K, ^{1}H NMR ($C_6D_5CD_3$) δ 0.69 (d, 3H, *J* = 7.92 Hz, C*H*$_3$, first diastereoisomer), 0.75 (d, 3H, *J* = 7.92 Hz, C*H*$_3$, second diastereoisomer), 2.49 (q, 1H, *J* = 7.92 Hz, *H*3, first diastereoisomer), 2.78 (q, 1H, *J* = 7.92 Hz, *H*3, second diastereoisomer), 6.61−6.85 (m, 3H, Ar), 7.52−7.68 (m, 2H, *H*2 for the first diastereoisomer and 1 Ar), 8.05 (t, 1H, *J* = 4.79 Hz, *H*2 for the second diastereoisomer); *T* = 283 K, ^{1}H NMR (CD_2Cl_2) δ 1.54 (d, 3H, *J* = 8.22 Hz, C*H*$_3$, first diastereoisomer), 1.67 (d, 3H, *J* = 8.22 Hz, C*H*$_3$, second diastereoisomer), 4.22 (q, 1H, *J* = 8.22 Hz, *H*3, second diastereoisomer), 4.34 (q, 1H, *J* = 8.22 Hz, *H*3, first diastereoisomer), 7.34−7.65 (m, 4H, Ar), 8.68 (two overlapping doublets, 1H, *H*2); *T* = 297 K, ^{1}H NMR (CD_2Cl_2) δ 1.61 (bs, 3H, C*H*$_3$), 4.28 (bs, 1H, *H*3), 7.36−7.66 (m, 4H, Ar), 8.68 (d, 1H, J_{HF} = 5.38 Hz, *H*2).

^{13}C NMR analyses at variable temperatures: *T* = 239 K, ^{13}C NMR (CD_2Cl_2) δ 12.23 (*C*H$_3$, first diastereoisomer), 12.38 (*C*H$_3$, second diastereoisomer), 47.64 (*C*3, first diastereoisomer), 47.72 (*C*3, second diastereoisomer), 117.88 (Ar), 124.15 (Ar), 128.95 (2 Ar), 138.56 (*C*3a), 146.52 (*C*7a), 179.81 (*C*2, second diastereoisomer), 180.19 (*C*2, first diastereoisomer).

Triethylammonium [Tris(pentafluorophenyl)](3-methyl-1*H*-indol-1-yl)borate (8a). A solution of triethylamine

(0.36 g, 3.56 mmol) in 10 mL of dichloromethane was added dropwise at room temperature under nitrogen atmosphere to a solution of **8** (2.2671 g, 3.52 mmol) in 10 mL of dichloromethane in a 25 mL Schlenk flask. During the addition the solution turned from light yellow to yellow. Exothermicity was not observed. After overnight stirring at room temperature, the final pink reaction mixture was evaporated in vacuo to give a pink solid, which was determined to be the desired product by ^{1}H NMR analysis in CD_2Cl_2 (2.630 g, 100%), mp 181.4−182.1 °C. An aliquot of the product was dissolved into 10 mL of CH_2Cl_2, and the resulting solution was stored at 5 °C for 1 day and then at −20 °C for 2 days. Crystals were isolated and analyzed by ^{1}H NMR in CD_2Cl_2. ^{1}H NMR (CD_2Cl_2) δ 1.04 [t, 9H, J = 7.24 Hz, N(CH_2CH_3)$_3$], 2.31 (d, 3H, J = 0.78 Hz, CH_3), 2.73 [q, 6H, J = 7.24 Hz, N(CH_2CH_3)$_3$], 3.61 (bs, 1H, N*H*), 6.87−6.96 (m, 2H, C*H*), 7.09 (bs, 1H, C*H*), 7.21−7.29 (m, 1H, C*H*), 7.40−7.48 (m, 1H, C*H*); ^{13}C NMR (CD_2Cl_2) δ 8.61 [N(CH_2CH_3)$_3$], 9.99 (CH_3), 47.35 [N(CH_2CH_3)$_3$], 107.11 (*C*3), 111.25 (*C*3a or *C*7a), 114.02, 116.74, 117.52, 119.42 (*C*4, *C*5, *C*6, *C*7), 131.00 (*C*7a or *C*3a), 133.07 (*C*2).

^{1}H NMR analyses at variable temperatures: T = 238 K, ^{1}H NMR (CD_2Cl_2) δ 0.98 [t, 9H, J = 7.24 Hz, N(CH_2CH_3)$_3$], 2.27 (d, 3H, J = 0.78 Hz, CH_3), 2.70 [q, 6H, J = 7.24 Hz, N(CH_2CH_3)$_3$], 4.11 (bs, 1H, N*H*), 6.85−6.94 (m, 2H, C*H*), 7.09 (bt, 1H, J = 3.67 Hz, C*H*), 7.16−7.23 (bm, 1H, C*H*), 7.38−7.47 (m, 1H, C*H*).

***N*-[Tris(pentafluorophenyl)borane]−5-Methoxy-3*H*-indole (9).** A solution of 5-methoxyindole (0.78 g, 5.25 mmol) in 10 mL of CH_2Cl_2 was added at 0 °C under nitrogen atmosphere to a solution of tris(pentafluorophenyl)borane (2.98 g, 5.79 mmol) in 20 mL of CH_2Cl_2 in a 50 mL Schlenk flask. During the addition, the color of the solution turned immediately from light yellow to yellow. The reaction mixture was allowed to warm to room temperature and stirred for 2 h, and then the solvent was removed in vacuo to give a white powder as product (yield = 100%): ^{1}H NMR (CD_2Cl_2) δ 3.85 (s, 3H, OCH_3), 4.21 (broad AB system, 2H, *H*3, *H*3′), 6.94 (dd, 1H, J = 9.11 Hz, J = 2.69 Hz, *H*6), 7.18 (d, 1H, J = 2.69 Hz, *H*4), 7.50 (d, 1H, J = 9.11 Hz, *H*7), 8.66 (d, 1H, J = 4.83 Hz, *H*2); ^{13}C NMR (CD_2Cl_2) δ 41.99 (*C*3), 56.20 (OCH_3), 110.45 (*C*4), 115.12 (*C*6), 118.94 (*C*7), 135.17 (*C*3a), 141.43 (*C*7a), 160.82 (*C*5), 172.87 (*C*2); NOESY (CD_2Cl_2) δ^1H/δ^1H 4.21/7.18 (*H*3/*H*4), 4.21/8.66 (*H*3/*H*2), 3.85/7.18 (OCH_3/*H*4), 3.85/6.94 (OCH_3/*H*6), 7.50/6.94 (*H*7/*H*6).

^{1}H NMR analysis at variable temperatures: T = 238 K, ^{1}H NMR (CD_2Cl_2) δ 3.82 (s, 3H, OCH_3), 4.25 (AB system, 2H, J = 26.16 Hz, *H*3, *H*3′), 6.90 (dd, 1H, J = 9.11 Hz, J = 2.32 Hz, *H*6), 7.16 (d, 1H, J = 2.32 Hz, *H*4), 7.46 (d, 1H, J = 9.11 Hz, *H*7), 8.65 (t, 1H, J = 4.50 Hz, *H*2).

Triethylammonium [Tris(pentafluorophenyl)](5-methoxy-1*H*-indol-1-yl)borate (9a). A solution of triethylamine (0.17 g, 1.70 mmol) in 10 mL of dichloromethane was added dropwise at room temperature under nitrogen atmosphere to a solution of **9** (1.12 g, 1.70 mmol) in 15 mL of dichloromethane in a 50 mL Schlenk flask. During the addition the solution turned from yellow to pink. Exothermicity was not observed. After 1 h of stirring at room temperature, the solvent was removed in vacuo to give a pink powder, which was determined to be the desired product by NMR analysis in CD_2Cl_2 (yield = 100%); mp 81.7−82.9 °C; ^{1}H NMR (CD_2Cl_2) δ 1.06 [t, 9H, J = 7.58 Hz, N(CH_2CH_3)$_3$], 2.85 [q, 6H, J = 7.58 Hz, N(CH_2CH_3)$_3$], 3.80 (s, 1H, OCH_3), 4.93 (bs, 1H, N*H*), 6.26 (bs,1H, *H*3), 6.59 (dd, 1H, J = 9.05 Hz, J = 2.69 Hz, *H*6), 7.00 (d, 1H, J = 2.69 Hz, *H*4), 7.19 (d, 1H, J = 9.05 Hz, *H*7), 7.31 (bs, 1H, *H*2); ^{13}C NMR (CD_2Cl_2) δ 8.89 [N(CH_2CH_3)$_3$], 47.89 (N(CH_2CH_3)$_3$), 56.79 (OCH_3), 97.78 (*C*3), 102.31 (*C*4), 109.60 (*C*6), 114.85 (*C*7), 130.81 (*C*3a), 135.89 (*C*2), 136.78 (*C*7a), 153.06 (*C*5).

***N*-[Tris(pentafluorophenyl)borane]−5-Benzyloxy-3*H*-indole (10).** A solution of 5-benzyloxyindole (0.88 g, 3.74 mmol) in 10 mL of CH_2Cl_2 was added at room temperature under nitrogen atmosphere to a solution of tris(pentafluorophenyl)borane (1.93 g, 3.75 mmol) in 20 mL of CH_2Cl_2 in a 50 mL Schlenk flask. Exothermicity was not observed. An orange solution was obtained; after 1 h of stirring, the solvent was removed in vacuo to give a white powder as product (2.75 g, 100%): ^{1}H NMR (CD_2Cl_2) δ 4.21 (broad AB system, 2H, *H*3, *H*3′), 5.11 (s, 2H, OCH_2), 7.02 (dd, 1H, J = 9.05 Hz, J = 2.45 Hz, *H*6), 7.29 (d, 1H, J = 2.45 Hz, *H*4), 7.35−7.52 (m, 5H, *Ar*), 7.61 (d, 1H, J = 9.05 Hz, *H*7), 8.65 (d, 1H, J = 4.89 Hz, *H*2); ^{13}C NMR (CD_2Cl_2) δ 42.04 (*C*3), 71.17 (OCH_2), 111.31 (*C*4), 116.11 (*C*6), 119.09 (*C*7), 128.08 (2 *ortho*- or *meta*-*C*H), 128.76 (*para*-*C*H), 129.14 (2 *meta*- or *ortho*-*C*H), 135.29 (*C*), 136.73 (*C*), 141.77 (*C*7a), 160.05 (*C*), 173.19 (*C*2).

***N*-[Tris(pentafluorophenyl)borane]−5-Chloro-3*H*-indole (11).** A solution of 5-chloroindole (0.66 g, 4.27 mmol) in 10 mL of CH_2Cl_2 was added at room temperature under nitrogen atmosphere to a solution of tris(pentafluorophenyl)-borane (2.32 g, 4.50 mmol) in 20 mL of CH_2Cl_2 in a 50 mL Schlenk flask. Exothermicity was not observed. A colorless solution was obtained; after 2 h of stirring, the solvent was removed in vacuo to give a white powder as product (yield = 100%): ^{1}H NMR (CD_2Cl_2) δ 4.30 (broad AB system, 2H, *H*3, *H*3′), 7.42 (dd, 1H, J = 9.05 Hz, J = 2.20 Hz, *H*6), 7.53 (d, 1H, J = 9.05 Hz, *H*7), 7.68 (dm, 1H, J = 2.20 Hz, *H*4), 8.80 (d, 1H, J_{HF} = 4.89 Hz, *H*2); ^{13}C NMR (CD_2Cl_2) δ 42.11 (*C*3), 119.23 (*C*7), 125.66 (*C*4), 129.72 (*C*6), 134.79 (*C*3a or *C*5), 135.55 (*C*5 or *C*3a), 146.47 (*C*7a), 175.46 (*C*2); NOESY (CD_2Cl_2) δ^1H/δ^1H 8.80/4.30 (*H*2/*H*3), 4.30/7.68 (*H*3/*H*4).

***N*-[Tris(pentafluorophenyl)borane]−2-Methyl-6,10b-dihydroindeno[2,1-*b*]indole (12).** 2-Methyl-5,6-dihydroindeno[2,1-*b*]indole (1.77 g, 8.1 mmol) was dissolved in 10 mL of CH_2Cl_2 and charged into a 50 mL Schlenk under nitrogen atmosphere. A solution of tris(pentafluorophenyl)borane (4.14 g, 8.1 mmol) in 25 mL of CH_2Cl_2 was added at room temperature under stirring. During the addition, the color of the solution turned immediately from green to dark brown; exothermicity was not observed. The reaction mixture was stirred at room temperature for 1 h, and then the solvent was removed in vacuo to give a brown solid as product (5.90 g, 100%): mp 160.5−166.1 °C; ^{1}H NMR (CD_2Cl_2) δ 2.46 (s, 3H, CH_3), 3.78 (d, 1H, J = 20.1 Hz, CH_2, *H*6b), 4.23 (dd, 1H, J = 20.1 Hz, J = 3.0 Hz, CH_2, *H*6a), 5.86 (s, 1H, *H*10b), 7.18 (d, 1H, J = 8.9 Hz, Ar, *H*3), 7.30−7.36 (m, 1H, Ar, *H*7), 7.33−7.43 (m, 2H, Ar, *H*8, *H*9), 7.45−7.53 (m, 1H, Ar, *H*4), 7.60−7.66 (m, 1H, Ar, *H*10), 7.68 (s, 1H, Ar, *H*1); ^{13}C NMR (CD_2Cl_2) δ 21.33 (CH_3), 35.72 (d, CH_2, J_{CF} = 10.8 Hz), 62.88 (CH_{10b}), 117.88 (m), 124.04, 125.31, 125.80, 129.18, 129.48, 129.98, 133.20, 134.07, 139.25, 141.19, 149.24 (d, J_{CF} = 4.2 Hz), 200.03 (peak assigned by a DEPT experiment); NOESY (CD_2Cl_2) δ^1H/δ^1H 5.86/4.23 (*H*10b/*H*6a), 5.86/7.68 (*H*10b/*H*1), 7.60−7.66/5.86 (*H*10/*H*10b), 7.68/2.46 (*H*1/CH_3), 7.18/2.46 (*H*3/CH_3), 7.30−7.36/3.78 (*H*7/*H*6b); COSY (CD_2Cl_2) δ^1H/δ^1H 7.68/7.18 (*H*1/*H*3), 7.18/7.45−7.53 (*H*3/*H*4), 7.45−7.53/2.46 (*H*4/CH_3).

Triethylammonium [Tris(pentafluorophenyl)](2-methyl-5,6-dihydroindeno[2,1-*b*]indol-5-yl)borate (12a). Triethylamine (0.23 mL, 1.67 mmol) was added dropwise at room temperature under nitrogen atmosphere to a suspension of **12** (1.22 g, 1.67 mmol) in 15 mL of dichloromethane in a 25 mL Schlenk flask. During the addition exothermicity was not observed. After 1 h of stirring at room temperature, the solvent was removed in vacuo to give a brown solid, which was determined to be the desired product by ^{1}H NMR analysis in CD_2Cl_2 (1.38 g, 100%): mp 75.3−80.4 °C; ^{1}H NMR (CD_2Cl_2) δ 0.90 [t, 9H, J = 7.3 Hz, N(CH_2CH_3)$_3$], 2.44 (s, 3H, CH_3), 2.63 [q, 6H, J = 7.3 Hz, N(CH_2CH_3)$_3$], 3.36 (s, 2H, CH_2), 4.40 (bs, 1H, N*H*), 6.78−7.51 (7H, m, Ar); ^{13}C NMR (CD_2Cl_2) δ 8.69 (NCH_2CH_3), 21.39 (CH_3), 34.09 (d, J_{CF} = 7.7 Hz, CH_2), 47.69 (NCH_2CH_3), 114.85 (m), 116.77, 117.49, 119.06, 121.72, 121.83, 123.28, 124.93, 127.20, 128.18, 140.30, 143.65, 144.80 (d, J_{CF} = 2.5 Hz), 155.60.

***N*-(Trichloroborane)−3*H*-Indole (13).** A solution of indole (1.79 g, 15.13 mmol) in 20 mL of dichloromethane was added in 5 min at −20 °C under nitrogen atmosphere to a solution of boron trichloride (1 M in heptane, 15 mL, 15.0

mmol) in 15 mL of dichloromethane in a 100 mL Schlenk flask. At the end of the addition a yellow suspension was formed. The reaction mixture was kept at −20 °C for 15 min and then allowed to warm to room temperature. The color of the suspension turned slowly from yellow to pink. A ^{1}H NMR analysis showed that the reaction was already complete after 1 h of stirring at room temperature. After 4 h of stirring at room temperature, the suspension was filtered on a G4 frit and the residue dried to give a pink powder, which was determined to be the desired product by ^{1}H NMR analysis in CD_2Cl_2 (2.79 g, 79.4%): mp 184.8−185.6 °C; ^{1}H NMR (CD_2Cl_2) δ 4.27 (bs, 2H, *H*3,*H*3′), 7.42−7.81 (m, 3H, Ar), 8.37−8.41 (m, 1H, Ar), 9.44−9.48 (m, 1H, *H*2); ^{1}H NMR ($C_2D_2Cl_4$) δ 4.19 (s, 2H, *H*3,*H*3′), 7.29−7.72 (m, 3H, Ar), 8.35−8.41 (m, 1H, Ar), 9.38−9.48 (m, 1H, *H*2).

The sample is not fully soluble in CD_2Cl_2 or $C_2D_2Cl_4$. Because of the low solubility of the complex, also at 120 °C in $C_2D_2Cl_4$, attempts to acquire a ^{13}C NMR failed. Nevertheless, the complex is stable at high temperature for a few hours.

The synthesis of *N*-(trichloroborane)−3*H*-indole was carried out also by using the same conditions reported above but by adding the boron trichloride solution in heptane to the indole solution in dichloromethane, obtaining the same results.

Triethylammonium (1*H*-Indol-1-yl)trichloroborate (13a). Triethylamine (0.86 mL, 6.14 mmol) was added dropwise at room temperature under nitrogen atmosphere to a suspension of **13** (1.44 g, 6.14 mmol) in 25 mL of dichloromethane in a 50 mL Schlenk flask. During the addition a light exothermicity was observed, and the starting pink suspension became an orange solution. After 2 h of stirring at room temperature, the solvent was removed in vacuo to give a red-orange sticky solid, which was determined to be the desired product by ^{1}H NMR analysis in CD_2Cl_2 (1.98 g, 96.1%): mp 176.7−178.1 °C; ^{1}H NMR (CD_2Cl_2) δ 1.27 [t, 9H, J = 7.34 Hz, N(CH_2CH_3)$_3$], 2.95 [m, 6H, J = 7.34 Hz, N(CH_2-CH_3)$_3$], 6.39 (d, 1H, J = 2.35 Hz, *H*3 or *H*2), 7.04 (t, 1H, J = 7.43 Hz, *H*5 or *H*6), 7.11 (t, 1H, J = 7.43 Hz, *H*6 or *H*5), 7.54 (d, 1H, J = 7.43 Hz, *H*4 or *H*7), 7.73 (d, 1H, J = 2.35 Hz, *H*2 or *H*3), 8.06 (d, 1H, J = 7.43 Hz, *H*7 or *H*4), 9.51 (bs, 1H, N*H*).

Because of the low solubility of the complex in different deuterated solvents, attempts to acquire a ^{13}C NMR spectrum failed.

Attempted Synthesis of *N*-(Triphenylborane)−3*H*-Indole. Triphenylborane (3.43 g, 14.2 mmol) was dissolved under nitrogen atmosphere into 48 mL of toluene in a 100 mL Schlenk flask equipped with a cooler. The resulting solution was cooled to 0 °C and slowly added to a solution of indole (1.68 g, 14.2 mmol) in 16 mL of toluene. No color change was observed during addition. The reaction mixture was allowed to warm to room temperature and stirred for 21 h. A ^{1}H NMR analysis of the reaction mixture showed exclusively the presence of starting materials. Then the reaction mixture was heated at 80 °C for 4 h. A second ^{1}H NMR analysis of the crude showed mainly unreacted indole and BPh_3.

Attempted Synthesis of *N*-(Trifluoroborane)−3*H*-Indole. Boron trifluoride diethyl etherate (5 mL, 5.60 g, 39.5 mmol) was added at room temperature to a solution of indole (4.63 g, 39.5 mmol) in 30 mL of dichloromethane under nitrogen atmosphere in a 50 mL Schlenk flask. At the end of the addition a white suspension was formed. After 30 min of stirring at room temperature, the reaction mixture was dried in vacuo to give a white powder, which became pink upon standing at room temperature. The color change indicates possible decomposition of the final product. Because the product was not soluble in CD_2Cl_2 or other different deuterated solvents, NMR characterization was not possible.

Phenyl-3,3′-dimethyl-2,2′-diindolylmethane.[13b] 3-Methylindole (15.12 g, 112.96 mmol) and benzaldehyde (6.07 g, 56.63 mmol) were dissolved under magnetic stirring into 100 mL of methanol in a 250 mL round-bottom flask. Then hydrochloric acid (37% aq, 4.65 mL, 55.96 mmol) was added dropwise at room temperature. During the addition the solution turned from colorless to yellow and a light exothermicity was observed. The reaction mixture was stirred for 3.5 h at room temperature with final formation of a yellow ochre suspension. The latter was neutralized by addition of a sodium hydroxide aqueous solution (2.24 g of NaOH in 50 mL of water). Additional water (∼50 mL) was added, and after 1 h of stirring at room temperature, the resulting suspension was filtered. The filtrate was discarded, whereas the residue was dried in vacuo to give a yellowish powder as product (19.64 g, purity = 93.8%, yield = 93.0%): mp 156.4−158.3 °C; ^{1}H NMR ($CDCl_3$) δ 2.21 (s, 6H, CH_3), 6.03 (s, 1H, C*H*Ph), 7.12−7.62 (m, 15H, Ar and N*H*); ^{13}C NMR ($CDCl_3$) δ 8.48 (CH_3), 40.80 (*C*HPh), 108.64 (*C*), 110.79 (*C*H), 118.43 (*C*H), 119.41 (*C*H), 121.58 (*C*H), 127.25 (*C*H), 128.41 (*C*H), 128.92 (*C*H), 129.46 (*C*), 133.30 (*C*), 135.19 (*C*), 139.98 (*C*) (peak assigned by a DEPT experiment); *m*/*z* (%) 351 (17) [M^+ + 1], 350 (69) [M^+], 349 (15), 335 (12), 273 (12), 257 (18), 256 (22), 221 (16), 220 (100), 219 (50), 218 (71), 217 (21), 207 (12), 206 (10), 205 (17), 204 (45), 175 (14), 144 (8), 131 (15), 130 (19), 129 (15), 128 (13), 77 (16).

***N*,*N*′-[Bis(trichloroborane)]−3,3′-Dihydro-3,3′-dimethyl-2,2′-diindolylmethane (14).** A solution of boron trichloride (1 M in heptane, 14 mL, 14.0 mmol) was added at 0 °C in 5 min under nitrogen atmosphere to a solution of phenyl-3,3′-dimethyl-2,2′-diindolylmethane (2.43 g, 6.9 mmol) in 27 mL of dichloromethane in a 100 mL Schlenk flask. At the end of the addition a dark green suspension was formed. The reaction mixture was kept at 0 °C for 15 min, then allowed to warm to room temperature, and stirred for 16 h. The solvent was evaporated in vacuo to give a dark green powder as product (3.51 g, 87.0%): ^{1}H NMR ($CDCl_3$) δ 0.96 (d, 6H, J = 7.58 Hz, CH_3), 4.24 (q, 2H, J = 7.58 Hz, C*H*), 7.13−7.56 (m, 14H, C*H*Ph and Ar); ^{13}C NMR ($CDCl_3$) δ 15.97 (CH_3), 43.42 (*C*H), 118.21 (*C*H), 122.63 (2*C*H), 124.76 (*C*H), 128.04 (*C*H), 128.38 (*C*H), 129.68 (*C*H), 130.52 (*C*H), 134.43 (*C*), 136.24 (*C*), 144.39 (*C*), 169.46 (*C*) (peak assigned by a DEPT experiment).

Attempted Synthesis of *N*,*N*′-[Tris(pentafluorophenyl)borane]−3,3′-Dihydro-3,3′-dimethyl-2,2′-diindolylmethane. A solution of phenyl-3,3′-dimethyl-2,2′-diindolylmethane (1.01 g, 2.74 mmol) in 10 mL of dichloromethane was added dropwise at 0 °C under nitrogen atmosphere to a solution of tris(pentafluorophenyl)borane (2.84 g, 5.51 mmol) in 15 mL of CH_2Cl_2 in a 50 mL Schlenk flask. At the end of the addition a black solution was formed. The reaction mixture was kept at 0 °C for 15 min, then allowed to warm to room temperature, and stirred for 20 h. Subsequent NMR analyses showed that the reaction did not afford any adduct: the starting phenyl-3,3′-dimethyl-2,2′-diindolylmethane was the only compound detected by ^{1}H NMR analysis after 20 h.

***N*-[Tris(pentafluorophenyl)borane]−7-Methyl-3*H*-indole (15).** A solution of 7-methylindole (0.45 g, 3.33 mmol) in 10 mL of dichloromethane was added at 0 °C under nitrogen atmosphere to a solution of tris(pentafluorophenyl)borane (1.70 g, 3.30 mmol) in 16 mL of dichloromethane in a 50 mL Schlenk flask. During the addition a color change from light yellow to deep yellow was observed. Exothermicity was not observed. At the end of the addition the solution was allowed to warm to room temperature and stirred for 5 days. During this time the reaction mixture color changed from dark yellow to orange and finally became red. After 5 min after mixing at room temperature, a mixture of 1:1.4 (% mol, calculated by ^{1}H NMR) of the starting 7-methylindole and the expected complex was formed together with lower amounts of byproducts. The subsequent ^{1}H NMR analyses showed both a slow conversion of 7-methylindole and a decomposition of **15** to a complex mixture of byproducts, which were neither isolated nor characterized. ^{1}H NMR (CD_2Cl_2) δ 2.35 (bs, 3H, CH_3), 4.21 (AB system, 2H, J = 26.41 Hz, *H*3,*H*3′), 6.91−7.59 (m, 3H, Ar), 8.97 (t, 1H, J_{HF} = 4.89 Hz, *H*2).

***N*-[Tris(pentafluorophenyl)borane]−2-Phenyl-3*H*-indole (16). (a) Experiment in CH_2Cl_2.** A solution of 2-phenylindole (0.99 g, 4.87 mmol) in 10 mL of dichloromethane was

added at 0 °C under nitrogen atmosphere to a solution of tris(pentafluorophenyl)borane (2.50 g, 4.85 mmol) in 20 mL of dichloromethane in a 50 mL Schlenk flask. At the end of the addition the yellow solution was allowed to warm to room temperature, stirred for 24 h, and followed by ^{1}H NMR analysis in CD_2Cl_2. After 1 h of stirring at room temperature, a 1:1 (% mol, calculated by ^{1}H NMR) mixture of the starting 2-phenylindole and the expected complex was formed. The ratio between starting material and product did not change during the 24 h. Attempts to shift the equilibrium to the desired product by the addition of a second equivalent of tris(pentafluorophenyl)borane failed. ^{1}H NMR (CD_2Cl_2) δ 4.47 (broad AB system, 2H, J = 23.87 Hz, *H*3,*H*3′), 7.10−7.78 (m, 9H, Ar).

(b) Experiment in Et_2O. The reaction was carried out by using the same conditions described in the previous experiment, but diethyl ether was used as solvent instead of dichloromethane. After 1 h of stirring at room temperature, a 2.4:1 (% mol, calculated by ^{1}H NMR) mixture of the starting 2-phenylindole and the expected complex was obtained. The ratio between starting material and product changed from 2.4:1 after 1 h to 2.8:1 after 24 h.

3-[Tris(pentafluorophenyl)borane]−1*H*-Imidazole (17). A colorless solution of imidazole (0.31 g, 4.50 mmol) in 5 mL of dichloromethane was added at room temperature under nitrogen atmosphere to a light yellow solution of tris(pentafluorophenyl)borane (2.33 g, 4.55 mmol) in 13 mL of dichloromethane in a 25 mL Schlenk flask. During the addition the color of the solution turned from light yellow to yellow. Exothermicity was not observed. The reaction mixture was stirred for 1 h at room temperature, and then the solvent was evaporated in vacuo to give a white powder as product (2.60 g, 99.6%): mp 214.9−217.8 °C; ^{1}H NMR (C_6D_6) δ 5.49 (t, 1H, J = 1.76 Hz, *H*5), 6.30 (bs, 1H, *H*4), 6.66 (bs, 1H, *H*2), 7.24 (bs, 1H, N*H*); NOESY (C_6D_6) δ^1H/δ^1H 7.24/6.66 (N*H*/*H*2), 7.24/5.49 (N*H*/*H*5), 6.30/5.49 (*H*4/*H*5); ^{1}H NMR (CD_2Cl_2) δ 7.18−7.24 (m, 2H, *H*4 and *H*5), 8.08 (bs, 1H, *H*2), 10.05 (bs, 1H, N*H*); ^{13}C NMR (CD_2Cl_2) δ 117.81 (*C*5), 126.66 (*C*4), 136.22 (*C*2).

Triethylammonium [Tris(pentafluorophenyl)](1*H*-imidazol-1-yl)borate (17a). A solution of triethylamine (0.231 g, 2.27 mmol) in 5 mL of dichloromethane was added dropwise at room temperature under nitrogen atmosphere to a solution of **17** (1.254 g, 2.16 mmol) in 15 mL of dichloromethane in a 25 mL Schlenk flask. During the addition the color of the solution turned from light yellow to yellow, and exothermicity was not observed. After overnight stirring at room temperature, a ^{1}H NMR analysis in CD_2Cl_2 showed complete conversion of the starting material, and then the solvent was removed in vacuo to give a white powder as product (1.35 g, 90.8%, purity = 99%): ^{1}H NMR (CD_2Cl_2) δ 1.27 [t, 9H, J = 7.24 Hz, $N(CH_2CH_3)_3$], 3.01 [q, 6H, J = 7.24 Hz, $N(CH_2CH_3)_3$], 6.93 (t, 1H, J = 1.47 Hz, *H*4 or *H*5), 7.00 (bs, 1H, *H*5 or *H*4), 7.62 (m, 1H, *H*2), 13.76 (m, 1H, N*H*); ^{13}C NMR (CD_2Cl_2) δ 9.02 [$N(CH_2CH_3)_3$], 45.82 [$N(CH_2CH_3)_3$], 121.92 (*C*4 or *C*5), 125.44 (*C*5 or *C*4), 138.89 (*C*2).

(a) Experiment in One Step. A solution of imidazole (0.1619 g, 2.38 mmol) in 5 mL of dichloromethane was added dropwise at room temperature under nitrogen atmosphere to a solution of tris(pentafluorophenyl)borane (1.3175 g, 2.56 mmol) in 15 mL of dichloromethane in a 50 mL Schlenk flask. After 1 h of stirring at room temperature, a ^{1}H NMR analysis in CD_2Cl_2 showed complete conversion of the starting material to the imidazole−$B(C_6F_5)_3$ complex. Then a solution of triethylamine (0.2604 g, 2.56 mmol) in 5 mL of dichloromethane was added at room temperature. After overnight stirring at the same temperature, the solvent was removed in vacuo to give a white powder as product (1.45 g, 88.5%, purity = 99%): mp 62.5−63.3 °C; ^{1}H NMR (CD_2Cl_2) δ 1.28 [t, 9H, J = 7.34 Hz, $N(CH_2CH_3)_3$], 3.02 [q, 6H, J = 7.34 Hz, $N(CH_2CH_3)_3$], 6.92 (t, 1H, J = 1.22 Hz, *H*4 or *H*5), 6.99 (bs, 1H, *H*5 or *H*4), 7.58 (m, 1H, *H*2), 14.21 (bs, 1H, N*H*); ^{1}H NMR (C_6D_6) δ 0.37 [t, 9H, J = 7.34 Hz, $N(CH_2CH_3)_3$], 1.73 [q, 6H, J = 7.34 Hz, $N(CH_2CH_3)_3$], 6.28 (m, 1H, *H*4 or *H*5), 6.89 (bs, 1H, *H*5 or *H*4), 7.44 (bs, 1H, *H*2), 13.30 (bs, 1H, N*H*); NOESY (C_6D_6) δ^1H/δ^1H 13.30/7.44 (N*H*/*H*2), 6.28/6.89 (*H*4/*H*5); ^{13}C NMR (C_6D_6) δ 7.99 ($N(CH_2CH_3)_3$), 44.63 ($N(CH_2CH_3)_3$), 122.39 (*C*4 or *C*5), 125.26 (*C*5 or *C*4), 138.83 (*C*2).

2-[Tris(pentafluorophenyl)borane]−1*H*-Pyrazole (18). Pyrazole (0.70 g, 10.08 mmol) was dissolved at room temperature under nitrogen atmosphere into 20 mL of dichloromethane in a 50 mL Schlenk flask. A light yellow solution of tris(pentafluorophenyl)borane (5.53 g, 10.74 mmol) in 20 mL of dichloromethane was added at room temperature in subsequent four steps (0.25 equiv each with respect to starting pyrazole). After every addition, the reaction mixture was stirred at room temperature for 15−20 min and followed by ^{1}H NMR analysis. At the end of the last addition the resulting white suspension was dried in vacuo to give a white powder as product (yield = 100%): ^{1}H NMR (CD_2Cl_2) δ 6.70 (q, 1H, J = 2.54 Hz, *H*4), 7.93 (d, 1H, J = 2.54 Hz, *H*3), 7.94 (d, 1H, J = 2.54 Hz, *H*5), 10.52 (bs, 1H, N*H*); ^{13}C NMR (CD_2Cl_2) δ 108.26 (*C*4), 133.62 (*C*5), 140.38 (*C*3); ^{1}H NMR (C_6D_6) δ 5.41 (q, 1H, J = 2.69 Hz, *H*4), 6.16 (t, 1H, J = 2.69 Hz, *H*5), 7.00 (bs, 1H, *H*3), 8.58 (bs, 1H, N*H*); ^{13}C NMR (C_6D_6) δ 106.79 (*C*4), 132.66 (*C*5), 139.59 (d, J_{CF} = 1.72 Hz, *C*3). The *H*3 and *H*5 protons in the ^{1}H NMR spectra were assigned by using the HSQC analysis. Indeed, the *H*3 proton is closer to $B(C_6F_5)_3$ than *H*5, and its intensity is lower due to the coupling with fluorine atoms of $B(C_6F_5)_3$.

By decoupling the N*H*, it appeared that the multiplicity in C_6D_6 of the *H*4 proton changed from a quartet to a triplet and that the multiplicity of the *H*5 proton changed from a triplet to a doublet; thus, both *H*4 and *H*5 couple with N*H*: ^{1}H NMR (C_6D_6) δ 5.41 (t, 1H, J = 2.69 Hz, *H*4), 6.16 (d, 1H, J = 2.69 Hz, *H*5), 7.00 (bs, 1H, *H*3), 8.58 (bs, 1H, N*H*).

^{1}H NMR analysis at variable temperatures: T = 215 K, ^{1}H NMR (CD_2Cl_2) δ 6.70 (q, 1H, J = 2.45 Hz, *H*4), 7.92 (bs, 1H, *H*5), 7.97 (t, 1H, J = 2.45 Hz, *H*3), 10.61 (m, 1H, N*H*). Attempts to link a second molecule of $B(C_6F_5)_3$ to the complex pyrazole−$B(C_6F_5)_3$ failed.

Triethylammonium [Tris(pentafluorophenyl)](1*H*-pyrazol-1-yl)borate (18a). A solution of triethylamine (0.264 g, 2.60 mmol) in 5 mL of dichloromethane was added dropwise at room temperature under nitrogen atmosphere to a solution of **18** (1.51 g, 2.60 mmol) in 15 mL of dichloromethane in a 25 mL Schlenk flask. A white suspension was obtained. After 1 h of stirring at room temperature, a ^{1}H NMR analysis in C_6D_6 showed complete conversion of the starting material, and then the solvent was removed in vacuo to give a white powder as product (1.74 g, 98.2%): ^{1}H NMR (C_6D_6) δ 0.18 [t, 9H, J = 7.30 Hz, $N(CH_2CH_3)_3$], 1.80 [q, 6H, J = 7.30 Hz, $N(CH_2CH_3)_3$], 5.93 (t, 1H, J = 1.96 Hz, *H*4), 6.60 (d, 1H, J = 1.96 Hz, *H*3 or *H*5), 7.53 (bs, 1H, *H*5 or *H*3), 9.67 (bs, 1H, N*H*); ^{1}H NMR (CD_2Cl_2) δ 1.14 [t, 9H, J = 7.34 Hz, $N(CH_2CH_3)_3$], 2.98 [q, 6H, J = 7.34 Hz, $N(CH_2CH_3)_3$], 6.30 (t, 1H, J = 2.20 Hz, *H*4), 7.48 (d, 1H, J = 2.20 Hz, *H*3), 7.66 (bs, 1H, *H*5), 10.81 (bs, 1H, N*H*); ^{13}C NMR (CD_2Cl_2) δ 8.19 [$N(CH_2CH_3)_3$], 46.49 [$N(CH_2CH_3)_3$], 104.26 (*C*4), 137.12 (*C*5), 138.66 (*C*3); NOESY (CD_2Cl_2) δ^1H/δ^1H 6.30/7.48 (*H*4/*H*3), 6.30/7.66 (*H*4/*H*5), 7.48/10.81 (*H*3/N*H*), 7.48/1.14 [*H*3/$N(CH_2CH_3)_3$], 7.48/2.98 [*H*3/$N(CH_2CH_3)_3$].

***N*-[Tris(pentafluorophenyl)borane]pyrrolidine (19).** A solution of pyrrolidine (0.34 g, 4.78 mmol) in 3 mL of dichloromethane was added at room temperature under nitrogen atmosphere to a solution of tris(pentafluorophenyl)borane (2.44 g, 4.77 mmol) in 15 mL of dichloromethane in a 25 mL Schlenk flask. A light exothermicity was observed. The reaction mixture was stirred for 30 min at room temperature, and then the solvent was evaporated in vacuo to give a white powder as product (yield = 100%): mp 205.0−206.9 °C; ^{1}H NMR (CD_2Cl_2) δ 1.84−2.09 (m, 4H, *H*3, *H*3′, *H*4, *H*4′), 2.68−2.86 (m, 2H, *H*2 and *H*5), 3.44−3.54 (m, 2H, *H*2′ and *H*5′), 6.30 (bs, 1H, N*H*); ^{13}C NMR (CD_2Cl_2) δ 23.86 (*C*3 and *C*4), 50.37 (*C*2 and *C*5).

***N*-[Tris(pentafluorophenyl)borane]indoline (20).** Indoline (0.57 g, 4.70 mmol) was added at room temperature under nitrogen atmosphere to a solution of tris(pentafluorophenyl)borane (2.41 g, 4.70 mmol) in 17 mL of dichloromethane in a 25 mL Schlenk flask. During the addition the color of the solution turned from light yellow to yellow. The reaction mixture was stirred for 1 h at room temperature, and then the solvent was evaporated in vacuo to give a whitish powder as product (2.95 g, 99.4%), mp 231.3−235.0 °C.

In a repeated experiment, a solution of indoline (0.60 g, 5.07 mmol) in 3 mL of dichloromethane was added at room temperature under nitrogen atmosphere to a solution of tris(pentafluorophenyl)borane (2.60 g, 5.07 mmol) in 15 mL of dichloromethane in a 25 mL Schlenk flask. A light exothermicity was observed. The reaction mixture was stirred for 30 min at room temperature, and then the solvent was evaporated in vacuo to give a white powder as product (yield = 100%): ^{1}H NMR (CD_2Cl_2) δ 2.16−2.34 (m, 1H, *H*3), 2.91−3.06 (m, 1H, *H*3′), 4.05−4.20 (m, 2H, *H*2,*H*2′), 7.10−7.40 (m, 4H, Ar), 8.15 (bs, 1H, N*H*); ^{13}C NMR (CD_2Cl_2) δ 29.29 (*C*3), 52.68 (t, *C*2, J_{CF} = 4.6 Hz), 120.64 (*C*7), 125.94 (*C*4), 128.57 (*C*5 or *C*6), 129.86 (*C*6 or *C*5), 135.51 (*C*3a or *C*7a), 140.35 (*C*7a or *C*3a).

***N*-[Tris(pentafluorophenyl)borane]−2-Methyl-1-pyrroline (21).** A solution of 2-methyl-1-pyrroline (0.39 g, 4.41 mmol) in 3 mL of dichloromethane was added at room temperature under nitrogen atmosphere to a solution of tris(pentafluorophenyl)borane (2.26 g, 4.41 mmol) in 15 mL of dichloromethane in a 25 mL Schlenk flask. A light exothermicity was observed. The reaction mixture was stirred for 30 min at room temperature, and then the solvent was evaporated in vacuo to give a white-gray powder as product (yield = 100%): mp 200.3−201.9 °C; ^{1}H NMR (CD_2Cl_2) δ 2.13 (s, 3H, C*H*$_3$), 1.94−2.36 (m, 2H, *H*4, *H*4′), 3.00−3.08 (m, 2H, *H*3, *H*3′), 4.00−4.58 (bm, 2H, *H*5, *H*5′); ^{13}C NMR (CD_2Cl_2) δ 19.65 (*C*H$_3$), 21.09 (*C*4), 42.64 (*C*3), 62.05 (*C*5), 191.95 (*C*2).

The complex **22** was analyzed at variable temperatures by ^{1}H NMR in CD_2Cl_2. By cooling the temperature from 298 to 238 K, the *H*4 and *H*4′ protons became a more complex multiplet, whereas the *H*5 or *H*5′ proton became a broad triplet.

Attempted Synthesis of Water-Free $B(C_6F_5)_3$. (a) $B(C_6F_5)_3$ (22.0 g) was suspended at room temperature under nitrogen atmosphere into 100 mL of dry hexane (<10 ppm of water) in a 250 mL Schlenk flask. The temperature was slowly increased to 60 °C with an oil bath. After 15 min of stirring at 60 °C, the borane was almost totally dissolved into the solvent. The mixture was then filtered on a G4 frit, keeping the temperature at 60 °C. The light yellow-beige filtrate was collected into a jacketed reactor, and then the temperature was cooled from 60 to 25 °C in 2 h. The crystallization of the product started at 50 °C under stirring. At the end the product was collected by filtration on a G4 frit under nitrogen at room temperature. After drying in vacuo, 10.0 g of $B(C_6F_5)_3$ was obtained as a white powder. The borane contained 4870 ppm of water by Karl Fischer analysis (∼0.5 wt %) and had an mp of 112.8−113.9 °C.

(b) $B(C_6F_5)_3$ (3.68 g, containing 0.2 wt % of water by Karl Fischer analysis corresponding to 0.41 mmol of water) was suspended at room temperature under nitrogen atmosphere into 100 mL of dry pentane (<10 ppm of water) in a 250 mL Schlenk flask. Almost all of the product was dissolved into the solvent. Then 24.0 mg of dry methylalumoxane (MAO, 0.41 mmol) was added at room temperature. After 10 min of stirring at the same temperature, a gray precipitate was formed. The mixture was decanted for 20 min and the supernatant liquid filtered on a G4 frit. The decanted gray precipitate was washed with an additional 50 mL of pentane, and all of the washings were passed through the frit. The different filtrates were collected and dried in vacuo to give a white powder as product. The latter contained <20 ppm of water by Karl Fischer analysis and <2 ppm of aluminum.

Synthesis of $(C_6F_5)_3B(OH_2)$.[5] A solution of tris(pentafluorophenyl)borane (0.3196 g, 0.6 mmol) in 15 mL of pentane was treated at room temperature with H_2O (0.0325 g, 1.8 mmol) in a 50 mL Schlenk flask. Neither a color change nor exothermicity was observed. The resulting suspension was stirred for 1 h at room temperature, and then an additional 2 equiv of $B(C_6F_5)_3$ (0.6181 g, 1.2 mmol) suspended in 10 mL of pentane was added. After 3 h of stirring at room temperature, the solvent was evaporated in vacuo, giving $(C_6F_5)_3B(OH_2)$ as a white solid (yield = 100%): ^{1}H NMR (C_6D_6) δ 4.56 (s, 2H, H_2O).

Reaction of Indole with $(C_6F_5)_3B(OH_2)$. A solution of $(C_6F_5)_3B(OH_2)$ (0.9064 g, 1.7 mmol) in 12 mL of toluene was added at room temperature to a solution of indole (0.2026 g, 1.7 mmol) in 8 mL of toluene in a 25 mL Schlenk flask. During the addition the solution became yellow, but exothermicity was not observed. The reaction mixture was stirred for 3 days at room temperature, and its path was constantly followed by ^{1}H NMR analysis. At the end the solvent was evaporated in vacuo to give **2** as a whitish solid (0.4841 g, yield = 45.3%). The low yield is due to the many aliquots taken for NMR analysis.

A possible intermediate species was observed in the NMR spectra made immediately after the mixing of the starting materials: ^{1}H NMR (CD_2Cl_2) δ 3.92 (dd, 2H, J = 8.61 Hz, J = 3.91 Hz), 5.87 (t, 1H, J = 8.61 Hz), 7.15−7.83 (m, 4H), 8.68 (bs, 1H); ^{13}C NMR (CD_2Cl_2) δ 35.33, 61.64, 113.03−132.42.

The progressive disappearance of NMR signals of the intermediate species matched with the increase of NMR signals of **2**.

Reaction of Indole with $(C_6F_5)_3B(OH_2)$ and $(C_6F_5)_3B$. A solution of indole (0.2081 g, 1.8 mmol) in 10 mL of dichloromethane was added at room temperature to a mixture of $(C_6F_5)_3B(OH_2)$ (0.2812 g, 0.5 mmol) and $(C_6F_5)_3B$ (0.6365 g, 1.2 mmol) in 15 mL of dichloromethane in a 50 mL Schlenk flask. During the addition the solution became yellow. The reaction mixture was stirred for 1 day at room temperature, and its path was constantly followed by ^{1}H NMR analysis. Then the solvent was evaporated in vacuo to give **2** as a whitish solid (0.9566 g, yield 84.6% with respect to starting indole).

X-ray Crystal Structure Analysis. Suitable crystals of **2**, **2a**, and **20** were mounted in air on a glass fiber tip onto a goniometer head. Single-crystal X-ray diffraction data were collected on a Siemens SMART CCD area detector diffractometer for **2** and **2a** and on an Enraf-Nonius CAD-4 diffractometer for **20**, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature [295(2) K].

For **2** and **2a** unit cell parameters were initially obtained from ∼100 reflections taken from 45 frames collected in three different ω regions and eventually refined against ∼3000 reflections with $3° \le \theta \le 25°$, whereas for **20** the setting angles of 25 randomly distributed intense reflections with $10° \le \theta \le 14°$ were processed by least-squares fitting.

For **2** and **2a** a full sphere of reciprocal space was scanned by 0.3° ω step, collecting 1800 frames (the exposure times were 40 and 20 s for **2** and **2a**, respectively). Intensity decay was monitored by re-collecting the initial 50 frames at the end of data collection and analyzing the duplicate reflections. After integration, an empirical absorption correction was made on the basis of the symmetry-equivalent reflection intensities measured (for **2**, 4745 reflections, with an average redundancy of 2.0; for **2a**, 11594 reflections, with an average redundancy of 3.8).[28]

For **20**, data collection was performed by the ω scan method with variable scan speed (maximum time per reflection of 60 s) and variable scan range (0.90 + 0.35 tan θ). Crystal stability under diffraction was checked by monitoring three standard reflections every 180 min. The measured intensities were corrected for Lorentz, polarization, and background effects and reduced to F_o^2. An empirical absorption correction was applied

TABLE 5. Summary of Crystal Data, Data Collection, and Structure Refinement Parameters for 2, 2a, and 20

	2	2a	20
formula	$C_{26}H_7BF_{15}N$	$C_{32}H_{22}BF_{15}N_2$	$C_{26}H_9BF_{15}N$
formula wt	629.14	730.33	631.15
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a (Å)	9.906(5)	12.058(5)	13.586(1)
b (Å)	10.969(6)	18.061(8)	10.882(1)
c (Å)	11.670(6)	14.683(7)	16.261(2)
α (deg)	107.17(1)		
β (deg)	93.02(1)	93.760(10)	98.06(1)
γ (deg)	101.54(1)		
V (Å^3)	1178.6(11)	3191(2)	2380.3(4)
Z	2	4	4
F(000)	620	1472	1248
density (g cm^{-3})	1.773	1.520	1.761
absorption coeff (mm^{-1})	0.187	0.150	0.185
crystal description	colorless plate	colorless block	colorless block
crystal size (mm)	0.18 × 0.10 × 0.04	0.26 × 0.26 × 0.24	0.30 × 0.28 × 0.28
θ range (deg)	$1.8 \le \theta \le 25.0$	$1.8 \le \theta \le 25.0$	$3.0 \le \theta \le 25.0$
index ranges	$-11 \le h \le 11$	$-14 \le h \le 14$	$-16 \le h \le 15$
	$-13 \le k \le 13$	$-21 \le k \le 21$	$0 \le k \le 12$
	$-13 \le l \le 13$	$-17 \le l \le 17$	$0 \le l \le 19$
intensity decay (%)	none	none	none
transmission factors (min, max)	0.870, 0.993	0.868, 0.965	0.936, 0.950
no. of measured reflns	8464	26047	4311
no. of ind reflns	4135	5640	4165
R_{int}, R_σ[a]	0.0249, 0.0381	0.0296, 0.0245	0.0146, 0.0116
no. of reflns with $I > 2\sigma(I)$	3272	3896	3447
no. of data/parameters	3272/388	3896/388	3447/388
weights (a, b)[b]	0.045, 0.3	0.05, 1.8	0.05, 0.6
goodness-of-fit $S(F^2)$[c]	1.039	1.107	1.047
$R(F)$[d]	0.0366	0.0492	0.0333
$wR(F^2)$[e]	0.0900	0.1235	0.0861
largest diff peak, hole (e Å^{-3})	0.211, −0.181	0.260, −0.200	0.210, −0.211

[a] $R_{int} = \sum|F_o^2 - F_{mean}^2|/\sum|F_o^2|$; $R_\sigma = \sum|\sigma(F_o^2)|/\sum|F_o^2|$. [b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. [c] $S = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters. [d] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [e] $wR(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

using ψ scan of three suitable reflections having χ values close to 90°.[29] Crystal data and data collection parameters are summarized in Table 5.

The structures were solved by direct methods (SIR97[30]) and subsequent Fourier synthesis; they were refined by full-matrix least-squares on F^2 (SHELX97[31]) using reflections with $I > 2\sigma(I)$. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from the internal library of SHELX97. Weights were assigned to individual observations according to the formula $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; a and b were chosen to give a flat analysis of variance in terms of F_o^2. Anisotropic parameters were assigned to all non-hydrogen atoms. All hydrogen atoms were clearly evidenced from difference Fourier maps; they were placed in idealized position and refined riding on their parent atom with an isotropic displacement parameter 1.2 times that of the pertinent parent atom.

The structure of **2a** is affected by a disorder of the triethylammonium cation. Because it was difficult to refine a consistent disordered model (possibly because of the large volume—252 Å^3—of the cavity occupied by the cation), its contribution was subtracted from the observed structure factor according to the BYPASS procedure,[32] as implemented in PLATON.[33]

The final difference electron density map showed no features of chemical significance, with the largest peaks lying close to the fluorine atoms of the pentafluorophenyl substituents. Final conventional agreement indices and other structure refinement parameters are listed in Table 5.

Computational Details. All of the reported structures represent stationary points on the potential energy surface. They were calculated with the Amsterdam Density Functional (ADF) program system,[34] developed by Baerends et al.[35,36] The electronic configurations of the molecular systems were described by sets for B, C, N, O, F (2*s*,2*p*) augmented with a single 3*d* function and a double-ζ STO basis set for hydrogen (1*s*), augmented with a single 2*p* function.[37,38] The frozen-core approximation was applied up to the [He] core for all of the non-hydrogen atoms. Energetics and geometries were evaluated by using the local exchange-correlation potential by Vosko et al.,[39] augmented in a self-consistent manner with Becke's[40] exchange gradient correction and Perdew's[41,42] correlation gradient correction (BP86). Geometry optimizations were terminated if the largest component of the Cartesian gradient was <0.003 au. Transition state geometry of the proton transfer from $H_2O{-}B(C_6F_5)_3$ to C_2 of pyrrole was approached by a linear-transit procedure, whereas all other degrees of

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freedom were optimized. A full transition state search was started from the geometry corresponding to the maximum along the linear-transit curve and terminated if the largest component of the Cartesian gradient was <0.002 au. Atomic coordinates for the optimized structures of $\mathbf{22}_{\mathbf{ind}}$ and $\mathbf{22}_{\mathbf{pyrr}}$ are reported in the Supporting Information.

Acknowledgment. We thank M. Colonnesi for the proton NMR spectra and Dr. Moskau (Bruker AG, CH) for the 2D $^{19}F-^{1}H$ experiments. We also thank Prof. F. Gasparrini, Università La Sapienza, Roma, for the PC version of the DNMR-6 program.

Supporting Information Available: Variable-temperature ^{1}H NMR spectra of compounds **4**, **5**, **7**, and **8**; 2D spectra of compounds **1**−**5**, **7**, **9**, **11**, **12**, **17**, **17a**, **18**, and **18a**; tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for compounds **2**, **2a**, and **20**; and atomic coordinates of the computed structures of compounds $\mathbf{22}_{\mathbf{ind}}$ and $\mathbf{22}_{\mathbf{pyrr}}$. This material is available free of charge via the Internet at http://pubs.acs.org.

JO020647X