

Synthesis and Reactivity of *N*-Heterocycle- $B(C_6F_5)_3$ Complexes. 3. Generation of *N*-Methylpyrrol-2-yl and *N*-Methylindol-2-yl Borate Zwitterions with Acidic sp^3 Carbons

Francesca Focante,[‡] Isabella Camurati,[†] Daniele Nanni,[‡] Rino Leardini,[‡] and Luigi Resconi^{*,†}

Basell Polyolefins, Centro Ricerche "G. Natta", I-44100 Ferrara, Italy, and
Dipartimento di Chimica Organica "A. Mangini", Università di Bologna,
Viale Risorgimento 4, I-40136 Bologna, Italy

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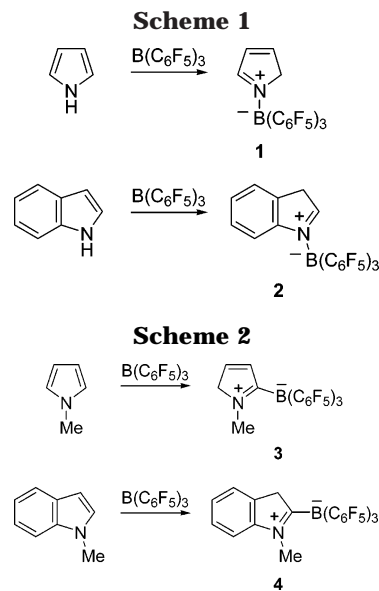
The stoichiometric reactions of *N*-methylpyrrole and *N*-methylindole with $B(C_6F_5)_3$ produce the zwitterionic species 2-[tris(pentafluorophenyl)borane]-5*H*-1-methylpyrrole (**3**) and 2-[tris(pentafluorophenyl)borane]-3*H*-1-methylindole (**4**), in which a $C(\alpha)$ –B bond and an acidic sp^3 methylene carbon are formed in the heterocyclic part of the molecule. Both derivatives present a restricted rotation around the $C(\alpha)$ –B and/or B – C_6F_5 bonds, and their rotational barriers (13.8 and 14.8 kcal mol^{−1} for **3** and **4**, respectively) were calculated from ¹H NMR experimental data. A kinetic study of the reaction, carried out by following the conversion by NMR, gave rate constant values (at 298 K in dichloromethane) of 3×10^{-5} and 6×10^{-5} M^{−1} s^{−1} for **3** and **4**, respectively. Complexes **3** and **4** react quantitatively with triethylamine to give the corresponding triethylammonium salts **5** and **6**. Both the zwitterionic complexes and their ammonium salts are efficient activators of Ind_2ZrMe_2 for the polymerization of ethylene.

Introduction

We have previously reported that pyrrole and indole react with tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, to give quantitative and instantaneous conversion to the 5*H*-pyrrole- $B(C_6F_5)_3$ complex **1** and the 3*H*-indole- $B(C_6F_5)_3$ complex **2**, respectively (Scheme 1).¹ Many *N*-*H*-pyrroles and -indoles with different substituents (e.g., R, RO, Ar, Cl) give the same reaction with a formal *N*-to-*C* hydrogen shift. Some of these adducts are efficient activators of group 4 metallocenes in the polymerization of olefins.² We now report the results of the reaction between $B(C_6F_5)_3$ and *N*-methylated pyrrole and indole. With these substrates, a B – $C(\alpha)$ bond is formed, and although the heterocycle lacks the potentially movable hydrogen at the 1-position, the reaction products again contain an acidic methylene group in the heterocyclic moiety, generated by a formal vinylic *C*–*H* activation.³

Results and Discussion

1. Synthesis and Characterization. The reaction of *N*-methylpyrrole or *N*-methylindole with 1 equiv of



$B(C_6F_5)_3$ at room temperature, in toluene or dichloromethane, gave high yields of compounds **3** and **4**, respectively (Scheme 2). In both cases the reaction was rather slow and reached 95% conversion after 4–10 days, depending on the initial concentration.

Mass spectra obtained by ESI technique revealed for both compounds a parent peak deriving from the mass addition of borane and heterocycle; however the detailed structures of the compounds were mainly characterized by NMR analyses. In particular, ¹H NMR in CD_2Cl_2 showed for **3** a broad singlet at 4.7 ppm for the

* Corresponding author. E-mail: luigi.resconi@basell.com.

[†] Basell Polyolefins.

[‡] Università di Bologna.

(1) Guidotti, S.; Camurati, I.; Focante, F.; Angellini, L.; Moscardi, G.; Resconi, L.; Leardini, R.; Nanni, D.; Mercandelli, P.; Sironi, A.; Beringhelli, T.; Maggioni, D. *J. Org. Chem.* **2003**, *68*, 5445.

(2) Resconi, L.; Guidotti, S. (Basell Polyolefins) Int. Pat. Appl. WO 01/62764 (priority 24.2.2000). Bonazza, A.; Camurati, I.; Guidotti, S.; Mascellani, N.; Resconi, L. *Macromol. Chem. Phys.* **2004**, *205* (3), 319.

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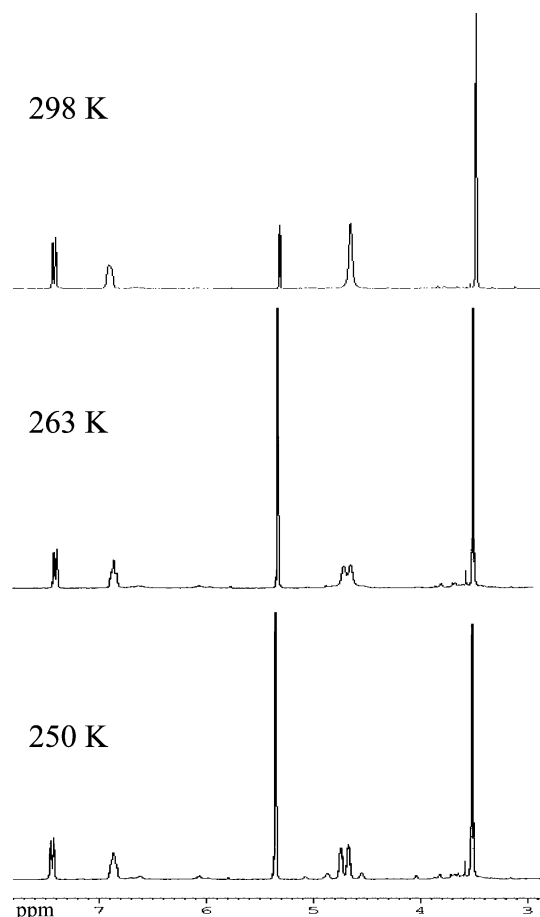


Figure 1. ^1H NMR spectra of **3** at variable temperature (in CD_2Cl_2).

α -methylene group, a singlet at 3.6 ppm for the *N*-methyl group, and the signals for the two vinylic protons (6.9 ppm, br s, H3, and 7.4 ppm, d, H4). DEPT, COSY, NOESY, HMBC, and HSQC experiments gave further support to the structure (see Experimental Section). Analogously, structure **4** was deduced by the presence in the ^1H NMR spectrum in CD_2Cl_2 of a diagnostic broad AB system at 4.6 ppm with a two-proton area value, revealing not only the presence of a CH_2 group, but also that these two protons are diastereotopic. For the same compound ^{13}C NMR revealed for carbon 2 a signal at a very low field (a multiplet, 214.3–217.4 ppm, likely due to a scalar spin–spin coupling with ^{19}F of the C_6F_5 rings, through nonbonding orbital overlap).⁴ Variable-temperature ^1H NMR experiments confirmed for both complexes the presence of a restricted rotation around some of the C–B bonds, likely due to steric interaction with the methyl group. Figure 1 shows the variable-temperature ^1H NMR spectra for compound **3**. At 298 K the methylene protons gave one slightly broad signal that, below 250 K, decoalesced into an AB-type spectrum.

Compound **4** showed the presence of diastereotopic protons at somewhat higher temperatures compared to **3**, the methylene signal being a sharp singlet at 346 K, a broad AB system at 298 K, and a well-defined one at 263 K (Figure 2).

As observed before,¹ the spectroscopic behavior of adducts **3** and **4** can be explained by assuming that

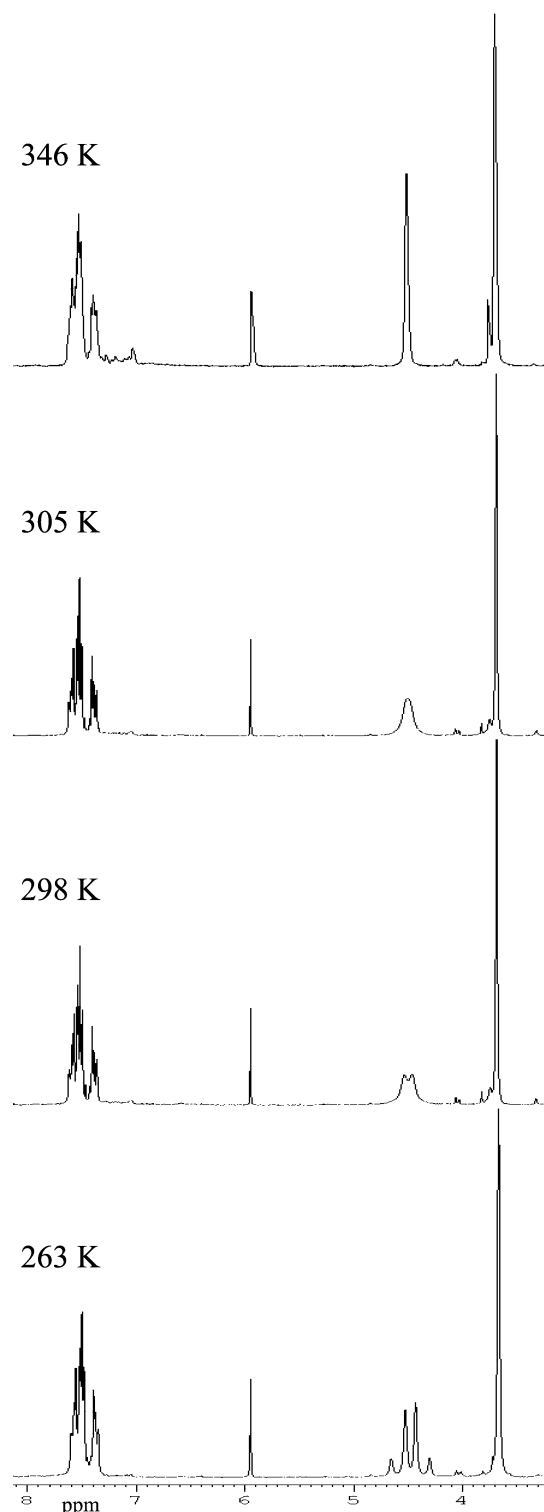


Figure 2. ^1H NMR spectra of **4** at variable temperature (in $\text{C}_2\text{D}_2\text{Cl}_4$).

these compounds are chiral molecules. The anisochronous methylene signals are therefore the result of pairs of stereolabile conformational enantiomers that can be detected by NMR techniques through the diastereotopicity of the methylene protons. The interconversion of the two atropisomers probably occurs by restricted rotations around the B–C(α) and/or the B– C_6F_5 bonds, as suggested for the previously reported B–N complexes.¹

(4) Mallory, F. B.; Mallory, C. W.; Ricker, W. M. *J. Am. Chem. Soc.* **1975**, *97*, 4770.

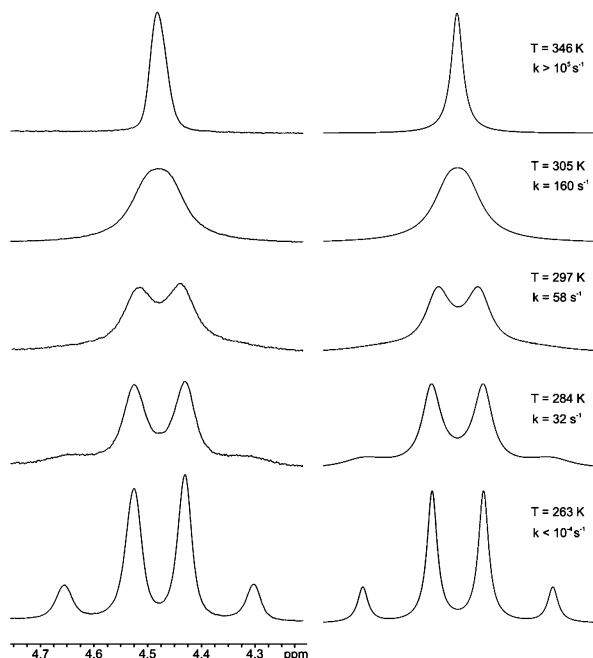


Figure 3. (Left) Experimental ¹H NMR signals of the methylene hydrogens of **4** as a function of temperature. (Right) Computer simulations obtained with the rate constants indicated.

The enantiomerization process was quantitatively studied for both **3** and **4**. Simulation of their ¹H NMR spectra at various temperatures allowed determination of the rate constant of interconversion at each temperature. For adduct **3** a virtually free rotation was observed above 300 K ($k > 10^5$ s⁻¹), whereas its two enantiomeric conformers do not interconvert on the NMR time scale below 250 K; simulation of the ¹H NMR spectra at intermediate temperatures gave rate constant values of 9 and 18 s⁻¹ at 256 and 263 K, respectively, from which we calculated a value of 13.8 ± 0.2 kcal mol⁻¹ for the activation barrier of the enantiomerization (ΔG^\ddagger). Compound **4** showed instead free rotation above 340 K and no interconversion below 260 K; simulation of the ¹H NMR spectra at intermediate temperatures gave rate constants of 160, 58, and 32 s⁻¹ at 305, 297, and 284 K, respectively, from which we calculated a ΔG^\ddagger value of 14.8 ± 0.2 kcal mol⁻¹ for the enantiomerization barrier. The simulation results for adduct **4** are shown in Figure 3.

Since both **3** and **4** have an *N*-Me iminium group linked to the boron atom and they differ only in the presence of sp²-CH or sp³-CH₂ moieties *beta* to the borate group, it is evident that the two methylenic protons of **4** bring about an increase as important as ca. 1 kcal mol⁻¹ with respect to the single vinylic proton of **3** in the enantiomerization process. The interconversion barrier is therefore originated mainly by the steric hindrance between the fluorinated rings and the *N*-methyl group, but the hydrogen atoms of the pyrrolic β -carbon play a role as well, although a minor one. It is also worth noting that the barrier calculated for **4** is strictly comparable to that obtained for *N*-[tris(pentafluorophenyl)borane]-2,4-dimethyl-5*H*-pyrrole (14.5 kcal mol⁻¹),¹ in which the borate moiety, although linked to a nitrogen atom, is surrounded by the same kind of bonds and groups. Another restricted rotation

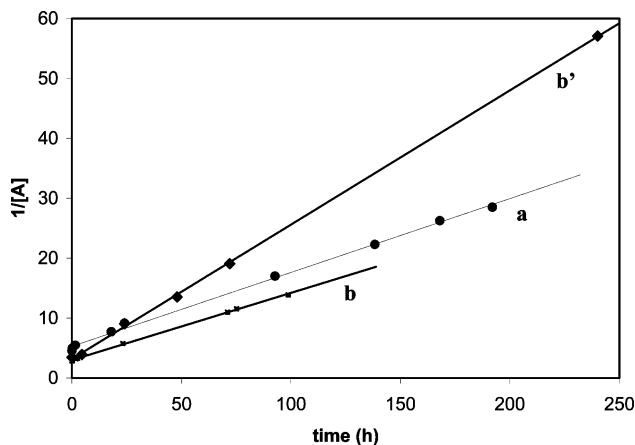
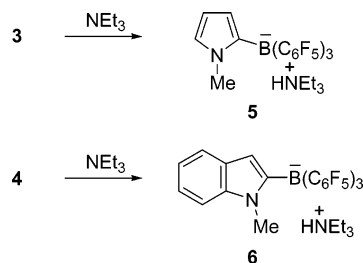


Figure 4. Plot of 1/[A] vs time for reaction A + B → C at 298 K, where A is the heterocycle, B is B(C₆F₅)₃, and C is the final adduct (plot a: synthesis of **3** in CH₂Cl₂; b: synthesis of **4** in C₆D₆, and b' synthesis of **4** in CH₂Cl₂).

Scheme 3



of congested imine-B(C₆F₅)₃ adducts has been recently reported by Piers and co-workers.⁵

The methylene groups in compounds **3** and **4** are acidic enough to protonate triethylamine: both complexes reacted quantitatively and instantaneously with 1 equiv of NEt₃, at room temperature in CH₂Cl₂, to give the corresponding triethylammonium salts, tris(pentafluorophenyl)-(1-methylpyrrol-2-yl)borate(1-) triethylammonium (**5**) and tris(pentafluorophenyl)-(1-methylindol-2-yl)borate(1-) triethylammonium (**6**), respectively (Scheme 3). Like in the case of **1** and **2**,¹ the driving force for this reaction is clearly the restoration of aromaticity in the five-membered heterocyclic ring.

Both structures (**5** and **6**) were characterized by ¹H NMR experiments, and the structure of compound **6** was also confirmed by X-ray diffraction analysis.⁶

2. Kinetic Treatment of Data. Both heterocycles (*N*-methylpyrrole or -indole) reacted slowly with B(C₆F₅)₃ (4–10 days at room temperature). The concentration values [A] for the starting heterocyclic substrate were deduced by the ¹H NMR spectra recorded at different times and were plotted as [A]⁻¹ versus time. Linear correlation curves, indicative of second-order reaction, were obtained for both compounds. The reaction of formation of **3** in CH₂Cl₂ at room temperature gave a rate constant value of 3×10^{-5} M⁻¹ s⁻¹ (Figure 4, curve a). The same value was calculated for compound **4** when the reaction was carried out in C₆D₆ at room temperature ($k = 3 \times 10^{-5}$ M⁻¹ s⁻¹, Figure 4, curve b), whereas the reaction in CH₂Cl₂ was much faster ($k = 6 \times 10^{-5}$

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(6) Sironi, A.; Mercandelli, P. Unpublished results.

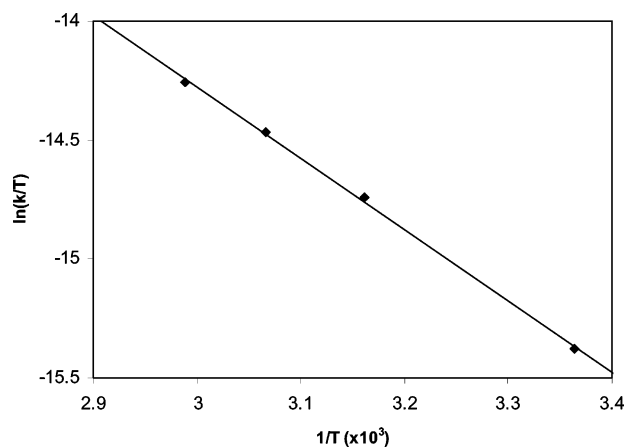
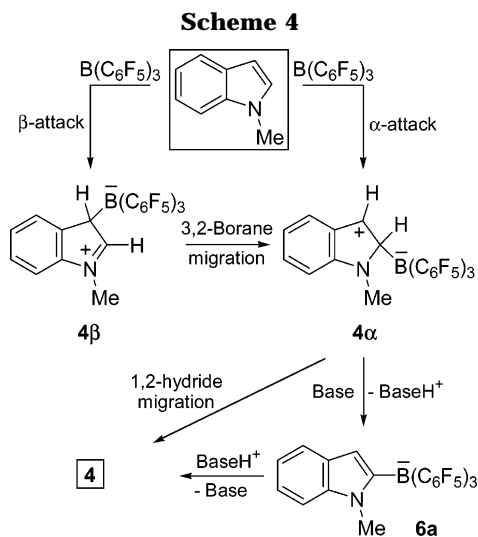
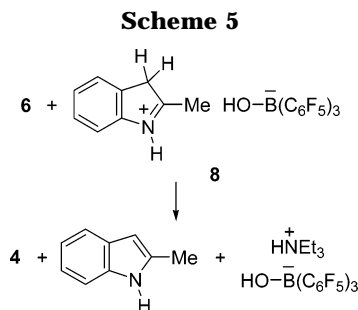


Figure 5. Eyring plot for the synthesis of **4** in $\text{C}_2\text{D}_2\text{Cl}_4$.



$\text{M}^{-1} \text{s}^{-1}$, Figure 4, curve b'). The difference in reaction rate between the two solvents is in agreement with their different polarity; in fact the dielectric constants⁷ are 2.28 and 8.93 respectively for benzene and dichloromethane. Figure 5 shows the temperature dependence of the rate constant of **4** in $\text{C}_2\text{D}_2\text{Cl}_4$ in the range 298–335 K. The Eyring plot gave the following activation parameters: $\Delta H^\ddagger = 6.6 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -60 \text{ eu}$.

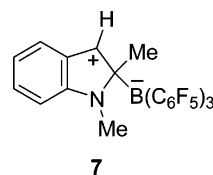
3. Mechanism of the Reaction between *N*-Methylpyrrole or *N*-Methylindole and Borane. The only species detectable by NMR techniques were the starting heterocycle and the final borate complex. It was not possible to isolate and characterize any reaction intermediate, and for this reason we assume that the first reaction step is a slow electrophilic attack that follows second-order kinetics and determines the global rate of the process. In the case of the formation of **4**, we can assume either an initial attack of the borane to C-3 (**4β**) followed by 1,2-migration to the α-position (**4α**) or a direct attack at C-2 yielding the intermediate **4α** in one step (Scheme 4). Although it has been demonstrated that direct attack at an α-position can also occur, electrophilic reagents strongly prefer to attack indoles at their β-carbons, even when that position carries a substituent;⁸ therefore, the migration route seems



more feasible. Intermediate **4α** can evolve to **4** either by 1,2-hydride migration from C-2 to C-3 or, more likely, by prior abstraction of the 2-proton by a base (probably free *N*-methylindole itself) followed by re-protonation at the nucleophilic β-position.

The 3,2-borane shift (or the direct attack at the 2-position) is probably due to some stabilizing effect of the type of charge separation: indeed, the negative boron and the positive nitrogen atom are closer in structure **4** compared to intermediate **4β**. A thermodynamic preference for the formation of the α-isomer is also suggested by theoretical calculations (DFT), which predict a difference of 8.4 kcal/mol between structures **4β** and **4**.

It is worth noting that 1,2-dimethylindole does not react with $\text{B}(\text{C}_6\text{F}_5)_3$. The lack of reaction may lend support to the preference of **4α** to undergo a base-catalyzed proton transfer from C-2 to C-3, rather than to rearrange by a 1,2-hydride migration. Indeed, if an anionotropic rearrangement were involved in intermediate **7**, the 2-methyl group would be expected to migrate easily to the 3-position, giving the 3-methyl-substituted analogue of **4**. However, we cannot exclude that the lack of any reaction could be due to some additional steric hindrance that would prevent attack of $\text{B}(\text{C}_6\text{F}_5)_3$ to the 3-position and/or its translocation to the 2-position.



We also found that the anion **6a** (the indolyl-borate) was instantaneously and quantitatively protonated to **4** by 3*H*-2-methylindolium (the cation of indolium salt **8**, Scheme 5), with concomitant formation of free 2-methylindole. Since the cation of **8** can be considered a species analogous to the generic BH^+ indicated in Scheme 4, this experiment demonstrates that indoles and the corresponding indolium cations can efficiently act as proton-transfer catalysts, according to our assumption on the last step of Scheme 4.

In the case of *N*-methylpyrrole, we can apply the same mechanism, but without the need of a borane rearrangement (Scheme 6). Indeed, $\text{B}(\text{C}_6\text{F}_5)_3$ can directly attack the α-position, which is the preferred one in electrophilic additions to pyrroles, giving intermediate **3α**; this can lose and recover its proton, owing to the catalytic action of free *N*-methylpyrrole, eventually yielding borate **3**. Analogously to 1,2-dimethylindole, 1,2,5-trimethylpyrrole did not react either with $\text{B}(\text{C}_6\text{F}_5)_3$.

(7) Lide, R. D. *Handbook of Chemistry and Physics*, 76th ed.; CRC Press: London, 1995, section 6.

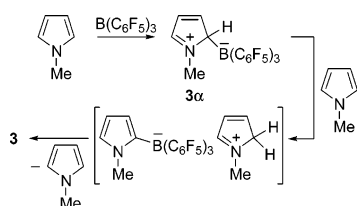
(8) Joule, J. A.; Mills, K. *Heterocyclic Chemistry*, IV ed.; Blackwell: London, 2000; Chapter 16.

Table 1. Ethylene Polymerization Results^a

cocatalyst	yield (g)	kg _{PE} /(mmol _{Zr} × h)	kg _{PE} /(g _{cat} × h) ^b	comments
TIBA	0	0	0	blank test
2	3.21 ± 0.36	12.9 ± 1.4	12.2	benchmark test average of three tests
3	2.43 ± 0.37	9.74 ± 1.5	9.8	average of four tests
4	1.60 ± 0.16	6.4 ± 0.7	6.4	average of three tests
5	7.61 ± 0.88	30.5 ± 3.5	27.4	average of three tests
6	1.74 ± 0.08	6.93 ± 0.3	5.9	average of two tests
9	5.71 ± 0.11	22.85 ± 0.45	16.0	average of two tests
10	7.05 ± 0.88	28.2 ± 3.5	22.9	average of two tests

^a Applied conditions: heptane 100 mL, scavenger TIBA 0.1 mmol, *P*(C₂) = 4 bar-g, *T*_p = 80 °C, time = 15 min, Ind₂ZrMe₂ = 1 μmol, B/Zr = 1.1 mol/mol, premix in 4 mL of toluene, no aging. ^bcat = zirconocene + activator.

Scheme 6



Both **4α** (or **4β**) and **3α** prefer to isomerize to **4** and **3**, respectively, to achieve structures with more substituted double bonds and lower internal steric hindrances; indeed, species **4** and **3** have the C–B bond in the same plane as the heterocycle.

4. Metallocene Activation. Compounds **3–6** are efficient activators of bis(indenyl)zirconium dimethyl in the polymerization of ethylene, likely generating, upon loss of methane, a zirconocene methyl cation–borate anion pair, in which the anion is sterically bulky and probably only very weakly coordinating. Table 1 shows the preliminary results obtained for ethylene polymerization with complexes **3–6**. Results using the reference activators [CPh₃⁺][B(C₆F₅)₄[−]] (**9**) and [HNMe₂Ph⁺][B(C₆F₅)₄[−]] (**10**) are also reported for comparison.⁹ Remarkably, the most active complex **5** is also more active than **9** and **10**. **3** is more active than **4**, likely because of the lower steric hindrance of the reactive CH₂ in **3** versus **4**.

Conclusions

N-Methylpyrrole and *N*-methylindole react with B(C₆F₅)₃ (1:1) in a novel one-pot reaction giving rise to unexpected zwitterionic adducts in which a C–B bond is generated and a formal α–α′ (or α–β for *N*-methylindole) hydrogen shift takes place. The reaction causes the loss of aromaticity in the five-membered ring, owing to the formation of an acidic methylene group. Both derivatives present a restricted rotation around the C(α)–B and/or B–Ar bonds, due to steric hindrance between the fluorinated rings and the *N*-methyl group, with the hydrogen atoms of the pyrrolic β-carbon playing a minor role. Their rotational barriers (13.8 and 14.8 kcal mol^{−1} for **3** and **4**, respectively) were calculated from ¹H NMR experimental data. Both adducts are able to protonate triethylamine, recovering their aromaticity and leading to the corresponding borate ammonium salts. The acidic character of the methylene moiety in **3** and **4**, as well as the stability of the borate anion in **5** and **6**, has been advantageously used for metallocene activation in ethylene polymerization. To explain the outcome of this novel reaction, we propose a mechanism

that includes a slow electrophilic attack of B(C₆F₅)₃ to the heterocycle followed by a fast structural rearrangement to the final products, which, in the case of **4**, also entails a 1,2-borane migration from C(3) to C(2). Further experiments are in progress to investigate this reaction.

Experimental Section

General Procedures and Starting Materials. All operations were performed under nitrogen by using conventional Schlenk-line techniques. Solvents were purified by degassing with N₂ and passing over activated (8 h, N₂ purge, 300 °C) Al₂O₃ and stored under nitrogen. Indole (Aldrich, purity 98% or Fluka, purity 99%), *N*-methylindole (Aldrich, purity 97%), 2-methylindole (Aldrich, purity 98%), 1,2-dimethylindole (Aldrich, purity 99%), 3-methylindole (Fluka, purity 98%), *N*-methylpyrrole (Aldrich, purity 99%), NEt₃ (Aldrich, purity 99.5%), and B(C₆F₅)₃ (Boulder) were used as received.

The ¹H and ¹³C NMR spectra were obtained using a Bruker DPX 200 spectrometer operating in the Fourier transform mode at 200.13 and 50.33 MHz, respectively. The samples were dissolved in CD₂Cl₂ or C₆D₆. As reference the residual peak of CHDCl₂ or C₆HD₅ in the ¹H spectra (5.35 and 7.15 ppm, respectively) and the peak of the solvent in the ¹³C spectra (53.80 ppm for CD₂Cl₂ and 128.00 ppm for C₆D₆) were used. 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; about 512 transients were stored for each spectrum. CD₂Cl₂ (Aldrich, 99.8% atom D) was used as received, whereas C₆D₆ (Aldrich, 99% atom D) was dried over activated 4 Å molecular sieves before use. Preparation of the samples was carried out under nitrogen using standard inert atmosphere techniques. Mass spectra (MS) were obtained by ESI technique from acetonitrile (**3**) or methanol (**4**) solutions of suitable samples. The melting points were obtained by using a capillary Electrothermal instrument. Bis(indenyl)zirconium dimethyl was prepared as previously described.¹⁰ The H₂O–B(C₆F₅)₃ complex was prepared as described in ref 11.

2-[Tris(pentafluorophenyl)borane]-5*H*-1-methylpyrrole (3**).** A light yellow solution of *N*-methylpyrrole (99%, 0.503 g, 6.1 mmol) (dichloromethane, 10 mL) was added at room temperature to a white-gray suspension of B(C₆F₅)₃ (99.4%, 3.18 g, 6.2 mmol) (dichloromethane, 10 mL). The resulting orange cloudy solution was stirred at room temperature for 3 days, and then the solvent was removed under reduced pressure. The obtained orange powder was suspended with a 1:2 dichloromethane/pentane mixture and filtered. The filtrate gave a dark pink solid (the desired product together with unidentified species), whereas the residue on the frit was a very light yellow powder (product **3**, 2.42 g, yield 66.5%), mp = 116.6–118.2 °C; ¹H NMR (CD₂Cl₂) δ 3.55 (s, 3 H, N-CH₃), 4.70 (br s, 2 H, H5, H5′), 6.91 (br s, 1 H, H3), 7.42 (d, *J* = 5.87

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(9) Chen, E.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

Hz, 1 H, *H4*); ^{13}C NMR (CD_2Cl_2) δ 38.12 (CH_3), 69.81 (C5), 137.33 (C3), 146.06 (C4); NOESY (CD_2Cl_2) $\delta^1\text{H}/\delta^1\text{H}$ 7.42/6.91 (*HA/H3*), 7.42/4.70 (*HA/H5*), 4.70/3.55 (*H5/N-CH3*); COSY (CD_2Cl_2) $\delta^1\text{H}/\delta^1\text{H}$ 7.42/6.91 (*HA/H3*), 7.42/4.70 (*HA/H5*), 4.70/3.55 (*H5/N-CH3*); ^1H NMR analysis at variable temperature, $T = -22^\circ\text{C}$, ^1H NMR (CD_2Cl_2) δ 3.52 (s, 3 H, CH_3), 4.71 (AB system, 2 H, *H5, H5'*), 6.87 (t, $J = 4.50$ Hz, 1 H, *H3*), 7.43 (d, $J = 5.87$ Hz, 1 H, *H4*); MS 592 ($M - 1$) $^-$. Anal. Calcd for $\text{C}_{23}\text{H}_7\text{BF}_{15}\text{N}$: C, 46.58; H, 1.19; N, 2.36. Found: C, 46.70; H, 1.19; N, 2.35.

2-[Tris(pentafluorophenyl)borane]-3*H*-1-methylindole (4). A yellow solution of *N*-methylindole (97%, 0.78 g, 5.8 mmol) in 10 mL of dichloromethane was added at room temperature to a white suspension of $\text{B}(\text{C}_6\text{F}_5)_3$ (99.4%, 2.97 g, 5.8 mmol) in 10 mL of dichloromethane in a 25 mL Schlenk flask. The resulting orange solution was stirred at room temperature for 10 days and analyzed by ^1H NMR at different times. During this time the color of the solution turned from orange to dark bordeaux; NMR analyses showed a slow conversion of the starting *N*-methylindole to product **4**. The solvent was evaporated in vacuo, and the solid obtained was suspended in a 9:1 pentane/dichloromethane mixture and filtered. The residue on the frit was a fuchsia solid (3.27 g, yield 87.8%), mp = 126.7–127.8 $^\circ\text{C}$; ^1H NMR (CD_2Cl_2) δ 3.77 (s, 3 H, N-CH_3), 4.59 (br AB system, 2 H, *H3, H3'*), 7.45–7.53 (m, 1 H, *H7*), 7.54–7.62 (m, 2 H, *H5* and *H6*), 7.63–7.71 (m, 1 H, *H4*); ^1H NMR (C_6D_6) δ 2.84 (s, 3 H, N-CH_3), 4.04 (br AB system, 2 H, *H3, H3'*); 6.42–6.51 (m, 1 H, *H7*), 6.81–6.97 (m, 3 H, *H4, H5*, and *H6*); ^{13}C NMR (CD_2Cl_2) δ 36.55 (CH_3), 48.33 (C3), 113.59 (C7), 125.22 (C4), 128.97 (C5 or C6), 129.22 (C6 or C5), 134.18 (C3a), 147.06 (C7a), 214.34–217.43 (m, C2); NOESY (CD_2Cl_2) $\delta^1\text{H}/\delta^1\text{H}$ 3.77/6.47 ($\text{N-CH}_3/\text{H7}$), 3.77/7.62 ($\text{N-CH}_3/\text{H6}$), 4.59/7.69 (*H3/H4*); NOESY (C_6D_6) $\delta^1\text{H}/\delta^1\text{H}$ 6.81–6.97/6.42–6.51 (*H6/H7*), 6.42–6.51/2.84 (*H7/N-CH3*); HMBC (CD_2Cl_2) $\delta^1\text{H}/\delta^{13}\text{C}$ 3.77/147.06 ($\text{N-CH}_3/\text{C7a}$), 7.46–7.70/134.18 (*HA/C3a*), 3.77/214.34–217.43 ($\text{N-CH}_3/\text{C2}$); ^1H NMR analysis at variable temperature, $T = -35^\circ\text{C}$, ^1H NMR (CD_2Cl_2) δ 3.79 (s, 3 H, N-CH_3), 4.61 (AB system, 2 H, *H3, H3'*), 7.48–7.69 (m, 4 H, Ar). MS 642 ($M - 1$) $^-$. Anal. Calcd for $\text{C}_{27}\text{H}_9\text{BF}_{15}\text{N}$: C, 50.42; H, 1.41; N, 2.18. Found: C, 50.66; H, 1.41; N, 2.17.

Tris(pentafluorophenyl)-(1-methylpyrrol-2-yl)borate-(1-) Triethylammonium (5). A colorless solution of triethylamine (99.5%, 0.167 g, 1.6 mmol) (dichloromethane, 6 mL) was added at room temperature to an orange solution of **3** (1.048 g, 1.6 mmol) (dichloromethane, 6 mL) in a 25 mL Schlenk flask. The resulting light yellow solution was stirred at room temperature for 1 h. Then the solvent was removed under reduced pressure to give a white-gray solid as product (0.892 g, yield 97.9%); ^1H NMR (CD_2Cl_2) δ 1.22 (t, 9 H, $J = 7.34$ Hz, $\text{N}(\text{CH}_2\text{CH}_3)_3$), 3.03 (q, 6 H, $J = 7.34$ Hz, $\text{N}(\text{CH}_2\text{CH}_3)_3$), 3.32 (s, 3 H, N-CH_3), 5.76 (br d, 1 H, $J = 2.64$ Hz, *H3*), 5.96 (d, 1 H, $J = 3.23$ Hz, *H4*), 6.10 (br s, 1 H, *NH*), 6.64 (br s, 1 H, *H5*); ^{13}C NMR (CD_2Cl_2) δ 8.82 ($\text{N}(\text{CH}_2\text{CH}_3)_3$), 35.94 (N-CH_3), 47.32 ($\text{N}(\text{CH}_2\text{CH}_3)_3$), 104.40 (C4), 111.85 (C3), 122.95 (C5), 146.20 (C2); NOESY (CD_2Cl_2) $\delta^1\text{H}/\delta^1\text{H}$ 6.64/3.32 (*H5/N-CH3*), 6.64/5.96 (*H5/H4*), 5.96/5.76 (*HA/H3*); COSY (CD_2Cl_2) $\delta^1\text{H}/\delta^1\text{H}$ 5.96/5.76 (*HA/H3*); HMBC (CD_2Cl_2) $\delta^1\text{H}/\delta^{13}\text{C}$ 3.32/146.20 ($\text{N-CH}_3/\text{C2}$). Anal. Calcd for $\text{C}_{23}\text{H}_{22}\text{BF}_{15}\text{N}_2$: C, 50.17; H, 3.19; N, 4.03. Found: C, 50.28; H, 3.18; N, 4.02.

Tris(pentafluorophenyl)-(1-methylindol-2-yl)borate-(1-) Triethylammonium (6). A colorless solution of triethylamine (99.5%, 0.167 g, 1.6 mmol) (dichloromethane, 6 mL) was added at room temperature to a bordeaux solution of **4** (1.048 g, 1.6 mmol) (dichloromethane, 4 mL) in a 10 mL Schlenk flask. The resulting solution was stirred at room temperature for 1 h, and its color turned from the initially orange to yellow. Then the solvent was removed in vacuo to give a yellow solid as product **6** (1.11 g, yield 93.2%), mp = 130.6–132.8 $^\circ\text{C}$; ^1H NMR (CD_2Cl_2) δ 1.03 (t, 9 H, $J = 7.24$ Hz, $\text{N}(\text{CH}_2\text{CH}_3)_3$), 2.60 (q, 6 H, $J = 7.24$ Hz, $\text{N}(\text{CH}_2\text{CH}_3)_3$), 3.51 (s, 3 H, N-CH_3), 4.40 (br s, 1 H, *NH*), 6.19 (s, 1 H, *H3*), 6.95–7.13 (m, 2 H, *H5, H6*),

7.23–7.29 (m, 1 H, *H7*), 7.41–7.48 (m, 1 H, *H4*); ^{13}C NMR (CD_2Cl_2) δ 8.56 ($\text{N}(\text{CH}_2\text{CH}_3)_3$), 31.84 (N-CH_3), 47.32 ($\text{N}(\text{CH}_2\text{CH}_3)_3$), 104.75 (C3), 109.35 (C7), 118.29 and 118.35 (C4 and C5), 119.19 (C6), 128.79 (C3a), 139.47 (C7a); NOESY (CD_2Cl_2) $\delta^1\text{H}/\delta^1\text{H}$ 6.19/7.48 (*H3/H4*), 3.51/7.23–7.29 ($\text{N-CH}_3/\text{H7}$); COSY $\delta^1\text{H}/\delta^1\text{H}$ 7.23/6.19 (*H7/H3*); HMBC (CD_2Cl_2) $\delta^1\text{H}/\delta^{13}\text{C}$ 3.51/139.47 ($\text{N-CH}_3/\text{C7a}$), 7.41–7.48/119.19 (*HA/C6*); 6.19/128.79 (*H3/C3a*). Anal. Calcd for $\text{C}_{33}\text{H}_{24}\text{BF}_{15}\text{N}_2$: C, 53.25; H, 3.25; N, 3.76. Found: C, 53.50; H, 3.24; N, 3.75.

Treatment of 1,2-Dimethylindole with $\text{B}(\text{C}_6\text{F}_5)_3$. A light pink solution of 1,2-dimethylindole (99%, 0.513 g, 3.5 mmol) (dichloromethane, 10 mL) was added at room temperature to a white-gray suspension of $\text{B}(\text{C}_6\text{F}_5)_3$ (99.4%, 1.797 g, 3.5 mmol) (dichloromethane, 10 mL) in a 25 mL Schlenk flask. The resulting orange suspension was stirred at room temperature for 10 days and analyzed by ^1H NMR at different times, but no reaction occurred, neither after 8 h of stirring at 40 $^\circ\text{C}$ in toluene solution. Only a small percentage of decomposition products was present.

Treatment of 1,2,5-Trimethylpyrrole with $\text{B}(\text{C}_6\text{F}_5)_3$. A very light yellow solution of 1,2,5-trimethylpyrrole (99%, 0.246 g, 2.2 mmol) (CH_2Cl_2 , 5 mL) was added at room temperature to a white-gray suspension of $\text{B}(\text{C}_6\text{F}_5)_3$ (99.4%, 1.165 g, 2.3 mmol) (CH_2Cl_2 , 5 mL) in a 10 mL Schlenk flask to give immediately an orange suspension. The reaction mixture was stirred at room temperature for a week and analyzed by ^1H NMR at different times: many unidentified byproducts were formed, but the main species was yet the starting trimethylpyrrole.

3*H*-2-Methylindolium Hydroxytris(pentafluorophenyl)borate(1-). A pink solution of 2-methylindole (0.15 g, 3.1 mmol) (pentane, 12 mL) was added at room temperature to a white suspension of $\text{H}_2\text{O-B}(\text{C}_6\text{F}_5)_3$ (1.66 g, 3.1 mmol) (dichloromethane, 12 mL) in a 25 mL Schlenk flask. The resulting mixture immediately became a pink suspension, which was stirred for 1 h and then dried in vacuo to give a light pink solid as product (**7**, 1.97 g, purity 90.4%, yield 86.2%); ^1H NMR (CD_2Cl_2) δ 2.72 (s, 3 H, CH_3), 7.43 (m, 3 H, Ar), 7.60 (m, 1 H, Ar); *N-H* and *H3, H3'* are not visible because of an acidic exchange reaction.

Protonation of Tris(pentafluorophenyl)-(1-methylindol-2-yl)borate(1-) Anion. A light pink solution of 3*H*-2-methylindolium hydroxytris(pentafluorophenyl)borate (**7**) (12.8 mg, 19 μmol) (dichloromethane, 4 mL) was added at room temperature to an orange solution of **6** (13.8 mg, 19 μmol) (dichloromethane, 4 mL) to give a light yellow solution. ^1H NMR analyses showed an instantaneous and complete conversion of reagents **7** and **6** in free 2-methylindole, **4**, and hydroxytris(pentafluorophenyl)borate triethylammonium. ^1H NMR of compound $[\text{HNEt}_3^+]\text{HO-B}(\text{C}_6\text{F}_5)_3^-$ (CD_2Cl_2): δ 1.16 (t, 9 H, $J = 7.24$ Hz, CH_3), 2.42 (br s, 1 H, *N-H* or *O-H*), 2.88 (q, 6 H, $J = 7.24$ Hz, CH_2), 9.76 (br s, 1 H, *O-H* or *N-H*).

Determination of the Kinetics for Synthesis of **3 or **4**.** The reactions of formation of compounds **3** and **4** follow the scheme $\text{A} + \text{B} \rightarrow \text{C}$, where A is the starting heterocycle (*N*-methylpyrrole or -indole), B is $\text{B}(\text{C}_6\text{F}_5)_3$, and C is complex **3** or **4**. The syntheses were performed starting from solutions of known concentration of A (where $[\text{A}]_0 = [\text{B}]_0$). Aliquots of the reaction mixture were taken at different times, dried, and analyzed by ^1H NMR. The only detectable species were the heterocycle A and the final complex C. Depending on the NMR area ratio of the methyl signals of both species and on the starting $[\text{A}]_0$ value, the concentration of the heterocycle A was therefore calculated at the corresponding time. Figure 4 collects plots of $[\text{A}]^{-1}$ versus time for reaction of formation of **3** and **4** at room temperature. Kinetics at higher temperature were calculated following the same methods, but the experiments were performed directly in deuterated solvent, and to keep the temperature constant in time, the NMR tubes were left at the temperature of analysis inside the instrument, and the spectra were recorded approximately every half hour. The

resulting kinetic constants calculated from each experiment were then plotted as $\ln(k/T)$ versus $1/T$ in Figure 5.

Ethylene Polymerization. Bis(indenyl)zirconium dimethyl (0.1 μ mol) was dissolved in 2 mL of toluene in a 10 mL Schlenk flask under a nitrogen atmosphere, and then the cocatalyst (solution in 2 mL of toluene) indicated in Table 1 was quickly added (Zr/cocat molar ratio 1:1.1). Ethylene polymerizations were carried out in a 260 mL Büchi glass autoclave equipped with magnetic stirrer, thermocouple, and feeding line for the monomer, purified with nitrogen, and kept in a thermostatic bath. Under ethylene purge, heptane (100 mL) and Al(*i*-Bu)₃ (0.1 mmol) were introduced, the temperature was brought to 80 °C, and the reactor was vented to remove residual nitrogen, then pressurized with ethylene up to 0.5 bar-g. The catalytic system, prepared as described above, was siphoned into the reactor by means of a Teflon cannula, and the ethylene partial pressure was raised to 4 bar-g. The polymerization was carried out at 80 °C for 15 min, by maintaining a constant ethylene partial pressure, then stopped

by degassing the reactor and by adding 2 mL of methanol. The polymer was precipitated with 200 mL of acetone, filtered, washed with acetone, and dried overnight at 60 °C under reduced pressure.

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Supporting Information Available: 2D NMR characterization of **3–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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