Protonation of the Heterocyclic Cp-Anion Equivalent [Pyrrolyl-B(C_6F_5)$_3$]Li − Formation of a Useful Neutral Brønsted Acid for the Generation of Homogeneous Metallocene Ziegler Catalysts

Gerald Kehr,[a] Rolf Roesmann,[a] Roland Fröhlich,[a][‡] Christiane Holst,[a][‡] and Gerhard Erker*[a]

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N-pyrrolyllithium (**1**) adds to $B(C_6F_5)_3$ to yield $[(C_4H_4N)B(C_6F_5)_3]Li$ (**3**). The corresponding monoetherate (**3**·OEt_2) was characterized by X-ray diffraction and shows an η^5 coordination of the pyrrolyl moiety to the lithium cation. Treatment of **3** with HCl in ether leads to H^+ addition at a pyrrolyl α-position to yield the neutral dipolar Brønsted acid system $[(C_4H_5N)B(C_6F_5)_3]$ (**4**). The reagent **4** can be used to protonate $Cp_2Zr(CH_3)_3$ to yield $[Cp_2Zr(CH_3)^+(C_4H_4N)B(C_6F_5)_3^-]$ (**6**) and methane. H^+ transfer from **4** to (butadiene)zirconocene results in the formation of the (π-allyl)metallocene salt $[(C_4H_7)ZrCp_2^+(C_4H_4N)B(C_6F_5)_3^-]$ **(8)**. In analogous reactions, the neutral Brønsted acid was employed as a protonating activator component for the generation of homogeneous Ziegler catalysts derived from a variety of (butadiene)- or (dimethyl)*ansa*-metallocenes. The systems generated by treatment with **4** show comparable activities in ethene or propene polymerization reactions as conventionally generated Group 4 metallocene Ziegler catalysts.

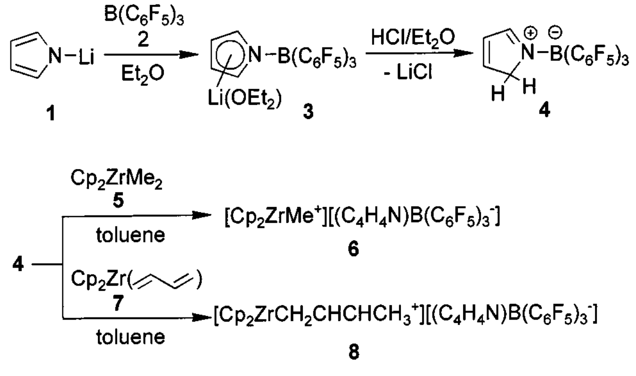
Introduction

The generation of homogeneous Group 4 metallocene Ziegler catalysts and related early and late transition metal catalyst systems is mostly carried out by treatment of the respective metal complex catalyst precursors with methylaluminoxane.[1] Alternatively, alkyl anion abstraction from, for example, $^RCp_2MR_2$ species, with the trityl cation[2] or with $B(C_6F_5)_3$ has also been reported,[3] as has the use of single component catalysts derived from $^RCp_2M$(butadiene) complexes by addition of $B(C_6F_5)_3$ or the related (pyrrolyl)$B(C_6F_5)_2$ Lewis acids.[4,5] In principle, formation of the active $[^RCpMR^+]$ catalyst species by protonation with a suitable Brønsted acid would be an alternative, provided sufficiently non-nucleophilic conditions could be maintained throughout the reaction. Ammonium salts have been successfully employed for this purpose, especially dimethylanilinium reagents such as $[PhNMe_2H^+]$ with $[BPh_4^-]$ or $[B(C_6F_5)_4^-]$ anions.[6] Sometimes low solubilities and the stoichiometric formation of a tertiary amine have complicated this protonation route for the generation of active homogeneous Ziegler catalysts. We here report the formation and some features of a neutral dipolar Brønsted acid reagent that may make the protonation route in some cases an attractive alternative to the activation methods presently used in homogeneous organometallic Ziegler catalyst formation and the chemistry of reactive organometallic cation systems.[7]

Results and Discussion

N-pyrrolyllithium (**1**) was treated with $B(C_6F_5)_3$ (**2**)[8] to yield the [(*N*-pyrrolyl)$B(C_6F_5)_3$]Li reagent **3** (Scheme 1). Complex **3** shows symmetrical pyrrolyl $^1H/^{13}C$ NMR resonances at δ = 6.72 (2,5-H) and 5.84 (3,4-H)/125.0 (C2,5) and 108.9 (C3,4), and a ^{11}B NMR signal at δ = −8.2 (in $[D_6]$benzene) indicating tetracoordinated boron. A ^7Li NMR resonance (in $[D_8]$THF) at δ = −2.6 points to a mononuclear geometry of the lithium compound **3** in this coordinating solvent.[9] Single crystals of **3**·OEt_2 were obtained from pentane/ether solution at 8 °C that allowed for characterization by an X-ray crystal structure analysis.

The structure shows that the pyrrolyl unit is bonded to a tetravalent boron atom [N1−B: 1.576(4) Å]. The pyrrolyl moiety of the $[(C_4H_4N)-B(C_6F_5)_3^-]$ anion exhibits a distorted η^5 coordination to the lithium atom.[10] The Li−N1 bond is short at 2.281(7) Å, the Li−C5 [2.350(8) Å]/Li−C2 [2.423(8) Å], and Li−C4 [2.492(9) Å]/Li−C3 [2.533(9) Å] linkages become increasingly longer, but all heavy atoms of the planar pyrrolyl framework are clearly within bonding



Scheme 1

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[a] Organisch-Chemisches Institut der Universität Münster,
Corrensstraße 40, D-48149 Münster, Germany
Fax: (internat.) +49-251/833-6503
E-mail: erker@uni-muenster.de

[‡] X-ray crystal structure analyses.

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distance of the lithium atom. Extensive bond delocalization is observed inside the C_4H_4N moiety (see Figure 1). The lithium atom in **3** is further coordinated to an ether molecule [O42−Li: 1.830(7) Å] and, remarkably, to two fluorine atoms from the *ortho* F−C bonds of two of the boron bound -C_6F_5 substituents [Li−F16: 2.041(7) Å, Li−F26: 2.467(8) Å]. This additional lithium-fluorine interaction,[11] which is in the same range of bond lengths as the Li−C(pyrrolyl) unit, makes the coordination geometry of the lithium atom in complex **3** distorted tetrahedral [bond angles O42−Li−pyrrolyl (centroid): 136.0°; O42−Li−F16: 105.4(3)°; O42−Li−F26: 118.5(4)°; F16−Li−F26: 81.2(3)°].

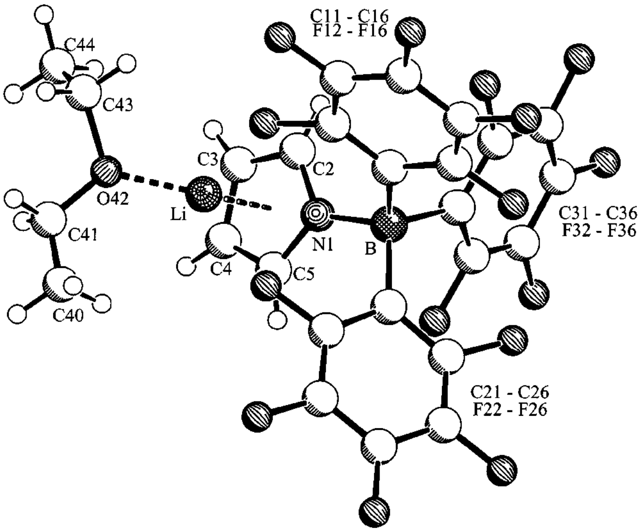


Figure 1. Molecular structure of complex **3**; selected bond lengths (Å) and angles (°): B−C21 1.637(5), B−C31 1.647(5), B−C11 1.656(5); C16−F16−Li 136.4(3), C26−F26−Li 136.4(2), N1−B−C21 109.4(3), N1−B−C31 102.5(2), N1−B−C11 112.6(3), C21−B−C31 115.8(3), C21−B−C11 104.1(3), C31−B−C11 112.7(3), C2−N1−B 125.0(3), C2−N1−C5 106.8(3), C5−N1−B 127.1(3); for additional values see text

Treatment of **3** with anhydrous HCl in ether resulted in protonation at an α-carbon atom of the pyrrol ring with formation of **4**. The neutral dipolar product was isolated in 57% yield after recrystallization from toluene. It shows four characteristic ^1H NMR resonances of the *N*-borylated pyrrolium ring system at δ = 7.35, 6.34, 5.45 and 3.53 in a 1:1:1:2 ratio {^{13}C NMR signals at δ = 171.1 (C2), 155.5 (C4), 127.2 (C3), 65.3 (C5) in [D_6]benzene; ^{15}N NMR resonance at δ = −145; ^{11}B NMR signal at δ = −7.6 in [D_8]toluene}.

The X-ray crystal structure analysis of **4** (single crystals from toluene at −18 °C; Figure 2) shows a planar pyrrolium ring system bonded to boron [N1−B6: 1.608(2) Å] that exhibits alternating double and single bonds [N1−C2: 1.298(2) Å; C2−C3: 1.431(3) Å; C3−C4: 1.318(3) Å; C4−C5: 1.474(3) Å; N1−C5: 1.449(2) Å; hydrogen atoms at the C_4H_5N ring were located from difference Fourier maps].

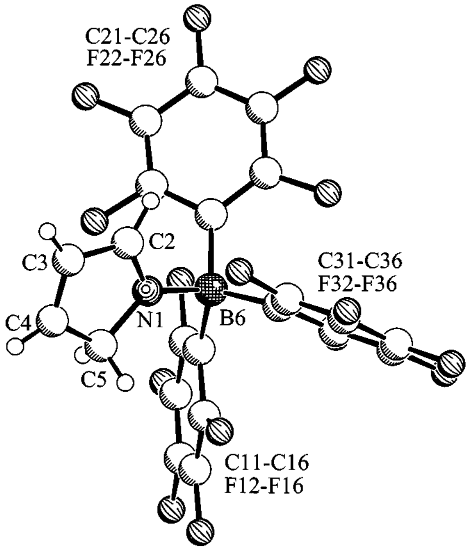
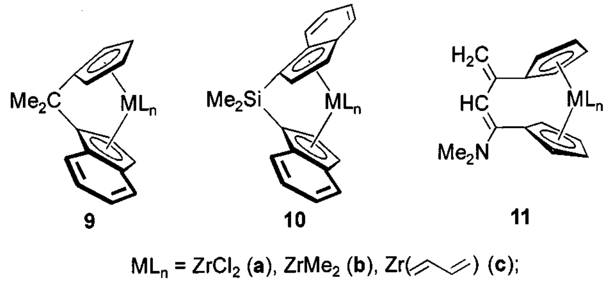


Figure 2. Molecular structure of **4**; selected bond lengths (Å) and angles (°): B6−C21 1.640(2), B6−C31 1.647(2), B6−C11 1.653(2); N1−B6−C21 105.13(12), N1−B6−C31 109.01(12), N1−B6−C11 106.37(12), C21−B6−C31 112.79(13), C21−B6−C11 114.36(13), C31−B6−C11 108.83(12), C2−N1−C5 107.61(14), C2−N1−B6 126.36(14), C5−N1−B6 125.98(13), N1−C2−C3 112.22(17), C4−C3−C2 106.83(18), C3−C4−C5 109.18(18), N1−C5−C4 104.05(16); for additional values see text

The neutral Brønsted acid **4** turns out to be well suited for the generation of group 4 metallocene cation complexes by protonation reactions of a variety of organometallic precursors. Two typical examples are the proton transfer reactions of **4** with dimethylzirconocene (**5**) and (η⁴-butadiene)-zirconocene (**7**, see Scheme 1). Compound **4** reacts with $Cp_2Zr(CH_3)_2$ (**5**) in toluene at ambient temperature during 1 h to yield cleanly the organometallic salt $[Cp_2ZrCH_3^+][(C_4H_4N)B(C_6F_5)_3^-]$ (**6**). The proton transfer reaction in this case results in the liberation of one equivalent of methane. Compound **4** rapidly transfers a proton to the butadiene ligand of **7** to yield a single [Cp_2Zr(*trans*-crotyl)$^+$][$(C_4H_4N)B(C_6F_5)_3^-$] isomer (**8**).

Both reactions were used for the generation of active homogeneous metallocene Ziegler catalysts for ethene polymerization in situ. In addition, the Brønsted acid **4** was employed in the generation of active ethene and propene polymerization catalysts from dimethyl- or η⁴-butadiene complexes of a series of *ansa*-metallocene frameworks (see Scheme 2).[12,13] The resulting catalysts were compared with their conventionally generated analogues [i.e. obtained by MAO treatment of the respective metallocene dichlorides, or $B(C_6F_5)_3$ treatment of the respective metallocene dimethyl complexes or -η⁴-butadiene complexes], and found to be comparable in activity and selectivity with these established procedures (see Table 1).[13] These reactions demonstrate that H^+ transfer from this new, readily available neutral proton source [$(C_4H_5N)B(C_6F_5)_3$] (**4**) provides an attractive alternative for the formation of reactive organometallic cations and related active catalyst systems, with concurrent generation of the essentially non-nucleophilic counter anion [$(C_4H_4N)B(C_6F_5)_3^-$]. A variety of interesting applications of the neutral Brønsted acid **4** and related systems in organometallic chemistry and catalysis can be envisioned. Further examples are being actively investigated in our laboratory.



Scheme 2

Table 1. A comparison of selected data concerning 1-alkene polymerization reactions at homogeneous metallocene Ziegler catalysts using different activation procedures

a) Ethene polymerization[a]

Precursor	µmol	Activator	µmol	t (min)	g PE	Act[b]	mp
5	59.5	$B(C_6F_5)_3$	58.6	60	9.9	169	128
5	35.7	**4**	36.3	30	6.4	359	127
7	33.6	$B(C_6F_5)_3$	35.2	30	10.0	583	128
7	33.6	**4**	34.5	30	8.6	501	130
9a[c]	34.0	MAO	36000	40	18.2	411[d]	[e]
9b	35.6	$B(C_6F_5)_3$	43.0	40	16.2	341[d]	[e]
9b[c]	29.3	**4**	29.4	40	13.8	354	129
9c[c]	27.4	**4**	27.6	60	36.9	673	[e]
11b[c]	29.0	**4**	29.4	15	5.6	386	129

b) Propene polymerization[c]

Precursor	µmol	Activator	µmol	t (min)	g PP	act[b]	%mmmm[f]
9a	34.0	MAO	36200	60	15.1	222	10[d]
9c	35.6	$B(C_6F_5)_3$	43.0	60	31.8	446	10[d]
9c	30.1	**4**	38.0	90	10.2	113	12
10a	22.6	MAO	36200	45	201.8	6700	69[d,g]
10c	39.3	$B(C_6F_5)_3$	43.0	45	63.6	1200	77[d,g]
10c	28.8	**4**	32.8	45	81.9	1900	88[g]

[a] Reactions at 20 °C, 1 bar, if not otherwise noted. – [b] In g polymer/mmol[Zr]·bar·h. – [c] 40 °C, 2 bar. – [d] From ref. 13. – [e] Not determined. – [f] From ^{13}C NMR pentade analysis. – [g] These reactions were not carried out under completely isothermal conditions because of their high exothermicities; that is probably the cause of the slightly different isotacticities observed.

Experimental Section

All reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. For additional general information including a description of the instrumentation used for physical characterization of the compounds see refs. 5 and 11a.

Preparation of $[(C_4H_4N)B(C_6F_5)_3]Li$ (3): Solid *N*-pyrrolyllithium[14] (0.53 g, 7.27 mmol) was mixed with solid $B(C_6F_5)_3$ (3.72 g, 7.27 mmol). Then, 50 mL of diethyl ether was added and the suspension stirred for 3 h at ambient temperature. Solvent was removed in vacuo and the residue suspended in pentane. The solid product was collected by filtration, washed with pentane (3 × 20 mL) and dried in vacuo to yield **3**$\cdot Et_2O$ (4.5 g, 91%), m.p. 137 °C, decomp. at 204 °C. – ^1H NMR (600 MHz, [D$_6$]benzene, 298 K): $\delta = 6.72$ (m, 2 H, 2,5-H), 5.84 (m, 2 H, 3,4-H), 2.80 (q, 4 H, CH_2 of Et_2O), 0.68 (t, 6 H, CH_3 of Et_2O). – ^{13}C NMR (150.7 MHz, [D$_6$]benzene, 298 K): $\delta = 148.2$ ($^1J_{FC} = 234$ Hz), 139.8 ($^1J_{FC} = 250$ Hz), 137.6 ($^1J_{FC} = 249$ Hz), 121.3 (br., *o*-, *p*-, *m*-, *ipso*-C of C_6F_5), 125.0 (C2,5), 108.9 (C3,4), 65.9, 14.0 (Et_2O). – ^{11}B NMR (64.2 MHz, [D$_6$]benzene, 300 K): $\delta = -8.2$ ($\nu_{1/2} \approx 50$ Hz). – ^7Li NMR (77.8 MHz, [D$_8$]THF, 300 K): $\delta = -2.6$ ($\nu_{1/2} \approx 2$ Hz). – ^{19}F NMR (282 MHz, [D$_6$]benzene, 300 K): $\delta = -134.9, -157.5, -162.7$ (*o*-, *p*-, *m*-F of C_6F_5). – $C_{26}H_{14}BF_{15}LiNO$ (659.1): calcd. C 47.38, H 2.14, N 2.13; found C 47.63, H 2.95, N 1.90.

X-ray Crystal Structure Analysis of 3: $C_{26}H_{14}BF_{15}LiNO$, $M = 659.13$, yellow crystal $0.20 \times 0.20 \times 0.10$ mm, $a = 11.478(2)$, $b = 15.266(6)$, $c = 15.539(2)$ Å, $\beta = 93.66(1)°$, $V = 2717.2(12)$ Å^3, $\rho_{calcd.} = 1.611$ g cm^{-3}, $\mu = 15.22$ cm^{-1}, empirical absorption correction by ψ scan data ($0.751 \leq T \leq 0.863$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 5820 reflections collected ($+h, -k, \pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 5540 independent ($R_{int} = 0.029$) and 2856 observed reflections [$I \geq 2\sigma(I)$], 408 refined parameters, $R = 0.062$, $wR2 = 0.166$, max. residual electron density 0.40 (−0.35) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Preparation of $[(C_4H_5N)B(C_6F_5)_3]$ (4): A 1 M solution of HCl in diethyl ether (3.00 mL, 3.00 mmol) was added dropwise with rapid stirring to a solution of **3**$\cdot Et_2O$ (1.50 g, 2.56 mmol) in 60 mL of ether. Volatiles were removed in vacuo after 30 min. and the residue stirred with pentane (20 mL). The solid was collected by filtration and extracted three times with toluene. Solvent was removed from the combined toluene phases in vacuo. The residue was recrystallized from toluene at -18 °C to yield **4** (852 mg, 57%), m.p. 178 °C. – ^1H NMR (600 MHz, [D$_6$]benzene, 298 K): $\delta = 7.35$ (br., $^1J_{CH} = 184$ Hz, 1 H, 2-H), 6.34 (m, $^1J_{CH} = 180$ Hz, 1 H, 4-H), 5.45 (m, $^1J_{CH} = 182$ Hz, 1 H, 3-H), 3.53 (br., $^1J_{CH} = 143$ Hz, 2 H, 5-H). – ^{13}C NMR (150.7 MHz, [D$_6$]benzene, 298 K): $\delta = 171.1$ (C2), 155.5 (C4), 148.2 ($^1J_{FC} = 241$ Hz), 140.6 ($^1J_{FC} = 253$ Hz), 137.6 ($^1J_{FC} = 249$ Hz), 118.5 (br., *o*-, *p*-, *m*-, *ipso*-C of C_6F_5), 127.2 (C3), 65.5 (C5). – ^{11}B NMR (192.2 MHz, [D$_6$]benzene, 298 K): $\delta = -7.6$ ($\nu_{1/2} \approx 90$ Hz). – ^{19}F NMR (563.7 MHz, [D$_8$]toluene, 298 K): $\delta = -132.3, 155.7, -162.6$ (*o*-, *p*-, *m*-F of C_6F_5). – $^1H,^{15}N$-GHMBC (600/60.7 MHz, [D$_8$]toluene, 213 K): $\delta = 6.93, 6.07, 5.20/-145$ (2-, 4-, 3-H/N). – $C_{22}H_5BF_{15}N$ (579.1): calcd. C 45.63, H 0.87, N 2.42; found C 45.50, H 1.11, N 2.27.

X-ray Crystal Structure Analysis of 4: $C_{22}H_5BF_{15}N$, $M = 579.08$, light yellow crystal $0.30 \times 0.10 \times 0.10$ mm, $a = 10.415(1)$, $b = 11.079(1)$, $c = 18.160(1)$ Å, $\beta = 98.54(1)°$, $V = 2072.2(3)$ Å^3, $\rho_{calcd.} = 1.856$ g cm^{-3}, $\mu = 2.04$ cm^{-1}, empirical absorption correction by SORTAV ($0.941 \leq T \leq 0.980$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 8760 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.65$ Å^{-1}, 4722 independent ($R_{int} = 0.022$) and 3772 observed reflections [$I \geq 2\sigma(I)$], 367 refined parameters, $R = 0.042$, $wR2 = 0.091$, max. residual electron density 0.30 (−0.21) e Å^{-3}, hydrogens from difference Fourier maps and refined as riding atoms.

Data sets were collected with Enraf–Nonius CAD4 and Nonius Kappa-CCD diffractometers, the latter one equipped with a rotating anode generator Nonius FR591. Programs used: data collection EXPRESS (Nonius B.V., **1994**) and COLLECT (Nonius B.V., **1998**), data reduction MolEN (K. Fair, Enraf–Nonius B.V., **1990**) and Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology* **1997**, *276*, 307–326), absorption correction for CCD data SORTAV (R. H. Blessing, *Acta Cryst.* **1995**, *A51*, 33–37; R.H.

Blessing, *J. Appl. Cryst.* **1997**, *30*, 421−426), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-144532 (**3**) and CCDC-144533 (**4**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

Reaction of $Cp_2Zr(CH_3)_2$ (5) with $[(C_4H_5N)B(C_6F_5)_3]$ (4); Generation of 6: Toluene (5 mL) was added to a solid mixture of **5** (101 mg, 0.40 mmol) and **4** (233 mg, 0.40 mmol). Pentane (80 mL) was added to the reaction mixture after 1 h to precipitate the product **6**, which was collected by filtration, washed with pentane (10 mL) and dried in vacuo. Yield of **6**: 210 mg, 64%. − ^{1}H NMR (600 MHz, [D$_8$]toluene, 298 K): δ = 6.98 (br., 2 H, pyrrolyl 2-H, 5-H), 5.27 (s, 10 H, Cp), 5.06 (m, 2 H, pyrrolyl 3-H, 4-H), -0.02 (s, 3 H, $Zr-CH_3$). − ^{13}C NMR (150.7 MHz, [D$_8$]toluene, 223 K): δ = 148.1 ($^1J_{CF}$ = 242 Hz), 139.7 ($^1J_{CF}$ = 249 Hz), 137.3 ($^1J_{CF}$ = 248 Hz), 120.7 (br., *o*-, *p*-, *m*-, *ipso*-C of C_6F_5), 137.2 ($^1J_{CH}$ = 189 Hz) and 101.8 ($^1J_{CH}$ = 166 Hz, pyrrolyl C2,5 and C3,4), 113.0 ($^1J_{CH}$ = 176 Hz, Cp), 40.2 ($^1J_{CH}$ = 120 Hz, $ZrCH_3$) (assignments confirmed by ^{1}H,^{1}H-GCOSY, ^{1}H,^{13}C-GHSQC and ^{1}H,^{13}C-GHMBC experiments). − ^{11}B NMR (64.2 MHz, [D$_8$]toluene, 298 K): δ = −8.7 ($\nu_{1/2}$ = 110 Hz). − ^{19}F NMR (563.7 MHz, [D$_8$]toluene, 223 K): δ = −130.9, −157.3, −163.2 (*o*-, *p*-, *m*-F of C_6F_5).

Reaction of (Butadiene)zirconocene (7) with 4; Generation of 8: Toluene (5 mL) was added at ambient temperature to a solid mixture of (*s-cis-/s-trans*-η^4-butadiene)$ZrCp_2$ (1:1) (**7**, 51 mg, 0.19 mmol) and **4** (107 mg, 0.19 mmol). The mixture was stirred for 30 min., then the solvent was removed in vacuo. The viscous residue was solidified by stirring with 50 mL of pentane. The product was collected by filtration, washed with pentane (2 × 10 mL) and dried in vacuo, yield of **8**: 106 mg (67%). − ^{1}H NMR (600 MHz, [D$_8$]toluene, 253 K): δ = 7.24, 4.87 (br., each 2 H, pyrrolyl), 4.66 (s, 10 H, Cp), 4.30 (dt, ^3J = 11 Hz, ^3J = 16 Hz, 1 H, $=CH-$), 3.37 (dq, ^3J = 6 Hz, ^3J = 16 Hz, 1 H, $=CH-CH_3$), 1.52 (d, ^3J = 11 Hz, 2 H, $=CH_2$), 1.28 (d, ^3J = 6 Hz, 3 H, CH_3). − ^{13}C NMR (150.7 MHz, [D$_8$]toluene, 253 K): δ = 148.3 ($^1J_{CF}$ = 244 Hz), 139.7 ($^1J_{CF}$ = 256 Hz), 137.4 ($^1J_{CF}$ = 249 Hz, *o*-, *p*-, *m*-C of C_6F_5), *ipso*-C of $-C_6F_5$ and pyrrolyl-C not observed, 123.2 ($^1J_{CH}$ = 150 Hz, $=CH-$), 108.0 ($^1J_{CH}$ = 177 Hz, Cp), 104.1 ($^1J_{CH}$ = 152 Hz, $=CH-CH_3$), 47.0 ($^1J_{CH}$ = 155 Hz, $=CH_2$), 18.6 ($^1J_{CH}$ = 126 Hz, CH_3) (assignment supported by ^{1}H,^{13}C-GHSQC). − ^{11}B NMR (64.2 MHz, [D$_8$]toluene, 298 K): δ = −8.8 ($\nu_{1/2}$ = 130 Hz). − ^{19}F NMR (563.7 MHz, [D$_8$]toluene, 223 K): δ = −130.8, −157.9, −163.5 (*o*-, *p*-, *m*-F of C_6F_5).

Polymerization Reactions with 4 as an Activator

a) Ethene Polymerization: A glass autoclave was charged with 300 mL of toluene and 2 mL of triisobutylaluminum, then thermostated for 1 h and the solution saturated with ethene (at 1 or 2 bar, see Table 1) for another hour. The catalyst was generated by treatment of the respective metallocene precursor with **4** in toluene, and this toluene solution was injected into the autoclave. The polymerization reaction was stopped by quenching with 50 mL aqueous HCl/methanol (1:5 v/v). The resulting polymer was washed subsequently with HCl, water, methanol and acetone and dried.

b) Propene Polymerization: Reactions were carried out analogously (at 2 bar). After quenching with HCl/CH_3OH, water (100 mL) was added. Stereoregular polypropylene samples were then collected by filtration and washed with HCl, water, methanol and acetone. Atactic polypropylene was extracted twice with toluene (200 mL); solvent was removed from the combined organic phases and the polymer dried in vacuo.

Acknowledgments

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