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Syntheses and properties of the novel co-catalysts *N*,*N*-dimethylanilinium- and trityl{tetrakis[4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl]borate}

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Dedicated to Professor Henri Brunner on the occasion of his 65th birthday

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Abstract

The syntheses and characterization of the novel co-catalysts trityl{tetrakis[4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl]borate} (**2**) and the corresponding *N*,*N*-dimethylaniliniumborate (**3**) is reported. Activation of dimethyl[*rac*-ethylenebis(indenyl)]zirconium(IV) with **2** or **3** forms a catalyst system for the homogeneous polymerization of ethene and propene, but also catalyzes the polymerization of 1-hexene. The molecular structure of the new, {tetrakis[4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl]borate} anion was determined by single-crystal X-ray structure analysis. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Co-catalyst; Zirconium; Metallocene; Olefin polymerization; Borates

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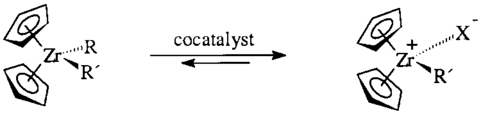
1. Introduction

Over the past decade there was intensive research activity concerning Group 4 metallocene complexes [1], because of their extraordinary advantages as olefin polymerization catalysts [2]. Therefore transformations concerning alkyl or hydride abstraction reactions from dialkyl- or dihydrido metallocenes by strong Lewis acids or Brønsted acids are of great interest [3]. The nature of the abstractor and the resulting anion X^-, as well as the coordinative and dynamic features of cation–anion pairing significantly influence the catalytic activity, lifetime, temperature stability of the catalyst as well as stereoregularity of the resulting polymer and chain transfer characteristics in Group 4 mediated homogeneous olefin polymerizations [3c].



Scheme 1. Activation of metallocene type catalysts. X = weakly coordinating anion; R, R′ = methyl or hydride.

This abstraction process yields highly electrophilic ion pairs (Scheme 1) which provide spectacular polymerization activity and selectivity.

Although a number of these ion pairs have been structurally characterized [4], simple functional models for homogeneous Ziegler–Natta catalysts remain scarce. Only few Lewis acids react with metallocenes to yield soluble, active catalyst systems. Even more problematic is the characterization of these active species. Suitable co-catalysts for the activation of metallocenes include perfluoroarylboranes [5], trityl- and *N*,*N*-dimethylanilinium borates, that form weakly coordinating anions on reaction with dialkyl-metallocenes [3e,6] and methylaluminoxane (MAO) [1,7]. Two features appear to be essential: (i) high Lewis-acidity of the electron deficient metal centers; (ii) lack of nucleophilic

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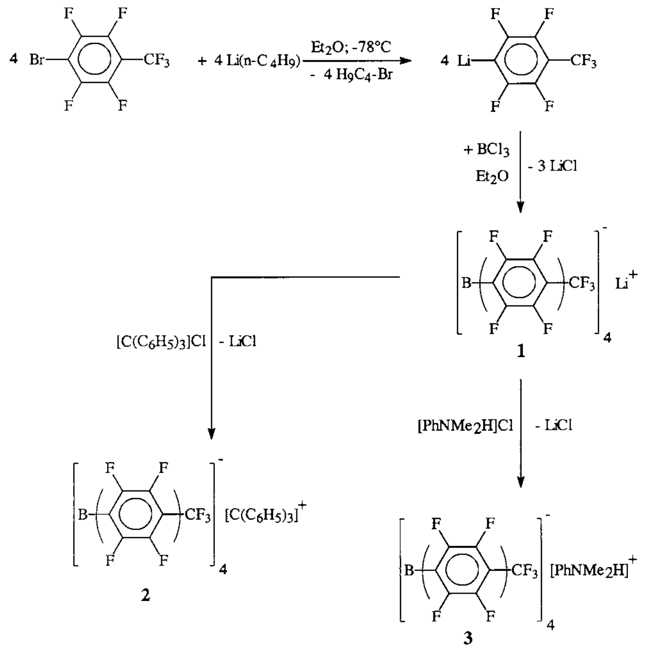

Scheme 2. Syntheses of compounds **1**, **2** and **3**.

Table 1
Crystal data and details of the structure determination for **3**

Empirical formula	$C_{28}BF_{28}$, $C_8H_{12}N$, C_3H_6O
Formula weight	1059.35
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
Unit cell dimensions	
a (Å)	12.754(2)
b (Å)	12.818(1)
c (Å)	14.749(2)
α (°)	97.474(14)
β (°)	115.012(14)
γ (°)	106.468(14)
V (Å^3)	2006.9(6)
Z	2
ρ_{calc} (g cm^{-3})	1.753
μ (mm)	0.2
Crystal size (mm)	0.61 × 0.025 × 0.20
Temperature (K)	173
λ (Å)	Mo–K$_\alpha$ 0.71073
$\theta_{min/max}$	2.0, 25.6
Total data	26 945
Unique data	7059 (0.041)
Observed data [$I>2\sigma(I)$]	4636
$R_1(F_o)$ [a]	0.0536
$wR_2(F_o^2)$ [b]	0.1663
Goodness-of-fit [c]	1.02
$\Delta/\rho_{min/max}$ (e Å^{-3})	−0.47, 1.34

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $wR=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
[c] $S=\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$.

substituents, which might serve as catalyst poison [3d]. Activation with trihaloboranes such as BF_3 and BCl_3, for instance, result in the formation of inactive metallocene halides due to the irreversible transfer of fluoride or chloride to the metal center. By activation with alkylaluminum halides often M(μ-Cl)Al structures are observed, that only exhibit modest activity [8]. Marks and coworkers investigated the relationship between thermal stability of metallocene borate ion pairs and their reactivity [3e]. For instance, the zirconocene-methyl complexes of the well known weakly coordinating $[B(C_6F_5)_4]^-$ anion are not stable at room temperature. The thermal decomposition of these ion pair complexes can be classified in (i) decomposition involving the counteranion (e.g. aryl group redistribution), and (ii) cation self decomposition (e.g. C–H activation). The first pathway can be suppressed by applying robust anions. Using strongly coordinating Lewis bases would block the second decomposition way, but Lewis base coordination also suppresses catalytic activity. Therefore the Lewis-basicity of the counteranion must be thoroughly tuned electronically and sterically with the Lewis acidity properties of the cation to receive optimal polymerization activities and thermal stability [3e].

2. Synthesis and structure

In order to receive an even less coordinating compound than the commonly used $[B(C_6F_5)_4]^-$ anion the *para*-positon of this compound was formally substituted by a trifluoromethyl group. The synthesis of the novel $[B(C_6F_4-CF_3)_4]^-$ anion resulted in the design of the corresponding trityl- (**2**) and *N*,*N*-dimethyl-anilinium salts (**3**). The advantages of this $[B(C_6F_4-CF_3)_4]^-$ anion are as follows: (i) good solubility of the co-catalyst and the resulting ion pairs, (ii) reduced coordination abilities, (iii) stability of the anion due to the perfluorinated nature of the ligand framework.

The synthesis of this new co-catalyst was performed according to Scheme 2 by reaction of 1.1 equivalents of *n*-BuLi with 1-bromo(4-trifluoromethyl)2,3,5,6-tetrafluorobenzene at −78°C in diethylether[1]. After addition of BCl_3 the Lithium at complex **1** can be isolated as crystalline solid. On subsequent reaction of **1** with CPh_3Cl yellow–orange crystals of the co-catalyst **2** were obtained in good yields. In an analogous manner activator **3** was synthesized by reaction of **1** with *N*,*N*-dimethylanilinium hydrochloride to yield colorless crystals. The structure of **3** is presented in Table 1 and Fig. 1. Most important bond lengths and bond angles are given in Table 2.

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[1] Caution! Lithiated perfluoraryl compounds have to be handled at low temperatures and should not be isolated, otherwise spontaneous decomposition with explosions may occur.

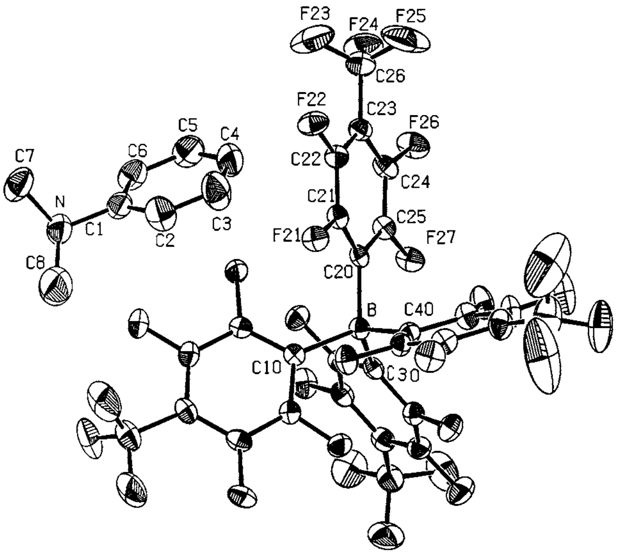

Fig. 1. ORTEP drawing of the molecular structure of *N*,*N*-dimethylaniline-{tetrakis[(4-trifluoromethyl)-2,3,5,6-tetrafluorophenyl]borate} (**3**). The ether molecules of crystallization and the hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

3. Catalytic performance

The activities obtained for the polymerization of ethylene, using dimethyl[*rac*-ethylenebis(indenyl)]-zirconium(IV) as precatalyst are presented in Table 3. In both cases, the activity decreases when the polymerization temperature is increased from 0°C to 60°C. At 80°C no activity is observed, neither for activation with **2** nor with **3**. The activation of the *ansa*-zirconocene $C_2H_4(Ind)_2ZrMe_2$ with tritylborate **2** gives slightly higher activities than with the corresponding anilinium derivative. This can be explained by the presence of a weak donation from the aniline, which may stabilize the Lewis acidic cationic metallocene and may therefore lower the catalytic activity. The activities produced by this new co-catalyst are lower than the activities known from ion pairs incorporating the $[B(C_6F_5)_4]^-$ anion or the MAO activated zirconocenes. The thermal stability of the ion pair produced with compound **2** or **3** is greatly enhanced. The resulting cationic metallocene complex starts to decompose at temperatures about 0°C, in contrast to the ion pair zirconocene/$[B(C_6F_5)_4]^-$ which is already thermally unstable at −20°C.

The produced polymers exhibit a molecular weight in the magnitude of 10^5 g mol^{-1} and a polydispersity of ca. 2. The molecular weights decrease when the polymerization temperature is increased due to a faster chain termination at higher temperatures. The polydispersities show a minimum at a temperature of 20°C, rising at higher and lower temperatures. At 0°C the activation of the precatalyst with the borate may not be quantitative, resulting in more than one polymerization active species and a broader molecular weight distribu-

Table 2
Selected bond distances and bond angles of **3**

C10–B	1.658(5)	C11–C10–B	119.4(3)	C45–C40–B	118.8(3)
C20–B	1.654(6)	C15–C10–B	127.7(3)	C7–N–C8	111.0(4)
C30–B	1.662(6)	C21–C20–B	119.5(3)	C1–N–C7	112.5(3)
C40–B	1.647(4)	C25–C20–B	126.6(3)	C1–N–C8	115.0(5)
N–C1	1.479(5)	C31–C30–B	118.7(3)		
N–C7	1.491(6)	C35–C30–B	127.3(3)		
N–C8	1.482(10)	C41–C40–B	128.1(3)		

Table 3
Results of ethene polymerization runs with co-catalysts **2** and **3**

Co-catalyst	t (°C)	Activity [a] after 5 min	Activity [a] after 45 min	Average activity [a]	M_w [b]	M_n [b]	D [b]
2	0	7.8×10^3	600	1.5×10^3	3.40×10^5	1.58×10^5	2.15
	20	7.3×10^3	600	1.3×10^3	3.30×10^5	1.59×10^5	2.08
	40	5.5×10^3	800	1.4×10^3	2.63×10^5	1.24×10^5	2.12
	60	3.5×10^3	900	1.4×10^3	2.31×10^5	1.07×10^5	2.16
	80	–	–	–	–	–	–
3	0	4.5×10^3	1.3×10^3	2.5×10^3	2.89×10^5	1.36×10^5	2.12
	20	2.1×10^3	1.2×10^3	1.4×10^3	2.72×10^5	1.35×10^5	2.01
	40	1.7×10^3	800	900	2.53×10^5	1.21×10^5	2.09
	60	1.4×10^3	400	600	2.19×10^5	1.03×10^5	2.12
	80	–	–	–	–	–	–

[a] kg PE (mol Zr × h × bar)$^{-1}$.

[b] Results from GPC at 135°C; precatalyst: dimethyl[*rac*-ethylenebis(indenyl)]zirconium(IV); reaction conditions: 2.0 bar ethene pressure; toluene as solvent; triisobutylaluminum as scavenger; reaction time 1 h.

Table 4
Results of propene polymerization runs with co-catalysts **2** and **3**

Co-catalyst	t (°C)	Activity [a] after 5 min	Activity [a] after 45 min	Average activity [a]	M_w [b]	M_n [b]	D [b]
2	0	3.2×10^3	700	1.4×10^3	7.17×10^4	3.30×10^4	2.17
	20	1.2×10^3	500	900	4.61×10^4	2.17×10^4	2.12
	40	600	150	300	3.98×10^4	1.96×10^4	2.03
	60	–	–	–	–	–	–
3	0	4.5×10^3	1.3×10^3	1.6×10^3	6.38×10^4	3.02×10^4	2.11
	20	4.1×10^3	900	1.3×10^3	4.01×10^4	2.27×10^4	2.07
	40	3.5×10^3	500	750	4.70×10^4	–	–
	60	–	–	–	–		

[a] kg PP (mol Zr × h × bar)$^{-1}$.

[b] Results from GPC at 135°C; precatalyst: dimethyl[*rac*-ethylenebis(indenyl)]zirconium(IV); reaction conditions: 2.0 bar ethene pressure; toluene as solvent; triisobutylaluminum as scavenger; reaction time 1 h.

tion of the obtained polymers. At temperatures of about 60°C a thermal decomposition of the active catalyst is likely to occur, also resulting in various polymerization-active and -inactive species.

The polymerization of propene is, according to Table 4, even more influenced by temperature. Thus, temperatures above 40°C lead to complete inactivity of the catalyst system. The activities are half of the observed ethylene polymerization activities. In the case of co-catalyst **2** the decrease of activity is, compared with the anilinium derivative **3**, more significant. The obtained polymers have been examined by ^{13}C-NMR and the isotacticities were determined to be higher than 95% isotactic.

Analogous to the polymerization of ethene, a decrease of product molecular weights is observed, when the polymerization temperature is increased. This decrease is more dramatic than in the polymerization of ethene, as can be seen in Tables 3 and 4. The molecular weight decreases from $6 \times 10^4/7 \times 10^4$ g mol^{-1} produced at 0°C to 4×10^3 g mol^{-1} at 40°C. Analogous to the ethene polymerization results, the polydispersities of the polymers decrease towards higher polymerization temperatures.

The polymerization of 1-hexene was performed at a polymerization temperature of -40°C. Both co-catalyst lead to a comparable catalyst activity of 120 kg poly-1-hexene (mol Zr × h × bar)$^{-1}$ for **2** and 110 kg poly-1-hexene (mol Zr × h × bar)$^{-1}$ for co-catalyst **3**.

The molecular weights of the poly-1-hexenes are 1.25×10^3 g mol^{-1} (polydispersity $D = 3.76$) for co-catalyst **2** and 1.16×10^3 g mol^{-1} (polydispersity $D = 3.45$) for co-catalyst **3**. The high polydispersities originate from the fact, that the temperature was not kept constant during the polymerization reaction, resulting in different activities of the catalyst and different length of the polymer chains. At temperatures around -40°C the activation of the *ansa*-zirconocene might not be complete, resulting in various active catalytic species.

4. Conclusions

The syntheses of the new co-catalysts **2** and **3** proceed via the lithiumborate **1**. Studies using these co-catalysts and dimethyl[*rac*-ethylenebis(indenyl)]-zirconium(IV) show a reduced activation potential, which is lower compared to conventional co-catalysts, e.g. MAO or [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]. It is shown that the stability of the ion pairs produced by dimethyl[*rac*-ethylenebis(indenyl)]zirconium and activators **2** and **3** strongly depend on the temperature. Thus, a significant deactivation is observed above 60°C for PE and above 40°C for PP. The ethene polymerization activities of the catalysts are twice as high as the corresponding propene polymerization activities. The polymerization of 1-hexene at -40°C shows comparatively moderate activity and results in highly viscous, polymeric products of high polydispersity.

5. Experimental

All experiments were carried out under an atmosphere of dry, purified nitrogen or argon using a glove box or standard Schlenk techniques. All solvents were dried and deoxygenated as described in [9] and kept under argon and molecular sieve (4 Å). NMR spectra were recorded on JEOL JNM GX-400 and Bruker DPX-400 instruments. The solvent signals were used for internal calibration. All spectra were obtained at room temperature (r.t.) unless otherwise stated. ^{19}F-NMR were referenced to external C$_6$H$_5$CF$_3$ and ^{11}B-NMR were referenced to external BF$_3$·Et$_2$O.

Polymer samples were dissolved in a mixture of 1,2,4-trichlorobenzene and $C_2D_2Cl_4$ and analyzed at 120°C. Elemental analysis was performed in the Microanalytical Laboratory of our institute.

The properties of the produced polymers were examined by a combination of high temperature gelpermeation chromatography, multi-angle light scattering and ^{13}C-NMR (100.5 MHz). The IR spectra were recorded on a Perkin–Elmer 1600 FTIR as KBr pellets. The melting points have been measured with a Bűchi apparatus and are uncorrected.

Dichloro[*rac*-ethylenebis(indenyl)]zirconium(IV) was purchased from Strem Chemicals and used as received. 1-Bromo-4-(trifluoromethyl)-2,3,5,6-tetrafluorobenzene was purchased from ABCR, *n*-BuLi, tritylchloride, BCl_3 (1 M in hexane) and *N*,*N*-dimethylaniline were purchased from Aldrich and used as received. 1-Hexene was purchased from Aldrich, purified by stirring over Na/K-alloy for 2 days and was freshly vacuum-transferred. Ethene (AGA Gas GmbH, grade 3.5) and propene (Linde AG, grade 2.8) were purified by passing two purification columns containing activated BTS-catalyst and molecular sieve (4 Å) before feeding the reactor.

Dimethyl[*rac*-ethylenebis(indenyl)]zirconium(IV) *rac*-$C_2H_4(Ind)_2ZrMe_2$ was prepared by the reaction of *rac*-$C_2H_4(Ind)_2ZrCl_2$ with $MgMe_2$ in toluene, followed by the purification of the product via crystallization from toluene.

5.1. *Lithium{tetrakis[(4-trifluoromethyl)-2,3,5,6-tetrafluorophenyl]borate}* (**1**)

To a stirred solution of 3.86 g (13 mmol) of 1-bromo-4-(trifluoromethyl)-2,3,5,6-tetrafluorobenzene in 50 ml of diethylether, cooled to −78°C, 1.1 equivalents of *n*-butyllithium were added via syringe. The reaction solution was stirred for 1 h at −78°C. Then, 0.25 equivalents of BCl_3 (1 M in hexane; 3.25 mmol; 3.25 ml) were added via syringe. This reaction mixture was kept at −78°C for 1 h and was afterwards allowed to come to r.t. overnight. The resulting suspension was filtered through celite and extracted twice with 30 ml of Et_2O. After concentrating the Et_2O phase, the product was crystallized from Et_2O at −30°C. Compound **1** was isolated by filtration and drying in vacuo to afford 2.8 g of off-white crystals in 83% yield.

Elemental analysis: Calc. for **1**·2Et_2O: C, 41,81; H, 1,95. Anal. Found: C, 42,07; H, 2,37%. ^{11}B-NMR ($CDCl_3$, 20 °C, ppm): $\delta = -16.84$ [s, 1B, $B(C_7F_7)_4$]. ^{19}F-NMR ($CDCl_3$, 20°C, ppm): $\delta = 6.61$ (t, $J = 21$ Hz, 12F, CF_3); −67.99 (br. s, 8F, *o*-F); −82.56 (br. s, 8F, *m*-F). ^{1}H-NMR ($CDCl_3$, 20°C, ppm): $\delta = 3.65$ (q, $J = 8$ Hz, 4H, Et_2O); 1.22 (t, $J = 8$ Hz, 6H, Et_2O). ^{13}C-NMR ($CDCl_3$, 20°C, ppm): $\delta = 14.3$ (s, 2C, Et_2O); 66,4 (s, 2C, Et_2O); 105.5; 121.47 (q, 4C, $J_{C-F} = 270$ Hz, CF_3); 133.5 (m, 4C); 141.5 (d, $J_{C-F} = 240$ Hz, 8C); 148.4 (d, $J_{C-F} = 270$ Hz, 8C). IR (Nujol, cm^{-1}): $\tilde{\nu} = 2925.8$ w; 2855.1 w; 1652.1 w; 1583.9 s; 1452.2 s; 1358.2 s; 1318.7 s; 1186.3 m; 1136.3 s; 990.5 w, 956.2 s; 768.2 w; 708.1 m; 681.9 w.

5.2. *Triphenylmethyl{tetrakis[(4-trifluormethyl)-2,3,5,6-tetrafluorophenyl]borate}* (**2**)

A total of 600 mg of **1** (0.58 mmol) was suspended in 10 ml of hexane. To this suspension 1.2 equivalents of CPh_3Cl (0.696 mmol, 194 mg) were added. Immediately, the suspension changed its color to red. After 2 days of stirring at r.t. the solution was filtered and the remaining yellow solid was extracted three times with 10 ml of dichloromethane. Onto this dark yellow–orange solution a layer of hexane was carefully added and after 2 days at −30°C, 610 mg of **2** (yield 94%) could be isolated after crystallization as yellow–orange crystals by filtration and drying in vacuo.

Elemental analysis: Calc. for **2**: C, 50.28; H, 1.34. Anal. Found: C, 50.03; H, 1.29%. ^{11}B-NMR ($CDCl_3$, 20°C, ppm): $\delta = -16.93$ [s, 1B, $B(C_7F_7)_4$]. ^{19}F-NMR ($CDCl_3$, 20°C, ppm): $\delta = 6.71$ (t, $J_{C-F} = 22$ Hz, 12F, CF_3); −67.68 (br. s, 8F, *o*-F); −82.46 (br. s, 8F, *m*-F). ^{1}H-NMR ($CDCl_3$, 20°C, ppm): $\delta = 7.60$ (br. 6H, aryl); 7.83 (br. 6H, aryl); 8.23 (br. 3H, *p*-aryl). ^{13}C-NMR ($CDCl_3$, 20°C, ppm): δ 105.5; 124,3; 125.6 (q, 4C, $J_{C-F} = 200$ Hz, CF_3); 130.7 (s, Trityl); 133.4 (m, 4C); 139.8 (s, Trityl); 142.4 (s, Trityl); 143.7 (s, Trityl); 142.7 (d, $J_{C-F} = 237$ Hz, 8C); 148,3 (d, $J_{C-F} = 239$ Hz, 8C); 210.8 (s, 1C, Ph_3C^+). IR (Nujol, cm^{-1}): $\tilde{\nu} = 2925.8$ w; 2855.1 w; 1652.1 w; 1583.9 s; 1452.2 s; 1358.2 s; 1318.7 s; 1186.3 m; 1136.3 s; 990.5 w, 956.2 s; 768.2 w; 708.1 m; 681.9 w.

5.3. *N,N-Dimethylanilinium{tetrakis-[(4-trifluoromethyl)-2,3,5,6-tetrafluorophenyl]borate}* (**3**)

A total of 600 mg of **1** (0.58 mmol) and 1.2 equivalents of *N*,*N*-dimethylanilinium hydrochloride (0.696 mmol, 110 mg) were combined in the reaction flask, followed by the addition of 20 ml of H_2O. The solution was stirred at r.t. overnight and the resulting off-white precipitate was filtered off and washed twice with 10 ml of H_2O and hexane. The remaining solid was dissolved in 10 ml of acetone. This solution was poured into 50 ml of cold H_2O. The resulting white precipitate was collected by filtration and afforded 500 mg of **3** (yield 86%) after drying in vacuo. Crystals were obtained from a dichloromethane–hexane mixture.

Elemental analysis: Calc. for **3**: C, 43.17; H, 1.20; N, 1.40. Anal. Found: C, 43.31; H, 1.50; N, 1.25%. ^{11}B-NMR ($CDCl_3$, 20°C, ppm): $\delta = -16.93$ [s, 1B, $B(C_7F_7)_4$]. ^{19}F-NMR ($CDCl_3$, 20°C, ppm): $\delta = 6,72$ (t, $J_{C-F} = 20$ Hz, 12F, CF_3); −67.84 (br. s, 8F, *o*-F); −82.19 (br. s, 8F, *m*-F). ^{1}H-NMR ($CDCl_3$, 20°C, ppm): $\delta = 3.28$ (s, 6H, NMe_2); 7.36–7.38 (m, 2H, aniline); 7.60–7.62 (m, 3H, aniline). ^{13}C-NMR ($CDCl_3$, 20°C, ppm): $\delta = 47.6$ (s, 2C, NMe_2); 105.5; 119.1 (s, aniline); 126.5 (q, 4C, $J_{C-F} = 200$ Hz, CF_3); 131.6 (s, aniline); 132.1 (s, aniline); 134.8 (m, 4C); 140.7 (s, aniline); 142.9 (d, $J_{C-F} = 257$ Hz, 8C); 148,3 (d, $J_{C-F} = 239$ Hz, 8C). IR (KBr, cm^{-1}): 2925.3 w; 2783.3 w; 1704.8 m; 1654.0 m; 1456.4 s; 1318.7 s; 1172.3 m; 1127.8 s; 990.2 m; 956.4 s; 775.9 m; 709.2 m; 681.5 m; 628.6 w; 573.8 w.

5.4. Ethene and propene polymerization and analytical procedures

A 0.5-l Bűchi glass autoclave, equipped with a press-flow gas controller was filled with ca. 230 ml of dry and oxygen-free toluene, 1.0 ml of triisobutylaluminum solution (25 wt% in toluene) and the desired amount of dimethyl[*rac*-ethylenebis(indenyl)]zirconium(IV), dissolved in toluene. The autoclave was pressurized with ethene or propene and thermostated to the desired reaction temperature.

One equivalent of **2** or **3**, respectively, was suspended in toluene or dissolved in 1,2-difluorobenzene. The vigorously stirred suspension or solution was transferred into the injection system via a canula. The injection system was then closed, the suspension or solution injected into the autoclave and the injection system was washed with an additional 5 ml of toluene. The pressure was kept constant during the polymerization and the amount of ethene or propene consumed by the catalyst during the polymerization reaction was measured. The polymerization was quenched after 1 h by adding 10 ml of methanol and the resulting polymer-suspension was poured into 250 ml of methanol/HCl (3:1) to precipitate the polymer and stirred for 16 h. After filtration the polymer was dried at 60°C in vacuo.

5.5. 1-Hexene polymerization procedure

In a glove box 12.5 mg of dimethyl[*rac*-ethylenebis(indenyl)]zirconium(IV) were combined with one equivalent of the the appropriate trityl- or *N*,*N*-dimethylanilinium-borate (**2** or **3**) and cooled to − 40°C. After the addition of 5 ml of toluene, cooled to − 40°C, the resulting reaction mixture was stirred at − 40°C for 5 min. After that time, 10 ml of 1-hexene were added and the mixture stirred at − 40°C for 1 h. The viscous solution was removed from the glove box and poured into 50 ml of acidic methanol (methanol/HCl = 3:1). The organic layer was separated and the aqueous solution extracted with toluene, the combined organic fractions washed with methanol, dilute HCl and water and the solvent evaporated in vacuo.

5.6. Molecular weight determination

The obtained polymers were analyzed using a combination of a Waters 150 CV-high-temperature-GPC at 135°C with 1,2,4-trichlorobenzene as a solvent and a modified Whyatt MiniDawn light scattering instrument. The calibration was performed with polystyrene standards and conversion into PE- and PP-calibration curves using Mark–Houwink parameters.

5.7. X-ray measurements and structure determination

A suitable colorless crystal of 0.61 × 0.25 × 0.20 mm was selected from a batch of crystals obtained by slow evaporation of a dichloromethane–ether solution. The crystal was fixed in a capillary with perfluorinated ether and mounted at the diffractometer. Data were collected at 173 K with an Image Plate system (STOE) using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å, Nonius FR 591 rotating anode). The structure was solved by direct methods [10] and the non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods based on F^2 [11]. A total of 26 945 reflections were measured and 7059 unique reflections ($R_{int} = 0.041$) were used in solution and refinement of the structure. Further details of data collection and refinement are given in Table 1. Most important bond length and bond angles are given in Table 2.

6. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 155149 for compound **3**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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