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Journal of Organometallic Chemistry 621 (2001) 184–189

Journal of Organo metallic Chemistry

Trimethylammonium[tetrakis(pentafluorophenoxy)borate], a safe way to synthesize novel co-catalysts for olefin polymerization

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Received 28 July 2000; accepted 29 September 2000

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

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Abstract

The synthesis and characterization of the novel co-catalyst trimethylammonium[tetrakis(pentafluorophenoxy)borate] (**1**) is reported. Activation of TIBA allkylated 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridyl-iron(II) chloride (**2**) using activator **1** forms an active catalyst system for homogeneous polymerization of ethene. The molecular structure of this new weakly coordinating anion was determined by single-crystal X-ray analysis. The straightforward synthesis of **1** is interesting for possible industrial applications. Polymerization experiments using activator **1** demonstrate higher activities than with the commonly used co-catalyst $[HNMe_2Ph][B(C_6F_5)_4]$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Co-catalysts; Olefin polymerization; Borates; Pentafluorophenol; Bisiminopyridines

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1. Introduction

Cationic Group 4 metallocene complexes have been a field of intensive research because of their extraordinary characteristics as olefin polymerization catalysts [1]. It was recently discovered by Brookhart [2] and Gibson [3], that also late transition metal chelate complexes based on iron, cobalt, nickel and palladium polymerize α-olefins to high molecular weight polymers. The nickel and palladium systems incorporate polar monomers such as methyl acrylate into the ethylene- and propylene-polymers [4]. Usually, for the transformation of the metallocene or the late transition metal precatalyst system into polymerization-active, cationic species, co-catalysts such as methylaluminoxane (MAO) or modified methylaluminoxane (MMAO) are used [1e,5]. But also fluorinated organoboranes or -borates are suitable as co-catalysts, as they form the active cationic species and weakly coordinating anions during the activation reaction [6,7]. The problem with these organoboranes or -borates is the sometimes pretentious synthesis: fluorinated Grignard and lithium compounds can spontaneously explode upon working at ordinary temperatures, especially when fluoro-substituents are in the *ortho*-position with regard to the metal [8].

Very commonly used activators are, for instance, ammonium borates [6d,e] as protolytic reagents. For their larger-scale production it is important to design organoborate compounds which provide a perfluorinated ligand framework. However, up to now there is no way of a straightforward synthesis without the latent danger of hazardous explosions.

Herein we report the synthesis of the novel compound $[HNMe_3][B(OC_6F_5)_4]$ (**1**) as an useful co-catalyst for the activation of late transition metal polymerization catalysts.

2. Results and discussion

Because of its high polymerization activity, 2,6-bis[1-(2,6-diisopropyl-phenylimino)ethyl]pyridyliron(II) chlo-

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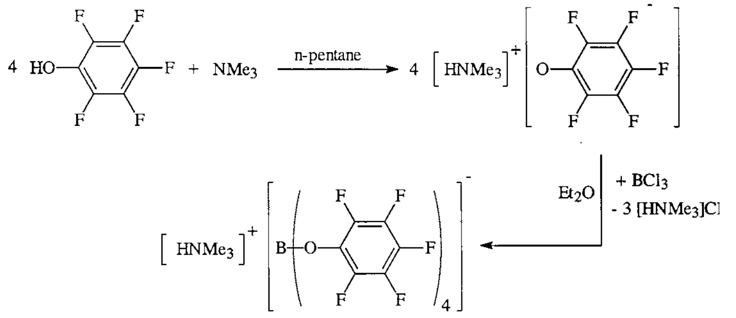
PII: S0022-328X(00)00861-5



Scheme 1. Synthesis of compound **1**.

ride (**2**) [2,3] was used for our investigations concerning polymerization activities.

The synthesis of **1** was performed according to Scheme 1 via the trimethylammoniumpentafluorophenolate $[HNMe_3][OC_6F_5]$ and subsequent reaction with BCl_3. This route is applicable to other ammonium borates such as the widely used *N*,*N*-dimethylanilinium derivative. The employed synthesis-strategy has the advantage of forming the co-catalyst in one step. This differs substantially from the conventional alkylorganoborates, that have to be treated additionally with ammonium hydrochloride derivatives in order to receive the final, protic co-catalyst.

Activator **1** was characterized by common standard techniques including elemental analysis, ^{11}B-, ^{19}F-, ^{1}H- and ^{13}C-NMR and IR. The compound was further subjected to single-crystal X-ray diffraction studies.

The crystal structure of the anionic portion of $[HNMe_3][B(OC_6F_5)_4]$ (**1**) is shown in Fig. 1. Specific data concerning crystal data, data collection and refinement are presented in Table 1.

The activation of 2,6-bis[1-(2,6-diisopropylimino-phenyl)ethyl]pyridyliron(II) chloride (**2**) was performed by an in situ alkylation of the bis(imino)pyridyl-iron(II) chloride with triisobutylaluminum and successive protonation of one alkyl group upon addition of co-catalyst **1** or $[PhNMe_2H][B(C_6F_5)_4]$ (Scheme 2).

To generate the polymerization active, cationic Fe-species, 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]-pyridyliron(II) chloride (**2**) was treated with $Al(^{i}Bu)_3$ in toluene to form the alkylated derivative **2a** (step 1). A dark green solution was formed within seconds. To this solution one equivalent of co-catalyst **1** was added (step 2). The color of the solution turned into deep purple while gas evolution could be observed. The resulting solution was stirred for 5 min at room temperature and afterwards injected into the reactor. Table 2 shows the measured activities at 0°C and 2.0 bar of ethene pressure. The overall polymerization activity of ion pair **3** was determined to 1400 kg PE (mol Fe h bar)$^{-1}$. The same procedure was used in case of co-catalyst $[PhNMe_2H][B(C_6F_5)_4]$. After addition of this conventional activator to precatalyst **2a** a change in color from dark green to brown was observed. This activated catalyst **4** provided an overall activity of 1000 kg PE (mol Fe h bar)$^{-1}$ using identical activation and polymerization conditions.

The comparatively low polymerization activities may originate from an incomplete activation of precatalyst **2**. Although the alkylation of **2** can be expected to be fast, as the extremely rapid in situ alkylation and activation of precatalyst **2** by MMAO shows, a complete conversion from **2** to **2a** is uncertain within the short reaction time of a few minutes. If we assume the alkylation to be complete after few minutes, the addition of the co-catalyst should give the active catalyst spontaneously, but up to now no evidence can be found for the completeness of the activation by the borate.

According to the data displayed in Table 2, the activated catalyst **3** shows comparatively high activity in the beginning of the polymerization process, but

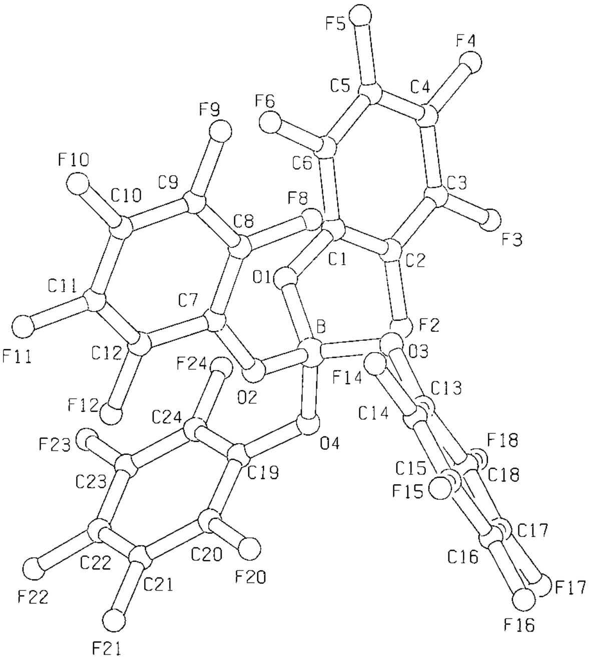


Fig. 1. Molecular structure of the [tetrakis(pentafluorophenoxy)-borate] anion. PLUTON style was used for clarity.

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

Formula weight	923.37
Crystal system	Monoclinic
Space group	$P21/c$ (no. 14)
Unit cell dimensions	
a (Å)	10.7302(2)
b (Å)	30.8172(6)
c (Å)	11.4044(2)
γ (°)	105.4720(10)
V (Å^3)	3634.48(12)
Z	4
ρ_{calc} (g cm^{-3})	1.688
μ (mm)	0.2
Crystal size (mm)	$0.33 \times 0.25 \times 0.20$
Temperature (K)	193
λ (Å)	Mo–K_α 0.71073
$\theta_{min/max}$	2.1/23.3
Total data	18 092
Unique data	5051 (0.041)
Observed data [$I > 2\sigma(I)$]	4208
$R_1(F_o)$ [a]	0.033
$wR_2(F_o^2)$ [b]	0.0841
Goodness-of-fit [c]	0.968
$\Delta/\rho_{min/max}$ (e Å^{-3})	−0.21, 0.20

[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] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.

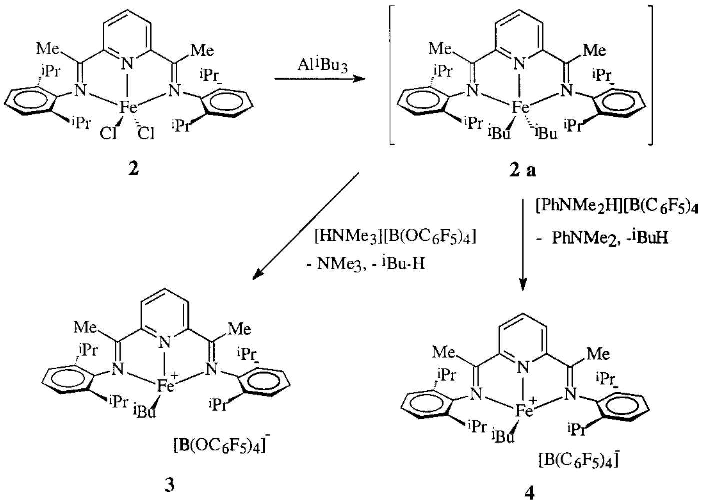
already after few minutes a significant decrease in activity can be detected. The behavior of the ion pair generated with the conventional co-catalyst [$HNMe_2$-Ph][$B(C_6F_5)_4$] is somewhat different. This system is not as active as catalyst **3** in the beginning, but the decrease in activity is slower. Thus, the activity of the catalyst system **4** seems to be more constant and the polymerization active species to be more stable during polymerization. The higher activity resulting in the use of co-catalyst **1** may originate from the lower donor ability of the borate counterion due to the significant change of the electronic properties of the boron center. Also, the different donor abilities of the reaction products NMe_3 and $PhNMe_2$ have to be taken into consideration. As a strong σ-donor, the produced trimethylamine can stabilize the active iron species more efficiently than the *N*,*N*-dimethylaniline resulting in a lower electron-deficiency of the catalytic center and therefore a lower polymerization activity of the resulting catalyst.

Analogous to the polymers obtained by the MMAO-activated bis(imino)pyridyliron(II) complex (**2**), reported by Gibson et al., the produced polymers are of bimodal molecular weight distribution with one polymer fraction of the molecular weight of ca. 10^6 g mol^{-1} and the low-molecular weight fraction of ca. 10^5 g mol^{-1}. Both catalysts, obtained by the activation of compound **2a** with the two borates [$HNMe_3$][$B(OC_6F_5)_4$] and [$PhNMe_2H$][$B(C_6F_5)_4$] produce nearly similar polymers, but the slightly higher molecular weights are produced by catalyst system **4**.

Attempts to crystallize these activated catalyst systems have not been successful up to now. Activation of zirconocenes, e.g. Cp_2ZrMe_2 and *rac*-$C_2H_4(Ind)_2ZrMe_2$ with this new type of co-catalyst did not succeed, probably due to the high oxophilicity of these early transition metal catalysts. No polymerization activity could be obtained at any polymerization conditions.

3. Conclusions

It has been shown that the synthesis of the new co-catalyst trimethylammonium tetrakis(pentafluorophenoxy)borate (1) is safe and straightforward. Co-catalyst **1** is capable of activating alkylated bis(imino)-



Scheme 2. Activation of compound **2a** with the borates **3** and **4**.

Table 2
Results of ethene polymerization runs

Compound	Co-catalyst	Activity [a] after 5 min	Activity [a] after 45 min	M_w [b]	M_n [b]	D
2a	[HNMe$_3$] [B(OC$_6$F$_5$)$_4$]	3600	500	9.85×10^5 (26%), 1.20×10^5 (74%)	8.22×10^5, 4.60×10^4	1.20, 2.61
2a	[HNMe$_2$Ph] [B(C$_6$F$_5$)$_4$]	1000	800	1.19×10^6 (29%), 2.03×10^5 (71%)	1.05×10^6, 8.65×10^4	1.14, 2.34

[a] kg PE (mol Fe h bar)$^{-1}$; determined in toluene, triisobutylaluminum as scavenger at 0°C and 2.0 bar ethene pressure.

[b] Results from GPC analysis at 135°C.

pyridyliron(II) complexes for olefin-polymerization. The achieved activity by activation of 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl)]pyridyliron(II) chloride is even higher than the activation by means of the commonly used co-catalyst [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$], the synthesis of which includes dangerous manipulations.

4. Experimental

All experiments were carried out under argon atmosphere using 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 a Bruker DPX-400 instrument. 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$_2$D$_2$Cl$_4$ and analyzed at 120°C. Elemental analysis were performed in the Microanalytical Laboratory of our institute.

The properties of the produced polymers were examined by a combination of high temperature-gel permeation 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.

Pentafluorophenol was purchased from ABCR, trimethylamine, triisobutylaluminum (1 M in toluene) and BCl$_3$ (1 M in hexane) were purchased from Aldrich and used as received. Ethene (AGA Gas GmbH, grade 3.5) was purified by passing two purification columns containing activated BTS-catalyst and molecular sieve (4 Å) before feeding the reactor.

*4.1. Trimethylammonium[tetrakis(pentafluorophenoxy)-borate] **(1)***

To a stirred solution of 7.25 g (39.4 mmol) of pentafluorophenol in 60 ml of absolute pentane, cooled to 0°C, 10 ml of NMe$_3$ (4.2 M in EtOH) were added slowly, upon which an immediate formation of a white solid was observed. After 2 h the cooled suspension was filtered and the remaining solid washed twice with 20 ml of pentane. The solid [HNMe$_3$][OC$_6$F$_5$], which was obtained by crystallization from Et$_2$O, was dissolved in 60 ml of diethylether, cooled to −30°C and 0.25 equivalents (9.8 ml) of BCl$_3$ (1 M in hexane) were added slowly with vigorous stirring via a syringe. After stirring for 1 h at −30°C the suspension was allowed to warm up to r.t. within 3 h. During this period a white precipitate formed. Then, the reaction mixture was heated to reflux overnight. After filtration and extraction with diethylether, the ether phase was concentrated. Compound **1** crystallized from diethylether at −30°C to afford 5.9 g (75%) yield.

Elemental analysis: Calc. for **1**: C, 40.36; H, 1,25; N, 1.74. Anal. Found: C, 40,27; H, 1,33; N, 1.83%. ^{11}B-NMR (CDCl$_3$, 20°C, ppm): $\delta = 0.996$ [s, 1B, B(OC$_6$F$_5$)$_4$]. ^{19}F-NMR (CDCl$_3$, −60°C, ppm): $\delta = -100.9$ (d, $J = 19$ Hz, 8F, *o*-F); −101.8 (*t*, 8F, *m*-F); −107.9 (br., 4F, *p*-F). ^{1}H-NMR (CDCl$_3$, 20°C, ppm): $\delta = 2.89$ (s, 9H, HN*Me*$_3$); 9.8 (v. br., 1H, *H*NMe$_3$). ^{13}C-NMR (CDCl$_3$, 20°C, ppm): $\delta = 45.8$ (s, 3C, Me); 124.5; 131.5; 134.5; 135.6 (d, $J_{C-F} = 246$ Hz, 4C); 137.9 (d, $J_{C-F} = 246$ Hz, 4C); 141.9 (d, $J_{C-F} = 243$ Hz, 4C). IR (Nujol, cm^{-1}): 3066.0 m; 2775.8 m; 2479.2w; 1518.5 s; 1482.0 s; 1314.6 w; 1251.9 w; 1164.5 m; 1025.0 s; 991.0 s; 949.1 m; 884.7 m; 632.6 m; 812.0 m; 565.0 w.

*4.2. Activation of the 2,6-bis[1-(diisopropylphenylimino)ethyl]pyridyl-iron(II) chloride **(2)** with trimethylammonium[tetrakis(pentafluorophenoxy)borate] **(1)***

A total of 61 mg (0.01 mmol) of **2** was suspended in 10 ml of toluene and 0.2 ml of a triisobutylaluminum-solution (1 M in toluene) were added dropwise and the resulting reaction mixture stirred for 2 min with a change in color from blue to deep green. Upon addition of one equivalent (80.3 mg, 0.1 mmol) of **1** (dissolved in 5 ml of 1,2-difluorobenzene), the color changed again from deep green to purple with gas evolution. This solution was stirred at r.t. for 5 min and used for the polymerization of ethene.

*4.3. Activation of the 2,6-bis[1-(diisopropylphenylimino)ethyl]pyridyl-iron(II) chloride **(2)** with N,N-dimethylanilinium[tetrakis(perfluorophenyl)borate]*

A total of 61 mg (0.01 mmol) of **2** was suspended in 10 ml of toluene and 0.2 ml of a triisobutylaluminum solution (1 M in toluene) were added dropwise and resulting reaction mixture stirred for 2 min with a change in color from blue to deep green. Upon addition of 80.1 mg (0.1 mmol) of *N*,*N*-dimethylanilinium [tetrakis(pentafluorophenyl)borate], dissolved in 5 ml of 1,2-difluorobenzene, the color changed again from deep green to brown with an evolution of gas. This solution was stirred at r.t. for 5 min and used for the polymerization of ethene.

4.4. Ethene polymerization and analytical procedures

4.4.1. Polymerization procedures

A 0.5 l Büchi glass autoclave, equipped with a press-flow gas controller was filled with ca. 230 ml of dry and oxygen-free toluene and 1.0 ml of triisobutylaluminum solution (25 wt.% in toluene). The autoclave was pressurized with ethene and thermostated to the reaction temperature. The catalyst solutions were transferred into the injection system via a syringe or a canula, the injection system closed, the solution injected into the autoclave and the injection system washed with additional 5 ml of toluene. The pressure was kept constant during the polymerization and the amount of ethene consumed by the catalyst 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 a methanol–HCl mixture (3:1) to precipitate the polymer and stirred for 16 h. After filtration the polymer was dried at 60°C in vacuo.

4.4.2. 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.

4.5. X-ray measurements and structure determination

A colorless crystal of 0.33 × 0.25 × 0.20 mm was selected from a batch of crystals obtained by slow evaporation of a hexane–ether solution. The crystal was fixed in a capillary with perfluorinated ether and mounted at the diffractometer. Data were collected at 193 K with an imaging 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 18 092 reflections were measured and 5051 unique reflections ($R_{\text{int}} = 0.041$) were used in solution and refinement of the structure. Further details of data collection and refinement are given in Table 1.

5. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 155150 for compound **1**. 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).

Acknowledgements

We are grateful to our coworker Mrs. A. Osterauer for experimental assistance. This work was generously supported by the Deutsche Forschungsgemeinschaft and the Bayerische Forschungsverbund Katalyse FORKAT.

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