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Synthesis and application in high-pressure polymerization of a titanium complex with a linked cyclopentadienyl-phenoxide ligand

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Abstract

The *ansa* half-sandwich complex [η^5:η^1-C_5H_4-$C(CH_3)_2$-2-C_6H_4O]$TiCl_2$ (**1**) has been prepared using two different ways, a 'one-pot' synthesis and a synthesis via thermolysis of the Ti trichloride precursor [η^5-C_5H_4-$C(CH_3)_2$-2-$C_6H_4OCH_3$]$TiCl_3$ (**3**). When activated with methylaluminoxane (**4**) or the cocatalyst system triisobutyl aluminum/$[Me_2PhNH]^+[B(C_6F_5)_4]^-$ (**5**), complex **1** could be used as a catalyst in high-pressure, high-temperature polymerization. The productivity of the catalyst system **1**/**4** in high-pressure polymerization of ethene is 400 t polymer mol^{-1} Ti, while the productivity of catalyst system **1**/**5** is only 6 t polymer mol^{-1} Ti. In ethene/1-hexene copolymerizations productivity and molecular weights decrease with increasing 1-hexene in the feed. The polymerization results were discussed and compared to results of high-pressure polymerization with the catalyst system $Me_2Si[IndH_4]_2ZrCl_2$/**4**. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Half-sandwich metallocene; Ethylene–1-olefin copolymerization

1. Introduction

Group 4 *ansa* half-sandwich complexes of the type [η^5:η^1-$C_5R_4(SiMe_2)NR'$]MCl_2 are of great technological interest as precursors of single site catalysts for the copolymerization of ethene with 1-olefins [1]. The amide donor is able to stabilize the electrophilic metal center, while the constrained geometry of the ligand opens up one side of the complex, resulting in high incorporation of the sterically more hindered 1-olefins into ethene/1-olefin copolymers [2]. Although synthetic routes to corresponding *ansa* half-sandwich complexes with other heteroatom donor-groups have already been described [3], little is known about their catalytic properties. Rieger found that ethylene-bridged fluorenyl alkoxide zirconium complexes were active for ethylene polymerization when used along with methylaluminoxane (**4**) [4]. Marks et al. have shown that a bidentate ligand containing a cyclopentadiene directly linked to the *ortho* position of phenol forms a constrained geometry Ti dibenzyl complex with $Ti(CH_2Ph)_4$, which is highly active for the polymerization of 1-olefins at room temperature after activation with cocatalysts [5]. Hessen et al. described a stable cationic [(Cp-alkoxide)$Ti(CH_2Ph)$]$^+$ species, which is active in catalytic propene polymerization [6].

The constrained geometry catalysts containing an amide donor ligand are remarkably stable and can be used in solution polymerization with temperatures up to 180°C, a crucial prerequisite for industrial application [1b,2]. However, nothing is known about the thermostability of the corresponding alkoxide catalysts.

In view of the potential of *ansa* half-sandwich complexes containing a bidentate mono-Cp-alkoxide ligand, we developed two synthetic routes leading to [η^5:η^1-C_5H_4-$C(CH_3)_2$-2-C_6H_4O]$TiCl_2$ (**1**), an *ansa* half-sandwich complex with a Cp-ligand linked to the phenoxide by an isopropyl bridge [7]. In order to exploit the performance of this type of complex for industrial polymerization processes, we performed high-temperature and high-pressure ethene/1-hexene copolymerizations with catalyst systems based on complex **1**.

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2. Results and discussion

2.1. Synthesis of [η^5:η^1-C_5H_4-$C(CH_3)_2$-2-C_6H_4O]$TiCl_2$ (1)

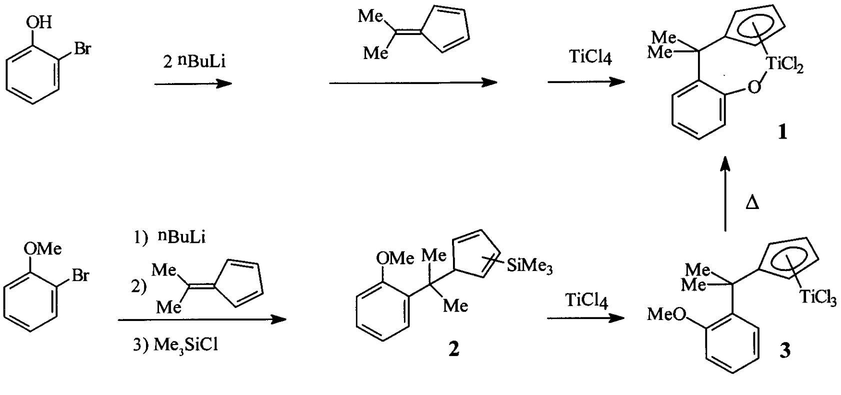
Both synthetic routes to [η^5:η^1-C_5H_4-$C(CH_3)_2$-2-C_6H_4O]$TiCl_2$ (**1**) are depicted in Scheme 1.

Route one shows a convenient 'one-pot' synthesis starting with the reaction of 2-bromophenol with two equivalents ^{n}BuLi. The resulting dilithio phenolate is reacted over-night with 6,6-dimethylfulvene to form the dilithio salt of the bidentate ligand. Further addition of $TiCl_4$ leads to complex **1**, which after precipitation of the crude product with hexane and recrystallization from hexane/dichloromethane, could be isolated as orange crystals in an overall yield of ca. 25%.

The other approach to complex **1** is more laborious and involves the isolation of the potential bidentate ligand system 2-methoxy-phenyl-1-methyl-ethyl-cyclopentadienyl-trimethylsilane (**2**), as well as thermolysis of the unbridged precursor complex [η^5-C_5H_4-$C(CH_3)_2$-2-$C_6H_4OCH_3$]$TiCl_3$ (**3**). The ligand system was synthesized in a one-pot procedure by treating 2-lithioanisole with 6,6-dimethylfulvene and subsequently quenching the reaction mixture with Me_3SiCl. After removal of the volatiles at 80°C and 10^{-2} mbar, the trimethylsilyl-functionalized ligand is obtained as a mixture of three isomers with a 10:1:1 ratio determined by ^{1}H-NMR [8]. Reaction of this ligand precursor with $TiCl_4$ produces a deep red solid which was identified as the half-sandwich Ti trichloride complex **3**. Attempts to crystallize the crude product failed, probably because of inter- and intramolecular coordination of the methoxy group, resulting in a non-crystalline precipitate. However, at room temperature the ^{1}H-NMR shows only one single isomer as was also found for (2-methoxyethyl)cyclopentadienyl titanium trichloride, an analogous half-sandwich complex, which shows a crystal structure with an intramolecular coordination of the methoxy group to the titanium atom [9]. Further attempts to purify the crude product by sublimation at 115°C and 10^{-2} mbar led to the *ansa* half-sandwich complex **1** by elimination of MeCl. The yields resulting from this solvent-free thermolysis are below 20%, probably due to intermolecular reactions. Hessen et al. have shown that analogous thermal elimination of MeCl from [$C_5Me_4(CH_2)_3OMe$]$TiCl_3$ performed in solution at elevated pressure results in better yields [6].

2.2. Polymerization properties of 1 under high temperature and high pressure

The properties of complex **1** as a catalyst for the polymerization of ethene were investigated under high-pressure and high-temperature conditions. Complex **1** was preactivated with either methylaluminoxane (MAO) (**4**) or triisobutyl aluminum/$[Me_2PhNH]^+[B(C_6F_5)_4]^-$ (**5**) as cocatalysts. The polymerizations were performed in a continuously operated autoclave at a temperature of 210°C and a pressure of 150 MPa (Section 3). Complex **1** was dissolved in toluene and activated with one of the above-described cocatalysts in a glass flask under an argon atmosphere. The activation of the titanocene (**1**) with cocatalyst **5** followed a two-step procedure as has already been successfully used for the activation of zirconocene dichlorides [10]. In the first step, **1** was dissolved in toluene and triisobutyl aluminum (TiBA) was added in order to alkylate the titanocene dichloride (**1**). Immediately after the desired amount of TiBA was added, the color of the solution changed from yellow to brown. In a second step, the addition of the activator $[Me_2PhNH]^+[B(C_6F_5)_4]^-$ further intensified the color. Using this catalyst solution for the polymerization of ethene yielded only 6 t polymer mol^{-1} Ti, whereas productivities of up to 400 t polymer mol^{-1} Ti were achieved using a catalyst solution containing **1** and MAO (**4**). The low productivity of the **1**/**5** catalyst system might be due to a rapid reduction of Ti^{IV} to Ti^{III} through the used surplus aluminum-alkyl $Al(^iBu)_3$. Ti^{III} species produced through direct reduction from Cp_2TiCl_2 with Et_2AlCl were shown to be inactive in ethene polymerization,



Scheme 1.

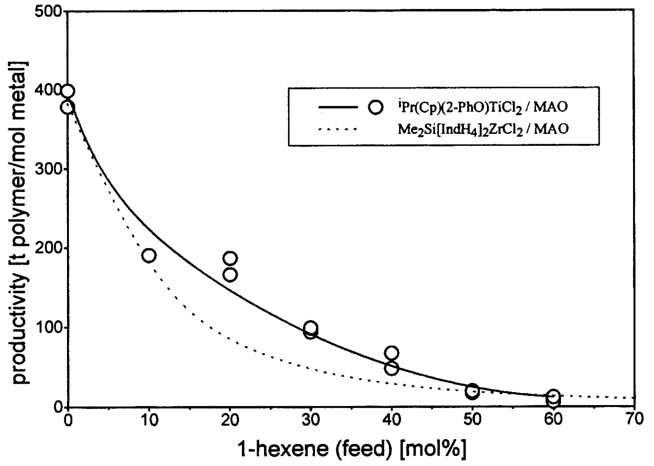


Fig. 1. Influence of 1-hexene in the feed on productivity, [Al]/[Zr] = 20 000.

whereas Ti^{IV} species are highly active towards ethene [11]. Therefore, the reduction of Ti^{IV} to inactive Ti^{III} by aluminum-alkyls is seen to be the predominant deactivation step in polymerizations with Cp_2TiCl_2/R_3Al systems [12]. In contrast to the titanocene-based system **1**/**5**, the zirconocene-based system $Me_2Si[Ind]_2ZrCl_2$/**5** could be employed successfully in high-pressure and high-temperature polymerization, probably due to the greater resistance of zirconium to reduction by aluminum-alkyls [10,13].

The preactivation of **1** with MAO (**4**) leads to a slight color change from the former yellow solution of **1** in toluene to a brighter yellow. The productivity of the **1**/**4** system is nearly the same to the one-found previously with the well-known catalyst system $Me_2Si[IndH_4]_2ZrCl_2$/**4** in high-pressure polymerization of ethene [14].

Ansa half-sandwich catalysts are often used in copolymerizations of ethene with higher α-olefins because they are known to incorporate comonomers more easily than *ansa* sandwich complexes [1,2]. In order to investigate the copolymerization behavior of the catalyst system **1**/**4** ethene/1-hexene copolymerizations were carried out with an increasing 1-hexene concentration in the feed from 0 to 60 mol%. The polymerization results of the catalyst system **1**/**4** were compared with copolymerization results obtained with the $Me_2Si[IndH_4]_2ZrCl_2$/**4** system [14]. Fig. 1 shows the productivities of the **1**/**4** and the $Me_2Si[IndH_4]_2ZrCl_2$/**4** system with respect to the 1-hexene ratio in the feed. In homopolymerizations of ethene, both catalysts show a productivity of ca. 400 t polymer mol^{-1} metal. With increasing comonomer fraction, the productivity decreases in both cases, but with the catalyst system containing the half sandwich complex **1**, the decrease is less steep. With more than 50 mol% 1-hexene in the feed, both catalysts show poor productivities below 20 t polymer mol^{-1} metal.

The number average molecular weight of the copolymers produced with **1**/**4** decreases from 43000 g mol^{-1} in ethene homopolymerization to 23000 g mol^{-1} in a copolymerization with 60 mol% 1-hexene in the feed. Independently from the decreasing average molecular weight, the polydispersity of the copolymers remains constant at 2, indicating that even in a high-pressure and high-temperature process only one active site is formed by **1**/**4**. The copolymerization parameters were evaluated in order to show the influence of the more open geometry of catalyst precursor **1** on the incorporation of comonomer. According to the equation of Mayo and Lewis [15], the parameters were determined by nonlinear regression methods [16] to $r_E = 27.8$ and $r_H = 0.04$ for the ${}^{i}Pr(Cp)(2\text{-}PhO)TiCl_2/MAO$ system. A comparison with the copolymerization parameters $r_E = 63$ and $r_H = 0.02$ of the $Me_2Si[IndH_4]_2ZrCl_2$/MAO catalyst system shows that the mono-cyclopentadienyl catalyst is able to incorporate two times more comonomer than the sterically more demanding bisindenyl complex [14]. The product of $r_E * r_H \approx 1$ for **1**/**4** indicates that a statistically random copolymer is formed.

3. Experimental

3.1. General comments

All experiments with air-sensitive materials were carried out in an argon atmosphere, using standard Schlenk techniques. Solvents were dried over Na–K-alloy (THF, hexane, toluene, diethyl ether) or calcium hydride (chloroform, dichloromethane), followed by distillation and storage under argon. ${}^{1}H$ (300 MHz) and ${}^{13}C$ (75 MHz) NMR spectra were recorded on either a Bruker ARX 300 or a Bruker AC 300 spectrometer. The mass spectra were determined by using a Varian MAT 311A instrument. The elemental analyses were obtained using a Perkin–Elmer CHN 240B instrument. Titanium tetrachloride was used as received from Aldrich.

3.2. Synthesis

3.2.1. $Me_3SiC_5H_4\text{-}C(CH_3)_2\text{-}2\text{-}C_6H_4OCH_3$ (2)

11.95 g (63.90 mmol) of 2-bromoanisole and 30 ml of diethyl ether were charged into a Schlenk flask and then 40 ml of ${}^{n}BuLi$ (64.0 mmol, 1.6 M in hexane) were added dropwise at 0°C while stirring. The resulting mixture was allowed to warm up to room temperature and stirred for another 1 h. Next, a solution of 6.78 g (63.90 mmol) of 6,6-dimetylfulvene in 10 ml diethyl ether was added to the reaction mixture. After being stirred for 2 h at room temperature, the solution was cooled down to −78°C, yielding a white precipitate of the lithio salt. The supernatant solution was decanted via a cannula and the residue suspended with an additional 50 ml of diethyl ether. The suspension was allowed to warm up to 0°C and a solution of 7.60 g (70.0 mmol) of Me_3SiCl in 10 ml diethyl ether was added. The resulting mixture was stirred overnight at room temperature. The reaction mixture was then filtered and concentrated by evaporation. The residue was suspended in hexane and filtered again to remove the rest of the LiCl. The volatiles were removed at 10^{-2} mbar and 80°C to yield 15.81 g (55.19 mmol, 86%) of a yellow oil (mixture of three isomers, 10:1:1 by ^{1}H-NMR). ^{1}H-NMR of the main isomer ($CDCl_3$, ppm): δ 0.00 (s, 9H, $SiMe_3$); 1.64 (s, 6H, CMe_2); 3.25 (s/br, 1H, Cp); 3.69 (s, 3H, OMe); 6.09 (br, 1H, Cp); 6.39 (br, 2H, Cp); 6.85–6.93 (m, 2H, Ar); 7.31–7.19 (m, 2H, Ar). ^{13}C-NMR of the main isomer ($CDCl_3$, ppm): δ −1.45 ($SiMe_3$); 28.56, 29.00 ($C(CH_3)_2$); 50.19 (*C*H of Cp); 55.27 (OMe); 112.05, 120.25, 128.10, 127.77 (*C*H of Ar); 124.69, 131.55, 132.75 (*C*H of Cp); 137.47 (C_q of Cp); 154.61, 158.54 (C_q of Ar). MS (EI): m/z 286 (M^+); 271 (M^+–CH_3); 73 ($SiMe_3$). Anal. Calc. for $C_{18}H_{26}O_1Si_1$: C, 75.46; H, 9.15. Found: C, 75.02; H, 9.14.

3.2.2. [η^5-C_5H_4-$C(CH_3)_2$-2-$C_6H_4OCH_3$]$TiCl_3$ (3)

1.30 g (6.85 mmol) of $TiCl_4$ and 30 ml CH_2Cl_2 were charged into a Schlenk flask, and then 1.95 g (6.81 mmol) of **2** in 10 ml CH_2Cl_2 were added dropwise with stirring at 0°C. The resulting mixture was allowed to warm up to room temperature and stirred overnight. The volatiles were removed under reduced pressure, leaving a black oily substance which was washed twice with 20 ml hexane to yield 2.37 g (6.47 mmol, 94%) of **3** as a deep red solid. ^{1}H-NMR ($CDCl_3$, ppm): δ 1.78 (s, 6H, CMe_2); 3.50 (s, 3H, OMe); 6.71 (t, 2H, Cp); 6.89 (d, 1H, Ar); 6.94 (t, 2H, Cp); 7.12–7.21 (m, 2H, Ar); 7.32 (d, 1H, Ar). MS (EI): m/z 366 (M^+); 331 (M^+–Cl).

3.2.3. [η^5-C_5H_4-$C(CH_3)_2$-2-C_6H_4O]$TiCl_2$ (1) via thermic elimination of MeCl from (3)

2.0 g (5.4 mmol) of **3** were charged into a sublimation apparatus and then heated to 110°C at 10^{-2} mbar. After 2 h, 250 mg (0.7 mmol, 13%) of **1** could be isolated as orange crystals from the cooling finger.

3.2.4. [η^5-C_5H_4-$C(CH_3)_2$-2-C_6H_4O]$TiCl_2$ (1) via a one-pot reaction

12.5 ml of ^{n}BuLi (20.0 mmol, 1.6 M in hexane) and 20 ml of diethyl ether were charged into a Schlenk flask. Then 1.73 g (10.0 mmol) of 2-bromophenol in 10 ml diethyl ether were added dropwise at 0°C while stirring. The resulting mixture was allowed to warm up to room temperature and stirred for another 2 h. Next, the solution was cooled down to −78°C, and a solution of 1.06 g (10.0 mmol) of 6,6-dimetylfulvene in 10 ml diethyl ether was added to the reaction mixture. The reaction mixture was allowed to warm up to room temperature and stirred overnight, yielding a white precipitate. The supernatant solution was decanted via a cannula and the residue dissolved in toluene. The resulting solution was cooled down again to −78°C and 1.90 g (10.0 mmol) $TiCl_4$ were added by rapid injection with a syringe. The reaction mixture was allowed to warm up to room temperature and stirred overnight. The resulting dark red solution was concentrated by evaporation to a volume of ca. 15 ml. Consequently, after addition of hexane, a reddish brown powder precipitated. Further crystallization from hexane–CH_2Cl_2 yielded 750 mg (2.4 mmol, 24%) of **1** as orange crystals. ^{1}H-NMR ($CDCl_3$, ppm): δ 1.55 (s, 6H, CMe_2); 6.07 (t, 2H, Cp); 6.76 (d, 1H, Ar); 6.91 (t 2H, Cp); 7.16–7.06 (m, 2H, Ar); 7.45 (d, 1H, Ar). ^{13}C-NMR ($CDCl_3$, ppm): δ 29.78 ($C(CH_3)_2$); 36.95 ($C(CH_3)_2$); 114.91, 125.29, 126.15, 127.56 (*C*H of Ar); 119.03, 121.76 (*C*H of Cp); 135.99 (C_q of Cp); 143,21, 162.38 (C_q of Ar). MS (EI): m/z 317 (M^+); 302 (M^+–CH_3); 266 (M^+–(CH_3, Cl)). Anal. Calc. for $C_{14}H_{14}Cl_2O_1Ti_1$: C, 53.04; H, 4.45. Found: C, 52.90; H, 4.44.

3.3. Activation of the catalyst precursor 1 with 4

2 mg (6.3 μmol) of the catalyst precursor **1** were dissolved in 2.0 ml of toluene and reacted with 23,5 ml of a MAO solution (30 wt% in toluene) to reach the necessary [Al]/[**1**]-ratio of 20 000 [17]. Prior to use, the solution was stirred for 30 min.

3.4. Activation of the catalyst precursor 1 with 5

14 mg (44 μmol) of the catalyst precursor **1** were dissolved in 10 ml of toluene and reacted with 2.2 ml (8.8 mmol) triisobutyl aluminum. After 15 min, the resulting solution was added to a solution of 5 mg (57 μmol) $[Me_2PhNH]^+[B(C_6F_5)_4]^-$ in toluene and stirred for further 30 min.

3.5. Polymerization procedure

The polymerization experiments were performed in a continuously operated high-pressure autoclave of 100-ml capacity. The apparatus and the polymerization technique are described with more detail in [13]. During polymerization, a pressure of 150 MPa and a residence time of 240 s were constantly maintained in the autoclave. The temperature was adjusted to 483 K by the amount of catalyst in the feed and an electric heater. The concentration of the comonomer in the feed was varied between 0 and 70 mol%. The highly concentrated catalyst solution was diluted with toluene (10 mol% in the feed) before entering the reactor.

After leaving the reactor, the pressure was released to normal. The polymer which separated from the unreacted monomers was collected for analysis. The productivity of the catalyst was determined from the amount of polymer obtained in one unit of time and the feed rate of the catalyst solution.

3.6. Polymer analysis

Gel permeation chromatograms (GPC) of the polymers were obtained at 140°C in 1,2,4-trichlorobenzene using a Waters model 150 C plus GPC and polystyrene calibration curves.

The incorporation of co-monomers was determined by infrared spectroscopy (IR) with a Bruker IFS 48 model.

4. Conclusions

The group 4 *ansa* half-sandwich complex **1** bearing a bidentate mono-Cp-alkoxid ligand was synthesized in a convenient one-pot synthesis. When activated with methylaluminoxane (**4**), complex **1** could be used as an active catalyst in high pressure polymerizations even at temperatures of 210°C. In high-pressure polymerization of ethene, the productivity of **1**/**4** was 400 t polymer mol^{-1} Ti. With increasing 1-hexene in the feed, the productivity decreases, resulting in a productivity curve shaped similarly to that found with the $Me_2Si[IndH_4]_2ZrCl_2$/**4** catalyst system. Due to the more open geometry of **1**, the **1**/**4** catalyst system has a higher tendency to incorporate 1-hexene into ethene/1-hexene copolymers than the catalyst system $Me_2Si[IndH_4]_2ZrCl_2$/**4**. In contrast to the findings with zirconocene dichlorides, the activation of the titanocene **1** with the binary cocatalyst system triisobutyl aluminum/$[Me_2PhNH]^+[B(C_6F_5)_4]^-$ (**5**) only results in poor productivity, probably due to reduction of Ti species.

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References

[1] (a) J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickias, R.K. Knight, G.W. Lai (Dow Chemical Co.) Eur. Pat. Appl. 416815, 1991. (b) J.A.M. Canich (Exxon Chemical Co.) Eur. Pat. Appl. 420436, 1991. (c) J.A.M. Canich, G.G. Hlatky, H.W. Turner (Exxon Chemical Co.) PCT Appl. 5026798, 1991.

[2] J.C. Stevens, in: J.W. Hightower, N.W. Delglass, E. Iglesia, A.T. Bell (Eds.), Studies in Surface Science and Catalysis, vol. 101, Elsevier, Amsterdam, 1996, p. 11.

[3] For reviews see: (a) J. Okuda, Comm. Inorg. Chem. 16 (1994) 185. (b) P. Jutzi, U. Siemeling, J. Organomet. Chem. 500 (1995) 175. (c) R.M. Waymouth, A.L. McKnight, Chem. Rev. 98 (1998) 2587. (d) J. Okuda, T. Eberle, Metallocenes, A. Togni, R.L. Halterman (Eds.), VCH-Wiley, Weinheim, 1999, p. 418.

[4] B. Rieger, J. Organomet. Chem. 420 (1991) C17.

[5] Y.-X. Chen, P.-F. Fu, C.L. Stern, T.J. Marks, Organometallics 16 (1997) 5958.

[6] E.E.C.G. Gielens, J.Y. Tiesnitsch, B. Hessen, J.H. Teuben, Organometallics 17 (1998) 1652.

[7] This type of complex is patented as a precursor of catalysts for the polymerization of olefins by Sumitomo Chemical Company, PCT Int. Appl. WO 97 03,002, 1997.

[8] For isomers and fluxionality of Cp compounds see: P. Jutzi, Chem. Rev. 86 (1986) 983.

[9] H. Quichen, Q. Yanlong, L. Guisheng, Transition Met. Chem. 15 (1990) 483.

[10] G. Luft, A. Dyroff, Ch. Götz, A. Rau, S. Schmitz, T. Wieczorek, R. Kliemesch, A. Gonioukh, Metallo-organic Catalysts for Synthesis and Polymerization, W. Kaminsky (Ed.), Springer-Verlag, New York, 1999, p. 651.

[11] D.S. Breslow, N.R. Newburg, J. Am. Chem. Soc. 79 (1957) 5072.

[12] H.J. Sinn, W. Kaminsky, Adv. Organomet. Chem. 18 (1980) 99.

[13] G. Luft, Ch. Götz, A. Rau, S. Schmitz, Chem. Eng. Technol. 21 (1998) 954.

[14] C. Bergemann, R. Cropp, G. Luft, J. Mol. Catal., A: Chem. 105 (1996) 87.

[15] F.R. Mayo, F.M. Lewis, J. Am. Chem. Soc. 66 (1944) 1594.

[16] M. Galimberti, F. Piemontesi, O. Fusco, I. Camurati, M. Destro, Macromolecules 31 (1998) 3409.

[17] G. Luft, High-Pressure Chemical Engineering, Ph.R. von Rohr, Ch. Trepp (Eds.), Elsevier, Amsterdam, 1996, p. 73.