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Amido functionalized *ansa* fluorenylidene half-sandwich complexes of zirconium as catalyst precursors for homogeneous ethylene polymerization

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Abstract

Amido functionalized *ansa* fluorenylidene half-sandwich complexes of zirconium have been prepared and characterized. After activation with methylalumoxane (MAO) these complexes can be used for catalytic ethylene polymerization. The variation of the substituent on the terminal nitrogen atom has a considerable influence on the catalyst activity.

Keywords: Zirconium; Half-sandwich *ansa* fluorenylidene complexes; NMR spectroscopy; Ethylene polymerization; Homogeneous polymerization

1. Introduction

The variation of the molecular structure of a catalyst can have a strong impact on the catalyst activity and the property of the produced polymer [1–10]. This empiric approach is a helpful tool to optimize catalysts. In this paper we report the preparation and characterization of various amido functionalized *ansa* fluorenylidene half-sandwich complexes of zirconium. We were interested in the influence of different substituents on the terminal nitrogen atom on the catalytic properties for ethylene polymerization of this comparatively new class of catalysts [11–21].

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2. Results and discussion

2.1. Synthesis of the ligand precursors

The ligand precursors were prepared according to the reaction scheme (Scheme 1).

All compounds were characterized by NMR spectroscopy (Table 1).

2.2. Preparation of the complexes

The amido functionalized *ansa* half-sandwich complexes were prepared according to Scheme 2.

These *ansa* half-sandwich complexes containing fluorenylidene ligands possess special symmetry features compared to the analogous indenylidene and organyl substituted cyclopentadienylidene derivatives [22–24]. They have a plane of symmetry that bisects the molecule in two mirror images. Due to the sp^2

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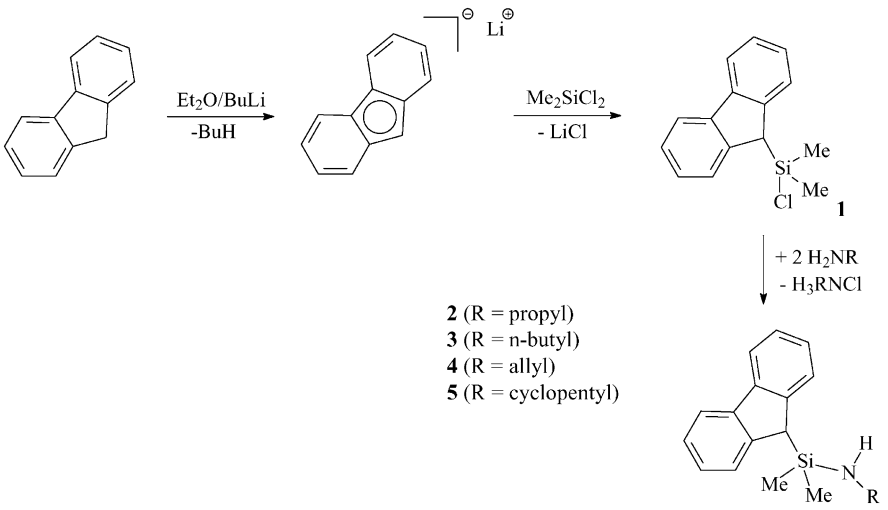
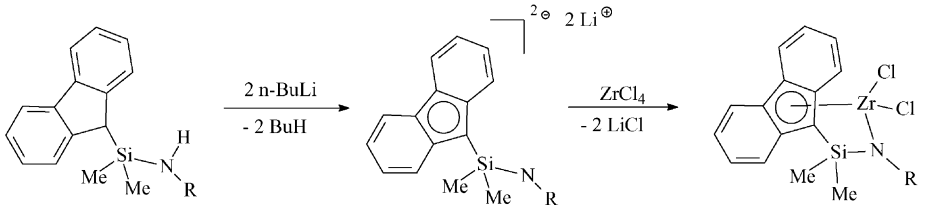


Scheme 1. Synthesis of the ligand precursors.

Table 1
NMR data of compounds **1–9**

Compound[a]	^{1}H NMR	^{13}C NMR	^{29}Si NMR
1	7.91 (d, 2H) [7.5], 7.72 (d, 2H), 7.43 (t, 2H) [7.5], 7.39 (t, 2H) [7.5], 4.14 (s, 1H), 0.23 (s, 6H)	C_q: 145.1, 143.2, 141.2; CH: 126.8, 126.5, 124.6, 120.5, 43.8; CH_3: 0.0	28.0
2	7.98 (d, 2H) [7.6], 7.68 (d, 2H) [7.6], 7.48 (m, 2H), 7.43 (m, 2H), 4.02 (s, 1H), 2.72 (m, 2H), 1.43 (m, 2H), 0.96 (t, 3H) [7.4], 0.06 (s, 6H)	C_q: 146.0, 141.0; CH: 126.7, 125.4, 124.5, 44.7; CH_2: 44.4, 28.0; CH_3: 11.8, −3.1	3.2
3	7.91 (d, 2H) [7.6], 7.63 (d, 2H) [7.6], 7.28 (m, 2H), 7.18 (m, 2H), 3.91 (s, 1H), 2.70 (m, 2H), 1.27 (m, 4H), 0.96 (t, 3H), 0.49 (br, 1H), 0.98 (s, 6H)	C_q: 145.5, 140.5; CH: 125.8, 124.9, 124.0, 119.7, 44.2; CH_2: 41.7, 36.7, 19.8; CH_3: 13.9, −3.6	3.1
4[b]	7.91 (d, 2H), [6.6], 7.71 (d, 2H) [6.6], 7.41 (m, 2H), 7.36 (m, 2H), 3.99 (s, 1H), 1.28 (s, 9H), −0.02 (s, 6H)	C_q: 146.0, 140.9, 51.8; CH: 126.0, 125.3, 124.6, 120.3, 45.2; CH_3: −0.6	−1.1
6	7.87 (d, 1H) [8.5], 7.75 (d, 1H) [8.5], 7.28 (m, 1H), 7.21 (m, 1H), 3.04 (m, 2H), 0.92 (m, 2H), 0.50 (t, 3H) 0.39 (s, 3H), 0.15 (s, 3H)	C_q: n.d. (DEPT); CH: 128.4, 128.3, 127.6, 126.0, 125.0, 121.2, 119.4, 114.3; CH_2: 65.9, 26.8; CH_3: 14.8, 2.3, 1.1	−20.7
7	8.74 (d, 1H) [8.5], 7.38 (d, 1H) [8.5], 7.29 (m, 1H), 6.92 (m, 1H), 3.60 (m, 2H), 1.53 (m, 2H), 1.38 (m, 2H), 1.01 (t, 3H), 0.51 (s, 3H), 0.43 (s, 3H)	C_q: n.d. (DEPT); CH: 129.8, 126.0, 123.8, 121.7, 121.2, 121.0, 119.7, 113.8; CH_2: 54.8, 37.2, 21.5; CH_3: 14.4, 2.7, 1.2	−20.8
8[b]	7.49 (d, 1H) [8.5], 7.32 (d, 1H) [8.5], 7.12 (m, 1H), 6.93 (m, 1H), 5.87 (m, 1H), 4.98 (m, 2H), 4.13 (m, 2H), 0.49 (s, 3H), 0.36 (s, 3H)	C_q: n.d. (DEPT); CH: 141.2, 129.0, 128.4, 128.0, 126.2, 123.8, 121.2, 120.2, 114.4; CH_2: 44.6; CH_3: 2.7, 0.8	−19.1
9	n.d.	C_q: 142.8, 135.0, 128.3, 128.0, 103.8; CH: 130.0, 125.8, 123.8, 121.7, 121.1, 120.9, 119.8, 113.5, 67.1; CH_2: 38.0, 35.9, 24.6, 23.8; CH_3: 4.6, 4.1	−23.0

[a] Compounds **1–4** in $CDCl_3$, **6–9** in C_6D_6, at 25°C.
[b] A more detailed assignment was not performed due to strong resonance overlap in the ^{1}H NMR spectrum.



6 (R = propyl)
7 (R = n-butyl)
8 (R = allyl)
9 (R = cyclopentyl)

Scheme 2. Synthesis of the amido functionalized complexes **6–9**.

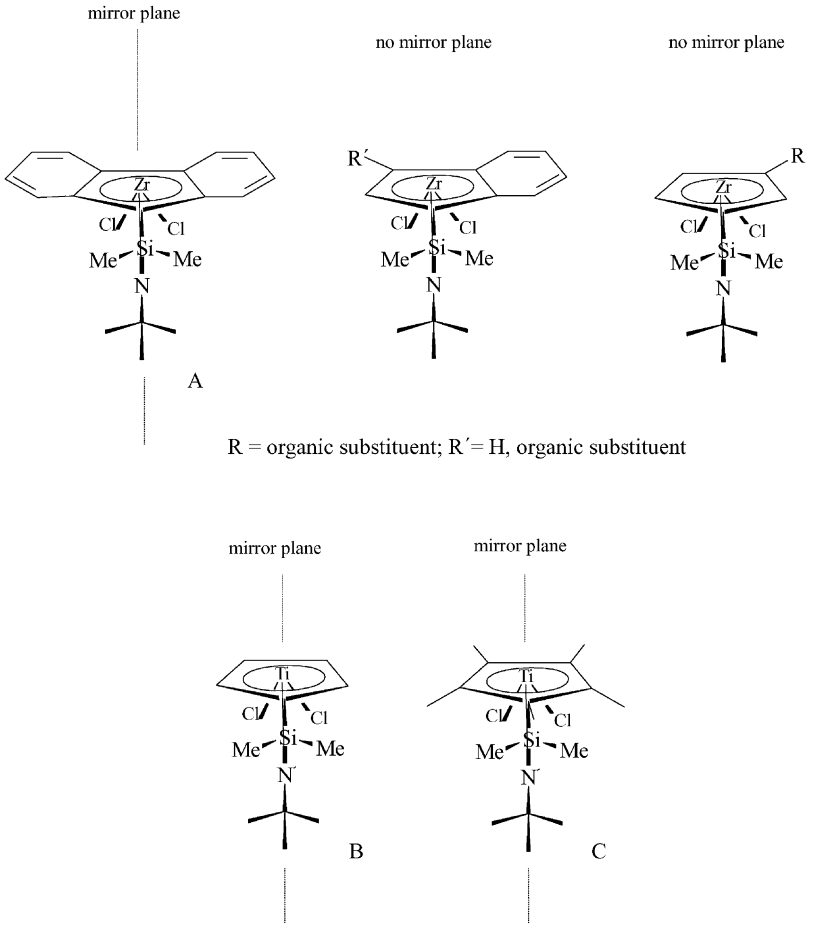


Fig. 1. Symmetric and asymmetric amido functionalized *ansa* half-sandwich complexes.

hybridization of the nitrogen atom its coordination sphere is trigonal planar, and therefore, it is part of the mirror plane. The fluorenylidene complex of this type A as well as the unsubstituted cyclopentadienylidene complex B and, the pentamethyl cyclopentadienylidene analogon C confirm this assumption [25–28] (Fig. 1). Consequently, both methyl groups on the silicon atom of compounds A, B and C should be homotopic. In the ^{1}H and ^{13}C NMR spectra, the two methyl groups on the silicon atom of these known complexes exhibit only one signal.

2.3. Characterization of **7**

Surprisingly complexes **6–9** do not show NMR signals as they can be expected for complexes of type A. Instead of one signal for the two methyl groups on the silicon atom two signals can be observed in each complex indicating diastereotopic methyl groups. In a similar manner, the fluorenylidene ligand shows different signals for every hydrogen atom and ^{13}C atom. This seems to be the consequence of asymmetry in these molecules.

In Fig. 2, the $^{13}C\{^{1}H\}$-DEPT135 NMR spectrum of compound **7** is shown. Quaternary carbon atoms are not excited with this selected pulse sequence. The positive phase exhibits CH_3 and CH groups, the negative phase CH_2 groups. Complexes **6–9** were characterized by NMR spectroscopy.

One reason for the asymmetry of compounds **6–9** could be the steric influence of the substituent on the nitrogen atom. A limited rotation of this aliphatic substituent could be responsible for the formation of an asymmetric center on the nitrogen atom. Consequently, no plane of symmetry is present in these molecules and the ^{13}C NMR signals for the methyl groups on the silicon atom appear as different resonances.

Another reason could derive from a ring slippage reaction [29–33] to give an exo coordinated η^3-bonded fluorenylidene ligand (Scheme 3).

2.4. Homogeneous ethylene polymerization

The amido functionalized fluorenylidene *ansa* half-sandwich complexes **6–9** can be activated with methylalumoxane (MAO) and used for catalytic ethylene polymerization.

They exhibit very low activities of less than 1 kg PE/mmol M h. When the nitrogen atom is functionalized with an *n*-propyl substituent or a

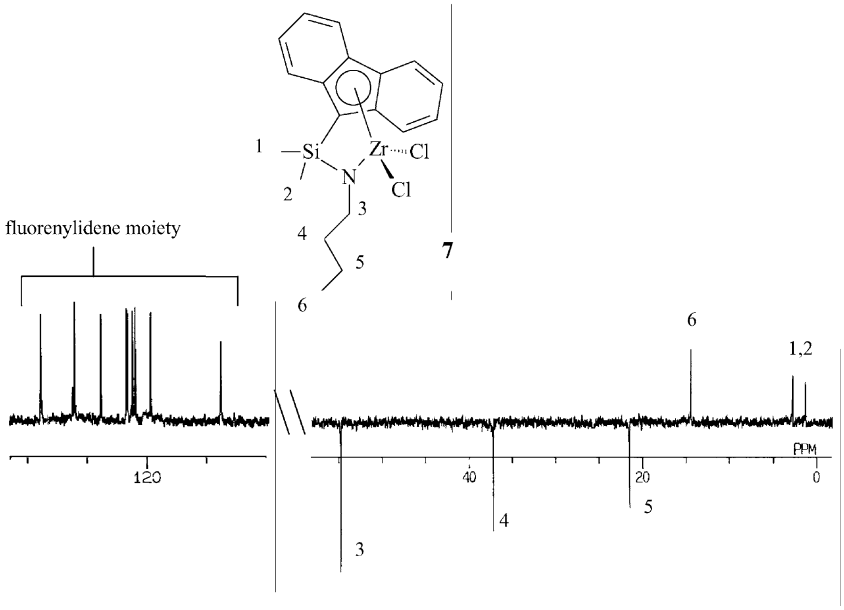


Fig. 2. The 67.80 MHz $^{13}C\{^{1}H\}$-DEPT135 NMR spectrum of compound **7** (25°C, C_6D_6). The compound has no plane of symmetry.

Scheme 3. Ring slippage reaction of *ansa* fluorenylidene amido half-sandwich complexes.

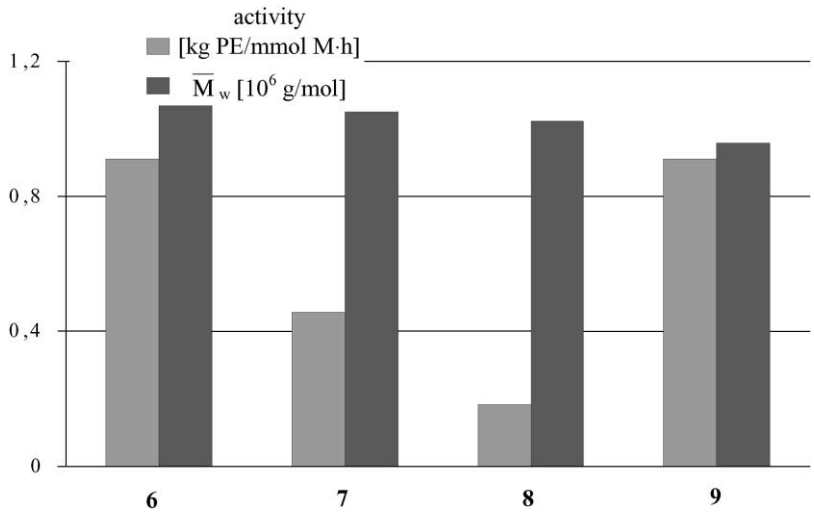


Fig. 3. Activities and average molecular weights $\overline{M}_w$ of the polyethylenes made from compounds **6–9**.

cyclopentyl substituent, the activity is only 900 g PE/mmol Zr h. The activity drops to about 50 or 75% for an *n*-butyl or an allyl substituent on the nitrogen atom.

The average molecular weight $\overline{M}_w$ of the obtained polymers is around 10^6 g/mol. The substituent on the nitrogen atom has only a small influence on the molecular weight of the polymers (Fig. 3).

There is no obvious reason for the low catalytic activity of this class of complexes. So far fluorenyl derivatives of metallocene complexes have been famous for their high activities in catalytic ethylene polymerization [34].

3. Experimental

All experimental work was routinely carried out with Schlenk technique. Dried and purified argon was used as inert gas. The solvents toluene, pentane, diethylether, tetrahydrofuran were purified by distillation over Na/K alloy. Ether was additionally distilled over lithium aluminum hydride. Methylene chloride was dried with CaH_2. Deuterated solvents such as deuterochloroform-d_1 and benzene-d_6 were dried over molecular sieves (300 pm), degassed and stored under inert gas atmosphere.

Prior to use commercial indene was distilled and stored at −30°C. Cyclopentadiene was freshly distilled from the dimer. Methylaluminoxane (MAO) was supplied by Witco Company, Bergkamen, as 30% solution in toluene. All the other starting materials were commercially available and were used without further purification.

3.1. NMR spectroscopy

The spectrometers Jeol JNM-EX 270 E and Bruker ARX 250 were available for the recording of NMR

spectra. The organometallic compounds were prepared under argon and measured at 25°C. The chemical shifts in ^{1}H NMR spectra are referred to the residual proton signal of the solvent ($\delta = 7.24$ ppm for chloroform, $\delta = 7.15$ ppm for benzene) and in ^{13}C NMR spectra to the solvent signal ($\delta = 77.0$ ppm for chloroform-d_1, $\delta = 128.0$ ppm for benzene-d_6). Tetramethylsilane ($\delta = 0.0$) was used as external standard for ^{29}Si NMR spectra.

3.2. Mass spectroscopy

The mass spectra were recorded with a VARIAN MAT CH7 instrument, GC–MS with a VARIAN 3700 gas chromatograph in combination with a VARIAN MAT 312 mass spectrometer.

3.3. Gas chromatography

Gas chromatograms were recorded using a Perkin-Elmer Auto System gas chromatograph with flame ionization detector (FID) and helium as carrier gas (1 ml/min).

Temperature program: starting phase, 3 min at 50°C; heating phase, 5°C/min (15 min); plateau phase: 310°C (15 min).

3.4. Differential scanning calorimetry (DSC)

The melting points of the polymer samples were determined using a Perkin-Elmer DSC-200 instrument. Therefore, 3–5 mg each of the dried polymer were fused into standard aluminum pans and measured using the following temperature program: first heating phase (20 K/min) from 320 to 470 K, cooling phase (20 K/min) to 320 K, second heating phase (10 K/min) from 320 to 470 K. The peak maximum of the second heating curve was indicated as melting point.

3.5. High temperature gel permeation chromatography (HT-GPC)

The polymers were measured with a Waters HT-GPC 150C apparatus. Four successive columns filled with cross-linked polystyrene were used for separation. The pore diameter of the individual particles was 500, 1000, 10,000 and 100,000 Å. For detection a RI Waters 401 refractometer was used. Degassed 1,2,4-trichlorobenzene was the eluent (flow rate 1 ml/min). The polymer samples were dissolved in boiling 1,2,4-trichlorobenzene. The measurements were conducted at 150°C. The apparatus was calibrated with polystyrene.

3.6. Synthesis procedure for fluorenyldimethylchlorosilane (**1**)

At −78°C 60 mmol fluorenyllithium in 100 ml diethylether were added slowly to 60 mmol of dimethyldichlorosilane in 100 ml diethylether and the mixture was stirred for 12 h. Subsequently, the reaction solution was filtered over sodium sulfate and the solvent was reduced to 70 ml volume. The compound precipitated at −36°C as a brown-yellow solid.

3.7. General synthesis procedure for the ligand precursors **2–5**

An amount of 80 mmol of fluorenyldimethylchlorosilane was dissolved in 200 ml methylene chloride and 200 mmol ^{t}butylamine were added quickly. After stirring for 12 h, the solvent was removed, the residue was dissolved in 200 ml pentane and the suspension was filtered over sodium sulfate. The solvent was reduced in volume. The ligand precursors were obtained quantitatively as yellow to light red oils.

3.8. Synthesis procedure for the ansa half-sandwiche complexes **6–9**

An amount of 18 mmol of the respective ligand precursor in diethylether was charged to a flask at −78°C and was mixed with 22.5 ml (36 mmol) *n*-butyllithium. The reaction mixture was stirred for 8 h at room temperature. Subsequently, the equimolar amount of zirconium tetrachloride (4.19 g) was added and the reaction solution was stirred for additional 12 h. The precipitating lithiumchloride was filtered, the ether was evaporated in vacuo and the residue was dissolved in pentane. The precipitating lithium salt was filtered again, the solvent was reduced in volume to almost dryness and the solution was stored at −78°C for 24 h. The complex precipitated as yellow-white solid and could be dried in vacuo. Yields: 19–24%.

Table 2
Polymerization data of the catalyst precursors **6–9**

Complex	Activity (g PE/mmol M h)	GPC $\overline{M}_w$ (g/mol), $\overline{M}_n$ (g/mol), HI	DSC mp[a] (°C), $\Delta\overline{H}_m$ (J/g), α[b]
6	912	1069000	137.7
		130000	80.1
		8.22	27.6
7	456	1051000	131.0
		148500	61.6
		7.07	21.2
8	913	957700	140.5
		20700	84.0
		4.63	29.0
9	182	1023000	137.3
		68540	76.3
		14.92	26.3

[a] Maximum of the melting peak during the second heating course of the DSC.
[b] $\alpha = \Delta\overline{H}_m/\Delta\overline{H}_m^\circ$ with $\Delta\overline{H}_m^\circ = 290$ J/g [33].

3.9. Characterization of *1–9* by NMR spectroscopy

Compounds **1–9** were characterized by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy (see Table 1).

3.10. Polymerization reactions

An amount of 10–15 mg of the corresponding complex was dissolved in 50 ml toluene. A solution containing 1–3 mg complex was taken and activated with MAO (30% in toluene) (Zr:Al = 1:2500). The catalyst solution was dissolved in 250 ml pentane, charged to a 1 l Büchi laboratory autoclave and thermostated at 60°C. Then an ethylene pressure of 10 bar was applied and the mixture was stirred for 1 h at 60(±2)°C. The obtained polymer was dried in vacuo. The polymerization results and the physical data of the polymers are presented in Table 2.

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