Dinuclear Transition Metal Complexes Consisting of an α-Diimine Complex Unit and a Half Sandwich Complex Unit as Dual Site Catalysts for the Polymerization of Ethylene

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Abstract

Dinuclear complexes consisting of an α-diimine complex unit with different ortho substituents at the aryl rings and a half sandwich complex unit were prepared, activated with methylaluminoxane (MAO) and tested for the polymerization of ethylene. The dinuclear catalysts bearing zirconium centers showed higher ethylene polymerization activities than the analogous titanium catalysts. Among the dinuclear catalysts with the same metal centers, the bulkier ortho substituents at the aryl moiety gave lower polymerization activities. The GPC spectra of the polyethylenes produced with the dinuclear catalysts displayed bimodal molecular weight distributions due to different active sites.

Keywords: Dinuclear complexes; Dual site ethylene polymerization catalysts; Bimodal resins.

Introduction

Brookhart and co-workers discovered the use of α-diimine complexes of nickel(II) and palladium(II) as homogeneous catalysts for the polymerization and oligomerization of olefins in 1995.[1-10] The use of these single site catalysts for olefin polymerization reactions can cause problems in industrial processing like extrusion or injection moulding due to the narrow molecular weight distributions (MWD) of the produced polymers. The solution is to develop catalysts which are able to produce polyolefins with broader MWDs.

There are several methods for the production of polyolefin resins with bimodal or broad molecular weight distributions: melt blending, reactor in series configuration, or a single reactor with dual site catalysts. This approach is very attractive because a dissymmetric dinuclear catalyst combines the advantages of the two mononuclear components and can be considered as the smallest possible reactor (nano technology) to produce bimodal resins. Due to the costly process required by the first and second method, the method of using dual site catalysts in a single reactor is widely employed.[11-35]

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In order to synthesize a dinuclear catalyst, the pathway is either to couple two mononuclear complexes or to prepare a potential organic ligand possessing two different moieties which are able to coordinate to two different metal centers.\cite{14,29,35-37} The latter pathway is the favorite because of the ease of separation and the higher stability of the free organic ligand compared to the complex during the purification process.

Herein, some α-diamine compounds bearing different ortho substituents at their aryl rings were modified to have cyclopentadienyl groups. These modified α-diamine compounds were used to prepare dinuclear complexes with only one metal salt. The ethylene polymerization activities of these dinuclear catalysts were investigated and the produced polyethylenes were analyzed via gel permeation chromatography (GPC) to test the bimodalities of the molecular weight distributions.

Results and discussion

Synthesis of the α-diamine compounds bearing chloropropyl groups

The α-diamine compounds 1-3 were synthesized by condensation reactions according to our previous work.\cite{38} Compounds 4-6 containing α-diamine moieties bearing chloropropyl groups at the backbone were synthesized via metalating the appropriate α-diamine compounds 1, 2, or 3 with a 1:1 mixture of n-butyllithium (n-BuLi) and N,N,N′,N′-tetramethylethylene-diamine (TMEDA). The resulting lithium salts were then reacted with 1-bromo-3-chloropropane to afford the corresponding products 4, 5, or 6 (Scheme 1). These compounds 4-6 were characterized by GC-MS and NMR spectroscopy.

Synthesis of the α-diamine compounds bearing cyclopentadienyl groups

Compounds 7-9 consist of α-diamine moieties combined with a cyclopentadienyl rest via a 1,4-butylene group. These compounds were synthesized by reacting the appropriate α-diamine compound 4, 5, or 6 with sodium cyclopentadienide (NaCp) to afford the corresponding products 7, 8, or 9. The synthesis steps are shown in Scheme 2. Compounds 7-9 were characterized by GC-MS and NMR spectroscopy. The \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra of compound 9 will be discussed as an example (Figures 1 and 2).
Scheme 1: The synthesis of the α-dilimine compounds 4-6 bearing chloropropyl groups.

Scheme 2: Synthesis of the α-dilimine compounds 7-9 bearing cyclopentadienyl groups.
The $^1$H NMR spectrum of compound 9 (Figure 1) shows a multiplet signal at $\delta = 7.12$ ppm which is assigned to the protons of the CH groups belonging to the aryl rings. The signals of the aromatic CH groups of the cyclopentadienyl moiety (33, 34, 35, 36) were observed at $\delta = 6.33, 6.17, 6.00$, and 5.85 ppm while the aliphatic one (32) appeared at $\delta = 2.86$ ppm. The CH groups of the isopropyl functions afford the signal at $\delta = 2.70$ ppm. The signal observed at $\delta = 2.53$ ppm was assigned to the methylene protons bearing the propylcyclopentadienyl moiety while the signal at $\delta = 2.25$ ppm was assigned to the protons of the methylene group attached to the cyclopentadienyl ring which is lower by 1.16 ppm than the signal of the analogous methylene group binding to the chloro group in the starting compound 6. The signal appearing at $\delta = 2.03$ ppm is produced by the protons of the methyl group at the backbone of the compound while the methylene groups 29 and 30 yield the multiplet at $\delta = 1.48$ ppm. The overlapping signals at $\delta = 1.25, 1.19, 1.15$ and 1.12 ppm are attributed to the methyl groups belonging to the isopropyl functions.

The $^{13}$C NMR spectrum of compound 9 (Figure 2) shows the signal of the imine carbon atom bearing the propylcyclopentadienyl group at $\delta = 171.2$ ppm which is higher by 3.2 ppm than the other imine carbon atom at $\delta = 168$ ppm. The signals belonging to the quaternary carbon atoms of the aromatic ring systems (6) and (5) appear at $\delta = 146.2$ and 145.7 ppm while the other quaternary carbon atoms (7, 8, 9, 10) arise at $\delta = 135.2$ and 135.0 ppm. The carbon atoms belonging to the aromatic CH groups of the cyclopentadienyl moiety produce the signals at $\delta = 134.5, 133.7, 132.4$, and 130.4 ppm. The signals at $\delta = 123.7$ and 123.6 ppm are attributed to the aromatic CH groups 15 and 16 while the aromatic CH groups (11, 12, 13, 14) yield the signals at $\delta = 123.0$ and 122.8 ppm. The carbon atom of the aliphatic CH group of the cyclopentadienyl moiety affords the signal at $\delta = 44.7$ ppm while the signal at $\delta = 43.1$
ppm arises from the methylene group connected to the propylcyclopentadienyl moiety. The methylene group bearing the cyclopentadienyl ligand gives the signal at $\delta = 41.2$ ppm which is lower by 3.4 ppm than the analogous methylene group binding to the chloro group of the starting compound 6. The signal at $\delta = 29.6$ ppm is assigned to the methylene group 29 while the methylene group 30 produces the signal at $\delta = 26.2$ ppm. Two signals overlapping at $\delta = 28.4$ ppm result from the CH groups of the isopropyl functions while the methyl groups of these functions generate the signals at $\delta = 23.2$, 23.1, 22.7, and 22.1 ppm. The carbon atom of the methyl group at the backbone of the compound structure yields the resonance signal at $\delta = 17.2$ ppm.

![Diagram of compound 9]

**Figure 2:** $^{13}$C NMR spectrum of the $\alpha$-diimine compound 9.

**Synthesis of the dinuclear complexes**

The appropriate $\alpha$-diimine compound bearing a cyclopentadienyl group (7, 8, or 9) was reacted with $n$-butyllithium ($n$-BuLi). The resulting lithium salt was then mixed with two equivalents of titanium tetrachloride (TiCl$_4$) or zirconium tetrachloride (ZrCl$_4$). The corresponding dinuclear complexes 7a, 7b, 8a, 8b, 9a and 9b were prepared from these mixtures by salt elimination reactions as shown in Scheme 3.
Scheme 3: Synthesis of the dinuclear complexes 7a, 7b, 8a, 8b, 9a and 9b.

These dinuclear complexes could not be analyzed by NMR spectroscopy because of their poor solubilities in prevalent NMR solvents. The complexes were characterized by mass spectroscopy and elemental analysis. The mass spectrum of complex 9b is discussed as an example (Figure 3).
The mass spectrum of complex 9b does not show a clear peak of the molecular ion at m/z = 938. Obviously the molecule does not survive the ionization process without decomposition. Various fragments could result from the loss of the ZrCl$_3$ unit and the ZrCl$_4$ group but this is not confirmed from the corresponding isotope patterns of chlorine and zirconium. A peak at m/z = 510 with an intensity of 7% speaks for the free ligand precursor while the fragmentation of the diimine ligand between the two diimine carbon atoms generates two imine moieties at m/z = 308 with an intensity of 12% and the base peak at m/z = 202.

Results of ethylene polymerization

The dinuclear complexes 7a, 7b, 8a, 8b, 9a and 9b were suspended in toluene and activated with methylaluminoxane (MAO); the M:Al ratio was 1:1500. The activated complexes were transferred to a 1 l Büchi laboratory autoclave under inert atmosphere and tested for the polymerization of ethylene (in 250 mL of n-pentane, 10 bar ethylene, and a polymerization temperature of 65 °C). The polymerization results are illustrated in Figure 4.
Figure 4: Polymerization activities of the dinuclear complexes 7a, 7b, 8a, 8b, 9a and 9b.

In consequence of the similar half sandwich metallocene complexes attached to the dinuclear precursors 7a, 7b, 8a, 8b, 9a and 9b, the polymerization activities of the dinuclear catalysts are expected to show a dependence on the variant metal centers of the α-diimine moiety and the size of the ortho substituents at the aryl rings of the catalyst structures.

The dinuclear catalysts 7b, 8b and 9b bearing zirconium centers showed higher ethylene polymerization activities than the analogous titanium catalysts 7a, 8a and 9a. This can be assigned to the better separation between the cationic active species of the catalysts and the anionic MAO species in the zirconium catalysts than in titanium ones.

The ethylene polymerization activities of both titanium and zirconium dinuclear catalysts demonstrated an obvious dependence on the size of the ortho substituents at the arene moieties. Among the dinuclear catalysts with the same metal centers, the catalysts bearing isopropyl substituents at the aryl rings (9a, 9b) showed the lowest polymerization activities while the catalysts having methyl substituents (7a, 7b) gave the highest activities. In general, the ethylene polymerization results reveal that the bulkier the substituents, the lower the polymerization activity. These results are compatible with the chain running mechanism which suggests that the bulky substituents can hinder the monomers from reaching the active catalytic centers due to their interaction with the axial coordination sites of the metal centers resulting in lower activities.\cite{38}
For comparison, the half sandwich complexes, cyclopentadienyltitanium trichloride (A) and cyclopentadienylzirconium trichloride (B) were activated with methylaluminoxane (MAO); the M:Al ratio was 1:1500. The activated complexes were tested for the polymerization of ethylene using the same polymerization conditions applied to the dinuclear catalysts 7a, 7b, 8a, 8b, 9a and 9b. The ethylene polymerization activity of catalyst A was 6750 kg PE / mol cat. h while the activity of catalyst B was 8130 kg PE / mol cat. h. These activities are lowered when the half sandwich complexes were coupled with α-diimine moieties to afford the dinuclear catalysts 7a, 7b, 8a, 8b, 9a and 9b. The coupling increases the steric hindrance around the active zirconium or titanium sites, prevents the ethylene molecules from reaching these sites, limits the growth rate of the polymer chain and leads to a reduced activity.

Samples of the polyethylenes produced with the dinuclear catalysts 7a, 7b, 8a and 8b and the half sandwich catalysts A and B were analyzed by gel permeation chromatography (GPC). The aim of this analysis was to test the bimodality of the produced polymer. The GPC results are summarized in Table 1.

Table 1: GPC results of the polyethylenes produced with the dinuclear complexes 7a, 7b, 8a and 8b and the half sandwich catalysts A and B.

<table>
<thead>
<tr>
<th>Complex Number</th>
<th>Mw (g/mol)</th>
<th>Mn (g/mol)</th>
<th>MWD</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>148100</td>
<td>5361</td>
<td>27.62</td>
</tr>
<tr>
<td>7b</td>
<td>172914</td>
<td>4800</td>
<td>36.02</td>
</tr>
<tr>
<td>8a</td>
<td>396920</td>
<td>23657</td>
<td>16.78</td>
</tr>
<tr>
<td>8b</td>
<td>407573</td>
<td>8026</td>
<td>50.78</td>
</tr>
<tr>
<td>A</td>
<td>345628</td>
<td>102821</td>
<td>3.36</td>
</tr>
<tr>
<td>B</td>
<td>429880</td>
<td>121921</td>
<td>3.53</td>
</tr>
</tbody>
</table>

The GPC results of polyethylenes produced with the dinuclear catalysts 7a, 7b, 8a and 8b displayed the desired broad or bimodal molecular weight distributions. These results can be assigned to the different active sites of the dinuclear catalysts. The molecular weights of the polyethylenes obtained with the half sandwich catalysts A and B are 345628 and 429880 g/mol. Therefore, the higher molecular weight fraction is estimated to be produced by catalyst A or B while the metal center of the α-diimine unit affords the lower fraction. The GPC spectra of polyethylenes produced with the dinuclear catalysts 7a (see Figure 5) and 7b (see Figure 6) will be discussed as examples and will be compared with the GPC spectra of polyethylenes produced with the mononuclear catalysts A and B.
Figure 5: GPC spectra of the polyethylenes produced with the mononuclear catalyst A (top) and the dinuclear catalyst 7a (bottom).
Figure 6: GPC spectra of the polyethylenes produced with the mononuclear catalyst B (top) and the dinuclear catalyst 7b (bottom).

The GPC spectra of the polyethylenes produced with the half sandwich catalysts A and B exhibit narrow molecular weight distributions with MWD = 3.36 and 3.53 while their dinuclear catalysts 7a and 7b afford polyethylenes with bimodal molecular weight distributions of MWD = 27.62 and 36.02.

Experimental Part

All experimental work was routinely carried out using Schlenk technique. Dried and purified argon was used as inert gas. n-Pentane, n-hexane, diethyl ether, toluene
and tetrahydrofuran were purified by distillation over Na/K alloy. Diethyl ether was additionally distilled over lithium aluminum hydride. Methylene chloride was first dried with phosphorus pentoxide and then with calcium hydride. Methanol and ethanol were dried over molecular sieves. Deuterated solvents (CDCl₃, CD₂Cl₂) for NMR spectroscopy were purchased from Euriso-Top and stored over molecular sieves (3 Å). Methylaluminoxane (30% in toluene) was purchased from Crompton (Bergkamen) and Albemarle (Baton Rouge, USA/Louvain, La Neuve, Belgium). Ethylene (3.0) and argon (4.8/5.0) were supplied by Rießner Company (Lichtenfels). All starting materials were commercially available and used without further purification.

**NMR spectroscopy**

NMR spectra were recorded with Bruker ARX (250 MHz), Varian Inova (300 MHz) or Varian Inova (400 MHz) spectrometers. The samples were prepared under inert atmosphere (argon) and routinely recorded at 25 °C. The chemical shifts in the ¹H NMR spectra are referred to the residual proton signal of the solvent (δ = 7.24 ppm for CDCl₃, δ = 5.32 ppm for CD₂Cl₂) and in ¹³C NMR spectra to the solvent signal (δ = 77.0 ppm for CDCl₃, δ = 53.5 ppm for CD₂Cl₂).

**Mass spectrometry**

Mass spectra were routinely recorded at the Zentrale Analytik of the University of Bayreuth with a VARIAN MAT CH-7 instrument (direct inlet, EI, E = 70 eV) and a VARIAN MAT 8500 spectrometer.

**GC/MS**

GC/MS spectra were recorded with a FOCUS Thermo gas chromatograph in combination with a DSQ mass detector. A 30 m HP-5 fused silica column (internal diameter 0.32 mm, film (dₕ = 0.25 μm), and flow 1 ml/min) was used and helium was applied as carrier gas. The routinely performed temperature program started at 50 °C and this temperature was maintained for 2 min. After a heating phase of twelve minutes (20 °C/min, the final temperature was 290 °C), the end temperature was held for 30 min (plateau phase).

At the Zentrale Analytik of the University of Bayreuth, GC/MS spectra were routinely recorded with a HP5890 gas chromatograph in combination with a MAT 95 mass detector.

**Gel permeation chromatography (GPC)**

GPC measurements were routinely performed by the analytical department at Saudi Basic Industries Corportion (SABIC) in Riyadh, Saudi Arabia.

**Elemental analysis**

The analyses were performed with a Vario EL III CHN instrument. Therefore, an amount of 4–6 mg of the complex was weighed into a standard tin pan. The tin pan was carefully closed and introduced into the auto sampler of the instrument. The raw
values of the carbon, hydrogen and nitrogen contents were multiplied with calibration factors (calibration compound: acetamide).

*Synthesis of the α-diimine compounds 1-3*

The compounds 1-3 were synthesized according to our previous work.[38] The yields were: 1, 79%; 2, 85%; 3, 87%. These compounds were characterized by GC-MS and NMR spectroscopy (Table 2).

*Synthesis of the α-diimine compounds 4-6 bearing chloropropyl groups*

A mixture of 3.3 mL (22 mmol) of N,N,N’,N’-tetramethylethylenediamine (TMEDA) and 13.75 mL (22 mmol) of n-butyllithium (1.6 M in n-hexane) was prepared in a pressure-equalizing dropping funnel containing 40 mL n-pentane. This mixture was added drop-wise to a stirred solution of 22 mmol of the appropriate α-diimine compound (1, 2 or 3) in 100 mL of n-pentane. Immediately the color of the solution changed from yellow to orange. The reaction mixture was stirred overnight. The next step was the addition of 2 equiv. of 1-bromo-3-chloropropane (44 mmol, 4.36 mL) and refluxing the reaction mixture for 24 h. Later, the reflux was stopped and the reaction mixture was allowed to cool down to room temperature. Removal of the solvent and the excess of 1-bromo-3-chloropropane by evaporation resulted in a viscous yellow liquid which was dissolved in n-pentane and dried and filtered over sodium sulfate. The solvent was removed and the resulting yellow thick liquid was purified by column chromatography on silica gel using n-hexane as eluant. The products were obtained after evaporating the solvents as viscous yellow liquids. Yields: 4, 72%; 5, 77%; 6, 74%. All compounds were characterized by GC/MS and NMR spectroscopy (Table 2).

*Synthesis of the α-diimine compounds bearing cyclopentadienyl groups (7-9)*

An amount of 3.52 g of sodium cyclopentadienide (40 mmol) was added to 40 mmol of the appropriate α-diimine compound bearing a chloropropyl group (4, 5 or 6) in 100 mL of THF. The reaction mixture was stirred at 60 °C for 36 h. The heating was stopped allowing the mixture to cool down to room temperature and the solvent was evaporated followed by the addition of n-pentane to the residue drying and filtering the resulting solution over sodium sulfate. The solvent was removed to afford the products as golden viscous liquids which were used in the subsequent reactions without further purification. Yields: 7, 75%; 8, 73%; 9, 82%. All compounds were characterized by GC/MS and NMR spectroscopy (Table 2).

*General synthesis of the dinuclear complexes 7a, 7b, 8a, 8b, 9a and 9b*

An amount of 5 mmol of n-butyllithium (1.6 M in n-hexane) was drop-wise added to 5 mmol of the appropriate α-diimine compound bearing a cyclopentadienyl group (7, 8 or 9) which was dissolved in 100 mL diethyl ether at −78°C. After warming up to room temperature, the mixture was stirred for 6 h. Subsequently, at −78°C, an amount of 10 mmol of titanium tetrachloride or zirconium tetrachloride was added and
the mixture was stirred for 36 h at room temperature. Then, the solvent was evaporated and the residue was extracted with dichloromethane and the solution was filtered over sodium sulfate. The solution was reduced in volume and the products were precipitated by adding n-pentane. The yields were 70-85%. The compounds were characterized by MS and elemental analysis (Table 3).

Table 2: Mass, $^1$H NMR, and $^{13}$C NMR spectra of compounds 1-9.

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Mass spectra $^{[m/z] (%)}$</th>
<th>$^1$H NMR [ppm]$^a$</th>
<th>$^{13}$C NMR [ppm]$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>292 (M$^+$), 277(24), 172(1), 146(100), 105(30)</td>
<td>7.5 (d,4H), 6.92 (t,2H), 2.02 (s,12H), 1.98 (s,6H).</td>
<td>Cq: 168, 148.3, 124.6 CH: 127.9, 123.2 CH$_3$: 17.8, 15.8</td>
</tr>
<tr>
<td>2</td>
<td>348 (M$^+$), 333(1), 319(91), 200(1), 174(100), 105(30)</td>
<td>7.1 (d,4H), 7.04 (t,2H), 2.37 (m,8H), 2.05 (s,6H), 1.15 (dd,12H).</td>
<td>Cq: 168, 147.5, 130.5 CH: 126.1, 123.5 CH$_2$: 24.7 CH$_3$: 16.2, 13.6</td>
</tr>
<tr>
<td>3</td>
<td>404 (M$^+$,0.8), 361(70), 212(1), 202(100), 160(23)</td>
<td>7.20 (d,4H), 7.13 (t,2H), 2.75 (sep,4H), 2.10 (s,6H), 1.22 (d,12H), 1.18 (dd,12H).</td>
<td>Cq: 168, 146, 135 CH: 123.8, 123, 28.5 CH$_3$: 22.8, 16.8</td>
</tr>
<tr>
<td>4</td>
<td>368 (M$^+$,1), 353(36), 317(100), 222(67), 146(94), 105(50)</td>
<td>7.06 (d,4H), 6.94 (t,2H), 3.38 (t,2H), 2.52 (t,2H), 2.04 (s,6H), 2.02 (s,6H), 2.01 (s,3H), 1.64 (m,4H).</td>
<td>Cq: 170.8, 167.5, 148.4, 147.8, 124.6 CH: 128.5, 128, 123.3, 123.3 CH$_2$: 44.4, 32.7, 28.3, 24.2 CH$_3$: 18, 16.3</td>
</tr>
<tr>
<td>5</td>
<td>424 (M$^+$), 395(2), 388(26), 359(100), 306(18), 214(94), 174(64), 105(20)</td>
<td>7.1 (d,4H), 7.02 (t,2H), 3.37 (t,2H), 2.52 (t,2H), 2.36 (m,8H), 2.03 (s,3H), 1.65 (m,4H), 1.18 (t,6H), 1.13 (t,6H).</td>
<td>Cq: 170.4, 167.7, 147.4, 146.9, 130.6, 130.3 CH: 126.1, 125.9, 123.6, 123.5 CH$_2$: 44.4, 32.8, 28.6, 24.8, 24 CH$_3$: 16.7, 13.9, 13.4</td>
</tr>
<tr>
<td>6</td>
<td>480 (M$^+$,1), 444(12), 437(36), 429(9), 401(91), 359(18), 278(87), 242(75), 202(100), 160(26)</td>
<td>7.20-7.14 (m,4H), 7.11 (t,2H), 3.41 (t,2H), 2.72 (sep,4H), 2.55 (t,2H), 2.07 (s,3H), 1.68 (m,4H), 1.25 (d,6H), 1.22 (d,6H), 1.19 (d,6H), 1.14 (d,6H).</td>
<td>Cq: 170.5, 168, 146.1, 145.6, 135.2, 134.9 CH: 123.8, 123.7, 123, 122.8, 28.5 CH$_2$: 44.6, 32.9, 28.9, 23.9 CH$_3$: 23.2, 22.7, 22.2, 22.1, 17.1</td>
</tr>
<tr>
<td>7</td>
<td>398(M$^+$,28), 383(32), 293(8), 252(100), 236(6), 146(64), 105(58)</td>
<td>7.05 (d,4H), 6.92 (t,2H), 6.34 (m,1H), 6.18 (m,1H), 5.98 (m,1H), 5.83 (m,1H), 2.86 (m,1H), 2.52 (t,2H), 2.23 (q,2H), 2.03 (s,3H), 2.01 (s,6H), 2.00 (s,6H), 1.46 (m,4H).</td>
<td>Cq: 171.5, 167.5, 148.5, 148, 124.7, 124.6 CH:134.6, 133.6, 132.3, 130.4, 128, 123.2, 44.7 CH$_2$: 43.1, 41.2, 29.3, 26.4 CH$_3$: 18, 16.3</td>
</tr>
<tr>
<td>Nr.</td>
<td>Mass spectra (<a href="%25">m/z</a>)</td>
<td>(^1^H) NMR [ppm](^a)</td>
<td>(^{13}C) NMR [ppm](^b)</td>
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<tr>
<td>8</td>
<td>454 (M(^+), 12), 425(100), 349(3), 280(53), 250(4), 174(42), 105(39)</td>
<td>7.10 (d, 4H), 7.01 (t, 2H), 6.34 (m, 1H), 6.18 (m, 1H), 5.98 (m, 1H), 5.84 (m, 1H), 2.86 (m, 1H), 2.52 (t, 2H), 2.35 (q, 8H), 2.22 (q, 2H), 2.02 (s, 3H), 1.46 (m, 4H), 1.16 (t, 6H), 1.13 (t, 6H).</td>
<td>Cq: 171.2, 167.7, 147.5, 147, 130.6, 130.4, 132.3, 130.4, 126.1, 125.8, 123.5, 123.4, 44.7. CH: 43.1, 41.2, 29.4, 26.3, 24.8, 24.7. CH(_3): 16.8, 13.8, 13.4.</td>
</tr>
<tr>
<td>9</td>
<td>510 (M(^+), 15), 467(50), 405(2), 308(100), 266(5), 202(52), 186(9), 160(14)</td>
<td>7.12 (m, 6H), 6.33 (m, 1H), 6.17 (m, 1H), 6.00 (m, 1H), 5.85 (m, 1H), 2.86 (m, 1H), 2.70 (m, 4H), 2.53 (t, 2H), 2.25 (q, 2H), 2.03 (s, 3H), 1.48 (m, 4H), 1.25 (d, 6H), 1.19 (d, 6H), 1.15 (d, 6H), 1.12 (d, 6H).</td>
<td>Cq: 171.2, 168, 146.2, 145.7, 135.2, 135, 130.4, 123.7, 123.6, 123.0, 122.8, 44.7, 28.4. CH(_2): 43.1, 41.2, 29.6, 26.2. CH(_3): 23.2, 23.1, 22.7, 22.1, 17.2.</td>
</tr>
</tbody>
</table>

\(^a\) 25 °C in chloroform-\(d_1\), rel. CHCl\(_3\), \(\delta = 7.24\) ppm

\(^b\) 25 °C in chloroform-\(d_1\), rel. CHCl\(_3\), \(\delta = 77.0\) ppm

Table 3: Mass spectra and elemental analyses of complexes 7a, 7b, 8a, 8b, 9a and 9b.
Activation of the complexes

An amount of 1–5 mg of the desired complex was suspended in 5 mL of toluene. Methylaluminoxane (30% in toluene, M:Al = 1:1500) was added resulting in an immediate color change. The mixture was added to a 1 l Schlenk flask filled with 250 ml n-pentane.

Polymerization of ethylene

The mixture of the complex and methylaluminoxane in n-pentane was transferred to a 1 l Büchi laboratory autoclave under inert atmosphere and thermostated at 65 °C. An ethylene pressure of 10 bar was applied for 1 h. After releasing the pressure, the polymer was filtered over a frit, washed with diluted hydrochloric acid, water, and acetone, and finally dried in vacuo.

Conclusions

Suitable dissymmetric dinuclear complexes can be activated with methylaluminoxane and are able to polymerize ethylene to give bimodal resins. This approach provides reactors on a molecular scale to produce different polyethylene chains that are connected via the catalyst.

Acknowledgement

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References