

Dissymmetric dinuclear transition metal complexes as dual site catalysts for the polymerization of ethylene

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ABSTRACT

A series of dissymmetric dinuclear complexes were synthesized, as dual site catalysts in ethylene polymerization, by coupling the allylated α -diimine complexes of the metals Ti, Zr, V, Ni and Pd with the *ansa*-zirconocene complex $[\text{C}_5\text{H}_4\text{-SiH(Me)-C}_5\text{H}_4]\text{ZrCl}_2$ possessing a hydride silane moiety. The different stages of syntheses included the formation of bis(cyclopentadienide)methyl silane which was utilized to prepare the silyl-bridged zirconocene complexes. The dinuclear complexes were prepared by mixing the latter complexes with allylated alpha-diimine via a hydrosilylation reaction using the Karstedt catalyst, platinum (0)1,3 divinyl-1,1,3,3,-tetramethyldisiloxane to react at room temperature for 40 h. These dinuclear complexes were activated with methylaluminoxane (MAO) and tested for the polymerization of ethylene. The dinuclear catalysts showed various activities depending on the nature of the metals and produced polyethylenes with broad or bimodal molecular weight distributions. The trend in polymerization activities was: Ni>Pd>V>Zr>Ti. The ethylene polymerization activities of the dinuclear catalysts were almost double the activities of their analogous alpha-diimine precursors. **Polyolefins J (2014) 1: 107-116**

Keywords: Dissymmetric dinuclear complexes; Ti, Zr, V, Ni, Pd; Dual site ethylene polymerization catalysts; Bimodal resins

INTRODUCTION

α -Diimine complexes of nickel(II), palladium(II) and other transition metals have proven as excellent single site catalysts for the polymerization and oligomerization of olefins [1-11]. However, the use of these single site catalysts for olefin polymerization has the disadvantage of producing polymers with narrow molecular weight distributions (MWD). This is due to identical active sites of the catalyst which may cause

problems in industrial scale processing like extrusion or injection molding. An elegant solution is to develop catalysts which are able to produce polyolefins with broader, bimodal or multimodal molecular weight distributions.

There exist several methods for the production of polyolefin resins with bimodal or broad molecular weight distributions: melt blending, reactors-in-series configuration, or a single reactor with a dual site catalyst. Melt blending suffers from the disadvantage

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of high costs [12]. The method with two reactors linked in series results in an expensive production due to the costly process required. The method of using dual site catalysts in a single reactor is the favored solution and it is widely employed [13-35]. In most cases, the mixtures of two mononuclear catalysts lead to resins with average molecular weights while the dinuclear catalysts containing combined ligand frameworks seem to produce resins with bimodal or broad molecular weight distributions when the metal centers are kept separated from each other by the ligand frameworks. The hydrosilylation reaction has been used to synthesize dinuclear or multinuclear complexes via coupling of two or more moieties where at least one contains a hydride silane unit and the other possesses an alkenyl group [36-40]. The two moieties can be either two mononuclear complexes or two organic compounds which can coordinate to different metal centers. Several electron-rich complexes of late transition metals such as Co(I), Rh(I), Ni(0), Pd(0), or Pt(0) are used to activate the hydrosilylation reaction while the most used catalysts are Speier's catalyst [41-44] (chloroplatinic acid, H_2PtCl_6) and Karstedt's catalyst [45-46] ($\text{Pt}_2\{[(\text{CH}_2=\text{CH})\text{Me}_2\text{Si}]_2\text{O}\}_3$).

In this paper, dissymmetric dinuclear complexes consisting of α -diimine compounds and an *ansa*-zirconocene unit were synthesized via a hydrosilylation reaction in the presence of Karstedt's catalyst. The ethylene polymerization activities of these dinuclear catalysts were investigated and compared to the summarized activities of their mononuclear precursors. Polyethylenes produced with the dinuclear catalysts were analyzed by gel permeation chromatography (GPC) to test the bimodalities of the molecular weight distributions.

EXPERIMENTAL

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 dried in two steps with phosphorus pentoxide and calcium hydride. Methanol and ethanol were dried over molecular sieves. Deuterated solvents (CDCl_3 , CD_2Cl_2) for NMR spectroscopy were purchased from

Euriso-Top and stored over molecular sieves (3Å). 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 Riebner 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 ($\delta = 7.24$ ppm for CDCl_3 , $\delta = 5.32$ ppm for CD_2Cl_2) and in ^{13}C NMR spectra to the solvent signal ($\delta = 77.0$ ppm for CDCl_3 , $\delta = 53.5$ ppm for CD_2Cl_2).

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.

Gel permeation chromatography (GPC)

GPC measurements were routinely performed by the Analytical Department at Saudi Basic Industries Corporation (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 autosampler of the instrument. The raw values of the carbon, hydrogen, and nitrogen contents were multiplied with calibration factors (calibration compound: acetamide).

Synthesis of bis(cyclopentadienyl)methyl silane ($\text{C}_5\text{H}_5\text{-SiHMe-C}_5\text{H}_5$)

Methyldichlorosilane (8.62 g, 75 mmol) in 80 mL of diethyl ether was cooled to -78°C and to this mixture sodium cyclopentadienide (13.2 g, 150 mmol), dissolved in 100 mL tetrahydrofuran, was slowly added over a period of 3 h. The solution was left to warm to room

Table 1. NMR spectra of complexes 1, 6, and 11

No.	¹ H NMR [δ in ppm] ^(a)	¹³ C NMR [δ in ppm] ^(b)
1	6.8-6.4(m,4H), 6.1(d,4H), 5.16(s,1H), 0.1(s,3H).	Cq: 108 CH: 130, 128, 115, 114 CH ₃ : -2
6	7.40(t,2H), 7.29(d,2H), 7.27(d,2H), 5.64(m,1H), 5.01(dd,2H), 3.10(sep,2H), 2.98(sep,2H), 2.54(t,2H), 2.21(q,2H), 2.13(s,3H), 1.54(d,6H), 1.47(d,6H), 1.29(d,6H), 1.23(d,6H).	Cq: 178.6, 174, 141.3, 140.9, 139.3 CH: 134.2, 129, 124, 29.5, 29.3 CH ₂ : 117.3, 32.6, 31 CH ₃ : 24.2, 23.5, 20.8
11	7.4-7.2(m,6H), 7-6(br,8H), 3.1(m,4H), 2.35(br,t,2H), 2.1(s,3H), 1.7(m,2H), 1.5(m,12H), 1.3(m,12H), 0.9(m,4H), 0.1(s,3H).	n. a. ^(c)

(a) 25°C in methylene chloride-d₂, rel. CH₂Cl₂, δ = 5.32 ppm; (b) 25°C in methylene chloride-d₂, rel. CH₂Cl₂, δ = 53.5 ppm; (c) not applicable

temperature with continuous stirring. The suspension was filtered and the solvents of the filtered solution were removed under reduced pressure to afford the final product MeSiH(C₅H₅)₂ as viscous clear yellow oil (12.3 g, 92%), a mixture of three stereoisomers. The product was used without purification in the next reaction.

Synthesis of the silyl bridged zirconocene complex 1

An amount of 100 mmol of (C₅H₅-SiHMe-C₅H₅) was dissolved in 200 mL diethylether and mixed with 200 mmol of n-butyllithium (1.6 M in n-hexane) at -78°C. After warming up to room temperature, the mixture was stirred for 4 h. Subsequently, at -78°C, 2.33 g (100 mmol) zirconium tetrachloride was added and stirred for 12 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 product was precipitated by adding n-pentane. The yield was 86%. The complex was characterized by mass and NMR spectroscopy and elemental analysis (Tables 1 and 2).

General synthesis of the allylated-diimine complexes 2-6

The allylated α-diimine complexes were synthesized according to our previous work [47]. The yields were 55-90%. All compounds were characterized by mass spectroscopy and elemental analysis (Table 2). Complex 6 was characterized by NMR spectroscopy (Table 1).

General synthesis of the dinuclear complexes 7-11

The appropriate allylated α-diimine complexes 2, 3, 4, 5, or 6 (2 mmol) were mixed with 2 mmol of

the silylene bridged zirconocene complex 1 in 100 mL toluene. The mixture was stirred and then a few drops of a solution of Karstedt's catalyst, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (0.1 M in xylene), were added. The reaction mixture was stirred at room temperature for 40 h. The mixture was then filtered through a glass frit and the resulting solid was washed several times with toluene and dried in vacuo to afford the dinuclear precursors. The yields were 40-90%. All precursors were characterized by mass spectroscopy and elemental analysis (Table 2). Complex 11 was characterized by NMR spectroscopy (Table 1).

Activation of the complexes

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

Polymerization of ethylene

The mixture 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.

RESULTS AND DISCUSSION

Synthesis of the silyl-bridged zirconocene complex 1

The first step was the reaction of methyldichlorosilane

Table 2. Mass spectra and elemental analyses of complexes 1-11

No.	Mass spectrum [m/z (%)]	Elemental analysis [%]
1	331(M^+ , 48), 317(18), 296(78), 259(23), 227(63), 192(15), 174(14), 162(25), 109(21)	Measured: C, 38.76; H, 3.53; N, - Calculated: C, 39.51; H, 3.62; N, -
2	634(M^+), 598(13), 563(25), 544(14), 526(36), 519(8), 444(50), 401(40), 357(15), 277(28), 242(64), 202(80), 190(15), 186(100), 117(34)	Measured: C, 58.79; H, 6.89; N, 4.15 Calculated: C, 58.69; H, 6.99; N, 4.42
3	674(M^+ , 8), 643(6), 633(10), 586(3), 502(5), 444(100), 401(33), 242(46), 202(42), 186(37), 176(13)	Measured: C, 55.07; H, 5.27; N, 4.03 Calculated: C, 54.94; H, 6.54; N, 4.13
4	598(M^+ , 7), 567(13), 529(3), 512(10), 494(12), 443(20), 427(27), 352(30), 254(48), 226(72), 177(29), 156(10), 105(58)	Measured: C, 59.83; H, 6.98; N, 4.80 Calculated: C, 61.85; H, 7.37; N, 4.65
5	662(M^+ , 10), 623(18), 619(15), 582(37), 578(52), 545(22), 502(45), 444(77), 399(38), 263(28), 242(73), 216(10), 202(100), 158(35), 120(26)	Measured: C, 55.63; H, 6.52; N, 4.01 Calculated: C, 56.14; H, 6.69; N, 4.22
6	621(M^+ , 7), 587(20), 580(35), 544(32), 463(48), 444(58), 240(45), 202(100), 118(38)	Measured: C, 60.18; H, 7.11; N, 4.38 Calculated: C, 59.86; H, 7.13; N, 4.50
7	966(M^+), 931(8), 922(15), 901(7), 878(25), 792(13), 618(22), 535(14), 444(100), 290(92), 238(38), 202(47), 186(35)	Measured: C, 49.15; H, 6.15; N, 2.92 Calculated: C, 52.07; H, 5.83; N, 2.89
8	1008(M^+), 977(3), 973(5), 888(3), 848(8), 835(5), 796(3), 775(10), 717(5), 595(6), 531(9), 462(7), 444(25), 369(6), 325(7), 254(24), 202(100), 162(48)	Measured: C, 48.15; H, 5.88; N, 2.80 Calculated: C, 49.84; H, 5.58; N, 2.77
9	934(M^+), 899(3), 802(5), 778(6), 774(10), 758(15), 751(16), 707(23), 672(20), 616(18), 509(29), 444(60), 364(42), 293(44), 252(48), 202(100)	Measured: C, 53.16; H, 6.47; N, 2.95 Calculated: C, 53.87; H, 6.03; N, 2.99
10	996(M^+), 965(3), 937(2), 904(2), 837(2), 778(4), 762(7), 710(12), 512(9), 456(10), 444(53), 427(44), 388(24), 271(52), 202(54), 186(51)	Measured: C, 49.97; H, 5.97; N, 2.58 Calculated: C, 50.57; H, 5.66; N, 2.81
11	955(M^+ , 5), 921(13), 884(16), 797(15), 779(20), 624(19), 445(35), 403(37), 467(18), 326(23), 269(34), 244(64), 202(76)	Measured: C, 51.50; H, 6.29; N, 3.16 Calculated: C, 52.74; H, 5.90; N, 2.93

with two equivalents of sodium cyclopentadienide to produce bis(cyclopentadienyl)methyl silane by salt elimination reaction. The next step was treating the bis(cyclopentadienyl)methyl silane with two equivalents of *n*-butyllithium (*n*-BuLi) followed by the addition of zirconium tetrachloride ($ZrCl_4$) to yield the silyl-bridged zirconocene complex 1 (Figure 1). The silylene-bridged zirconocene complex 1 was characterized by mass spectroscopy and NMR spectroscopy and elemental analysis.

Synthesis of the allylated α -diimine complexes

The allylated α -diimine complexes 2-6 were synthesized according to our previous work [47] (Figure 2).

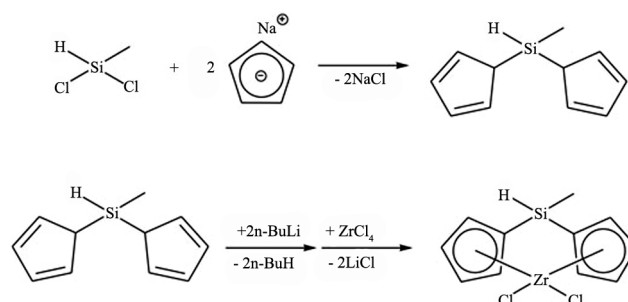
Synthesis of the dinuclear complexes

The silylene-bridged zirconocene complex 1 was coupled with the α -diimine complexes 2-6 via a hydrosilylation reaction in the presence of Karstedt's catalyst, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (0.1 M in xylene), to produce the

corresponding dinuclear precursors 7-11 (Figure 3).

The dinuclear complexes 7-11 were characterized by mass spectroscopy and elemental analysis. Due to either the paramagnetism of these complexes or the poor solubility in prevalent NMR solvents, only complex 11 was characterized by NMR spectroscopy. The 1H NMR spectrum of complex 11 is shown in Figure 4.

The 1H NMR spectrum of complex 11 shows a multiplet at $\delta = 7.40$ -7.20 ppm which is assigned to the protons of the aromatic phenyl rings while the

**Figure 1.** Synthesis of the silylene-bridged zirconocene complex 1

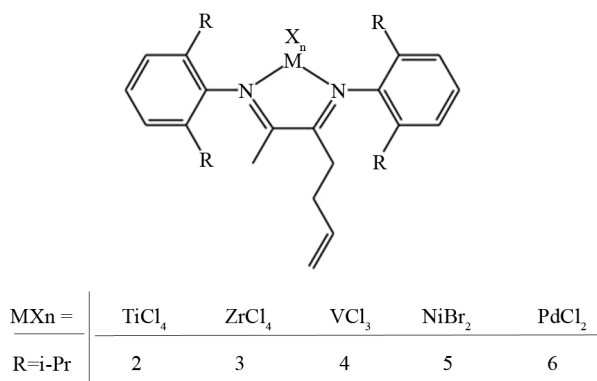


Figure 2. Synthesis of the allylated α -diimine complexes 2-6

signals at $\delta = 7.00$, 6.50, 6.20, and 6.00 ppm are attributed to the protons of the cyclopentadienyl rings. The CH groups of the isopropyl functions yield the multiplet at $\delta = 3.10$ ppm while the methylene group (2) produces the signal at $\delta = 2.35$ ppm. The singlet at $\delta = 2.10$ ppm is assigned to the methyl group bonded to the diimine moiety while the methylene group (21) affords the signal at $\delta = 1.70$ ppm. The methyl groups of the isopropyl functions produce broad signals at $\delta = 1.50$ and 1.30 ppm. The methylene groups (22, 23) generate a broad signal at $\delta = 0.90$ ppm, while the singlet at $\delta = 0.10$ ppm is attributed to the methyl group attached to the silicon atom.

The ^1H NMR spectrum of complex 11 proves the completion of the hydrosilylation reaction when it was compared with the ^1H NMR spectra of the starting complexes 6 and 1 (Figure 5). The spectrum of

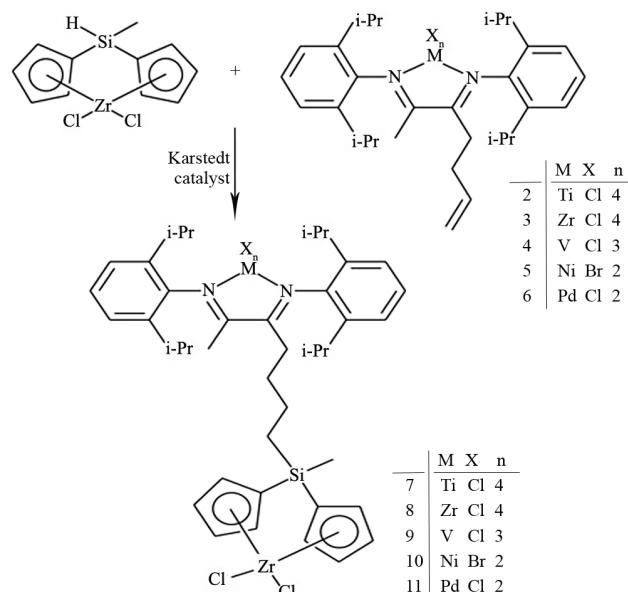


Figure 3. Synthesis of the dinuclear complexes 7-11

complex 11 shows the disappearance of three proton signals: The two signals observed in the spectrum of complex 6 at $\delta = 5.64$ and 5.01 ppm are assigned to the protons of the terminal double bond ($-\text{CH}=\text{CH}_2$) of the allyl group. The signal produced by the proton of the silane group in the spectrum of complex 1 has appeared at $\delta = 5.16$ ppm.

The disappearance of these signals can be explained by completion of the hydrosilylation reaction. The evidence of this addition is observed from the formation

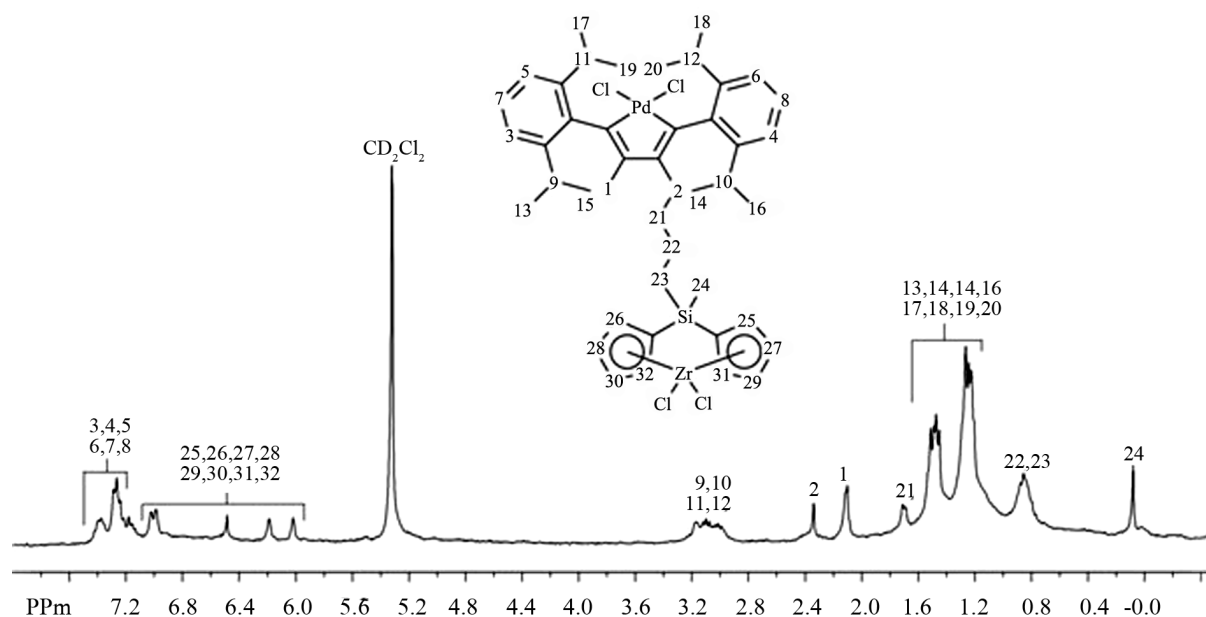


Figure 4. ^1H NMR spectrum of the dinuclear complex 11

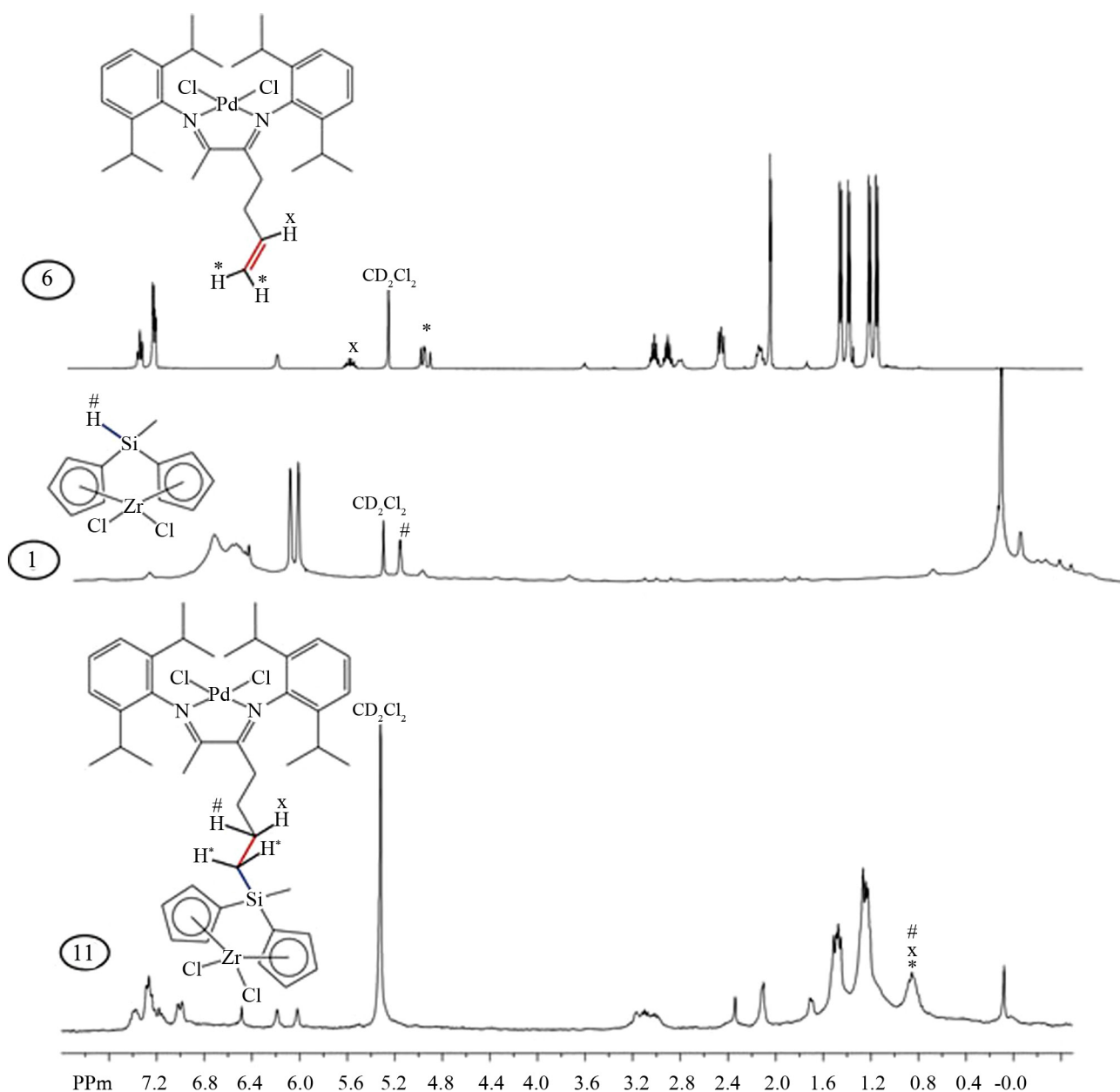


Figure 5. Comparison of the ^1H NMR spectrum of the dinuclear complex 11 with the spectra of complexes 6 and 1

of a new signal at $\delta = 0.90$ ppm which is attributed to the methylene groups of the linkage $-\text{CH}_2-\text{CH}_2-\text{Si}$ -replacing the terminal double bond of the allyl group $-\text{CH}=\text{CH}_2$. Hence, ^1H NMR spectroscopy has assisted to evince and monitor the hydrosilylation reaction.

Results of ethylene polymerization reactions

The complexes 1-11 were suspended in toluene and activated with methylaluminoxane (MAO) (M:Al = 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, polymerization

temperature of 65°C for 60 min).

The ethylene polymerization activity of the silylene-bridged zirconocene catalyst 1 was 16130 kg PE / mol.cat.h. The polymerization results of catalysts 2-11 are listed in Table 3.

The ethylene polymerization activities of the dinuclear catalysts 7-11 were almost double the activities of their analogous α -diimine precursors 2-6. The silylene-bridged zirconocene moiety is the same for all the dinuclear complexes. Therefore, the ethylene polymerization activities of these dinuclear catalysts showed dependency on the variant metal centers of the α -diimine moiety. The trend in polymerization

Table 3. Comparison of polymerization activities of dinuclear catalysts 7-11 versus the catalysts 2-6

Complex No.	Activity (kg PE / mol cat. h)	Complex No.	Activity (kg PE / mol cat. h)
2	761	7	1731
3	1119	8	3528
4	3428	9	6973
5	3980	10	8409
6	0	11	7523

activities was: Ni > Pd > V > Zr > Ti. The mononuclear complex 6 which was used to prepare the dinuclear precursor 11 showed no polymerization activity while the dinuclear catalyst 11 produced polyethylene with the second highest activity among the dinuclear series 7-11. This result can be explained hereinafter. The inactivity of catalyst 6 is assigned to the allyl function at the α -diimine ligand that can block the active site at the metal and is then deactivating the catalyst. In the hydrosilylation reaction used to prepare the dinuclear precursor 11, the allyl function of complex 6 reacted with the silane group of complex 1 and disappeared upon forming the silyl-alkyl link coupling the two dinuclear moieties. Consequently, both catalytic parts of the dinuclear catalyst 11 can polymerize ethylene.

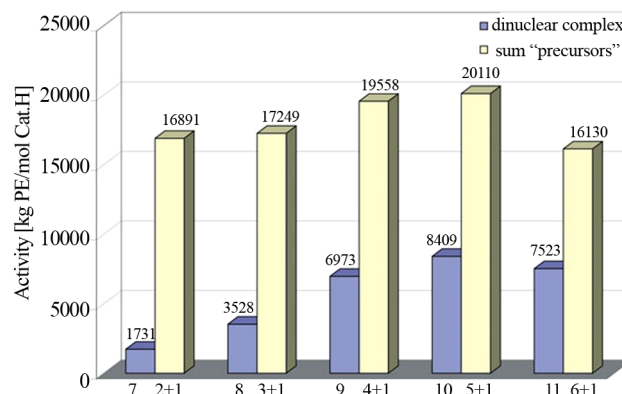
The dinuclear catalysts 7-11 showed lower polymerization activities compared to the summarized activities of their mononuclear precursors (Figure 6).

These low activities are attributed to the reduced activity of the silylene-bridged zirconocene complex when coupled with the α -diimine precursors 2-6. The coupling increases the steric hindrance around the active zirconium sites and prevents the ethylene molecules from reaching these sites leading to reduced activity. This effect is even stronger when the interactions of the cationic catalyst molecules and the anionic bulky MAO anions are considered.

Polyethylene samples produced with the single site catalyst 1, the α -diimine nickel catalyst 5, and the dinuclear catalysts 8-10 were analyzed by gel permeation chromatography (GPC). The GPC results

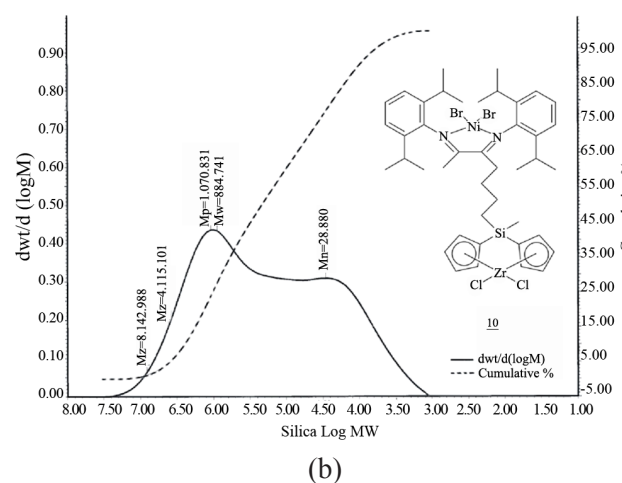
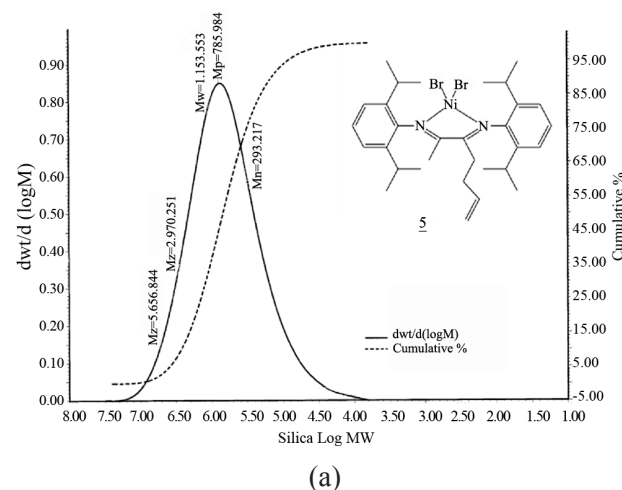
Table 4. GPC results of polyethylenes produced with the mononuclear catalysts 1 and 5 and the dinuclear catalysts 8-10

Complex number	M_w (g/mol)	M_n (g/mol)	MWD
1	200745	69556	2.89
5	1153553	293217	3.93
8	392266	8323	47.13
9	763410	10251	74.47
10	884741	28880	39.43

**Figure 6.** Comparison of ethylene polymerization activities of dinuclear complexes 7-11 and their "precursor" complexes

are summarized in Table 4.

The GPC spectra of the polyethylenes produced with the dinuclear catalysts displayed the desired broad or bimodal molecular weight distributions due to the dual site catalysts. The molecular weight of

**Figure 7.** GPC spectra of polyethylenes produced with mononuclear catalyst 5 (a) and the dinuclear catalyst 10 (b)

the polyethylene resulting from the silylene-bridged zirconocene catalyst 1 is 200745 g/mol. Consequently, the *ansa*-zirconocene unit of the dinuclear precursors is estimated to produce the lower molecular weight fraction. The GPC spectrum of polyethylene produced with the dinuclear catalyst 10 is discussed as an example and it is compared to the GPC spectrum of polyethylene produced with its mononuclear catalyst 5 (Figure 7).

The GPC spectrum of the polyethylene resulting from the nickel catalyst 5 shows a narrow molecular weight distribution (MWD = 3.93) while a broad molecular weight distribution (MWD = 39.43) is afforded by the polyethylene of the dinuclear catalyst 10. The nickel center of the dinuclear catalyst 10 yielded the higher molecular weight fraction.

CONCLUSION

Suitable dissymmetric dinuclear complexes of the metals Ti, Zr, V, Ni and Pd can be activated with methyl aluminoxane and then be applied as dual site ethylene polymerization catalysts to produce bimodal resins.

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