Olefin Polymerization and Copolymerization by Complexes Bearing [ONNO]-Type Salan Ligands: Effect of Ligand Structure and Metal Type (Titanium, Zirconium, and Vanadium)

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ABSTRACT: A series of novel titanium(IV) complexes bearing tetradentate [ONNO] salan type ligands: [Ti{2,2'-(OC₆H₃-5-t-Bu)₂-NHRNH}Cl₂] (Lig¹TiCl₂: $R = C_2H_4$; Lig²TiCl₂: $R = C_4H_8$; Lig³⁻ TiCl₂: $R = C_6H_{12}$) and $[Ti\{2,2'-(OC_6H_2-3,5-di-t-Bu)_2-NHC_6H_{12}NH\}$ Cl₂] (Lig⁴TiCl₂) were synthesized and used in the (co)polymerization of olefins. Vanadium and zirconium complexes: [M{2,2'- $(OC_6H_3-3,5-di-t-Bu)_2-NHC_6H_{12}NHC_2]$ (Lig⁴VCl₂: M = V; Lig⁴ZrCl₂: M = Zr) were also synthesized for comparative investigations. All the complexes turned out active in 1-octene polymerization after activation by MAO and/or Al(i-Bu)₃/[Ph₃C][B(C₆F₅)₄]. The catalytic performance of titanium complexes was strictly dependent on their structures and it improves for the increasing length of the aliphatic linkage between nitrogen atoms (Lig¹TiCl₂ << Lig²TiCl₂ < Lig³TiCl₂) and declines after adding additional tert-Bu group on the aromatic rings (Lig³TiCl₂ < Lig⁴TiCl₂). The activity of all titanium complexes in ethylene polymerization

INTRODUCTION The so-called postmetallocene complexes, after activation, have been used for about two decades as catalysts in ethylene and α -olefin homopolymerization and copolymerization processes.¹⁻⁷ In particular, attention was paid to the development of complexes bearing dianionic ancillary tetradentate ligands, amongst which [ONNO]-type salan ligands for Group 4 metal centers can be distinguished:⁸⁻²⁰ mainly for Zr⁸⁻²⁰ and occasionally Ti^{9,10,17,20} and $\mathrm{Hf}^{9,10}$ ones. The salan ligands are attractive because their structures can be modified easily by introduction various substituents on aromatic rings and/or by changing bridge between donor nitrogen atoms. That way of tailoring the coordination environment around the metal centre may affect the catalytic properties of the produced complexes. The diamine-bis(phenolate) complexes of this type were used in homopolymerization of ethylene¹⁴ and propylene,9,14,16,18,19 in propylene/ethylene copolymerization,19 and in polymerization of higher α -olefins^{8-12,14,15,17,20} or other monomers.^{10,12,13,21}

was moderate and the properties of polyethylene was dependent on the ligand structure, cocatalyst type, and reaction conditions. The Et₂AlCl-activated complexes gave polymers with lover molecular weights and bimodal distribution, whereas ultra-high molecular weight PE (up to 3588 kg mol⁻¹) and narrow MWD was formed for MAO as a cocatalyst. Vanadium complex yielded PE with the highest productivity (1925.3 kg mol_v⁻¹), with high molecular weight (1986 kg mol⁻¹) and with very narrow molecular weight distribution (1.5). Copolymerization tests showed that titanium complexes yielded ethylene/1-octene copolymers, whereas vanadium catalysts produced product mixtures. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 2111–2123

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The salan ligands that possess an aliphatic bridge between the two amine donors produce C_2 -symmetric octahedral complexes having the two labile groups in the *cis* position, which makes them appropriate precatalysts for polymerization of olefins.⁸ Such complexes, having appropriate substituents on the phenolate rings and having appropriate metallic centers, can produce highly isospecific PP and iPP-block-PE,19 or low-molecularweight atactic and ultrahigh-molecular-weight poly(1-hexene) of different isotacticities.¹⁷ They are also active in isospecific and living 1-hexene polymerization.8 The chiral salan complexes are based on *trans*-1,2-diaminocyclohexane¹² and the chiral bipyrrolidine²⁰ backbone. The former produce poly (α -olefin)s whose isotacticity depends on the ligand's bulk: non-bulky groups lead to atactic polymers, whereas complexes with tert-Bu and 1-adamantyl substituents lead to highly isotactic products.¹² The complexes with salan ligands arranged around chiral 2,2'-bipyrrolidine are relatively high isospecific ([mmmm] = 87%) in 1-hexene polymerization.²⁰ The salan zirconium complex with the binaphthyl-amine bis(phenolate)

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SCHEME 1 A route for the synthesis of salans.

ligand turned out to produce atactic PP and isotactic polymers of higher α -olefins.¹⁴ The salophen ligands containing the aromatic linkage between nitrogen atoms, which are closely analogous to salan ligands, formed complexes which are highly active in 1-hexene polymerization.²² The activity of some of them was considerably higher than that of salan complexes but the produced polymers were atactic.²² The *C*₁-symmetric achiral and chiral zirconium complexes with salan ligands were also derived from nonsymmetric salan ligands which bear a halo-substituted phenolate ring and an alkyl-substituted phenolate ring.^{11,15,16} These [ONNO']ZrBn₂ complexes yielded low-molecular-weight polypropylene with different tacticity, from atactic to isotactic ([*mmmm*] = 78%),¹⁶ and from atactic to highly isotactic poly(1-hexene).¹⁵

The nonchiral salan ligands and appropriate salan complexes, as introduced until today, were based on the N,N'-dimethyl-ethylenediamine or ethylenediamine backbone only.^{8–11,15,17–19,21} We therefore decided to expand that family of ligands and complexes. The new salan precursors were synthesized (Scheme 1), featuring the hexanediamine, butanediamine, and ethylenediamine backbones, and either *tert*-butyl phenolates or di-*tert*-butyl phenolates. They were then used for the synthesis of titanium, zirconium, and vanadium complexes; their catalytic properties were investigated in 1-octene and ethylene homopolymerization and in ethylene/1-octene copolymerization processes. In particular, we were interested in the research of vanadium systems as only salan complexes of Group 4 transition metal had been reported in literature until now.

EXPERIMENTAL

All air-sensitive and/or moisture-sensitive compounds were handled under an inert atmosphere, using standard Schlenk line techniques and a glove box.

Materials

Argon (grade 5.0, Linde Gas), methylaluminoxane (MAO) (10 wt %, Sigma-Aldrich), Et₂AlCl (1.0 M, Sigma-Aldrich), EtAlCl₂ (25%, Sigma-Aldrich), and (i-Bu)₃Al (1.1 M, Agros Organic), $[Ph_3C][B(C_6F_5)_4]$ (Strem Chemicals), $B(C_6F_5)_3$ (98%, Strem Chemical), NaH (60%, Sigma-Aldrich), TiCl₄, ZrCl₄, VCl₄ (Sigma-Aldrich), CDCl₃ (99.8%, Sigma-Aldrich), 1,2-dichlorobenzene-d₄ (Deutero GmbH), DMSO-d₆ (99.8%, Euriso-top), ethylenediamine (99.5%, POCH), MgSO₄ (POCH), NaBH₄ (98%, Sigma-Aldrich), butanediamine (99%, Sigma-Aldrich), 4-t-butylophenol (99%, Sigma-Aldrich), 2,4-di-t-butylophenol (99%, Sigma-Aldrich), hexanediamine (98%, Sigma-Aldrich), silica gel (0.063-0.2 mm, Fluka Chemika) were used as received. Tetrahydrofurane, hexane, and toluene were refluxed over sodium/benzophenone or sodium (toluene). 1-Octene (98%, Sigma-Aldrich) was dried under argon over 4A molecular sieves. Ethylene (Grade 3.0, Linde Gas) and nitrogen (Messer) were used after having been passed through a column with sodium metal supported on Al₂O₃. Chloroform, methylene chloride, ethanol, and methanol (POCH) were used after previous distillation.

General Methods

The infrared spectra were recorded with the Nicole Nexus 2002 Fourier transform infrared (FTIR) spectrometer.

Samples for FTIR analysis were prepared as follows: PEs, copolymers, and salans were made as powder pills with KBr, poly(1-olefin)s were placed between two KBr plates and the complexes were analyzed in nujol. Compositions of copolymers were found by the modified IR method.²³ The ¹H NMR and ¹³C NMR spectra of the ligands as well as of the homoand copolymers were recorded with the Ultrashield Bruker spectrometer (400 MHz). The copolymers were analyzed in 1,2-dichlorobenzene-d₄ at 120 °C. The peak of the residual undeuterated solvent at 7.249 was chosen as the internal reference for the ¹H NMR analysis, and the chemical shifts in the ¹³C NMR analysis were referenced internally to the major backbone methylene carbon resonance, which was taken to be 30.00 ppm. The samples of ligands (10 mg) and poly(1-octene)s were dissolved in CDCl₃ and the analysis was performed at room temperature. The melting temperatures $(T_{\rm m})$ of PEs and copolymers, their crystallinity (χ) , and glass transition temperatures (T_g) of poly(1-olefin)s were determined by differential scanning calorimetry (DSC) with a 2010 DSC calorimeter from TA Instruments at the heating rate 10 °C min⁻¹ (unless otherwise stated). Molecular weights and molecular weight distributions of (co)polymers were determined by gel permeation chromatography using an Alliance 135 GPCV 2000 apparatus equipped with two columns: HT 3 and HT 6E, at 135 °C, using 1,2,4-trichlorobenzene $(1.0 \text{ mL min}^{-1})$ as a solvent. The average molar mass values were calculated from the polystyrene calibration curve obtained with narrow PDI standards. The molecular weights of poly(1-olefin)s were determined at 100 °C.

Synthesis of 5-t-butyl-2-hydroxybenzaldehyde

5-*t*-butyl-2-hydroxybenzaldehyde was prepared in accordance with the procedure presented in ref. 24.

¹H NMR: δ 1.32 (s, 9H, Ar—C(CH₃)₃); 6.92 (d, *J* = 8.72, 1H, Ar—H); 7.50 (d, *J* = 7.50–7.51, 1H, Ar—H); 7.57 (dd, *J* = 8.72; 2.51 Hz, Ar—H); 9.87 (s, 1H, Ar—CHO); 10.87 (s, 1H, Ar—OH). ¹³C NMR: δ 30.68 (3C, C(CH₃)₃); 33.52 (1C, C(CH₃)₃); 116.65 (1C, Ar); 119.47 (1C, Ar); 129.21 (1C, Ar); 134.14 (1C, Ar); 142.20 (1C, Ar); 158.92 (1C, Ar); 196.29 (1C, CHO).

Synthesis of 3,5-di-t-butyl-2-hydroxybenzaldehyde

3,5-Di-*t*-butyl-2-hydroxybenzaldehyde was synthesized exactly in the same way as 5-*t*-butyl-2-hydroxybenzaldehyde.

¹H NMR: δ 1.33 (s, 9H, Ar—C(CH₃)₃); 1.44 (s, 9H, Ar—C(CH₃)₃); 7.35 (d, J = 2.51 Hz, 1H, Ar—H); 7.60 (d, J = 2.51 Hz, 1H, Ar—H); 9.87 (s, 1H, CHO); 11.65 (s, 1H, Ar—OH). ¹³C NMR: δ 28.72 (3C, C(CH₃)₃); 30.77 (3C, C(CH₃)₃); 33.70 (1C, C(CH₃)₃); 34.48 (1C, C(CH₃)₃); 119.43 (1C, Ar); 127.32 (1C, Ar); 131.37 (1C, Ar); 137.03 (1C, Ar); 141.08 (1C, Ar); 158.55 (1C, Ar); 196.83 (1C, CHO).

Synthesis of Ligands

The ligands were prepared according to literature procedure²⁵ by reaction of 5-*t*-butyl-2-hydroxybenzaldehyde or 3,5-*t*-butyl-2-hydroxybenzaldehyde with appropriate diamine followed by reduction of resulting salens to sal-

ans with NaBH₄. In case of $Lig^{2-4}H_2$ different procedure for isolation was applied. First, they were extracted with methylene chloride and then purified by flesh chromatography. All ligands were recrystallized from hexane.

N,N-bis(5-*t*-butyl-2-hydroxybenzyl)-1,2-diaminoethane (Lig¹H₂)

 $T_{\rm m} = 161.5-164.0$ °C, ¹H NMR: δ 1.28 (s, 18H, Ar—C(CH₃)₃); 2.86 (s, 4H, CH₂-NH); 3.99 (s, 4H, NH-CH₂-Ar); 6.77 (d, J = 8.47 Hz, 2H, Ar—H); 6.98 (d, J = 2.38, 2H, Ar—H); 7.19 (dd, J = 8.5; 2.4 Hz, 2H, Ar—H). ¹³C NMR: δ 31.04 (6C, C(CH₃)3); 33.41 (2C, C(CH₃)₃); 47.47 (2C, (CH₂—NH); 52.52 (2C, NH-CH₂-Ar); 115.26 (2C, Ar); 120.85 (2C, Ar); 124.72 (2C, Ar); 125.07 (2C, Ar); 141.34 (2C, Ar); 154.91 (2C, Ar). FTIR (cm⁻¹) 3259 (NH); 2958 (CH₃); 2901 (CH₂); 1612, 1516, 1454 (C=C Ar); 1282, 1267 (Ph—O); 1392 (OH); 1377, 1362 (C(CH₃)₃).

N,N-bis(5-t-butyl-2-hydroxybenzyl) – 1,2-diaminobutane (Lig²H₂)

*T*_m = 119.0–124.0 °C, ¹H NMR: δ 1.28 (s, 18H, Ar—C(CH₃)₃); 1.60 (m, 4H, (CH₂)₂); 2.70 (m, 4H, CH₂-NH); 3.98 9(s, 4H, NH—CH₂—Ar); 6.76 (d, *J* = 8.53, 2H, Ar—H); 6.98 (d, *J* = 2.51, 2H, Ar—H); 7.18 (dd, *J* = 8.53, 2.51 Hz, 2H, Ar—H). ¹³C NMR: δ 26.70 (2C, (CH₂)₂); 31.05 (6C, C(CH₃)₃); 33.41 (2C, C(CH₃)₃); 47.94 (2C, CH₂—NH); 52.61 (2C, NH—CH₂—Ar); 115.20 (2C, Ar); 121.15 (2C, Ar); 124.57 (2C, Ar); 124.87 (2C, Ar); 141.13 (2C, Ar); 155.17 (2C, Ar). FTIR (cm⁻¹) 3291 (NH); 2957 (CH₃); 2924 (CH₂); 1613, 1514, 1452 (C=C Ar); 1277 (Ph-O); 1390 (OH); 1386, 1362 (C(CH₃)₃; 747 ((CH₂)_n; $n \ge 4$).

N,N-bis(5-*t*-butyl-2-hydroxybenzyl)-1,2-diaminohexane (Lig³H₂)

 $T_{\rm m}$ = 84.0–85.5 °C, ¹H NMR: δ 1.28 (s, 18H, Ar—C(CH₃)₃); 1.37 (m, 4H, (CH₂)₂); 1.54 (m, 4H, —CH₂—); 2.68 (t, *J* = 7 Hz, 4H, —CH₂—NH—); 3.98 (s, 4H, NH-CH₂-Ar); 6.76 (d, *J* = 8,47 Hz, 2H, Ar—H); 6.98 (d, *J* = 2.38 Hz, 4H, Ar—H); 7.17 (dd, *J* = 8.41; 2.5 Hz, Ar—H). ¹³C NMR: δ 26.37 (2C, (CH₂)₂); 28.96 (2C, —CH₂—); 31.05 (6C, C(CH₃)); 33.40 (2C, C(CH₃)₃); 48.14 (2C, CH₂—NH); 52.63 (2C, NH—CH₂—Ar); 115.18 (2C, Ar); 121.26 (2C, Ar); 124.51 (2C, Ar); 124.81 (2C, Ar); 141.03 (2C, Ar); 155.26 (2C, Ar). FTIR (cm⁻¹) 3283 (NH); 2960 (CH₃); 2930 (CH₂); 1615, 1597, 1503 (C=C Ar); 1260 (Ph-O); 1399 (OH); 1376, 1361 (C(CH₃)₃; 728 ((CH₂)_n; n ≥ 4).

N,N-bis(3,5-di-*t*-butyl-2-hydroxybenzyl)-1,2diaminohexane (Lig⁴H₂)

 $T_{\rm m} = 110.5-112.5$ °C, ¹H NMR: δ 1.30 (s, 18H, Ar—C(CH₃)₃);1.37 (m, 4H, (CH₂)₂); 1.44 (s, 18H, Ar—C(CH₃)₃); 1.56 (m, 4H, —CH₂—); 2.70 (t, *J* = 7,03 Hz, 4H, CH₂-NH); 3.96 (s, 4H, NH—CH₂-Ar); 6.88 (d, *J* = 2.26, 2H, Ar—H), 7.24 (d, *J* = 2.26, Ar—H). ¹³C NMR: δ 26.39 (2C, (CH₂)₂); 28.96 (2C, —CH₂—); 29.10 (6C, C(CH₃)₃); 31.15 (6C, C(CH₃)₃); 33.59 (2C, C(CH₃)₃); 34.35 (2C, C(CH₃)₃); 48.12 (2C, CH₂—NH); 53.04 (2C, NH-CH₂-Ar); 121.64 (2C, Ar);



122.32 (2C, Ar); 122.53 (2C, Ar); 135.31 (2C, Ar); 139.80 (2C, Ar); 154.19 (2C, Ar). FTIR (cm⁻¹) 3312 (NH); 2957 (CH₃); 2902 (CH₂); 1605, 1460 (C=C Ar); 1254, 1238 (Ph-O); 1390 (OH); 1377, 1360 (C(CH₃)₃; 725 ((CH₂)_n; $n \ge 4$).

Synthesis of $[Ti{2,2'-(OC_6H_3-5-t-Bu)_2-NHC_2H_4NH}Cl_2]$ (Lig¹TiCl₂)

NaH (0.10 g; 2.60 mmol) was added portionwise to a solution of ${\rm Lig}^1{\rm H}_2$ (0.50 g; 1.30 mmol) in 50 mL THF, with stirring, at room temperature. When the addition operation was completed, the mixture was stirred for 1 h. After that time, the solution of titanium tetrachloride (0.14 cm³; 1.30 mmol) in 20 mL toluene was added dropwise which changed the coloration to dark-red. The reaction mixture was stirred for another 3 h at room temperature and then it was filtered to remove insoluble impurities. The solvent was expelled under reduced pressure to obtain 0.69 g of a dark-red powder.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 10.00 (s, 2H, N-H), 7.46 (d, ₄ *J* = 2.3 Hz, 2H, Ar—H), 7.25 (dd, ₃ *J* = 8.4 Hz, ₄ *J* = 2.3 Hz, 2H, Ar—H), 6.87 (d, ₃ *J* = 8.4 Hz, 2H, Ar—H), 4.12 (br, 4H, Ar—CH₂-N), 1.24 (s, 18H, C(CH₃)₃), the additional signals at the shift values 3.64 (t, *J* = 6.7 Hz, 2H) 3.40 (t, *J* = 6.3 Hz, 2H), 1.72 (m, 2H), 1.51 (m, 2H), N-CH₂-CH₂-N] suggests the possibility of the existence of the complex in two conformations in the ratio 1:1. FTIR (cm⁻¹) 1265, 1246 (Ph-O); 1601, 1523, 1456 (C=C Ar); 1376, 1365 (C(CH₃)₃).

Synthesis of $[Ti{2,2'-(OC_6H_3-5-t-Bu)_2-NHC_4H_8NH}Cl_2]$ (Lig²TiCl₂)

The complex $\rm Lig^2 TiCl_2$ was synthesized in the same way as $\rm Lig^1 TiCl_2$ by reacting 0.73 mmol (0.3 g) of $\rm Lig^2 H_2$ with 1.45 mmol NaH (0.06 g) and a solution of TiCl_4 (0.08 mL; 0.73 mmol) in toluene (15 mL). The second stage of the synthesis was conducted for 2 h. The procedure yielded 0.83 g of a dark-red solid.

¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 9.99$ (s, 2H, N—H), 7.49 (d, $_4 J = 2.1$ Hz, 2H, Ar—H), 7.22 (dd, $_3 J = 8.6$ Hz, $_4 J = 2.1$ Hz, 2H, Ar—H), 6.88 (d, $_3 J = 8.6$ Hz, 2H, Ar—H), 4.02 (br, 4H, Ar—CH₂-N), 2.89 (br, 4H, N—CH₂—CH₂—CH₂—CH₂—CH₂—N), 1.74 (br, 4H, N—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—N), 1.74 (br, 4H, N—CH₂=N) suggests the possibility of the existence of the complex in two conformations in the ratio 8:1. There are also present signals at shift values 3.59 (m) and 1.76 (m), derived from THF. The ratio 8:1 (complex:THF). FTIR (cm⁻¹) 1267 (Ph-O); 1598, 1504, 1459 (C=C Ar); 1377, 1366 (C(CH₃)₃); 721 ((CH₂)_n, $n \ge 4$).

Synthesis of $[Ti{2,2'-(OC_6H_3-5-t-Bu)_2-NHC_6H_{12}NH}Cl_2]$ (Lig³TiCl₂)

The complex $\rm Lig^3TiCl_2$ was synthesized in the same way as $\rm Lig^1TiCl_2$ by reacting 1.13 mmol (0.5 g) of $\rm Lig^3H_2$ with 2.27 mmol NaH (0.09 g) and a solution of TiCl_4 (0.12 mL; 1.13 mmol) in toluene (15 mL). The procedure yielded 0.87 g of a dark-red solid.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 9.97 (s, 2H, N-H), 7.46 (d, ₄ *J* = 2.3 Hz, 2H, Ar—H), 7.23 (dd, ₃ *J* = 8.6 Hz, ₄ *J* = 2.3 Hz, 2H, Ar—H), 6.87 (d, ₃ *J* = 8.6 Hz, 2H, Ar—H), 4.03 (br, 4H, Ar—CH₂— N), 2.85 (br, 4H, N—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—N), 1.65 (br, 4H, N—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—N), 1.30 (br, 4H, N—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—N), 1.30 (br, 4H, N—CH₂—CH₂—CH₂—CH₂—CH₂—N), 1.24 (s, 18H, C(CH₃)₃). There are also present signals at shift values 3.60 (m) and 1.76 (m), derived from THF. The ratio 8:1 (complex:THF). FTIR (cm⁻¹) 1251 (Ph-O); 1593, 1563, 1508 (C=C Ar); 1376, 1364 (C(CH₃)₃); 728 ((CH₂)_n, $n \ge 4$).

Synthesis of $[Ti{2,2'-(OC_6H_3-3,5-di-t-Bu)_2-NHC_6H_{12}NH}C_2]$ (Lig⁴TiCl₂)

The complex $\rm Lig^4TiCl_2$ was synthesized in the same way as $\rm Lig^2TiCl_2$ by reacting 0.90 mmol (0.5 g) of $\rm Lig^4H_2$ with 1.81 mmol NaH (0.07 g) and a solution of TiCl_4 (0.10 mL; 0.90 mmol) in toluene (15 mL). The procedure yielded 0.60 g of a dark-red solid.

¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 8.63$ (s, 2H, N-H), 7.24 (d, 4 *J* = 7.15 Hz, 2H, Ar—H), 7.17 (d, 4 *J* = 7.15 Hz, 2H, Ar—H), 4.17 (br, 4H, Ar—CH₂–N), 2.94 (br, 4H, N—CH₂—CH₂—CH₂—CH₂— CH₂—CH₂—CH₂—N), 1.63 (br, 4H, N—CH₂—CH₂—CH₂—CH₂— CH₂—CH₂—CH₂—N), 1.36, 1.26 (br, 40H, 2xC(CH₃)₃, N—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—N). FTIR (cm⁻¹) 1231, 1218 (Ph-O); 1597, 1457 (C=C Ar); 1364, 1376 (C(CH₃)₃); 720 ((CH₂)_n, $n \ge 4$).

Synthesis of $[V{2,2'-(0C_6H_3-3,5-di-t-Bu)_2-NHC_6H_{12}NH}Cl_2]$ (Lig⁴VCl₂)

The complex Lig^4VCl_2 was synthesized in the same way as $\text{Lig}^1\text{TiCl}_2$ by reacting 1.27 mmol (0.7 g) of Lig^4H_2 with 2.53 mmol NaH (0.10 g) and a solution of VCl₄ (0.13 mL; 1.27 mmol) in toluene (15 mL). The second stage of the synthesis was conducted for 4 hours. The procedure yielded 0.55 g of a dark-green solid. FTIR (cm⁻¹) 1236, 1231 (Ph-O); 1593, 1452 (C=C Ar); 1375, 1365 (C(CH_3)_3); 721 ((CH_2)_n, $n \ge 4$).

Synthesis of $[Zr{2,2'-(OC_6H_3-3,5-di-t-Bu)_2-NHC_6H_{12}NH}C_2]$ (Lig⁴ZrCl₂)

The complex $\text{Lig}^{4}\text{ZrCl}_{2}$ was synthesized in the similar way to that for $\text{Lig}^{1}\text{TiCl}_{2}$ but the salan deprotonation step was omitted. The reaction involved 0.80 mmol (0.44 g) of $\text{Lig}^{4}\text{H}_{2}$, 0.80 mmol (0.18 g) of ZrCl_{4} (0.08 mL; 0.73 mmol) and 50 mL of toluene. The reaction was performed for 46 h. The procedure yielded 0.32 g of a white solid.

¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 8.59$ (s, 2H, N-H), 7.29 (d, ₄*J* = 2.5 Hz, 2H, Ar—H), 7.26 (d, ₄*J* = 2.5 Hz, 2H, Ar—H), 4.10 (br, 4H, Ar—CH₂-N), 2.94 (br, 4H, N—CH₂—CH₂—CH₂— CH₂—CH₂—CH₂—N), 1.65 (br, 4H, N—CH₂—CH₂—CH₂— CH₂—CH₂—CH₂—N), 1.37(s, 18H, C(CH₃)₃), 1.34 (br, 4H, N—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—N), 1.26 (s, 18H, C(CH₃)₃). FTIR (cm⁻¹) 1225 (Ph-O); 1603, 1452 (C=C Ar); 1375, 1364 (C(CH₃)₃); 722 ((CH₂)_n, $n \ge 4$).

General Procedure for Ethylene Polymerization and Copolymerization

The ethylene polymerization reactions were performed in a Büchi glass autoclave equipped with the magnetic stirrer and



SCHEME 2 A route for the synthesis of complexes.

heating-cooling jacket. Initially, 150 mL of toluene and the required amounts of the activator was charged to the autoclave, and when the required temperature was reached, the complex was introduced to the reactor. Then, the ethylene gas was fed. The ethylene feed pressure (5 bar) and the reactor temperature were kept constant throughout the runs. After the prescribed time, that is 30 min, the ethylene gas feed was stopped and the obtained mixture was transferred to a dilute solution of hydrochloric acid in methanol. The polymer was filtered, washed a few times with methanol and dried under vacuum. The ethylene/1-octene copolymerization process followed the same procedure as ethylene homopolymerization and the only difference was that 1-olefin was charged to the reactor after the solvent had been added there.

General Procedure for 1-Octene Polymerization

The monomer (6 mL; 37 mmol) and the organoaluminium activator were added to a 100 mL flask. After the required temperature level had been reached (30, 60, or 80 °C), the complex was added to the reaction mixture. When $[Ph_3C][B(C_6F_5)_4]$ was used as an activator, it was added as the final component. The mixture was stirred for the prescribed period of time (120 min), and the reaction was terminated by adding the HCl/MeOH solution. The obtained product was washed with methanol and dried.

RESULTS AND DISCUSSION

Synthesis of Ligands and Complexes

Single-step and multi-step methods are known and utilized for the production of salans; those methods involve phenols,^{26–29} aldehydes,^{25,30,31} or 1,3-bis(2'-hydroxy-5'-methylbenzyl)imida-

zolidine^{32,33} as parent substances. Our research was based on a two-step synthesis process to which the aldehyde compound was fed as obtained from the Reimer-Tiemann reaction (Scheme 1).^{24,34} The reaction of aldehyde and diamine (with a suitable chain length) produced salens (Scheme 1) which precipitated from the reaction mixtures as yellow sediments. Salens were reduced with sodium borohydride at another stage (Scheme 1) to yield corresponding salans. $Lig^{1}H_{2}$ and $Lig^{3}H_{2}$ were obtained as white precipitates, while $Lig^{2}H_{2}$ and Lig⁴H₂ were recovered from the reaction mixtures by adding water and extracting the resulting aqueous solutions with methylene chloride. The ligands $Lig^{2-4}H_2$ were additionally purified by flash chromatography. Four salan structures were synthesized within this work. Two of them, containing the butylene and hexylene linkages between the nitrogen atoms and one t-Bu group in each phenolate ring (Lig^2H_2) and $Lig^{3}H_{2}$) have not so far been reported in literature.

The complexes with salan ligands may be obtained directly from salans^{28,35,36} or from their salts¹⁴ under various reaction conditions, that is at various temperatures and with the use of various solvents. The salan complexes of titanium and vanadium were prepared in a two-stage process in our research. The first stage, deprotonation of salans with the use of sodium hydride, was performed in tetrahydrofuran (Lig¹⁻³H₂) or in toluene (Lig⁴H₂) at room temperature. At another stage, the *in situ* ligand salts were reacted with the toluene solution of metal tetrachloride (Scheme 2). The reactions were conducted at room temperature over 2 to 4 h, and then, after removing impurities by filtration, the solvent was removed under reduced pressure. The obtained titanium complexes were red-colored and the vanadium complex was



Entry	Complex	Activator	<i>T</i> (°C)	Yield (g)	Productivity (kg mol _{Ti} ⁻¹)	C (%)	<i>M</i> _w (g mol ⁻¹)	M _w / M _n
MP5	Lig ¹ TiCl ₂	MAO	30	0.012	0.40	0.28	-	-
MP6	Lig ¹ TiCl ₂	Et ₂ AICI	30	0.005	0.17	0.12	-	-
MP11	Lig ¹ TiCl ₂	Al(iBu) ₃ /B	30	0.240	8.00	5.71	236,000	428
MP18	Lig ¹ TiCl ₂	MAO	60	traces	-	-	-	-
MP12	Lig ² TiCl ₂	MAO	30	0.930	31.00	22.12	-	-
MP14	Lig ² TiCl ₂	Al(iBu) ₃ /B	30	0.012	0.40	0.28	-	-
MP16	Lig ² TiCl ₂	MAO	60	0.789	26.30	18.77	-	-
MP9	Lig ³ TiCl ₂	MAO	RT	0.764	25.47	18.17	-	-
MP3	Lig ³ TiCl ₂	MAO	30	0.969	32.30	23.05	-	-
MP4	Lig ³ TiCl ₂	Al(iBu) ₃ /B	30	0.022	0.73	0.52	-	-
MP1	Lig ³ TiCl ₂	MAO	60	0.546	18.20	12.99	-	-
MP13	Lig ⁴ TiCl ₂	MAO	30	0.189	6.30	4.49	-	-
MP15	Lig ⁴ TiCl ₂	Al(iBu) ₃ /B	30	0.026	0.87	0.62	-	-
MP17	Lig ⁴ TiCl ₂	MAO	60	0.238	7.93	5.66	37,207	100

TABLE 1 Data for 1-Octene Polymerization by Lig¹⁻⁴TiCl₂ Complexes

Polymerization conditions: 0.03 mmol of complex; 3 mmol of organoaluminium activator; 1-octene (6.0 mL, 37.47 mmol); 2 h; $AI(iBu)_3/B = AI(iBu)_3/[Ph_3C][B(C_6F_5)_4]$, 0.45 mmol/0.045 mmol; C-conversion; RT-room temperature.

green-colored. The zirconium complex, because of poor solubility of zirconium tetrachloride and the complex itself in toluene, was prepared with no salan deprotonation step. The reaction of zirconium tetrachloride and toluene solution of salan (Scheme 2) was conducted at room temperature over 46 h.

The FTIR analysis revealed that the bands which represented stretching vibrations of Ph—O in the spectra of complexes were shifted towards lower frequencies, when compared with their locations in the spectra of corresponding salans. Some changes were also apparent within the range which is specific for stretching vibrations of N—H. There are intensive bands in the spectra of salans: at 3259 cm^{-1} for $\text{Lig}^{1}\text{H}_{2}$, at 3291 cm^{-1} for $\text{Lig}^{2}\text{H}_{2}$, at 3283 cm^{-1} for $\text{Lig}^{3}\text{H}_{2}$ and at 3312 cm^{-1} for $\text{Lig}^{4}\text{H}_{2}$. In the spectra of complexes, that band is either absent or its height is very low and it is shifted toward lower frequencies ($\text{Lig}^{1}\text{TiCl}_{2}$, $\text{Lig}^{4}\text{ZrCl}_{2}$). Those changes speak for the formation of complex compounds.

Additionally, the bands were identified in the FTIR spectra of complexes $\text{Lig}^2\text{TiCl}_2$ and $\text{Lig}^3\text{TiCl}_2$ which represent stretching vibrations in the C—O-C group which suggests the presence of solvent (THF) molecules, either fixed by coordination or encapsulated in the crystal lattice.

Polymerization of 1-Octene

Zirconium and titanium complexes with salan ligands are usually tested as precatalysts for α -olefin polymerization in combination with MAO and Al(*i*-Bu)₃/[Ph₃C][B(C₆F₅)₄] or B(C₆F₅)₃.^{9,10,12,14,17,20} The titanium complexes synthesized by us were activated with the use of the first two compounds and they were tested in 1-octene polymerization (neat monomer) at 30 °C (Table 1). The complexes Lig²⁻⁴TiCl₂ were remarkably more active in conjunction with MAO than

with $Al(i-Bu)_3/[Ph_3C][B(C_6F_5)_4]$. A reverse relation was observed only for the complex $\mathrm{Lig}^{1}\mathrm{Ti}\mathrm{Cl}_{2}.$ The activity performance for the catalytic systems Lig¹⁻³TiCl₂/MAO with one tert-butyl group on the aromatic rings was improving up to the following pattern: Lig¹TiCl₂ << Lig²TiCl₂ < Lig³TiCl₂ (Fig. 1). Hence, a higher length of the aliphatic bridge [from $(CH_2)_2$ to $(CH_2)_4$ turned out to improve considerably the catalytic activity of the complex studied, probably due to improved accessibility of the active site for coordination of a higher 1-olefin. Any further extension of the connecting link between donor nitrogen atoms does not matter much. The relation between the catalytic activity and the type of the bridge in a complex was the same also at higher temperatures, that is at 60 °C (Fig. 1). At the same time, however, higher reaction temperatures resulted in lower reaction yields in each case which was evidence of no thermal stability of the tested catalysts. The activity of the system Lig³TiCl₂/MAO at ambient temperature (entry MP9) was lower than at 30 °C and higher than at 60 °C. The complex Lig⁴TiCl₂, which had the additional *tert*-butyl group on its



FIGURE 1 Effect of ligand structure and reaction temperature on the yield of 1-octene polymerization catalyzed by Lig¹⁻⁴TiCl₂/MAO.

Entry	Complex	Activator	<i>T</i> (°C)	Yield (g)	Productivity (kg mol _M ⁻¹)	C (%)	<i>M</i> _n (g mol ⁻¹)	M _w ∕ M _n
MP35	Lig ⁴ VCl ₂	Et ₂ AICI	RT	0.039	1.30	0.93	-	-
MP34	Lig ⁴ VCl ₂	MAO	RT	0.105	3.50	2.50	234,000	125
MP39	Lig^4VCI_2	MAO	30	0.092	3.07	2.19	-	-
MP56	Lig ⁴ ZrCl ₂	Al(iBu) ₃ /B	30	0	-	-	-	-
MP33	Lig ⁴ ZrCl ₂	Al(iBu) ₃ /B	80	0.127	4.23	3.02	316	1.3
MP32	Lig ⁴ ZrCl ₂	MAO	80	0	-	-	-	_

TABLE 2 Data for 1-Octene Polymerization by Lig⁴MCl₂ (M = Zr, V) Complexes

Polymerization conditions: 0.03 mmol of complex; 3 mmol of organoaluminium activator; 1-octene (6.0 mL, 37.47 mmol); 2 h; $Al(iBu)_3/B = Al(iBu)_3/[Ph_3C][B(C_6F_5)_4]$, 0.45 mmol/0.045 mmol; C-conversion; RT-room temperature.

aromatic rings, turned out less active than its equivalent with only one *tert*-butyl group ($\text{Lig}^{3}\text{TiCl}_{2}$) (Table 1, Entries MP3 and MP13). Yet, it was thermally more stable than complexes with one *tert*-Bu substituent (Fig. 1).

No attempt has been made so far to investigate the catalytic performance of salan-type titanium complexes together with simple organoaluminium compounds. Thus, the complex $\text{Lig}^{1}\text{TiCl}_{2}$ was also used in 1-octene polymerization, after its activation with Et₂AlCl. This catalytic system showed however a very low activity (entry MP6).

The vanadium complex Lig⁴VCl₂, just like Lig¹TiCl₂, turned out poor catalyst in conjunction with Et₂AlCl (Table 2, entry MP35). The efficiency of MAO activated complex was not much higher, 2.5% only. That catalyst was used at ambient temperature since increased reaction temperatures up to 30 °C had a low but negative impact on the process yield (Table 2, Entries MP34 and MP39). Lig⁴ZrCl₂ was active in conjunction with Al(*i*Bu)₃/[Ph₃C][B(C₆F₅)₄], its activity was rather low and polymer was obtained only at high temperature (MP33). The monomer conversion after 2 h exceeded 3%.

The products obtained from polymerization of 1-octene, when catalyzed by the systems $\text{Lig}^{1}\text{TiCl}_2/\text{Al}(i-\text{Bu})_3/[\text{Ph}_3\text{C}]$ [B(C₆F₅)₄] and $\text{Lig}^{4}\text{VCl}_2/\text{MAO}$, had the form of sticky, gluey solids [Fig. 2(a)]. The GPC analysis revealed that those products had high molecular weights (higher than 200,000 g mol⁻¹). The MWD for those polymers was very wide as the



FIGURE 2 Poly(1-octene)s synthesized with Lig $^{4}VCI_{2}/MAO$ (a) and Lig $^{2}TiCI_{2}/MAO$ (b).

products contained two fractions of macromolecules with clearly diversified molecular weights: very high and very low, which can be observed in GPC chromatograms (Fig. 3). As regards other catalytic systems, the products were oils [Fig. 2(b)], irrespective of the catalyst composition and reaction conditions. Among them the only product with higher degree of polymerization and a higher average molecular weight, about 37,200 g mol⁻¹ (Fig. 3), was produced by the catalytic system $\text{Lig}^4\text{TiCl}_2/\text{MAO}$. The other products were low-viscosity liquids and could not be analyzed with GPC.

The poly(1-octene)s with higher molecular weight, samples MP11 and MP 34, were analyzed by $^{13}\text{C-NMR}$. The obtained spectra indicate that catalysts Lig^1TiCl_2/Al(iBu)_3/[Ph_3C] [B(C_6F_5)_4] and Lig^4VCl_2/MAO produced about 67% and 46% isotactic polymers, respectively.

Obtained products were analyzed by FTIR method to see if the cocatalyst type and complex structure had any effect on the macromolecules structure and thus on the reaction mechanism. The examples of FTIR spectra were provided in Figure 4. The spectra for the products obtained with the use of titanium complexes, irrespective of their structures, and MAO as the activator contain high-intensity bands which are specific for unsaturated terminal groups: *trans*-vinylene group (ca., 967 cm⁻¹) and vinyl group (910 cm⁻¹, 993 cm⁻¹). There is also a



FIGURE 3 GPC traces of the products of 1-octene polymerization obtained with: $1-\text{Lig}^4\text{VCl}_2/\text{MAO}$ (MP34); $2-\text{Lig}^1\text{TiCl}_2/\text{AI}(iBu)_3/[Ph_3C][B(C_6F_5)_4]$ (MP11); $3-\text{Lig}^4\text{TiCl}_2/\text{MAO}$ (MP17).



FIGURE 4 FTIR spectra (section $500-2250 \text{ cm}^{-1}$) of products produced by: $1-\text{Lig}^{4}\text{TiCl}_{2}/\text{MAO}$ (MP13); $2-\text{Lig}^{4}\text{VCl}_{2}/\text{MAO}$ (MP39).

band at about 890 cm⁻¹ which represents the vinylidene group but that peak is very low. Vinylidene groups are formed as a result of the β -elimination reaction of the hydrogen atom after 1,2-insertion of 1-octene (Scheme 3, eq 1) or as a result of the β -H transfer reaction to the monomer (Scheme 3, eq 2). The *trans*-vinylene and vinyl groups as present within polymer chains may be formed by the β -elimination reaction after 2,1-insertion of 1-octene (eq 3) and β -alkyl elimination reaction, respectively (eq 4). As regards the spectra for the products obtained with the use of the catalytic systems Lig⁴VCl₂/ MAO and Lig⁴ZrCl₂/Al (*i*-Bu)₃/[Ph₃C][B(C₆F₅)₄], only highintensity peaks for vinylidene and *trans*-vinyl groups at 967 and 890 cm⁻³ were present.

Products which had been synthesized with the use of $\rm Lig^4VCl_2$ and $\rm Lig^{1-4}TiCl_2$, activated by MAO, were also investigated by the 1H NMR method. The 1H NMR spectra showed

the same differences in the types of terminal groups of poly(1-octene)s produced by the vanadium and titanium catalytic systems as observed in FTIR spectra. Additionally, in case of products given by Lig¹⁻³TiCl₂/MAO, very low signals were present at about 5.1 ppm; they are indicative of a small share of 1,1,2-trisubstituted groups. Such tri-substituted end groups can be formed in re-arrangement of the polymer chain which is then terminated by β -H transfer.³⁷ That signal was invisible in the spectrum of poly(1-octene) produced by Lig⁴TiCl₂/MAO, while the fraction of vinylidene groups was clearly higher in that polymer (the shares of vinylidene groups in terminal groups of the product obtained from $\text{Lig}^{3}\text{TiCl}_{2}$ and $\text{Lig}^{4}\text{TiCl}_{2}$ systems amounted to 1.3% and 13.4%, respectively). Hence, the chain termination reactions were controlled by the type of transition metal in the complex, and by the presence of the additional *t*-Bu substituent.

The thermal properties of some samples were also investigated by means of DSC. When the products were heated up at 5 °C min⁻¹ within -100 to 50 °C no exotherms and/or endotherms caused by crystallization and/or melting were observed. Only the glass transition temperatures were visible in thermograms, with the values close to -90 °C for oils (MP13: -89.0 °C). Some higher T_g was noted for the sticky solid product MP34 (-75.4 °C) which could resulted from the molecular weight of that polymer which was higher.

Ethylene Polymerization and Copolymerization

With Et₂AlCl as a cocatalyst, ethylene polymerization tests promoted by Lig¹⁻⁴TiCl₂ under 5 bar of ethylene, at 30 and 50 °C were performed. The typical results were summarized in Table 3. The performance of the complexes Lig¹⁻³TiCl₂ was found a bit better at 50 °C than at 30 °C, while the activity of Lig⁴TiCl₂ was independent on temperature in practice. At 50 °C, the catalytic activity of the complexes changed in the line: Lig²TiCl₂ < Lig⁴TiCl₂ < Lig¹TiCl₂ < Lig³TiCl₂ (Fig. 5). A

$$Cat - CH_2 - CH - CH_2 - CH - P \qquad \xrightarrow{\beta - H} \qquad CH_2 - CH_2 - CH_2 - CH - P + Cat - H$$

$$I_{C_6H_{13}} = C_{6H_{13}} - C_{6H_{13}} = C_{6H_{13}} - C_{6H_{13}} \qquad (1)$$

$$Cat - CH_{2} - CH - CH_{2} - CH - P + C_{8}H_{16} \xrightarrow{B - H \text{ to } C_{8}H_{16}} CH_{2} - CH_$$





SCHEME 3 Termination reaction.

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TABLE 3 Results of Ethylene Polymerization Catalyzed by Salan Complexes

Entry	Complex	Activator	<i>T</i> (°C)	Yield (g)	Productivity (kg mol _M ⁻¹)	<i>T</i> _m (°C)	χ (%)	<i>M</i> _w ·10 ^{−3} (g mol ^{−1})	M _w / M _n
MP45	Lig ¹ TiCl ₂	Et ₂ AICI	30	1.407	20.1	129.9 ^a	-	140	92.5 ^b
MP53	Lig ¹ TiCl ₂	Et ₂ AICI	50	1.527	21.8	106.4; 124.9	-	72	241.6
MP47	Lig ¹ TiCl ₂	MAO	50	1.116	15.9	135.5	66	775	3.4
MP20	Lig ² TiCl ₂	Et ₂ AICI	30	1.691	24.2	128.5 ^ª	84	563	146.5 ^b
MP22	Lig ² TiCl ₂	Et ₂ AICI	50	1.978	28.3	92.0; 105.4; 122.7	-	89	78.9
MP23	Lig ² TiCl ₂	MAO	50	0.218	3.1	134.5	28	-	-
MP8	Lig ³ TiCl ₂	Et ₂ AICI	30	1.284	18.3	126.8 ^a	83	253	147.5 ^b
MP19	Lig ³ TiCl ₂	Et ₂ AICI	50	1.332	19.0	96.8; 106.7; 121.9	-	56	-
MP7	Lig ³ TiCl ₂	MAO	50	0.074	1.1	133.9	10	-	-
MP24	Lig ⁴ TiCl ₂	Et ₂ AICI	30	1.894	27.1	129.0 ^a	83	2,250	996.9 ^b
MP38	Lig ⁴ TiCl ₂	Et ₂ AICI	50	1.847	26.4	93.0; 105.3; 122.6	-	1.6	-
MP42	Lig ⁴ TiCl ₂	MAO	50	1.196	17.1	135.7	61	3,588	3.4
MP43	Lig ⁴ VCl ₂ ^c	MAO	30	0.157	224.3	133.5	31	-	-
MP26	Lig ⁴ VCl ₂ ^c	EtAICI ₂	30	1.348	1,925.3	138.4	57	1,968	1.5
MP31	Lig ⁴ ZrCl ₂	MAO	65	0.451	6.4	136.9	50	987	7.7
MP37	$Lig^{4}ZrCl_{2}$	MAO	80	0.311	4.4	138.0	50	-	-

Polymerization conditions: 0.07 mmol of complex; 10.5 mmol of MAO; 7 mmol of Et_2AlCl; 4 mmol of EtAlCl₂; 5 bar of ethylene, 30 min; $\chi-$ crystallinity.

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<sup>a</sup> Broad peak with shoulder.
<sup>b</sup> Bimodal.
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^c 0.0007 mmol of complex.

similar trend was observed at 30 °C. The activity of all titanium complexes activated by MAO was tested at 50 °C. It was lower than the activity of the same complexes activated by Et_2AlCl , and the catalysts containing Lig^4TiCl_2 and Lig^1TiCl_2 were most active. The fact which is noteworthy is that these two complexes showed the lowest activity in 1-octene polymerization. The reason was a larger size of the monomer to be inserted into the polymer chain; it was more difficult for the reaction catalyzed by a more sterically hindered complex to convert a bigger molecule (1-octene) than a smaller one (ethylene).

The activator type was essential for the product properties. In general, MAO-activated complexes produced linear polyethylenes with high melting points (133.9–135.7 °C), whereas titanium complexes activated by Et₂AlCl gave prod-



FIGURE 5 Effect of ligand structure and type of activator on productivity of titanium catalysts at 50 °C.

ucts with lower melting points (128.5–129.9 °C) when polymerization was performed at 30 °C. On DSC curves of these polymers the melting endotherms with shoulders are observed. For polyethylenes produced at 50 °C more than one melting points were obtained and they were placed at lower temperatures region. The examples of PE thermograms were presented in Figure 6.

The molecular weight values for polyethylenes synthesized with $Lig^{1-4}TiCl_2/Et_2AlCl$ were relatively low and they were strongly dependent on the reaction temperature (Table 3). The increase in temperature from 30 to 50 °C resulted in a



FIGURE 6 Thermograms of polyethylene synthesized with: 1– $Lig^{2}TiCl_{2}/MAO$ (MP23) at 50 °C; 2– $Lig^{2}TiCl_{2}/EtAlCl_{2}$ (MP20A) at 30 °C; 3– $Lig^{2}TiCl_{2}/EtAlCl_{2}$ at 50 °C (MP22).



FIGURE 7 GPC traces of PEs produced by: $1-\text{Lig}^{4}\text{TiCl}_{2}/\text{EtAlCl}_{2}$ (MP38) at 50 °C; $2-\text{Lig}^{4}\text{TiCl}_{2}/\text{EtAlCl}_{2}$ at 30 °C (MP24); $3-\text{Lig}^{4}\text{TiCl}_{2}/\text{MAO}$ (MP42) at 50 °C.

few times lower values of M_w . The molecular weight distribution patterns for PE were bimodal, irrespective of the reaction temperature, with the higher and lower molecular weight fractions being clearly separated (Fig. 7). Polymer with bimodal molecular weight distribution is usually created by the presence of two type of active sites. One site produces high molecular weight fraction and the other gives low molecular weight fraction. The share of the lower molecular weight fraction was growing for higher temperatures (Fig. 7, Curves 1 and 2).

The average molecular weight values and molecular weight distributions for each fraction were calculated for selected polymers (Table 4). The average values of M_w for higher molecular weight fractions fell within 1310-3063 kg mol⁻¹, and higher M_w values within that fraction were noted for the products obtained at lower temperatures and with the use of the catalyst with the additional *t*-Bu groups ($\text{Lig}^{4}\text{TiCl}_{2}$). Similar relations could be observed for the fraction of very low molecular weight products, of the order of several thousand (1500-8000 g mol⁻¹). The molecular weight distributions were very narrow for both fractions. To verify whether liquid oligomers were produced in addition to low molecular weight PE in some polymerization processes (MP20 and MP24), the liquid post-reaction mixtures were analyzed by the GC-MS method. No oligomers were found present. Hence, activation of titanium complexes with diethylchloroaluminium produced two types of active sites, with clearly different catalytic performances.

The molecular weight value of PE was also significantly affected by the ligand structure. The increasing number of $-CH_2$ — groups in the bridge decreased the average molecular weight, while the additional *t*-Bu group on the ligand rings produced substantially higher values. That might result from steric changes around the active site. The steric hindrance arising from a shorter bridge and/or the presence of an additional *t*-Bu group restrict the polymer chain termination reactions. The use of MAO instead of Et₂AlCl also increased the M_w value of polymers considerably. The MAO-activated complexes produced polyethylenes with M_w over 3 million g mol⁻¹ and with not very narrow distributions of molecular weights, $M_w/M_n = 3.4$ (the GPC curves had significant shoulders, Fig. 7, curve 3).

Highly interesting, the FTIR spectra for polyethylenes obtained in the presence of Lig¹⁻⁴TiCl₂/Et₂AlCl showed not only the vinyl terminal groups, which are typical for ethylene polymerization and which are formed by the β -hydrogen elimination and/or transfer to the monomer, but also high absorption bands at 888 cm⁻¹ which were indicative for the vinylidene groups in polyethylene macromolecules. Those terminal groups in ethylene homopolymerization could be produced by reinsertion of vinyl terminated chains (macromers) into the growing polyethylene chain. That incorporation could yield branched PE structures. To learn more about the PE macromolecules, the ¹³C NMR spectra were taken for two polymers: MP8a and MP19a. Those spectra, however, did not confirm the presence of any branching in PE chains; there were only peaks at 14.02, 22.85, 29.56, 30.00, and 32.17 ppm which come from low molecular weights in the test PE sample. There was no signal for tertiary carbon atoms. Thus, addition of the ethylene macromer molecule was probably followed by the chain termination reaction.

The ethylene polymerization experiments were also conducted in the presence of the salan complex of vanadium, activated by MAO or EtAlCl₂, at 30 °C (Table 3, Entries MP43 and MP26). The catalytic system Lig⁴VCl₂/EtAlCl₂ turned out definitely superior in terms of activity. It also yielded a polymer product with a higher melting point. Moreover, its structure was linear (1.4 group CH₃/1000 CH₂), its molecular weight was high (19,60,000 g mol⁻¹) and its MWD was very narrow (1.54). This can indicate that the used catalyst is a single-site one. MAO-activated Lig⁴ZrCl₂ was also used in

TABLE 4 Molecular Weight and Molecular Weight Distribution of Selected Bimodal Polyethylenes Produced by Titanium Complexes Activated by Et₂AICI

Entry	Complex	<i>T</i> (°C)	Total		Peak 1		Peak 2		
			<i>M</i> _w ·10 ⁻³ (g mol ⁻¹)	$M_{\rm w}/M_{\rm n}$	$M_{\rm w}$ ·10 ⁻³ (g mol ⁻¹)	$M_{\rm w}/M_{\rm n}$	$M_{\rm w} \cdot 10^{-3} \ ({\rm g \ mol}^{-1})$	$M_{\rm w}/M_{\rm n}$	
MP45	Lig ¹ TiCl ₂	30	140	92.5	1,310	1.7	4.4	3.1	
MP53	Lig ¹ TiCl ₂	50	72	241.6	1,681	1.6	2.4	2.4	
MP24	Lig ⁴ TiCl ₂	30	2,250	996.9	3,063	1.6	8.0	2.9	
MP38	Lig ⁴ TiCl ₂	50	1.6	-	2,264	2.4	1.5	1.9	

TABLE 5 Results of Ethylene/1-Octene Copolymerization by the Lig⁴VCl₂/EtAlCl₂ and Lig⁴TiCl₂/MAO Catalytic Systems

Entry	Complex	Activator	1-Octfeed (mol dm ⁻³)	Yield (g)	Productivity (kg mol _M ⁻¹)	T _m (°C)	χ (%)	1-Oct in copolymer (mol%)	<i>M</i> _w 10 ⁻³ (g mol ⁻¹)	$M_{\rm w}/M_{\rm n}$
MP48	Lig ⁴ TiCl ₂	MAO	0	0.705	10.1	135.6	59	-	1,232	4.1 ^a
MP49			0.20	2.662	38.0	-	-	1.6	930	4.1
MP50			0.39	3.550	50.7	126.9 ^b	33	2.6	-	-
MP51			0.56	3.228	46.1	-	-	-	836	14.4 ^c
MP52			0.73	2.737	39.1	122.3 ^b	27	3.7 ^d	229	17.6 ^c
MP26	Lig^4VCI_2	EtAICI ₂	0	1.411	2,015.9	138.4	57	-	1,968	1.5
MP29			0.20	0.836	1,193.5	124.6 ^b	38	-	291	2.6
MP27			0.39	0.349	498.2	108.7; 128.6	-	5.7	238	2.7
MP30			0.56	0.335	478.4	131.3	37	-	-	-
MP28			0.73	0.138	197.6	127.9	19	8.0	263	2.4

Polymerization conditions: 0.0007 mmol of Lig⁴VCl₂; 0.07 mmol of Lig⁴ TiCl₂; 4 mmol of EtAlCl₂; 10.5 mmol of MAO; 5 bar of ethylene, 30 min, 150 cm³ of toluene (solvent); 30 °C; χ -crystallinity.

^a Bimodal.

^b Broad peak. ^c Bimodal—ir

^c Bimodal-in chromatogram an additional, low intensity, and low molecular weight peak can be seen.

^d Polymer analyzed in the form of foil.

polymerization of ethylene but its activity was clearly low in that process.

The complexes Lig^4MCl_2 (where M = Ti or V) after activation by MAO and EtAlCl₂, respectively, were used in ethylene copolymerization with 1-octene. It was for the first time that the copolymerization process of ethylene and a higher olefin in the presence of salan complexes of titanium and vanadium was researched. The reaction conditions were exactly the same as adopted for ethylene homopolymerization when catalyzed by those systems. Both the catalysts were homogeneous but the observed performance was different in the process studied. As regards the titanium catalyst, addition of a comonomer and increasing its concentration to 0.39 mol dm⁻³ improved the activity of the catalyst versus its performance in the homopolymerization process. A further increase of the comonomer concentration in the reaction medium, up to 0.73 mol dm^{-3} , lowered the process yield but its value was still nearly four times higher than in homopolymerization. In contrast, the catalyst Lig⁴VCl₂/EtAlCl₂ exhibited a lower activity when a comonomer was added and its activity was declining for the growing comonomer concentration in the reaction medium. The change in the reaction rate for copolymerization of olefins versus homopolymerization is known as the "comonomer effect" ant it was described in numerous reports.³⁸⁻⁴¹ The extent of that effect can be different for different catalytic systems and different comonomers, and the reasons for that effect may have chemical or physical grounds,³⁸ like for example modification of active sites and increase in the number of catalytic centers, changes in monomer diffusion, changes in propagation constant (k_p).^{38,39,42}

Incorporation of 1-octene into the polyethylene chain makes another important marker for the catalytic performance. The data in Table 5 indicate that the titanium catalyst offers a moderate ability only to incorporate a comonomer. The incorporation level reaches 1.6 mol % at the concentration of 0.2 mol dm^{-3} and it grows up to 3.7 mol % for 0.73 mol dm^{-3} of 1-octene in the medium. An increase in the comonomer incorporation leads to changes in the polymer properties. The polymer crystallinity and the melting point become decreased and the melting peaks for copolymers are definitely wider than those for PEs. The increasing initial 1-octene concentration gradually decreases the molecular weight of the resultant copolymers while the molecular weight distribution broadens and even, at higher comonomer incorporation levels, it becomes bimodal with a very low share of the low molecular weight fraction. Thus, the obtained copolymers are heterogeneous. The ¹³C NMR spectrum of the poly(ethylene-co-1-octene) copolymer, containing about 3.7 mol % of 1-octene units, produced at the highest comonomer concentration in the feed (0.73 mol dm^{-3}) is similar to those presented in other papers for copolymers with not very high comonomer contents, and it exhibits the signals at 14.06 ppm (CH₃), 22.88 ppm (CH₂(2)), 27.37 ppm (CH₂(5) and β —CH₂), 30.04 ppm (ϵ —CH₂, δ —CH₂ and CH₂(4)), 32.24 ppm (CH₂(3)), 34.63 ppm (α-CH₂, 6-CH₂), and 38.29 ppm (CH). There are no resonances within 40 to 42 ppm for carbon in the block type sequence or at about 25 ppm for carbon in the alternative sequence.

As regards copolymerization in the presence of a vanadium complex, the changes in the properties of the polymer product for changing comonomer concentrations are not unequivocal. The melting points for copolymers obtained at higher comonomer concentrations in the reaction medium are higher than $T_{\rm m}$ for copolymers obtained at lower concentrations, and the share of built-in comonomer segments, as found by the FTIR method, is growing. This can suggests the



presence of mixed products. The copolymer product was split into two fractions. One of them, which was insoluble in boiling hexane, was an ethylene homopolymer. The other fraction, which was soluble in boiling hexane, was a copolymerization product. As the amount of the product was very low it was impossible to investigate for further specifications of the fractions.

CONCLUSIONS

In summary, we synthesized a series of new titanium(IV) complexes bearing tetradentate [ONNO]-type salan ligands. Those complexes differ in the type of the linkage between the donor nitrogen atoms and in the number of *t*-Bu groups on the aromatic rings (one or two). The vanadium and zirconium complexes with hexene bridges were also prepared as reference comparative materials. These have not been so far reported in literature, either.

All the complexes exhibited catalytic activities towards 1octene polymerization in the presence of MAO and/or borates as a cocatalyst, producing oily products. Only two catalytic systems: $Lig^{1}TiCl_{2}/Al(i-Bu)_{3}/[Ph_{3}C][B(C_{6}F_{5})_{4}]$ and $Lig^{4}VCl_{2}/MAO$, produced solid materials with high average molecular weights and bimodal distribution.

Polymerization of ethylene in the presence of salen complexes has not so far been investigated in practice,¹⁴ while there is completely no information available on their use in copolymerization of ethylene and higher olefins. The studied catalysts show moderate activity in both processes and – just alike in homopolymerization of 1-octene—the activator type and the complex structure, for example, the type of linkage between nitrogen atoms, the presence of additional *t*-Bu group on each aromatic ring, and the transition metal type, greatly influenced the catalytic activities and molecular weight of the polymeric products. Investigations revealed also that the titanium catalyst gave the copolymer product with moderate incorporation and typical microstructure, while the vanadium catalyst produced the mixture of homopolymer and copolymer.

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