

Bis(salicylaldiminato)titanium Complexes Containing Bulky Imine Substituents: Synthesis, Characterization and Ethene Polymerization Studies

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A series of titanium complexes bearing two anionic [N, O⁻] bidentate salicylaldiminato ligands, namely bis[(*N*-salicylidene)anilinato]titanium(IV) dichloride (**1**), bis[(*N*-salicylidene)-2,6-dimethylanilinato]titanium(IV) dichloride (**2**), bis[(*N*-salicylidene)-2,6-di-*i*-propylanilinato]titanium(IV) dichloride (**3**), bis[(*N*-salicylidene)-(1-naphthalenylimino)]titanium(IV) dichloride (**4**), bis[(*N*-salicylidene)-2,6-difluoroanilinato]titanium(IV) dichloride (**5**), and bis[(*N*-3-fluorosallylidene)-2,6-difluoroanilinato]titanium(IV) dichloride (**6**) have been synthesized with good yields by a two-step procedure. The X-ray structure analysis reveals that in complex **2**, titanium has a distorted octahedral coordination sphere in which the oxygen atoms and the chloride ligands form the basal plane. Both the chloride and the phenoxy moieties have a *cis* orientation and the angle between the chloride ligands is 93.05°.

The imine nitrogen atoms complete the octahedral coordination of the Ti center by occupying the axial positions. The newly synthesized (**2** and **4–6**) and already known complexes (**1** and **3**) were introduced in detailed ethene-polymerization studies. The activities achieved were low to moderate depending on the size and nature of the imino substituents. The polyethenes (PEs) produced had high molar masses, and the modalities of the molecular weight distributions varied with polymerization temperature. Based on the results of *ab initio* calculations and on the experimental data obtained, an explanation for uni- and bimodal polymerization behavior and the differences in catalytic activities are given.

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Introduction

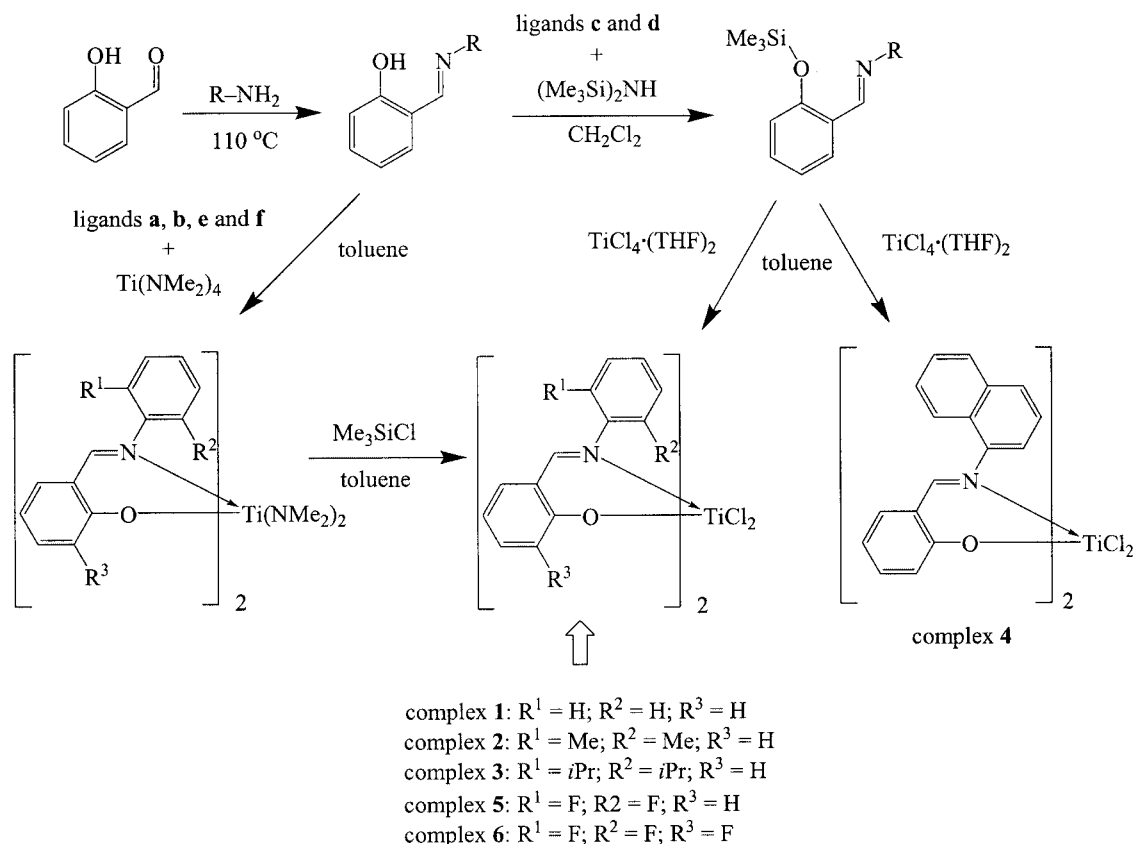
In the middle of the 80s chiral group 4 *ansa*-metallocenes were successfully used for the first time in the homogeneous polymerization of isotactic polypropene with excellent activities when activated with methylaluminoxane (MAO).^[1–3] This fundamental observation initiated intensive research activities in academia as well as in the polyolefin industry, and a lot of theoretical and synthetic resources were focused on the development and the understanding of metallocene-catalyzed polymerization reactions.^[4,5] At the same time there have also been significant efforts to transfer this know-how to other types of metal complexes that are mainly based on titanium and zirconium. An enormous increase in the number of publications on non-metallocene olefin polymerization catalysis started in the middle of the 90s, and this seems to be an ongoing trend as the research has spread from group 4 metals to nearly all other transi-

tion metals. Non-metallocene catalysts and their ethene polymerization properties have been reviewed rather extensively.^[6–8]

Fujita and coworkers at Mitsui Chemicals have so far reported the most efficient homogeneous non-metallocene catalysts for ethene polymerization. An activity as high as 80 kg_{PE}/(mmol·bar·h) was achieved for a MAO-activated bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]zirconium(IV) dichloride catalyst precursor.^[9] These types of catalysts are sensitive to the applied substituent pattern on the ligand framework, and depending on the ligand structure, the polymerization activities can vary from 0.1 to 10 kg_{PE}/(mmol·bar·h).^[9–12] The structure of the catalyst precursor as well as the polymerization conditions also influence the properties of polyethene. As an augmentation to our earlier studies on non-metallocene polymerization catalysis,^[13–15] we report herein a straightforward and efficient synthetic strategy to prepare (salicylaldiminato)-based titanium dichlorides. The ethene polymerization reactions of the newly synthesized (**2** and **4–6**) and already known complexes (**1** and **3**) with different aromatic substituents on the imine nitrogen atom were studied in order to evaluate the steric and electronic influences caused by the ligand substituents on the polymerization properties (Scheme 1).

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Scheme 1. Schematic presentation of the synthesis and the (salicylaldiminato)titanium complexes studied.

Results and Discussion

Synthesis of Ligand Precursors

Ligands containing phenoxy-imino groups are well known and are common in coordination chemistry. In our case, the synthesis of the ligands (**a–d**) was performed by the direct reaction between salicylaldehyde and the corresponding aniline by heating the reaction mixture in an oil bath at 110 °C in an open, round-bottomed flask overnight to ensure evaporation of water.^[16–18] The novel ligands (**e** and **f**) were synthesized in a similar manner to ligands (**a–d**) with two exceptions: the former ligands required a catalytic amount of sulfuric acid to achieve high yields, and the reactions were performed in toluene. The crude products from the reactions with all ligands were isolated in high yields. The color of ligand **d** was dark brown, **e** and **f** were orange, and the others were yellow. According to ^1H NMR spectroscopy all these salicylaldimines were pure and no further purifications were required.

Synthesis of Complexes

There are several methods that can be used successfully in the complexation of salicylaldiminato ligands with group 4 metals. *n*BuLi is consistently applied as reagent for ligand deprotonation, and in subsequent complex preparation, metal halides are employed. The yields of the desired bis(sa-

licylaldiminato)titanium dichloride complexes achieved with *n*BuLi varied between (20–80) percent depending on the corresponding ligand.^[11] This method produces the insoluble LiCl salt as a side product, and in the case in which the desired metal complex has low solubility, further purification of the product might be complicated as, for example, filtration causes problems. Another interesting complexation method was published by Erker et al., which afforded complexes by direct reaction between TiCl_4 and the salicylaldimine ligand in yields of around 60%.^[19] The main target in the complex preparation described here was to find a synthesis route that consists of a few high-yield steps and where side products are either volatile or otherwise easily removable. Two improved routes for the preparation of bis(salicylaldiminato)titanium dichlorides from the ligand precursors (**a–f**) were developed, and they both fulfill the above-mentioned requirements and are described below.

Method A

The silylation of the phenolic hydroxyl group with a common silylation reagent like trimethylsilyl chloride has been known to be quantitative under mild reaction conditions. Unfortunately, its use with compounds that contain nitrogen can lead to the formation of the undesired intramolecular iminium salt through elimination of HCl. To avoid salt formation, Me_3SiCl was replaced by 1,1,1,3,3,3-hexamethyldisilazane.^[20] It is suitable in this context because hexamethyldisilazane residues (bp. 125 °C) as well as

the by-product 1-trimethylsilylamine (bp. 57 °C) can be easily removed in vacuo after formation of the desired silyl compound.

Complex preparation with silyl-substituted ligand precursors has some limitations. The silylated phenoxy-imine compounds react fast and unselectively with TiCl_4 . This phenomenon was observed, for example, in the complexation of the silylated ligand precursor **a**. Together with the desired 1:2 complex (L_2TiCl_2), complexes with the stoichiometry LTiCl_3 and L_3TiCl were also observed. We assume that the observed unselectivity is due to lack of the steric bulkiness of the aniline substituents; with ligand precursors (**c** and **d**) that have bulky substituents, the complexation proceeded selectively by simple treatment of two molar equivalents of silylated ligand with $\text{TiCl}_4 \cdot (\text{THF})_2$ at -78°C (Scheme 1).^[21] After the reaction, toluene and the by-product trimethylsilylchloride were removed under vacuum, and the corresponding complexes **3** and **4** were isolated with nearly quantitative yields.

Method B

Method B consisted of two steps that were easy to perform as a one-pot reaction. Compounds containing a phenolic hydroxyl proton are susceptible to direct metallation with $\text{Ti}(\text{NMe}_2)_4$ followed by cleavage of dimethylamine.^[22,23] With this method the formation of the bis(salicylaldiminato) $\text{Ti}(\text{NMe}_2)_2$ complexes was smooth and proceeded with higher selectivity than with method A, e.g. complexation of the ligand precursors (**a**, **b**, **e** and **f**) with $\text{Ti}(\text{NMe}_2)_4$ produced only the desired 1:2 complexes ($\text{L}_2\text{Ti}(\text{NMe}_2)_2$). Despite the low boiling point of the released $(\text{Me})_2\text{NH}$, the complete removal of this by-product does not occur even after an extended period under vacuum at 50°C . This might be due to partial coordination of dimethylamine to the titanium complex. Free rotation of the amine methyl groups is prohibited and therefore in the ^1H NMR spectrum, the signal for the methyl groups are split into two peaks $\delta = 1.69$ and 2.3 ppm.

Titanium amido complexes are known to be less active catalyst precursors in ethene polymerization than their dichloro derivatives,^[24] and hence the obtained bis(salicylaldiminato) $\text{Ti}(\text{NMe}_2)_2$ complexes were converted directly to the corresponding bis(salicylaldiminato) TiCl_2 complex with excess chlorotrimethylsilane.^[22] The chlorinated complexes formed selectively and quantitatively. The progress of the chlorination reaction can be followed by ^1H NMR spectroscopy. When 75% of the amido groups were converted to chlorides, three different signals from the imine protons can be detected. For example, in the spectrum of complex **1**, one signal can be assigned to L_2TiCl_2 ($\delta = 8.06$ ppm) and two to $\text{L}_2\text{TiClNMe}_2$ ($\delta = 7.92$ and 8.22 ppm). Further, the signals for the methyl groups in $\text{L}_2\text{TiClNMe}_2$ appear as two distinct broad signals at $\delta = 3.6$ and 4.0 ppm. When the reaction was continued, signals from the dimethylamido group gradually disappeared, and in the end, only one imine signal at $\delta = 8.06$ ppm remained. After the removal of the coordinated $(\text{Me})_2\text{NH}$, the only by-product from the chlorination procedure was soluble $\text{Me}_3\text{SiNMe}_2$, which was

easy to remove by recrystallization of the bis(salicylaldiminato) TiCl_2 complexes. If the coordinated $(\text{Me})_2\text{NH}$ was not removed before chlorination was started, it was possible to observe an additional broad signal at $\delta = 9.0$ ppm in the ^1H NMR spectrum, which is evidence for the formation of a salt-like by-product between $(\text{Me})_2\text{NH}$ and Me_3SiCl . However, after refluxing and removal of the solvent, only traces of the by-product remained. The isolated yields for all complexes prepared by method B were above 90%.

X-ray Studies of Complex 2

Red crystals of complex **2** suitable for X-ray determination were grown at -20°C from a saturated toluene solution. The solid-state structure is shown in Figure 1, and crystallographic data as well as selected bond lengths and angles are given in Table 1 and Table 2. The titanium center has a distorted octahedral coordination and is located in the plane of the O_2Cl_2 core. The oxygen atoms are oriented *cis* to each other with nearly equidistant bond lengths ($\text{Ti}-\text{O1} = 1.8432 \text{ \AA}$ and $\text{Ti}-\text{O2} = 1.8629 \text{ \AA}$). The octahedral coordination of Ti is accomplished by a *trans* orientation of the imine nitrogen atoms with a dihedral angle of 178.69° . Because of the different coordination mode, the $\text{Ti}-\text{N}$ bonds are significantly longer than the $\text{Ti}-\text{O}$ bonds ($\text{Ti}-\text{N1} = 2.21068 \text{ \AA}$ and $\text{Ti}-\text{N2} = 2.1949 \text{ \AA}$). The chloride ligands

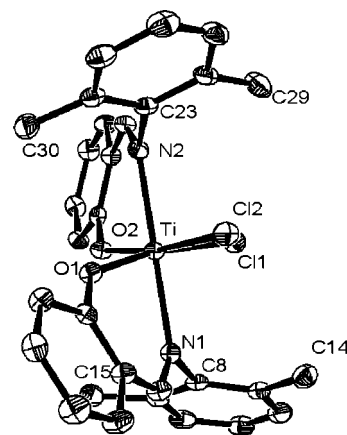


Figure 1. ORTEP plot of **2** with thermal ellipsoids drawn at 50% probability level. All hydrogen atoms are omitted for clarity.

Table 1. Selected crystallographic data for complex **2**.^[29]

Chemical formula	$\text{C}_{30}\text{H}_{28}\text{Cl}_2\text{N}_2\text{O}_2\text{Ti}$
Formula weight	567.34
Temperature [K]	150(2)
Wavelength [$\text{\AA}$]	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
<i>a</i> [$\text{\AA}$]	10.6183
<i>b</i> [$\text{\AA}$]	10.7983
<i>c</i> [$\text{\AA}$]	13.4618
α [$^\circ$]	77.596
β [$^\circ$]	85.990
γ [$^\circ$]	68.124
Volume [$\text{\AA}^3$]	1398.86

are *cis* oriented and they almost form a right angle (89.90 Å) with equivalent bond lengths (2.33 Å). In general, the bond lengths and angles resemble those reported earlier for bis[(*N*-salicylidene)-2,6-diisopropylanilinato]titanium(IV) dichloride.^[19]

Table 2. Selected bond lengths and angles for complex **2**.

Bond lengths [Å]		Bond angles [°]	
Ti–Cl1	2.333(1)	O2–Ti–N2	81.87(7)
Ti–Cl2	2.332(1)	O1–Ti–N2	98.92(7)
Ti–N1	2.211(2)	O2–Ti–N1	97.02(7)
Ti–N2	2.195(2)	O1–Ti–N1	81.81(7)
Ti–O1	1.843(5)	N2–Ti–Cl2	88.89(5)
Ti–O2	1.863(2)	N1–Ti–Cl2	92.22(5)
O1–C1	1.340(3)	O2–Ti–Cl1	89.62(5)
O2–C16	1.338(3)	O1–Ti–Cl1	170.29(5)
N1–C7	1.300(3)	N2–Ti–Cl1	90.71(5)
N1–C8	1.452(3)	N1–Ti–Cl1	88.59(5)
N2–C22	1.292(3)	Cl–Ti–Cl	89.90(2)
N2–C23	1.456(3)	O–Ti–O	92.98(7)
		N–Ti–N	178.69(7)

Ethene Polymerization

Herein the series of new (**2**, **4–6**) and already known (**1** and **3**) bis(salicylaldiminato)TiCl₂ complexes with different substituents were introduced in detailed polymerizations after MAO activation to investigate the influence of the ligand structure on the ethene polymerization properties. Because of simple phenyl substitution on the imine nitrogen, **1**/MAO was considered as a reference catalyst. The activity of **1**/MAO, which was 67 kg_{PE}/(mol_{Ti}·h·bar) at (60 °C, 3 bar), rose slowly but constantly with increasing monomer pressure (Table 3). When the pressure was kept constant (5 bar), the activity was enhanced with elevated temperatures and a maximum of 143 kg_{PE}/(mol_{Ti}·h·bar) was achieved at 80 °C. Under harsher polymerization conditions (100 °C, 10 bar), the activity was not significantly better. Irrespective of the applied polymerization conditions, molar

masses were between 300–500 kg/mol and the polydispersity (PD) values obtained were narrow. Catalyst **2**/MAO carrying 2,6-methyl-substituted anilines had activities of less than 10 kg_{PE}/(mol_{Ti}·h·bar) under all polymerization conditions, but the molar masses of the polyethenes were twice as high than those obtained with **1**/MAO. All GPC chromatograms represented polymers with unimodal and narrow polydispersities. A subtle tailing toward the low molar mass region was observed only for polymerizations at 80 °C.

The replacement of 2,6-methyl substituents with isopropyl groups further increases the steric congestion around the catalytic active metal center and results in a quite interesting polymerization behavior for **3**/MAO. The polymer produced was clearly bimodal, and the relative ratios between the two molar mass areas varied as a function of temperature. At 40 °C, the distribution curves partly overlapped and therefore the PD value was broad (≈ 14). The average value for the molar mass was around 600 kg/mol. At 60 °C, the catalyst had a distinct bimodal behavior, as two separate curves with narrow distribution were recorded. Molar masses of the separate peaks were 100 and 1000 kg/mol, which is consistent with two active sites. At 80 °C, the molar mass was 350 kg/mol, and the distribution curve was more or less unimodal again with a small shoulder at around 100 kg/mol. Polymerization activities were lower throughout than those with **1**/MAO under similar conditions as they remained below 50 kg_{PE}/(mol_{Ti}·h·bar).

Under the applied polymerization conditions, the activity of naphthyl-substituted **4**/MAO remained below 30 kg_{PE}/(mol_{Ti}·h·bar), and the polymer had a bimodal character. At 40 °C, the distribution curves overlapped, and as a consequence, the observed curve was rather broad and almost flat from the top. This complicated the determination of accurate molar mass values, but the average value for the molar masses was around 800 kg/mol. Polymers prepared at 80 °C have molar masses of 600 kg/mol and a compar-

Table 3. Selected ethene polymerization results with MAO-activated complexes **1**-, **2**- and **3**/MAO ([Al]/[Ti] = 2000) polymerization time 50 min.

Run	Complex	Cat. [μmol]	<i>T</i> _p [°C] ^[a]	<i>p</i> [bar] ^[b]	Activity ^[c]	<i>M</i> _w [kg/mol]	<i>M</i> _w / <i>M</i> _n	<i>T</i> _m [°C]
1	1	20	60	3	67	430	2.6	136
2	1	20	40	5	63	340	2.3	140
3	1	20	60	5	80	330	2.2	135
4	1	20	80	5	143	520	3.5	133
5	1	10	60	10	72	370	2.7	141
6	2	10	60	3	8	380	6.9	136
7	2	5	40	5	6	940	2.4	140
8	2	5	60	5	3	740	9.0	135
9	2	5	80	5	9	600	7.3	133
10	2	10	60	10	5	870	4.3	141
11	3	20	60	3	18	710	17.8	133
12	3	20	60	5	26	1060	49.5	134
13	3	20	60	10	14	750	44	135
14	3	20	40	5	21	615	8.9	133
15	3	20	80	5	18	600	8.9	133

[a] Polymerization temperature. [b] Monomer pressure. [c] Activity in (10³ g_{PE})/(mol_{Ti}·h·bar). [d] Onset melting temperatures of the polyethenes after heating the samples to 230 °C and cooling down again to 30 °C (cooling and heating rate 20 °C/min).

Table 4. Selected ethene polymerization results with MAO-activated complexes **4**-, **5**- and **6**/MAO ([Al]/[Ti] = 2000) polymerization time 50 min.

Run	Complex	Cat. [μmol]	T_p [$^{\circ}\text{C}$] ^[a]	p [bar] ^[b]	Activity ^[c]	M_w [kg/mol]	M_w/M_n	T_m [$^{\circ}\text{C}$]
16	4	20	60	3	19	480	18.2	128
17	4	20	60	5	21	600	14.9	136
18	4	20	60	10	19	480	7.9	135
19	4	20	40	5	42	615	8.9	134
20	4	20	80	5	8	630	7.5	134
21	5	20	60	3	20	270	6.8	136
22	5	20	60	5	36	590	7.0	136
23	5	10	60	10	95	1540	1.5	142
24	5	20	40	5	162	910	1.9	142
25	5	20	80	5	41	950	6.6	135
26	5	10	100	10	265	1090	1.6	144
27	6	10	60	3	37	460	3.0	137
28	6	10	60	5	72	1990	3.0	143
29	6	10	60	10	713	1520	3.8	144
30	6	10	40	5	194	690	4.5	143
31	6	10	80	5	120	620/30	1.4/1.4	143

[a] Polymerization temperature. [b] Monomer pressure. [c] Activity in ($10^3 \text{ g}_{\text{PE}}/(\text{mol}_{\text{Ti}} \cdot \text{h} \cdot \text{bar})$). [d] Onset melting temperatures of the polyethenes after heating the samples to 230 $^{\circ}\text{C}$ and cooling down again to 30 $^{\circ}\text{C}$ (cooling and heating rate 20 $^{\circ}\text{C}/\text{min}$).

tively unimodal distribution curve. Only a small shoulder was observed around the 100 kg/mol region.

The replacement of aniline with 2,6-difluoroaniline changes the catalyst performance considerably. At 40 $^{\circ}\text{C}$, the activity of **5**/MAO [$165 \text{ kg}_{\text{PE}}/(\text{mol}_{\text{Ti}} \cdot \text{h} \cdot \text{bar})$] was significantly higher than **1**/MAO [$63 \text{ kg}_{\text{PE}}/(\text{mol}_{\text{Ti}} \cdot \text{h} \cdot \text{bar})$], but by increasing the temperature its activity decreased to same level as catalyst **1**/MAO. This, together with the fact that the molar mass distributions were considerably expanded with a bimodal behavior at higher temperatures, might indicate changes in the catalytically active species. Catalyst **5**/MAO showed a rather linear enhancement of its activity with increasing ethene pressure. Actually, the highest activity for **5**/MAO [$265 \text{ kg}_{\text{PE}}/(\text{mol}_{\text{Ti}} \cdot \text{h} \cdot \text{bar})$] was achieved at 100 $^{\circ}\text{C}$ and 10 bar. At lower ethene pressures, the catalyst tended to produce polymers with bimodal distributions; however, with sufficient monomer concentrations, single-center behavior of the catalyst appeared, and polydispersities of the polymers were below 2.

In general, **6**/MAO had similar trends in the variation of polymerization conditions as **5**/MAO. It was slightly more

tolerant against thermal changes since only a bimodal distribution curve was observed at 80 $^{\circ}\text{C}$. The catalyst **6**/MAO revealed the highest activity, 713 $\text{kg}_{\text{PE}}/(\text{mol}_{\text{Ti}} \cdot \text{h} \cdot \text{bar})$ and gave polyethene with the highest molar mass (2000 kg/mol) (Table 4, runs 28 and 29). The molar mass distribution of polyethene was less than four and unimodal under all conditions. Only at 80 $^{\circ}\text{C}$ was the PE formed bimodal, and the chromatogram consisted of two overlapping curves with equal areas (Figure 2, Figure 3).

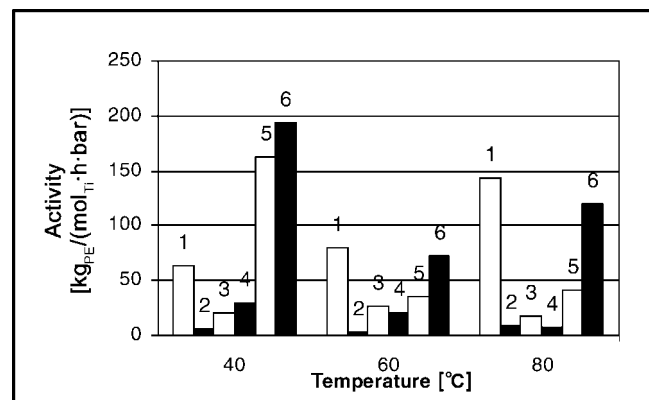


Figure 2. Activities of the catalysts (**1**–**6**)/MAO at different temperatures in ethene polymerization at 5 bar.

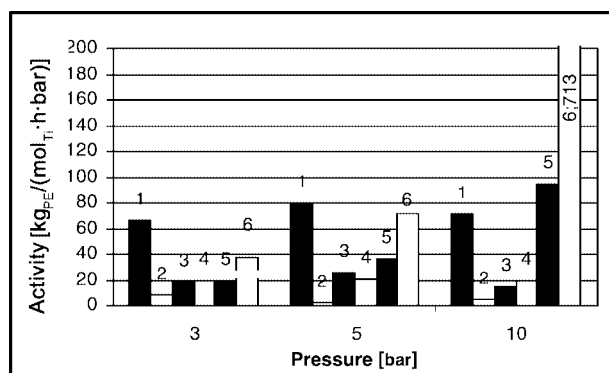


Figure 3. Activities of the catalysts (**1**–**6**)/MAO at different pressures in ethene polymerization at 60 $^{\circ}\text{C}$.

Correlation Between Complex Structure and Polymerization Behavior

Bis(salicylaldiminato)TiCl₂ complexes have three isomers that could be considered as active precatalysts in ethene polymerization as they all have chloride ions in a *cis* position (Figure 4). In two of the possible conformations, the imine nitrogen atoms are in *cis*- and the oxygen atoms, in *trans* positions, or vice versa. In the third conformation both the nitrogen and oxygen atoms occupy the *cis* orientation. The existence of all of these isomers has been experimentally verified by crystal-structure determination.^[19,25] The com-

plexes bearing bulky imino substituents have nitrogen atoms in a *cis* orientation, while complexes having fluorine or hydrogen at the 2,6-positions in the anilino part favor a *trans* orientation.

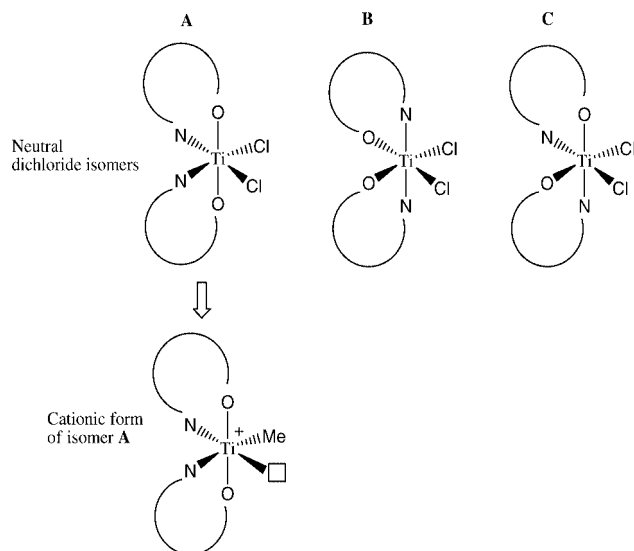


Figure 4. Schematic presentation of the neutral and active isomers in ethene polymerization.

The structures of the complexes calculated with *ab initio* methods^[26,27] and those measured experimentally by X-ray diffraction are indeed in good agreement for complexes 1–3. According to the solid-state structure, in complex 1, the imine nitrogen atoms are in *cis* positions (Figure 4, A), and this conformer has a significantly lower energy than the isomer in which the nitrogen atoms occupy the axial corners of the octahedra (Figure 4, B). Due to steric interactions, the increasing bulkiness on the aniline moiety raises the energy level of the *cis* isomer, and the *trans* isomer is favored. This is in accordance with the solid-state structures of complexes 2 and 3. The structural data for the rest of the complexes studied were calculated by theoretical methods only: *trans* isomer for complex 4, while for 5 and 6, which both have 2,6-fluoroaniline, the *cis* isomer was the most stable isomer.

In the solid state, complex 1 has the imine nitrogen atoms *cis* to each other, and the angle between the chloride ligands is 97°. In complex 2, which carries 2,6-dimethylaniline, the imine moieties are *trans* to each other (179°), and the angle between the chloride ligands is reduced to 89°. When the size of the aniline substituents is increased, the angle between the nitrogen atoms (172°) in 3 becomes smaller, and the angle between chloride ligands increases (94°). By comparing the polymerization activities and the geometries of the complexes, a clear dependence can be observed – the catalyst precursors that prefer the imine nitrogen atoms in the *cis* position, 1, 5 and 6, are more active in ethene polymerization than those that have a *trans* configuration. In any event, this observation does not provide answers to the question “what will happen after activation and why does PE have uni- and bimodal distribution curves”. Therefore, the stability of the bis(salicylaldiminato)Ti⁺–Me species was

the subject of further calculations as the stability of the metal cation is one of the crucial parameters which determines polymerization activity of a certain catalytic species (Figure 4).^[28]

The energy differences between the dichloro complexes and corresponding monomethyl cation forms were calculated for each isomer. According to the data, the relative stability of the structural isomers is altered after activation, e.g. complex 6 prefers a *cis* orientation but for the cation, the *trans* isomer has the lowest energy (Table 5). This phenomenon complicates the direct comparison of the calculated stability values and the experimental polymerization activities, and raises the question whether the species responsible for the catalytic activity has the same conformation as the corresponding dichloro complex. In fact, elegant ¹⁵N NMR spectroscopic studies by Fujita et al. indicate that some of the bis(salicylaldiminato)ZrCl₂ complexes possess fluxional behavior, and intramolecular change of the complex geometry can occur.^[29]

Table 5. The relative stability energies E_{Rel} in kJ/mol of the dichloro complexes 1–6 $E_{\text{Rel}}(\text{Cl}_2)$ and their cationic forms $E_{\text{Rel}}(\text{Ti}^+)$ including different isomeric structures. The most stable isomer has been marked. In the calculations the *trans* isomer of each catalyst precursor has been chosen as a point of reference. The stability of Ti⁺ was compared with the cationic form of TiCl₄.

Complex	$E_{\text{Rel}}(\text{Cl}_2)$	$E_{\text{Rel}}(\text{Ti}^+)$	Stability of Ti ⁺
1- <i>cis</i>	–21	0	–435
1- <i>ciscis</i>	–8	0	–448
1- <i>trans</i>	0	0	–456
2- <i>cis</i>	40	0	–479
2- <i>ciscis</i>	48	79	–409
2- <i>trans</i>	0	0	–439
3- <i>cis</i>	43	–26	–495
3- <i>ciscis</i>	65	0	–491
3- <i>trans</i>	0	0	–426
4- <i>cis</i>	3	0	–453
4- <i>ciscis</i>	13	0	–463
4- <i>trans</i>	0	0	–450
5- <i>cis</i>	–7	15	–440
5- <i>ciscis</i>	31	3	–490
5- <i>trans</i>	0	0	–462
6- <i>cis</i>	–17	10	–437
6- <i>ciscis</i>	21	5	–479
6- <i>trans</i>	0	0	–464

Whenever the conformation of the catalyst changes, one of the coordination bonds is released, after which rotation of the ligand can take place. This gives an option that the *cis* or *trans* isomers can be converted directly into the *ciscis* isomer, which is also the required intermediate isomer if ever the exchange between *cis* and *trans* isomer takes place. Taking this possibility into account, the observed activities as well as the multisite behaviors of the complexes can be rationalized.

In the series complexes, 1 prefers a *cis* conformation, and after MAO activation, it produces polyethene with good activity. At low polymerization temperatures, 1/MAO gives PE with unimodal PD, while at higher temperatures, bimodal behavior is apparent. According to the calculations, all cationic isomers have an equal possibility of occurring,

while the *trans* geometry gives the most stable active center and it should be the dominant species in the polymerization (Table 5). The neutral and cationic form of **2** prefers the *trans* isomer, and in addition the *cis* isomer is located significantly higher in energy and, therefore, the geometry of the catalyst is frozen to the initial *trans* conformer with low stability. This is in accordance with the observed low activity and unimodal behavior of the catalyst. As a neutral complex, **3** favors the *trans* conformer, while in the cationic form the *cis* isomer is more favorable. Because the *cis* intermediate is low in energy such a change in the coordination sphere is easily achievable and is reflected in the polymerization behavior of **3**/MAO. The interchange of catalyst geometries can be seen as a broad distribution curve at 40 °C, bimodal at 60 °C, but at 100 °C, PE with narrow PD (1.84) is obtained, which implicates the presence of only one type of active center (*cis*). Complex **4** prefers the *cis* form, but after activation all isomers have an equal possibility of occurring – the stability of the *cis* isomer is only slightly favorable. Therefore, under certain conditions, **4**/MAO produced PE with trimodal character. Before activation, **5** and **6** adopt a *cis* conformation, but in the cationic form the *trans* isomers are slightly favored. In fact, catalyst **6**/MAO produces PE with a high activity and mainly with a unimodal distribution. Only at 80 °C is the polymer clearly bimodal, which is in accordance with the presence of the higher energy *cis* isomer. Due to the lower energy gap between the *trans*- and *cis* isomers, **5**/MAO is more prone to produce bimodal PE.

In addition to the stability of the cation, the steric shielding of the catalyst is also one of the crucial factors that determine the activity in polymerization. In the series of catalysts, **3** exhibits the highest calculated stability value but only medium catalytic activity has been detected. This raises the question about the steric shielding of the metal center. In fact, Fujita et al. have also reported the deleterious effects of aniline's alkyl substituents on the catalytic activity and they suggested that the alkyl groups increase the steric congestion around the active site.^[12,30] We assume that the low activity of **3** as well as **2** and **4**, combined with low stability of the cation, arises from the same origin. Tuning of the size of the substituent has a significant influence on the average polymerization activity.^[31]

Electron-withdrawing fluoro substituents on aniline have been considered as highly desirable as they give catalyst precursors with highest activities. We assume that the coordination between imino-N and Ti weakens, and affords, therefore, rapid intramolecular exchange towards the conformation with the highest stability even at low polymerization temperatures (25 °C and below). When the polymerization temperature is increased (above 60 °C), the catalyst precursor with aniline (**1**) possesses similar or even higher activities than that bearing 2,6-difluoro aniline (**5**).

Conclusions

Bis(salicylaldiminato)TiCl₂ complexes are often described as catalyst precursors that are able to produce poly-

ethene with narrow polydispersities, and even a living polymerization of α -olefins has been reported.^[11] The series of bis(salicylaldiminato) catalysts described here possess a tunable multisite character with high activity. Similar multisite behavior of bis(salicylaldiminato)TiCl₂ catalyst precursors has been reported only for bis[(3-(3,5-dicumyl)salicylidene)anilinato]zirconium(IV) dichloride; depending on polymerization conditions uni-, bi- and trimodal polyethene have been obtained.^[29]

Subtle variations in the ligand structure and polymerization conditions can significantly change the polymer properties. What is apparent from this study is the fact that the structure of the catalyst precursor does not predict the polymerization properties of the activated complex. The most important factor is the conformation of the active catalyst. The catalysts studied here are prone to change their coordination sphere after the activation process, and the relative stability energies of the different cation isomers vary with the ligand substituents. The relative stabilities of the different isomers depend on the ligand substituents. Different conformers of the active species can be present at the same time, which is seen by a multimodal behavior in polymerization. The ratio of the active species present in polymerization can be also fine tuned by the reaction temperature. In this series of catalysts, the metal cations with a *trans* conformation possess highest activities. For example, the activity of the catalyst **1**/MAO is three times greater than that of catalysts **3**/MAO and **4**/MAO, for which the most stable isomer is the *cis* isomer. It is reasonable to assume that in the *trans* conformation, the active center is sterically protected by the imino substituents. As a conclusion, the phenomenon described above illustrates the fluxional character of bis(salicylaldiminato)TiCl₂ complexes, which depends on the ligand substituents, and is therefore unique for each catalyst.

Experimental Section

All organometallic syntheses were performed under argon using standard Schlenk techniques and dry solvents.

Materials: Toluene, *n*-hexane, and tetrahydrofuran (THF) of HPLC grade were dried and purified by refluxing over sodium and benzophenone, followed by distillation under argon. Dichloromethane (CH₂Cl₂) was dried and purified over CaH₂ by refluxing for 4 h and subsequent distillation. Toluene, *n*-hexane, and THF were stored with sodium flakes under argon. Salicylaldehyde (Fluka), 3-fluorosalicylaldehyde (Aldrich), 3-*tert*-butylsalicylaldehyde (Aldrich), aniline (Aldrich), 2,6-dimethylaniline (Aldrich), 2,6-diisopropylaniline (Aldrich), naphthylamine (Aldrich), 2,6-difluoroaniline (Aldrich), 2,3,4,5,6-pentafluoroaniline (Aldrich), Tetrakis(dimethylamino)titanium (Aldrich), and TiCl₄ (Riedel-de Haën) were used as received, methylaluminoxane (MAO, 30 wt.-% solution in toluene) was received from Borealis Polymers Oy.

¹H- and ¹³C NMR spectra were collected on a Varian Gemini 2000 (200 MHz) spectrometer. Chemical shifts were referenced internally with respect to CHCl₃ (δ = 7.27 and 77.23 ppm, respectively). Mass spectra (EI) were acquired by a JEOL-SX102 spectrometer. DSC

measurements (melting point) were performed on a Perkin–Elmer DSC-2, calibrated with indium (temperature scanning 20 °C/min). Scan area was from 25 °C to 232 °C. Mass average molecular weights (M_w), number average molecular weights (M_n), and molecular weight distribution (MWD, M_w/M_n) of the polyethene samples were determined by GPC (Waters Alliance GPCV 2000, high-temperature gel chromatographic device). HMW7, 2*HMWGE and HMW2 Waters Styrogel columns were used for GPC. Measurements were performed in 1,2,4-trichlorobenzene (TCB) at 160 °C relative to polyethene standards, and 2,6-di-*tert*-butyl-4-methylphenol was used as a stabilizer.

Syntheses of the Compounds a–f

***N*-(Salicylidene)aniline (a):** Fully detailed analyses can be found in the literature.^[16] Salicylaldehyde (5 mL, 1.146 g/mL, 0.047 mol) and aniline (4.82 mL, 93.13 g/mol, 0.047 mol) were added to a 100-mL round-bottomed flask at room temperature and were warmed to 120 °C. The heated mixture was stirred overnight. The crude product was recrystallized from propanol (8.34 g, 90%). ¹H NMR (200 MHz, CDCl₃, 29 °C): δ = 6.93–7.08 (m, 2 H, H–Ph) 7.26–8.63 (m, 5 H, H–Ph), 8.63 (s, 1 H, CNH), 13.31 (s, 1 H, OH) ppm.

***N*-(Salicylidene)-2,6-dimethylaniline (b):** Fully detailed analyses can be found in the literature.^[17] Compound **b** was prepared by a similar method as described above for **a**. Salicylaldehyde (5 mL, 1.146 g/mL, 0.047 mol) and 2,6-dimethylaniline (5.9 mL, 121.18 g/mol, 0.047 mol) were mixed. The product was isolated as yellow crystals. Yield: 9.53 g, 90%. ¹H NMR (200 MHz, CDCl₃, 29 °C): δ = 2.24 (s, 6 H, CH₃), 6.95–7.12 (m, 5 H, H–Ph), 7.35–7.48 (m, 2 H, H–Ph), 8.37 (s, 1 H, CNH), 13.13 (s, 1 H, OH) ppm. MS (EI): m/z = 224–225 with appropriate isotope ratio for [C₁₅H₁₅NO⁺].

***N*-(Salicylidene)-2,6-diisopropylaniline (c):** Fully detailed analyses can be found in the literature.^[17] Compound **c** was prepared by a similar method as described above for **a**. Salicylaldehyde (5 mL, 1.146 g/mL, 0.047 mol) and 2,6-diisopropylaniline (17.7 mL, 177.29 g/mol, 0.047 mol) were mixed. The product was isolated as yellow crystals. Yield: 10.58 g, 80%. ¹H NMR (200 MHz, CDCl₃, 29 °C): δ = 1.26 (d, 12 H, CH₃), 3.08 (sept, 2 H, CH), 7.05–7.55 (m, 7 H, H–Ar), 8.39 (s, 1 H, CNH), 13.18 (s, 1 H, OH) ppm.

***N*-Naphthylsalicylaldimine (d):** Fully detailed analyses can be found in the literature.^[18] Compound **d** was prepared by a similar method as described above for **a**. Salicylaldehyde (5 mL, 1.146 g/mL, 0.047 mol) and naphthylamine (6.73 g, 0.047 mol) were mixed. The product was isolated as a brown powder. Yield: 8.14 g, 70%. ¹H NMR (200 MHz, CDCl₃, 29 °C): δ = 6.67–6.97 (m, 3 H, H–Ar), 7.12–7.32 (m, 3 H, H–Ar), 7.49–7.53 (m, 2 H, H–Ar), 7.56–7.65 (m, 2 H, H–Ar), 7.95–8.03 (m, 2 H, H–Ar), 8.42 (s, 1 H, CNH) ppm.

***N*-(Salicylidene)-2,6-difluoroaniline (e):** Salicylaldehyde (5 mL, 1.146 g/mL, 0.047 mol) and 2,6-difluoroaniline (5.1 mL, 1.199 g/mL, 0.047 mol) were added to a 100-mL round-bottomed flask at room temperature. To the mixture were added a catalytic amount of concentrated sulfuric acid and toluene (40 mL), and the mixture was warmed to 110 °C. The heated mixture was stirred overnight. The formed imine was dissolved in CH₂Cl₂, dried with solid Na₂SO₄, and the mixture was filtered. The product was isolated as an orange–yellow powder. Yield: 9.86 g, 90%. ¹H NMR (200 MHz, CDCl₃, 29 °C): δ = 6.93–7.22 (m, 5 H, H–Ar), 7.38 and 7.42 (d, 2 H, H–Ar), 8.88 (s, 1 H, CNH), 12.94 (s, 1 H, OH) ppm. ¹³C{¹H} NMR (50.3 MHz, CDCl₃, 29 °C): δ = 107.27 (Ar), 112.05–112.53 (m, 2 H, Ar), 117.76 (Ar), 119.34 (Ar), 126.71 (t, 1 H, Ar), 132.98 (Ar), 134.12 (Ar), 153.64 and 153.75 (d, Ar), 158.65 and 158.79 (d, Ar), 161.63 (Ar), 168.93 (t, Ar) ppm. MS (EI): m/z = 233–234 with appropriate isotope ratio for [C₁₃H₉F₂NO⁺].

***N*-(3-Fluorosalicylidene)-2,6-difluoroaniline (f):** Compound **f** was prepared by a similar method as described above for **e**. 3-Fluorosalicylaldehyde (1.0 g, 0.00713 mol) and 2,6-difluoroaniline (0.77 mL, 0.00713 mol) were mixed. The product was isolated as an orange–yellow powder. Yield: 1.61 g, 90%. ¹H NMR (200 MHz, CDCl₃, 29 °C): δ = 6.84–8.94 (m, 6 H, H–Ar), 8.94 (s, 1 H, CNH), 13.21 (s, 1 H, OH) ppm. MS (EI): m/z = 250–251 with appropriate isotope ratio for [C₁₃H₈F₃NO⁺].

Syntheses of the Complexes 1–6

Bis[*N*-(salicylidene)anilinato]titanium(IV) Dichloride (1): Fully detailed analyses of complex **1** can be found in the literature.^[19] Compound **a** (2.0 g, 0.010 mol) was dissolved in toluene (60 mL), and cooled to –78 °C, after which it was slowly transferred with a syringe to a precooled solution of toluene (60 mL) and Ti(NMe₂)₄ (1.2 mL, 224.21 g/mol, 0.0050 mol). The solution obtained was stirred overnight at room temperature. Quantitative formation of the complex bis(dimethylamino)bis[*N*-(salicylidene)anilinato]titanium was observed. ¹H NMR (200 MHz, CDCl₃, 29 °C): δ = 1.69 (s, 6 H, HNMe₂), 2.30 (s, 6 H, HNMe₂), 3.5 (b, 12 H, TiNMe₂), 4.83 (s, 2 H, HNMe₂), 5.89 and 5.93 (d, 2 H, H–Ar), 6.58–7.57 (m, 16 H, H–Ar), 8.49 (s, 2 H, CNH) ppm. MS (EI): m/z = 528 with appropriate isotope ratio for [C₃₀H₃₂N₄O₂Ti⁺]. The amount of the solvent was reduced to 40 mL, and trimethylsilylchloride (20× excess, 25 mL, 0.856 g/mL, 0.2 mol) was added at room temperature. The reaction mixture was stirred overnight, followed by 2 h of heating in refluxing toluene and removal of side-product residues at 70 °C in vacuo. The procedure was repeated twice (may be necessary). Traces of unidentified amine compounds were still observed by ¹H NMR spectroscopy, otherwise the product was pure according to EA, NMR, MS. Yield: 2.55 g, 98%. ¹H NMR (200 MHz, CDCl₃, 29 °C): δ = 6.47 and 6.51 (d, 2 H, H–Ar), 6.98–7.34 (m, 16 H, H–Ar), 8.27 (s, 2 H, CNH) ppm. MS (EI): m/z = 511 with appropriate isotope ratio for [C₂₆H₂₀Cl₂N₂O₂Ti⁺]. C₂₆H₂₀Cl₂N₂O₂Ti: calcd. C 61.08, H 3.94, N 5.48; found C 61.22, H 4.01, N 5.57.

Bis[*N*-(salicylidene)-2,6-dimethylanilinato]titanium(IV) Dichloride (2): Complex **2** was prepared by a similar method as described above for **1**.

Analyses of the quantitative formation of the intermediate product bis(dimethylamino)bis[*N*-(salicylidene)-2,6-dimethylanilinato]titanium. ¹H NMR (200 MHz, CDCl₃, 29 °C): δ = 2.16 (s, 6 H, Ar–CH₃), 2.35 (s, 6 H, Ar–CH₃), 2.56 (s, 6 H, NCH₃), 2.87 (s, 6 H, CH₃, NCH₃), 6.37 and 6.41 (d, 2 H, H–Ar), 6.59 (t, 2 H, H–Ar), 7.00–7.27 (m, 10 H, H–Ar), 8.06 (s, 2 H, CNH) ppm. MS (EI): m/z = 584 with appropriate isotope ratio for [C₃₄H₄₀N₄O₂Ti⁺].

Analyses of the final product. The product was isolated as yellow crystals. Yield: 2.55 g, 90%. ¹H NMR (200 MHz, CDCl₃, 29 °C): δ = 2.47 and 2.50 (d, 12 H, Ar–CH₃), 6.76 and 6.80 (d, 2 H, Ar), 6.98–7.17 (m, 8 H, H–Ar), 7.53–7.65 (m, 4 H, H–Ar), 8.38 (s, 2 H, CNH) ppm. ¹³C{¹H} NMR (50.3 MHz, CDCl₃, 29 °C): δ = 19.15 (s, Ar–CH₃), 19.85 (s, Ar–CH₃), 115.48 (Ar), 122.11 (Ar), 124.34 (Ar), 126.95 (Ar), 127.81 (Ar), 129.06 (Ar), 130.11 (Ar), 131.54 (Ar), 134.64 (Ar), 137.04 (Ar), 154.01 (Ar), 164.01 (Ar), 169.58 (Ar) ppm. MS (EI): m/z = 566 with appropriate isotope ratio for [C₃₀H₂₈Cl₂N₂O₂Ti⁺].

Bis[*N*-(salicylidene)-2,6-diisopropylanilinato]titanium(IV) Dichloride (3): Fully detailed analyses of the complex **3** can be found in the literature.^[19] Compound **c** (3.0 g, 10.6 mmol) was dissolved in dry CH₂Cl₂ (30 mL) in a Schlenk flask, under argon. Hexamethylsilazane (3.0 mL, 0.765 g/mL, 14.22 mmol) was added to the solution with a syringe. The reaction mixture was kept at room temperature

and was stirred overnight. Evaporation of excess hexamethylsilazane and by-products under vacuum at 50 °C over 5 h purified the product. The silylated *N*-(salicylidene)-2,6-diisopropylaniline was a slightly yellow, viscous liquid. The yield was quantitative (3.15 g). ¹H NMR (200 MHz, CDCl₃, 29 °C): δ = 0.37 (s, 9 H, SiCH₃), 1.28 (d, 12 H, CH₃), (sept, 2 H, CH), 6.97 (d, 1 H, H-Ar), 7.15–7.33 (m, 4 H, H-Ar), 8.45 (t, 1 H, H-Ar), 8.29 (d, 1 H, H-Ar), 8.62 (s, 1 H, CNH) ppm. The silylated compound **c** (3.55 g, 10.07 mmol) was dissolved in dry THF (60 mL) in a Schlenk flask, and cooled to the freezing point of THF with liquid nitrogen. The same cooling procedure was performed with TiCl₄·(THF)₂ (2.23 g, 5.04 mmol), which was dissolved on THF (150 mL). Precooled silylated compound **c** was slowly transferred to the titanium solution with syringe under an argon flow. The solution immediately turned to light red. The reaction mixture was stirred overnight, and allowed to come to room temperature. During that time, the color of the mixture turned to deep red. The titanium complex was purified by evaporation of the formed trimethylsilylchloride and THF. Recrystallization was performed from *n*-hexane/THF (7:1). Yield: 2.91 g, 85%. ¹H NMR (200 MHz, CDCl₃, 29 °C): δ = 1.14 (d, 12 H, CH₃), 1.30 (d, 6 H, CH₃), 1.46 (d, 6 H, CH₃), 1.90 (4 H, THF), 3.62 (sept, 4 H, CH), 3.80 (4 H, THF), 6.78 (d, 2 H, H-Ar), 7.10 (t, 2 H, H-Ar), 7.17 (m, 6 H, H-Ar), 7.48 (m, 4 H, H-Ar), 8.42 (s, 1 H, CNH) ppm. MS (EI): *m/z* = 679–684 with appropriate isotope ratio for [C₃₈H₄₄N₂O₂TiCl₂]⁺. C₃₈H₄₄N₂O₂TiCl₂: calcd. C 67.16, H 6.53, N 4.12, Ti 7.05; found C 66.84, H 6.71, N 4.26, Ti 7.17.

Bis[*N*-(naphthylsalicylaldiminato)titanium(IV) Dichloride (4): Complex **4** was prepared by a similar method as described above for **3**. Silylated compound **d** was a slightly yellow, viscous liquid. The yield was quantitative (3.39 g). ¹H NMR (200 MHz, CDCl₃, 29 °C): δ = 0.33 (s, 9 H, SiCH₃), 6.90–7.20 (m, 3 H, H-Ar), 7.18–7.58 (m, 4 H, H-Ar), 7.77 (d, 1 H, aromatic), 7.85 (m, 1 H, H-Ar), 8.38 (m, 1 H, H-Ar), 8.90 (s, 1 H, CNH) ppm. MS (EI): *m/z* = 319–322 with appropriate isotope ratio for [C₂₀H₂₁NOSi]⁺. The desired titanium complex precipitated out as a powder from an *n*-hexane/THF (5:1) solution. Yield: 2.62 g, 90%. ¹H NMR (200 MHz, CDCl₃, 29 °C): δ = 1.86 (4 H, THF), 3.76 (4 H, THF), 5.62 (d, 1 H, H-Ar), 6.02 (d, 1 H, H-Ar), 6.20 (d, 1 H, H-Ar), 6.50–8.40 (m, 19 H, H-Ar), 8.70 (s, 2 H, CNH) ppm. ¹³C{¹H} NMR (50.3 MHz, CDCl₃, 29 °C): δ = 25.85 (THF), 68.28 (THF), 116.24 (Ar), 116.76 (Ar), 117.52 (Ar), 119.00 (Ar), 119.23 (Ar), 121.56 (Ar), 121.92 (Ar), 122.54 (Ar), 123.56 (Ar), 123.99 (Ar), 125.00 (Ar), 125.24 (Ar), 125.76 (Ar), 126.88 (Ar), 123.99 (Ar), 125.00 (Ar), 125.24 (Ar), 125.76 (Ar), 126.88 (Ar), 127.80 (Ar), 128.44 (Ar), 133.87 (Ar), 134.69 (Ar), 135.02 (Ar), 136.33 (Ar), 137.06 (Ar), 149.60 (Ar), 162.13 (Ar), 162.53 (Ar), 168.47 (Ar), 169.05 (Ar), 169.62 (Ar) ppm. MS (EI): *m/z* = 610–615 with appropriate isotope ratio for [C₃₄H₂₄N₂O₂TiCl₂]⁺. C₃₄H₂₄N₂O₂TiCl₂: calcd. C 66.83, H 3.93, N 4.58, Cl 11.62, Ti 7.86; found: C 64.89, H 4.41, N 4.18, Cl 10.14, Ti 8.69.

Bis[*N*-(salicylidene)-2,6-difluoroanilinato)titanium(IV) Dichloride (5): Complex **5** was prepared by a similar method as described above for **1**. Yield: 2.33 g, 80%. ¹H NMR (200 MHz, CDCl₃, 29 °C): δ = 6.43–6.47 (m, 4 H, H-Ar), 6.97–7.01 (m, 6 H, H-Ar), 7.36–7.40 (m, 4 H, H-Ar), 8.25 (s, 2 H, CNH) ppm. MS (EI): *m/z* = 583–586 with appropriate isotope ratio for [C₂₆H₁₆Cl₂F₄N₂O₂Ti]⁺. C₂₆H₁₆Cl₂F₄N₂O₂Ti: calcd. C 53.55, H 2.77, N 4.80; found C 53.16, H 3.16, N 4.4.

Bis[*N*-(3-fluorosallylidene)-2,6-difluoroanilinato)titanium(IV) Dichloride (6): Complex **6** was prepared by a similar method as described above for **1**. Yield: 1.11 g, 90%. ¹H NMR (200 MHz, CDCl₃, 29 °C): δ = 6.30 (b, 2 H, H-Ar), 6.88–7.40 (m, 10 H,

H-Ar), 8.30 (s, 2 H, CNH) ppm. MS (EI) *m/z* = 619–620 with appropriate isotope ratio for [C₂₆H₁₄Cl₂F₆N₂O₂Ti]⁺. C₂₆H₁₄Cl₂F₆N₂O₂Ti: calcd. C 50.44, H 2.28, N 4.52; found C 49.91, H 2.46, N 4.10.

Polymerization Experiments: Polymerization runs were performed in a Büchi 1.0-dm³ stainless steel autoclave equipped with a Julabo ATS-3 and Lauda RK 20 temperature controlling unit. Mechanical stirring was applied with a stirring speed of 800 r.p.m. During polymerization, the partial pressure of ethene and the temperature were kept constant. Ethene consumption was measured with a calibrated mass flow meter and monitored online together with the temperature and pressure inside the vessel by using the Genie™ computer program for data acquisition.

Toluene (250 cm³) and the cocatalyst (MAO) were introduced to the argon-purged reactor. Once the polymerization temperature had been reached, the vessel was charged with ethene to the appropriate pressure. Polymerization was started by injecting 20 cm³ of the catalyst precursor solution (5–20 μmol solution in toluene) into the reactor. The polymerization was completed by pouring the contents of the vessel into methanol, acidified with a small amount of concentrated hydrochloric acid. The solid polyethene was collected by filtration, washed with methanol, and dried overnight at 70 °C.

X-ray Crystallographic Study: A single crystal of compound **2** was selected for the X-ray measurement and mounted on the glass fibre using the oil-drop method (Kottke & Stalke, 1993). Data were collected at 120(2) K with a Nonius KappaCCD diffractometer. The intensity data were corrected for Lorentz and polarization^[32] effects and for absorption by multi-scan method.^[33] The structures were solved by direct methods (SHELXS-97).^[34] The refinements and graphics were performed by using the SHELXL-97 and SHELXTL/PC program packages, respectively.^[35] All non-hydrogen atoms were refined anisotropically. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms.

X-ray Data for Complex 2: *Z*, calculated density 2, 1.347 Mg/m³, absorption coefficient 0.527 mm⁻¹, *F*(000) 588, crystal size 0.35 × 0.15 × 0.10 mm, *θ* range for data collection 2.08 to 26°, reflections collected 27130, unique reflections 5489 (*R*_{int} = 0.0925), completeness to *θ* = 26.00: 99.7%, absorption correction semi empirical from equivalents, max. and min. transmission 0.9492 and 0.8372, refinement method full-matrix least-squares on *F*², data/restraints/parameters 5489/0/339, goodness of fit on *F*² = 1.120, final *R* indices [*I* > 2σ(*I*)] *R*₁ = 0.0492, *wR*₂ = 0.01252, *R* indices (all data) *R*₁ = 0.0570, *wR*₂ = 0.1298, extinction coefficient 0.0098(19), largest diff. peak and hole 0.538 and -0.672 e Å⁻³ (see also: Table 1, Table 2, and Figure 1).

CCDC-235033 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Theoretical Calculations: Geometry optimisations were performed at the HF/3-21G* level, which has been shown to provide reliable structures for group 4 transition-metal complexes, especially for titanium-based complexes. Based on our earlier studies, neither increasing the size of the basis set nor inclusion of electron correlation at the MP2 level has a significant influence on the geometries, but would certainly increase calculation times. Single-point MP2 calculations were performed to confirm the relative stability order of conformations of the studied titanium complexes. At the single-point calculations, basis set 6-31G* for C, H, O and N, and

equal-level generated basis set for Ti were used. The stability orders, produced by both methods, are generally in good agreement with each other. The geometry minima were confirmed by frequency calculations. All calculations were carried out by the Gaussian 03 program package.^[26]

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