Alkylphenyl-Substituted Bis(salicylaldiminato) Titanium Catalysts in Ethene Polymerization

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Received November 10, 2006

Titanium complexes bearing anionic [N,O$^-$] bidentate salicylaldiminato ligands were synthesized with excellent yields via one- or two-step processes. The common feature of these catalyst precursors is the presence of aliphatic substituents (adamantyl, benzyl, $(CH_2)_2$Ph, $(CH_2)_3$Ph, and *i*-Pr) at the aldimino moieties. X-ray structure analysis of the benzyl-substituted complex revealed a distorted octahedral geometry, wherein nitrogen and chlorine atoms form the basal plane while the oxygen atoms of the phenoxy moieties complete the coordination sphere of the Ti center by occupying the axial positions. However, according to dynamic ^{1}H NMR measurements, these complexes can possess different structural isomers in solution, even at room temperature. After MAO activation, the catalysts displayed a range of catalytic activities [3−1700 $kg_{PE}/(mol_{Ti}\cdot h\cdot bar)$]. The complex with ethylphenyl substituents was the most active in the series. In general, the $(CH_2)_2$Ph- and $(CH_2)_3$Ph-substituted catalysts produce PE with unimodal molar mass distribution, while the benzyl-, adamantyl-, and isopropyl-substituted catalysts tend to produce high molar mass bimodal PE with low activity. Computational methods were used to interpret the polymerization results, particularly the catalytic activity.

Introduction

Only a few catalyst classes have appeared[1] that possess catalytic activities to challenge zirconium-based metallocenes[2] in the area of homogeneous catalysts for ethene polymerization. The discovery of competitive late transition metal catalysts based on iron as well as nickel and palladium complexes bearing tridentate 2,6-bis-imino(pyridine) or bidentate diimine ligands, respectively, initiated intensive research on this topic more than a decade ago.[3] Schiff base group 4 metal complexes have been known since the 1960s,[4] but during the last 10 years they have attracted considerable attention as possible catalyst precursors for olefin polymerization.[5] Phenoxyimine ligands are especially attractive, as they are easily prepared via a classical imine condensation reaction between a suitable salicylaldehyde and any primary amine. The modification possibilities for these ligands are, therefore, plentiful. In addition, upon coordination of phenoxyimine ligands to the metal, the chlorides adopt a *cis* orientation,[5e,6] which is generally considered to be a prerequisite for efficient polymerization catalysts. In this context Fujita et al. developed novel ligand combinations for group 4 metals and reported the most efficient homogeneous nonmetallocene catalysts for ethene polymerization to date. In these highly active Ti complexes, fluorinated aromatic substituents at the imine nitrogen together with either a *t*-Bu or cumyl group at the 3-position adjacent to the phenoxy oxygen are the distinctive features.[6b,7]

One of the phenoxy-imine catalysts studied, bearing bulky 3,5-dicumyl substituents and unsubstituted phenyl at the imine nitrogen, had unusual behavior. First it produced multimodal

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10.1021/om0610391 CCC: $37.00
Publication on Web 06/14/2007

PE, and second the ratios of the different molar mass fractions and polymerization activities alternated with reaction temperature.[8] A similar phenomenon was observed in our studies concerning bis(phenoxyanilinato)titanium catalysts, where the production of multimodal PE was frequent.[9] Molecular modeling of these bis(phenoxyanilinato)titanium catalysts revealed interesting results, which correlate well with the experimental polymerization data. According to ab initio calculations, the relative stabilization energies of the structural isomers of these complexes can change after activation. Therefore, the cationic complex formed does not necessarily have to adopt the same orientation with the salicylaldiminato ligands as that of the initial dichloro complex.[9] Such fluxional behavior is well known also for neutral titanium dichloro complexes and is dependent on the ligand substitution pattern.[8]

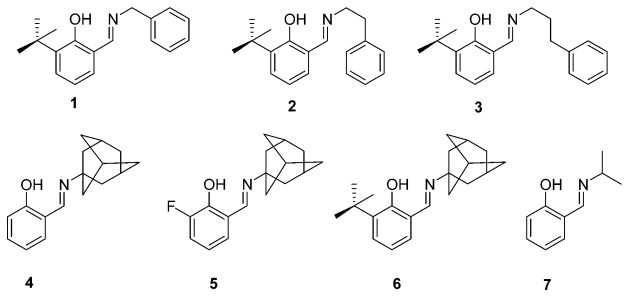
The observed multimodal polymerization behavior for bis(phenoxyanilinato)titanium catalysts may be due to changes in the orientation of the salicylaldiminato ligands, leading to simultaneous polymerization with different structural isomers. Furthermore, according to calculations, a common feature of the most active (phenoxyanilinato)titanium catalyst precursors was their tendency to change their coordination sphere by moving the imine nitrogens from *cis* to *trans* positions upon activation.[9] To gain further understanding of these fluxional catalysts, we extended our studies toward alkylphenyl ($Ph(CH_2)_n$, $n = 1$, 2, and 3) substituted titanium complexes, which also tend to change the orientation of their imino nitrogens from *cis* to *trans* upon activation. In addition, the polymerization behavior of these alkylphenyl-substituted titanium complexes was compared with alkyl-substituted complexes bearing rather small (isopropyl) as well as sterically bulky (adamantyl) imino substituents.

Results and Discussion

Ligands and Complexes. Imine ligands **1**−**7** were prepared via a classical condensation reaction between aldehydes and amines (Scheme 1). As reported previously,[9] amines can be efficiently converted to salicylaldimines by simple mixing of salicylaldehyde and the corresponding aliphatic amine and heating overnight at 110 °C in the absence of solvent. Crude products from the syntheses were isolated with high yields as bright yellow powders, and according to ^{1}H NMR spectra, all of these salicylaldimines were pure as such.

Titanium dichloro complexes (**1-Ti**, **2-Ti**, and **3-Ti**) (Scheme 2) were synthesized via direct metalation of the ligand precursors **1**−**3** with $Ti(NMe_2)_4$, followed by replacement of the amido groups with chlorines using excess Me_3SiCl.[9,10] The intermediate

Scheme 1. Schematic Representation of Ligand Precursors 1−7



$L_2Ti(NMe_2)_2$ and the resulting dichloro derivatives were formed with practically quantitative yields. The amido complexes possessed sharp singlet resonances in the ^{1}H NMR ($CDCl_3$) spectra for the imino protons, indicating the presence of the C_2-symmetric *cis* or *trans* isomer, solely. When converted to their dichloro analogues, **1-Ti** and **2-Ti** according to the calculations and crystallographic data obtain the *cis*-configuration,[11] while for **3-Ti**, the ^{1}H NMR spectra revealed three singlets with the intensity ratio 1:4:1, indicating a mixture of *cis* (singlet) and *cis,cis* (two singlets) isomers (2:1). After purification of the complex at slightly higher temperatures, the intensity ratio of *cis* and *cis,cis* isomers changed to 5:1 (NMR measured at room temperature), indicating different temperature-dependent stabilities for the isomers.

To gain a more detailed understanding of the fluxional behavior of **3-Ti**, dynamic ^{1}H NMR (C_6D_5Br) measurements were carried out. For these studies **3-Ti** was isolated and purified separately at low temperatures to increase the yield of the *cis,cis* isomer, the ratio now being 1:2 for *cis* and *cis,cis* isomers. In the spectrum of **3-Ti** at room temperature there are three equal size resonances arising from CH═N ligand protons together with an aromatic signal in the same region (7.65 ppm) (Figure 1). The imine proton signals at 7.81 and 7.66 ppm can be assigned to the *cis,cis* configuration (C_1-symmetry), while the third imino signal at 7.73 ppm can be assigned to the *cis* configuration (C_2-symmetry). When the temperature increases, the signals due to the *cis,cis* imino protons shift closer to the signal at 7.73 ppm (C_2-symmetric complex), but the coalescence point was not reached up to 75 °C, which was the highest possible temperature for these measurements. However, in the purification process the temperature of the solution was always increased above 80 °C, leading to a higher yield of the *cis* isomer at the expense of the *cis,cis* isomer. Although the coalescence point was not reached in these measurements, it is clear that at high temperatures there is a chance for the *cis,cis* isomer to be converted to the *cis* isomer.

The titanium complexes bearing ligands **4**, **5**, and **7**, i.e., those without the *tert*-butyl substituent next to the phenol group, were most efficiently synthesized via silylation of the ligand precursors using 1,1,1,3,3,3-hexamethyldisilazane followed by reaction with $TiCl_4$. This method gave nearly quantitative yields of the desired titanium complexes **4-Ti**, **5-Ti**, and **7-Ti** (Scheme 2).[9,12] These titanium complexes can also be prepared simply by the

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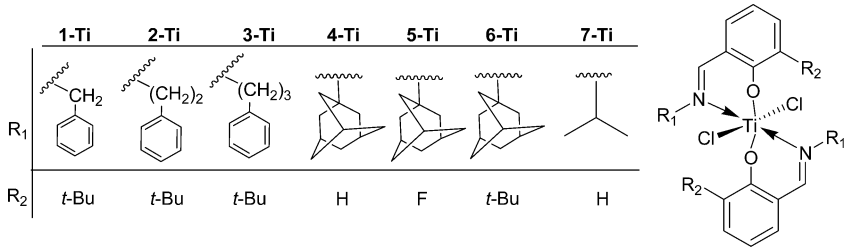
(11) NOE measurements were carried out with complex **1-Ti** to find out whether the singlet imine resonance is arising from the *cis* or *trans* isomer. In both isomers there is a NOE effect between the benzyl CH_2 group and the phenoxy *tert*-butyl group. According to the modeling, in the *cis* isomer the distance for the NOE is shorter (∼2.5 Å) than for the *trans* isomer (∼3.2 Å). The NOE effect with two mixing time (300 and 500 ms) values gave a distance close to 2.4 Å, which supports the *cis* configuration.

Scheme 2. Schematic Representation of the Catalyst Precursors Studied Herein[a]



[a] Complexes having nitrogens in a *cis* configuration (**1-Ti**−**4-Ti**) and complexes having a *trans* configuration (**5-Ti**−**7-Ti**) according to HF calculations (Table 3) are shown.

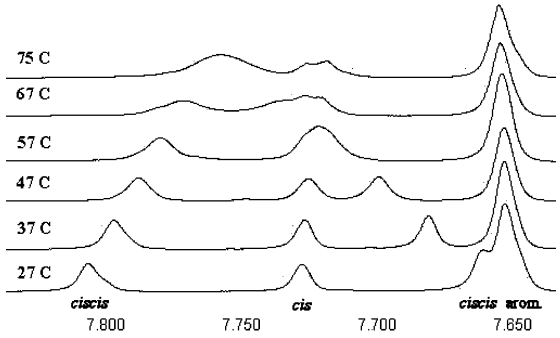


Figure 1. ^{1}H NMR spectrum of complex **3-Ti** shown at ambient and higher temperatures.

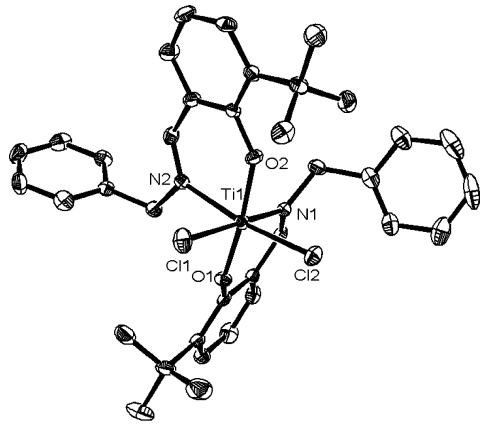


Figure 2. ORTEP plot of **1-Ti** with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms are removed for clarity.

combination of 2 molar equiv of the neutral salicylaldimines with titanium tetrachloride. This method was especially applicable for the most sterically bulky ligand **6**, and the complex **6-Ti** was quantitatively formed (Scheme 2). The solubility of complexes **4-Ti**−**7-Ti** in common deuterated solvents was very poor, and as a result ^{13}C spectra with satisfactory resolution could not be obtained.

Red crystals of complex **1-Ti** suitable for X-ray determination were grown at room temperature from a saturated toluene solution (Figure 2). The X-ray data showed that the titanium center is located in the plane of the N_2Cl_2 core, and the *trans* orientation of the phenoxy oxygens with the O−Ti−O bond angle of 168.48° (Table 1 and Table 2) leads to a distorted octahedral coordination. The chlorides have a *cis* orientation with a Cl−Ti−Cl bond angle of 96.85° and almost equivalent bond lengths (2.30 and 2.31 Å). In general, the bond distances

Table 1. Crystallographic Data for Complex 1-Ti

chemical formula	$C_{36}H_{40}Cl_2N_2O_2Ti$
fw	651.50
space group	$P2_1/c$
a, Å	10.238(2)
b, Å	13.299(1)
c, Å	24.412(4)
α, deg	90
β, deg	90.371(8)
γ, deg	90
V, Å^3	3323.8(9)
d_{calc}, g cm^{-3}	1.302
Z	4
μ, mm^{-1}	0.452
λ, Å	0.71073
T, K	173(2)
R^a	0.0544
$R_w{}^b$	0.1012

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$ for observed reflections [$I > 2\sigma(I)$]. [b] $R_w = \{\sum[w(F_o^2 - F_c^2)]/\sum[w(F_o^2)^2]\}^{1/2}$ for all data.

Table 2. Selected Structural Parameters for Complex 1-Ti

bond lengths, Å (exptl)		bond angles, deg (exptl)	
Ti−Cl1	2.311(1)	O−Ti−O	168.48(7)
Ti−Cl2	2.303(1)	O2−Ti−N2	81.37(8)
Ti−N1	2.187(2)	O1−Ti−N2	88.06(8)
Ti−N2	2.247(2)	O2−Ti−N1	92.35(8)
Ti−O1	1.873(2)	O1−Ti−N1	82.01(8)
Ti−O2	1.850(2)	O1−Ti−Cl1	91.25(5)
N2−C32	1.499(3)	O2−Ti−Cl1	93.20(6)
O1−C1	1.339(3)	N1−Ti−Cl2	89.96(6)
O2−C21	1.348(3)	N2−Ti−Cl2	171.80(6)
N1−C11	1.299(4)	N−Ti−N	84.38(7)
N1−C12	1.489(4)	N2−Ti−Cl1	89.42(5)
N2−C31	1.296(3)	N1−Ti−Cl1	170.97(6)
		Cl−Ti−Cl	96.85(3)

and angles resemble the ones earlier reported for bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride.[7g]

Correlation between Complex Structure and Polymerization Behavior. There are five different possible coordination geometries for bis(salicylaldiminato)titanium dichloride complexes, three of which have chlorides in *cis* positions and are therefore considered as suitable catalyst precursors for olefin polymerization.[5e,6b] In the first of these catalytically active conformations, the imine nitrogens are in *cis* positions, while the oxygens have *trans* orientations (Scheme 3, *cis*). In another conformation both the nitrogens and the oxygens have *cis* orientations (Scheme 3, *cis*,*cis*), while in the third the nitrogens occupy *trans* positions and the oxygens occupy *cis* positions (Scheme 3, *trans*). All of these isomers have been previously observed in X-ray studies for (phenoxyimino)$_2$TiCl$_2$ complexes.[6,13] The remaining two geometries are related to complexes having a large Cl−Ti−Cl angle (close to 180°) and are

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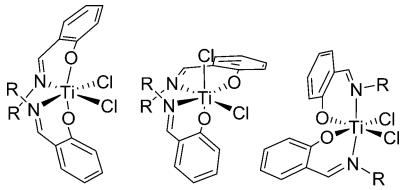
Scheme 3. Schematic Representation of Different Coordination Geometries for Octahedral Dichloro Complexes Having Chlorides in *cis* Form[a]



cis *ciscis* *trans*

In the *cis* isomer the imino nitrogens are in a *cis* while the phenoxy oxygens are in a *trans* configuration. In *cis*,*cis* both the nitrogens and the oxygens have a *cis* orientation, and in the *trans* isomer the nitrogens are in a *trans* while the oxygens are in a *cis* configuration.

Table 3. Relative Stabilization Energies (E_{Rel}) in kJ/mol of the Dichloro Complexes (1-Ti−7-Ti), $E_{Rel}(Cl_2)$, and Their Cationic Forms, $E_{Rel}(Ti^+Me)$, Including Different Isomeric Structures[a]

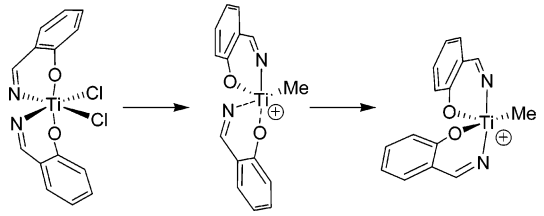
complex	$E_{Rel}(Cl_2)$	$E_{Rel}(Ti^+Me)$
1-Ti_*cis*	**−4**	0
1-Ti_*cis*,*cis*	−1	−17
1-Ti_*trans*	0	**−49**
2-Ti_*cis*	**−3**	0
2-Ti_*cis*,*cis*	2	−22
2-Ti_*trans*	0	**−45**
3-Ti_*cis*	**−1**	0
3-Ti_*cis*,*cis*	4	7
3-Ti_*trans*	0	**−16**
4-Ti_*cis*	**−2**	**0**
4-Ti_*cis*,*cis*	21	47
4-Ti_*trans*	0	2
5-Ti_*cis*	17	**0**
5-Ti_*cis*,*cis*	39	82
5-Ti_*trans*	**0**	**0**
6-Ti_*cis*	8	**−5**
6-Ti_*cis*,*cis*	9	2
6-Ti_*trans*	**0**	0
7-Ti_*cis*	3	**0**
7-Ti_*cis*,*cis*	14	61
7-Ti_*trans*	**0**	**0**

[a] The most stable isomer has been marked. In calculations the *trans* isomer of each catalyst precursor has been chosen as a point of reference. See Scheme 3 for the definition of different coordination geometries.

known for complexes bearing salen-type Schiff base ligands.[4,5b] The presence of this large Cl−Ti−Cl angle is apparently accountable for the low activities of catalysts with these geometries in α-olefin polymerization, and hence they have been omitted from the ab initio calculations.

Geometry prediction of aryl-substituted phenoxyimino complexes using HF calculations has been successfully utilized in earlier studies.[9] Similar stabilization energy values for the different isomers can be obtained using DFT; however the structures calculated using HF are finalized faster. HF calculations are important for resolution of the geometries of the complexes synthesized herein, as only one of them (complex **1-Ti**) could be determined by single-crystal X-ray measurements. The geometry of the X-ray crystal structure obtained for complex **1-Ti** is in good agreement with the HF-calculated one (Table 3). It can be seen from the calculated data that the stabilization energies of the three different isomers of complex **1-Ti** are quite close to each other (Table 3), the *cis* configuration being only 3 kJ/mol more stable than the corresponding *cis*,*cis* geometry. In the case of complex **3-Ti**, which possesses more than one geometry in solution, the calculated energy difference between the *cis* and *trans* isomers was only 1 kJ/mol. The structures of the titanium dichloro complexes studied herein (**1-Ti**−**7-Ti**) can be divided into two groups according to their

Scheme 4. Schematic Representation of the Activation Procedure of the Bis(salicylaldiminato) Titanium Dichloride Complex Starting from a *cis* Orientation and Ending with the Cationic Complex with a *trans* Orientation (1-Ti−3-Ti)



coordination geometries as predicted by ab initio calculations: complexes **1-Ti**−**4-Ti** have *cis* while complexes **5-Ti**, **6-Ti**, and **7-Ti** have *trans* configurations.

Observations in previous work have shown that knowledge of the geometry of the dichloro complex for aryl-substituted bis(salicylaldiminato)titanium catalysts does not necessarily allow ethene polymerization behavior for the corresponding catalysts to be reliably predicted.[9] According to these studies, the relative stabilization energies of the different isomers are changed markedly when the complexes are activated. This may lead to a change in the stability order for the isomers. The alkylphenyl-substituted catalyst precursors (**1**−**3**)**-Ti** have a tendency to change their coordination sphere by moving the imine nitrogens from the *cis* to the *trans* position upon activation (Scheme 4), as was the case for the most active bis(phenoxyanilinato)titanium catalysts.[9] Since the geometry of the neutral complexes has a tendency to change upon MAO activation, the structure of the cationic species is required before any detailed structure−polymerization correlations can be made.

The benzyl group as a substituent at the imine nitrogen is interesting, as it is capable of rotation and therefore can provide substantial steric shielding.[14] However, as shown with unbridged metallocene catalysts, benzyl substitution can retard the catalytic activity via coordination from the *ortho*-carbon of the phenyl ring to the cationic metal center.[15] The solid-state structure of **1-Ti** shows that the benzyl substituents point outward from the titanium center as a result of the *cis* geometry (Figure 2). According to calculations, the *trans* geometry is very close in energy to *cis* geometry (Table 3) and structural transformation from *cis* to *trans* brings the benzyl substituents into the vicinity of the titanium center, as shown in Figure 3. When activated, the *trans* conformer is the most stable and it gives the benzyl groups an opportunity to interact with the catalytically active, cationic metal center (Table 3). As a consequence, MAO-activated **1-Ti** revealed low activities in ethene polymerizations, giving a maximum of 40 $kg_{PE}/(mol_{Ti}\cdot h\cdot bar)$ at 80 °C (Table 4). In 3 bar ethene pressure two separable molar mass areas appeared in the GPC chromatograph, the lower of which decreases with increasing monomer concentration. We assume that this particular phenomenon is linked to the benzyl substit-

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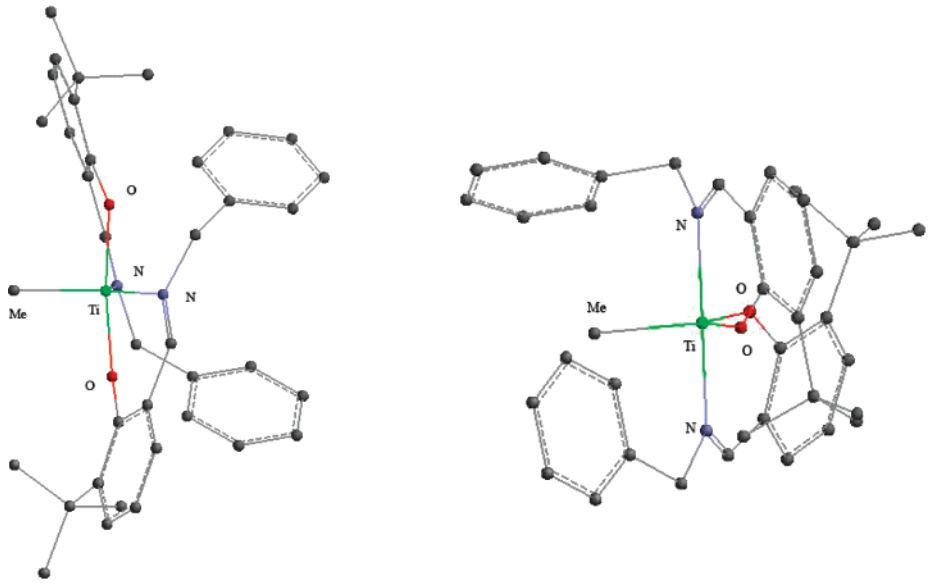

Figure 3. *Cis* (left) and *trans* (right) geometries of complex **1-Ti** calculated by the HF-method at the 3-21G* level.

Table 4. Selected Ethene Polymerization Results with Catalysts (1-Ti−7-Ti) after MAO Activation[a]

run	complex	cat. (μmol)	m (g)	T_p (°C)[b]	p (bar)[c]	activity[d]	M_w (kg/mol)	M_w/M_n	T_m (°C)[e]
1	**1-Ti**	10	0.03	60	3	1	600/8	2.1/1.7	135
2	**1-Ti**	10	0.16	40	5	4	45	1.8	135
3	**1-Ti**	10	0.155	60	5	4	740/10	2.2/1.4	137
4	**1-Ti**	10	1.58	80	5	40	230/4	1.9/2.0	139
5	**1-Ti**	10	0.45	60	10	6	790/6	2.0/2.4	135
6	**2-Ti**	5	5.58	60	3	1120	520	2.1	136
7	**2-Ti**	5	5.81	40	5	700	580	2.2	137
8	**2-Ti**	5	9.52	60	5	1140	435	2.2	136
9	**2-Ti**	5	10.33	80	5	1240	375	1.9	136
10	**2-Ti**	2.5	7.25	60	10	1740	220	2.0	136
11	**3-Ti**	5	4.94	60	3	990	160	2.1	137
12	**3-Ti**	5	4.51	40	5	540	160	2.1	138
13	**3-Ti**	5	7.39	60	5	890	95	2.8	136
14	**3-Ti**	5	1.87	80	5	220	120	2.1	135
15	**3-Ti**	5	7.05	60	10	850	140	2.0	134
16	**4-Ti**	20	1.28	60	5	20	400	21.8	137
17	**5-Ti**	10	5.03	60	5	130	710	20.9	135
18	**6-Ti**	10	1.09	60	5	30	950	3.5	140
19	**7-Ti**	10	0.06	60	3	3	605	4.3	141
20	**7-Ti**	10	0.08	40	5	2	630	4.7	143
21	**7-Ti**	10	0.11	60	5	3	560	3.3	140
22	**7-Ti**	10	0.30	80	5	8	1130	3.5	138
23	**7-Ti**	10	0.38	60	10	5	720	3.4	143

[a] Polymerization conditions: [Al]/[Ti] = 2000, 200 mL of toluene, polymerization times **2-Ti** and **3-Ti**, 20 min; runs 10 and 15, 10 min; and **1-Ti** and **4-Ti**−**7-Ti**, 45 min. [b] Polymerization temperature. [c] Monomer pressure. [d] Activity in (kg PE)/(mol·[Ti]·h·bar). [e] Onset melting temperatures of the polyethenes after heating the samples to 230 °C and cooling again to 30 °C (cooling and heating rate 20 °C/min).

uents, which tend to block the active site at lower pressures. At higher ethene concentrations this trend fades away.

The catalyst **2-Ti**/MAO possesses an ethyl group that acts as a link between the phenyl group and the imine nitrogen. As shown in Figure 4, the energetically favored *anti*-staggered ethyl spacers force the phenyl rings away from the cationic metal center, thus reducing the possibility for metal−phenyl interactions. This small change in the ligand structure has a dramatic influence on catalytic activity. Activities as high as 1700 $kg_{PE}/(mol_{Ti}\cdot h\cdot bar)$ were observed, and the polymerization properties of the catalyst resemble those typical of single-center catalysts, e.g., metallocenes. The polydispersity values were around 2, and the molar mass obtained varied between 200 and 600 kg/mol. Catalytic activities were increased at elevated temperatures and pressures. A small decrease in molar mass was observed when the temperature was raised from 40 to 80 °C (Table 4). Further lengthening of the spacer between the imino nitrogen and the phenyl ring has a slightly deteriorating effect on catalytic activity. Average activities recorded for **3-Ti**/MAO bearing propylphenyl imino substituents were in the range 220−1100 $kg_{PE}/(mol_{Ti}\cdot h\cdot bar)$ and were dependent on the polymerization temperature. This catalyst also produced unimodal PE with narrow polydispersities, as is typical for single-center catalysts.

A series of alkyl-substituted complexes bearing either sterically bulky adamantyl or small isopropyl groups at the imine fragment were studied in order to illustrate the effect of alkyl phenyl substitution on the activity of the catalysts **2-Ti** and **3-Ti**. The adamantyl group was chosen to investigate whether bulky alkyl substituents have a major effect on the activity of these catalysts. Unlike the alkylphenyl-substituted complexes, **6-Ti** (adamantyl substituents) favors the *trans* geometry for the dichloro complex, while the *cis* geometry is preferred for its methyl cation (Table 2). In ethene polymerizations **6-Ti**/MAO showed low activities (below 10 $kg_{PE}/(mol_{Ti}\cdot h\cdot bar)$ in conjunction with broad molar mass distribution (MMD) values (3.4−4.7), indicating the multicenter behavior of the catalyst (Table

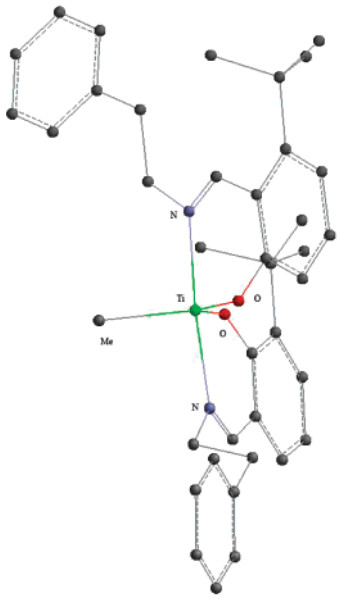

Figure 4. Calculated structure of the *trans* isomer of complex **2-Ti**. The most favorable conformer of the staggered ethyl linker forces the phenyl rings away from the metal center, thus reducing possible metal−phenyl interactions and increasing the steric protection of the cationic metal center.

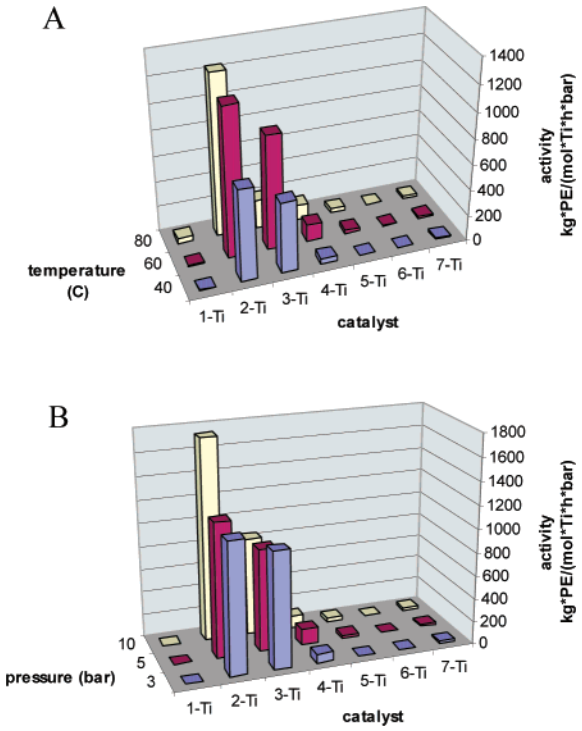

Figure 5. (a) Activities of the catalysts (**1-Ti**−**7-Ti**)/MAO at different temperatures in ethene polymerization at 5 bar. (b) Activities of the catalysts (**1-Ti**−**7-Ti**)/MAO at different pressures in ethene polymerization at 60 °C.

4). To reduce the steric hindrance around the catalytic metal center, the *tert*-butyl group at the 3-position of the phenoxy group was replaced by an electron-withdrawing fluorine substituent. As a result of this change **5-Ti** favors the *trans* geometry, both in the dichloro as well as in the cationic form. However, the average polymerization activities are only slightly improved, being below 40 $kg_{PE}/(mol_{Ti}\cdot h\cdot bar)$ at all polymerization conditions. The catalyst **4-Ti**, without a substituent at the 3-position, gave the highest activities in the adamantyl series (below 130 $kg_{PE}/(mol_{Ti}\cdot h\cdot bar)$ and produced clearly bimodal PE. The isopropyl group, as a model for small alkyl substituents at the imine nitrogen, was also studied. This catalyst **7-Ti** showed low activities (less than 30 $kg_{PE}/(mol_{Ti}\cdot h\cdot bar)$) and produced multimodal MMD at all polymerization conditions. Polymerization activities for (**1**−**7**)**-Ti** as a function of temperature and monomer pressure are summarized in Figure 5.

Conclusions

Upon activation with MAO, the alkyl-substituted bis(salicylaldiminato) catalysts **1-Ti**−**7-Ti** displayed a range of catalytic activities [3−1700 $kg_{PE}/(mol_{Ti}\cdot h\cdot bar)$] in ethene polymerization. The polymerization results strongly suggest that alkyl substitution at the imino nitrogen atoms has an essential role in determining the catalytic properties. The most active catalysts were **2-Ti** and **3-Ti**, both of which contain alkylphenyl substituents. When activated, these bis(salicylaldiminato)$TiCl_2$ complexes tend to change the relative coordination of the phenoxyimine ligands from *cis* to *trans*, as seen previously with moderately active phenyl-substituted bis(salicylaldiminato) catalysts.[9] Even though there is no unambiguous explanation for the observed structure−activity relationship, the *trans* configuration of imine nitrogens leads to an arrangement of imine substituents that provides improved steric protection for the cationic metal center, which in turn might lead to increased activities. Although the cation of **7-Ti** may adopt the *trans* configuration, the presence of sterically small imine substituents increases the likelihood of side-reactions[16] detrimental for catalytic activities. According to HF calculations, catalysts bearing sterically bulky adamantyl substituents (**4-Ti**, **5-Ti**, and **6-Ti**) do not undergo the *cis*-to-*trans* transformation, which was observed with the alkylphenyl-substituted catalysts **1-Ti**−**3-Ti**. These may be the reasons for the observed lower activities of **4-Ti**−**7-Ti**. The alkylphenyl substituents introduced here appear to possess both the geometry and steric properties that lead to highly active and thermally stable alkyl-substituted bis(salicylaldiminato) catalysts.

Experimental Section

General Comments. All organometallic syntheses were performed under argon atmosphere using Schlenk techniques. Toluene (HPLC grade) was dried and purified by refluxing over sodium and benzophenone followed by distillation under an argon atmosphere. Dichloromethane (CH_2Cl_2) was dried and purified over CaH_2 by refluxing for 4 h followed by distillation. Toluene was stored over sodium flakes under an argon atmosphere. Salicylaldehyde (Fluka), 3-fluorosalicylaldehyde (Aldrich), 3-tertbutylsalicylaldehyde (Aldrich), benzylamine (Aldrich), 2-phenylethylamine (Aldrich), 3-phenyl-1-propylamine (Aldrich), adamantylamine (Aldrich), 1,1,1,3,3,3-hexamethyldisilazane (Aldrich), tetrakis(dimethylamino)titanium (Aldrich), and $TiCl_4$ (Riedel-de Haën) were used as received, methylaluminoxane (MAO, 30 wt % solution in toluene) was purchased from Borealis Polymers Oy (Finland).

^1H and ^{13}C NMR spectra were collected on a Varian Gemini 2000 (200 MHz). Chemical shifts were referenced with respect to $CHCl_3$. EI mass spectra were acquired using a JEOL-SX102 instrument. DSC measurements (melting point) were performed

(16) Possible side-reactions of the activated species in polymerization conditions are extensively studied for metallocene catalysts. (a) *Ziegler Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H.-H., Eds.; Springer-Verlag: Berlin, 1995. (b) Bryliakov, K. P.; Kravtsov, E. A.; Pennington, D. A.; Lancaster, S. J.; Bochmann, M.; Brintzinger, H.-H.; Talsi, E. P. *Organometallics* **2005**, *24*, 5660−5664. For reviews see refs 2b−d.

using a Perkin-Elmer DSC-2, calibrated with indium (temperature scanning 20 °C/min). The scan area was from 25 to 232 °C. Mass average molar mass (M_w), number average molar mass (M_n), and molar mass distribution (MMD, M_w/M_n) of the polyethylene samples were determined by GPC (Waters Alliance GPCV 2000, high-temperature gel chromatographic device). The GPC had HMW7, 2*HMWGE, and HMW2 Waters Styrogel columns. Measurements were carried out in 1,2,4-trichlorobenzene (TCB) at 160 °C relative to polyethylene (PE) standards. 2,6-Di-*tert*-butyl-4-methylphenol was used as a stabilizer.

Synthesis of Compounds 1−7. Benzyl-*N*-(3-*tert*-butylsalicylaldimine) (1). *tert*-Butylsalicylaldehyde (2.5 mL, 0.0146 mol) and benzylamine (1.59 mL, 0.0146 mol) were mixed in a 100 mL round-bottom flask. The reaction mixture was heated to 120 °C and stirred over night. The crude product (yellow powder) was recrystallized from propanol (3.82 g, 98%). Anal. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 81.00; H, 7.02; N, 5.09. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H 13.96 (s, OH), 8.46 (s, CNH), 7.42−7.13 (m, 7H, H-Ar), 7.17, 7.13 (d, 1H, H-Ar), 6.83 (t, 1H, H-Ar), 4.81 (2H, CH_2), 1.44 (s, 9H, CH_3). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C 166.47 (CNH), 160.61 (COH), 138.44 (Ar), 137.62 (Ar), 129.99 (Ar), 129.69 (Ar), 128.84 (Ar), 128.09 (Ar), 127.52 (Ar), 118.89 (Ar), 118.05 (Ar), 63.38 (CH_2), 35.04 (CH), 29.55 (CH_3). MS(EI) *m*/*z*: 267 with appropriate isotope ratio for $C_{14}H_{13}NO^+$.

2-Phenylethyl-*N*-(3-*tert*-butylsalicylaldimine) (2) was prepared by a similar method to that described for **1**. *tert*-Butylsalicylaldehyde (2.5 mL, 0.0146 mol) and 2-phenylethylamine (1.84 mL, 0.0146 mol) were used to obtain **2** (4.02 g, 98%). Anal. Calcd for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98. Found: C, 80.18; H, 8.44; N, 4.76. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H 14.08 (s, OH), 8.26 (s, CNH), 7.38−7.22 (m, 6H, H-Ar), 7.09, 7.05 (d, 1H, H-Ar), 6.80 (t, 1H, H-Ar), 3.84 (t, 2H, NCH_2), 3.04 (t, 2H, Ar-CH_2), 1.46 (s, 9H, CH_3). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C 165.98 (CNH), 160.71 (COH), 139.52 (Ar), 137.58 (Ar), 129.76 (Ar), 129.47 (Ar), 129.09 (Ar), 128.69 (Ar), 126.54 (Ar), 118.80 (Ar), 117.88 (Ar), 61.18 (NCH_2), 37.73 (CMe_3) 35.04 (Ar-CH_2), 29.55 (CH_3). MS(EI) *m*/*z*: 281 with appropriate isotope ratio for $C_{15}H_{15}NO^+$.

3-Phenylpropyl-*N*-(3-*tert*-butylsalicylaldimine) (3) was prepared by a similar method to that described for **1**. *tert*-Butylsalicylaldehyde (2.5 mL, 0.0146 mol) and 3-phenylpropylamine (2.08 mL, 0.0146 mol) were used to obtain **3** (4.22 g, 98%). Anal. Calcd for $C_{20}H_{25}NO$: C, 81.36; H, 8.53; N, 4.74. Found: C, 81.58; H, 8.73; N, 4.44. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H 14.15 (s, OH), 8.34 (s, NCNH), 7.33−7.07 (m, 7H, H-Ar), 6.82 (t, 1H, H-Ar), 3.61 (t, 2H, CNH), 2.76 (t, 2H, Ar-CH_2), 2.07 (sept, 2H, CCH_2C), 1.46 (s, 9H, CH_3). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C 165.84 (CNH), 160.78 (COH), 141.74 (Ar), 137.61 (Ar), 129.70 (Ar), 129.43 (Ar), 128.69 (Ar), 128.62 (Ar), 126.14 (Ar), 118.87 (Ar), 117.89 (Ar), 58.89 (CNH_2), 35.05 (CMe_3) 35.04 (Ar-CH_2), 32.49 (CH_2CCH_2), 29.55 (CH_3). MS(EI) *m*/*z*: 295 with appropriate isotope ratio for $C_{16}H_{17}NO^+$.

Adamantylsalicylaldimine (4) preparation has been described in the literature[17] and was prepared here with high yield by the method described for **1**. Salicylaldehyde (2.5 mL, 1.146 g/mL, 0.0235 mol) and 1-adamantylamine (3.55 g, 0.0235 mol) were mixed to obtain **4** (5.9 g, 98%). Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 80.27; H, 8.72; N, 5.26. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H 14.52 (s, OH), 8.32 (s, CNH), 7.21−7.32 (m, 2H, H-Ar), 6.79−7.32 (m, 2H, H-Ar), 2.18 (w, 3H, CH), 1.83 (w, 6H, CH_2), 1.73 (w, 6H, CH_2). MS(EI) *m*/*z*: 255 with appropriate isotope ratio for $C_{17}H_{21}NO^+$.

Adamantyl-*N*-(3-fluorosalicylaldimine) (5) was prepared by a similar method to that described for **1**. 3-Fluorosalicylaldehyde (1.0 g, 7.138 mmol) and 1-adamantylamine (1.08 g, 7.138 mmol) were mixed to obtain **5** (1.85 g, 95%). Anal. Calcd for $C_{17}H_{20}FNO$: C, 74.70; H, 7.37; N, 5.12. Found: C, 74.88; H, 7.79; N, 4.89. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ 15.17 (s, OH), 8.26 (s, CNH), 7.24−6.59 (H-Ar), 2.20 (w, 3H, CH), 1.89 (w, 6H, CH_2), 1.76 (w, 6H, CH_2). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C 159.21 (CF), 137.75 (Ar), 129.24 (Ar), 128.43 (Ar), 126.78 (Ar), 126.71 (Ar), 118.62 (Ar), 118.27 (Ar), 118.27 (Ar), 115.78 (Ar), 115.65 (Ar), 57.14 (CN), 42.98 (CH_2), 36.31 (CH), 29.46 (CH). MS(EI) *m*/*z*: 273 with appropriate isotope ratio for $C_{17}H_{20}FNO^+$.

Adamantyl-*N*-(3-*tert*-butylsalicylaldimine) (6) was prepared by a similar method to that described for **1**. 3-*tert*-Butylsalicylaldehyde (2.5 mL, 0.0146 mol) and 1-adamantylamine (2.21 g, 0.0146 mol) were mixed to obtain **6** (4.54 g, 100%). Anal. Calcd for $C_{21}H_{29}NO$: C, 80.98; H, 9.38; N, 4.50. Found: C, 80.62; H, 9.83; N, 4.27. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ 14.85 (s, OH), 8.35 (s, NCH), 7.29, 7.24 (d, 1H, H-Ar), 7.13, 7.10 (d, 1H, H-Ar), 6.79 (t, 2H, H-Ar), 2.20 (w, 3H, CH), 1.89 (w, 6H, CH_2), 1.76 (w, 6H, CH_2), 1.46 (s, 9H, CH_3). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C 161.66 (COH), 160.09 (CNH), 137.75 (Ar), 129.88 (Ar), 129.12 (Ar), 118.97 (Ar), 117.42 (Ar), 57.20 (CN), 43.25 (CH_2), 36.59 (CH_2), 35.03 (CH), 29.65 (CH_3), 29.58 (CH). MS(EI) *m*/*z*: 311 with appropriate isotope ratio for $C_{21}H_{29}NO^+$.

***N*-Isopropylsalicylaldimine (7)** was prepared according to the literature procedure.[18]

Synthesis of Complexes (1−7)-Ti. Bis(κ*N*,κ*O*-*N*-benzyl-3-*tert*-butylsalicylaldiminato)TiCl$_2$ (1-Ti). A precooled (−78 °C) toluene solution (40 mL) of **1** (2.67 g, 0.010 mol) was slowly added via a syringe to a precooled toluene solution (40 mL) of $Ti(NMe_2)_4$ (1.2 mL, 5 mmol). The reaction mixture was warmed to ambient temperature and stirred overnight. Quantitative formation of bis(κN,κO-*N*-benzyl-3-*tert*-butylsalicylaldiminato)$Ti(NMe_2)_2$ was observed. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H 7.70 (s, 2H, CNH), 7.44−7.17 (m, 12H, H-Ar), 6.95−6.90 (m, 2H, H-Ar), 6.67 (t, 2H, H-Ar), 4.41, 4.00 (d, 4H, CH_2), 3.36 (s, 12H, NCH_3), 1.60 (s, 18H, CH_3). MS (EI) *m*/*z*: 668 with appropriate isotope ratio for $C_{40}H_{52}N_4O_2Ti^+$. The amount of solvent was reduced to 40 mL, and an excess of trimethylsilylchloride (12.7 mL, 0.1 mol, 20 equiv) was added at ambient temperature. The reaction mixture was stirred overnight followed by refluxing for 2 h in toluene and removal of side-product residues at 70 °C under vacuum (3.25 g, 100%). Anal. Calcd for $C_{36}H_{40}Cl_2N_2O_2Ti$: C, 66.37; H, 6.19; N, 4.30. Found: C, 66.55; H, 6.61; N, 3.96. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H 7.74 (s, 2H, CNH), 7.74−6.85 (m, 16H, H-Ar), 5.00, 4.65 (d, 4H, CH_2). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 29 °C): δ_C 167.22 (CNH), 162.18 (CO), 139.60 (Ar), 138.23 (Ar), 136.52 (Ar), 134.15 (Ar), 133.30 (Ar), 130.92 (Ar), 129.66 (Ar), 129.54 (Ar), 129.10 (Ar), 128.69 (Ar), 126.03 (Ar), 125.48 (Ar), 121.33 (Ar), 63.95 (CH_2), 35.77 (CH), 30.37 (CH_3). MS (EI) *m*/*z*: 651 with appropriate isotope ratio for $C_{36}H_{40}Cl_2N_2O_2Ti^+$.

Bis(κ*N*,κ*O*-(2-phenylethyl)-*N*-3-*tert*-butylsalicylaldiminato)-TiCl$_2$ (2-Ti) was prepared by a similar method to that described for **1-Ti**. **2** (2.81 g, 0.010 mol) $Ti(NMe_2)_4$ (1.2 mL, 5 mmol) were used. Bis(κ*N*,κ*O*-2-phenylethyl-*N*-3-*tert*-butylsalicylaldiminato)Ti-$(NMe_2)_2$: ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H 7.95 (s, 2H, CNH), 7.52, 7.48 (d, 2H, H-Ar), 7.30−7.02 (m, 12H, H-Ar), 6.79 (t, 2H, H-Ar), 3.28 (s, 12H, NCH_3), 3.9−3.2 (m, 8H, CH_2), 1.55 (s, 18H, CH_3) ppm. Complex **2**: 3.39 g, 100%. Anal. Calcd for $C_{36}H_{40}Cl_2N_2O_2Ti$: C, 67.16; H, 6.53; N, 4.12; Found: C, 66.97; H, 6.66; N, 4.02. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H 7.64, 7.61 (d, 2H, H-Ar), 7.49 (s, 2H CNH), 7.40−6.80 (m, 14H, H-Ar), 4.00−3.90 (m, 4H, NCH_2), 3.60−3.40 (m, 4H, NCH_2), 3.15−2.95 (m, 4H, Ar-CH_2), 2.90−2.70 (m, 4H, Ar-CH_2), 1.63 (s, 18H, CH_3). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C 166.26 (CNH), 161.13 (CO), 139.53 (Ar), 138.24 (Ar), 137.84 (Ar), 134.10 (Ar),

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132.61 (Ar), 129.51 (Ar), 128.91 (Ar), 128.80 (Ar), 126.89 (Ar), 124.64 (Ar), 121.46 (Ar), 63.15 (NCH_2), 36.83 (Ar-CH_2) 35.41 (CMe_3), 30.13 (CH_3). MS(EI) *m/z*: 679 with appropriate isotope ratio for $C_{38}H_{44}Cl_2\ N_2O_2Ti^+$.

Bis(κ*N*,κ*O*-(3-phenylpropyl)-*N*-(-3-*tert*-butyl-salicylaldiminato)TiCl$_2$ (3-Ti) was prepared by a similar method to that described for **1-Ti**. **3** (2.95 g, 0.010 mol) and $Ti(NMe_2)_4$ (1.2 mL, 5 mmol) were used. Bis(κ*N*,κ*O*-3-phenyl-1-propyl-*N*-3-*tert*-butylsalicylaldiminato)$Ti(NMe_2)_2$: ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H 7.98 (s, 2H, CNH), 7.53, 7.49 (d, 2H, H-Ar), 7.26−7.09 (m, 12H, H-Ar), 6.96, 6.93 (d, 2H, H-Ar), 6.80 (t, 2H, H-Ar) 3.26 (s, 12H, NCH_3), 2.95−1.2 (m, 12H, CH_2), 1.63 (s, 18H, CH_3). The complex **3-Ti** (3.53 g, 100%): Anal. Calcd for $C_{40}H_{48}Cl_2\ N_2O_2Ti$: C, 67.90; H, 6.84, N 3.96. Found: C, 68.09; H, 7.19, N 3.79. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ (*cis*,*cis*) 8.20 (s, CNH), (*cis*) 8.02 (s, CNH), (*cis*,*cis*) 7.84 (s, CNH), 7.65, 7.62 (d, 2H, H-Ar), 7.30−7.11 (m, 10H, H-Ar), 7.02 (t, 2H, H-Ar), 6.86, 6.83 (d, 2H, H-Ar), 3.70−3.50 (m, 4H, NCH_2), 2.45−2.20 (m, 4H, Ar-CH_2), 1.9−1.7 (m, 4H, CCH_2C), 1.63 (s, 18H, CH_3) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C 169.37 (CNH), 166.76 (CNH), 166.55 (CNH), 162.45 (CO), 162.30 (CO), 161.71 (CO), 142.11 (Ar), 141.27 (Ar), 141.10 (Ar), 139.92 (Ar), 138.48 (Ar), 138.43 (Ar), 134.66 (Ar), 133.74 (Ar), 133.68 (Ar), 133.35 (Ar), 133.33 (Ar), 132.80 (Ar), 129.80 (Ar), 129.41 (Ar), 129.24 (Ar), 129.21 (Ar), 129.18 (Ar), 129.16 (Ar), 129.06 (Ar), 128.99 (Ar), 128.93 (Ar), 128.90 (Ar), 126.96 (Ar), 126.80 (Ar), 126.66 (Ar), 126.59 (Ar), 125.54 (Ar), 124.88 (Ar), 122.59 (Ar), 122.08 (Ar), 65.57 (NCH_2), 62.02 (NCH_2), 61.93 (NCH_2), 35.92 (CMe_3), 35.75 (CMe_3), 35.66 (CMe_3) 34.10 (Ar-CH_2), 33.98 (Ar-CH_2), 33.80 (Ar-CH_2), 33.64 (CH_2-CCH_2), 33.26 (CH_2CCH_2), 33.02 (CH_2CCH_2), 30.60 (CH_3), 30.46 (CH_3), 30.32 (CH_3). MS(EI) *m/z*: 706 with appropriate isotope ratio for $C_{40}H_{48}Cl_2\ N_2O_2Ti^+$.

Bis(κ*N*,κ*O*-*N*-adamantylsalicylaldiminato)TiCl$_2$ (4-Ti). Hexamethylsilazane (3.0 mL, 14.22 mmol) was added to solution of **4** (2.7 g, 10.60 mmol) in dry CH_2Cl_2 (30 mL) via a syringe. The reaction mixture was stirred overnight. The silylated phenoxyimine was isolated as yellow, viscose liquid. The excess of hexamethylsilazane and byproducts were evaporated under vacuum at 50 °C. The silylated compound **4**: 3.47 g, 100%. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ 8.61 (s, CNH), 7.96, 7.92 (d, H-Ar), 7.28, 7.27 (d, H-Ar), 7.00 (t, H-Ar), 6.83, 6.79 (d, H-Ar), 2.18 (w, 3H, CH), 1.81 (w, 6H, CH_2), 1.75 (w, 6H, CH_2), 0.29 (s, 9H, $SiMe_3$) ppm. The precooled (−78 °C) silylated **4** (3.47 g, 10.60 mmol) in toluene (40 mL) was slowly added via syringe to a precooled solution of toluene (20 mL) and $TiCl_4$ (0.58 mL, 5.30 mmol). The reaction mixture was warmed to ambient temperature and stirred overnight. Both toluene and the trimethylsilylchloride formed were removed under vacuum at 50 °C. Complex **4-Ti**: 3.32 g, 100%. Anal. Calcd for $C_{34}H_{40}Cl_2\ N_2O_2Ti$: C, 65.08; H, 6.43; N, 4.46. Found: C, 65.21; H, 6.54; N, 4.31. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ 8.05 (s, 2H, CNH), 7.60−6.80 (m, 8H, H-Ar), 2.45−1.40 (m, 30H, adamantyl) ppm. MS(EI) *m/z*: 626 with approppriate isotope ratio for $C_{34}H_{40}Cl_2N_2O_2Ti^+$.

Bis(κ*N*,κ*O*-*N*-adamantyl-3-fluorosalicylaldiminato)TiCl$_2$ (5-Ti) was prepared by a similar method to that described for **4-Ti**. Hexamethylsilazane (3.0 mL, 14.22 mmol), **5** (2.89 g, 10.60 mmol), and $TiCl_4$ (0.58 mL, 5.30 mmol) were used. The silylated compound **5** (3.66 g, 100%): ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ 8.61 (s, CNH), 7.96, 7.92 (d, H-Ar), 7.28, 7.27 (d, H-Ar), 7.00 (t, H-Ar), 7.75−6.85 (m, 3H, H-Ar), 2.18 (w, 3H, CH), 1.81 (w, 6H, CH_2), 1.75 (w, 6H, CH_2), 0.29 (s, 9H, CH_3) ppm. Complex **5-Ti**: 3.16 g, 90%. Anal. Calcd for $C_{34}H_{38}Cl_2F_2\ N_2O_2Ti$: C, 61.55; H, 5.77; N, 4.22. Found: C, 61.19; H, 5.46; N, 4.06. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ 8.63 (s, 2H, CNH), 7.10−6.80 (m, 6H, H-Ar), 2.46 (w, 6H, CH), 2.24 (w, 12H, CH_2), 1.74 (w, 12H, CH_2) ppm. MS(EI) *m/z*: 662 with appropriate isotope ratio for $C_{34}H_{38}Cl_2F_2\ N_2O_2Ti^+$.

Bis(κ*N*,κ*O*-*N*-adamantyl-3-*tert*-butylsalicylaldiminato)TiCl$_2$ (6-Ti). A precooled (−78 °C) solution of **6** (3.15 g, 0.010 mol) in toluene (40 mL) was slowly added via syringe to a solution of $TiCl_4$ (5 mmol, 0.55 mL) precooled (−78 °C) in toluene (40 mL). The reaction mixture was warmed to ambient temperature and stirred overnight. The product precipitated out and was isolated from the liquid phase (3.69 g, 100%). Anal. Calcd for $C_{42}H_{56}Cl_2N_2O_2Ti$: C, 68.02; H, 7.63; N, 3.79. Found: C, 67.36; H, 7.63; N, 3.80. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ 8.50 (s, 2H, CNH), 8.02, 7.97 (d, 2H, H-Ar), 7.63−7.00 (m, 4H, H-Ar), 2.02 (b, 6H, CH), 1.82 (s, 12H, CH_2), 1.58 (b, 12H, CH_2), 1.46 (s, 18H, CH_3). MS(EI) *m/z*: 738 with appropriate isotope ratio for $C_{42}H_{56}Cl_2N_2O_2Ti^+$.

Bis(κ*N*,κ*O*-*N*-isopropylsalicylaldiminato)TiCl$_2$ (7-Ti)[19] was prepared by a similar method to that described for **4-Ti**. Hexamethylsilazane (3.0 mL, 14.22 mmol), **7** (1.73 g, 10.60 mmol) (2.49 g, 100%), and $TiCl_4$ (0.58 mL, 5.30 mmol) were used. The silylated compound **7** (2.7 g, 10.60 mmol): ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ 8.69 (s, CNH), 7.914, 7.91 (d, H-Ar), 7.28, 7.72 (d, H-Ar), 6.99 (t, H-Ar), 6.83, 6.79 (d, H-Ar), 3.54 (s, Me_2CH), 1.28, 1.25 (d, 6H, CH_3), 0.29 (s, 9H, $SiMe_3$) ppm. MS(EI) *m/z*: 235 with appropriate isotope ratio for $C_{13}H_{21}NOSi^+$. Complex **7-Ti**: 2.34 g, 100%. Anal. Calcd for $C_{38}H_{44}N_2O_2TiCl_2$: C, 54.20; H, 5.46; N, 6.32. Found: C, 54.05; H, 5.79; N, 6.46. MS(EI) *m/z*: 443 with appropriate isotope ratio for $C_{20}H_{24}N_2O_2TiCl_2^+$.

Polymerization Experiments. Polymerizations were performed in a Büchi 1.0 L stainless steel autoclave equipped with Julabo ATS-3 and Lauda RK 20 temperature-controlling units. Toluene (200 mL) and the cocatalyst (MAO) were introduced to the argon-purged autoclave reactor. Once the polymerization temperature was reached, the reactor was charged with ethylene to the appropriate pressure. Polymerizations were initiated by injecting 20 mL of the catalyst precursor solution (2.5−20 μmol solution in toluene) into the reactor. Mechanical stirring was applied at a speed of 800 rpm. During the polymerizations the partial pressure of ethylene and the temperature were maintained constant. Ethylene consumption was measured using a calibrated mass flow meter and monitored together with the autoclave temperature and pressure. The polymerization reaction was terminated by pouring the contents of the reactor into methanol, which was then acidified with a small amount of concentrated hydrochloride acid. The solid polyethylene was collected by filtration, washed with methanol, and dried overnight at 70 °C.

X-ray Crystallographic Study. Crystallographic data of compound **1-Ti** were collected with a Nonius KappaCCD area-detector diffractometer at 173(2) K using Mo Kα radiation (graphite

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monochromator), 0.71073 Å. Data reduction: COLLECT.[20a] Absorption correction: SADABS.[20b] Structure solution: SIR 2002.[20c] Refinement: SHELX-97.[20d] Graphics: SHELXTL.[20e] All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were refined to calculated positions.

Theoretical Calculations. Geometry optimizations 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.[21,22] On the basis of 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; however these would certainly increase calculation times. Single-point MP2 calculations were performed to confirm the relative stabilization order of conformations of the studied titanium complexes. For single-point calculations, the basis set 6-31G* for C, H, O, and N and a generated basis set of equal level for Ti were used. The stabilization orders produced by both methods were generally in good agreement with each other. Geometry minima were confirmed by frequency calculations. All calculations were carried out by the Gaussian 03 program package.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM0610391

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