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Ethene Polymerization Behavior of MAO-Activated Dichloridotitanium Complexes Bearing Bi- and Tetradentate Salicylaldimine Derivatives

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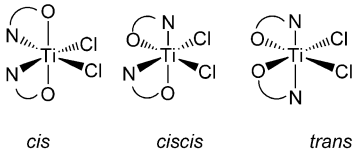
New chiral bridged tetradentate $(N_2O_2)Ti^{IV}Cl_2$-type complexes bearing dimethylbiphenyl (**1-Ti**–**3-Ti**) and previously published binaphthyl-bridged (**4-Ti**) complex were synthesized with high yields. This was achieved by treating the corresponding Schiff-base ligand (H_2L) precursors with $Ti(NMe_2)_4$, followed by conversion of these diamido complexes to $LTiCl_2$ derivatives by the addition of excess of Me_3SiCl. A series of unbridged titanium complexes **5-Ti**–**8-Ti** with similar substituents at the phenoxy group were studied and their polymerization properties, after methylaluminoxane (MAO) activation, compared with the above bridged complexes. It was found that the catalysts bearing chiral tetradentate biaryl-bridged salicylaldimine ligands produce multimodal polyethylene (PE) with low activity [below 10 $kg_{PE}/(mol_{Ti}\,h\,bar)$] while their unbridged analogues provide activities that are 10–1000 times greater under similar reaction conditions. The reasons for this dramatic difference in polymerization activities are discussed based on the stabilities of the different cationic species configurations.

Introduction

Group 4 metal-based bis(salicylaldiminato) dichlorido complexes are known for their high activities in ethene polymerisation upon activation with MAO.[1] In highly active titanium and zirconium complexes fluorinated-[1] or alkylphenyl[2] groups at the imine nitrogen and *t*Bu or cumyl substituents at the 3-position adjacent to the phenoxy oxygen are distinctive features. These highly active catalysts polymerize ethene with narrow polydispersity values typical for single-site catalysts. However, considerable number of bis(salicylaldiminato)Ti catalysts have low polymerization activities and tend to give multimodal polyethylene. According to our previous results, various active species in polymerization is linked to simultaneous presence of different structural isomers of catalysts.[3]

As shown before, substituents on the salicylaldiminato ligands have an effect on the geometry of the dichlorido complexes. Three different octahedral configurations have been determined by X-ray structure analysis.[4,5] In these solid-state structures, the imine nitrogen atoms as well as the phenoxy oxygens have either *cis*, *ciscis* or *trans* orientation towards each other while the chlorides adopt a *cis* orientation (Scheme 1).



Scheme 1. Octahedral configurations for bis(salicylaldiminato)-$TiCl_2$ complexes wherein chlorides occupy *cis* orientation. R can be any aromatic or aliphatic substituent. *cis* (*cis*-N, *trans*-O and *cis*-Cl, C_2 symmetry), *ciscis* (*cis*-N, *cis*-O and *cis*-Cl, C_1 symmetry) and *trans* (*trans*-N, *cis*-O and *cis*-Cl, C_2 symmetry) abbreviations are related to the orientation of imine nitrogen atoms in the complexes.

In solution, the dichloride complexes can have mixture of different coordination geometries and their relative ratios are dependent upon salicylaldiminato ligand substituents.[2,6,7]

Besides of substituents in salicylaldiminato ligands also co-ligands have an influence for the coordination geometries of the complexes and their relative ratios. This phenomenon is clearly observable when converting bis(salicylaldiminato)Ti amido complexes to corresponding chloride analogues.[2,7] According to the recent calculation results the coordination geometries can further change when dichloride complexes are activated with MAO. The relative stabilization energies of the cationic Ti isomers do not necessarily follow the same pattern as their corresponding neutral chloride analogues.[2] The change in geometry subsequent to activation and the magnitude of the change is dependent upon the ligand substituents as well as the applied reaction conditions. As a consequence solid-state structures of dichlorido complexes cannot be used to predict their po-

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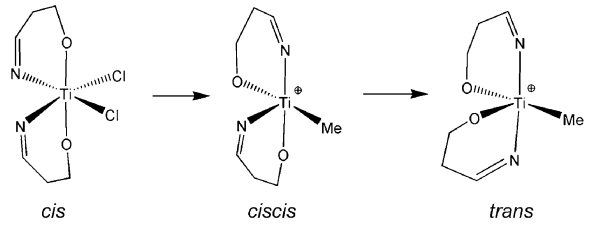
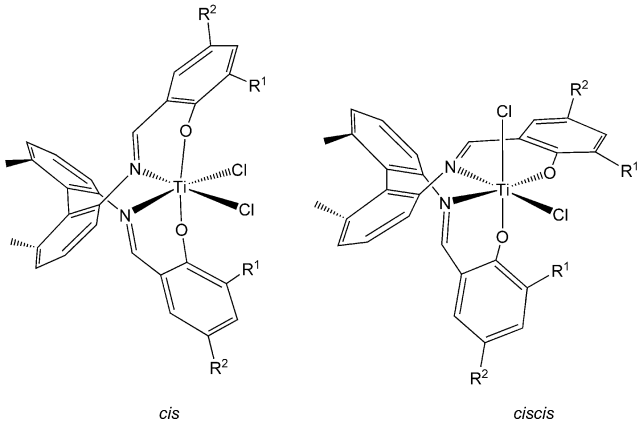
lymerization behavior. In fact, our previous results have demonstrated that the most active bis(salicylaldiminato) catalysts bearing alkyl[2] and aromatic[3] imino substituents are those complexes which tend to change the relative orientation of their imine nitrogen atoms from *cis* to *trans* upon activation (Scheme 2).



Scheme 2. Schematic representation of the plausible *cis* to *trans* change in complex configuration during the activation procedure. *cis* and *trans* abbreviations are related to the orientation of imine nitrogen atoms in complexes.

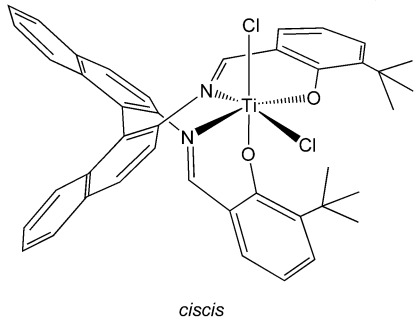
To further attest the benefit of the *cis* to *trans* change on catalytic activity, a series of biphenyl bridged (**1-Ti**–**3-Ti**, Scheme 3), binaphthyl bridged (**4-Ti**, Scheme 4) and unbridged Ti complexes (**5-Ti**–**8-Ti**, see Schemes 5 and 6) were studied to compare their polymerization properties after MAO activation. The bridging in **1-Ti**–**4-Ti** prevents any possible *cis* to *trans* isomerisation of the imino nitrogen atoms.



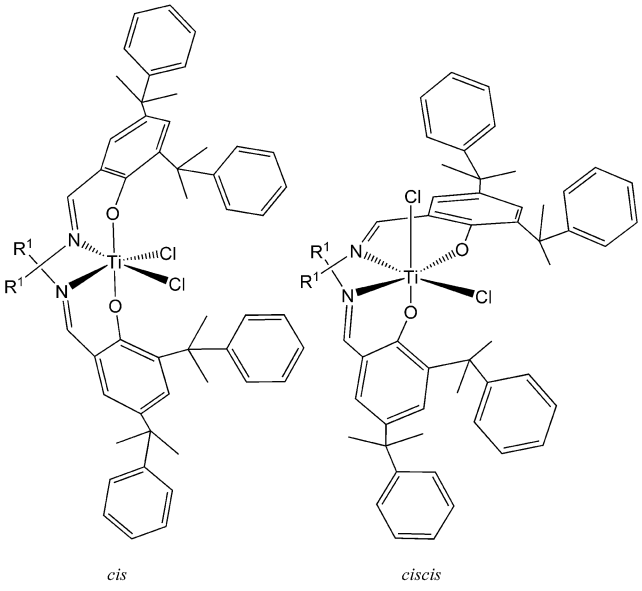
Scheme 3. The dimethylbiphenyl bridged titanium dichloride complexes (**1-Ti**–**3-Ti**) possess the *cis* or *ciscis* configuration or their combinations at room temp. in solution. **1-Ti** (R^1 = R^2 = H, *cis* and *ciscis* configurations in ratio of 1:4), **2-Ti** (R^1 = *tert*-butyl, R^2 = H, *ciscis* configuration) and **3-Ti** (R^1 = R^2 = cumyl, *cis* configuration).

The basic salen-type ligands, having an ethylene linkage between the imino nitrogen atoms, favour planar coordination with Group 4 metals which results in the chlorides being forced to adopt a *trans* (≈ 180°) orientation. These types of conformers are known to have low activities in α-olefin polymerisation.[8]

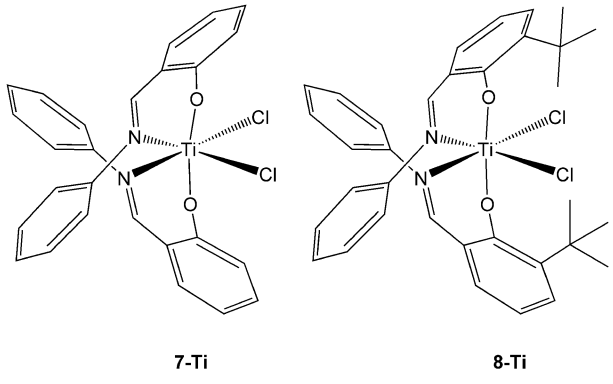
Therefore our interest was drawn towards the study of chiral tetradentate biaryl-iminophenolate ligand systems wherein the rigid biaryl bridge forces both the chlorides and



Scheme 4. The binaphthyl-bridged titanium dichloride complex **4-Ti** possesses the *ciscis* configuration in solution.



Scheme 5. In solution the unbridged complex **5-Ti** (R^1 = CH_2CH_2Ph) possesses both the *cis* and the *ciscis* configurations in ratio of 1:2 while complex **6-Ti** (R^1 = Ph) possesses *ciscis* configuration.



Scheme 6. Schematic presentation of complexes **7-Ti** and **8-Ti**.

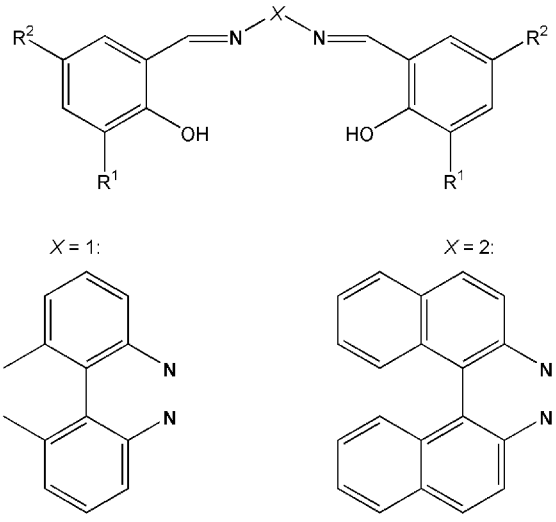
imino nitrogen atoms to occupy *cis* coordination sites in C_1 and C_2-symmetric complexes.[7,9,10] Intriguingly, despite of the attractive octahedral symmetry and similar substitution pattern with the most active bis(salicylaldiminato) catalysts

those with tetradentate ligands have only low activity in polymerization. It is also worth to notice, that in *ciscis*-type complexes the Ti–O, Ti–N, and Ti–Cl bond lengths and even O–Ti–O and Cl–Ti–Cl bond angles for bidentate and tetradentate phenoxy-iminotitanium(IV) complexes are very close to each other and therefore do not explain the dramatic difference in catalytic activity in ethene polymerization.[5,9]

Results and Discussion

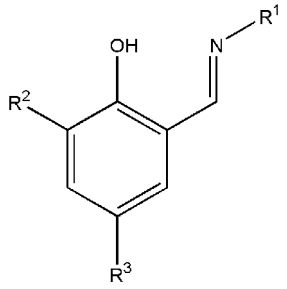
Preparation of Ligands and Complexes

As shown previously with *N*-(salicylidene)anilines,[2] the Schiff base condensation reaction occurs efficiently when carried out in toluene solution in round-bottomed flask at temperature above 100 °C. By this method three 6,6′-dimethylbiphenyl (**1**–**3**) and previously published binaphthyl-bridged ligand precursors (**4**) (Scheme 7) as well as 2-phenylethyl-*N*-(3,5-dicumylsalicylaldimine) (**5**) and phenyl-*N*-(3,5-dicumylsalicylaldimine) (**6**) (Scheme 8) were obtained with very high yields from their corresponding salicylaldehydes and amines.



Scheme 7. Schematic representation of the biaryl-bridged salicylaldimine ligand precursors **1**–**4**. **1**: $X = 1$, $R^1 = R^2 = H$; **2**: $X = 1$, R^1 = *tert*-butyl, $R^2 = H$; **3**: $X = 1$, $R^1 = R^2 = CMe_2Ph$; **4**: X = 2, R^1 = *tert*-butyl, $R^2 = H$.

Direct metallation of the ligand precursors with $Ti(NMe_2)_4$, followed by chlorination of the formed bis(dimethyl)amido titanium complexes using an excess of chlorotrimethylsilane, proved to be a highly selective and simple method of synthesis for complexes (**1-Ti**–**3-Ti**) bearing the 6,6′-dimethylbiphenyl moiety and for complex **4-Ti** with a binaphthyl bridge between the salicylaldimine moieties (see Schemes 3 and 4).[9] However, this method was not directly suitable for the synthesis of complex **5-Ti** (Scheme 5) as the chlorination procedure resulted in the formation of an amino salt which could not been completely removed under vacuum and lead to a 5–6% deficit in the carbon proportion. However, the amino salt was nearly completely removed by the addition of a slight excess of triethylamine which led to the pure complex being obtained with 90% yield.[4]



Scheme 8. Schematic representation of the bidentate ligand precursors **5**–**8**. **5**: $R^1 = CH_2CH_2Ph$, $R^2 = R^3 = CMe_2Ph$; **6**: R^1 = Ph, $R^2 = R^3 = CMe_2Ph$; **7**: R^1 = Ph, $R^2 = R^3$ = H; **8**: R^1 = Ph, R^2 = *tert*-butyl, R^3 = H.

Attempts to prepare complex **6-Ti** by direct metallation were not successful. Although treatment of compound **6** with $Ti(NMe_2)_4$ resulted in formation of the desired titanium amido complex intermediate, the chlorination procedure was unselective. After chlorination, substantial amounts of amido signals (NMe_2) including an additional sharp signal at 8.5 ppm were detected by ^{1}H NMR spectroscopy. The peak at 8.5 ppm indicates the presence of non coordinating imine. Therefore, the preparation of complex **6-Ti** required the use of the traditional route via lithium salt followed by complexation with $TiCl_4$. By heating the lithium salt together with $TiCl_4$ at 85 °C for two days the complex was obtained with nearly quantitative yield. Complex **6-Ti** was discovered to be very sensitive and hence all NMR samples were prepared in a glovebox under argon atmosphere. Even traces of moisture can lead to the detachment of the phenoxy imine ligand, as testified by the appearance of two new sharp resonances at δ = 8.52 ppm and 8.62 ppm in ^{1}H NMR indicating the presence of uncoordinated imines.

Configurations of Amido and Chlorido Complexes

The amido derivative of complex **1-Ti** possesses indistinguishable imino and amido proton signals in its ^{1}H-NMR spectrum possibly caused by presence of *cis* and *ciscis* isomers and hindered rotation of ligands. When the NMe_2 ligands of **1-Ti** are replaced by chlorides, three slightly broad imine proton signals appears, a singlet from the *cis* isomer together with two separate singlets from the *ciscis* isomer, the ratio being 1:4. In order to gain insight into the possible fluxional behaviour of **1-Ti** in its dichloride form, dynamic ^{1}H NMR (C_6D_6) measurements were carried out. The results of this study revealed that both of the isomers seem to be stable even at 67 °C as no changes in ratio or in the positions of the imine signals were observed.[7]

For complex **2-Ti** which bears a *tert*-butyl group at the phenoxy moiety, both the amido and dichloro derivatives adopt the *ciscis* geometry while both the amido and dichloro derivatives of cumyl-substituted complex **3-Ti**

adopt the *cis* geometry exclusively. In the case of the amido derivative of complex **4-Ti**, one sharp singlet from the imino protons (δ = 7.82 ppm) is observed indicating the presence of the *cis* isomer. Upon subsequent chlorination two sharp resonances is observed indicating conversion of the complex from *cis* to the *ciscis* isomeric form.[9] A similar phenomenon was previously observed by Scott et al. for a comparable, 6,6′-dimethylbiphenyl-bridged bis(3,5-di-*tert*-butylsalicylaldimino)$TiCl_2$ complex.[7]

As for the bridged complex **4-Ti**, the unbridged complexes are prone to configurational changes upon chlorination. The amido derivative of complex **6-Ti** revealed a sharp singlet in ^{1}H NMR indicating a possible C_2-symmetric *cis* configuration while the corresponding dichlorido complex adopts a C_1-symmetric *ciscis* structure resolved from its HSQC spectra (Scheme 5).

Due to overlapping signals arising from different isomers, the ^{1}H-NMR spectrum of amido derivative **5-Ti** was ambiguous. The configuration of the corresponding dichloride complex was resolved using ^{13}C-NMR revealing three imino signals arising from *cis* and *ciscis* isomers in the estimated ratio of 1:2 (see Supporting Information). It can be concluded that the geometries of studied complexes can vary and their configurations are dependent upon the substituents at the phenoxy *ortho* position as well as on the anionic monodentate co-ligands present (Cl and NMe_2).

Ethene Polymerization

The bridged Ti complexes **1-Ti**–**4-Ti** were activated with an excess of methylaluminoxane (MAO) (Al/Ti ratio 2000) and used in ethene polymerisation. The structure of precatalysts of **2-Ti**/MAO and **4-Ti**/MAO are similar, the only difference being the chiral backbone (see Schemes 3 and 4). In fact, this structural difference has only a minor influence on polymerisation behavior. Regardless of the applied polymerisation temperature and monomer pressure, polymerisation activities of both **2-Ti**/MAO and **4-Ti**/MAO were very low [1–6 $kg_{PE}/(mol_{Ti}\,h\,bar)$] and they produced, in general, PE with unimodal but slightly broadened distribution curves (Table 1). Interestingly, at certain polymerisation conditions (6 bar, 40 °C) both catalysts exhibited bimodal behavior, particularly **2-Ti**/MAO which produced PE with two clearly distinguishable distribution curves. The highest molar mass polymers were achieved either at low temperatures or low pressures (Table 1).

Catalyst **1-Ti**/MAO, although missing *ortho tert*-butyl groups and therefore having reduced steric bulkiness around the active center, has comparable activity with **2-Ti**/MAO and **4-Ti**/MAO[10] (Table 1). The major difference between these three catalysts is that **1-Ti**/MAO tends to form bimodal PE at all polymerization conditions. Curiously, **1-Ti**/MAO produced clearly unimodal PE at 4 bar and 60 °C. Catalyst **3-Ti**/MAO, bearing sterically bulky cumyl substituents, differs from the other bridged catalysts in that it has slightly increased activity [10–20 $kg_{PE}/(mol_{Ti}\,h\,bar)$] and the ability to produce trimodal PE under all polymerisation conditions (Figure 1). For example, the molecular mass distribution curve (MMD) of PE at 80 °C consists of three separate, almost equal molecular mass areas with each having narrow PDI values (1.5–2.0). The molecular mass of the polymer in the high M_w-region is close to 1000 kg/mol. In the middle region the molecular mass is around 30 kg/mol while in the low region it is only few kg/mol. The relative sizes of these molecular mass areas are dependent on the polymerisation temperatures. At 60 °C the MMD curve consists mostly of high and average M_w areas while at 40 °C the average M_w area is favored. It is worth noting that **3-Ti**/MAO produces comparable trimodal PE to a similarly substituted unbridged bis(salicylaldiminato) zirconium catalyst, although the latter is more active.[6] This phenomenon is discussed in more detail in the following section.

For the bridged Ti complexes **1-Ti**–**4-Ti**/MAO, ethene consumption during 40 min polymerization reactions is stable. Thus, the observed average low activities and various modalities of PE cannot be explained by deactivation of the catalyst during the polymerisation. Based on the low

Table 1. Ethene polymerisation results with complexes (1-Ti–6-Ti). Reaction conditions: runs 1–20 [Al]/[Ti] = 2000, time 40 min; run 21 [Al]/[Ti] = 2000, time 141 s; runs 22–24 [Al]/[Ti] = 5000, time 500 s; run 25 [Al]/[Ti] = 5000, time 134 s; run 26 [Al]/[Ti] = 5000, time 200 s; run 27 [Al]/[Ti] = 5000, time 300 s.

Run	Complex	Yield [g]	Cat. [μmol]	T[a] [°C]	p[b] [bar]	Act.[c]	M_w [kg/mol]	M_w/M_n
1	**1-Ti**	0.48	20	60	4	9	930	3.9
2	**1-Ti**	0.24	20	40	6	4	620	3.9
3	**1-Ti**	0.40	20	60	6	5	900	6.5
4	**1-Ti**	0.72	20	80	6	9	320	5.2
5	**1-Ti**	0.75	20	60	8	7	560	12.8
6	**2-Ti**	0.21	20	60	4	4	1020	3.6
7	**2-Ti**	0.08	20	40	6	1	580	9.2
8	**2-Ti**	0.08	20	60	6	1	970	3.6
9	**2-Ti**	0.08	20	80	6	1	490	3.3
10	**2-Ti**	0.32	20	60	8	3	180	2.3
11	**3-Ti**	0.64	20	60	4	12	1060/30/3	1.5[d]
12	**3-Ti**	0.80	20	40	6	10	1090/34/1	1.5[d]
13	**3-Ti**	1.76	20	60	6	22	1040/34/3	1.5[d]
14	**3-Ti**	0.96	20	80	6	12	1250/32/1	1.5[d]
15	**3-Ti**	1.60	20	60	8	15	890/30/3	1.5[d]
16	**4-Ti**	0.21	20	60	4	4	570	3.9
17	**4-Ti**	0.40	20	40	6	5	600	7.6
18	**4-Ti**	0.40	20	60	6	5	360	3.7
19	**4-Ti**	0.08	20	80	6	1	330	3.7
20	**4-Ti**	0.64	20	60	8	6	390	2.2
21	**5-Ti**	7.30		60	4	6210	110	2.1
22	**5-Ti**	2.63	2	40	4	2360	120	2.1
23	**5-Ti**	5.17	2	60	4	4650	110	2
24	**5-Ti**	3.46	2	80	4	3110	110	1.9
25	**6-Ti**	6.70	2	60	4	22500	370	2
26	**6-Ti**	1.86	2	60	2	8370	380	2.1
27	**6-Ti**	1.55	2	40	4	4650	380	2
28	**6-Ti**	0.54	2	80	4	2460	635	3.3
29	**7-Ti**[8]	–	20	80	5	143	520	3.5
30	**8-Ti**[14]	3.14	5	75	0.1	380000	44[e]	≈ 2

[a] Polymerisation temperature. [b] Monomer pressure. [c] Activity in $(kg\ PE)/(mol_{Ti}\,h\,bar)$. [d] PDI values were between 1–2. Exact values can′t be given due to overlapping of molecular mass areas. [e] Molecular mass value is given as a viscosity average molecular mass M_v.

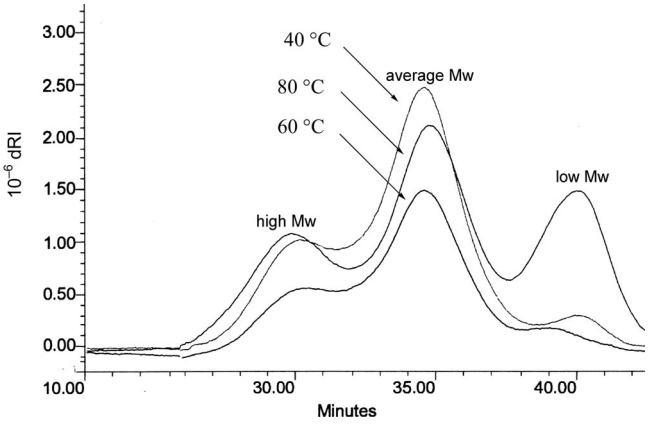


Figure 1. Molecular mass distribution curve of trimodal PE polymerized with MAO activated complex **3-Ti** at different temperatures.

polymerisation activities recorded for the series of bridged catalysts, it can be summarized that neither the *cis* nor *ciscis* geometry provides a Ti-center of high activity. Alternative explanation for low activity was presented by e.g. Scott et al. who proposed that during complex activation process one of the imino groups is replaced with amido one.[7]

In order to identify the influence of bridging on catalytic properties, a series of unbridged complexes were chosen for study under similar polymerization conditions. This series included a new non-bridged complex (**5-Ti**/MAO) and the previously reported **6-Ti**/MAO,[11] **7-Ti**/MAO[3,4] and **8-Ti**/MAO[12] (see Scheme 5 and 6). This series of unbridged complexes covers the same range of *o*-substitution patterns as present in the series of bridged complexes studied above. These selected unbridged complexes also have *cis* and/or *ciscis* orientation of their imine nitrogen atoms in the dichloro form as was the case for the bridged complexes.

Catalyst **5-Ti**/MAO bearing a cumyl substituent in the *o*-position and an ethylphenyl group at imino nitrogen had high catalytic activity 6,000 $kg_{PE}/(mol_{Ti}\,h\,bar)$ at 60 °C and 4 bar ethylene (Table 1). This catalyst also had appreciable thermal stability as is evident from its activity at 80 °C which was 70% of that achieved at 60 °C. The polymerization properties of the catalyst resemble those typical for single center catalysts e.g. metallocenes. Typical polydispersity values were 2 and the obtained molecular masses were 100 kg/mol. At 80 °C traces of high M_w PE were obtained.

At 60 °C and 4 bar ethylene, the activity of **6-Ti**/MAO (having a phenyl group at imino nitrogen) is remarkably high over very short polymerization times. During a short two minute polymerization run, the activity was over 20,000 $kg_{PE}/(mol_{Ti}\,h\,bar)$; however after three minutes the activity decreased to 8,000 $kg_{PE}/(mol_{Ti}\,h\,bar)$ which is close to the literature reported values.[13] **5-Ti**/MAO and **6-Ti**/MAO produce PE with narrow PDI values indicating the presence of one active catalytic centre.

At the highest temperature studied (80 °C) the activity of **6-Ti**/MAO was clearly reduced and PE with broad PDI was obtained. Accordingly, **6-Ti**/MAO appears to have lower thermal stability than **5-Ti**/MAO.

Under similar polymerization conditions the previously published **7-Ti**/MAO having a phenyl group at imino nitrogen and H at *ortho*-position has low activity and produces PE with a slightly broadened PDI of 3.5.[3] Conversely, very high activities have been reported for **8-Ti**/MAO bearing *ortho tert*-butyl groups and a phenyl group at imino nitrogen. **8-Ti**/MAO produces PE with narrow PDI (≈ 2)[11] (Scheme 6).

Correlation between Complex Structure and Polymerisation Behaviour

In order to find a correlation between the structure of the bridged and the unbridged complexes **1-Ti**–**8-Ti** and their polymerisation properties, all complexes were subjected to ab initio calculations. Unfortunately the ab initio calculations failed with complexes **3-Ti**, **5-Ti** and **6-Ti** due to their large and freely rotating cumyl groups. Despite this setback, the data-set produced from the remaining complexes provides an interesting insight into the polymerisation behaviour of these catalysts.

The calculations concerning relative stabilisation energies of the bridged dichlorido complexes **1-Ti**, **2-Ti** and **4-Ti** are in accordance with the experimental results. In these complexes the relative stabilisation energies of *cis* and *ciscis* conformers are very close to each other (Table 2). Therefore, depending on the conditions it follows that both conformers may be present in solution. Similarly, when activated, both isomers of the cationic species have the same stability. Thus under certain polymerisation conditions, bimodal PE or unimodal with slightly broadened distribution curves is expected.

Table 2. The relative stabilisation energies (E_{Rel} = kJ/mol) for different isomeric structures of dichloro as well as cationic derivatives of **1-Ti**, **2-Ti**, **4-Ti**, **7-Ti** and **8-Ti** $E_{Rel}(Cl_2)$ and $E_{Rel}(Ti^+)$, respectively. In these calculations, the *cis* isomer has been chosen as a point of reference for the bridged and the *trans* isomer for the non-bridged complexes. For the complexes **1-Ti**–**4-Ti** stability energies of *trans* isomers were left out of table due to high values (<+200 kj/mol). $E_{Rel}(Ti^+)$ stands for the methylated cationic form of the titanium dichloride complex (Scheme 2).

Complex	$E_{Rel}(Cl_2)$	$E_{Rel}(Ti^+)$
1-Ti_*cis*	0.9	0.0
1-Ti_*ciscis*	0	0.0
2-Ti_*cis*	0	0.0
2-Ti_*ciscis*	0.1	0.0
4-Ti_*cis*	1.6	0.0
4-Ti_*ciscis*	0	0.0
7-Ti_*cis*	–21	0.0
7-Ti_*ciscis*	–8	0.0
7-Ti_*trans*	0	0.0
8-Ti_*cis*	2.6	26.4
8-Ti_*ciscis*	0.0	5.4
8-Ti_*trans*	18.8	0.0

In our earlier studies with a series of non-bridged bis(phenoxyimine)titanium catalysts, we found that the highest activities in ethene polymerisation are achieved with com-

plexes which are, according to calculations, prone to adopt the *trans* orientation of the imino nitrogen atoms upon activation.[2,3] This orientation brings the imine substituents into the frontal position and thus steric shielding of the active centre increases. As shown below, this appears to be crucial for catalytic activity.

The bridged **1-Ti** and unbridged **7-Ti** have otherwise similar ligand environments, both of which consist of unsubstituted phenoxy and imino phenyl groups. However, the polymerisation activity of the unbridged complex is ten times higher. Ab initio calculations concerning the cationic **7-Ti** revealed that all three isomers (*cis*, *ciscis* and *trans*) have similar stabilisation energies and so are equally likely to be present. This decreases the fraction of the highly active *trans* isomer present and hence the increase in activity is limited to ten-fold only.[3] The presence of various isomers of the active species is also reflected in the relatively broad PDI (≈ 3.5).

Both the bridged **2-Ti** and unbridged **8-Ti** have *ortho tert*-butyl substituents that in the case of latter one has been shown previously to increase the catalytic activity of these types of complexes.[12] This *tert*-butyl substituent effect is not evident in the case of the bridged **2-Ti** as its activity shows no further increase from that of **1-Ti**. Conversely, however, the unbridged **8-Ti** has an activity superior than that of **7-Ti** (Table 1) which demonstrates that the *tert*-butyl substituent effect is operational for the unbridged type complexes.

These findings were once again supported by the calculations which showed that the *trans* geometry is clearly favoured for the cationic form of **8-Ti** which explains it high activity. This isomeric form cannot exist for **2-Ti** due to bridging which results in this complex having low activity which is not enhanced by the presence of *tert*-butyl substituents. As the *trans* form of the cationic **8-Ti** is preferable, only one active centre is present in polymerization and unimodal PE with very high activity is observed.[12] The difference between the bridged and the unbridged catalysts in polymerisation activity is 10,000-fold.

The cumyl-substituted, bridged **3-Ti** and unbridged **6-Ti** complexes make up the third catalytic pair studied. The unbridged **6-Ti** polymerizes ethene with high activity [8000 kg PE/(mol_{Ti} h bar)] and produces unimodal PE (PDI = 2.0). **3-Ti** has the highest activity in the series of the bridged complexes [up to 20 kg PE/(mol_{Ti} h bar)] and produces trimodal PE. It must be noted, however, that the activity of the bridged **3-Ti** is 400 times lower than the activity of the unbridged **6-Ti**.

Since the existence of the *trans* geometry in **3-Ti** is prevented by bridging, possible *cis* and *ciscis* conformers leads to catalytic species with low activities. As **6-Ti** is highly active and produce PE with unimodal, narrow PDI it can be concluded that the *trans* geometry of the catalytically active **6-Ti** is prevalent. It is worth to notice that the unbridged **6-Ti** was prone to changes in the coordination geometry when amido ligands are changed to chlorines.

The observation that the cumyl-substituted, bridged **3-Ti** produce trimodal PE is interesting. As the third isomer (*trans*) is missing in **3-Ti**, the explanation for the trimodality can arise from interaction of the bulky cumyl substituents with the cationic metal center. In our previous studies concerning bis(salicylaldiminato) catalysts bearing bulky benzyl substituents, which are sterically quite similar to the corresponding cumyl ones used herein, we observed that increased proximity of these substituents to the active site results in dramatic decreases in polymerization activity and leads to the formation of multimodal PE.[2] The freely rotating aromatic ring may form a temporary steric blockade preventing polymer chain growth and hence causing the formation of low molecular mass PE.

Conclusions

Titanium complexes can undergo changes in geometry during their synthesis. The direction and magnitude of these changes are dependent on both the co-ligands present and the *ortho* substituents of the phenoxy group. According to ab initio calculations the same structural isomerization remains present when the catalytically active species are generated. This finding underlines the fact that the isomeric form present in the solid-state structure of such dichlorido complexes is not necessarily the same isomer that is responsible for catalytic activity in ethene polymerization.

After MAO activation, the differences in catalytic activities between non-bridged bis(salicylaldiminato)$TiCl_2$ and their bridged, chiral tetradentate analogues are at best 10,000-fold, the former being more active. As demonstrated in this study using the series of catalysts, this significant difference in catalytic activity arises from the bridging itself rather than the *ortho* ligand substituents. We previously reported that structural isomerisation can be a significant factor in the generation of active species with high catalytic activity. These observations are now further supported by the obtained results.

The bridged complexes **1-Ti**, **2-Ti** and **4-Ti** have two possible structural isomers (*cis* and *ciscis*), which based on ab initio calculations, have similar stabilization energies. As shown, neither of these two isomers is capable of providing high polymerization activity. This finding helps to answer the question of why titanium dichlorido complexes bearing tetradentate biaryl-bridged salicylaldimine ligands have low activity in ethene polymerizations after MAO activation. Additionally, the relatively equal stabilization energies of the two isomers lead to the generation of polymers with bimodal distribution. Bridging in these complexes prevent the presence of the *trans* isomer, which appears to be the most active isomeric form. For example, according to the calculations the cation of non-bridged **8-Ti** prefers the *trans* isomer. The consequence of this is a 10,000 fold increase in activity from its bridged analogue **2-Ti**, which as a result of its constricted isomeric freedom exists in its *cis* and/or *ciscis* forms only. *trans* orientation of the imine nitrogen atoms brings the imine substituents into the frontal position and thus steric shielding of the active centre increases. This appears to be crucial for catalytic activity.

Experimental Section

General: All manipulations of air- and water-sensitive compounds were carried out under dry argon using standard Schlenk techniques. HPLC-grade toluene was dried and purified by refluxing over sodium followed by distillation under argon. Benzophenone was used to detect the absence of water. Toluene was stored over sodium under argon. Salicylaldehyde (Fluka), 3-*tert*-butylsalicylaldehyde (Aldrich), 2,4-bis(α,α′-dimethylbenzyl)phenol (Aldrich), 2,2′-diamino-6,6′-dimethylbiphenyl (MCAT), 2,2′-diaminobinaphthyl (Aldrich), chlorotrimethylsilane (98%) (Aldrich) and tetrakis(dimethylamino)titanium (Aldrich) were used as received, methylaluminoxane (MAO, 30 wt.-% solution in toluene) was purchased from Borealis Polymers Oy. ^{1}H and ^{13}C NMR spectra were collected on a Varian Gemini 2000 (200 MHz). Chemical shifts are referenced with respect to $CHCl_3$. For the complexes **1-Ti**–**6-Ti** complete list of ^{13}C resonances are presented in ESI. Dynamic NMR measurements were carried out with a Varian spectrometer (500 MHz), deuterated benzene was used as solvent, the temperature scan area was from 27–67 °C. Mass spectra (EI) were acquired by JEOL-SX102. DSC measurements (melting point) were performed on a Perkin–Elmer DSC-2, calibrated with indium (temperature scanning 20 °C/min). The scan area was from 25–232 °C. Mass average molecular weights (M_w), number average molecular weights (M_n) and molecular weight distribution (MWD, M_w/M_n) of the polyethylene samples were determined by GPC (Waters Alliance GPCV 2000, high temperature gel chromatographic device). GPC had HMW7, 2*HMWGE and HMW2 Waters Styrogel columns. Measurements were carried out in 1,2,4-trichlrobentzene (TCB) at 160 °C relative to polystyrene (PS) standards. 2,6-Di-*tert*-butyl-4-methylphenol was used as a stabilizer. For the earlier published but differently synthesized ligand precursors (1,4) and complexes (4-Ti) only selected experimental information was included. All the synthezied ligand precursors and complexes precipitated out of solution as yellow powder and as dark red powder respectively.

Synthesis of Ligand Precursors 1–6

2,2′-Bis[(2-hydroxybenzylidene)amino]-6,6′-dimethyl-1,1′-biphenyl (1):[14] A 50 mL round-bottomed flask was charged with salicylaldehyde (1.00 mL, 9.42 mmol) and 2,2′-diamino-6,6′-dimethylbiphenyl (1.0 g, 4.71 mmol) The reactants were dissolved in 20 mL of toluene and heated at 110 °C for overnight. The raw product (yellow powder) was recrystallized from 2-propanol (yield 1.94 g, 98%). ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H = 12.33 (s, 2 H, 2 × OH), 8.54 (s, 2 H, 2 × NCH), 7.45–6.68 (m, 14 H, aromatic), 2.09 (s, 6 H, 2 × CH_3) ppm.

2,2′-Bis[(3-*tert*-butyl-2-hydroxybenzylidene)amino]-6,6′-dimethyl-1,1′-biphenyl (2) was prepared by a similar method as described for **1**. 3-*tert*-Butylsalicylaldehyde (1.61 mL, 9.42 mmol) and 2,2′-diamino-6,6′-dimethylbiphenyl (1.0 g, 4.71 mmol) were used (yield 2.25 g, 90%, yellow powder). $C_{36}H_{40}N_2O_2$ (532.7): calcd. C 81.17, H 7.57, N 5.26; found C 81.30, H 7.28, N 5.52. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H = 13.11 (s, 2 H, 2 × OH), 8.46 (s, 2 H, 2 × NCH), 7.40–6.74 (m, 12 H, Ar), 2.10 (s, 6 H, 2 × CH_3), 1.33 (s, 18 H, CH_3) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C = 162.1 (CN), 160.8 (CO), 146.9, 137.4, 130.5, 130.0, 128.6, 119.2, 117.9, 115.4 (Ar), 35.0 (CMe_3), 29.4 (CH_3), 20.0 (Ar-CH_3) ppm. MS (EI), *m*/*z*: 532–534 [with appropriate isotope ratio for ($C_{36}H_{40}N_2O_2^+$)].

2,2′-Bis{[3,5-bis(α,α′-dimethylbenzyl)-2-hydroxybenzylidene]amino}-6,6′-dimethyl-1,1′-biphenyl (3) was prepared by a similar method as described above for **1**. 3,5-Bis(α,α′-dimethylbenzyl)salicylaldehydes[15] (0.5 g, 1.40 mmol) and 2,2′-diamino-6,6′-dimethylbiphenyl (0.15 g, 0.70 mmol) were used. The product was recrystallized from 2-propanol (yield 0.56 g, 90%). $C_{64}H_{64}N_2O_2$ (893.2): calcd. C 86.06, H 7.22, N 3.14; found C 85.87, H 7.12, N 2.62. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H = 12.51 (s, 2 H, 2 × OH), 8.09 (s, 2 H, 2 × NCH), 7.33–6.96 (m, 6 H, Ar), 6.83 and 6.79 (both s, each 1 H, Ar) 1.91 (s, 6 H, 2 × Ar-CH_3), 1.69 (s, 12 H, 4 × CH_3), 1.55 and 1.52 (12 H, 4 × CH_3) ppm. MS (EI), *m*/*z*: 892–894 [with appropriate isotope ratio for ($C_{64}H_{64}N_2O_2^+$)].

2,2′-Bis[(3-*tert*-butyl-2-hydroxybenzylidene)amino]-1,1′-binaphthyl (4):[9] Preparation by a similar method as described above for **1**, starting from 3-*tert*-butylsalicylaldehyde (1.61 mL, 9.42 mmol) and 2,2′-diaminobinaphthyl (1.34 g, 4.71 mmol) (yield 2.78 g, 98%). ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H = 12.94 (s, 2 H, 2 × OH), 8.62 (s, 2 H, 2 × NCH), 8.08 (d, 2 H, Ar), 7.98 (d, 2 H, Ar), 7.63–7.18 (m, 10 H, Ar), 7.03 (d, 2 H, Ar), 6.70 (t, 2 H, Ar), 1.22 (s, 18 H, 6 × CH_3) ppm.

1-{[3,5-Bis(α,α′-dimethylbenzyl)-2-hydroxybenzylidene]amino}-2-phenylethane (5): Preparation by a similar method as described above for **1**, starting from 2-phenylethylamine (0.2 mL, 1.59 mmol) and 3,5-bis(α,α′-dimethylbenzyl)salicylaldehyde (0.57 g, 1.59 mmol). $C_{33}H_{35}NO$ (461.6): calcd. C 85.86, H 7.64, N 3.03; found C 85.79, H 7.85, N 2.84. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H = 13.44 (s, 1 H, OH), 8.15 (s, 1 H, CNH), 7.35–7.14 (m, 16 H, Ar-H), 6.97, 6.96 (d, 1 H, Ar-H), 3.68 (t, 2 H, NCH_2), 2.88 (t, 2 H, Ar-CH_2), 1.70 and 1.68 (both s, each 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C = 165.8 (CN), 158.0 (CO), 151.0, 150.9, 139.6, 139.5, 136.3, 129.0, 129.0, 128.6, 128.2, 128.0, 126.9, 126.5, 125.8, 125.2, 118.1, 61.2 (NCH_2), 42.6 (CMe_2), 42.3 (CMe_2), 37.7 (Ar-CH_2), 31.1 (CH_3), 29.6 (CH_3) ppm. MS (EI), *m*/*z*: 461 with appropriate isotope ratio for ($C_{33}H_{35}NO^+$).

{[3,5-Bis(α,α′-dimethylbenzyl)-2-hydroxybenzylidene]amino}benzene (6): Preparation by a similar method as described above for **1**, starting from aniline (0.254 mL, 2.79 mmol) and 3,5-bis(α,α′-dimethylbenzyl)salicylaldehyde (0.57 g, 2.79 mmol) (yield 80%, 0.96 g). $C_{31}H_{31}NO$ (433.6): calcd. C 85.87, H 7.21, N 3.23; found C 85.87, H 7.22, N 3.24. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H = 13.33 (s, 1 H, OH), 8.53 (s, 1 H, CNH), 7.47–7.16 (m, 17 H, H-Ar), 1.78 and 1.74 (both s, each 6 H, 2 × CH_3) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C = 163.5 (CN), 158.0 (CO), 150.7, 148.8, 140.3, 136.6, 130.0, 129.4, 129.0, 128.3, 128.1, 126.9, 126.7, 125.9, 125.8, 125.4, 121.3, 118.7, 42.7 (CMe_2), 42.4 (CMe_2), 31.1 (CH_3), 29.6 (CH_3) ppm. MS (EI), *m*/*z*: 433 with appropriate isotope ratio for ($C_{31}H_{31}NO^+$).

Synthesis of Ti Complexes

1-Ti: Compound **1** (0.79 g, 1.88 mmol) was poured into precooled toluene (60 mL) solution of $Ti(NMe_2)_4$ (0.44 mL, 1.88 mmol). The reaction mixture was warmed to ambient temperature and stirred overnight. Quantitative formation of complex $LTi(NMe_2)_2$ was observed. The reaction was continued by decreasing the amount of solution to 20 mL followed by addition of trimethylsilyl chloride (5 mL, 20 mmol) at room temperature. Reaction mixture was stirred overnight followed by removal of solvent and side products at 70 °C in vacuo (yield 0.99 g, 98%). $C_{28}H_{22}Cl_2N_2O_2Ti$ (537.3): calcd. C 62.60, H 4.13, N 5.21; found C 62.16, H 4.35, N 5.28. ^{1}H NMR [200 MHz, $CDCl_3$, 29 °C, mixture of two isomers in solution, 25% C_2 isomer (*cis*)]: δ_H = 8.49 (s, 2 H, NCH, *cis*), 8.34 and 8.20 (both s, each 1 H, NCH, *ciscis*), 7.59–6.63 (m, 14 H, aromatic), 2.17 (s, 3 H, CH_3), 1.99 (s, 3 H, CH_3) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C = 167.1, 166.8, 165.5 (CN), 164.2, 164.0, 163.7 (CO), 151.5, 150.3, 150.0, 137.5–116.6 (m, Ar), 20.2,

20.0, 19.96 (Ar-CH_3) ppm. MS (EI) *m/z*: 537–539 with appropriate isotope ratio for ($C_{28}H_{22}Cl_2N_2O_2Ti^+$).

2-Ti was prepared by a similar method as described below for **1-Ti**. Compound **2** (1.0 g, 1.87 mmol) and $Ti(NMe_2)_4$ (0.44 mL, 1.87 mmol) were used (yield 1.19 g, 98%). $C_{36}H_{38}Cl_2N_2O_2Ti$ (649.5): calcd. C 66.57, H 5.90, N 4.31; found C 66.59, H 5.77, N 4.10. ^1H NMR ($CDCl_3$): δ = 8.34 (s, 1 H, NCH), 8.17 (s, 1 H, NCH), 7.68–6.88 (m, 10 H, Ar), 6.56–6.52 (2 H, Ar), 2.16 (s, 3 H, CH_3), 1.98 (s, 3 H, CH_3), 1.52 (s, 9 H, CH_3), 1.39 (s, 9 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C = 167.3 (CNH), 165.9 (CNH), 163.4 (CO), 163.2 (CO), 151.6, 150.3, 138.1–121.8 (m, Ar), 35.8, 35.3, 35.2 (CMe_3), 29.9, 29.7 (CCH_3), 20.1, 20.0 (Ar-CH_3) ppm. MS (EI) *m/z*: 649–651 with appropriate isotope ratio for ($C_{36}H_{38}N_2O_2Ti^+$).

3-Ti was prepared by a similar method as described above for **1-Ti**. Compound **3** (0.84 g, 0.94 mmol) and $Ti(NMe_2)_4$ (0.22 mL, 0.94 mmol) were used. Pure complex **3-Ti** with traces of amino salt was obtained (yield 0.93 g, 98%): $C_{64}H_{62}Cl_2N_2O_2Ti$ (1010.0): calcd. C 76.11, H 6.19, N 2.77; found C 75.63, H 6.91, N 3.27. ^1H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H = 7.86 (s, 2 H, 2 × NCH), 7.55–6.61 (m, 28 H, Ar), 4.99 (s, 1 H, Ar), 4.95 (s, 1 H, Ar), 2.08 (s, 6 H, 2 × Ar-CH_3), 1.85 (s, 3 H, CH_3), 1.72 and 1.71 (both s, each 3 H, 2 × CH_3), 1.65 (s, 6 H, 2 × CH_3), 1.62 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C = 167.5 (CNH), 165.4 (CNH), 160.9 (CO), 160.8 (CO), 151.4, 150.6, 150.3, 150.3, 149.7, 143.6, 143.4, 138.1–121.7 (m, Ar), 42.9, 41.8, 33.2, 32.0, 31.1, 31.0, 30.8, 27.1, 21.7, 20.1, 19.9 ppm. MS (EI) *m/z*: 1010–1012 with appropriate isotope ratio for ($C_{64}H_{62}Cl_2N_2O_2Ti^+$).

4-Ti[9] was prepared by a similar method as described above for **1-Ti**. Compound **4** (1.14 g, 1.88 mmol) and $Ti(NMe_2)_4$ (0.44 mL, 1.88 mmol) were used (yield 0.99 g, 98%). ^1H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H = 8.42 (s, 1 H, NCH), 8.16 (s, 1 H, NCH), 8.05–6.88 (m, 16 H, Ar), 6.80 (t, 2 H, Ar), 1.54 (s, 9 H, 3 × CH_3), 1.42 (s, 9 H, 3 × CH_3) ppm.

5-Ti: Compound **5** (0.83 g, 1.88 mmol) was poured into precooled toluene (60 mL) solution of $Ti(NMe_2)_4$ (0.44 mL, 1.88 mmol). The reaction mixture was warmed to ambient temperature and stirred overnight. The reaction was continued by decreasing the amount of solution to 20 mL followed by addition of trimethylsilyl chloride (5 mL, 20 mmol) at room temperature. Reaction mixture was stirred overnight followed by removal of solvent and side products at 70 °C in vacuo. The purification process was continued by solvating chlorinated complex to 40 mL of toluene and dry triethylamine (0.39 mL, 2.8 mmol) followed by several hours of stirring. Thereafter the formed amino salt was allowed to precipitate and removed from the main solution. Solvent and residual triethylamine were removed at 70 °C in vacuo and pure complex with traces of amino salt was obtained (1.20 g, 90%). $C_{66}H_{68}Cl_2N_2O_2Ti$ (1040.0): calcd. C 76.22, H 6.59, N 2.69; found C 75.62, H 5.86, N 2.67. ^1H NMR [20 MHz, $CDCl_3$, 29 °C, mixture of two isomers in solution, 33% C_2 isomer (*cis*)]: δ_H = 7.78–6.68 (m, Ar-H), 6.60–6.30 (m, Ar-H), 3.80–2.70 (m, CH_2), 2.17–1.27 (m, CH_3 region) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C = 168.3 (CNH), 165.9 (CNH), 164.4 (CNH), 159.6 (CO), 159.5 (CO), 159.4 (CO), 150.5 (Ar), 150.1–125.4 (m, Ar), 124.3, 124.2, 123.2, 65.0 (NCH_2), 60.8 (NCH_2), 59.6 (NCH_2), 43.0–41.8 (m, CCH_3 and Ar-CH_2), 33.5–26.0 (m, CH_3) ppm. MS (EI), *m/z*: 1040 with appropriate isotope ratio for ($C_{66}H_{70}Cl_2N_2O_2Ti^+$).

6-Ti: *n*-Butyllithium (1.6 M in hexanes, 1.31 mL, 2.1 mmol) was added dropwise to a solution of ligand precursor **6** (0.86 g, 2.0 mmol) in toluene (40 mL) at –78 °C. The solution was warmed to room temperature and stirred for 2 h and then added dropwise via cannula to a solution of $TiCl_4$ (0.11 mL, 1.00 mmol) in toluene (20 mL) at –78 °C. The resulting solution was warmed up to 85 °C and stirred under nitrogen for 48 h. The reaction mixture was filtered through Celite followed by removal of the solvent in vacuo. The complex was pure as such (99%, 0.98 g). $C_{62}H_{60}Cl_2N_2O_2Ti$ (983.9): calcd. C 75.68, H 6.15, N 2.85; found C 75.71, H 6.69, N 2.60. ^1H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H = 7.68 and 7.34 (s, 2 H, 2 × NCH), 7.85–6.20 (m, 34 H, Ar-H), 2.16–1.25 (m, 24 H, 8 × CH_3) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C = 169.0 (CNH), 165.6 (CNH), 160.4 (CO), 159.5 (CO), 155.6, 151.3, 150.2, 149.3, 149.2, 144.2, 144.1, 137.1, 136.8, 133.5, 132.1, 131.8, 131.7, 129.4–121.2, (m, Ar), 43.0, 42.8, 42.0 (m, CCH_3), 32.7–26.5 (m, C*Me*) ppm. MS (EI), *m/z*: 982 with appropriate isotope ratio for ($C_{62}H_{60}Cl_2N_2O_2Ti^+$).

Polymerization Experiments

Polymerizations were performed in a 1.0 L Büchi stainless steel autoclave equipped with Julabo ATS-3 and Lauda RK 20 temperature controlling units. Toluene (200 mL) and the co-catalyst (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 (2–20 μmol solution in toluene) into the reactor. Mechanical stirring was applied at a speed of 800 r.p.m. 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.

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.[16,17] Based on 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 stabilizations 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 (see also the footnote on the first page of this article): selected ^1H and ^{13}C NMR spectra of the titanium complexes **1-Ti** to **6-Ti**, dynamic NMR spectrum of **1-Ti**, HSQC spectrum of **6-Ti**, all of the ^{13}C NMR resonances of the titanium complexes **1-Ti** to **3-Ti**, **5-Ti** and **6-Ti** and ^1H NMR resonances of the complexes **5-Ti** and **6-Ti**.

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