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# Tridentate Aryloxy-Based Titanium Catalysts towards Ethylene Oligomerization and Polymerization

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**Keywords:** Titanium / Tridentate ligands / Homogeneous catalysis / Oligomerization / Polymerization

A series of tridentate aryloxy-based ligands were synthesized and characterized for their coordination behaviour towards $Ti^{IV}$. Coordination studies revealed that the nature of the central atom (amine vs. ether) and the type of bridging spacer (aromatic vs. aliphatic) are important aryloxy ligand parameters and influence the ligand coordination mode and the formation of stable titanium complexes. This series of titanium complexes were evaluated in ethylene oligomerization and polymerization after activation with methylaluminoxane (MAO) and showed the preferential formation of polyethylene. In some cases, the formation of a small amount of 1-hexene suggests the existence of several catalytic centres in the reaction mixture.

## Introduction

Coordination chemistry and organometallic chemistry are at the very heart of homogeneous transition-metal catalysis. The identification and fine-tuning of catalyst parameters, in terms of activity and selectivity, continue to represent great challenges for ligand design, coordination chemistry and organometallic chemistry. Although the combination of the electronic and steric properties of the ligand has been recognized as a powerful tool for catalyst optimization, predictions remain very difficult. Therefore, to a large extent, catalyst discovery still relies on a delicate interplay between intuition, laboratory experience and, in many cases, lucky breaks. A strategy that has emerged to accelerate catalyst development is based on the evaluation of structurally diverse and meaningful ligand libraries through high-throughput screening techniques. This approach has been remarkably valid in the field of olefin polymerization catalysis, for which the screening of ligand libraries has enabled the fine-tuning of the physical properties of polyolefinic materials.[1] In this research area, ligands such as phenoxyimines (FI) have attracted great interest owing to their synthetic accessibility and easy structural diversification (**I**; Figure 1), which makes this class of ligands very attractive for lead identification and catalysis optimization.[2–4] In the course of their investigations on this type of ligands, Fujita and co-workers discovered that the introduction of an additional donor group can completely switch the catalyst activity from polymerization to highly active and selective trimerization.[5] On the basis of systematic investigations,[5c] several structural variations of these FI tridentate ligands were proposed, and the additional pendant 2-methoxybiphenyl donor was identified as a critical feature to induce 1-hexene selectivity (**IIa**; Figure 1). Along the same lines, we and other groups have reported on the application of bidentate aryloxy-based $Ti^{IV}$ systems and contributed to the further development of this ligand family for selective ethylene oligomerization.[6]

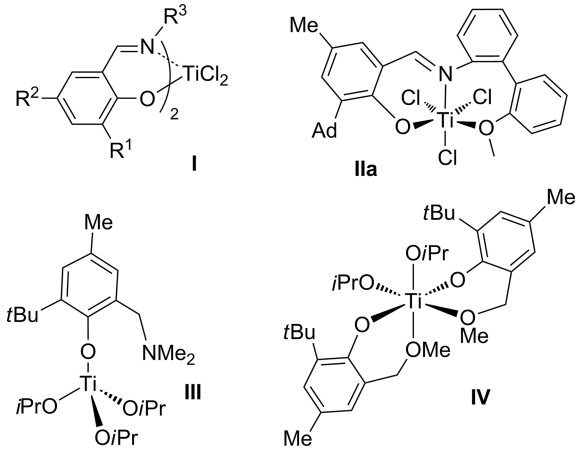


Figure 1. Titanium aryloxy complexes.

Depending on the structure of the aryloxy ligand (steric hindrance, nature of the heteroatom and nature of the spacer group), mono-aryloxy or bis-aryloxy complexes can be obtained (**III** and **IV**; Figure 1).[6a,6b] Upon activation

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with methylaluminoxane (MAO), catalysts derived from **III** and **IV** are poorly active towards ethylene with a selectivity oriented towards polymers (>95%).

In light of this and the potential impact of a third coordination donor of the aryloxy-based $Ti^{IV}$ complexes, we decided to further study this ligand family through the evaluation of a small library of tridentate aryloxy-based ligands (Figure 2) derived from the aryloxy amine and aryloxy ether ligands found in structures **III** and **IV** (Figure 1).[7] For both ligand families, special attention was devoted to the role of the spacer group between the nitrogen or oxygen atom linked to the aryloxy group and the third donor group (fixed as OMe in this study; Figure 2). By this means, we wished to gain a better insight into the critical parameters that influence the coordination mode of this class of ligand, the stability of the resulting titanium complexes and their reactivity as catalysts in ethylene oligomerization versus polymerization.

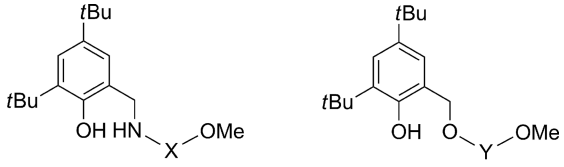
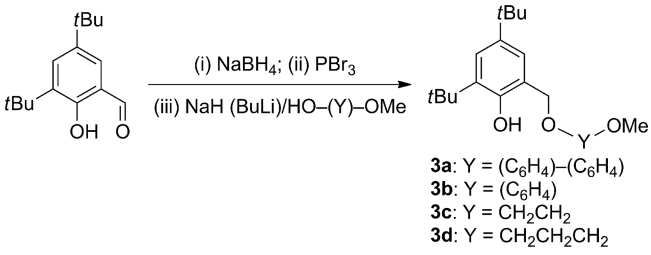



Figure 2. Ligand platforms used in this study.

## Results and Discussion

The aryloxy amine ligands **2a**–**2d** were prepared by the procedure displayed in Scheme 1. It should be noted that a potentially noninnocent NH group was chosen in the structure. Indeed, such NH moieties are deprotonated upon MAO activation,[8] which leads to an overall dianionic ligand, unlike the recently evaluated NMe analogues.[9] This deprotonation proved to be of special interest for $R_2P$–NH–$PR_2/Cr^{III}$ systems in the selective trimerization of ethylene to 1-hexene.[10] The Schiff base condensation of the commercial 3,5-di(*tert*-butyl)salicylaldehyde with the appropriate amine provided the corresponding aryloxy imine ligands **1a**–**1d**.[5a] These intermediates were then reduced by $NaBH_4$ to the desired aryloxy amine ligands **2a**–**2d** in excellent yields.[11] All of the compounds were characterized by $^1H$ and $^{13}C$ NMR spectroscopy and mass spectrometry.

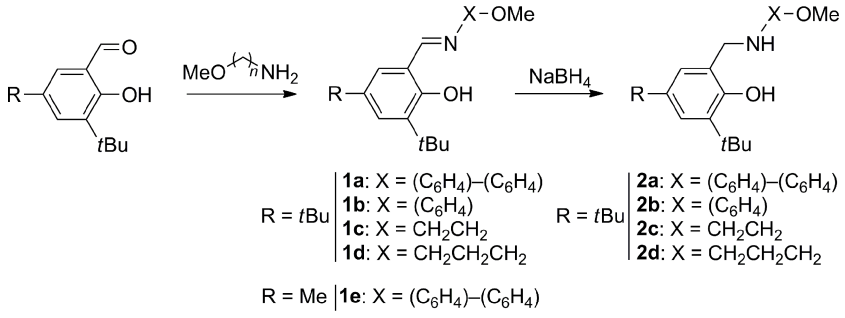
The aryloxy ether ligands were obtained by following a second route, which is shown in Scheme 2. The first step is the reduction of 3,5-di-*tert*-butylsalicylaldehyde to the corresponding alcohol[12] and the subsequent bromination to 3,5-di-*tert*-butyl-2-hydroxybenzyl bromide.[13] The reparation of ligands **3a**–**3d** was then readily achieved by reaction of this highly reactive intermediate with the corresponding deprotonated alcohol HO–(Y)–OMe. All of the compounds were characterized by $^1H$ and $^{13}C$ NMR spectroscopy and mass spectrometry.




Scheme 2. Synthetic route to tridentate aryloxy ether ligands.

In addition, crystals of ligand **3a** were grown from a saturated pentane solution, and the structure was determined by X-ray crystallography (Figure 3). The solid-state structure shows intramolecular H-bond interactions between the phenolic hydrogen atom and the ether and methoxy functionalities. Similarities with the analogous tridentate aryloxy amine ligand described by McGuinness et al. can be observed.[9] The distance between O32 and H541 is comparable to that of the H bond between the NMe group and the phenolic hydrogen atom reported previously (2.004/2.028 Å). In both structures, the distortion angles between the phenol and ether (or NMe) moieties are also similar [107.9(4)/112.31(9)°].

With these eight new ligands in hand, the synthesis of the respective titanium(IV) complexes was studied. The synthesis relies on a classical procedure in which ligands **2a**–**2d** or **3a**–**3d** are treated with 1.1 equiv. of $TiCl_4$ in toluene at –78 °C. Quite surprisingly, however, this procedure, which is efficient for **1a** and **1b**, failed to deliver the corresponding complexes cleanly with the saturated ligands **2a** and **2b** or with ligands **3a** and **3b**. Alternative synthetic strategies were followed, such as reactions with less acidic titanium precur-




Scheme 1. Synthetic route to tridentate aryloxy amine ligands.

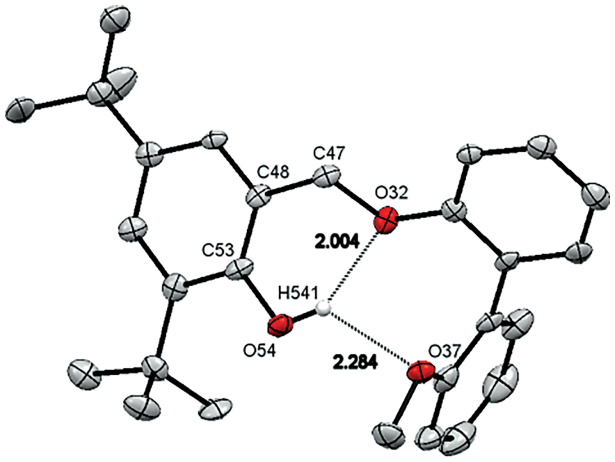
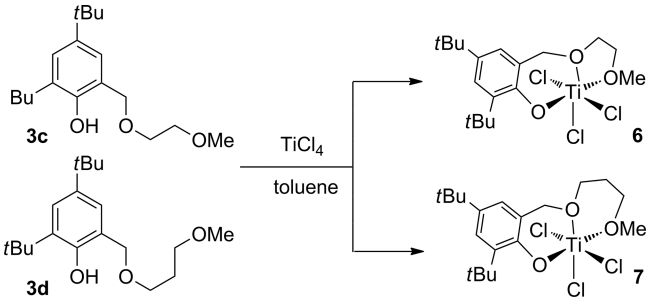



Figure 3. ORTEP diagram of the molecular structure of ligand **3a** (CCDC-1405437). The thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity except for the phenolic hydrogen atom. Selected bond length [Å] and angles [°]: C53–O54 1.392(6), C47–O32 1.467(6), O54–H541 0.855(3), O32–H541 2.004(3), O37–H541 2.284(4); C48–C53–O54 122.0(4), C48–C47–O32 107.9(4), C53–O54–H541 103.8(3).

sors such $TiCl_4(THF)_2$ (THF = tetrahydrofuran) or the use of a silylated phenol derivative before the reaction with the titanium precursor [$TiCl_4$ or $TiCl_4(THF)_2$], but none of these reactions were successful. We were not able to identify the decomposition products precisely, but $^1H$ NMR spectroscopy of the bulk product showed the disappearance of the methylene group. The stability of the methylene group linked to the phenol moiety has been reported to be poor in some instances, especially if highly acidic compounds such as $TiCl_4$ are used and, thus, can be evoked to explain these disappointing results.[14]

On the other hand, the classical synthesis proved successful with ligands **2c**–**2d** (Scheme 3) and **3c**–**3d** (Scheme 4).

With ligand **2c**, the hexacoordinate complex **4** was obtained. Crystals of **4** were grown by slow diffusion of heptane into a dichloromethane solution of the complex (Figure 4). Interestingly, **4** adopts a distorted octahedral geometry with the ligand arranged in a meridional fashion. The five-membered N(23)–O(26) chelate ring of **4** adopts a distorted folded conformation, which results in an inclination of this ring of ca. 40° to the equatorial plane [Ti, O(7), C(8), C(9), C(22)].




Scheme 4. Synthesis of **6** and **7**.

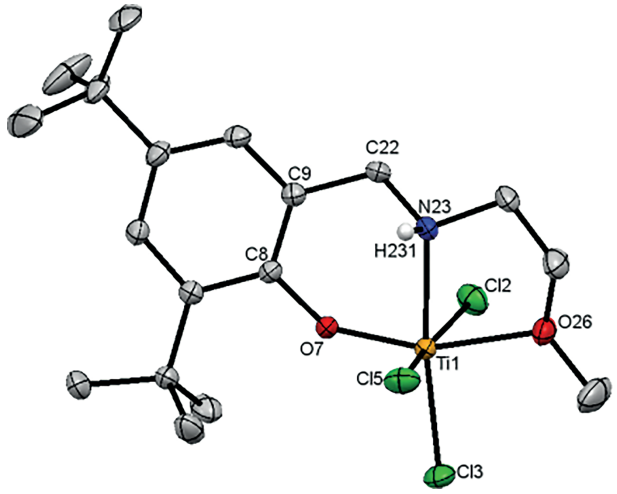
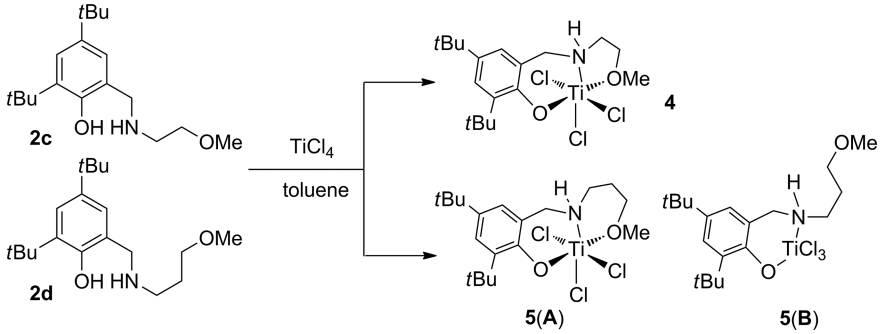



Figure 4. ORTEP diagram of the molecular structure of **4** (CCDC-1405434). The thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity except for that of the amine group. Selected bond length [Å] and angles [°]: Ti–Cl2 2.3112(6), Ti–Cl3 2.2700(5), Ti–Cl5 2.3675(6), Ti–O7 1.7617(12), Ti–N23 2.1943(14), Ti–O26 2.1715(13); Cl2–Ti–Cl3 95.19(2), Cl2–Ti–Cl5 166.37(2), Cl3–Ti–Cl5 92.18(2), O7–Ti–N23 83.41(5), O7–Ti–O26 158.75(5), N23–Ti–O26 75.36(5), Ti–O7–C8 144.40(11).

Interestingly, under similar conditions, the reaction of ligand **2d** with $TiCl_4$ led to a mixture of two complexes, **5(A)** and **5(B)**, in a 73:27 ratio (Scheme 3). The $^1H$ NMR spectrum of **5(A)** is characterized by the signal of a methoxy group at $\delta$ = 4.23 ppm, which is in accordance with a tridentate chelation to the titanium centre, as depicted in Scheme 3. In contrast, the $^1H$ NMR spectrum of **5(B)** displays a broad singlet at $\delta$ = 7.85 ppm for the NH group,




Scheme 3. Synthesis of complexes **4** and **5**.

whereas the pendant methoxy group exhibits a singlet at $\delta$ = 3.40 ppm, identical to the chemical shift of this group in the free ligand. Moreover, the absence of signals corresponding to diastereotopic protons, typical for an ABX system, further confirmed the ligand arrangement in **5(B)** depicted in Scheme 3.

From this mixture, crystals of **5(A)** suitable for X-ray diffraction were grown by the diffusion of heptane into a dichloromethane solution of the bulk product. The solid-state analysis revealed an octahedral geometry at the titanium centre, which possesses meridional chlorido ligands (Figure 5).

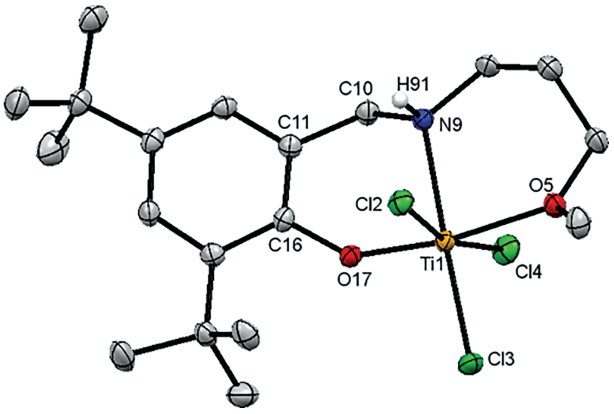



Figure 5. ORTEP diagram of the molecular structure of **5(A)** (CCDC-1405435). The thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity except for that of the amine group. Selected bond length [Å] and angles [°]: Ti–Cl2 2.3727(6), Ti–Cl3 2.2781(6), Ti–Cl4 2.3184(6), Ti–O5 2.1541(14), Ti–N9 2.2314(16), Ti–O17 1.7703(13); Cl2–Ti–Cl3 94.56(2), Cl2–Ti–Cl4 165.11(2), Cl3–Ti–Cl4 95.62(2), O5–Ti–N9 87.85(6), O5–Ti–O17 171.10(6), N9–Ti–O17 84.30(6), C16–O17–Ti 143.24(12), N9–Ti–Cl3 177.45(5).

Complexes **6** and **7** were obtained in turn from ligands **3c** and **3d**, respectively (Scheme 4).

Complex **6** appeared as a dark red powder that is highly soluble in $CH_2Cl_2$. Crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into a $CH_2Cl_2$ solution of **6**. Similarly to the amine analogue **4**, complex **6** adopts a distorted octahedral geometry with the ligand arranged in a meridional fashion (Figure 6). The Ti–N23 bond in **4** is slightly longer [2.1943(14) Å] than the Ti–O5 bond in **6** [2.151(3) Å]. This bond lengthening can be explained by the weaker titanium–amine interaction in **4** compared with the titanium–ether interaction in **6**. The other Ti–O and Ti–Cl bonds in **4** and **6** are very similar.

Contrary to ligand **2d**, ligand **3d** led to the formation of a single complex (**7**) in solution; complex **7** was also isolated as a dark red solid. Despite several attempts, we were not able to isolate crystals of **7** for X-ray diffraction analysis. However, the $^1$H NMR spectroscopic data are consistent with the effective formation of a $\kappa^3$-(OOO)-titanium chelated system, as proved by the chemical shift of the OMe signal at $\delta$ = 4.25 ppm, significantly downfield from that of the free ligand.

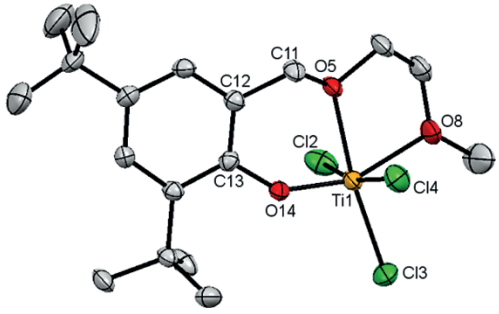



Figure 6. ORTEP diagram of the molecular structure of **6** (CCDC-1405436). The thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond length [Å] and angles [°]: Ti–O14 1.765(2), Ti–O5 2.151(3), Ti–O8 2.146(2), Ti–Cl3 2.259(1), Ti–Cl2 2.312(2), Ti–Cl4 2.336(2); Cl2–Ti–Cl3 94.05(5), Cl2–Ti–Cl4 167.03(5), Cl3–Ti–Cl4 93.25(5), O8–Ti–O5 74.7(1), O8–Ti–O14 157.6(1), O5–Ti–O14 83.9(1), Ti–O14–C13 143.4(2).

To summarize, the coordination studies revealed that the nature of the spacer group X or Y (aryl vs. alkyl) has a major influence on the stability of the ligands in the coordination sphere of the metal centre. Ligands bearing biphenyl and aryl spacers such as **2a**–**2b** and **3a**–**3b** led to decomposition, whereas ligands **2c**–**2d** and **3c**–**3d** provided the expected Ti complexes.

The reactivity of the Ti complexes **4**–**7** was evaluated towards ethylene poly- and oligomerization with MAO as a cocatalyst (Table 1). As a benchmark in this study, we used **IIb** [featuring a *t*Bu moiety instead of the adamantyl (Ad) moiety in **IIa**; Figure 1], which was synthesized by following the procedure described previously.[5a] Complex **IIb** exhibited high activity [294 kg($C_2H_4$)/g(Ti)/h] and selectivity towards 1-hexene (86% $C_6$, >99.5% $C_6^{=1}$). The main byproduct was a $C_{10}$ olefin mixture, which can be explained by the co-trimerization of 1-hexene with two ethylene molecules.[5a,9,15] Low amounts of butenes, octenes and $C_{14}$ olefins were also detected in the liquid phase (less than 0.5%). After drying, 2% of polyethylene (PE) can be isolated from the reaction mixture. The activity as well as the selectivity with complex **IIb** appeared similar to those of the original system **IIa**, developed by Fujita et al.[5a] Nevertheless, a small decrease of 1-hexene selectivity was observed. The steric impact of the adamantyl group in **IIa** (vs. *t*Bu for **IIb**) can be evoked to explain this result. Some of the PE properties were obtained from differential scanning calorimetry (DSC) analysis. This material melts/softens at ca. 126 °C. By following the method described by Tait and coworkers,[16] the crystallinity of this PE was estimated to be ca. 29%. The microstructure was accessible through $^{13}$C NMR spectroscopy analysis. The material formed was an ethylene/1-hexene copolymer with the incorporation of ca. 1% of 1-hexene in the polymeric chain. This analysis showed good agreement with the DSC thermal analysis. Moreover, the absence of a signal corresponding to the extremity of the polymeric chain suggests an elevated molecular weight.

Table 1. Ethylene oligo-/polymerization for **IIb** and **4**–**7**.[a]

| Entry | Catalyst | Activity[b] | $C_6$ [%] (1-$C_6$)[c,d] | $C_{10}$ [%][c,d] | PE [%][e] |
|---|---|---|---|---|---|
| 1[f,g] | **IIb** | 294 | 86 (99+) | 12 | 2 |
| 2 | **4** | 4 | – | – | 99+ |
| 3 | **5** | 4 | – | – | 99+ |
| 4 | **6** | 7 | 4 (92) | <1 | 93 |
| 5 | **7** | 8 | 3 (88) | <1 | 94 |

[a] Catalyst (5 μmol), MAO (500 equiv.), toluene (10 mL), 30 bar, 30 °C, 1 h. [b] In kg($C_2H_4$)/g(Ti)/h. For catalysts producing essentially PE, the activities in kg(PE)/mol(Ti)/bar/h are 6 (Entries 2 and 3), 11 (Entry 4) and 12 (Entry 5). [c] In wt.-%. [d] Traces of $C_4$, $C_8$ and $C_{10+}$ olefins. [e] In wt.-% (calculated from isolated solid). [f] 2 μmol catalyst. [g] Reaction time 30 min.[17]

Under identical conditions, the amine-based $Ti^{IV}$ complexes **4** and **5** (Table 1, Entries 2–3) produce solely polyethylene. Under these reaction conditions, the swelling of the polyethylene in contact with the solvent in the reactor prevents the recovery of sufficient liquid phase for analysis. Similarly, the ether-based $Ti^{IV}$ complexes **6** and **7** also predominantly produce polyethylene (93 and 94%, respectively). Interestingly, for both **6** and **7**, small but significant amounts of 1-hexene were produced (Table 1, Entries 4 and 5); therefore, several active species compete in the reaction media. The physical properties of the polymers produced with **6** and **7** seem to be different to those obtained with **IIb**. They melt/soften at 136–138 °C, which is significantly higher than the value for the PE produced with **IIb**. Furthermore, the crystallinity of these materials appeared to be ca. 41–45%, which is once again significantly higher than the value for **IIb**. The microstructures, $M_n$ values and $M_w$ values of theses polyethylenes were not accessible owing to the insolubility of the material even at high temperature; this suggests that linear polyethylene with an ultrahigh molecular weight is formed.

## Conclusions

We have reported the synthesis and characterization of a library of aryloxy-based titanium complexes. Coordination studies revealed that both the nature of the central heteroelement (amine vs. ether) and the type of bridging spacer (aromatic vs. aliphatic) are crucial ligand features for the formation of stable titanium complexes. For the tridentate aryloxy–$Ti^{IV}$ complexes studied, decomposition occurs if aromatic spacers are used. If aliphatic spacer groups are used, the complexes obtained adopt distorted octahedral geometries with the ligand arranged in a meridional fashion. Furthermore, when activated with MAO, these $Ti^{IV}$ precatalysts produced polyethylene in 93–99%. Only with the Ti complexes bearing the "O,O,O" ligand could a significant amount of 1-hexene be detected. Further investigations are currently in progress to identify the specific feature of the tridentate aryloxyimine–$Ti^{IV}$ complexes responsible for the selective production of 1-hexene.

## Experimental Section

**General:** Unless stated otherwise, reactions were performed under argon by standard Schlenk techniques. Anhydrous $CH_2Cl_2$, toluene and pentane were purified with a solvent purification system (SPS-M-Braun). NMR spectra ($^1H$, $^{31}P$ and $^{13}C$) were recorded with a Bruker AV 300 MHz spectrometer at 303 K unless stated otherwise. NMR spectra of polymers ($^{13}C$) were recorded with a Bruker DRX 400 MHz spectrometer equipped with a PSEX 10 mm probe. Deuterated solvents were purchased from Sigma–Aldrich or Eurisotop. $CD_2Cl_2$ was used as a solvent, if not further specified. GC analyses were performed with an Agilent 6850 series II device equipped with an autosampler and fitted with PONA columns. GC–MS analyses were conducted with an Agilent 6890 N apparatus equipped with a PONA or HP-5-MS column and an Agilent 5975B inert XL EI/CI MSD mass spectrometer. With exception of the compounds given below, all reagents were purchased from commercial suppliers and used without further purification. DSC analyses were performed with a TA Instruments Q100 analyzer. MAO was supplied by Chemtura as a 10% solution in toluene. 3-*tert*-Butyl-5-methylsalicylaldehyde,[18] 2-(2′-methoxyphenyl)aniline,[19] 2,4-di-*tert*-butyl-6-(hydroxymethyl)phenol,[12] 2,4-di-*tert*-butyl-6-(bromomethyl)phenol[13] and 2-hydroxy-2′-methoxybiphenyl[20] were prepared according to literature methods. CCDC-1405437 (for **3a**), -1405434 (for **4**), -1405435 [for **5**(**A**)] and -1405436 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Ligand 1e Used in IIb:** To a solution of 3-*tert*-butyl-5-methylsalicylaldehyde (0.786 g, 3.95 mmol) in MeOH (15 mL) was added a solution of 2-(2′-methoxyphenyl)aniline (0.759 g, 3.95 mmol) in MeOH (5 mL) and a few drops of acetic acid. The reaction mixture was stirred at room temperature overnight. The product precipitated from the reaction solution as orange solid and was isolated by filtration (0.959 g, yield 65%). MS (EI+): *m*/*z* = 373 $[M]^+$. $^1H$ NMR (300 MHz, $CD_2Cl_2$): δ = 13.32 (s, 1 H, O*H*), 8.51 (s, 1 H, N=C*H*), 7.51–7.30 (m, 4 H, Ar-*H*), 7.27–7.19 (m, 2 H, Ar-*H*), 7.15 (d, *J* = 2.1 Hz, 1 H, Ar-*H*), 7.06–6.92 (m, 3 H, Ar-*H*) 3.72 (s, 3 H, O$CH_3$), 2.27 (s, 3 H, Ar-$CH_3$), 1.35 [s, 9 H, Ar-C($CH_3$)$_3$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz): δ = 163.5 (CH), 158.6 (C), 157.0 (C), 147.8 (C), 137.5 (C), 134.6 (C), 131.7 (CH), 131.7 (CH), 131.4 (CH), 130.6 (CH), 129.4 (CH), 129.0 (CH), 128.9 (CH), 127.2 (C), 126.8 (CH), 120.7 (CH), 119.2 (C), 118.4 (CH), 111.0 (CH), 55.5 ($CH_3$), 35.0 (C), 29.4 ($CH_3$), 20.7 ($CH_3$) ppm.

**General Procedure for the Synthesis of Ligands 1a–1d:** Ligands **1a**–**1d** were synthesized by condensation reactions of 3,5-di-*tert*-butylsalicylaldehyde (1.0 equiv.) with the corresponding amine (1.0 equiv.) in MeOH (0.6 M). The reaction mixture was stirred at room temperature overnight. Compounds **1a** and **1b** precipitated from their reaction solutions and were isolated by filtration. Ligands **1c** and **1d** were isolated as oils after concentration under high vacuum.

**Ligand 1a:** Yield 84% (orange solid). MS (EI+): *m*/*z* = 415 $[M]^+$. $^1H$ NMR (300 MHz, $CD_2Cl_2$): δ = 13.38 (br. s, 1 H, O*H*), 8.61 (s, 1 H, N=C*H*), 7.51–7.45 (m, 1 H, Ar-*H*), 7.42–7.36 (m, 4 H, Ar-*H*), 7.29–7.21 (m, 3 H, Ar-*H*), 7.07–6.98 (m, 2 H, Ar-*H*), 3.76 (s, 3 H, O$CH_3$), 1.39 [s, 9 H, Ar-C($CH_3$)$_3$], 1.33 [s, 9 H, Ar-C($CH_3$)$_3$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz): δ = 163.8 (CH), 158.5 (C), 157.1 (C), 147.9 (C), 140.7 (C), 136.9 (C), 134.6 (C), 131.7 (CH), 131.4 (CH), 129.4 (CH), 129.0 (CH), 128.9 (C), 128.1 (CH), 127.1 (CH), 126.7 (CH), 120.7 (CH), 118.8 (C), 118.3 (CH), 110.9 (CH), 55.5 ($CH_3$), 35.3 (C), 34.4 (C), 31.6 ($CH_3$), 29.4 ($CH_3$) ppm.

**Ligand 1b:** Yield 95% (yellow solid). MS (EI+): *m*/*z* = 339 $[M]^+$. $^1H$ NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 8.72 (s, 1 H, N=C*H*), 7.47 (d, *J* = 2.5 Hz, 1 H, Ar-*H*), 7.29–7.18 (m, 3 H, Ar-*H*), 7.06–6.97 (m, 2 H, Ar-*H*), 3.92 (s, 3 H, OC$H_3$), 1.49 [s, 9 H, Ar-C(C$H_3$)$_3$], 1.35 [s, 9 H, Ar-C(C$H_3$)$_3$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz): $\delta$ = 164.3 (CH), 158.9 (C), 153.4 (C), 140.9 (C), 138.1 (C), 137.3 (C), 128.3 (CH), 128.0 (CH), 127.2 (CH), 121.4 (CH), 120.3 (CH), 119.0 (C), 112.4 (CH), 56.3 ($CH_3$), 35.5 (C), 34.5 (C), 31.7 ($CH_3$), 29.7 ($CH_3$) ppm.

**Ligand 1c:** Yield 73% (yellow oil). MS (EI+): *m*/*z* = 291 $[M]^+$. $^1H$ NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 13.77 (br s, 1 H, O*H*), 8.37 (s, 1 H, N=C*H*), 7.38 (d, *J* = 2.4 Hz, 1 H, Ar-*H*), 7.12 (d, *J* = 2.4 Hz, 1 H, Ar-*H*), 3.75 (m, 2 H, CH=NC$H_2$), 3.67 (m, 2 H, $CH_3$OC$H_2$), 3.36 (s, 3 H, OC$H_3$), 1.43 [s, 9 H, Ar-C(C$H_3$)$_3$], 1.31 [s, 9 H, Ar-C(C$H_3$)$_3$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz): $\delta$ = 167.9 (CH), 158.4 (C), 140.5 (C), 136.9 (C), 127.3 (CH), 126.5 (CH), 118.4 (C), 72.4 ($CH_2$), 59.4 ($CH_3$), 59.0 ($CH_2$), 35.3 (C), 34.5 (C), 31.7 ($CH_3$), 29.6 ($CH_3$) ppm.

**Ligand 1d:** Yield 96% (yellow oil). MS (EI+): *m*/*z* = 305 $[M]^+$. $^1H$ NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 13.86 (br s, 1 H, O*H*), 8.41 (s, 1 H, N=C*H*), 7.37 (d, *J* = 2.5 Hz, 1 H, Ar-*H*), 7.11 (d, *J* = 2.5 Hz, 1 H, Ar-*H*), 3.66 (td, *J* = 6.8, *J* = 1.2 Hz, 2 H, CH=NC$H_2$), 3.46 (t, *J* = 6.1 Hz, 2 H, $CH_3$OC$H_2$), 3.32 (s, 3 H, OC$H_3$), 1.95 (quin, *J* = 6.6 Hz, 2 H, $CH_2$C$H_2$CH$_2$), 1.43 [s, 9 H, Ar-C(C$H_3$)$_3$], 1.31 [s, 9 H, Ar-C(C$H_3$)$_3$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz): $\delta$ = 166.7 (CH), 158.5 (C), 140.5 (C), 136.9 (C), 127.1 (CH), 126.3 (CH), 118.4 (C), 70.4 ($CH_2$), 58.7 ($CH_3$), 56.6 ($CH_2$), 35.3 (C), 34.5 (C), 31.7 ($CH_3$), 31.3 ($CH_2$), 29.6 ($CH_3$) ppm.

**General Procedure for the Synthesis of Ligands 2a–2d:** To a solution of **1a**–**1d** (1 equiv.) in MeOH (0.5 M) at 0 °C was added $NaBH_4$ (3 equiv.) in one portion. The reaction mixture was warmed to room temperature and stirred for 16 h. The solvent was removed with a rotary evaporator, and the solid obtained was dissolved in $Et_2O$ (20 mL), washed with a saturated $NaHCO_3$ solution (3× 10 mL), dried with $MgSO_4$, which was removed by filtration, and the filtrate concentrated.

**Ligand 2a:** Yield 90% (white foam). MS (EI+): *m*/*z* = 417 $[M]^+$. $^1H$ NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 8.88 (br s, 1 H, O*H* or N*H*), 7.41–7.31 (m, 2 H, Ar-*H*), 7.25–7.22 (m, 2 H, Ar-*H*), 7.16–6.98 (m, 6 H, Ar-*H*), 4.34 (m, 2 H, Ar-C$H_2$N), 3.83 (s, 3 H, OC$H_3$), 1.37 [s, 9 H, Ar-C(C$H_3$)$_3$], 1.27 [s, 9 H, Ar-C(C$H_3$)$_3$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz): $\delta$ = 157.2 (C), 154.0 (C), 145.5 (C), 141.7 (C), 136.4 (C), 132.1 (CH), 131.1 (CH), 129.9 (CH), 129.0 (CH), 128.6 (C), 127.6 (C), 123.9 (C), 123.6 (CH), 122.8 (CH), 121.4 (CH), 120.4 (CH), 113.8 (CH), 111.2 (CH), 55.9 ($CH_3$), 49.6 ($CH_2$), 35.2 (C), 34.5 (C), 31.7 ($CH_3$), 29.8 ($CH_3$) ppm.

**Ligand 2b:** Yield 99% (white solid). MS (EI+): *m*/*z* = 341 $[M]^+$. $^1H$ NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 8.71 (br s, 1 H, O*H* or N*H*), 7.32 (d, *J* = 2.4 Hz, 1 H, Ar-*H*), 7.31 (d, *J* = 2.4 Hz, 1 H, Ar-*H*), 7.09–6.88 (m, 4 H, Ar-*H*), 4.55 (br s, 1 H, O*H* or N*H*), 4.37 (s, 2 H, Ar-C$H_2$N), 3.84 (s, 3 H, OC$H_3$), 1.42 [s, 9 H, Ar-C(C$H_3$)$_3$], 1.31 [s, 9 H Ar-C(C$H_3$)$_3$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz): $\delta$ = 154.0 (C), 149.2 (C), 141.9 (C), 137.7 (C), 136.5 (C), 124.1 (CH), 123.7 (CH), 123.3 (CH), 121.5 (CH), 120.6 (CH), 114.4 (CH), 110.4 (CH), 55.9 ($CH_3$), 49.8 ($CH_2$), 35.3 (C), 34.6 (C), 31.8 ($CH_3$), 29.9 ($CH_3$) ppm.

**Ligand 2c:** Yield 99% (colourless oil). MS (EI+): *m*/*z* = 447 $[M]^+$. $^1H$ NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.19 (d, *J* = 2.4 Hz, 1 H, Ar-*H*), 6.87 (d, *J* = 2.4 Hz, 1 H, Ar-*H*), 3.95 (s, 2 H, Ar-C$H_2$N), 3.51 (t, *J* = 5.1 Hz, 2 H, NHC$H_2$CH$_2$), 3.34 (s, 3 H, OC$H_3$), 2.82 (t, *J* = 5.1 Hz, 2 H, $CH_2$C$H_2$OCH$_3$), 1.43 [s, 9 H, Ar-C(C$H_3$)$_3$], 1.30 [s, 9 H, Ar-C(C$H_3$)$_3$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz): $\delta$ = 155.2 (C), 140.7 (C), 135.9 (C), 123.7 (CH), 123.1 (CH), 122.6 (C), 71.4 ($CH_2$), 58.9 ($CH_3$), 53.8 ($CH_2$), 48.3 ($CH_2$), 35.2 (C), 34.4 (C), 31.8 ($CH_3$), 29.7 ($CH_3$) ppm.

**Ligand 2d:** Yield 99% (colourless oil). MS (EI+): *m*/*z* = 461 $[M]^+$. $^1H$ NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.19 (d, *J* = 2.5 Hz, 1 H, Ar-*H*), 6.88 (d, *J* = 2.5 Hz, 1 H, Ar-*H*), 3.94 (s, 2 H, Ar-C$H_2$N), 3.45 (t, *J* = 6.1 Hz, 2 H, NHC$H_2$CH$_2$), 3.30 (s, 3 H, OC$H_3$), 2.76 (t, *J* = 6.7 Hz, 2 H, $CH_2$C$H_2$OCH$_3$), 1.79 (m, 2 H, $CH_2$C$H_2$CH$_2$), 1.41 [s, 9 H, Ar-C(C$H_3$)$_3$], 1.28 [s, 9 H, Ar-C(C$H_3$)$_3$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz): $\delta$ = 155.3 (C), 140.7 (C), 135.9 (C), 123.6 (CH), 123.0 (CH), 122.8 (C), 71.5 ($CH_2$), 58.8 ($CH_3$), 53.9 ($CH_2$) 46.8 ($CH_2$), 35.2 (C), 34.4 (C), 31.8 ($CH_3$), 29.8 ($CH_2$), 29.6 ($CH_3$) ppm.

**Ligand 3a:** To a solution of 2-(2′-methoxyphenyl)phenol (1.379 g, 6.89 mmol) in pentane (20 mL) and $Et_2O$ (10 mL) in a Schlenk flask was added dropwise tetramethylethylenediamine (TMEDA; 0.800 g, 6.89 mmol). After 10 min, *n*BuLi was added (1.33 M in hexane, 5.30 mL, 7.05 mmol) at –78 °C. The mixture was stirred at room temperature for 4 h. A solution of 6-(bromomethyl)-2,4-di-*tert*-butylphenol (2.06 g, 6.89 mmol) in $Et_2O$ (3 mL) was added. The mixture was stirred overnight. The volatiles were removed, water (20 mL) and dichloromethane (20 mL) were added, and the organic phase was separated and washed with aqueous 1 M HCl (10 mL) and water (20 mL). The organic phase was then dried with $MgSO_4$ and filtered, and the volatiles were removed in vacuo to give a yellow oil. The residue was precipitated in pentane to give the ligand **3a** (0.669 g, yield 23%) as a white solid. MS (EI+): *m*/*z* = 418 $[M]^+$. $^1H$ NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.48–6.93 (m, 11 H, Ar-*H* and O*H*), 5.08 (s, 2 H, Ar-C$H_2$O), 3.82 (s, 3 H, OC$H_3$), 1.37 [s, 9 H, Ar-C(C$H_3$)$_3$], 1.26 [s, 9 H, Ar-C(C$H_3$)$_3$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz): $\delta$ = 156.9 (C), 155.6 (C), 152.9 (C), 142.1 (C), 136.9 (C), 131.6 (CH), 131.3 (CH), 129.2 (CH), 129.1 (CH), 128.8 (C), 127.9 (C), 124.6 (CH), 124.0 (CH), 121.9 (C), 121.6 (CH), 121.1 (CH), 111.6 (CH), 111.1 (CH), 70.5 ($CH_2$), 56.1 ($CH_3$), 35.1 (C), 34.3 (C), 31.5 ($CH_3$), 29.7 ($CH_3$) ppm.

**Ligand 3b:** To a solution of 2-methoxyphenol (0.415 g, 0.33 mmol) in pentane (10 mL) and $Et_2O$ (5 mL) in a Schlenk flask, TMEDA (0.388 g, 0.33 mmol) was added dropwise. After 10 min, *n*BuLi (1.7 M in hexane, 1.97 mL, 0.33 mmol) was added at –78 °C. The mixture was stirred at room temperature for 4 h. A solution of 6-(bromomethyl)-2,4-di-*tert*-butylphenol (1.00 g, 0.33 mmol) in $Et_2O$ (2 mL) was added. The mixture was stirred overnight. The volatiles were removed, water (20 mL) and dichloromethane (20 mL) were added, and the organic phase was separated and washed with aqueous 1 M HCl (10 mL) and water (20 mL). The organic phase was then dried with $MgSO_4$ and filtered, and the volatiles were removed in vacuo to give a yellow oil. The residue was precipitated in cold pentane to give the ligand **3b** (0.351 g, yield 31%) as a white solid. MS (EI+): *m*/*z* = 342 $[M]^+$. $^1H$ NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.65 (s, 1 H, O*H*), 7.32 (d, *J* = 2.6 Hz, 1 H, Ar-*H*), 7.18–6.90 (m, 5 H, Ar-*H*), 5.06 (s, 2 H, Ar-C$H_2$O), 3.92 (s, 3 H, OC$H_3$), 1.45 [s, 9 H, Ar-C(C$H_3$)$_3$], 1.30 [s, 9 H, Ar-C(C$H_3$)$_3$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz): $\delta$ = 153.5 (C), 151.4 (C), 147.6 (C), 142.0 (C), 136.9 (C), 124.9 (CH), 124.4 (CH), 124.2 (CH), 122.1 (C), 121.5 (CH), 118.7 (CH), 112.3 (CH), 74.2 ($CH_2$), 56.2 ($CH_3$), 35.3 (C), 34.5 (C), 31.7 ($CH_3$), 29.8 ($CH_3$) ppm.

**Ligand 3c:** To a suspension of NaH (5.20 g, 130.3 mmol) in THF (60 mL) in a Schlenk flask, 2-methoxyethanol (7.63 g, 100.2 mmol) was added dropwise at room temperature. The mixture was stirred for 4 h. A solution of 6-(bromomethyl)-2,4-di-*tert*-butylphenol (10.0 g, 33.4 mmol) in THF (60 mL) was added. The mixture was heated under reflux overnight. Upon cooling, water (50 mL) was added, and the organic phase was separated, washed with aqueous 1 M HCl (30 mL) and water (50 mL). The organic phase was then

dried with $MgSO_4$ and filtered, and the volatiles were removed in vacuo to give the ligand **3c** (8.70 g, yield 88%) as a yellow oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.61–7.50 (br. s, 1 H, O*H*), 7.27 (d, *J* = 2.4 Hz, 1 H, Ar-*H*), 6.90 (d, *J* = 2.4 Hz, 1 H, Ar-*H*), 4.71 (s, 2 H, Ar-C$H_2$O), 3.74–3.69 (m, 2 H, $CH_3OCH_2$), 3.62–3.57 (m, 2 H, $CH_2OCH_2$), 3.41 (s, 3 H, $OCH_3$), 1.43 [s, 9 H, Ar-C($CH_3$)$_3$], 1.29 [s, 9 H, Ar-C($CH_3$)$_3$] ppm. $^{13}$C{$^1$H} NMR (75 MHz): $\delta$ = 153.2 (C), 141.5 (C), 136.4 (C), 124.2 (CH), 123.4 (CH), 122.0 (C), 73.7 ($CH_2$), 71.6 ($CH_2$), 69.4 ($CH_2$), 59.1 ($CH_3$), 35.1 (C), 34.3 (C), 31.7 ($CH_3$), 29.8 ($CH_3$) ppm.

**Ligand 3d:** To a suspension of NaH (0.239 g, 9.96 mmol) in THF (20 mL) in a Schlenk flask, 3-methoxypropan-1-ol (0.464 g, 5.15 mmol) was added dropwise at room temperature. The mixture was stirred for 4 h. A solution of 6-(bromomethyl)-2,4-di-*tert*-butylphenol (1.009 g, 3.37 mmol) in THF (10 mL) was added. The mixture was heated under reflux overnight. Upon cooling, water (20 mL) was added, and the organic phase was separated and washed with aqueous 1 M HCl (10 mL) and water (20 mL). The organic phase was then dried with $MgSO_4$ and filtered, and the volatiles were removed in vacuo to give a yellow residue. Column chromatography (EtOAc/heptane, 1:10, v/v) gave the ligand **3d** (0.220 g, yield 21%) as a colourless oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.69 (s, 1 H, O*H*), 7.26 (d, *J* = 2.6 Hz, 1 H, Ar-*H*), 6.88 (d, *J* = 2.6 Hz, 1 H, Ar-*H*), 4.66 (s, 2 H, Ar-C$H_2$O), 3.66 (t, *J* = 6.1 Hz, 2 H, $CH_2OCH_2$), 3.49 (t, *J* = 6.1 Hz, 2 H, $CH_3OCH_2$), 3.35 (s, 3 H, $OCH_3$), 1.91 (quint, *J* = 6.1 Hz, 2 H, $CH_2CH_2CH_2$), 1.42 [s, 9 H, Ar-C($CH_3$)$_3$], 1.28 [s, 9 H, Ar-C($CH_3$)$_3$] ppm. $^{13}$C{$^1$H} NMR (75 MHz): $\delta$ = 153.1 (C), 141.5 (C), 136.4 (C), 124.1 (CH), 123.1 (CH), 122.1 (C), 73.6 ($CH_2$), 69.9 ($CH_2$), 68.2 ($CH_2$), 58.9 ($CH_3$), 35.1 (C), 34.3 (C), 31.8 ($CH_3$), 29.8 ($CH_2$), 29.8 ($CH_3$) ppm.

**Complex IIb:** To a solution of freshly distilled $TiCl_4$ (0.355 g, 1.87 mmol) in toluene at –78 °C in a Schlenk flask, a solution of ligand **1e** (0.636 g, 1.70 mmol) in toluene was added dropwise. The mixture was allowed to return to room temperature and then stirred overnight. The volatiles were removed under reduced pressure, and pentane was added to precipitate the complex. The solid was isolated by filtration with a cannula, washed twice with pentane and dried under vacuum. Complex **IIb** was obtained as a dark red solid (0.770 g, yield 88%). $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 8.14 (s, 1 H, N=C*H*), 7.56–7.45 (m, 3 H, Ar-*H*), 7.42–7.27 (m, 5 H, Ar-*H*), 7.20–7.11 (m, 2 H, Ar-*H*), 4.34 (s, 3 H, $OCH_3$), 2.34 (s, 3 H, Ar-C$H_3$), 1.50 [s, 9 H, Ar-C($CH_3$)$_3$] ppm. $^{13}$C{$^1$H} NMR (75 MHz): $\delta$ = 169.3 (CH), 162.0 (C), 158.5 (C), 152.0 (C), 136.6 (C), 136.1 (CH), 134.6 (C), 133.1 (CH), 131.7 (2 C, CH), 131.1 (C), 130.5 (C), 130.2 (CH), 129.5 (CH), 128.2 (CH), 127.8 (CH), 127.6 (C), 126.2 (CH), 123.5 (CH), 72.5 ($CH_3$), 35.4 (C), 30.0 ($CH_3$), 21.1 ($CH_3$) ppm. $C_{25}H_{26}Cl_3NO_2Ti$ (526.74): calcd. C 57.01, H 4.98, N 2.66; found C 56.87, H 5.09, N 2.65.

**General Procedure for the Preparation of the Titanium Complexes 4 and 5:** To a solution of freshly distilled $TiCl_4$ (1.1 equiv.) in toluene at –78 °C in a Schlenk flask, a solution of the ligand (1.0 equiv.) in toluene was added dropwise. The mixture was allowed to return to room temperature and then warmed to 50 °C for 3 h as a stream of argon was bubbled through to facilitate the release of HCl. After the reaction mixture had cooled to room temperature, the volatiles were removed under reduced pressure, and pentane was added to precipitate the complex. The solid was isolated by filtration with a cannula and dried under vacuum.

**Complex 4:** The general procedure was applied with $TiCl_4$ (0.100 g, 0.53 mmol) and **2c** (0.141 g, 0.48 mmol) in toluene (10 mL). The removal of the volatiles gave **4** (0.180 g, yield 75%). Single crystals were grown by slow diffusion of heptane into a saturated solution of **4** in dichloromethane. $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.36 (d, *J* = 2.0 Hz, 1 H, Ar-*H*), 7.11 (d, *J* = 2.0 Hz, 1 H, Ar-*H*), 4.58 (m, 1 H, C$H_2$), 4.36 (m, 1 H, C$H_2$), 4.26 (s, 3 H, $OCH_3$), 4.17 (m, 1 H, C$H_2$), 3.86 (m, 1 H, C$H_2$), 3.64 (m, 1 H, C$H_2$), 3.182 (m, 1 H, C$H_2$), 1.54 [s, 9 H, C($CH_3$)$_3$], 1.31 [s, 9 H, C($CH_3$)$_3$] ppm. $^{13}$C{$^1$H} NMR (75 MHz): $\delta$ = 161.2 (C), 148.5 (C), 135.9 (C), 128.9 (C), 124.8 (CH), 124.3 (CH), 75.3 ($CH_2$), 67.0 ($CH_3$), 55.6 ($CH_2$), 50.5 ($CH_2$), 35.8 (C), 35.1 (C), 31.5 ($CH_3$), 30.5 ($CH_3$) ppm. $C_{18}H_{30}Cl_3NO_2Ti$ (446.70): calcd. C 48.40, H 6.77, N 3.14; found C 48.35, H 6.79, N 3.05.

**Complex 5:** The general procedure was applied with $TiCl_4$ (0.209 g, 1.1 mmol) and **2d** (0.307 g, 1.0 mmol) in toluene (10 mL). The removal of the volatiles gave **5** as a red solid (0.322 g, yield 70%). The analysis of the complex by NMR spectroscopy showed the formation of two complexes **5(A)**/**5(B)** in a 73:23 ratio. Single crystals of **5(A)** were grown by slow diffusion of heptane into a dichloromethane solution. $C_{19}H_{32}Cl_3NO_2Ti$ (460.73): calcd. C 49.54, H 7.00, N 3.04; found C 49.37, H 7.08, N 2.94.

**Compound 5(A):** $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.34 (d, *J* = 2.3 Hz, 1 H, Ar-*H*), 7.11 (d, *J* = 2.1 Hz, 1 H, Ar-*H*), 4.86 (td, *J* = 11.6, *J* = 2.1 Hz, 1 H, C$H_2$), 4.54 (t, *J* = 12.8 Hz, 1 H, C$H_2$), 4.23 (s, 3 H, $OCH_3$), 4.08 (dt, *J* = 11.7, *J* = 3.4 Hz, 1 H, C$H_2$), 3.57 (dd, *J* = 13.8, *J* = 2.1 Hz, 1 H, C$H_2$), 3.23 (td, *J* = 12.0, *J* = 2.1 Hz, 1 H, C$H_2$), 3.13 (m, 1 H, C$H_2$), 2.35 (m, 1 H, C$H_2$), 1.96 (m, 1 H, C$H_2$), 1.54 [s, 9 H, C($CH_3$)$_3$], 1.31 [s, 9 H, C($CH_3$)$_3$] ppm. $^{13}$C{$^1$H} NMR (75 MHz): $\delta$ = 163.2 (C), 148.2 (C), 135.8 (C), 130.0 (C), 124.7 (CH), 124.3 (CH), 78.5 ($CH_2$), 69.4 ($CH_3$), 57.2 ($CH_2$), 52.4 ($CH_2$), 35.7 (C), 35.1 (C), 31.5 ($CH_3$), 30.4 ($CH_3$), 26.9 ($CH_2$) ppm.

**Compound 5(B):** $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.91 (br. s, 1 H, N*H*), 7.51 (d, *J* = 2.0 Hz, 1 H, Ar-*H*), 7.16 (d, *J* = 2.0 Hz, 1 H, Ar-*H*), 4.51 (br. s, 2 H, C$H_2$), 3.75 (m, 2 H, C$H_2$), 3.52 (br. s, 2 H, C$H_2$), 3.40 (s, 3 H, $OCH_3$), 2.11 (m, 2 H, C$H_2$), 1.57 [s, 9 H, C($CH_3$)$_3$], 1.32 [s, 9 H, C($CH_3$)$_3$] ppm. $^{13}$C{$^1$H} NMR (75 MHz): $\delta$ = 148.7 (C), 140.4 (C), 127.1 (CH), 126.6 (CH), 123.1 (C), 73.5 ($CH_2$), 59.9 ($CH_3$), 50.1 ($CH_2$), 48.8 ($CH_2$), 36.1 (C), 35.2 (C), 31.4 ($CH_3$), 31.2 ($CH_3$), 25.1 ($CH_2$) ppm.

**General Procedure for the Preparation of the Titanium Complexes 6 and 7:** To a solution of freshly distilled $TiCl_4$ (1.1 equiv.) in toluene at –78 °C in a Schlenk flask, a solution of the ligand (1.0 equiv.) in toluene was added dropwise. The mixture was allowed to return to room temperature and stirred overnight. The solution was concentrated, and pentane was added to precipitate the complex. The solid was isolated by filtration with a cannula, washed three times with pentane and dried under vacuum.

**Complex 6:** The general procedure was applied with $TiCl_4$ (0.188 g, 0.99 mmol) and **3c** (0.264 g, 0.90 mmol) in toluene (10 mL). The removal of the volatiles gave **6** (0.300 g, yield 74%) as a dark red solid. Single crystals were grown by slow diffusion of pentane into a solution of **6** in dichloromethane. $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.39 (d, *J* = 2.3 Hz, 1 H, Ar-*H*), 7.08 (d, *J* = 2.3 Hz, 1 H, Ar-*H*), 5.10 (s, 2 H, Ar-C$H_2$O), 4.35 (br. s, 4 H, $CH_3OCH_2$ and $CH_2OCH_2$), 4.26 (s, 3 H, $OCH_3$), 1.54 [s, 9 H, Ar-C($CH_3$)$_3$], 1.31 [s, 9 H, Ar-C($CH_3$)$_3$] ppm. $^{13}$C{$^1$H} NMR (75 MHz): $\delta$ = 161.4 (C), 148.8 (C), 135.6 (C), 126.4 (C), 125.0 (CH), 123.6 (CH), 78.5 ($CH_2$), 73.7 ($CH_2$), 73.3 ($CH_2$), 67.4 ($CH_3$), 35.8 (C), 35.2 (C), 31.5 ($CH_3$), 30.5 ($CH_3$) ppm. $C_{18}H_{29}Cl_3O_3Ti$ (447.68): calcd. C 48.30, H 6.53; found C 48.16, H 6.65.

**Complex 7:** The general procedure was applied with $TiCl_4$ (0.144 g, 0.76 mmol) and **3d** (0.215 g, 0.69 mmol) in toluene (10 mL). The removal of the volatiles gave **7** (0.174 g, yield 55%) as a dark red solid. $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.39 (d, *J* = 2.3 Hz, 1 H,

Ar-*H*), 7.08 (d, $J$ = 2.3 Hz, 1 H, Ar-*H*), 5.15 (s, 2 H, Ar-C$H_2$O), 4.42 (t, $J$ = 5.5 Hz, 2 H, $CH_2OCH_2$), 4.29 (t, $J$ = 5.2 Hz, 2 H, $CH_3OCH_2$), 4.25 (s, 3 H, $OCH_3$), 2.41 (quint, $J$ = 5.5 Hz, 2 H, $CH_2CH_2CH_2$), 1.54 [s, 9 H, Ar-C($CH_3$)$_3$], 1.31 [s, 9 H, Ar-C($CH_3$)$_3$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz): $\delta$ = 162.7 (C), 148.6 (C), 135.5 (C), 127.5 (C), 124.9 (CH), 123.5 (CH), 80.5 ($CH_2$), 78.1 ($CH_2$), 77.5 ($CH_2$), 69.3 ($CH_3$), 35.7 (C), 35.2 (C), 31.5 ($CH_3$), 30.5 ($CH_3$), 27.9 ($CH_2$) ppm. $C_{19}H_{31}Cl_3O_3Ti$ (461.71): calcd. C 49.43, H 6.77; found C 49.35, H 6.63.

**Oligomerization Procedure:** The catalytic experiments were performed in a 35 mL stainless-steel autoclave equipped with a mechanical stirrer. In a typical procedure, the autoclave was preheated to 100 °C and flushed with nitrogen. After cooling to room temperature, the autoclave was filled with MAO (500 equiv.) in toluene. After 5 min, the titanium precatalyst in toluene was added to the reactor (total solvent volume 10 mL). The reactor was then pressurized with ethylene and heated at 30 °C. During the reaction, the pressure was maintained with a replenishing flow of ethylene. After 1 h, the reaction was stopped, and the autoclave was cooled to 10 °C and depressurized. The residual MAO was quenched with acidified methanol. The organic phase was recovered and weighed after separation from a solution (5 mL) of $H_2SO_4$ (10%). The composition of the organic phase was then determined by GC analysis. If solid polyethylene formed, it was recovered from the reaction mixture by filtration, dried at 100 °C for 16 h and weighed. The thermal analysis of the polymers was conducted with a DSC Q100 analyzer (TA Instruments). The samples (< 10 mg) were heated to 150 °C and subsequently cooled to 0 or –70 °C at a rate of 10 °C/min. A second heating cycle to 180 °C was used for data analysis. The NMR spectra of the polymer were recorded with the samples in a mixture of deuterated and nondeuterated *o*-dichlorobenzene as the solvent at 393 K.

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[1] a) J. Tian, G. W. Coates, *Angew. Chem. Int. Ed.* **2000**, *39*, 3626–3629; *Angew. Chem.* **2000**, *112*, 3772; b) D. J. Jones, V. C. Gibson, S. M. Green, P. J. Maddox, *Chem. Commun.* **2002**, 1038–1039; c) V. Murphy, X. H. Bei, T. R. Boussie, O. Brummer, G. M. Diamond, C. Goh, K. A. Hall, A. M. Lapointe, M. Leclerc, J. M. Longmire, J. A. W. Shoemaker, H. Turner, W. H. Weinberg, *Chem. Rec.* **2002**, *2*, 278–289; d) V. Murphy, A. F. Volpe, W. H. Weinberg, *Curr. Opin. Chem. Biol.* **2003**, *7*, 427–433; e) T. R. Boussie, G. M. Diamond, C. Goh, K. A. Hall, A. M. LaPointe, M. Leclerc, C. Lund, V. Murphy, J. A. W. Shoemaker, U. Tracht, H. Turner, J. Zhang, T. Uno, R. K. Rosen, J. C. Stevens, *J. Am. Chem. Soc.* **2003**, *125*, 4306–4317; f) N. Adams, H. J. Arts, P. D. Bolton, D. Cowell, S. R. Dubberley, N. Friederichs, C. M. Grant, M. Kranenburg, A. J. Sealey, B. Wang, P. J. Wilson, A. R. Cowley, P. Mountford, M. Schroder, *Chem. Commun.* **2004**, 434–435; g) D. J. Jones, V. C. Gibson, S. M. Green, P. J. Maddox, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **2005**, *127*, 11037–11046; h) D. C. Webster, *Macromol. Chem. Phys.* **2008**, *209*, 237–246.

[2] a) T. R. Younkin, *Science* **2000**, *287*, 460–462; b) V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283–315; c) R. K. J. Bott, D. L. Hughes, M. Schormann, M. Bochmann, S. J. Lancaster, *J. Organomet. Chem.* **2003**, *665*, 135–149; d) W. Q. Hu, X. L. Sun, C. Wang, Y. Gao, Y. Tang, L. P. Shi, W. Xia, J. Sun, H. L. Dai, X. Q. Li, X. L. Yao, X. R. Wang, *Organometallics* **2004**, *23*, 1684–1688; e) D. A. Pennington, W. Clegg, S. J. Coles, R. W. Harrington, M. B. Hursthouse, D. L. Hughes, M. E. Light, M. Schormann, M. Bochmann, S. J. Lancaster, *Dalton Trans.* **2005**, 561–571; f) C. Wang, X.-L. Sun, Y.-H. Guo, Y. Gao, B. Liu, Z. Ma, W. Xia, L.-P. Shi, Y. Tang, *Macromol. Rapid Commun.* **2005**, *26*, 1609–1614; g) C. Wang, Z. Ma, X. L. Sun, Y. Gao, Y. H. Guo, Y. Tang, L. P. Shi, *Organometallics* **2006**, *25*, 3259–3266; h) M. Gao, C. Wang, X. Sun, C. T. Qian, Z. Ma, S. H. Bu, Y. Tang, Z. W. Xie, *Macromol. Rapid Commun.* **2007**, *28*, 1511–1516; i) H. Zhang, S. Katao, K. Nomura, J. Huang, *Organometallics* **2007**, *26*, 5967–5977; j) T. Q. Xu, J. Liu, G. P. Wu, X. B. Lu, *Inorg. Chem.* **2011**, *50*, 10884–10892; k) X.-C. Shi, G.-X. Jin, *Organometallics* **2012**, *31*, 7198–7205; l) L. Zhang, X. Luo, W. Gao, J. Zhang, Y. Mu, *Organometallics* **2013**, *32*, 6277–6285.

[3] T. Matsugi, T. Fujita, *Chem. Soc. Rev.* **2008**, *37*, 1264–1277.

[4] a) S. Matsui, Y. Tohi, M. Mitani, J. Saito, H. Makio, H. Tanaka, M. Nitabaru, T. Nakano, T. Fujita, *Chem. Lett.* **1999**, 1065–1066; b) M. Mitani, R. Furuyama, J. Mohri, J. Saito, S. Ishii, H. Terao, T. Nakano, H. Tanaka, T. Fujita, *J. Am. Chem. Soc.* **2003**, *125*, 4293–4305; c) Y. Suzuki, Y. Inoue, H. Tanaka, T. Fujita, *Macromol. Rapid Commun.* **2004**, *25*, 493–497; d) A. V. Prasad, H. Makio, J. Saito, M. Onda, T. Fujita, *Chem. Lett.* **2004**, *33*, 250–251; e) H. Makio, T. Fujita, *Acc. Chem. Res.* **2009**, *42*, 1532–1544; f) H. Terao, A. Iwashita, N. Matsukawa, S. Ishii, M. Mitani, H. Tanaka, T. Nakano, T. Fujita, *ACS Catal.* **2011**, *1*, 254–265.

[5] a) Y. Suzuki, S. Kinoshita, A. Shibahara, S. Ishii, K. Kawamura, Y. Inoue, T. Fujita, *Organometallics* **2010**, *29*, 2394–2396; b) S. Kinoshita, K. Kawamura, T. Fujita, *Chem. Asian J.* **2011**, *6*, 284–290; c) Y. Suzuki, S. Kinoshita, A. Shibahara, N. Yoshimura, I. Hara, T. Hamada, K. Kawamura, K. Tsurugi, Y. Saito, S. Ishii, Y. Nakayama, N. Matsukawa, S. Murata, WO 2009005003 A1, **2009**.

[6] a) J. B. Cazaux, P. Braunstein, L. Magna, L. Saussine, H. Olivier-Bourbigou, *Eur. J. Inorg. Chem.* **2012**, 2942–2950; b) F. Grasset, J. B. Cazaux, L. Magna, P. Braunstein, H. Oliver-Bourbigou, *Dalton Trans.* **2012**, *41*, 10396–10404; c) J. A. Suttil, D. S. McGuinness, M. Pichler, M. G. Gardiner, D. H. Morgan, S. J. Evans, *Dalton Trans.* **2012**, *41*, 6625–6633; d) J. A. Suttil, D. S. McGuinness, M. G. Gardiner, S. J. Evans, *Dalton Trans.* **2013**, *42*, 4185–4196.

[7] For a review on tridentate ligands in group IV metal catalysts for α-olefin homo-/copolymerization, see: C. Redshaw, Y. Tang, *Chem. Soc. Rev.* **2012**, *41*, 4484–4510.

[8] a) D. C. H. Oakes, B. S. Kimberley, V. C. Gibson, D. J. Jones, A. J. P. White, D. J. Williams, *Chem. Commun.* **2004**, 2174–2175; b) D. C. H. Oakes, V. C. Gibson, A. J. P. White, D. J. Williams, *Inorg. Chem.* **2006**, *45*, 3476–3477.

[9] J. A. Suttil, M. F. Shaw, D. S. McGuinness, M. G. Gardiner, S. J. Evans, *Dalton Trans.* **2013**, *42*, 9129–9138.

[10] a) D. S. McGuinness, P. Wasserscheid, D. H. Morgan, J. T. Dixon, *Organometallics* **2005**, *24*, 552–556; b) D. S. McGuinness, D. B. Brown, R. P. Tooze, F. M. Hess, J. T. Dixon, A. M. Z. Slawin, *Organometallics* **2006**, *25*, 3605–3610; c) D. S. McGuinness, A. J. Rucklidge, R. P. Tooze, A. M. Z. Slawin, *Organometallics* **2007**, *26*, 2561–2569.

[11] G. Alesso, M. Sanz, M. E. G. Mosquera, T. Cuenca, *Eur. J. Inorg. Chem.* **2008**, 4638–4649.

[12] Y. L. Choi, H. S. Lim, H. J. Lim, J. N. Heo, *Org. Lett.* **2012**, *14*, 5102–5105.

[13] A. Sokolowski, J. Müller, T. Weyhermüller, R. Schnepf, P. Hildebrandt, K. Hildenbrand, E. Bothe, K. Wieghardt, *J. Am. Chem. Soc.* **1997**, *119*, 8889–8900.

[14] T. Tsuritani, H. Shinokubo, K. Oshima, *Tetrahedron Lett.* **1999**, *40*, 8121–8124.

 

[15] a) A. Sattler, J. A. Labinger, J. E. Bercaw, *Organometallics* **2013**, *32*, 6899–6902; b) A. Sattler, D. G. VanderVelde, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2014**, *136*, 10790–10800.
[16] J. Justino, A. R. Dias, J. Ascenso, M. M. Marques, P. J. T. Tait, *Polym. Int.* **1997**, *44*, 407–412.
[17] The reaction was stopped after 30 min, because we reached the maximum ethylene consumption in relation to the volume capacity of our autoclaves.
[18] T. V. Hansen, L. Skattebol, *Tetrahedron Lett.* **2005**, *46*, 3829–3830.
[19] P. K. Agarwal, S. K. Sharma, D. Sawant, B. Kundu, *Tetrahedron* **2009**, *65*, 1153–1161.
[20] D. C. Harrowven, T. Woodcock, P. D. Howes, *Tetrahedron Lett.* **2002**, *43*, 9327–9329.

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