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High temperature ethylene polymerization catalyzed by titanium(IV) complexes with tetradentate aminophenolate ligands in *cis*-O, N, N chelating mode†

Ruiguo Zhao, Taotao Liu, Liying Wang and Haiyan Ma*

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A series of titanium trichloride complexes **1a–4a**, **7a–10a** ligated with claw-type tetradentate aminophenolate ligands were synthesized from the direct reaction of $TiCl_4(THF)_2$ with 1 equiv. of the corresponding aminophenol in the presence of triethylamine. For comparison purposes, titanium isopropoxide complexes **5e–8e** were also synthesized *via* the reaction of $Ti(O^iPr)_4$ and 1 equiv. of the proligand. Similar reactions of $ZrCl_4(THF)_2$ with the corresponding aminophenol ligands in the presence of triethylamine only allowed the isolation of zirconium complex **8b**. The X-ray diffraction studies reveal that titanium trichloride complexes **2a**, **9a** and titanium triisopropoxide complex **5e** all possess a distorted octahedral geometry with the tetradentate aminophenolate ligand in *cis*-O, N, N chelating mode, where the methoxy group of the aryl unit does not coordinate with the metal center in the solid state. Upon activation with MMAO, these titanium and zirconium(IV) complexes exhibited moderate to high catalytic activities for ethylene polymerization at 30–120 °C, producing high-molecular-weight polyethylenes with broad distributions (M_w/M_n = 10.2–34.8). The activities of titanium trichloride complexes are significantly higher than those of titanium isopropoxide and zirconium trichloride complexes at high temperatures. The highest activity of 15 456 kg (mol-Ti h)$^{-1}$ could be achieved by titanium trichloride complex **8a** with bromo groups on both *ortho*- and *para*-positions of the phenolate ring of the ligand at 120 °C.

Introduction

Since the discovery of metallocene–MAO catalytic systems for olefin polymerization, great achievements have been made in the fields of syntheses and catalytic applications of well-defined metallocene complexes.[1–16] But when people found that non-metallocene complexes of a variety of metals, including early,[17–24] middle[25–30] and late transition metals[31–42] as well as rare earth metals,[43–46] could also act as efficient catalysts for olefin polymerization and moreover they were readily accessible in comparison to metallocene complexes, the study on developing non-metallocene catalysts attracted considerable attention and became another hotspot in the field of olefin polymerization. For group 4 non-metallocene catalysts in particular,[47–62] upon activation with a suitable cocatalyst, their performance in catalytic olefin polymerization can meet and even exceed those of metallocene catalysts in many aspects. For example, the phenoxy-imine and pyrrolide-imine group 4 complexes developed by Fujita and co-workers, namely FI and PI catalysts,[63–78] when activated with MAO (methylaluminoxane) or MMAO (modified-methylaluminoxane), exhibited unprecedented activities for olefin polymerization. Furthermore, they can be used to precisely control polymer microstructures, achieve living polymerization of ethylene and propylene, generate highly isotactic and syndiotactic polypropylenes, and willfully produce polyolefins of low molecular weight to millions of ultra-high molecular weight. Besides all the attractive properties displayed by non-metallocene catalysts, one noticeable drawback is that non-metallocene complexes are generally less stable at high reaction temperatures which are however required by industrial polymerization processes.[12] This drawback to a great extent limits potential industrial applications of the vast majority of non-metallocene complexes.

So far, some thermally stable non-metallocene complexes for olefin polymerization have been obtained through the utili-

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Shanghai Key Laboratory of Functional Materials Chemistry and Laboratory of Organometallic Chemistry, East China University of Science and Technology, Shanghai 200237, P. R. China. E-mail: haiyanma@ecust.edu.cn; Fax: +86 21 64253519

† Electronic supplementary information (ESI) available: Figures, tables, and CIF files, giving NMR spectra of complexes **1c**, **1a–4a**, **6a–10a**, **8b** and **5e–8e**, ^1H NMR spectrum of typical polymer obtained by **8a**–MMAO (entry 17), variable-temperature ^1H NMR spectra of **2a** and **5e** in toluene-d_8, X-ray crystallographic data for complexes **2a**, **9a**, **8b** and **5e**. CCDC 968903 (**2a**), 968904 (**9a**), 991086 (**5e**) and 968905 (**8b**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt01122h

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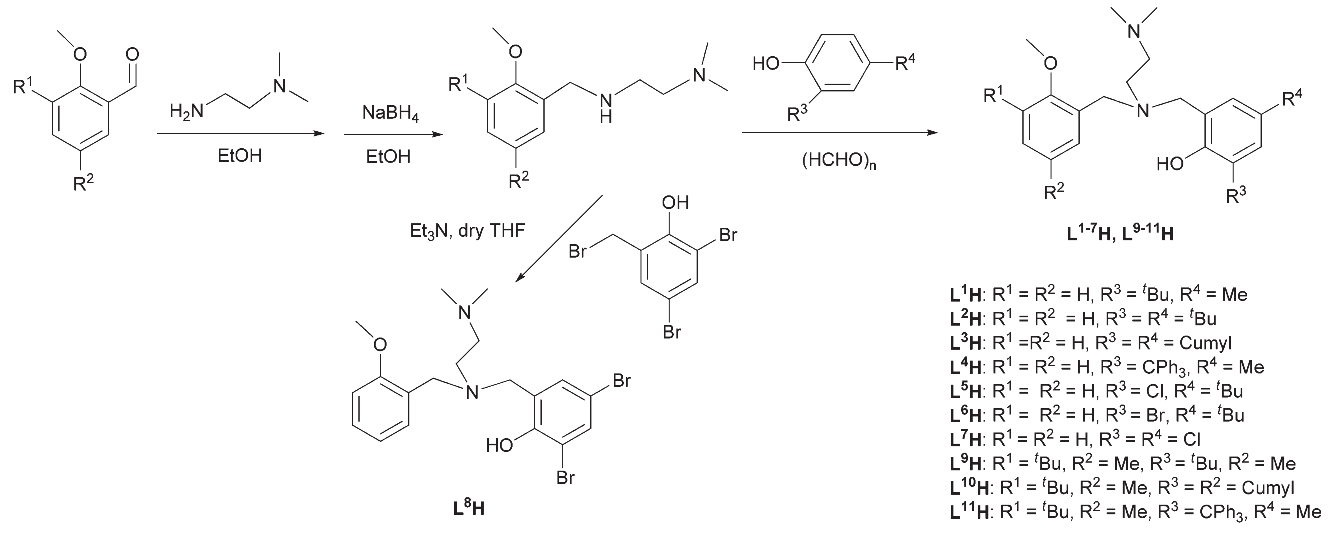
zation of ligands with multiple donor groups. For instance, Janiak and co-workers[79] reported that β-diketonato zirconium complexes bearing two different substituents on the α-position showed high catalytic activities for ethylene polymerization at 70 °C, which could meet and even exceed that of Cp_2ZrCl_2 under the same conditions. Fujita's group[80] reported that, upon activation with MAO, a FI-type catalyst, $[3\text{-}^t\text{Bu-2-(O)-}C_6H_3CH{=}NPh]_2TiCl_2$, was highly active in catalyzing ethylene polymerization (47 800 kg PE $(\text{mol-Ti h})^{-1}$) at 75 °C with *n*-heptane as the solvent. Sun and coworkers[81] reported a series of bis(6-benzimidazolylpyridine-2-carboxylimidate) titanium complexes bearing different substituents on the *N*-imino moiety which were capable of catalyzing the living polymerization of ethylene and exhibited high catalytic activities at 80 °C in the presence of MAO (5040–9720 kg PE $(\text{mol-Ti h})^{-1}$). There are only a few examples of group 4 non-metallocene catalysts that are thermal stable and active at temperatures close to or higher than 100 °C. In 2009, Chan and co-workers[82] reported some titanium complexes supported by pyridine-2-phenolate-6-(σ-aryl) ancillary ligands which displayed excellent ethylene polymerization activities up to 22 000 kg PE $(\text{mol-Ti h})^{-1}$ at 100 °C with borate as cocatalyst. Tang's group[83] developed a series of tridentate titanium complexes $[O^-N(H)X]TiCl_3$ (X = S or P), which exhibited good thermal stability and high activities toward ethylene polymerization at 110 °C, and the highest activity of 5400 kg PE $(\text{mol-Ti h atm})^{-1}$ was achieved. Very recently, our group[84] reported a series of novel eight-coordinate zirconium dichloride complexes bearing two pyridylimino phenolate ligands which possessed excellent thermal stability and long lifetime. Upon activation with MMAO, these complexes displayed high activities up to 1040 kg PE $(\text{mol-Zr h})^{-1}$ at 140 °C in *o*-xylene toward ethylene polymerization, and a lifetime of nearly 5 h at 140 °C could be obtained together with a satisfactory activity of 420 kg PE $(\text{mol-Zr h})^{-1}$. From the above exciting reports, it is deduced that the existence of multiple donor groups within the ligand framework may play an essential role in stabilizing the active center, thus leading to great enhancement of thermal stability and catalytic activity at high temperature. Inspired by these results, we are interested to obtain titanium and zirconium complexes supported with uninegative multidentate aminophenolate ligands. In this work, a straightforward and efficient synthetic strategy to prepare titanium, zirconium trichloride complexes and titanium isopropoxide complexes, ligated with tetradentate $ONNO^-$-type aminophenolate ligands, was reported. The ethylene polymerization reactions of the synthesized titanium and zirconium complexes with various substituents on the phenolate ring and the pendant group were studied. In the presence of MMAO, titanium trichloride complexes showed moderate to high activities in catalyzing ethylene polymerization even at high temperatures of 100–160 °C.

Results and discussion

Synthesis and characterization of titanium and zirconium complexes

The claw-type aminophenol proligands **$L^{1-7}H$** and **$L^{9-11}H$** were synthesized according to the reported method as illustrated in Scheme 1:[85,86] the condensation reaction of *N*,*N*-dimethyl-1,2-ethanediamine with the benzaldehyde derivative in refluxing ethanol yielded the corresponding Schiff-base compounds, which were sequentially reduced to amines with excess $NaBH_4$; without further purification, the resultant secondary amines were subjected to Mannich reactions with substituted phenols to afford the target proligands. Analytically pure aminophenol proligands were obtained through column chromatography as colorless to light yellow oily substances or white powders in moderate yields. A similar route was adopted to synthesize the proligand **L^8H**, but no target product could be isolated. Alter-



Scheme 1 Synthesis and structures of the proligands $L^{1-11}H$.

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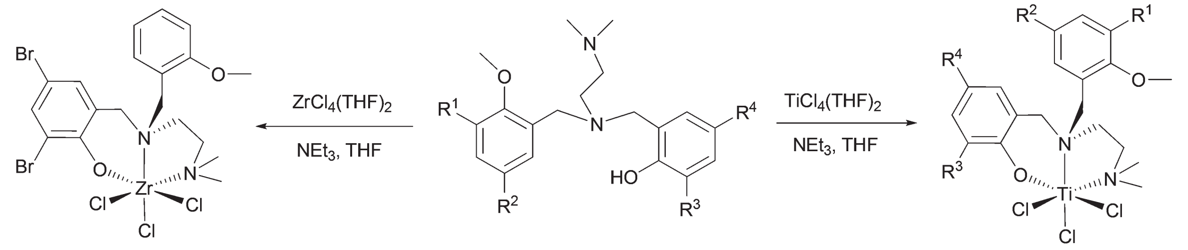


8b

$L^{1-11}H$

1a: $R^1 = R^2 = H$, $R^3 = {}^tBu$, $R^4 = Me$
2a: $R^1 = R^2 = H$, $R^3 = R^4 = {}^tBu$
3a: $R^1 = R^2 = H$, $R^3 = R^4$ = cumyl
4a: $R^1 = R^2 = H$, $R^3 = CPh_3$, $R^4 = Me$
6a: $R^1 = R^2 = H$, $R^3 = Br$, $R^4 = {}^tBu$
7a: $R^1 = R^2 = H$, $R^3 = R^4 = C$
8a: $R^1 = R^2 = Br$, $R^3 = R^4 = H$
9a: $R^1 = {}^tBu$, $R^2 = Me$, $R^3 = {}^tBu$, $R^2 = Me$
10a: $R^1 = {}^tBu$, $R^2 = Me$, $R^3 = R^2$ = cumyl

Scheme 2 Synthesis of titanium and zirconium complexes.

natively, the resultant secondary amine was reacted with 6-bromomethyl-2,4-dibromophenol to give readily the desired product in high yield (Scheme 1).[87–89]

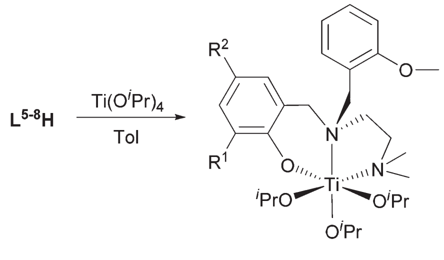
The first attempt to synthesize the target titanium trichloride complex **1a** was performed by reacting the neutral proligand $\mathbf{L^1H}$ with $TiCl_4$ in 1 : 1 molar ratio in toluene.[90] After a normal work-up procedure, a pale orange powder and a red powder were isolated sequentially. The former is likely a titanium hydrochloride adduct $(L^1H)TiCl_4{\cdot}HCl$ (**1c**), as characterized by the existence of two "active hydrogens" at 10.75 and 10.22 ppm in its ^1H NMR spectrum (see ESI†).[81,84] The latter is the target titanium complex **1a** but contaminated with a small amount of **1c**, which however could not be further purified *via* repetitive recrystallization procedures. In view of the formation of **1c**, the reaction of $TiCl_4(THF)_2$ with 1 equiv. of the neutral proligand $\mathbf{L^1H}$ in the presence of excess triethylamine was carried out, which finally enabled the isolation of analytically pure **1a**, shown in Scheme 2.[91]

Similar reactions of the neutral proligands $\mathbf{L^{2-4}H}$, $\mathbf{L^{7-10}H}$ with 1 equiv. of $TiCl_4(THF)_2$ in the presence of excess triethylamine in THF readily afforded the target titanium trichloride complexes **2a–4a**, **7a–10a** as red to deep red crystalline solids in moderate to high yields (Scheme 2). The corresponding titanium trichloride complexes ligated with ligands $\mathbf{L^5}$ and $\mathbf{L^{11}}$ could not be obtained *via* a similar approach, while the reaction of proligand $\mathbf{L^6H}$ with $TiCl_4(THF)_2$ in the presence of triethylamine did enable the isolation of a red powder characterized as complex **6a** mainly, which however could not be purified *via* recrystallization probably due to the close solubility of the target complex and impurities in toluene. Possibly, due to the substitution of halogen atoms in the ligand framework, complexes **7a** and **8a** are slightly soluble in toluene or THF, which is in contrast to the satisfactory solubility of complexes **1a–4a**, **9a** and **10a** in toluene. Furthermore, a shiny red crystal was accidentally gained from a saturated solution of complex **8a** in toluene. X-ray diffraction analysis revealed that it is a binuclear, oxygen-bridged titanium complex (**8d**, *vide post*), probably formed by a partially hydrolysis reaction of **8a** with a trace amount of water contained in the solvent.[92]

Because of the unsuccessful preparation or purification of titanium trichloride complexes **5a**, **6a**, titanium isopropoxide complexes **5e–8e** bearing halogen substituted aminophenolate ligands were synthesized *via* the reaction of the neutral proligands $\mathbf{L^{5-8}H}$ with 1 equiv. of $Ti(O^iPr)_4$ in toluene (Scheme 3).[93] In comparison with the corresponding trichloride complexes, all the titanium isopropoxide complexes could be easily purified and isolated in moderate yields as colorless crystals, since they are fairly soluble in hexane.

The strategy of adding excess triethylamine to trap hydrogen chloride was further used in the synthesis of the corresponding zirconium trichloride complexes. Proligands $\mathbf{L^1H}$, $\mathbf{L^2H}$ and $\mathbf{L^{7-10}H}$ were treated with 1 equiv. of $ZrCl_4(THF)_2$ in the presence of excess triethylamine in THF. However, from the reaction mixtures, only complex **8b** was successfully isolated *via* recrystallization with a mixture of toluene and THF. The other reactions generated unidentifiable substances and no target zirconium complex could be detected spectroscopically.

The stoichiometric structures of all the synthesized titanium and zirconium complexes were confirmed on the basis of ^1H and ^{13}C NMR spectroscopy as well as elemental analysis. The ^1H NMR spectrum of **1a** in $CDCl_3$ shows the disappearance of the phenoxy proton signal of $\mathbf{L^1H}$ at δ 10.67 ppm. The



5e: $R^1 = Cl$, $R^2 = {}^tBu$
6e: $R^1 = Br$, $R^2 = {}^tBu$
7e: $R^1 = R^2 = Cl$
8e: $R^1 = R^2 = Br$

Scheme 3 Synthesis of titanium isopropoxide complexes **5e–8e**.

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resonances of the methyl protons of the dimethylamido group $N(CH_3)_2$ appear as two sharp singlets and four doublets are observed for the two bridging methylene units of Ar–CH_2–N moieties as compared to the singlet in the free ligand. Furthermore, four multiplets accounting for the ethylene protons ($NCH_2CH_2NMe_2$) are displayed. All these features indicate the coordination of both amino units of the ligand to the titanium center. In contrast to these obvious differences displayed in the spectra of complex **1a** and free ligand **L^{1}H**, it is found that the sharp resonance assignable to Ar–OCH_3 in complex **1** hardly changes when compared to that of the free ligand. Similar phenomena are also witnessed in the proton NMR spectra of the rest of the titanium and zirconium complexes. Therefore, it is suggested that the methoxy group of the tetradentate aminophenolate ligand in these complexes does not take part in a coordination with the metal center, as they behave in the solid state (*vide post*).

Noticeably, careful analysis of the ^{1}H NMR spectra of the trichloride complexes indicates that in addition to the main set of signal peaks attributable to the aminophenolate ligand, there exists a series of small peaks in the vicinity of the former signals, which are also consistent with the stoichiometric structure of the ligand. For example, in the ^{1}H NMR spectrum of complex **1a**, the proton resonance of *tert*-butyl group is observed at δ 1.55 ppm as one sharp singlet; in addition, one small singlet at 1.56 ppm can also be observed. Similarly, the methyl protons of the dimethylamido group ($N(CH_3)_2$) resonate at δ 3.12, 2.63 ppm as two big sharp singlets and at δ 3.44, 3.18 ppm as two small singlets, respectively. The ratio of all minor signals is in correspondence to that of ligand **L^1**. All these indicate that complex **1a** has two isomers in solution. A similar event also occurs for titanium complexes **2a–4a** and **7a–10a** as well as zirconium complex **8b**. Hexa-coordinated titanium complexes supported by a tridentate ligand adopting *cis*- or *trans*-configurations have been reported previously.[83,94] According to this, there are two conceivable configurational isomers for octahedral complexes featuring a prochiral tridentate aminophenolate ligand, of which both of the chiral-at-metal *cis*- and *trans*-isomers exist as two stereoisomers, respectively (Fig. 1). On the basis of X-ray diffraction studies of complexes **2a**, **9a** and **8d**, where in each case the tetradentate aminophenolate ligand is coordinated to the metal center in a *cis*-O, N, N chelating mode in the solid state, it is believed that the *cis*-isomer should be dominant in solution for this series of complexes. Moreover, the possibility of isomerization of two isomers of complex **2a** was further studied by variable temperature ^{1}H NMR spectroscopy in the temperature range of 20 to 100 °C in toluene-d_8 (see ESI†). It can be noted that with the increase of temperature, the proportion of the *trans*-isomer increases slightly, but with all signals still in a relatively sharp state, implying that some isomerization processes do occur, but the structures of the isomers are not as fluxional as we anticipated.

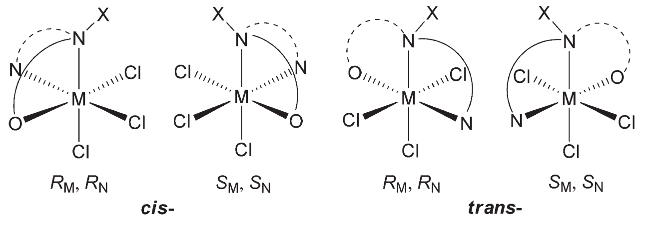

Fig. 1 Possible octahedral configuration isomers of titanium and zirconium complexes with the tridentate prochiral aminophenolate ligand.

Different patterns are displayed in the ^{1}H NMR spectra of titanium isopropoxide complexes **5e–8e**. At ambient temperature, except for complex **7e**, the aliphatic protons of the corresponding ligand in complexes **5e**, **6e** and **8e** all resonate as broad signals, whereas in the low field region some small peaks could be observed in addition to the well-coupled, dominant resonances. Therefore, the existence of isomers is suggested for these titanium isopropoxide complexes and the *cis*-isomer should be the major one according to the X-ray molecular structure of **5e**. The variable temperature ^{1}H NMR spectra of complex **5e** further indicate that a similar coordination mode of the ligand wrapping around the metal center as that of the titanium trichloride complexes could be observed below 0 °C (see ESI†). Four well-coupled doublets attributable to the two Ar–CH_2–N units and four multiplets accounting for the ethylene protons ($NCH_2CH_2NMe_2$) as well as two sharp $N(CH_3)_2$ signals are displayed, indicative of the coordination of two nitrogen donors to the metal center. The participation of the aromatic methoxy group to coordinating with the metal center is not observed. As the temperature increases, the signals of all the aliphatic protons of **5e** become broad and coalesce gradually and finally become sharp again at about 80 °C. Two singlets accounting for the Ar–CH_2–N units and one singlet for the $N(CH_3)_2$ unit imply either the dissociation of the nitrogen donors from the metal center or a fast coordination–dissociation equilibrium. All these features suggest that complexes **5e–8e** are more fluxional in solution than their trichloride analogues.

X-ray molecular structures of titanium complexes 2a, 9a, 8d and 5e

Single crystals of complexes **2a**, **9a**, **8d** and **5e** suitable for X-ray diffraction studies were obtained from saturated toluene solutions at −20 °C. The molecular structures of complexes **2a**, **9a**, **8d** and **5e** are given in Fig. 2–5.

In the solid state, complex **2a** possesses a distorted octahedral geometry, where the titanium center is coordinated by the aminophenolate ligand in a *cis*-chelating mode through two nitrogen atoms of the diamino moieties and the phenolate oxygen atom of the ligand. The distance from O2 to Ti atom is 5.127 Å, much larger than the sum of atomic radii of titanium and oxygen ($r_{(Ti)}$ = 2.110 Å, $r_{(O)}$ = 1.520 Å),[95] demonstrating that the aryl ether oxygen atom is not involved in coordination with the metal center. The Ti–O1 bond length is 1.791(5) Å; the Ti–N bond lengths are 2.343(6) and 2.300(7) Å; and the Ti–Cl bond lengths are 2.340(2), 2.296(3) and 2.276(3) Å. All these bond distances are in agreement with those observed for related N- and O-functionalized titanium dichloride complexes.[17,82]

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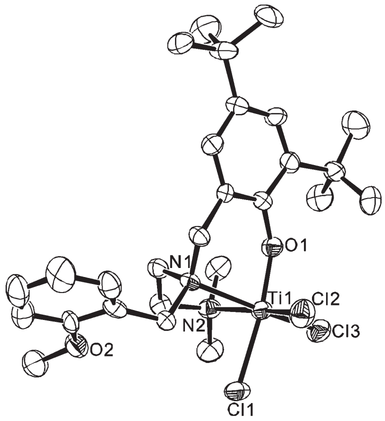

Fig. 2 Molecular structure of complex **2a** with thermal ellipsoids drawn at the 30% level, hydrogen atoms and uncoordinated solvent are omitted for clarity. The selected bond lengths (Å) and angles (°): Ti–O1 1.791(5), Ti–N1 2.343(6), Ti–N2 2.300(7), Ti–Cl3 2.276(3), Ti–Cl1 2.340(2), Ti–Cl2 2.296(3), N2–Ti–N1 77.9(2), Cl2–Ti–N1 90.23(17), Cl3–Ti–Cl2 102.90(11), O1–Ti–N2 91.8(2), Cl3–Ti–N2 89.34(19), O1–Ti–N1 81.1(2), O1–Ti–Cl1 171.81(19).

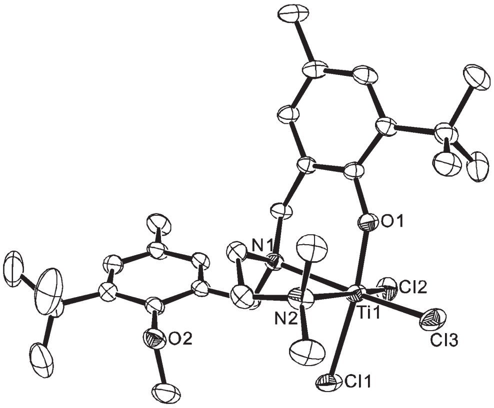

Fig. 3 Molecular structure of complex **9a** with thermal ellipsoids drawn at the 30% level, hydrogen atoms are omitted for clarity. The selected bond lengths (Å) and angles (°): Ti1–O1 1.783(3), Ti1–N2 2.310(4), Ti1–Cl3 2.2721(18), Ti1–N1 2.326(4), Ti1–Cl2 2.282(2), Ti1–Cl1 2.3493(19), Cl3–Ti1–Cl2 103.08(7), Cl3–Ti1–N2 90.10(13), O1–Ti1–N2 91.95(16), O1–Ti1–N1 81.77(14), Cl2–Ti1–N1 89.72(10), O1–Ti1–Cl1 172.81(11), N2–Ti1–N1 77.49(15).

The sum of specific angles around the Ti center (N1–Ti1–Cl2, Cl3–Ti1–Cl2, N2–Ti1–Cl3 and N2–Ti1–N1) is 360.37°, very close to the ideal 360°, proving that Ti, N1, N2, Cl2, Cl3 are nearly perfectly coplanar. On the basis of this lead, O1, Ti1, Cl1 (O1–Ti1–Cl1 = 171.18(19)°) occupy the axial position of the octahedron with O1 and Cl1 located on the upper or lower side of the above plane, respectively. Furthermore, the N1–Ti1–N2, O1–Ti1–N1, and O1–Ti1–N2 bond angles are 77.9(2)°, 81.2(2)° and 91.8(2)°, close to 90°, indicating that the three coordinated heteroatoms O1, N1 and N2 are located in a *cis*-fashion and therefore three chloride ligands are also located in a *cis*-position to each other, which is beneficial to the polymerization of olefins.[17]

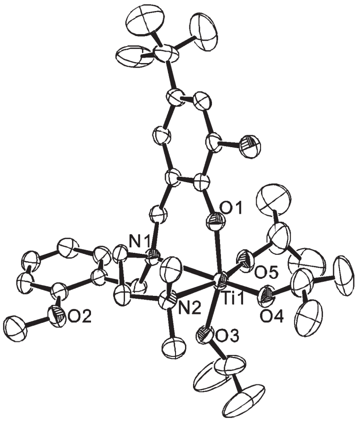

Fig. 4 Molecular structure of complex **5e** with thermal ellipsoids drawn at the 30% level, hydrogen atoms and uncoordinated solvent are omitted for clarity. The selected bond lengths (Å) and angles (°): Ti1–O1 1.949(3), Ti1–O3 1.836(3), Ti1–O4 1.787(3), Ti1–O5 1.808(3), Ti1–N2 2.387(4), Ti1–N1 2.390(3), O4–Ti1–O5 104.58(15), O3–Ti1–O1 160.37(13), O4–Ti1–N2 90.30(14), O1–Ti1–N2 81.73(13), O5–Ti1–N1 88.82(13), O1–Ti1–N1 79.06(11), N2–Ti1–N1 76.07(12).

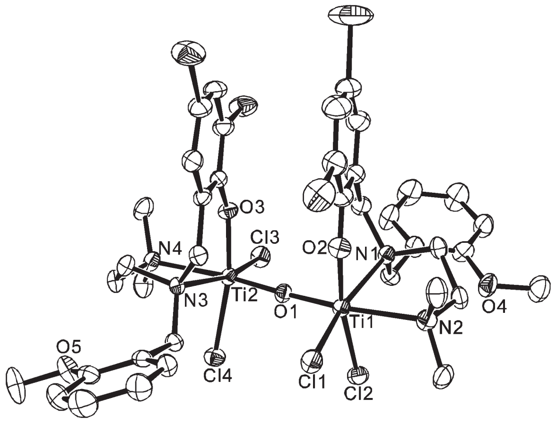

Fig. 5 Molecular structure of complex **8d** with thermal ellipsoids drawn at the 30% level, hydrogen atoms and uncoordinated solvent are omitted for clarity. The selected bond lengths (Å) and angles (°): Ti1–O1 1.831(5), Ti2–O1 1.801(5), Ti2–O1–Ti1 177.4(3), O1–Ti1–N2 170.2(2), O1–Ti2–N4 167.9(2).

Complexes **9a** and **5e** show similar molecular structures to that of **2a.** The geometry around titanium is a distorted octahedron and the ligand coordinates in *cis*-fashion. Much larger distances from methoxy oxygen to Ti atom (**9a:** 5.221 and **5e:** 6.006 Å) than the sum of atomic radii of titanium and oxygen indicate that the aryl ether oxygen is not coordinated too. Although the pendant aryl ether group is located far away from the metal center, when ^{t}Bu and Me groups are introduced to the pedant group in **9a**, the steric influence of the bulky aryl ether ring on bond lengths still exists. The bond length of Ti1–N1 is slightly shorter than that in **2a** (2.326(4) *versus* 2.343(6) Å), while the bond length of Ti1–N2 is slightly longer (2.310(4) *versus* 2.300(7) Å). As for complex **5e**, due to the replacement of chloride ligands by isopropoxide groups, the

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bond angles of O1–Ti–N1, O1–Ti–N2 and N1–Ti–N2 are slightly larger and the Ti–O1, Ti–N1, and Ti–N2 bond lengths are slightly longer than those observed in complexes **2a** and **9a**, respectively.

Complex **8d** is the hydrolysis product of complex **8a**, and possesses an oxygen-bridged binuclear structure. Each titanium center has a distorted octahedral geometry with the tetradentate aminophenolate ligand in tridentate, *cis*-O, N, N chelating mode, which is similar to those of **2a**, **9a** and **5e**. The Ti1–O1–Ti2 bond angle is 177.4(3)°, almost equal to 180°, showing that the two titanium atoms linked by the bridging oxygen atom are nearly linear. The Ti1–O1 bond length is 1.831(5) Å, slightly longer than Ti2–O1 (1.801(5) Å), and the N2–Ti1–O3 bond angle is 170.2(2)°, slightly larger than N4–Ti2–O3 (167.9(2)°), indicating that **8d** has a asymmetric C_1-configuration.

Ethylene polymerization

Ethylene polymerizations using the synthesized titanium and zirconium complexes as precatalysts under different conditions were examined and the results are summarized in Tables 1–3. When activated with MMAO, titanium isopropoxide complexes **5e–8e** and zirconium complex **8b** exhibit moderate catalytic activities for ethylene polymerization. More efficient than the titanium isopropoxide and zirconium trichloride analogues, in conjunction with MMAO, titanium trichloride complexes **1a–4a**, **7a–10a** show good activities for ethylene polymerization even at high temperatures. The ligand structure, reaction temperature and the molar ratio of Al/Ti influence both the activities of the complexes and the molecular weights of the resultant polyethylenes.

Upon treatment of 1000 equiv. of MMAO as cocatalyst at 1 MPa of ethylene pressure, titanium trichloride complexes **1a–4a** and **7a–10a** show moderate to high activities at high temperatures of 100 °C and 120 °C, affording linear polyethylenes of high molecular weights (Table 1). The data in Table 1 demonstrate that the steric and electronic effects of the substituents on the *ortho*- and *para*-positions of the phenolate ring of the ligand exert significant influence on the catalytic activities of these complexes. Complexes **7a** and **8a** with halogen groups on the *ortho*- and *para*-positions of the phenolate ring show much higher activities than complexes **1a–4a** with alkyl or aralkyl substituents for ethylene polymerization at 120 °C (entries 13, 16 *versus* entries 2, 5, 8, 10), suggesting that the electronic effect of the substituents may have played a significant role in ethylene polymerization. For example, the catalytic activity of complex **8a** with bromo groups substituted on the *ortho*- and *para*-positions reaches 2082 kg (mol-Ti h)$^{-1}$ at 120 °C, whereas complex **2a** with *o*-^{t}Bu and *p*-^{t}Bu provides an activity of 852 kg (mol-Ti h)$^{-1}$ under the same conditions. At the same time, for complexes **7a** and **8a** with halogen substitution, an obvious increase of the catalytic activity is observed when chloro groups are replaced by bromo groups, which might be attributable to the increase of the steric bulkiness of

Table 1 Ethylene polymerization catalyzed by complexes **1a–4a**, **7a–10a** and **8b**^{a}

Entry	Cat.	Al/M	Temp. (°C)	PE (mg)	Activity (kg (mol-M h)$^{-1}$)	$M_\eta{}^b$ (10^4 g mol^{-1})	$T_m{}^c$ (°C)
1	**1a** (*o*-^{t}Bu, *p*-Me)	1000	100	63	378	*	133.4
2	**1a** (*o*-^{t}Bu, *p*-Me)	1000	120	111	666	18.2	134.6
3	**1a** (*o*-^{t}Bu, *p*-Me)	5000	120	158	948	7.73	133.7
4	**2a** (*o*,*p*-^{t}Bu$_2$)	1000	100	92	552	*	132.5
5	**2a** (*o*,*p*-^{t}Bu$_2$)	1000	120	142	852	14.4	133.6
6	**2a** (*o*,*p*-^{t}Bu$_2$)	5000	120	277	1662	5.34^d	133.7
7	**3a** (*o*,*p*-cumyl$_2$)	1000	100	66	396	18.8	135.2
8	**3a** (*o*,*p*-cumyl$_2$)	1000	120	76	456	6.88	134.5
9	**4a** (*o*-CPh$_3$, *p*-Me)	1000	100	78	468	21.4	133.8
10	**4a** (*o*-CPh$_3$, *p*-Me)	1000	120	128	768	8.18	134.2
11	**4a** (*o*-CPh$_3$, *p*-Me)	5000	120	212	1272	2.73	133.2
12	**7a** (*o*,*p*-Cl$_2$)	1000	100	196	1176	25.1	133.6
13	**7a** (*o*,*p*-Cl$_2$)	1000	120	257	1542	14.0	134.2
14	**7a** (*o*,*p*-Cl$_2$)	5000	120	396	2376	8.32	134.7
15	**8a** (*o*,*p*-Br$_2$)	1000	100	320	1920	25.5^d	134.6
16	**8a** (*o*,*p*-Br$_2$)	1000	120	347	2082	9.54^d	133.7
17	**8a** (*o*,*p*-Br$_2$)	5000	120	695	4170	6.33^d	134.5
18	**9a** (*o*-^{t}Bu, *p*-Me)	1000	100	62	372	*	132.8
19	**9a** (*o*-^{t}Bu, *p*-Me)	1000	120	84	504	15.4	133.6
20	**9a** (*o*-^{t}Bu, *p*-Me)	5000	120	97	582	9.85	135.2
21	**10a** (*o*,*p*-cumyl$_2$)	1000	100	48	288	18.3	—
22	**10a** (*o*,*p*-cumyl$_2$)	1000	120	64	384	6.32	133.9
23	**8b** (*o*-, *p*-Br$_2$)	1000	100	64	384	55.1	134.3
24	**8b** (*o*-, *p*-Br$_2$)	1000	120	51	306	46.4	—

^{a} Conditions: toluene as solvent, [Cat.] = 0.04 μmol mL^{-1}, V_{total} = 25 mL, MMAO as cocatalyst, 1 MPa of ethylene, 10 min. ^{b} Intrinsic viscosity was determined in decahydronaphthalene at 135 °C by Ubbelohde viscometer technique, and the viscosity average molecular weights were calculated using the relation:[96] $[\eta] = 6.67 \times 10^{-4} M_\eta^{0.67}$, in unit of 10^4 g mol^{-1}; * insoluble. ^{c} Determined by DSC at a heating rate of 10 °C min^{-1}. ^{d} M_w and M_w/M_n were determined by GPC, using 1,3,5-trichlorobenzene as solvent at 160 °C, in unit of 10^4 g mol^{-1}. For entry 6, $M_w = 4.92 \times 10^4$ g mol^{-1}, $M_w/M_n = 16.8$; for entry 15, $M_w = 34.8 \times 10^4$ g mol^{-1}, $M_w/M_n = 16.4$; for entry 16, $M_w = 10.1 \times 10^4$ g mol^{-1}, $M_w/M_n = 10.2$; for entry 17, $M_w = 7.25 \times 10^4$ g mol^{-1}, $M_w/M_n = 13.7$.

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Table 2 Ethylene polymerization catalyzed by complex **8a** under different conditions[a]

Entry	Cat. (μmol mL^{-1})	Temp. (°C)	Al/Ti	Yield (mg)	Activity (kg (mol-Ti h)$^{-1}$)	M_η[b] (10^4 g mol^{-1})	T_m[c] (°C)
25	**8a** (0.04)	30	1000	123	738	*	134.4
26	**8a** (0.04)	50	1000	133	798	*	133.8
27	**8a** (0.04)	80	1000	162	972	40.7	133.5
28[d]	**8a** (0.04)	120	1000	318	954	9.60	132.0
29[d]	**8a** (0.04)	140	1000	394	1182	5.76	133.6
30[d]	**8a** (0.04)	160	1000	462	1386	2.68	135.2
31	**8a** (0.04)	120	2000	487	2922	8.59	133.9
32	**8a** (0.02)	120	1000	238	2856	12.8	134.6
33[e]	**8a** (0.02)	120	5000	644	15 456	9.94	133.9
34[e]	**8a** (0.004)	120	5000	74	8880	13.6	135.2
35	**8a** (0.04)	100	1000/100[f]	358	2148	22.3	133.4
36	**8a** (0.04)	120	1000/100[f]	367	2202	9.38	133.8

[a] In toluene, 25 mL, MMAO as cocatalyst, 1 MPa of ethylene, 10 min. [b] M_η measured by the Ubbelohde calibrated viscometer technique, * insoluble. [c] Determined by DSC. [d] In 1,3,5-trimethylbenzene, 50 mL. [e] 5 min. [f] $Al_{(MMAO)}/Al_{AliBu3}/Ti$ = 1000/100/1.

Table 3 Ethylene polymerization catalyzed by complexes **5e–8e**[a]

Entry	Cat.	Temp. (°C)	Al/Ti	Yield (mg)	Activity (kg (mol-Ti h)$^{-1}$)	M_η[b] (10^4 g mol^{-1})
37	**5e** (*o*-Cl, *p*-^{t}Bu)	25	1000	311	207	3.48
38	**5e** (*o*-Cl, *p*-^{t}Bu)	50	1000	606	404	3.25
39	**5e** (*o*-Cl, *p*-^{t}Bu)	80	1000	512	341	3.06[c]
40	**6e** (*o*-Br, *p*-^{t}Bu)	50	1000	362	241	0.96
41	**7e** (*o*,*p*-Cl_2)	50	1000	515	343	25.2
42	**8e** (*o*,*p*-Br_2)	50	1000	162	110	5.56

[a] Solvent: toluene, 25 mL; MMAO as cocatalyst, [Cat.] = 0.12 μmol mL^{-1}, 0.5 MPa of ethylene, 30 min. [b] M_η measured by the Ubbelohde calibrated viscometer technique. [c] M_w and M_w/M_n were determined by GPC, using 1,3,5-trichlorobenzene as solvent at 160 °C, in unit of 10^4 g mol^{-1}. For entry 39, $M_w = 13.6 \times 10^4$ g mol^{-1}, $M_w/M_n = 34.8$.

the bromo group.[97] However, the space effect of the *ortho*- and *para*-substituents of the phenolate ring is complicated for alkyl or aralkyl substituted complexes **1a–4a**. Complex **4a** with an *ortho*-trityl group on the phenolate ring exhibits higher activity than complex **3a** with *o*,*p*-cumyl groups, but is less active than complex **2a** with *o*,*p*-*tert*-butyl groups at 120 °C (entries 2, 5 and 10). At present we do not have a reasonable explanation, it is tentatively suggested that probably a cooperative effect of the steric bulkiness and the electronic nature of these substituents might be responsible for this unusual phenomenon. Moreover, the substituents on the pendant aryl ethyl group of the ligand also have a slight impact on the catalytic activity of the corresponding titanium complex. When two H atoms of the pendant aryl ring are replaced by *tert*-butyl and methyl groups separately (**9a** and **10a**), reduced activities of 504 kg (mol-Ti h)$^{-1}$ and 384 kg (mol-Ti h)$^{-1}$ are produced in comparison to those of complexes **1a** and **3a** (entries 19 and 22 *vs.* entries 2 and 8). It seems that although the pendant aryl group is located far away from the metal center according to the X-ray diffraction studies, it does exhibit a certain influence on the polymerization likely by hindering the coordination/insertion of ethylene monomer.

In comparison to the high activities of titanium analogues at high temperatures, zirconium trichloride complex **8b** is significantly less active. At 120 °C, with a Al/M molar ratio of 1000, titanium complex **8a** shows an activity of 2082 kg (mol-Ti h)$^{-1}$, while the activity of zirconium complex **8b** is only 306 kg (mol-Ti h)$^{-1}$, suggesting that the zirconium complex is markedly less thermally stable than the titanium analogues.

It is found that the molecular weights of the resultant polymers are closely dependent on the structure of the catalysts. In general, increasing the steric hindrance of the substituents in the ligand framework results in an obvious decrease of the molecular weights of the obtained polymers.[98] Under the polymerization conditions of Al/Ti = 1000 and 120 °C, with the variation of the *ortho*-substituent of the phenolate ring from *tert*-butyl (**1a**, **2a** and **9a**) to cumyl (**3a**, **10a**) and CPh_3 (**4a**), a sharp decrease of M_η values of the resulted polyethylenes from 144–182 kg mol^{-1} to 63.2–81.8 kg mol^{-1} could be observed (entries 2, 5, 8, 10, 19, 22, respectively). It is also the case for the polymers obtained by complexes **7a** and **8a** (entries 13, 16). Although being less active than titanium analogues zirconium complex **8b** provides polyethylenes with much higher molecular weights of 464–551 kg mol^{-1} at high temperatures of 100–120 °C. Furthermore, polyethylenes with very broad molecular weight distributions (M_w/M_n = 10.2–16.8) are obtained as indicated by the GPC measurements for typical polymer samples (entries 6, 15, 16 and 17), which suggest the presence of multiple active species. From the ^{1}H NMR spectra of these titanium complexes, the existence of isomers is conclusive. The variable temperature ^{1}H NMR study of complex **2a** further indicates the somewhat rigid configur-

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ation of these complexes at high temperature. Therefore, the widely distributed GPC traces might be a result of multiple active sites of different nature generated from different isomers, although possible species generated from some decomposition pathways might not be ruled out. Moreover, the obtained PEs possess melting points in the range 133–136 °C, typical for linear polyethylene.[97]

The polymerization temperature also exerts a crucial influence on the catalytic activities of these titanium and zirconium trichloride complexes. As illustrated in Fig. 6, with the increase of the polymerization temperature from 30 °C to 120 °C, the activities of titanium complexes **1a–4a**, **7a** and **8a** increase to a great extent, so for complexes **9a** and **10a** from 80 to 120 °C. For instance, in the presence of MMAO, the most active titanium complex **8a** displays a moderate activity of 738 kg (mol-Ti h)$^{-1}$ toward ethylene polymerization at 30 °C, while nearly a three-fold increase of the activity could be obtained at 120 °C (2082 kg (mol-Ti h)$^{-1}$). As for zirconium complex **8b**, the optimal temperature is around 80 °C, at which the highest activity of 678 kg (mol-Zr h)$^{-1}$ could be obtained with a Al/Zr molar ratio of 1000. All these indicate the superior thermal stability of this series of titanium trichloride complexes. To have further insight into the thermal stability of these titanium complexes, ethylene polymerizations catalyzed by the **8a**–MMAO catalytic system were carried out at higher temperatures of 120–160 °C in trimethylbenzene. As depicted by the data in Table 2, an increasing tendency of the activities could still be observed with the temperature elevating from 120 °C to 160 °C (from 954 kg (mol-Ti h)$^{-1}$ to 1386 kg (mol-Ti h)$^{-1}$, entries 28–30), suggesting that the *in situ* formed catalytic species are quite stable even at a high temperature of 160 °C. Tang's group reported[83] that, in the presence of MMAO, titanium trichloride complexes supported by tridentate aminophenolate ligand [$O^-N(H)X$] (X = S, P) showed high activity toward ethylene polymerization at 90 °C. However, a further increase of polymerization temperature led to a decline of the activity. Therefore, it is conceivable that the additional OMe group in the ligand framework of these complexes might play a crucial role in stabilizing the active species during the polymerization, although it isn't coordinated to the metal in the precatalyst. It is worthy of note that, under similar conditions, using **8a**–MMAO as the catalytic system for ethylene polymerization, a higher activity of 2082 kg (mol-Ti h)$^{-1}$ could be reached in toluene than that in trimethylbenzene (entry 16 *vs*. 28). Similar phenomena have also been reported in the literature recently.[83] It is conceivable that the polarity and the steric bulkiness of the solvent molecule might be the likely factors.

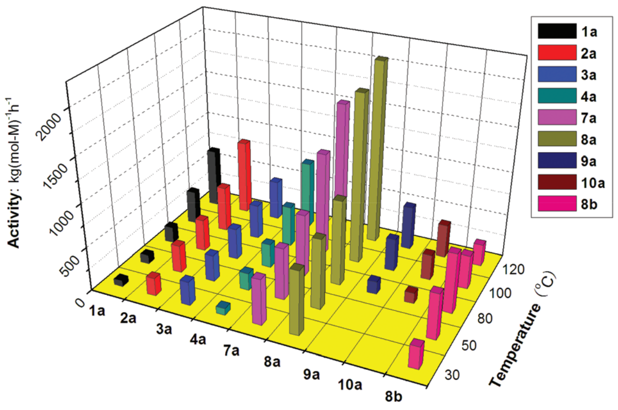

Fig. 6 The influence of polymerization temperature on the catalytic activities of complexes **1a–4a**, **7a–10a** and **8b** (polymerization conditions: toluene as solvent, [Cat.] = 0.04 μmol mL^{-1}, MMAO as cocatalyst, 1 MPa of ethylene pressure, 10 min).

It is noticeable that the polymerization temperature influences the molecular weights of the resultant polymers remarkably. Polyethylenes obtained at lower temperatures (<100 °C) are in general insoluble in decahydronaphthalene at 135 °C, indicative of the ultra-high-molecular-weight nature, especially for polymers obtained by complexes **1a**, **2a** and **9a** with less.

As observed for most of the catalytic olefin polymerization systems, the activity of these titanium complexes toward ethylene polymerization is also influenced by the molar ratio of Al/Ti. With the increase of Al/Ti ratio from 1000 to 5000, the activity of complex **8a** is increased from 2082 kg (mol-Ti h)$^{-1}$ to 4170 kg (mol-Ti h)$^{-1}$ (entries 16 and 17). A similar trend is also found for the other complexes. According to literature reports, with MAO as cocatalyst, the addition of a small amount of alkyl aluminium could normally enhance the catalytic activity of the corresponding system.[99,100] Therefore, the same strategy was adopted for ethylene polymerizations catalyzed by **8a**–MMAO at 100 and 120 °C, as expected the addition of 100 equiv. of Al^iBu_3 slightly increased the activity from 1920 kg (mol-Ti h)$^{-1}$ and 2082 kg (mol-Ti h)$^{-1}$ to 2148 kg (mol-Ti h)$^{-1}$ and 2202 kg (mol-Ti h)$^{-1}$, respectively (entry 15 *vs*. 35 and 16 *vs*. 36). The influence of the Al/Ti molar ratio on the polymer molecular weight was also investigated. The results shown in Tables 1 and 2 indicate that, in general, under otherwise the same conditions, the molecular weight of the obtained PE decreases dramatically with the increase of the Al/Ti molar ratio. From the ^1H NMR spectrum of a typical polyethylene sample obtained by **8a** at 120 °C, no obvious alkenyl hydrogen signals could be detected, implying that the dominant termination process is chain transfer to aluminum[17,101,102] instead of the β-hydride elimination reaction.[101]

Moreover, the catalytic activity depends on the catalyst concentration. For **8a**, the effect of catalyst concentration on activity was studied in the range of 0.04 to 0.004 μmol mL^{-1}, the highest activity of 15 456 kg (mol-Ti h)$^{-1}$ was obtained with a catalyst concentration of 0.02 μmol mL^{-1} (entry 33).

For a comparison purpose, titanium isopropoxide complexes **5e–8e** were tested as precatalysts for the polymerization of ethylene using MMAO as the cocatalyst, and the results are illustrated in Table 3. For **5e**–MMAO, when the Al/Ti molar ratio is 1000, changing polymerization temperature from 25 to 80 °C, the highest activity of 404 kg (mol of Ti h)$^{-1}$ is achieved at 50 °C (entries 37–39). This trend demonstrates that the titanium isopropoxide complexes are less thermally stable than the corresponding trichloride complexes. Meanwhile, much

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lower activities are obtained by these titanium isopropoxide complexes in comparison to titanium trichloride analogues under similar conditions. Among complexes **5e**–**8e**, complex **5e** with a chloro group on the *ortho*-position of the phenolate ring is most active and exhibits significantly higher activity than **6e** with an *ortho*-bromo group for ethylene polymerization at 50 °C (entry 38 *vs.* 40). A similar order is also found for complexes **7e** and **8e**. On the other hand, when compared with complex **7e** with chloro groups on both *ortho*- and *para*-positions of the phenolate ring, the activity of complex **5e** with a *para-tert*-butyl group is slightly higher. It brings an ambivalent situation for understanding the effect of substituents, either by steric effect or by electronic effect. We tentatively suggest that different influences of the *ortho*- and *para*-substituents might be involved. In addition, the observed very broad polydispersity indices of the polymer sample obtained by **5e** (M_w/M_n = 34.8, entry 39) indicated the presence of multiple active sites in these catalyst systems, which might be due to the fluxional nature of this series of titanium isopropoxide complexes above 0 °C.

Conclusions

A series of novel titanium and zirconium complexes supported by tetradentate aminophenolate ligands in tridentate, *cis*-O, N, N chelating mode were prepared and characterized. In the presence of MMAO, these complexes show moderate to high activities in catalyzing ethylene polymerization and afford high molecular weight polymers with broad molecular weight distributions. Moreover, the active species generated *in situ* from titanium trichloride complexes upon treatment with MMAO possess unusual thermal stability even at high temperatures of 120–160 °C. In comparison to titanium trichloride complexes, zirconium trichloride complexes and titanium isopropoxide complexes are less active and thermally stable. The electronic properties and steric hindrances of the substituents of the ligands remarkably affect the catalytic activities of these complexes, and complex **8a** with bromo groups on both the *ortho*- and *para*-positions of the phenolate ring of the ligand exhibits the highest activity among them. The highest activity for ethylene polymerization was achieved as 15 456 kg (mol-Ti h)$^{-1}$ at 120 °C by complex **8a**. These results and the easy modification feature of these complexes are helpful in developing efficient catalysts having potentially industrial applications.

Experimental

General considerations

All air- and/or moisture-sensitive compounds were manipulated using standard Schlenk techniques or in a glovebox under an argon atmosphere. Solvents for air- and moisture-sensitive reactions, for example, toluene, THF, and *n*-hexane were refluxed with sodium–benzophenone and distilled prior to use under argon. Dichloromethane and triethylamine were dried over calcium hydride before use. $CDCl_3$ was distilled from CaH_2 and stored under argon. 3-*tert*-Butyl-2-methoxy-5-methylbenzaldehyde, 2-chloro-4-*tert*-butylphenol, 2-bromo-4-*tert*-butylphenol, 2,4-dibromo-6-bromomethyl phenol, and proligands **L$^{1-3}$H**, **L^{7}H**, **L^{9}H**, and **L^{10}H** were prepared according to literature procedures.[85–87] $TiCl_4(THF)_2$ and $ZrCl_4(THF)_2$ were prepared according to literature procedures.[103] 1,3,5-Trimethylbenzene was purchased from Acros and distilled with sodium before use. Al^iBu_3, *n*-BuLi, $TiCl_4$, and $ZrCl_4$ were purchased from J&K, Aldrich or Acros. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-400 (^1H: 400 MHz, ^{13}C: 100 MHz) spectrometer at room temperature unless otherwise stated. Elemental compositions were determined by an EA-1106 elements analyzer. The melting points of the compounds were measured by WRS-1B digital melting point tester and reported without correction. The molecular weights of the polyethylenes were measured in decahydronaphthalene at 135 °C by a Ubbelohde viscometer according to the following equation:[96] $[\eta] = (6.77 \times 10^{-4})M_\eta^{0.67}$. The ^1H NMR spectrum of a typical polymer sample was recorded on a Varian 400 NMR spectrometer at 100 °C using a mixed solvent of *o*-dichlorobenzene and C_6D_6 (4 : 1). The melting temperatures (T_m) of polymers were measured by differential scanning calorimetry (DSC) (V2.3C TA) at a heating rate of 10 °C min^{-1} from −20 to 200 °C. Molecular weights and molecular weight distributions of the polyethylenes were measured on a PL-GPC 220 instrument at 160 °C with 1,2,4-trichlorobenzene as the eluent.

Synthesis of proligands and titanium and zirconium complexes

2-{[(2-(Dimethylamino)ethyl)(2-methoxybenzyl)amino]methyl}-4-methyl-6-tritylphenol (L^{4}H). To a solution of 2-methoxybenzaldehyde (4.08 g, 30.0 mmol) in ethanol (30 mL) was added *N*,*N*-dimethyl-1,2-ethanediamine (3.9 mL, 30 mmol), and the mixture was refluxed for 12 h. After cooling the reaction mixture to 0 °C, $NaBH_4$ (2.27 g, 60 mmol) was slowly added. The solution was refluxed for another 12 h and then cooled to room temperature. The reaction was quenched with 20 mL of water and all the volatiles were evaporated. The resulting viscous residue was extracted with petroleum ether (3 × 30 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and filtered. The filtrate was evaporated *in vacuo* to afford a light yellow oil. 4-Methyl-2-tritylphenol (10.5 g, 30.0 mmol) and paraformaldehyde (1.80 g, 60.0 mmol) were added to the solution of the above light yellow oil in ethanol (30 mL). The reaction mixture was refluxed for 12 h and then cooled to ambient temperature. All the volatiles were evaporated to give a white solid, which was recrystallized with a mixture of solvents (PE/EA = 5 : 1) to afford the target proligand **L^{4}H** as colorless crystals (9.96 g, 56.6%). mp: 138.3–139.5 °C. (Found: C, 81.73; H, 7.34; N, 4.68. Calc. for $C_{39}H_{42}N_2O_2$: C, 82.07; H, 7.42; N, 4.91%); δ_H (400 MHz, $CDCl_3$) 10.63 (1 H, bs, ArO*H*), 7.34–7.07 (16 H, m, Ar*H*), 6.93–6.71 (5 H, m, Ar*H*), 3.64 (2 H, s, $ArCH_2N$), 3.58 (3 H, s, $ArOCH_3$), 3.53 (2 H, s, $ArCH_2N$), 2.45–2.35 (2 H, m, $N(CH_2)_2N$), 2.22–2.12 (2 H, m, $N(CH_2)_2N$), 2.15 (3 H, s, $ArCH_3$), 2.01 (6 H, s, $N(CH_3)_2$).

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δ_{C} (100 MHz, $\mathrm{CDCl_3}$) 158.0, 154.2, 146.4, 133.7, 131.5, 131.3, 131.1, 130.6, 128.9, 128.6, 127.3, 126.9, 126.1, 125.5, 125.2, 122.9, 120.4, 110.2, (all Ar*C*), 63.4 (Ar*C*Ph$_3$), 57.8 (O*C*H$_3$), 56.0 (N(*C*H$_2$)$_2$N), 55.1 (N(*C*H$_2$)$_2$N), 52.6 (Ar*C*H$_2$N), 50.4 (Ar*C*H$_2$N), 45.4 (N(*C*H$_3$)$_2$), 21.0 (Ar*C*H$_3$).

4-*tert*-Butyl-2-chloro-6-{[(2-(dimethylamino)ethyl)(2-methoxybenzyl)amino]methyl}phenol ($\mathbf{L^5H}$). Proligand $\mathbf{L^5H}$ was synthesized in the same manner as that for $\mathbf{L^4H}$ with 2-chloro-4-*tert*-butylphenol (5.54 g, 30.0 mmol) as the starting material. After work-up, a light yellow oil was obtained, which was purified by chromatography (PE/EA = 4 : 1) and then recrystallization with absolute alcohol. The target product $\mathbf{L^5H}$ was isolated as colorless crystals (6.29 g, 51.8%). mp: 107.1–108.4 °C. (Found: C, 68.00; H, 8.19; N, 6.59. Calc. for $\mathrm{C_{23}H_{33}ClN_2O_2}$: C, 68.21; H, 8.21; N, 6.92%); δ_{H} (400 MHz, $\mathrm{CDCl_3}$) 11.20 (1 H, bs, ArO*H*), 7.26–7.17 (3 H, m, Ar*H*), 6.93–6.86 (2 H, m, Ar*H*), 6.84 (1 H, d, ^3J = 8.1 Hz, Ar*H*), 3.81 (3 H, s, ArOC*H*$_3$), 3.72 (2 H, s, ArC*H*$_2$N), 3.65 (2 H, s, ArC*H*$_2$N), 2.58 (2 H, t, ^3J = 6.6 Hz, N(C*H*$_2$)$_2$N), 2.48 (2 H, t, ^3J = 6.6 Hz, N(C*H*$_2$)$_2$N), 2.14 (6 H, s, N(C*H*$_3$)$_2$), 1.26 (9 H, s, ArC(C*H*$_3$)$_3$). δ_{C} (100 MHz, $\mathrm{CDCl_3}$) 158.1, 151.2, 141.9, 131.6, 128.9, 125.9, 125.4, 124.6, 123.8, 120.3, 120.2, 110.4, (all Ar*C*), 57.1 (O*C*H$_3$), 56.4 (N(*C*H$_2$)$_2$N), 55.2 (N(*C*H$_2$)$_2$N), 53.0 (Ar*C*H$_2$N), 50.4 (Ar*C*H$_2$N), 45.3 (N(*C*H$_3$)$_2$), 34.0 (Ar*C*(CH$_3$)$_3$), 31.5 (ArC(*C*H$_3$)$_3$).

2-Bromo-4-*tert*-butyl-6-{[(2-(dimethylamino)ethyl)(2-methoxybenzyl)amino]methyl}phenol ($\mathbf{L^6H}$). Proligand $\mathbf{L^6H}$ was synthesized in the same manner as that for $\mathbf{L^4H}$ with 2-bromo-4-*tert*-butylphenol (6.67 g, 30.0 mmol) as the starting material. After work-up, a light yellow oil was obtained, which was purified by chromatography (PE/EA = 4 : 1) and then recrystallization with absolute alcohol. The target product $\mathbf{L^6H}$ was isolated as colourless crystals (7.90 g, 58.6%). mp: 142.3–143.4 °C. (Found: C, 61.46; H, 7.30; N, 6.26. Calc. for $\mathrm{C_{23}H_{33}BrN_2O_2}$: C, 61.47; H, 7.40; N, 6.23%); δ_{H} (400 MHz, $\mathrm{CDCl_3}$) 11.06 (1 H, bs, ArO*H*), 7.38 (1 H, d, ^4J = 2.2 Hz, Ar*H*), 7.26–7.18 (2 H, m, Ar*H*), 6.93 (1 H, d, ^4J = 2.2 Hz, Ar*H*), 6.89 (1 H, t, ^3J = 7.4 Hz, Ar*H*), 6.84 (1 H, d, ^3J = 8.2 Hz, Ar*H*), 3.82 (3 H, s, ArOC*H*$_3$), 3.73 (2 H, s, ArC*H*$_2$N), 3.65 (2 H, s, ArC*H*$_2$N), 2.58 (2 H, t, ^3J = 6.8 Hz, N(C*H*$_2$)$_2$N), 2.48 (2 H, t, ^3J = 6.8 Hz, N(C*H*$_2$)$_2$N), 2.13 (s, 6H, N(C*H*$_3$)$_2$), 1.25 (s, 9H, ArC(C*H*$_3$)$_3$). δ_{C} (100 MHz, $\mathrm{CDCl_3}$) 158.1, 152.2, 142.5, 131.6, 128.9, 128.8, 125.4, 125.3, 123.7, 120.3, 110.5, 109.9, (all Ar*C*), 57.4 (O*C*H$_3$), 56.4 (N(*C*H$_3$)$_2$), 55.2 (N(*C*H$_3$)$_2$), 53.0 (Ar*C*H$_2$N), 50.5 (Ar*C*H$_2$N), 45.4 (N(*C*H$_3$)$_2$), 34.0 (Ar*C*(CH$_3$)$_3$), 31.5 (ArC(*C*H$_3$)$_3$).

2,4-Dibromo-6-{[(2-(dimethylamino)ethyl)(2-methoxybenzyl)amino]methyl}phenol ($\mathbf{L^8H}$). To a solution of 2-methoxybenzaldehyde (4.08 g, 30.0 mmol) in ethanol (30 mL) was added *N*,*N*-dimethyl-1,2-ethanediamine (3.9 mL, 30 mmol), and the mixture was refluxed for 12 h. After cooling the reaction mixture to 0 °C, $\mathrm{NaBH_4}$ (2.27 g, 60 mmol) was slowly added. The solution was refluxed for another 12 h and then cooled to room temperature. The reaction was quenched with 20 mL of water and all the volatiles were evaporated. The resulting viscous residue was extracted with petroleum ether (3 × 30 mL). The combined organic phase was dried over anhydrous $\mathrm{MgSO_4}$ and filtered. The filtrate was evaporated *in vacuo* to give a light yellow oil. 2,4-Dibromo-6-(bromomethyl)phenol (10.34 g, 30.00 mmol) and triethylamine (4.5 mL) were added to the solution of the above light yellow oil in THF (30 mL) under argon. The reaction mixture was stirred for 3 h in the dark, and then the solvent was evaporated to dryness and the brown crude product was purified by chromatography (PE/EA = 4 : 1) and then recrystallization with petroleum ether. The target product $\mathbf{L^8H}$ was isolated as colourless crystals (9.97 g, 70.4%). mp: 138.3–139.5 °C. (Found: C, 48.03; H, 5.20; N, 5.84. Calc. for $\mathrm{C_{19}H_{24}Br_2N_2O_2}$: C, 48.33; H, 5.12; N, 5.93%); δ_{H} (400 MHz, $\mathrm{CDCl_3}$) 7.53 (1 H, d, ^4J = 2.2 Hz, Ar*H*) 7.23 (1 H, t, ^3J = 7.4 Hz, Ar*H*), 7.15 (1 H, d, ^3J = 7.4 Hz, Ar*H*), 7.07 (1 H, d, ^4J = 2.2 Hz, Ar*H*), 6.88 (1 H, t, ^3J = 7.4 Hz, Ar*H*), 6.83 (1 H, d, ^3J = 7.4 Hz, Ar*H*), 3.78 (3 H, s, ArOC*H*$_3$), 3.64 (2 H, s, ArC*H*$_2$N), 3.60 (2 H, s, ArC*H*$_2$N), 2.56 (2 H, t, ^3J = 6.5 Hz, N(C*H*$_2$)$_2$N), 2.48 (2 H, t, ^3J = 6.5 Hz, N(C*H*$_2$)$_2$N), 2.13 (6 H, s, N(C*H*$_3$)$_2$). δ_{C} ($\mathrm{CDCl_3}$, 100 MHz) 158.2, 154.4, 134.1, 131.7, 131.3, 129.2, 126.5, 125.1, 120.3, 111.4, 110.5, 109.8 (all Ar*C*), 56.0 (N(*C*H$_2$)$_2$N), 56.0 (N(*C*H$_2$)$_2$N), 55.2 (ArO*C*H$_3$), 53.1 (Ar*C*H$_2$N), 49.9(Ar*C*H$_2$N), 45.1 (N(*C*H$_3$)$_2$).

2-{[(3-*tert*-Butyl-2-methoxy-5-methylbenzyl)(2-(dimethyl amino)ethyl)amino]methyl}-4-methyl-6-tritylphenol ($\mathbf{L^{11}H}$). Proligand $\mathbf{L^{11}H}$ was synthesized in the same manner as for that $\mathbf{L^4H}$ with 3-*tert*-butyl-2-methoxy-5-methylbenzaldehyde (6.18 g, 30.0 mmol) as the starting material. The target product $\mathbf{L^{11}H}$ was obtained as a colourless crystals (8.76 g, 45.6%). mp: 137.5–138.7 °C. (Found: C, 81.99; H, 8.23; N, 4.34. Calc. for $\mathrm{C_{44}H_{52}N_2O_2}$: C, 82.46; H, 8.18; N, 4.37%); δ_{H} (400 MHz, $\mathrm{CDCl_3}$) 10.46 (1 H, bs, ArO*H*), 7.26–7.09 (15 H, m, Ar*H*), 6.96 (1 H, d, ^4J = 1.6 Hz, Ar*H*), 6.89 (1 H, s, Ar*H*), 6.81 (1 H, s, Ar*H*), 6.69 (1 H, s, Ar*H*), 3.63 (2 H, s, ArC*H*$_2$N), 3.59 (3 H, s, ArOC*H*$_3$), 3.55 (2 H, s, ArC*H*$_2$N), 2.36–2.28 (2 H, m, N(C*H*$_2$)$_2$N), 2.25–2.20 (2 H, m, N(C*H*$_2$)$_2$N), 2.17 (6 H, s, ArC*H*$_3$), 1.97 (6 H, s, N(C*H*$_3$)$_2$), 1.35 (9 H, s, ArC(C*H*$_3$)$_3$). δ_{C} (100 MHz, $\mathrm{CDCl_3}$) 156.5, 154.0, 146.2, 142.0, 133.7, 132.4, 131.1, 130.7, 130.5, 129.2, 129.1, 125.2, 126.8, 126.8, 126.2, 123.0 (all Ar*C*), 63.3 (*C*Ph$_3$), 62.3 (O*C*H$_3$), 57.7 (N(*C*H$_2$)$_2$N), 55.7 (N(*C*H$_2$)$_2$N), 52.1 (Ar*C*H$_2$N), 49.9 (Ar*C*H$_2$N), 45.1 (N(*C*H$_3$)$_2$), 34.7 (Ar*C*(CH$_3$)$_3$), 31.1 (ArC(*C*H$_3$)$_3$), 21.2 (Ar*C*H$_3$), 20.9 (Ar*C*H$_3$).

$\mathbf{L^1TiCl_3}$ (1a). A solution of $\mathbf{L^1H}$ (0.769 g, 2.00 mmol) and triethylamine (0.6 mL, 4 mmol) in 30 mL of THF was added dropwise *via* a syringe to a mixture of $\mathrm{TiCl_4(THF)_2}$ (0.644 g, 2.00 mmol) in 20 mL of THF which was pre-cooled to −78 °C with a liquid nitrogen–alcohol bath. The mixture was then warmed to room temperature and stirred for 24 h. The resulting dark red suspension was filtered. All the volatiles of the filtrate were removed *in vacuo*, and the residue was re-dissolved in toluene (100 mL) and filtered. The red solution was concentrated to 50 mL and kept at −20 °C. The target complex **1a** was collected as red solids after filtration and drying (0.884 g, 82.2%). **1a** was characterized to be a mixture of isomers, the molar ratio of *cis*-**1a**/*trans*-**1a** = 10 : 1. mp: 211.5–212.4 °C. (Found: C, 56.96; H, 6.79; N, 4.44. Calc. for $\mathrm{C_{24}H_{35}Cl_3N_2O_2Ti{\cdot}(0.6C_7H_8)}$: C, 57.11; H, 6.76; N, 4.72%); NMR spectroscopic data for *cis*-**1a**: δ_{H} (400 MHz, $\mathrm{CDCl_3}$) 7.41 (1 H, td, ^3J = 8.3, ^4J = 1.7 Hz, Ar*H*), 7.21 (1 H, dd, ^3J = 7.5, ^4J = 1.7 Hz, Ar*H*), 7.08

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(s, 1H, Ar*H*), 7.02 (1 H, t, ^3J = 7.5 Hz, Ar*H*), 6.97 (1 H, d, ^3J = 8.3 Hz, Ar*H*), 6.67 (1 H, s, Ar*H*), 5.45 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 4.60 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 4.21 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 3.94–3.81(1 H, m, N(C*H*$_2$)$_2$N), 3.81 (3 H, s, OC*H*$_3$), 3.59 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 3.11 (3 H, s, N(C*H*$_3$)$_2$), 2.85–2.74 (1 H, m, N(C*H*$_2$)$_2$N), 2.67–2.56 (1 H, m, N(C*H*$_2$)$_2$N), 2.60 (3 H, s, N(C*H*$_3$)$_2$), 2.26 (3 H, s, ArC*H*$_3$), 2.30–2.21 (1 H, m, N(C*H*$_2$)$_2$N), 1.55 (9 H, s, C(C*H*$_3$)$_3$). δ_C (100 MHz, CDCl$_3$): 159.0, 157.6, 137.6, 135.2, 134.0, 130.8, 129.8, 128.9, 127.5, 120.4, 120.6, 111.3 (all Ar*C*), 61.4 (O*C*H$_3$), 59.2 (N(*C*H$_2$)$_2$N), 57.6 (N(*C*H$_2$)$_2$N), 55.5 (Ar*C*H$_2$N), 55.0 (Ar*C*H$_2$N), 50.9 (N(*C*H$_3$)$_2$), 48.5 (N(*C*H$_3$)$_2$), 35.0 (*C*(CH$_3$)$_3$), 30.3 (C(*C*H$_3$)$_3$), 21.0 (Ar*C*H$_3$).

L^{2}TiCl$_3$ (2a). Complex **2a** was synthesized in a similar manner to that described for **1a**, using **L^{2}H** (0.853 g, 2.00 mmol), triethylamine (0.6 mL, 4 mmol), and TiCl$_4$(THF)$_2$ (0.644 g, 2.00 mmol) as the starting materials. Red crystals were obtained (0.819 g, 70.6%), which were characterized to be a mixture of two isomers, the molar ratio of *cis*-**2a**/*trans*-**2a** = 10 : 2. mp: 178.5–180.2 °C. (Found: C, 57.96; H, 7.31; N, 4.32. Calc. for C$_{27}$H$_{41}$Cl$_3$N$_2$O$_2$Ti·(0.4C$_7$H$_8$): C, 58.04; H, 7.22; N, 4.54%); NMR spectroscopic data for *cis*-**2a**: δ_H (400 MHz, CDCl$_3$) 7.44 (1 H, t, ^3J = 7.6 Hz, Ar*H*), 7.30 (1 H, s, Ar*H*), 7.25 (1 H, d, ^3J = 8.0 Hz, Ar*H*), 7.06 (1 H, t, ^3J = 7.6 Hz, Ar*H*), 6.99 (1 H, d, ^3J = 8.0 Hz, Ar*H*), 6.78 (1 H, s, Ar*H*), 5.48 (1 H, d, ^2J = 14.6 Hz, ArC*H*$_2$N), 4.62 (1 H, d, ^2J = 14.6 Hz, ArC*H*$_2$N), 4.22 (1 H, d, ^2J = 14.6 Hz, ArC*H*$_2$N), 3.95–3.84 (1 H, m, N(C*H*$_2$)$_2$N), 3.82 (3 H, s, OC*H*$_3$), 3.62 (1 H, d, ^2J = 14.6 Hz, ArC*H*$_2$N), 3.12 (3 H, s, N(C*H*$_3$)$_2$), 2.88–2.77(1 H, m, N(C*H*$_2$)$_2$N), 2.62 (3 H, s, N(C*H*$_3$)$_2$), 2.68–2.58 (1 H, m, N(C*H*$_2$)$_2$N), 2.28–2.21 (1 H, m, N(C*H*$_2$)$_2$N), 1.56 (9 H, s, C(C*H*$_3$)$_3$), 1.25 (9 H, s, C(C*H*$_3$)$_3$). δ_C (100 MHz, CDCl$_3$): 159.0, 157.3, 147.1, 137.0, 135.3, 130.7, 129.3, 125.2, 123.8, 120.6, 120.4, 111.2 (all Ar*C*), 61.8 (O*C*H$_3$), 59.2 (N(*C*H$_2$)$_2$N), 57.6 (N(*C*H$_2$)$_2$N), 55.5 (Ar*C*H$_2$N), 55.1 (Ar*C*H$_2$N), 51.1 (N(*C*H$_3$)$_2$), 48.6 (N(*C*H$_3$)$_2$), 35.3 (*C*(CH$_3$)$_3$), 34.7 (*C*(CH$_3$)$_3$), 31.4 (C(*C*H$_3$)$_3$), 30.3 (C(*C*H$_3$)$_3$).

L^{3}TiCl$_3$ (3a). Complex **3a** was synthesized in a similar manner to that described for **1a**, using proligand **L^{3}H** (1.102 g, 2.000 mmol), triethylamine (0.6 mL, 4 mmol), and TiCl$_4$(THF)$_2$ (0.644 g, 2.00 mmol) as starting materials. After crystallization in toluene, pure *cis*-**3a** was obtained as red crystals (0.712 g, 50.6%). mp: 238.6–239.7 °C. (Found: C, 62.68; H, 6.56; N, 3.97. Calc. for C$_{37}$H$_{45}$Cl$_3$N$_2$O$_2$Ti: C, 63.13; H, 6.44; N, 3.98%); NMR spectroscopic data for *cis*-**3a**: δ_H (400 MHz, CDCl$_3$) 7.40 (1 H, td, ^3J = 8.1 Hz, ^4J = 1.8 Hz, Ar*H*), 7.34–7.28 (5 H, m, Ar*H*), 7.24–7.16 (6 H, m, Ar*H*), 7.09 (1 H, t, ^3J = 7.3 Hz, Ar*H*), 7.02 (1 H, t, ^3J = 7.3 Hz, Ar*H*), 6.94 (1 H, d, ^3J = 8.1 Hz, Ar*H*), 6.77 (1 H, d, ^4J = 1.8 Hz, Ar*H*), 5.34 (1 H, d, ^2J = 14.6 Hz, ArC*H*$_2$N), 4.57 (1 H, d, ^2J = 14.6 Hz, ArC*H*$_2$N), 4.11 (1 H, d, ^2J = 14.6 Hz, ArC*H*$_2$N), 3.76 (3 H, s, OC*H*$_3$), 3.70–3.59 (1 H, m, N(C*H*$_2$)$_2$N), 3.54 (1 H, d, ^2J = 14.6 Hz, ArC*H*$_2$N), 2.81 (3 H, s, N(C*H*$_3$)$_2$), 2.63–2.53 (1 H, m, N(C*H*$_2$)$_2$N), 2.49–2.41 (1 H, m, N(C*H*$_2$)$_2$N), 2.09 (3 H, s, N(C*H*$_3$)$_2$), 2.03–1.95 (1 H, m, N(C*H*$_2$)$_2$N), 1.67 (6 H, s, C(C*H*$_3$)$_2$Ph), 1.46 (3 H, s, C(C*H*$_3$)$_2$Ph), 1.40 (3 H, s, C(C*H*$_3$)$_2$Ph). δ_C (100 MHz, CDCl$_3$) 158.9, 156.9, 150.0, 146.0, 136.4, 135.4, 130.6, 129.4, 128.1, 127.9, 126.7, 126.6, 126.6, 126.6, 125.8, 125.6, 120.7, 120.6, 111.2 (all Ar*C*), 61.9 (O*C*H$_3$), 58.9 (N(*C*H$_2$)$_2$N), 57.6 (N(*C*H$_2$)$_2$N), 55.4 (Ar*C*H$_2$N), 54.9 (Ar*C*H$_2$N), 48.6 (N(*C*H$_3$)$_2$), 48.5 (N(*C*H$_3$)$_2$), 42.9 (*C*(CH$_3$)$_2$Ph), 42.4 (*C*(CH$_3$)$_2$Ph), 34.9 (C(*C*H$_3$)$_2$Ph), 30.9 (C(*C*H$_3$)$_2$Ph), 30.9 (C(*C*H$_3$)$_2$Ph), 26.0 (C(*C*H$_3$)$_2$Ph).

L^{4}TiCl$_3$ (4a). Complex **4a** was synthesized in a similar manner to that described for **1a**, using proligand **L^{4}H** (1.143 g, 2.00 mmol), triethylamine (0.6 mL, 4 mmol), and TiCl$_4$(THF)$_2$ (0.644 g, 2.00 mmol) as starting materials. After crystallization in toluene, pure *cis*-**4a** was obtained as red crystals (0.527 g, 36.4%). mp: 197.2–198.1 °C. (Found: C, 64.03; H, 5.82; N, 3.47. Calc. for C$_{39}$H$_{41}$Cl$_3$N$_2$O$_2$Ti: C, 64.70; H, 5.71; N, 3.87%); NMR spectroscopic data for *cis*-**4a**: δ_H (400 MHz, CDCl$_3$) 7.44–7.37 (1 H, m, Ar*H*), 7.34–7.11 (1 6H, m, Ar*H*), 7.02 (1 H, t, ^3J = 7.4 Hz, Ar*H*), 6.95 (1 H, d, ^3J = 9.2 Hz, Ar*H*), 6.93 (1 H, d, ^4J = 2.5 Hz, Ar*H*), 6.80 (1 H, s, Ar*H*), 5.28 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 4.80 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 4.25 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 3.77 (3 H, s, ArOC*H*$_3$), 3.67–3.57 (1 H, m, N(C*H*$_2$)$_2$N), 3.57 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 2.73 (3 H, s, N(C*H*$_3$)$_2$), 2.56–2.43 (1 H, m, N(C*H*$_2$)$_2$N), 2.49 (1 H, d, ^2J = 13.2 Hz, N(C*H*$_2$)$_2$N), 2.19 (3 H, s, ArC*H*$_3$), 1.87 (1 H, d, ^2J = 13.2 Hz, N(C*H*$_2$)$_2$N), 1.20 (3 H, s, N(C*H*$_3$)$_2$). δ_C (100 MHz, CDCl$_3$) 159.0, 157.4, 135.2, 133.9, 133.2, 133.0, 131.0, 130.6, 130.3, 129.8, 127.6, 127.4, 125.9, 125.6, 120.6, 120.5, 111.2 (all Ar*C*), 63.6 (*C*Ph$_3$), 61.8 (O*C*H$_3$), 59.0 (N(*C*H$_2$)$_2$N), 57.5 (N(*C*H$_2$)$_2$N), 55.4 (Ar*C*H$_2$N), 55.1 (Ar*C*H$_2$N), 48.6 (N(*C*H$_3$)$_2$), 47.9 (N(*C*H$_3$)$_2$), 21.1 (Ar*C*H$_3$).

Attempted synthesis of L^{6}TiCl$_3$ (6a). Complex **6a** was synthesized in a similar manner to that described for **1a**, using proligand **L^{6}H** (0.899 g, 2.00 mmol), triethylamine (0.6 mL, 4 mmol), and TiCl$_4$(THF)$_2$ (0.644 g, 2.00 mmol) as starting materials. The product collected through crystallization, giving **6a** as red–orange powder (0.181 g, 15.0%). (Found: C, 44.32; H, 5.37; N, 4.71. Calc. for C$_{23}$H$_{32}$BrCl$_3$N$_2$O$_2$Ti: C, 45.84; H, 5.35; N, 4.65%); δ_H (400 MHz, CDCl$_3$) 7.48 (1 H, d, ^4J = 2.0 Hz, Ar*H*), 7.46–7.40 (1 H, m, Ar*H*), 7.29–7.24 (1 H, m, Ar*H*), 7.10–7.03 (1 H, m, Ar*H*), 6.99 (1 H, d, ^3J = 8.1 Hz, Ar*H*), 6.88 (1 H, d, ^4J = 2.0 Hz, Ar*H*), 5.44 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 4.70 (1 H, d, ^2J = 14.8 Hz, ArC*H*$_2$N), 4.21 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 3.95–3.75(2 H, m, N(C*H*$_2$)$_2$N), 3.82 (3 H, s, ArOC*H*$_3$), 3.62 (1 H, d, ^2J = 14.8 Hz, ArC*H*$_2$N), 3.12 (3 H, s, N(C*H*$_3$)$_2$), 2.63 (3 H, s, N(C*H*$_3$)$_2$), 2.65–2.58 (1 H, m, N(C*H*$_2$)$_2$N), 2.25–2.18 (1 H, m, N(C*H*$_2$)$_2$N), 1.24 (9 H, s, Ar(C*H*$_3$)$_3$).

L^{7}TiCl$_3$ (7a). Complex **7a** was synthesized in a similar manner to that described for **1a**, using proligand **L^{7}H** (0.767 g, 2.00 mmol), triethylamine (0.6 mL, 4 mmol), and TiCl$_4$(THF)$_2$ (0.644 g, 2.00 mmol) as starting materials. Pure *cis*-**7a** was obtained as red–orange powder (0.642 g, 59.8%). mp: 189.4–190.6 °C. (Found: C, 48.83; H, 5.18; N, 4.33. Calc. for C$_{19}$H$_{23}$Cl$_5$N$_2$O$_2$Ti·(0.9C$_7$H$_8$): C, 49.05; H, 4.91; N, 4.52%); NMR spectroscopic data for *cis*-**7a** δ_H (400 MHz, CDCl$_3$) 7.46–7.38 (1 H, m, Ar*H*), 7.33 (1 H, d, ^3J = 2.2 Hz, Ar*H*), 7.20 (1 H, dd, ^3J = 7.4 Hz, ^4J = 2.2 Hz, Ar*H*), 7.03 (1 H, t, ^3J = 7.4 Hz, Ar*H*), 6.98 (1 H, d, ^3J = 8.3 Hz, Ar*H*), 6.90 (1 H, d, ^4J = 2.2 Hz, Ar*H*), 5.38 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 4.67 (1 H, d, ^2J = 14.9 Hz, ArC*H*$_2$N), 4.22 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 3.87–3.76 (1 H,

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m, N(C*H*$_2$)$_2$N), 3.82 (3 H, s, OC*H*$_3$), 3.57 (1 H, d, ^2J = 14.9 Hz, ArC*H*$_2$N), 3.12 (3 H, s, N(C*H*$_3$)$_2$), 2.60 (3 H, s, N(C*H*$_3$)$_2$), 2.68–2.51 (2 H, m, N(C*H*$_2$)$_2$N), 2.94–2.21 (1 H, m, N(C*H*$_2$)$_2$N). δ_C (100 MHz, CDCl$_3$) 158.8, 154.3, 135.1, 131.1, 130.2, 129.4, 128.6, 128.4, 122.1, 120.7, 120.1, 111.4 (all Ar*C*), 60.1 (O*C*H$_3$), 58.8 (N(*C*H$_2$)$_2$N), 57.7 (N(*C*H$_2$)$_2$N), 55.6 (Ar*C*H$_2$N), 55.5 (Ar*C*H$_2$N), 49.7 (N(*C*H$_3$)$_2$), 48.2 (N(*C*H$_3$)$_2$).

L^{8}TiCl$_3$ (8a). Complex **8a** was synthesized in a similar manner to that described for **1a**, using proligand **L^{8}H** (0.944 g, 2.00 mmol), triethylamine (0.6 mL, 4 mmol), and TiCl$_4$(THF)$_2$ (0.644 g, 2.00 mmol) as starting materials. Pure *cis*-**8a** was obtained as red crystals (0.695 g, 55.6%). mp 186.9–187.8 °C. (Found: C, 37.16; H, 4.41; N, 3.80. Calc. for $C_{19}H_{23}Br_2Cl_2N_2O_2$-Ti·(0.1$C_7H_8$): C, 37.28; H, 3.78; N, 4.41%). NMR spectroscopic data for *cis*-**8a**: δ_H (400 MHz, CDCl$_3$) 7.65 (1 H, d, ^4J = 2.0 Hz, Ar*H*), 7.42 (1 H, t, ^3J = 7.3 Hz, Ar*H*), 7.22–7.17 (1 H, m, Ar*H*), 7.08 (1 H, d, ^4J = 2.0 Hz, Ar*H*), 7.03 (1 H, t, ^3J = 7.3 Hz, Ar*H*), 6.98 (1 H, d, ^3J = 8.3 Hz, Ar*H*), 5.37 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 4.69 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 4.23 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 3.80 (3 H, s, OC*H*$_3$), 3.86–3.75 (1 H, m, N(C*H*$_2$)$_2$N), 3.57 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 3.12 (3 H, s, N(C*H*$_3$)$_2$), 2.61 (3 H, s, N(C*H*$_3$)$_2$), 2.68–2.52 (2 H, m, N(C*H*$_2$)$_2$N), 2.28–2.19 (1 H, m, N(C*H*$_2$)$_2$N). Due to the poor solubility of complex **8a** in CDCl$_3$, the ^{13}C NMR spectrum could not be obtained.

L^{9}TiCl$_3$ (9a). Complex **9a** was synthesized in a similar manner to that described for **1a**, using proligand **L^{9}H** (0.910 g, 2.00 mmol), triethylamine (0.6 mL, 4 mmol), and TiCl$_4$(THF)$_2$ (0.644 g, 2.00 mmol) as starting materials. Red crystals were isolated (0.518 g, 42.6%), which was characterized to be a mixture of two isomers, the molar ratio of *cis*-**9a**/*trans*-**9a** = 10 : 1. mp: 226.7–227.5 °C. (Found: C, 58.98 H, 7.62; N, 3.92. Calc. for $C_{29}H_{45}Cl_3N_2O_2Ti$·(0.4C_7H_8): C, 59.24; H, 7.53; N, 4.34%); NMR spectroscopic data for *cis*-**9a**: δ_H (400 MHz, CDCl$_3$) 7.21 (1 H, s, Ar*H*), 7.07 (1 H, s, Ar*H*), 6.86 (1 H, s, Ar*H*), 6.61 (1 H, s, Ar*H*), 5.43 (1 H, d, ^2J = 14.6 Hz, ArC*H*$_2$N), 4.56 (1 H, d, ^2J = 14.6 Hz, ArC*H*$_2$N), 4.27 (1 H, d, ^2J = 14.6 Hz, ArC*H*$_2$N), 3.84–3.73 (1 H, m, N(C*H*$_2$)$_2$N), 3.82 (3 H, s, OC*H*$_3$), 3.40 (1 H, d, ^2J = 14.6 Hz, ArC*H*$_2$N), 3.11 (3 H, s, N(C*H*$_3$)$_2$), 2.72–2.61 (1 H, m, N(C*H*$_2$)$_2$N), 2.59–2.49 (1 H, m, N(C*H*$_2$)$_2$N), 2.56 (3 H, s, N(C*H*$_3$)$_2$), 2.34 (3 H, s, ArC*H*$_3$), 2.26 (3 H, s, ArC*H*$_3$), 2.29–2.19 (1 H, m, N(C*H*$_2$)$_2$N), 1.55 (9 H, s, C(C*H*$_3$)$_3$), 1.36 (9 H, s, C(C*H*$_3$)$_3$). δ_C (100 MHz, CDCl$_3$) 158.4, 157.8, 143.7, 137.7, 134.0, 133.9, 132.7, 129.9, 129.7, 128.9, 127.6, 125.2 (all Ar*C*), 63.4 (O*C*H$_3$), 61.2 (N(*C*H$_2$)$_2$N), 59.6 (N(*C*H$_2$)$_2$N), 58.4 (Ar*C*H$_2$N), 55.2 (Ar*C*H$_2$N), 50.6 (N(*C*H$_3$)$_2$), 47.9 (N(*C*H$_3$)$_2$), 35.1 (*C*(CH$_3$)$_3$), 35.0 (*C*(CH$_3$)$_3$), 31.1 (C(*C*H$_3$)$_3$), 30.4 (C(*C*H$_3$)$_3$), 21.1 (Ar*C*H$_3$), 21.1 (Ar*C*H$_3$).

L^{10}TiCl$_3$ (10a). Complex **10a** was synthesized in a similar manner to that described for **1a**, using proligand **L^{10}H** (1.242 g, 2.00 mmol), triethylamine (0.6 mL, 4 mmol), and TiCl$_4$(THF)$_2$ (0.644 g, 2.00 mmol) as starting materials. Pure *cis*-**10a** was obtained as red–orange crystals (0.565 g, 36.5%). mp: 271.2–273.0 °C. (Found: C, 64.89; H, 7.13; N, 3.62. Calc. for $C_{42}H_{55}Cl_3N_2O_2Ti$: C, 65.16; H, 7.16; N, 3.62%); NMR spectroscopic data for *cis*-**10a**: δ_H (400 MHz, CDCl$_3$) 7.34–7.12 (11 H, m, Ar*H*), 7.08 (1 H, t, ^3J = 7.2 Hz, Ar*H*), 6.80 (1 H, s, Ar*H*), 6.69 (1 H, s, Ar*H*), 5.25 (1 H, d, ^2J = 14.6 Hz, ArC*H*$_2$N), 4.57 (1 H, d, ^2J = 14.6 Hz, ArC*H*$_2$N), 4.23 (1 H, d, ^2J = 14.6 Hz, ArC*H*$_2$N), 3.75 (3 H, s, OC*H*$_3$), 3.63–2.43 (1 H, m, N(C*H*$_2$)$_2$N), 3.32 (1 H, d, ^2J = 14.6 Hz, ArC*H*$_2$N), 2.80 (3 H, s, N(C*H*$_3$)$_2$), 2.53–2.42 (1 H, m, N(C*H*$_2$)$_2$N), 2.42–2.34 (1 H, m, N(C*H*$_2$)$_2$N), 2.31 (3 H, s, N(C*H*$_3$)$_2$), 2.08 (3 H, s, ArC*H*$_3$), 2.04–1.96 (1 H, m, N(C*H*$_2$)$_2$N), 1.67 (3 H, s, C(C*H*$_3$)$_2$Ph), 1.66 (3 H, s, C(C*H*$_3$)$_2$Ph), 1.45 (3 H, s, C(C*H*$_3$)$_2$Ph), 1.38 (3 H, s. C(C*H*$_3$)$_2$Ph), 1.35 (9 H, s, C(C*H*$_3$)$_3$). δ_C (100 MHz, CDCl$_3$) 158.5, 157.0, 150.1, 150.0, 146.3, 143.7, 136.4, 133.5, 132.8, 129.7, 129.7, 128.2, 128.0, 126.8, 126.7, 126.6, 125.9, 125.7, 125.2 (all Ar*C*), 63.3 (O*C*H$_3$), 61.6 (N(*C*H$_2$)$_2$N), 59.1 (N(*C*H$_2$)$_2$N), 58.4 (Ar*C*H$_2$N), 55.0 (Ar*C*H$_2$N), 48.5 (N(*C*H$_3$)$_2$), 48.0 (N(*C*H$_3$)$_2$), 43.0 (*C*(CH$_3$)$_2$Ph), 42.4 (*C*(CH$_3$)$_2$Ph), 35.0 (*C*(CH$_3$)$_3$), 34.5 (C(*C*H$_3$)$_2$Ph), 31.1 (C(*C*H$_3$)$_3$ and C(*C*H$_3$)$_2$Ph overlapped), 30.9 (C(*C*H$_3$)$_2$Ph), 26.0 (C(*C*H$_3$)$_2$Ph), 21.2 (Ar*C*H$_3$).

L^{8}ZrCl$_3$ (8b). Complex **8b** was synthesized in a similar manner to that described for **1a**, using proligand **L^{8}H** (0.944 g, 2.00 mmol), triethylamine (0.6 mL, 4 mmol), and ZrCl$_4$(THF)$_2$ (0.750 g, 2.00 mmol) as starting materials. Pure *cis*-**8b** was obtained as colourless crystals (0.531 g, 42.5%). mp: 234.3–235.6 °C. (Found: C, 36.50; H, 3.83; N, 3.69. Calc. for $C_{19}H_{23}Br_2Cl_3N_2O_2Zr$·(0.3$C_7H_8$): C, 36.39; H, 3.68; N, 4.02%); NMR spectroscopic data for *cis*-**8b**: δ_H (400 MHz, CDCl$_3$) 7.63 (s, 1H, Ar*H*), 7.50–7.37 (1 H, m, Ar*H*), 7.31–7.12 (2 H, m, Ar*H*), 7.11–6.88 (2 H, m, Ar*H*), 5.31 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 4.62 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 4.27 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 3.84 (3 H, s, OC*H*$_3$), 3.92–3.72(1 H, m, N(C*H*$_2$)$_2$N), 3.58 (1 H, d, ^2J = 14.5 Hz, ArC*H*$_2$N), 3.03 (3 H, s, N(C*H*$_3$)$_2$), 2.70–2.59 (2 H, m, N(C*H*$_2$)$_2$N), 2.48 (3 H, s, N(C*H*$_3$)$_2$), 2.32–2.24 (1 H, m, N(C*H*$_2$)$_2$N). Due to the poor solubility of the complex **8b** in CDCl$_3$, the ^{13}C NMR spectrum could not be obtained.

L^{5}Ti(O^{i}Pr)$_3$ (5e). Ti(O^{i}Pr)$_4$ (0.40 mL, 1.3 mmol) was added dropwise *via* a syringe to the solution of proligand **L^{5}H** (0.520 g, 1.28 mmol) in 10 mL of dry toluene. The mixture was stirred at room temperature for 3 h. Then all the volatiles were removed *in vacuo*, and the residue was re-dissolved in *n*-hexane (10 mL) and filtered. The pale yellow solution was concentrated to 5 mL and kept at −20 °C. Complex **5e** was isolated as colourless crystals (0.490 g, 60.9%). (Found: C, 60.93; H, 8.31; N, 4.45. Calc. for $C_{32}H_{53}ClN_2O_5Ti$: C, 61.09; H, 8.49; N, 4.45%); δ_H (CDCl$_3$, 400 MHz) 7.44 (1 H, t, ^3J = 8.0 Hz, Ar*H*), 7.29 (2 H, m, Ar*H*), 7.09 (1 H, t, ^3J = 7.4 Hz, Ar*H*), 7.03 (1 H, d, ^3J = 8.0 Hz, Ar*H*), 6.65 (1 H, s, Ar*H*), 5.02 (4 H, br, ArC*H*$_2$ and C*H*(CH$_3$)$_2$ overlapped), 4.28 (2 H, br, ArC*H*$_2$), 3.88 (3 H, s, C*H*$_3$OAr), 3.53–3.25 (2 H, br, NC*H*$_2$CH$_2$N and ArC*H*$_2$ overlapped), 2.42 (9 H, br, N(C*H*$_3$)$_2$ and NC*H*$_2$C*H*$_2$N overlapped), 1.31 (18 H, br, CH(C*H*$_3$)$_2$), 1.26 (9 H, s, C(C*H*$_3$)$_3$). δ_C (CDCl$_3$, 100 MHz) 159.3, 156.0, 138.1, 135.0, 129.5, 126.0, 125.3, 124.6, 122.8, 121.5, 120.1, 111.1 (all Ar*C*), 59.1 (*C*H$_3$O), 57.1 (Ar*C*H$_2$N), 55.3 (N(*C*H$_2$)$_2$N), 53.0 (N(*C*H$_3$)$_2$), 45.8 (N(*C*H$_3$)$_2$), 33.8 (*C*(CH$_3$)$_3$), 31.6 (C(*C*H$_3$)$_3$), 26.2 (CH(*C*H$_3$)$_2$).

L^{6}Ti(O^{i}Pr)$_3$ (6e). Complex **6e** was synthesized in a similar manner to that described for **5e**, using proligand **L^{6}H** (1.15 g, 2.56 mmol), and Ti(O^{i}Pr)$_4$ (0.80 mL, 2.60 mmol) as starting

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materials. Pure **6e** was obtained as colourless crystals (1.15 g, 62.3%). (Found: C, 56.76; H, 7.79; N, 4.25. Calc. for $C_{32}H_{53}BrN_2O_5Ti$: C, 57.06; H, 7.93; N, 4.16%); δ_H ($CDCl_3$, 400 MHz) 7.37 (2 H, br, Ar*H*), 7.22 (1 H, dd, ^3J = 7.4 Hz, ^4J = 1.6 Hz, Ar*H*), 7.02 (1 H, td, ^3J = 7.4 Hz, ^4J = 0.9 Hz, Ar*H*), 6.97 (1 H, d, ^3J = 8.2 Hz, Ar*H*), 6.62 (1 H, d, ^4J = 2.5 Hz, Ar*H*), 4.87 (4 H, br, ArCH_2 and $CH(CH_3)_2$ overlapped), 4.20 (2 H, br, ArCH_2), 3.81 (3 H, s, CH_3OAr), 3.33 (2 H, br, NCH_2CH_2N and ArCH_2 overlapped), 2.34 (9 H, br, $N(CH_3)_2$ and NCH_2CH_2N overlapped), 1.24 (18 H, br, $CH(CH_3)_2$), 1.19 (9 H, s, $C(CH_3)_3$). δ_C ($CDCl_3$, 100 MHz) 159.3, 156.8, 138.6, 135.0, 129.5, 129.0, 126.2, 124.4, 122.8, 120.1, 112.5, 111.1 (all Ar*C*), 59.3 (CH_3O), 57.1 (ArCH_2N), 55.3 ($N(CH_2)_2N$), 53.0 ($N(CH_3)_2$), 45.8 ($N(CH_3)_2$), 33.8 ($C(CH_3)_3$), 31.6 ($C(CH_3)_3$), 26.3 ($CH(CH_3)_2$).

$L^7Ti(O^iPr)_3$ (7e). Complex **7e** was synthesized in a similar manner to that described for **5e**, using proligand **L^7H** (0.490 g, 1.28 mmol), and $Ti(O^iPr)_4$ (0.40 mL, 1.3 mmol) as starting materials. Pure **7e** was obtained as colourless crystals (0.480 g, 62.3%). (Found: C, 55.31; H, 7.34; N, 4.62. Calc. for $C_{28}H_{44}Cl_2N_2O_5Ti$: C, 55.36; H, 7.30; N, 4.61%); δ_H ($CDCl_3$, 400 MHz) 7.36 (1 H, t, ^3J = 7.8 Hz, Ar*H*), 7.16 (2 H, m, Ar*H*), 6.97 (2 H, m, Ar*H*), 6.63 (1 H, s, Ar*H*), 5.23 (1 H, s, ArCH_2), 4.84–4.94 (3 H, br, $CH(CH_3)_2$), 4.28 (1 H, d, ^2J = 12.6 Hz, ArCH_2), 4.05 (1 H, d, ^2J = 12.6 Hz, ArCH_2), 3.80 (3 H, s, CH_3OAr), 3.38 (1 H, m, CH_2CH_2), 3.16 (1 H, d, ^2J = 12.6 Hz, ArCH_2), 2.66 (3 H, s, $N(CH_3)_2$), 2.35 (2 H, m, NCH_2CH_2N), 2.12 (3 H, s, $N(CH_3)_2$), 1.93 (1 H, m, NCH_2CH_2N), 1.30–1.10 (18 H, br, $CH(CH_3)_2$). δ_C ($CDCl_3$, 100 MHz) 159.1, 157.4, 134.8, 129.7, 128.5, 128.1, 126.1, 123.0, 122.0, 120.1, 118.0, 110.9 (all Ar*C*), 58.2 (CH_3OAr), 56.9 ($N(CH_2)_2N$), 55.2 ($CH(CH_3)_2$), 52.9 ($N(CH_3)_2$), 45.7 ($N(CH_3)_2$), 26.2 ($CH(CH_3)_2$).

$L^8Ti(O^iPr)_3$ (8e). Complex **8e** was synthesized in a similar manner to that described for **5e**, using proligand **L^8H** (0.900 g, 1.92 mmol), and $Ti(O^iPr)_4$ (0.60 mL, 1.92 mmol) as starting materials. Pure **8e** was obtained as colourless crystals (0.800 g, 61.5%). (Found: C, 48.27; H, 6.31; N, 3.99. Calc. for $C_{28}H_{44}Br_2N_2O_5Ti$: C, 48.30; H, 6.37; N, 4.02%); δ_H ($CDCl_3$, 400 MHz) 7.48 (1 H, d, ^4J = 2.5 Hz, Ar*H*), 7.36 (1 H, td, ^3J = 8.2 Hz, ^4J = 2.5 Hz, Ar*H*), 7.15 (1 H, dd, ^3J = 7.4 Hz, ^4J = 1.7 Hz, Ar*H*), 7.00–6.94 (2 H, m, Ar*H*), 6.78 (1 H, d, ^4J = 2.5 Hz, Ar*H*), 5.26 (1 H, s, ArCH_2), 4.81–4.95 (3 H, br, $CH(CH_3)_2$), 4.28 (1 H, bs, ArCH_2), 4.05 (1 H, bs, ArCH_2), 3.81 (3 H, s, CH_3OAr), 3.38 (1 H, m, CH_2CH_2), 3.16 (1 H, d, ^2J = 12.6 Hz, ArCH_2), 2.65 (3 H, bs, $N(CH_3)_2$), 2.35 (2 H, t, ^3J = 5.2 Hz, NCH_2CH_2N), 2.13 (3 H, s, $N(CH_3)_2$), 1.90 (1 H, br, NCH_2CH_2N), 1.23 (18 H, br, $CH(CH_3)_2$). δ_C ($CDCl_3$, 100 MHz) 159.1, 158.6, 134.8, 134.0, 131.6 129.8, 126.5, 122.0, 120.1, 114.0, 111.0, 105.1 (all Ar*C*), 58.3 (CH_3O), 57.0 (ArCH_2N), 55.2 ($CH(CH_3)_2$), 53.0 ($N(CH_2)_2N$), 45.7 ($N(CH_3)_2$), 26.3 ($CH(CH_3)_2$).

X-ray crystallography

Single crystals of *cis*-**2a**, *cis*-**9a**, **8d** and **5e** were obtained from their saturated toluene solutions at room temperature, respectively. The crystals were mounted on glass fibers using an oil drop. The intensity data were collected on a Bruker SMART APEX II diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 298 K. These structures were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. All calculations were performed using the SHELXTL program.[104,105]

Ethylene polymerization

Toluene and MMAO (2.5 M in toluene) were introduced to a thoroughly dried 50 mL steel autoclave equipped with a magnetic stirrer. The autoclave was placed in a bath at the desired temperature for 10 min, and saturated with ethylene (1.5 atm). The polymerization reaction was started by adding a toluene solution of the desired catalyst precursor with a syringe to bring the total volume of the solution to 25 mL. The vessel was pressurized to 10 atm with ethylene immediately, and the pressure was kept by continuous feeding of ethylene. The reaction mixture was stirred at the desired temperature. After the polymerization was carried for a certain time interval, the reactor was cooled to room temperature and then the polymerization reaction was quenched with 3% HCl in ethanol (50 mL). The precipitated polymer was filtered, washed with water and ethanol, and then dried overnight in a vacuum oven at 60 °C to constant weight.

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