

Chiral Diamine Bis(phenolate) Ti^{IV} and Zr^{IV} Complexes – Synthesis, Structures and Reactivity

Sónia Barroso,^[a] Pedro Adão,^[a] M. Teresa Duarte,^[a] Auke Meetsma,^[b]
João Costa Pessoa,^[a] Marco W. Bouwkamp,^[b] and Ana M. Martins^{*[a]}

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Neutral and cationic titanium and zirconium diamine bis(phenolate) complexes supported by chiral ligands L¹ and L² are described [L¹ = (*R*)-6,6'-{1-(dimethylamino)propan-2-ylazanediyl}bis(methylene)-bis(2,4-di-*tert*-butylphenolate); L² = (*S*)-6,6'-{1-(1-ethylpyrrolidin-2-yl)methylazanediyl}bis(methylene)-bis(2,4-di-*tert*-butylphenolate)]. Complexes [TiL(OiPr)₂] [L = L¹ (1), L² (2)], [TiL²X(OiPr)] [X = Cl (3), CH₂Ph (4)], [TiL¹(CH₂Ph)₂] (5), [ZrLCl₂] [L = L¹ (6), L² (7)] and [ZrL(CH₂Ph)₂] [L = L¹ (8), L² (9)] are C₁-symmetric species readily prepared in moderate to high yields. Cationic compounds were obtained from complexes 5, 8 and 9

through reactions with B(C₆F₅)₃. The monocationic species reveal the η²-binding character of the benzyl groups and noncoordinated [B(C₆F₅)₃(CH₂Ph)][−]. Complexes 5–9 were tested in the polymerization of ethylene and propylene upon activation with modified methylaluminoxane (MMAO), B(C₆F₅)₃ or [NHMe₂Ph]⁺ as cocatalysts. The [ZrL¹Cl₂]/MMAO and [ZrL¹(CH₂Ph)₂]/B(C₆F₅)₃ systems revealed high activities in the polymerization of propylene (2.1 × 10³ and 1.5 × 10³ g_{pol}mmol_{cat}^{−1}h^{−1}, respectively), leading to atactic polypropylene, whereas the titanium complexes showed no activity.

Introduction

There has been a growing interest in the development of postmetallocene single-site transition metal catalysts for alkene polymerization in order to achieve control over the stereochemistry and molecular weight of the polymers.^[1] In recent years, group 4 transition metal complexes supported by chelating ligands containing nitrogen and/or oxygen coordinating sites have received considerable attention as active catalysts for olefin polymerization.^[1,2] Aryloxy ligands are particularly attractive since they form strong metal–oxygen bonds with electropositive group 4 metals, which are expected to stabilize the resulting complexes.

Group 4 amine bis(phenolate) metal complexes are effective catalysts for 1-hexene,^[3] 4-methylpentene,^[4] vinylcyclohexane^[4] and propylene polymerization,^[5] and for ethylene/1-hexene copolymerization.^[6] Evaluation of structural modifications in the activity of titanium and zirconium diamine bis(phenolate) catalysts has shown the importance of the bulkiness and electronic properties of the phenolate substituents in 1-hexene polymerization. When activated

with B(C₆F₅)₃, [TiL^{Cl}(CH₂Ph)₂] (Figure 1) was found to be highly active in 1-hexene polymerization giving the highest molecular weight poly(1-hexene) ever prepared at room temperature.^[3b] In addition, the presence of an extra donor on the sidearm proved to be crucial for the stabilization of active catalytic species and it has been found to suppress chain transfer reactions.^[3a,3b] Dibenzyltitanium and zirconium diamine bis(phenolate) complexes [ML^{tBu}(CH₂Ph)₂] (M = Ti, Zr, Figure 1), featuring a nitrogen donor on a sidearm, led to exceptionally high activities in the polymerization of 1-hexene and, in the case of titanium, to living polymerization.^[3a,3b] The diamine bis(phenolate) zirconium complex [ZrL^{tBu}(CH₂Ph)₂] and its dichloride analogue

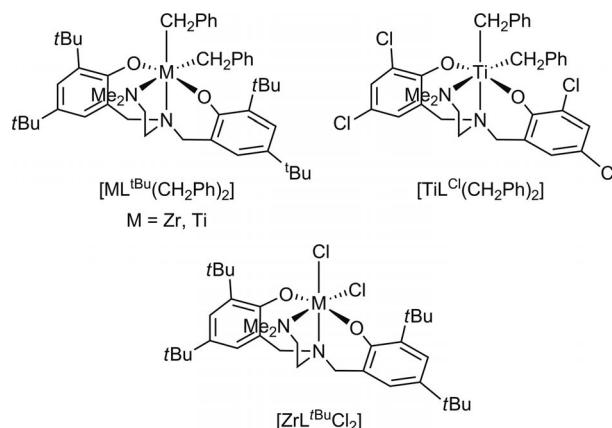


Figure 1. Diamine bis(phenolate) Ti^{IV} and Zr^{IV} complexes active in α -olefin polymerization.

[a] Centro de Química Estrutural, Instituto Superior Técnico, Universidade Técnica de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
E-mail: ana.martins@ist.utl.pt

[b] Molecular Inorganic Chemistry Group, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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[ZrL^tBuCl₂] (Figure 1) were found to be active propylene polymerization catalysts, upon activation with MAO, leading to high molecular weight, atactic polypropylene.^[5]

In view of these results, chiral derivatives of titanium and zirconium diamine bis(phenolate) complexes could be good candidates for the stereoselective polymerization of α -olefins. In fact, Kol and coworkers have recently reported a variety of chiral dianionic ligands of the type [N₂O₂] and their corresponding zirconium and titanium complexes for the stereoselective polymerization of α -olefins.^[7] However, the only example of a chiral tripodal diamine bis(phenolate) complex reported to date is a molybdenum compound and no catalytic applications have been described.^[8]

As part of our research with diamine bis(phenolate) complexes of group 3, 4 and 5 metals^[9] we undertook the preparation of chiral tripodal diamine bis(phenol) ligand precursors. Attempts to introduce chirality in the benzylic methylene protons were hampered by the formation of 1,3-benzoxazines.^[10] In view of these results we decided to adopt a different strategy and introduce chirality in the carbon chain of the ethylenediamine sidearm (**H₂L¹** in Figure 2).^[9b] Herein we describe a new chiral diamine bis(phenolate) ligand precursor displaying a ethylpyrrolidine moiety in the sidearm (**H₂L²** in Figure 2) together with neutral and cationic titanium and zirconium complexes supported by these two chiral ligands. The results obtained with these complexes as ethylene and propylene polymerization catalysts are also included.

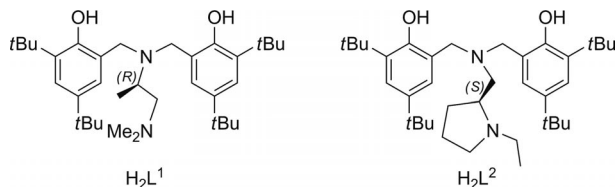


Figure 2. Chiral diamine bis(phenol) ligand precursors employed in this work.

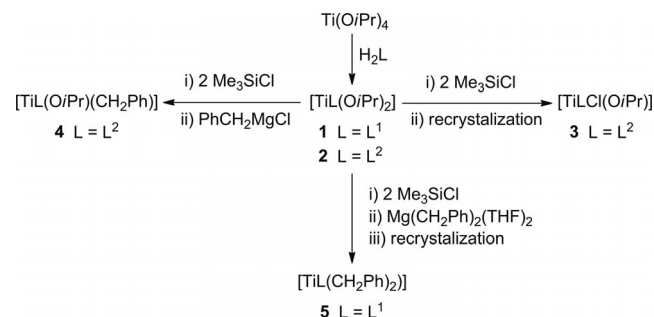
Results and Discussion

Synthesis and Characterization of the Ligands and Neutral Complexes

Chiral ligand precursor **H₂L²** (Figure 2), was prepared by a single-step Mannich condensation reaction of a substituted phenol, formaldehyde and an optically pure diamine, (*S*)-(1-ethylpyrrolidin-2-yl)methanamine, following reported procedures.^[11] The ¹H NMR spectrum of **H₂L²** displays only two sets of resonances for the *tert*-butyl groups and for the aromatic protons. However, the resonances assigned to the diamine moiety and the benzylic protons are consistent with a C₁-symmetric compound. Thus, the benzylic protons are diastereotopic, appearing as an AB system and all the resonances assigned to the diamine moiety are nonequivalent.

Scheme 1 shows the reactions performed to prepare the new chiral titanium complexes. [TiL¹(O*i*Pr)₂] (**1**) and [Ti-

L²(O*i*Pr)₂] (**2**) were obtained as yellow crystalline solids, in good yields, by treating the ligand precursors **H₂L¹** and **H₂L²**, respectively, with Ti(O*i*Pr)₄ in a 1:1 ratio. The compounds are stable to hydrolysis and do not show any sign of decomposition after several days in air. The ¹H NMR spectra of **1** and **2** feature two different isopropoxide groups and distinct resonances for the aromatic and aliphatic protons of the ancillary ligands pointing to rigid C₁-symmetric chelates on the NMR time scale.



Scheme 1. Synthesis of titanium complexes.

The chirality of **1** and **2** was further confirmed by the CD spectra of THF solutions of both compounds (Figure 3). Although the diamine sidearm moiety is different in the two complexes, the CD spectra of **1** and **2** show that the bands in the range close to 280 nm are nearly mirror images of each other.^[12] This is probably due to the similarity between the skeletons of L¹ and L² and the opposite configurations of their chiral carbon atoms (*R* in L¹ and *S* in L²). Moreover, the CD spectrum of **2** is more intense than that of **1**, which may be related to the existence of an extra source of chirality upon coordination of the ethylpyrrolidine heterocycle of L².^[13]

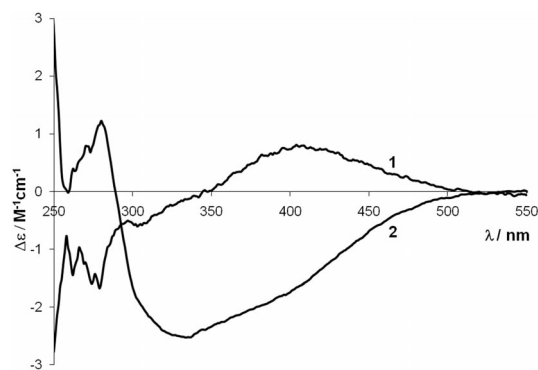


Figure 3. CD spectra of **1** and **2** in THF.

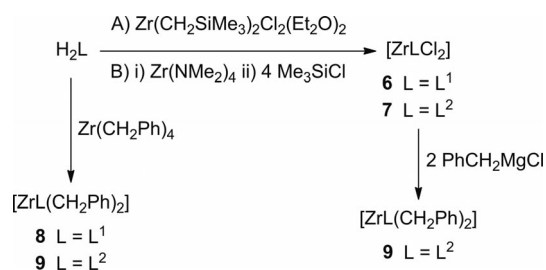
The reaction of M–OR groups with Me₃SiCl is a known procedure for the replacement of alkoxide by chloride ligands as a result of the formation of strong silicon–oxygen bonds.^[3a,3d] Aiming to prepare [TiL²Cl₂], **2** was treated with 2 equiv. of Me₃SiCl in dichloromethane. The NMR spectrum of the crude product revealed a complex mixture. Nevertheless, crystals of [TiL²Cl(O*i*Pr)] (**3**) suitable for X-ray diffraction were obtained by recrystallization of the mixture from toluene.

Sequential addition of Me₃SiCl and PhCH₂MgCl to a solution of **2** led to [TiL²(O*i*Pr)(CH₂Ph)] (**4**), which was isolated in 70% yield. The NMR spectrum of **4** is consistent with a C₁-symmetric species. The two benzylic methylene protons of L² appear as two AX systems giving rise to four doublets [δ = 3.85 and 2.84 ppm (²J_{HH} = 14.5 Hz); δ = 3.78 and 3.10 ppm (²J_{HH} = 13.4 Hz)], whereas the methylene protons of the benzyl ligand appear as one AB system [δ = 3.01 and 3.92 ppm (²J_{HH} = 8.7 Hz)]. A NOESY experiment pointed out a spatial correlation between the isopropoxide group and the *ortho*-*t*Bu groups attesting its coordination *trans* to the tripodal nitrogen. In addition, the NOESY spectrum shows spatial correlations between one of the *ortho*-*t*Bu groups and the protons of the methyl group of the ethylpyrrolidine moiety attesting for its static coordination to the metal on the NMR time scale. As a result the epimerization of this chiral centre in solution is blocked.

The reaction of **1** with Me₃SiCl followed by the addition of Mg(CH₂Ph)₂(THF)₂ led, upon recrystallization from cold pentane, to the isolation of the dibenzyl complex [TiL¹(CH₂Ph)₂] (**5**). The ¹H NMR spectrum of **5** indicates the formation of a rigid C₁-symmetric species. The benzylic methylene protons of L¹ are observed as two AB systems, whereas the methylene protons of the benzyl ligands appear as two AX systems. The NMR spectrum is comparable to that previously published for the nonchiral analogue of **5**, [TiL^{*t*Bu}(CH₂Ph)₂].^[3a,3d] Complex **5** is thermally unstable in solution at room temperature but can be kept in the solid state at -37 °C for several weeks. All attempts to obtain crystals of **5** suitable for X-ray diffraction were unsuccessful.

The reactions performed for the preparation of the new chiral zirconium complexes are shown in Scheme 2. Upon protonolysis of Zr(CH₂SiMe₃)₂Cl₂(Et₂O)₂ with the neutral ligand precursors H₂L¹ and H₂L² in THF, SiMe₄ elimination was observed affording [ZrL¹Cl₂] (**6**) and [ZrL²Cl₂] (**7**) in 48 and 16% isolated yield, respectively. The low yields obtained in these reactions are surprising since this procedure is a known entry to the chemistry of zirconium supported by a variety of ligands.^[14] In view of this, an alternative method, consisting of the formation of [ZrL¹(NMe)₂] and [ZrL²(NMe)₂] intermediates, was attempted. Thus, the reactions of H₂L¹ and H₂L² with Zr(NMe₂)₄ followed by in situ addition of excess Me₃SiCl led to the isolation of complexes **6** and **7** in 68 and 57% yield, respectively, as light yellow solids. The ¹H NMR spectrum of **6** is consistent with a C₁-symmetric species displaying two AX spin systems for the benzylic methylene protons of the ligand. The coordination of the NMe₂ moiety was confirmed by a NOESY experiment. The ¹H NMR spectrum of **7** is consistent with the presence of two isomers of C₁ symmetry. The NOESY experiment has shown that there is no dynamic exchange between them. Although many resonances of the minor species are overlapped by the resonances of the major one, the AX spin systems are appreciably different due to the benzylic methylene protons, which is possibly related to ring current effects caused by different locations of these nuclei in relation to the phenolate rings. The two isomers might

result either from *trans/cis*-phenolate coordination or from diastereomers associated with the chirality of the N2 nitrogen upon bonding to the zirconium, as shown in Figure 4. Isomers of *trans/cis*-phenolate coordination have been reported for [ZrL^{*t*Bu}Cl₂], which also has a diamine bis(phenolate) donor set bearing a pyridine donor on the side-arm.^[14b] However, if *trans/cis*-phenolate coordination is assumed for **7**, three different types of isomers would be expected, as shown in Scheme 3. If the two possible configurations, *R/S*, resulting from the coordination of N2 are also considered, six diastereoisomers might be expected. The two isomers observed in the ¹H NMR spectrum of **7** are tentatively assigned to *trans*-phenolate species with *S* and *R* configuration at N2 in accordance with the geometry observed for compounds **1–6**.



Scheme 2. Synthesis of zirconium complexes.

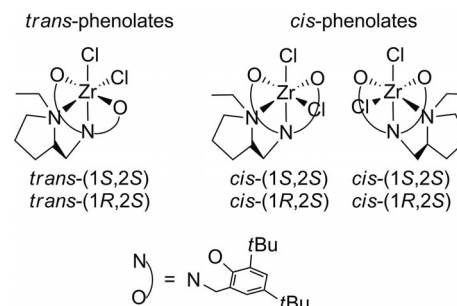
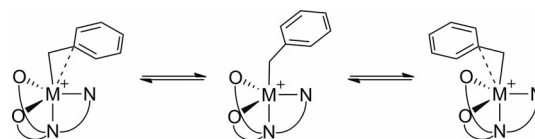
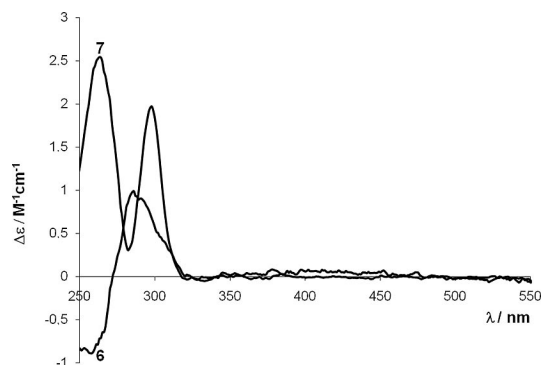


Figure 4. Possible isomers of **7**.



Scheme 3.

The chirality of **6** and **7** was further confirmed by the CD spectra of THF solutions of the complexes (Figure 5). No bands are observed in the visible region of the CD spectra due to the absence of charge transfer bands in that region, also reflected in the light colour of the complexes (pale yellow). As observed for **1** and **2**, the CD spectrum of **6** is more intense than that of **7**, due to the additional chiral centre.^[15]

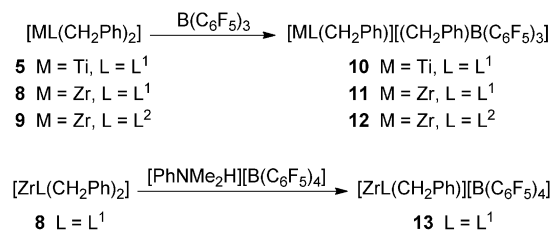
Figure 5. CD spectra of **6** and **7** in THF.

Compounds $[\text{ZrL}^1(\text{CH}_2\text{Ph})_2]$ (**8**) and $[\text{ZrL}^2(\text{CH}_2\text{Ph})_2]$ (**9**) were obtained by single-step metathesis reactions between tetrabenzylzirconium and the ligand precursors. Surprisingly, according to ^1H NMR spectroscopic data, only one isomer was obtained for **9**, suggesting that formation of two isomers observed for **7** is blocked by the steric bulk of the benzyl group. This assumption was confirmed by the reaction of **7** (mixture of isomers) with 2 equiv. of PhCH_2MgCl that led to the formation of one isomer of **9** in 59% isolated yield. The ^1H and ^{13}C NMR spectra of **8** and **9** are consistent with C_1 -symmetric species. The two dibenzyl complexes show characteristic AB systems for the diastereotopic methylene protons of the benzyl ligands in their ^1H NMR spectra ($\delta = 2.55\text{--}2.96$ ppm). In the ^{13}C NMR spectra the ZrCH_2Ph methylene group is found in the range $\delta = 66\text{--}70$ ppm with small $^1J_{\text{CH}}$ (112–124 Hz). The latter value and the observation of downfield resonances for the *ipso*-carbons suggest η^1 -coordination of the benzyl ligands.^[15] For both complexes, the NOESY spectra show spatial correlations that confirm the coordination of the ethylpyrrolidine and dimethylamine nitrogen atoms to the metal centre and *trans* configuration of the phenolate groups. The tripodal ligand forces the two benzyl ligands to be mutually *cis*.

Generation and Characterization of Cationic Species

The reactions of tris(pentafluorophenyl)borane with **5**, **8** and **9** proceed rapidly and quantitatively at room temperature in $[\text{D}_5]\text{bromobenzene}$, through the abstraction of one benzyl group and formation of the corresponding cationic species as shown in Scheme 4. In solution, $[\text{ZrL}^1(\text{CH}_2\text{Ph})_2][\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3]$ (**11**) is stable for several days at room temperature, whereas $[\text{TiL}^1(\text{CH}_2\text{Ph})_2][\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3]$ (**10**) decomposes gradually at room temperature over one or two days and is only stable at -35°C . $[\text{ZrL}^2(\text{CH}_2\text{Ph})_2][\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3]$ (**12**) is unstable and decomposes over a couple of hours even at low temperatures. The high instability of the titanium vs. the zirconium complexes follows the trend observed for first row metal organometallic compounds and is related to weaker metal–ligand bonds.^[16] The lower stability of **12** is likely associated with the high steric

bulk of the amine sidearm of L^2 and the presence of $\beta\text{-H}$ atoms in the ethylpyrrolidine moiety that may provide $\beta\text{-H}$ elimination as an accessible decomposition pathway.



Scheme 4. Generation of the cationic species.

The new complexes were characterised by ^1H , ^{13}C and ^{19}F NMR spectra as monocationic species with a noncoordinated $[\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3]^-$ anion.^[15] The ^1H and ^{13}C NMR spectra of **10**, **11** and **12** are consistent with C_1 -symmetric species resembling their neutral precursors. The resonances corresponding to the MCH_2Ph methylene protons show up as broad singlets in the ^1H NMR spectra of the three complexes indicating that the rotation of the benzyl group is constrained.

Relevant chemical shifts for the neutral precursors **5**, **8** and **9** and the corresponding cationic species **10**, **11** and **12** are listed in Table 1. The assessment of the benzyl coordination mode by NMR is often obscured by fluxional processes. However, in static systems η^2 -benzyl ligands in cationic species are usually characterized by downfield-shifted methylene proton resonances and highfield shifts for the *ipso* and the methylene carbon signals when compared to the neutral precursors. A high $^1J_{\text{CH}}$ for the methylene group (> 130 Hz) is also an indication of η^2 -benzyl coordination.^[17] The upfield shift (> 29 ppm) of the TiCH_2Ph carbon resonance in the ^{13}C NMR spectrum of **10**, the high $^1J_{\text{CH}}$ value for ZrCH_2Ph (139 Hz) and the upfield shift of the *ipso* carbon in the ^{13}C NMR spectrum of **11** and the upfield shift of the *ipso* carbon resonance in the ^{13}C NMR spectrum of **12** are suggestive of η^2 -benzyl coordination to the metal. Although no downfield shift of methylene proton resonances was observed for the cationic species, it is important to mention that these experiments were run at room temperature and that fluxional processes occurring in these conditions may obscure the identification of all criteria. The broad resonances due to the benzyl methylene protons are

Table 1. Selected ^1H and ^{13}C NMR spectroscopic data for compounds **5** and **8–12**.

	^1H NMR (δ , ppm) MCH_2 [$^1J_{\text{HH}}$, Hz]	^{13}C NMR (δ , ppm) MCH_2Ph [$^1J_{\text{CH}}$, Hz]	C_{ipso} MCH_2Ph
5	3.56 and 3.34 [8.4]; 3.26 and 2.79 [9.5]	98.6, 85.1	155.2, 148.2
10	3.25, br.	55.6	147.4
8	2.79 and 2.67; 2.67 and 2.55 [9.8]	68.6 [123], 66.6 [121]	150.2, 148.0
11	2.94, br.	72.6 [139]	131.6
9	2.96 and 2.79; 2.86 and 2.79	69.1 [124], 68.3 [112]	148.9, 148.6
12	2.55, br.	68.8	135.8

an indication that equilibrium between two η^2 -benzyl isomers takes place in solution as shown in Scheme 3.

The reaction of **8** with [PhNMe₂H][B(C₆F₅)₄] in [D₅]bromobenzene leads to [ZrL²(CH₂Ph)][B(C₆F₅)₄] (**13**) with the release of toluene and PhNMe₂ (Scheme 4). The ¹H and ¹³C NMR spectra of **13** indicate a cationic species similar to **11**, and the ¹⁹F NMR spectrum confirms the presence of the [B(C₆F₅)₄][−] anion.

Catalytic Studies – Ethylene and Propylene Polymerization

The chiral titanium and zirconium complexes were screened for their potential application as catalyst precursors in ethylene and propylene polymerization and the results are presented in Table 2. The activities are based on the observed productivity over the 30 min run time extrapolated to 1 h and they do not take into account possible differences in activity profiles for the various catalysts over the run time. These values are to be used as relative measures of catalyst efficiency rather than absolute activities. All polymers obtained were analysed by high-temperature gel permeation chromatography (HT-GPC).

Upon activation with MMAO, **6** and **7** exhibit low activities^[18] in the polymerization of ethylene. Molecular weight analysis of the resulting polymers show narrow polydispersity (PDI = 1.4) for the polyethylene (PE) obtained from **6**, whereas a very wide PDI was obtained with **7**. In the polymerization of propylene, **6** was found to be highly active, with an activity of 2.1×10^3 g_{pol}mmol_{cat}^{−1}h^{−1}, whereas **7** was inactive.

Complex **8**, activated with B(C₆F₅)₃ and in the presence of the scavenger tri(isobutyl)aluminoxane (TIBAO), gave the highest activities for the polymerization of ethylene and propylene. These reactions are highly exothermic and are accompanied by heating of the mixture. Complex **9** was inactive in the same conditions, which is possibly related to the instability of **12** discussed above. Complex **8** led to polypropylene (PP) with a polymodal distribution and low molecular weight (7.4×10^3 g mol^{−1}), contrasting with its non-chiral analogue [ZrL^{tBu}(CH₂Ph)₂], which was found to be active in the polymerization of propylene, upon activation with MAO, yielding PP with a high molecular weight ($M_w = 3.6 \times 10^5$ g mol^{−1}) and a narrow PDI of 1.8.^[5] [ZrL^{tBu}(CH₂Ph)₂] was also shown to be highly reactive in the polymerization of 1-hexene.^[5] Therefore, the performance of **8** was also tested in the polymerization of 1-hexene but it showed no activity.

The mixture of **5** and B(C₆F₅)₃ was found to be inactive in the polymerization of ethylene and propylene, even in the presence of a scavenger. This result contrasts with those published for the nonchiral analogue of **5**, [TiL^{tBu}(CH₂Ph)₂], which was found to lead to living polymerization of 1-hexene.^[3a]

To investigate the influence of the cocatalyst, [PhNMe₂H][B(C₆F₅)₄] was also used to activate **8** in the presence of TIBAO. Under these conditions, the activity of **8** was lower for the polymerization of ethylene and higher for the polymerization of propylene in comparison to the activities obtained using [B(C₆F₅)₃]. However, these small differences were not significant.

Table 2. Data for ethylene, propylene and 1-hexene polymerization.^[a]

Precatalyst	Activator (equiv.)	Scavenger (equiv.)	<i>m</i> _{pol} [g]	Activity ^[b]	<i>M</i> _w [g mol ^{−1}]	<i>M</i> _n [g mol ^{−1}]	PDI (<i>M</i> _w / <i>M</i> _n)
Ethylene polymerization ^[c]							
6	MMAO (200)		0.090	4 × 10 ¹	1.1 × 10 ³	8.1 × 10 ²	1.4
7	MMAO (200)		0.017	7	6.9 × 10 ⁵	2.9 × 10 ³	240.9
8	B(C ₆ F ₅) ₃ (1)		traces				
9	B(C ₆ F ₅) ₃ (1)		traces				
5	B(C ₆ F ₅) ₃ (1)	TIBAO (20)	traces				
8	B(C ₆ F ₅) ₃ (1)	TIBAO (20)	1.395	5.6 × 10 ²	2.1 × 10 ⁴	5.4 × 10 ³	3.8
9	B(C ₆ F ₅) ₃ (1)	TIBAO (20)	traces				
8	[NHMe ₂ Ph] [B(C ₆ F ₅) ₄] (1)	TIBAO (20)	0.993	3.8 × 10 ²	3.7 × 10 ⁴	1.1 × 10 ⁴	3.4
Propylene polymerization ^[c]							
6	MMAO (200)		5.314	2.1 × 10 ³	7.5 × 10 ³	2.1 × 10 ³	3.6
7	MMAO (200)		traces				
8	B(C ₆ F ₅) ₃ (1)		traces				
9	B(C ₆ F ₅) ₃ (1)		traces				
5	B(C ₆ F ₅) ₃ (1)	TIBAO (20)	traces				
8	B(C ₆ F ₅) ₃ (1)	TIBAO (20)	3.665	1.5 × 10 ³	7.4 × 10 ³	1.3 × 10 ³	5.8
9	B(C ₆ F ₅) ₃ (1)	TIBAO (20)	traces				
8	[NHMe ₂ Ph] [B(C ₆ F ₅) ₄] (1)	TIBAO (20)	7.454	3.0 × 10 ³	8.0 × 10 ³	1.2 × 10 ³	6.5
1-Hexene polymerization ^[d]							
6	MMAO (200)		1.343	5.4 × 10 ²	4.5 × 10 ³	2.1 × 10 ³	2.2
8	B(C ₆ F ₅) ₃ (1)		n.d.				

[a] Precatalyst: 5 μmol; *t* = 30 min. [b] g_{pol}mmol_{cat}^{−1}h^{−1}. [c] Monomer pressure: 5 bar. [d] Monomer: 9 mL (6.06 g).

Despite the chirality of the catalyst precursors no enantioselectivity was achieved since all PP samples obtained were atactic according to ^{13}C NMR spectra.

Aiming to obtain information about the catalytic reactions, one equivalent of ethylene was added, at ambient temperature, to a NMR tube containing a $[\text{D}_5]$ bromobenzene solution of **11**. Upon stirring for a few minutes, the ^1H NMR spectrum indicates the presence of **11** and a new C_1 -symmetric species that seems to present an interaction between the zirconium and ethylene. Indeed, ethylene resonances in the mixture appear as one singlet at $\delta = 5.13$ ppm in the ^1H NMR spectrum and give rise to a signal at $\delta = 75.7$ in the ^{13}C NMR spectrum (^1H $\delta = 5.29$ ppm, ^{13}C $\delta = 123.9$ ppm for free ethylene).^[19] After 24 h stirring no significant changes were observed in the ^1H NMR spectrum. Upon addition of excess ethylene (+5 equiv.) the solution becomes slightly turbid and broadening of the NMR signals is observed. The resonances assigned to **11** disappear, indicating that its conversion to new compound(s) is complete. The NMR spectroscopic data did not allow further conclusions but indicate that **11** interacts with ethylene in solution.

Single-Crystal X-ray Diffraction Studies

Suitable crystals for X-ray diffraction were obtained for H_2L^1 , H_2L^2 , **3**, **6** and **8**.

H_2L^1 crystallizes in the orthorhombic system, space group $Pbca$, with two symmetry-independent molecules in the asymmetric unit as depicted in Figure 6. H_2L^2 crystallizes in the monoclinic system, space group $P2_1$ with four symmetry-independent molecules in the asymmetric unit as depicted in Figure 7. The configurations adopted by both compounds in the solid state are determined by $\text{O} \cdots \text{H} \cdots \text{N}$ and $\text{O} \cdots \text{H} \cdots \text{O}$ intramolecular hydrogen bond interactions. Selected structural parameters for H_2L^1 and H_2L^2 and a more detailed description are given in the Supporting Information.

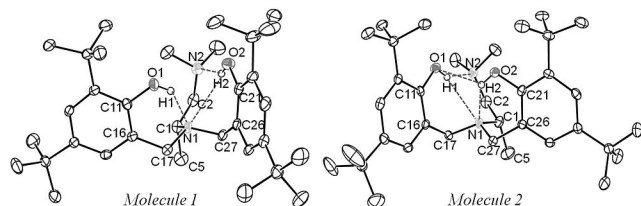


Figure 6. ORTEP diagram of H_2L^1 , 40% probability level ellipsoids. Hydrogen atoms are omitted for clarity.

An ORTEP diagram of the molecular structure of **3** is shown in Figure 8 and selected structural parameters are listed in Table 3. The compound crystallizes in the triclinic system, space group $P1$, with one molecule of **3** and one toluene solvate molecule in the asymmetric unit. The titanium centre displays a distorted octahedral geometry with the equatorial plane defined by atoms O1, O2 and N2 of the diamine bis(phenolate) ligand and C11, and the axial

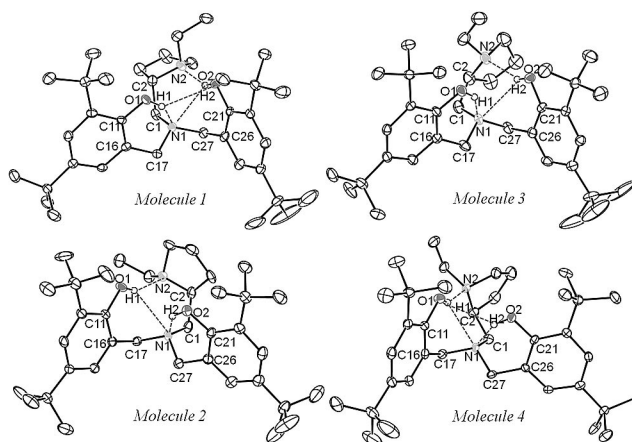


Figure 7. ORTEP diagram of H_2L^2 , 40% probability level ellipsoids. Hydrogen atoms are omitted for clarity.

positions are occupied by the tripodal nitrogen N1 and by O3 of the isopropoxide ligand. The titanium atom is slightly displaced from the equatorial plane [0.24(1) Å], in the direction of the isopropoxide ligand. The phenolate groups display *trans* configuration, folding towards the chloride ligand with a narrow dihedral angle of 121(1)° between the planes containing the phenolate rings, reflecting the bulkiness of the heterocyclic amine. The pyrrolidine cycle is coordinated to the metal through the nitrogen atom N2. Chiral atoms N2 and C2 have *S* configuration, and the five-membered metallacycle is defined by Ti1–N1–C1–C2–N2, which displays δ conformation. The least square plane containing the pyrrolidine ring defines a dihedral angle of 72.6(6)° with the equatorial plane and dihedral angles of 24.2(7) and 64.1(8)° with the planes containing the phenolate rings (planes that include C11 and C21, respectively). The relatively short Ti1–O3 bond length [1.79(1) Å] is consistent with a pronounced π -donation from the isopropoxide oxygen atom to the metal. This effect is commonly observed in titanium(IV) alkoxy derivatives^[20] and is more pronounced for this type of ligand than for the phenoxide groups, which display Ti–O bond lengths of 1.89(1) Å.

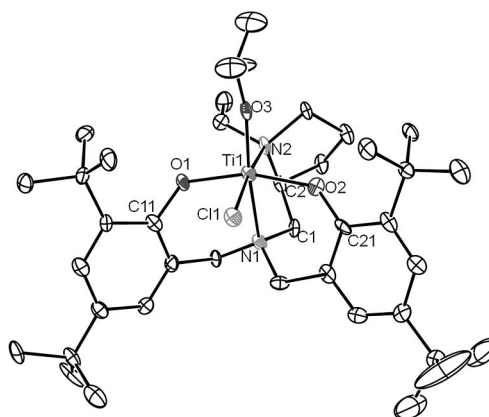


Figure 8. ORTEP diagram of **3**, 40% probability level ellipsoids. Hydrogen atoms are omitted for clarity.

Table 3. Selected structural parameters for **3**, **6** and **8**.^[a]

	3	6	8		3	6	8
Distances [Å]							
M(1)–O(1)	1.89(1)	1.979(5)	1.996(1)	M(1)–X(1)	1.79(1)	2.422(2)	2.310(2)
M(1)–O(2)	1.89(1)	1.978(6)	1.989(2)	M(1)–X(2)	2.37(0)	2.441(3)	2.345(2)
M(1)–N(1)	2.31(1)	2.393(7)	2.453(2)	M(1)–C(72)			3.002(2)
M(1)–N(2)	2.32(1)	2.437(7)	2.610(2)	M(1)–C(82)			3.314(2)
M(1)–equat. plane ^[b]	0.244(2)	0.239(2)	0.209(2)				
Angles [°]							
O(1)–M(1)–O(2)	161.4(4)	160.8(2)	160.5(1)	O(2)–M(1)–N(2)	91.5(4)	87.8(2)	87.7(1)
O(1)–M(1)–N(1)	83.8(4)	80.8(2)	80.8(1)	O(2)–M(1)–X(2)	86.4(3)	99.6(2)	91.7(1)
O(1)–M(1)–X(1)	98.8(4)	98.6(2)	98.8(1)	N(1)–M(1)–X(1)	164.1(4)	160.7(2)	149.9(1)
O(1)–M(1)–N(2)	91.2(4)	87.4(2)	85.9(1)	N(1)–M(1)–N(2)	75.7(4)	74.5(2)	69.8(1)
O(1)–M(1)–X(2)	87.9(3)	92.3(2)	93.2(1)	N(1)–M(1)–X(2)	95.0(3)	99.4(2)	105.8(1)
O(2)–M(1)–N(1)	79.1(4)	80.0(2)	79.7(1)	X(1)–M(1)–X(2)	100.8(3)	99.9(1)	104.3(1)
O(2)–M(1)–X(1)	99.6(4)	99.6(2)	98.2(1)	N(2)–M(1)–X(2)	170.7(3)	173.8(2)	175.6(1)
X(1)–M(1)–N(2)	88.5(4)	86.3(2)	80.1(1)	M(1)–C(71)–C(72)			102.5(1)
M(1)–O(1)–C(11)	130.7(7)	145.2(5)	145.3(1)	M(1)–C(81)–C(82)			118.4(1)
M(1)–O(2)–C(21)	135.3(8)	146.9(5)	145.7(1)	θ ^[c]	120.7(7)	157.2(3)	152.7(1)

[a] M = Ti in **3** and Zr in **6** and **8**; X(1) = O(3) in **3**, Cl(1) in **6** and C(71) in **8**; X(2) = Cl(1) in **3**, Cl(2) in **6** and C(81) in **8**. [b] The equatorial plane is defined by atoms O(1), O(2), N(2) and X(2). [c] θ is the dihedral angle between the planes containing the phenolate rings.

The molecular structure of complex **6** is depicted in Figure 9 and selected structural parameters are listed in Table 3. The compound crystallizes from toluene in the monoclinic system, space group $P2_1/c$, with one molecule in the asymmetric unit. Compound **6** displays distorted octahedral geometry with the equatorial plane defined by atoms O1, O2, N2 and Cl2, and the axial positions occupied by the tripodal nitrogen N1 and Cl1. The zirconium atom is slightly away from the equatorial plane [0.227(3) Å] in the direction of Cl1. The overall structural parameters of **6** are comparable to the nonchiral analogue [ZrL^{Bu}Cl₂].^[5] The structure presents the phenolate groups in *trans* configuration, bending towards the sidearm with a dihedral angle of 157.2(3)° between the planes containing the phenolate rings. Despite the formal absence of a mirror plane in the molecule, the overall ligand core remains quasisymmetrical because the C₂ chain of the diamine moiety is twisted to accommodate the extra methyl group away from the phenolate groups, thus nearly bisecting the angle between them.

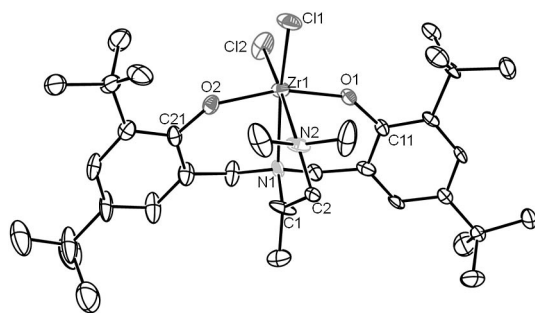


Figure 9. ORTEP diagram of **6**, 40% probability level ellipsoids. Hydrogen atoms and a disordered carbon atom are omitted for clarity.

The molecular structure of **8** is depicted in Figure 10 and selected structural parameters are listed in Table 3. The compound crystallizes from toluene in the monoclinic system, space group $P2_1/c$, with one molecule of **8** and one toluene solvate molecule in the asymmetric unit. The geometry around the zirconium centre is again distorted octahedral with the equatorial plane defined by atoms O1, O2 and N2 of L¹ and C81 of one of the benzyl ligands, whereas the axial positions are occupied by the tripodal nitrogen N1 and C71 of the other benzyl ligand. The phenolate groups are mutually *trans*, in accordance with the discussion of the NMR results, and bend towards the dimethylamine sidearm defining a dihedral angle of 152.7(1)°. The zirconium atom is slightly away from the equatorial plane [0.209(2) Å] in the direction of the benzyl ligand. The NMe₂ moiety is weakly bonded to the metal as indicated by the long Zr1–N2 bond

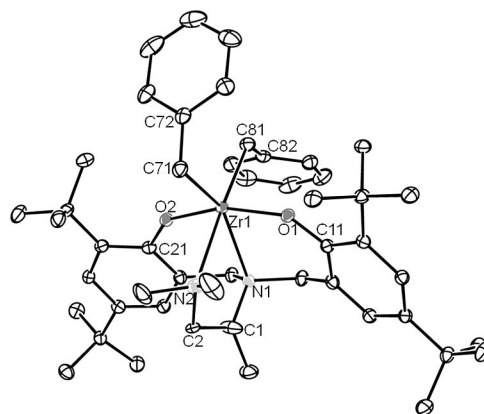


Figure 10. ORTEP diagram of **8**, 40% probability level ellipsoids. Hydrogen atoms and a disordered carbon atom are omitted for clarity.

length of 2.610(2) Å. In general the structure of **8** resembles that of **6**. The longer Zr–N bond lengths in **8** may be attributed to a richer metal centre and higher steric bulk caused by the benzyl ligands.

There is a noticeable difference in the bonding mode of the two benzyl ligands in the structure of **8**. The narrower Zr1–C71–C72 angle [102.5(1) vs. 118.4(1)°], as well as the shorter Zr1–C72 distance [3.002(2) vs. 3.314(2) Å] observed in one benzyl group (Figure 10), point to partial η^2 -binding to the Zr.^[3c,17]

As shown in Figure 11 the arrangement around the tripodal nitrogen N1 in **3** is helical, whereas the structures of **6** and **8** present a nearly symmetric arrangement of the phenolates that bend towards the sidearm.

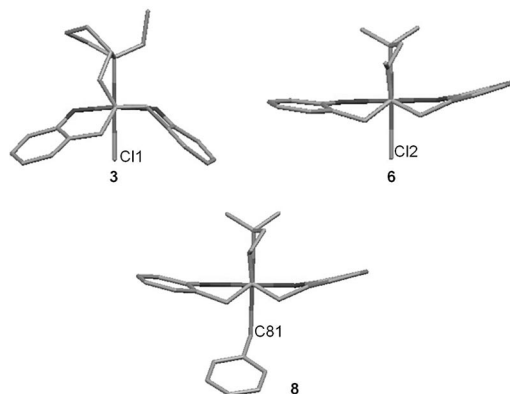


Figure 11. Wireframe diagrams of **3**, **6** and **8** viewed along the N1–M axis (M = Ti in **3**, Zr in **6** and **8**). Groups in *trans* position relative to the tripodal nitrogen (OiPr in **3**, Cl1 in **6** and CH₂Ph in **8**) and the *tert*-butyl groups are omitted for clarity.

The centrosymmetric space groups obtained for the structures of **H₂L¹**, **6** and **8** indicate that the resolution of the racemic diamine for the preparation of ligand precursor **H₂L¹** was not efficient.

Conclusions

New chiral neutral and cationic diamine bis(phenolate) complexes were prepared and characterized. With the exception of [TiL(OiPr)₂] [L = L¹ (**1**), L² (**2**)], the titanium compounds are, in general, less stable than the zirconium analogues. The compounds derived from L¹ are closely related to their nonchiral analogues concerning their structures and properties. The presence of the methyl group α to the tripodal nitrogen atom does not impose a significant change in the complex structures because the torsion of the sidearm C₂ chain releases the steric bulk that results from the presence of the substituent. In general, the compounds supported by L² are less stable than those bearing L¹. This feature is related to the high steric bulk imposed by the ethylpyrrolidine moiety and to the presence of β -H atoms, which may provide an extra decomposition pathway. Furthermore, the presence of two chiral centres [C_(S) and N_(R/S)] upon coordination of L² gives rise to the formation of one pair of diastereomers for [ZrL²Cl₂] (**7**). Replacement

of the chloride ions by benzyl groups leads to a unique stereoisomer, possibly due to steric constraints.

Compounds **5**, **8** and **9** were used as precursors for cationic complexes formed upon removal of one benzyl ligand. The NMR spectra of these species are indicative of η^2 -benzyl coordination. Assessment of the catalytic properties of the compounds revealed high activities in the polymerization of propylene [2126 and 1466 g_{pol}mmol_{cat}^{−1}h^{−1} for [ZrL¹Cl₂]/MMAO and [ZrL¹(CH₂Ph)₂]/B(C₆F₅)₃ systems, respectively] yielding atactic polypropylene. Conversely, the titanium complexes showed very low activities in the polymerization of ethylene and propylene.

Experimental Section

General: All preparations and subsequent manipulations of air/moisture sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk line and glovebox techniques. Reagents were purchased from commercial suppliers. **H₂L¹**, Zr(CH₂Ph)₄, B(C₆F₅)₃, Zr(CH₂SiMe₃)₂Cl₂(Et₂O)₂ and Mg(CH₂Ph)₂(THF)₂ were prepared according to literature procedures.^[9b,16,21] Solvents (THF, toluene, pentane) were dried by percolation under a nitrogen atmosphere through columns of alumina, molecular sieves, and supported copper oxygen scavenger (BASF R3-11) or by distillation with Na/K alloy (THF, hexane, Et₂O, [D₈]THF, C₆D₆). C₆D₅Br and CH₂Cl₂ were dried with CaH₂ and distilled under reduced pressure. [D₈]Toluene and CD₂Cl₂ were dried with molecular sieves (4 Å) and degassed by the freeze-pump-thaw method. NMR spectra were recorded with Varian Inova 500, Varian Gemini VXR 400, Varian VXR 300 and Bruker Avance II+ 300 and 400 MHz (UltraShield Magnet) NMR instruments. ¹H and ¹³C chemical shifts (δ) are expressed in ppm relative to Me₄Si, whereas ¹⁹F nucleus was referenced to an external reference capillary with CF₃COOH.

Synthetic Procedures

H₂L²: The diamine used to prepare **H₂L²**, (S)-(1-ethylpyrrolidin-2-yl)methanamine, was obtained optically active pure from commercial suppliers. A solution of 2,4-di-*tert*-butylphenol (4.13 g, 20.00 mmol), (S)-(–)-2-aminomethyl-1-ethylpyrrolidine (1.35 mL, 12.30 mmol) and 36% aqueous formaldehyde (1.65 mL, 22.00 mmol) in methanol (10 mL) was stirred at room temperature for 3 d. The mixture was cooled to –20 °C overnight leading to the formation of a sticky precipitate. The supernatant solution was decanted and the solid was redissolved in MeOH. Upon cooling, the compound precipitated out of solution. The solid was separated by filtration and washed thoroughly with ice cold methanol to give an off-white solid in 30% yield. The compound was further purified by recrystallization from methanol. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 9.69 (br., 2 H, OH), 7.20 (d, ⁴J_{HH} = 2.2 Hz, 2 H, CH-Ar), 6.87 (d, ⁴J_{HH} = 2.2 Hz, 2 H, CH-Ar), 3.87 (d, ²J_{HH} = 13.3 Hz, 2 H, ArCH₂N), 3.43 (d, ²J_{HH} = 13.2 Hz, 2 H, ArCH₂N), 3.35 (m, 1 H, CH₂), 3.04 (m, 1 H, CH₂CH₃), 2.66 (m, 2 H, CH₂, CH), 2.48 (m, 1 H, NCH₂), 2.25 (m, 2 H, CH₂CH₃, CH₂), 1.90 (m, 1 H, CH₂), 1.68 (m, 2 H, CH₂), 1.48 (m, 1 H, CH₂), 1.39 [s, 18 H, C(CH₃)₃], 1.27 [s, 18 H, C(CH₃)₃], 1.20 (t, ³J_{HH} = 7.2 Hz, 3 H, CH₂CH₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C): δ = 153.6, 140.1, 136.0 and 121.8 (C_{ipso}-Ar), 124.9 and 123.3 (CH-Ar), 64.4 (CH), 58.5 (ArCH₂N), 54.0 (CH₂), 53.6 (CH₂), 50.0 (CH₂CH₃), 34.9 and 34.1 [C(CH₃)₃], 31.7 and 29.6 [C(CH₃)₃], 28.5 (CH₂), 22.8 (CH₂), 13.0 (CH₂CH₃) ppm. C₃₇H₆₀N₂O₂·0.1(CH₃OH)

(567.66); calcd. C 78.44, H 10.72, N 4.93; found C 78.36, H 11.21, N 4.94.

[TiL¹(OiPr)₂] (1): A solution of **H₂L¹** (323 mg, 0.6 mmol) in Et₂O was slowly added to a 1 M solution of Ti(OiPr)₄ in Et₂O (0.6 mL, 0.6 mmol) in the same solvent. The solution was stirred for 2 h at room temperature. Evaporation of all the volatiles under reduced pressure led to a yellow solid in 62% yield. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 7.58 (d, ⁴J_{HH} = 2.5 Hz, 1 H, *p*-CH-Ar), 7.56 (d, ⁴J_{HH} = 2.5 Hz, 1 H, *p*-CH-Ar), 7.07 (d, ⁴J_{HH} = 2.4 Hz, 1 H, *o*-CH-Ar), 7.04 (d, ⁴J_{HH} = 2.5 Hz, 1 H, *o*-CH-Ar), 5.25 [sept, ³J_{HH} = 6.1 Hz, 1 H, CH(CH₃)₂], 4.75 [sept, ³J_{HH} = 6.1 Hz, 1 H, CH(CH₃)₂], 4.66 (d, ²J_{HH} = 13.8 Hz, 1 H, NCH₂Ar), 3.51 (d, ²J_{HH} = 13.2 Hz, 1 H, NCH₂Ar), 3.39 (d, ²J_{HH} = 13.2 Hz, 1 H, NCH₂Ar), 3.29 (d, ²J_{HH} = 13.9 Hz, 1 H, NCH₂Ar), 3.19 [m, 1 H, NCH(CH₃)-CH₂N], 2.47 [t, 1 H, NCH(CH₃)CH₂N], 2.34 [s, 3 H, N(CH₃)₂], 2.04 [s, 3 H, N(CH₃)₂], 1.79 [s, 9 H, C(CH₃)₃], 1.76 [s, 9 H, C(CH₃)₃], 1.53 [d, ³J_{HH} = 6.1 Hz, 3 H, CH(CH₃)₂], 1.50 [d, ³J_{HH} = 6.1 Hz, 3 H, CH(CH₃)₂], 1.44 [s, 9 H, C(CH₃)₃], 1.41 [s, 9 H, C(CH₃)₃], 1.12 [m, 1 H, NCH(CH₃)CH₂N], 0.99 [d, ³J_{HH} = 6.1 Hz, 3 H, CH(CH₃)₂], 0.88 [d, ³J_{HH} = 6.1 Hz, 3 H, CH(CH₃)₂], 0.59 [d, ³J_{HH} = 6.7 Hz, 3 H, NCH(CH₃)CH₂N] ppm. ¹³C{¹H} NMR (75 MHz, C₆D₆, 25 °C): δ = 163.4, 160.1, 139.5, 139.2, 136.2, 134.7, 125.9 and 124.4 (C_{ipso}-Ar), 124.7 and 124.3 (CH-Ar), 77.9 and 77.8 [CH(CH₃)₂], 64.6 [NCH(CH₃)CH₂N], 62.1 and 57.3 (NCH₂Ar), 53.0 [NCH(CH₃)CH₂N], 51.3 and 50.1 [N(CH₃)₂], 36.1, 35.9 and 34.7 [C(CH₃)₃], 32.5, 32.4, 31.5 and 31.4 [C(CH₃)₃], 27.6, 27.5, 26.7 and 26.5 [CH(CH₃)₂], 8.7 [NCH(CH₃)CH₂N] ppm. C₄₁H₇₀N₂O₄Ti·3.5(C₃H₈O) (912.61): calcd. C 67.73, H 10.82, N 3.07; found C 67.79, H 11.04, N 2.84.

[TiL²(OiPr)₂] (2): A solution of **H₂L²** (339 mg, 0.6 mmol) in Et₂O was slowly added to a 1 M solution of Ti(OiPr)₄ in Et₂O (0.6 mL, 0.6 mmol) in the same solvent. The solution was stirred for 2 h at room temperature. Evaporation of all the volatiles under reduced pressure led to a yellow solid in 64% yield. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 7.58 (d, ⁴J_{HH} = 2.4 Hz, 1 H, *p*-CH-Ar), 7.51 (d, ⁴J_{HH} = 2.3 Hz, 1 H, *p*-CH-Ar), 7.18 (d, ⁴J_{HH} = 2.5 Hz, 1 H, *o*-CH-Ar), 6.69 (d, ⁴J_{HH} = 2.2 Hz, 1 H, *o*-CH-Ar), 5.14 [sept, ³J_{HH} = 6.1 Hz, 1 H, CH(CH₃)₂], 4.90 (d, ²J_{HH} = 14.4 Hz, 1 H, NCH₂Ar), 4.29 [sept, ³J_{HH} = 6.1 Hz, 1 H, CH(CH₃)₂], 4.10 (m, 1 H, CH₂), 3.89 (d, ²J_{HH} = 12.3 Hz, 1 H, NCH₂Ar), 3.29 (m, 2 H, CH₂CH₃), 3.19 (d, ²J_{HH} = 14.6 Hz, 1 H, NCH₂Ar), 2.96 (m, 1 H, NCH₂CH), 2.86 (t, ²J_{HH} = 12.4 Hz, 1 H, CH₂), 2.69 (d, ²J_{HH} = 12.4 Hz, 1 H, NCH₂Ar), 2.63 (m, 1 H, CH₂), 1.79 [s, 9 H, C(CH₃)₃], 1.77 [s, 9 H, C(CH₃)₃], 1.51 [d, ³J_{HH} = 3.8 Hz, 3 H, CH(CH₃)₂], 1.49 [d, ³J_{HH} = 3.8 Hz, 3 H, CH(CH₃)₂], 1.47 [s, 9 H, C(CH₃)₃], 1.44 (m, 2 H, CH₂), 1.38 (m, 1 H, CH₂), 1.34 [s, 9 H, C(CH₃)₃], 1.20 (m, 1 H, NCH₂CH), 0.92 (t, ³J_{HH} = 7.2 Hz, 3 H, CH₂CH₃), 0.72 [d, ³J_{HH} = 6.1 Hz, 3 H, CH(CH₃)₂], 0.55 (m, 1 H, NCH₂CH), 0.48 [d, ³J_{HH} = 6.1 Hz, 3 H, CH(CH₃)₂] ppm. ¹³C{¹H} NMR (101 MHz, C₆D₆, 25 °C): δ = 164.4, 159.7, 139.6, 139.2, 136.6, 134.5 and 125.0 (C_{ipso}-Ar), 124.3, 124.1 and 124.0 (CH-Ar), 123.5 (C_{ipso}-Ar), 123.0 (CH-Ar), 78.0 and 77.9 [CH(CH₃)₂], 63.6 (NCH₂Ar), 62.9 (NCH₂CH), 61.8 (NCH₂Ar), 61.1, 54.7 and 53.4 (CH₂), 36.1, 35.8, 34.7 and 34.6 [C(CH₃)₃], 32.6, 32.4, 31.3 and 31.3 [C(CH₃)₃], 29.2 (CH₂), 27.3, 27.2, 26.2 and 25.8 [CH(CH₃)₂], 25.2 (CH₂), 11.0 (CH₂CH₃) ppm. C₄₃H₇₂N₂O₄Ti·2.5(C₃H₈O) (878.56): calcd. C 68.99, H 10.55, N 3.19; found C 68.66, H 10.26, N 3.19.

[TiL²Cl(OiPr)] (3): A 1 M solution of Si(Me)₃Cl in CH₂Cl₂ (5.00 mL, 5.00 mmol) was added to a solution of **2** (1.82 g, 2.50 mmol) in CH₂Cl₂ and the mixture was stirred for 2 h at room temperature. All the volatiles were removed under reduced pressure to give an orange solid. Analysis of the NMR spectroscopic data

revealed a complex mixture of compounds. Orange crystals of **3** were obtained from a toluene solution of the mixture at -37 °C. The small amount of crystals obtained prevented further characterization.

[TiL²(OiPr)(CH₂Ph)] (4): A 1 M solution of Si(Me)₃Cl in CH₂Cl₂ (0.42 mL, 0.42 mmol) was added to a solution of **2** (153.1 mg, 0.21 mmol) in CH₂Cl₂ and the mixture was stirred for 2 h at room temperature. All the volatiles were removed under reduced pressure. The residue was redissolved in Et₂O and a 1 M solution of PhCH₂MgCl in Et₂O (0.42 mL, 0.42 mmol) was added and the mixture was further stirred for 2 h at room temperature. The solution was filtered and the solvent was evaporated under reduced pressure to give a red solid in 70% yield. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 7.64 (s, 1 H, *p*-CH-Ar), 7.59 (s, 1 H, *p*-CH-Ar), 7.09 (s, 1 H, *o*-CH-Ar), 6.96 (m, 2 H, CH₂Ph), 6.92 (s, 1 H, *o*-CH-Ar), 6.83 (d, ³J_{HH} = 7.7 Hz, 2 H, CH₂Ph), 6.75 (t, ³J_{HH} = 7.2 Hz, 1 H, CH₂Ph), 5.14 [sept, ³J_{HH} = 6.0 Hz, 1 H, CH(CH₃)₂], 3.85 (d, ²J_{HH} = 14.5 Hz, 1 H, NCH₂Ar), 3.78 (d, ²J_{HH} = 13.4 Hz, 1 H, NCH₂Ar), 3.10 (d, ²J_{HH} = 13.4 Hz, 1 H, NCH₂Ar), 3.01 (d, ²J_{HH} = 8.7 Hz, 1 H, CH₂Ph), 2.92 (d, ²J_{HH} = 8.7 Hz, 1 H, CH₂Ph), 2.84 (d, ²J_{HH} = 14.5 Hz, 1 H, NCH₂Ar), 2.74 (m, 1 H, CH₂), 2.70 (m, 1 H, CH₂), 2.60 (m, 1 H, NCH₂CH), 2.58 (m, 1 H, CH₂CH₃), 2.23 (m, 1 H, CH₂), 1.98 (m, 1 H, CH₂CH₃), 1.86 [s, 9 H, C(CH₃)₃], 1.82 [s, 9 H, C(CH₃)₃], 1.51 [m, 7 H, CH₂, CH(CH₃)₂], 1.43 [s, 9 H, C(CH₃)₃], 1.39 [s, 9 H, C(CH₃)₃], 1.14 (m, 1 H, CH₂), 0.85 (m, 2 H, CH₂), 0.62 (t, ³J_{HH} = 7.1 Hz, 3 H, CH₂CH₃), 0.30 (m, 1 H, CH₂) ppm. ¹³C{¹H} NMR (75 MHz, C₆D₆, 25 °C): δ = 161.5, 159.4, 152.1, 141.2, 140.7, 136.7, 135.6 and 129.7 (C_{ipso}-Ar), 128.7, 127.9 and 127.3 (CH-Ph), 127.0 and 125.9 (C_{ipso}-Ph), 124.9, 124.8, 124.2 and 123.9 (CH-Ar), 121.5 (CH-Ph), 79.8 [CH(CH₃)₂], 76.1 (CH₂Ph), 65.5 and 65.1 (NCH₂Ar), 63.5 (NCH₂CH), 62.5, 50.8 and 50.1 (CH₂), 36.3, 36.2 and 34.8 [C(CH₃)₃], 32.5, 32.4, 31.8 and 31.3 [C(CH₃)₃], 27.3 (CH₂), 26.8 and 26.5 [CH(CH₃)₂], 22.6 (CH₂), 11.7 (CH₂CH₃) ppm. C₄₈H₇₅N₂O₃Ti·1.7(CH₂Cl₂) (919.80): calcd. C 64.82, H 8.58, N 3.04; found C 64.85, H 8.48, N 3.04.

[TiL¹(CH₂Ph)₂] (5): A 1 M solution of Si(Me)₃Cl in CH₂Cl₂ (6.00 mL, 6.00 mmol) was added to a solution of **2** (1.76 g, 2.50 mmol) in CH₂Cl₂ and the mixture was further stirred for 2 h at room temperature. The solvent was evaporated to dryness and the residue was redissolved in THF and treated with a solution of Mg(CH₂Ph)₂(THF)₂ (0.88 g, 2.50 mmol) in THF. The mixture was stirred at room temperature for 4 h and then evaporated to dryness leading to a residue that was extracted in pentane. After filtration the solution was cooled to -54 °C leading to a microcrystalline dark red solid in 41% yield that was separated by filtration and dried in vacuo. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ = 7.89 (d, ³J_{HH} = 7.4 Hz, 2 H, CH₂Ph), 7.74 (d, ⁴J_{HH} = 2.1 Hz, 1 H, CH-Ar), 7.70 (d, ⁴J_{HH} = 2.1 Hz, 1 H, CH-Ar), 7.41 (t, ³J_{HH} = 7.6 Hz, 2 H, CH₂Ph), 7.00 (m, 4 H, CH-Ar, CH₂Ph), 6.90 (d, ⁴J_{HH} = 2.1 Hz, 1 H, CH-Ar), 6.60 (t, ³J_{HH} = 7.5 Hz, 2 H, CH₂Ph), 6.48 (t, ³J_{HH} = 7.2 Hz, 1 H, CH₂Ph), 3.56 (d, ²J_{HH} = 8.4 Hz, 1 H, CH₂Ph), 3.34 (d, ²J_{HH} = 8.4 Hz, 1 H, CH₂Ph), 3.26 (d, ²J_{HH} = 9.5 Hz, 1 H, CH₂Ph), 2.98 (d, ²J_{HH} = 14.1 Hz, 1 H, ArCH₂N), 2.79 (m, ²J_{HH} = 8.9 Hz, 2 H, CH₂Ph, ArCH₂N), 2.63 (d, ²J_{HH} = 14.1 Hz, 1 H, ArCH₂N), 2.52 [m, 1 H, NCH(CH₃)CH₂N], 2.39 (d, ²J_{HH} = 14.0 Hz, 1 H, ArCH₂N), 2.19 [s, 18 H, C(CH₃)₃], 2.05 [m, 1 H, NCH(CH₃)CH₂N], 1.85 [s, 3 H, N(CH₃)₂], 1.82 [s, 3 H, N(CH₃)₂], 1.36 [s, 9 H, C(CH₃)₃], 1.35 [s, 9 H, C(CH₃)₃], 0.53 [m, 1 H, NCH(CH₃)CH₂N], 0.51 [d, ³J_{HH} = 6.5 Hz, 3 H, NCH(CH₃)CH₂N] ppm. ¹³C{¹H} NMR (126 MHz, C₆D₆, 25 °C): δ = 161.1 and 160.1 (C_{ipso}-Ar), 155.2 and 148.2 (C_{ipso}-Ph), 141.6, 141.2, 136.1 and 135.3 (C_{ipso}-Ar), 128.8 and 128.6 (CH₂Ph), 128.5 and 127.0 (C_{ipso}-Ar), 126.9, 126.7 and 126.2 (CH₂Ph), 124.7, 124.4, 124.3 and

124.0 (CH-Ar), 122.0 and 121.9 (CH₂Ph), 98.6 and 85.1 (CH₂Ph), 65.7 [NCH(CH₃)CH₂N], 61.0 and 56.8 (ArCH₂N), 50.6 [NCH(CH₃)CH₂N], 37.9, 36.0, 35.8 and 34.2 [C(CH₃)₃], 31.8, 31.7 and 31.3 [C(CH₃)₃], 31.2 [N(CH₃)₂], 31.1 [C(CH₃)₃], 30.8 [N(CH₃)₂], 7.5 [NCH(CH₃)CH₂N] ppm. C₄₉H₇₀N₂O₂Ti·0.5(C₄H₈O) (802.44): calcd. C 76.28, H 9.29, N 3.49; found C 76.31, H 9.37, N 3.33.

[ZrL¹Cl₂] (6). Method A: A solution of H₂L¹ (1.35 g, 2.50 mmol) in THF was added to a solution of Zr(CH₂SiMe₃)₂Cl₂(Et₂O)₂ (1.12 g, 2.50 mmol) in the same solvent. The mixture was stirred at room temperature for 12 h and a white precipitate appeared. The yellow solution was filtered and the solvents evaporated to dryness under reduced pressure to give a light yellow solid in 48% yield.

Method B: A solution of H₂L¹ (323 mg, 0.6 mmol) in Et₂O was added to a solution of Zr(NMe₂)₄ (161 mg, 0.6 mmol) in the same solvent. The mixture was stirred at room temperature for 2 h. The yellow solution was evaporated to dryness under reduced pressure. The residue was redissolved in CH₂Cl₂ and Si(Me)₃Cl 1 M in CH₂Cl₂ (2.4 mL, 2.4 mmol) was slowly added to the solution. The mixture was stirred at room temperature for 2 h and the yellow solution was evaporated to dryness under reduced pressure. The residue was washed with *n*-hexane and dried in vacuo to give a light yellow solid in 68% yield. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 7.61 (s, 1 H, CH-Ar), 7.55 (s, 1 H, CH-Ar), 6.92 (s, 2 H, CH-Ar), 4.41 (d, ²J_{HH} = 14.1 Hz, 1 H, ArCH₂N), 4.06 (d, ²J_{HH} = 14.3 Hz, 1 H, ArCH₂N), 2.95 [m, 3 H, ArCH₂N, NCH(CH₃)CH₂N], 2.38 [t, ²J_{HH} = 13.1 Hz, 1 H, NCH(CH₃)CH₂N], 2.09 [s, 3 H, N(CH₃)₂], 1.71 [s, 18 H, C(CH₃)₃], 1.69 [s, 3 H, N(CH₃)₂], 1.39 [s, 9 H, C(CH₃)₃], 1.37 [s, 9 H, C(CH₃)₃], 0.75 [d, ²J_{HH} = 13.0 Hz, 1 H, NCH(CH₃)CH₂N], 0.54 [d, ³J_{HH} = 6.6 Hz, 3 H, NCH(CH₃)CH₂N] ppm. ¹³C-{¹H} NMR (101 MHz, C₆D₆, 25 °C): δ = 158.2, 156.9, 142.7, 142.5, 138.0, 136.9, 126.7 and 125.5 (C_{ipso}-Ar), 125.5, 125.4, 125.1 and 124.7 (CH-Ar), 66.1 [NCH(CH₃)CH₂N], 62.5 and 58.1 (ArCH₂N), 53.2 [NCH(CH₃)CH₂N], 51.7 and 48.2 [N(CH₃)₂], 36.1, 36.0, 34.9 and 34.8 [C(CH₃)₃], 32.3, 32.2, 31.4 and 31.0 [C(CH₃)₃], 8.3 [NCH(CH₃)CH₂N] ppm. C₃₅H₃₆Cl₂N₂O₂Zr·0.6(CH₂Cl₂) (749.51): calcd. C 57.02, H 7.69, N 3.74; found C 57.01, H 8.48, N 3.36.

[ZrL²Cl₂] (7). Method A: A solution of H₂L² (1.41 g, 2.50 mmol) in THF was added to a solution of Zr(CH₂SiMe₃)₂Cl₂(Et₂O)₂ (1.12 g, 2.50 mmol) in the same solvent. The mixture was stirred at room temperature for 12 h and a white precipitate appeared. The yellow solution was filtered and the solvents evaporated to dryness under reduced pressure to give a light yellow solid; yield 0.28 g, 16%.

Method B: A solution of H₂L² (339 mg, 0.6 mmol) in Et₂O was added to a solution of Zr(NMe₂)₄ (161 mg, 0.6 mmol) in the same solvent. The solution was stirred at room temperature for 2 h. The yellow solution was evaporated to dryness under reduced pressure. The residue was redissolved in CH₂Cl₂ and Si(Me)₃Cl 1 M in CH₂Cl₂ (2.4 mL, 2.4 mmol) was slowly added to the solution. The mixture was stirred at room temperature for 2 h. The yellow solution was evaporated to dryness under reduced pressure. The residue was washed with *n*-hexane and dried in vacuo to give a light yellow solid; yield 250 mg, 57%. The analysis of NMR spectroscopic data revealed a mixture of isomers in variable ratios (from 100:1 to 3:1). **Major isomer:** ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 7.60 (s, 1 H, CH-Ar), 7.58 (s, 1 H, CH-Ar), 7.05 (s, 1 H, CH-Ar), 6.94 (s, 1 H, CH-Ar), 4.79 (d, ²J_{HH} = 13.8 Hz, 1 H, ArCH₂N), 3.95 (d, ²J_{HH} = 13.1 Hz, 1 H, ArCH₂N), 3.19 (m, 1 H, CH₂CH₃), 3.07 (m, 2 H, ArCH₂N, CH₂), 2.89 (m, 2 H, ArCH₂N, CH), 2.69 (m, 2 H, CH₂), 2.20 (m, 1 H, CH₂CH₃), 1.74 [s, 18 H, C(CH₃)₃], 1.53 (m, 1 H, CH₂), 1.40 [s, 9 H, C(CH₃)₃], 1.35 [s, 9 H, C(CH₃)₃], 0.80 (m, 1 H,

CH₂), 0.70 (m, 3 H, CH₂, CH₂CH₃), 0.21 (m, 1 H, CH₂) ppm. ¹³C-{¹H} NMR (101 MHz, C₆D₆, 25 °C): δ = 156.3, 142.7, 142.4, 138.0, 136.9 and 126.9 (C_{ipso}-Ar), 125.8, 125.2, 125.1 and 124.5 (CH-Ar), 66.2 (CH), 65.7 and 65.2 (ArCH₂N), 59.4, 52.0 and 51.5 (CH₂), 36.1, 35.9, 34.9 and 34.8 [C(CH₃)₃], 32.3, 32.2, 31.5, 31.0 [C(CH₃)₃], 27.1 and 22.5 (CH₂), 11.2 (CH₂CH₃) ppm. **Minor isomer:** ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 7.52 (d, ⁴J_{HH} = 2.1 Hz, 1 H, CH-Ar), 7.48 (d, ⁴J_{HH} = 2.1 Hz, 1 H, CH-Ar), 7.12 (d, ⁴J_{HH} = 1.9 Hz, 1 H, CH-Ar), 7.09 (d, ⁴J_{HH} = 1.8 Hz, 1 H, CH-Ar), 5.68 (d, ²J_{HH} = 14.2 Hz, 1 H, ArCH₂N), 5.42 (d, ²J_{HH} = 13.1 Hz, 1 H, ArCH₂N), 3.33 (d, ²J_{HH} = 14.2 Hz, 1 H, ArCH₂N), 3.25 (d, ²J_{HH} = 13.2 Hz, 1 H, ArCH₂N), 1.74 [s, 9 H, C(CH₃)₃], 1.45 [s, 9 H, C(CH₃)₃], 1.44 [s, 9 H, C(CH₃)₃], 1.40 [s, 9 H, C(CH₃)₃] ppm. The other peaks are overlapped by the peaks of the major isomer. ¹³C-{¹H} NMR (101 MHz, C₆D₆, 25 °C): δ = 158.9, 157.6, 140.6, 140.5, 135.7 and 126.2 (C_{ipso}-Ar), 126.2, 125.4 and 125.1 (CH-Ar), 125.0 (C_{ipso}-Ar), 124.8 (CH-Ar), 66.6 (ArCH₂N), 66.4 (CH), 66.2 (ArCH₂N), 59.0, 51.4 and 49.2 (CH₂), 36.0, 35.8, 35.7 and 34.7 [C(CH₃)₃], 32.4, 32.3, 31.9, 30.6 [C(CH₃)₃], 26.2 and 21.2 (CH₂), 11.9 (CH₂CH₃) ppm. C₃₇H₃₈Cl₂N₂O₂Zr·(C₄H₈O) (796.64): calcd. C 57.02, H 7.69, N 3.74; found C 57.01, H 8.48, N 3.36.

[ZrL¹(CH₂Ph)₂] (8): A solution of H₂L¹ (456 mg, 1 mmol) in toluene was slowly added to a solution of Zr(CH₂Ph)₄ (539 mg, 1 mmol) in the same solvent. The solution was stirred at room temperature for 2 h. All the volatiles were removed under reduced pressure and the residue was washed with pentane to give a yellow solid; yield 670 mg, 83%. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ = 7.73 (d, ³J_{HH} = 7.4 Hz, 2 H, CH₂Ph), 7.63 (d, ⁴J_{HH} = 2.4 Hz, 1 H, CH-Ar), 7.58 (d, ⁴J_{HH} = 2.4 Hz, 1 H, CH-Ar), 7.39 (t, ³J_{HH} = 7.7 Hz, 2 H, CH₂Ph), 7.04 (t, ³J_{HH} = 7.3 Hz, 1 H, CH₂Ph), 6.96 (d, ⁴J_{HH} = 2.3 Hz, 1 H, CH-Ar), 6.90 (m, 3 H CH-Ar, CH₂Ph), 6.72 (t, ³J_{HH} = 7.6 Hz, 2 H, CH₂Ph), 6.56 (t, ³J_{HH} = 7.2 Hz, 1 H, CH₂Ph), 3.36 (d, ²J_{HH} = 14.3 Hz, 1 H, ArCH₂N), 3.06 (d, ²J_{HH} = 14.3 Hz, 1 H, ArCH₂N), 2.90 (d, ²J_{HH} = 14.3 Hz, 1 H, ArCH₂N), 2.79 [m, 3 H, CH₂Ph, ArCH₂N, NCH(CH₃)CH₂N], 2.67 (m, 2 H, CH₂Ph), 2.55 (d, ²J_{HH} = 9.8 Hz, 1 H, CH₂Ph), 2.20 [t, ²J_{HH} = 13.0 Hz, 1 H, NCH(CH₃)CH₂N], 1.89 [s, 9 H, C(CH₃)₃], 1.88 [s, 9 H, C(CH₃)₃], 1.71 (s, 3 H, NCH₃), 1.39 (s, 3 H, NCH₃), 1.35 [s, 9 H, C(CH₃)₃], 1.34 [s, 9 H, C(CH₃)₃], 0.68 [dd, ³J_{HH} = 3.0, ²J_{HH} = 13.0 Hz, 1 H, NCH(CH₃)CH₂N], 0.62 [d, ³J_{HH} = 6.7 Hz, 3 H, NCH(CH₃)CH₂N] ppm. ¹³C-{¹H} NMR (126 MHz, C₆D₆, 25 °C): δ = 159.0 and 158.0 (C_{ipso}-Ar), 150.2 and 148.0 (C_{ipso}-Ph), 141.8, 141.4, 137.1 and 136.4 (C_{ipso}-Ar), 128.8, 128.1, 127.8 and 127.6 (CH₂Ph), 127.0 and 126.1 (C_{ipso}-Ar), 125.2, 125.1, 124.9 and 124.7 (CH-Ar), 122.6 and 120.6 (CH₂Ph), 68.6 (CH₂Ph), 66.6 [CH₂Ph, NCH(CH₃)CH₂N], 61.0 and 57.2 (ArCH₂N), 51.6 [NCH(CH₃)CH₂N], 49.7 and 46.7 [N(CH₃)₂], 36.1, 36.0, 34.8 and 34.7 [C(CH₃)₃], 32.3, 31.3 and 31.0 [C(CH₃)₃], 8.2 [NCH(CH₃)CH₂N] ppm. ¹³C NMR (101 MHz, C₆D₆, 25 °C): δ = 68.6 (t, ¹J_{CH} = 123 Hz, ZrCH₂Ph), 66.6 (t, ¹J_{CH} = 121 Hz, ZrCH₂Ph) ppm. C₄₉H₇₀N₂O₂Zr (809.77): calcd. C 72.63, H 8.71, N 3.46; found C 71.70, H 8.72, N 3.44; the low carbon content obtained results from the extreme instability of the complex; although the NMR spectra reveal the high purity of the compound (see Supporting Information), attempts to obtain good elemental analysis failed.

[ZrL²(CH₂Ph)₂] (9). Method A: A solution of H₂L² (220 mg, 0.48 mmol) in toluene was slowly added to a solution of Zr(CH₂Ph)₄ (273 mg, 0.48 mmol) in the same solvent. After stirring for 2 h at room temperature the volatiles were removed under reduced pressure and the residue was washed with pentane to give a yellow solid; yield 404 mg, 70%.

Method B: A 1 M solution of PhCH₂MgCl in Et₂O (0.56 mL, 0.51 mmol) was slowly added to a solution of **7** in Et₂O (185 mg,

0.26 mmol) and the mixture was stirred for 2 h. The yellow solution was filtered and the solvent removed under reduced pressure to give a yellow solid; yield 213 mg, 59%. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ = 7.59 (m, 4 H, CH-Ar, CH₂Ph), 7.37 (t, ³J_{HH} = 7.7 Hz, 2 H, CH₂Ph), 7.02 (t, ³J_{HH} = 7.1 Hz, 1 H, CH₂Ph), 6.94 (m, 3 H, CH-Ar, CH₂Ph), 6.86 (s, 1 H, CH-Ar), 6.76 (t, ³J_{HH} = 7.6 Hz, 2 H, CH₂Ph), 6.59 (t, ³J_{HH} = 6.9 Hz, 1 H, CH₂Ph), 3.64 (d, ²J_{HH} = 13.4 Hz, 1 H, ArCH₂N), 2.93 (m, 2 H, ArCH₂N, CH₂Ph), 2.86 (m, 2 H, CH₂Ph, CH₂), 2.79 (m, 2 H, CH₂Ph), 2.73 (m, 2 H, ArCH₂N, CH), 2.58 (m, 2 H, ArCH₂N, CH₂), 2.37 (m, 2 H, CH₂), 2.24 (m, 1 H, CH₂), 1.91 [s, 9 H, C(CH₃)₃], 1.79 [s, 9 H, C(CH₃)₃], 1.35 [s, 9 H, C(CH₃)₃], 1.34 [s, 9 H, C(CH₃)₃], 1.29 (m, 1 H, CH₂), 0.88 (m, 2 H, CH₂), 0.68 (m, 1 H, CH₂), 0.36 (t, ²J_{HH} = 10.9 Hz, 1 H, CH₂), 0.29 (t, ³J_{HH} = 7.3 Hz, 3 H, CH₂CH₃) ppm. ¹³C-{¹H} NMR (126 MHz, C₆D₆, 25 °C): δ = 158.6 and 157.4 (*C*_{ipso}-Ar), 148.9 and 148.6 (*C*_{ipso}-Ph), 141.9, 141.5, 137.1 and 136.6 (*C*_{ipso}-Ar), 129.2, 128.7, 128.2 and 127.9 (CH₂Ph), 126.6 and 126.1 (*C*_{ipso}-Ar), 125.2, 124.7 and 124.3 (CH-Ar), 122.2 and 120.7 (CH₂Ph), 69.1 and 68.3 (CH₂Ph), 65.7 and 64.6 (ArCH₂N), 64.2 (CH), 60.0, 52.2 and 51.9 (CH₂), 36.1, 36.0, 34.8 and 34.7 [C(CH₃)₃], 32.3, 32.2, 31.3, 31.1 [C(CH₃)₃], 28.7 and 23.6 (CH₂), 11.7 (CH₂CH₃) ppm. ¹³C NMR (101 MHz, C₆D₆, 25 °C): δ = 69.1 (t, ¹J_{CH} = 124 Hz, ZrCH₂Ph), 68.3 (t, ¹J_{CH} = 112 Hz, ZrCH₂Ph) ppm. EA calculated for C₅₁H₇₂N₂O₂Zr (835.78): C 73.24, H 8.68, N 3.35; found C 71.34, H 8.65, N 3.34; the low carbon content obtained results from the extreme instability of the complex; although the NMR spectra reveal the high purity of the compound (see Supporting Information), attempts to obtain good elemental analysis failed.

[TiL¹(CH₂Ph)][PhCH₂B(C₆F₅)₃] (10): In a NMR tube, **5** (7.00 mg, 9.13 μmol) was treated with one equivalent of B(C₆F₅)₃ (4.67 mg, 9.13 μmol) in C₆D₅Br (0.6 mL). After 10 min, the NMR spectrum of the dark orange solution revealed the quantitative formation of **10**. ¹H NMR (500 MHz, C₆D₅Br, 25 °C): δ = 7.44 (s, 1 H, CH-Ar), 7.39 (s, 1 H, CH-Ar), 7.27 (m, 4 H, CH₂Ph), 7.23 (s, 1 H, CH-Ar), 7.10 (m, 2 H, CH₂Ph), 7.06 (m, 1 H, CH₂Ph), 6.92 (m, 2 H, CH₂Ph), 6.83 (s, 1 H, CH-Ar), 6.78 (t, ³J_{HH} = 6.5 Hz, 1 H, CH₂Ph), 3.77 (d, ²J_{HH} = 14.1 Hz, 1 H, ArCH₂N), 3.70 (m, 2 H, ArCH₂N), 3.36 (d, ²J_{HH} = 13.9 Hz, 1 H, ArCH₂N), 3.29 (s, 2 H, BCH₂Ph), 3.25 (s, 2 H, TiCH₂Ph), 2.90 [m, 2 H, NCH(CH₃)CH₂N], NCH(CH₃)CH₂N], 2.22 [s, 3 H, N(CH₃)₂], 2.19 [s, 3 H, N(CH₃)₂], 2.09 [m, 1 H, NCH(CH₃)CH₂N], 1.46, 1.37, 1.32 and 1.20 [s, 9 H, C(CH₃)₃], 0.74 [d, ³J_{HH} = 4.4 Hz, 3 H, NCH(CH₃)CH₂N] ppm. ¹³C-{¹H} NMR (126 MHz, C₆D₅Br, 25 °C): δ = 161.7 and 159.7 (*C*_{ipso}-Ar), 149.4 [br., B(C₆F₅)₃], 148.6 (*C*_{ipso}-PhCH₂B), 147.6 [br., B(C₆F₅)₃], 147.4 (*C*_{ipso}-PhCH₂Ti), 147.4 and 145.2 (*C*_{ipso}-Ar), 138.5, 137.4, 136.5 and 135.5 [br., B(C₆F₅)₃], 135.1 and 134.8 (*C*_{ipso}-Ar), 131.2, 129.6, 128.8, 128.4, 128.2, 127.8, 127.0, 126.4 and 125.8 (CH₂Ph), 125.1, 124.9 and 124.8 (CH-Ar), 123.8 and 123.6 (*C*_{ipso}-Ar), 122.7 (CH₂Ph), 104.0 (ArCH₂N), 68.6 [NCH(CH₃)CH₂N], 55.6 (TiCH₂Ph), 52.4 [NCH(CH₃)CH₂N], 50.2 [N(CH₃)₂], 49.8 (ArCH₂N), 47.9 [N(CH₃)₂], 34.9, 34.7, 34.5 and 34.3 [C(CH₃)₃], 31.4 (BCH₂Ph), 31.2, 31.1, 29.9 and 29.8 [C(CH₃)₃], 7.0 [NCH(CH₃)CH₂N] ppm. ¹⁹F NMR (376 MHz, C₆D₅Br, 25 °C): δ = -130.59 (br., 6 F, *o*-C₆F₅), -163.66 (br., 3 F, *p*-C₆F₅), -166.46 (br., 6 F, *m*-C₆F₅) ppm. [Δδ(*m,p-F*)] = 2.80.

[ZrL¹(CH₂Ph)][PhCH₂B(C₆F₅)₃] (11): In a NMR tube, **8** (8.00 mg, 9.87 μmol) was treated with one equivalent of B(C₆F₅)₃ (5.00 mg, 9.87 μmol) in C₆D₅Br (0.6 mL). After 10 min, the NMR spectrum of the light yellow solution revealed the quantitative formation of **11**. ¹H NMR (500 MHz, C₆D₅Br, 25 °C): δ = 7.50 (m, 4 H, CH-Ar, CH₂Ph), 7.19 (t, 2 H, ³J_{HH} = 7.5 Hz, CH₂Ph), 7.11 (m, 3 H, CH₂Ph), 7.07 (d, 1 H, ⁴J_{HH} = 1.9 Hz, CH-Ar), 6.99 (d, 1 H, ⁴J_{HH} = 2.1 Hz, CH-Ar), 6.92 (t, 2 H, ³J_{HH} = 7.6 Hz, CH₂Ph), 6.77 (t, 1

H, ³J_{HH} = 7.3 Hz, CH₂Ph), 3.61 (d, 1 H, ²J_{HH} = 14.3 Hz, ArCH₂N), 3.51 (d, 1 H, ²J_{HH} = 14.4 Hz, ArCH₂N), 3.39 (d, 1 H, ²J_{HH} = 14.5 Hz, ArCH₂N), 3.31 (s, 2 H, BCH₂Ph), 3.28 (d, 1 H, ²J_{HH} = 14.5 Hz, ArCH₂N), 2.98 [m, 1 H, NCH(CH₃)CH₂N], 2.94 (s, 2 H, ZrCH₂Ph), 2.47 [m, 1 H, NCH(CH₃)CH₂N], 2.04 [s, 3 H, N(CH₃)₂], 1.77 [s, 3 H, N(CH₃)₂], 1.52 [s, 18 H, C(CH₃)₃], 1.33 [m, 1 H, NCH(CH₃)CH₂], 1.32 [s, 9 H, C(CH₃)₃], 1.30 [s, 9 H, C(CH₃)₃], 0.92 [d, 3 H, ³J_{HH} = 6.6 Hz, NCH(CH₃)CH₂N] ppm. ¹³C-{¹H} NMR (126 MHz, C₆D₅Br, 25 °C): δ 155.5 and 154.8 (*C*_{ipso}-Ar), 149.5 [br., B(C₆F₅)₃], 148.8 (*C*_{ipso}-PhCH₂B), 147.6 [br., B(C₆F₅)₃], 144.8 and 144.7 (*C*_{ipso}-Ar), 138.5, 137.5 and 136.5 [br., B(C₆F₅)₃], 135.8 (*C*_{ipso}-Ar), 135.5 [br., B(C₆F₅)₃], 135.2 (*C*_{ipso}-Ar), 134.3 and 131.8 (CH₂Ph), 131.6 (*C*_{ipso}-PhCH₂Zr), 131.2, 129.6, 128.9, 127.0 and 126.4 (CH₂Ph), 125.6 and 125.5 (CH-Ar), 125.2 (*C*_{ipso}-Ar), 125.2 and 125.0 (CH-Ar), 124.3 (*C*_{ipso}-Ar), 122.6, 122.5 and 121.9 (CH₂Ph), 72.6 (ZrCH₂Ph), 67.5 [NCH(CH₃)CH₂N], 60.9 (ArCH₂N), 57.0 (ArCH₂N), 52.3 [NCH(CH₃)CH₂N], 52.0 and 47.4 [N(CH₃)₂], 35.0, 34.9 and 34.2 [C(CH₃)₃], 31.45 (BCH₂Ph), 31.33, 31.29 and 30.0 [C(CH₃)₃], 7.4 [NCH(CH₃)CH₂N] ppm. ¹³C NMR (126 MHz, C₆D₅Br, 25 °C): δ 72.6 (t, ¹J_{CH} = 139 Hz, ZrCH₂Ph) ppm. ¹⁹F NMR (376 MHz, C₆D₅Br, 25 °C): δ -130.16 (d, 6 F, ³J_{FF} = 22.6 Hz, *o*-C₆F₅), -163.59 (t, 3 F, ³J_{FF} = 22.6 Hz, *p*-C₆F₅), -166.30 (t, 6 F, ³J_{FF} = 22.6 Hz, *m*-C₆F₅) ppm. [Δδ(*m,p-F*)] = 2.71.

[ZrL²(CH₂Ph)][PhCH₂B(C₆F₅)₃] (12): In a NMR tube, **9** (7.00 mg, 8.37 μmol) was treated with one equivalent of B(C₆F₅)₃ (4.28 mg, 8.37 μmol) in C₆D₅Br (0.6 mL). After 10 min, the NMR spectrum of the light yellow solution revealed the quantitative formation of **12**. ¹H NMR (500 MHz, C₆D₅Br, 25 °C): δ = 7.43 (m, 5 H, CH-Ar, CH₂Ph), 7.37 (s, 1 H, CH-Ar), 7.25 (s, 1 H, CH-Ar), 7.13 (d, ³J_{HH} = 7.2 Hz, 3 H, CH₂Ph), 6.96 (m, 2 H, CH₂Ph), 6.85 (s, 1 H, CH-Ar), 6.81 (t, ³J_{HH} = 7.1 Hz, 1 H, CH₂Ph), 4.42 (d, ²J_{HH} = 13.4 Hz, 1 H, ArCH₂N), 3.62 (m, 1 H, CH), 3.52 (d, ²J_{HH} = 14.8 Hz, 1 H, ArCH₂N), 3.33 (s, 2 H, BCH₂Ph), 3.17 (d, ²J_{HH} = 14.9 Hz, 1 H, ArCH₂N), 3.10 (d, ²J_{HH} = 13.5 Hz, 1 H, ArCH₂N), 2.97 (m, 1 H, CH₂), 2.73 (t, ³J_{HH} = 9.1 Hz, 1 H, CH₂), 2.55 (s, 2 H, ZrCH₂Ph), 2.49 (t, ²J_{HH} = 13.5 Hz, 1 H, CH₂), 2.40 (m, 2 H, CH₂CH₃), 2.02 (d, ²J_{HH} = 13.4 Hz, 1 H, CH₂), 1.69 (m, 1 H, CH₂), 1.47 (m, 1 H, CH₂), 1.34 [s, 9 H, C(CH₃)₃], 1.27 [s, 9 H, C(CH₃)₃], 1.23 [s, 9 H, C(CH₃)₃], 1.20 [s, 9 H, C(CH₃)₃], 1.20 (1 H, CH₂), 0.97 (t, ³J_{HH} = 6.8 Hz, 1 H, CH₂CH₃), 0.90 (m, 1 H, CH₂) ppm. ¹³C-{¹H} NMR (126 MHz, C₆D₅Br, 25 °C): δ = 157.7 and 155.3 (*C*_{ipso}-Ar), 149.4 [br., B(C₆F₅)₃], 148.6 (*C*_{ipso}-PhCH₂B), 147.5 [br., B(C₆F₅)₃], 145.5 and 145.4 (*C*_{ipso}-Ar), 138.5 and 137.5 [br., B(C₆F₅)₃], 136.8 (*C*_{ipso}-Ar), and 136.5 [br., B(C₆F₅)₃], 136.1 (*C*_{ipso}-Ar), 135.8 (*C*_{ipso}-PhCH₂Zr), 135.5 [br., B(C₆F₅)₃], 132.9, 131.2, 129.6, 128.8, 128.4, 127.1 and 126.4 (CH₂Ph), 125.4 and 125.2 (CH-Ar), 122.8 and 122.4 (CH₂Ph), 122.0 (*C*_{ipso}-Ar), 121.9 (CH-Ar), 121.6 (*C*_{ipso}-Ar), 68.8 (ZrCH₂Ph), 64.4 (CH), 59.2 and 58.3 (ArCH₂N), 56.6 and 55.5 (CH₂), 52.9 (CH₂CH₃), 34.8, 34.5, 34.3 and 34.1 [C(CH₃)₃], 31.4 (BCH₂Ph), 31.3, 31.2, 30.2 and 29.7 [C(CH₃)₃], 24.3 and 21.5 (CH₂), 14.6 (CH₂CH₃) ppm. ¹⁹F NMR (376 MHz, C₆D₅Br, 25 °C): δ = -130.68 (d, ³J_{FF} = 22.6 Hz, 6 F, *o*-C₆F₅), -163.60 (t, ³J_{FF} = 18.8 Hz, 3 F, *p*-C₆F₅), -166.44 (t, ³J_{FF} = 22.6 Hz, 6 F, *m*-C₆F₅) ppm. [Δδ(*m,p-F*)] = 2.84.

[ZrL¹(CH₂Ph)][B(C₆F₅)₄] (13): In a NMR tube, **8** (7.00 mg, 8.64 μmol) was treated with one equivalent of [PhNMe₂H][B(C₆F₅)₄] (6.92 mg, 8.64 μmol) in C₆D₅Br (0.6 mL). After 10 min, the NMR spectrum of the light yellow solution revealed the quantitative formation of **13**, toluene and free PhNMe₂. ¹H NMR (500 MHz, C₆D₅Br, 25 °C): δ = 7.54 (m, 4 H, CH-Ar, CH₂Ph), 7.18 [m, 6 H, NPh(CH₃)₂, CH₃Ph, CH₂Ph], 7.07 (m, 5 H, CH-Ar, CH₂Ph, CH₃Ph), 6.98 (s, 1 H, CH-Ar), 6.80 [t, 1 H, ³J_{HH} = 7.1 Hz, NPh(CH₃)₂], 6.60 [m, 2 H, NPh(CH₃)₂], 3.55 (d, 1 H, ²J_{HH} =

14.3 Hz, ArCH₂N), 3.46 (d, 1 H, ²J_{HH} = 14.4 Hz, ArCH₂N), 3.33 (d, 1 H, ²J_{HH} = 14.2 Hz, ArCH₂N), 3.21 (d, 1 H, ²J_{HH} = 14.3 Hz, ArCH₂N), 2.94 [m, 3 H, NCH(CH₃)CH₂N, ZrCH₂Ph], 2.56 [s, 6 H, NPh(CH₃)₂], 2.45 [t, 1 H, ²J_{HH} = 13.3 Hz, NCH(CH₃)CH₂N], 2.18 (s, 3 H, CH₃Ph), 2.00 [s, 3 H, N(CH₃)₂], 1.72 [s, 3 H, N(CH₃)₂], 1.54 [s, 9 H, C(CH₃)₃], 1.53 [s, 9 H, C(CH₃)₃], 1.34 [s, 9 H, C(CH₃)₃], 1.33 [s, 9 H, C(CH₃)₃], 1.26 [m, 1 H, NCH(CH₃)-CH₂N], 0.88 [d, 3 H, ³J_{HH} = 6.4 Hz, NCH(CH₃)CH₂N] ppm. ¹³C-{¹H} NMR (126 MHz, C₆D₅Br, 25 °C): δ = 155.6 and 154.9 (*C*_{ipso}-Ar), 149.5 and 147.5 [br., B(C₆F₅)₃], 144.9 and 144.8 (*C*_{ipso}-Ar), 139.3 [br., B(C₆F₅)₃], 137.4 [br., B(C₆F₅)₃], 135.9 (*C*_{ipso}-Ar), 135.5 [br., B(C₆F₅)₃], 135.2 (*C*_{ipso}-Ar), 134.2 and 131.8 (*Ph*), 131.5 (*C*_{ipso}-PhCH₂Zr), 131.2, 129.6, 129.2, 128.9, 128.1 and 127.9 (*Ph*), 126.4, 125.5 and 125.3 (CH-Ar), 125.2 (*C*_{ipso}-Ar), 124.9 (CH-Ar), 124.2 (*C*_{ipso}-Ar), 122.4, 121.9, 118.5 and 113.3 (*Ph*), 72.5 (ZrCH₂Ph), 67.4 [NCH(CH₃)CH₂N], 60.8 and 56.8 (ArCH₂N), 52.2 [NCH(CH₃)-CH₂N], 51.9 and 47.3 [N(CH₃)₂], 41.0 [NPh(CH₃)₂], 35.0, 34.9 and 34.2 [C(CH₃)₃], 31.23, 31.18 and 30.0 [C(CH₃)₃], 21.2 (CH₃Ph), 7.1 [NCH(CH₃)CH₂N] ppm. ¹⁹F NMR (470 MHz, C₆D₅Br, 25 °C): δ = -132.14 (br., 8 F, *o*-C₆F₅), -162.54 (t, 4 F, ³J_{FF} = 23.5 Hz, *p*-C₆F₅), -166.38 (t, 8 F, ³J_{FF} = 18.8 Hz, *m*-C₆F₅) ppm.

General Procedure for Small-Scale Ethylene and Propylene Polymerization: In the glovebox, precatalyst stock solutions were prepared (0.01 M) in toluene (2 mL, **6** and **7**) or bromobenzene (2 mL, **5**, **8** and **9**) and stored at -37 °C. B(C₆F₅)₃, [PhNMe₂H][B(C₆F₅)₄] (0.01 M in bromobenzene) and TIBAO (0.1 M in toluene) stock solutions were also prepared and stored. In the polymerization runs with **6** and **7**, a 100 mL Büchi glass autoclave containing one Teflon®-coated stirrer bar was charged with dry toluene (9 mL), precatalyst solution (0.5 mL) and MMAO (0.533 mL, 7 % Al in heptanes) and then pressurized with 5 bar of the monomer. In the polymerization runs with **5**, **8** and **9**, a 100 mL Büchi glass autoclave with a Teflon® coated stirrer bar was charged with dry toluene (9 mL), precatalyst solution (0.5 mL) and B(C₆F₅)₃ or [PhNMe₂H][B(C₆F₅)₄] solution (0.5 mL) and then pressurized with the monomer to a pressure of 5 bar. When TIBAO was added as a scavenger the autoclaves were charged with toluene (8 mL), precatalyst solution (0.5 mL), TIBAO solution (1 mL) and B(C₆F₅)₃ or

[PhNMe₂H][B(C₆F₅)₄] solution (0.5 mL) and then pressurized with the monomer to a pressure of 5 bar. The mixture in the reactor was stirred for 30 min with continuous supply of monomer. The polymerization was ended by venting the reactor and subsequent addition of acidified methanol (5% HCl).

Polyethylene: The polymeric material was collected and washed several times with ethanol and dried in a vacuum oven at 80 °C overnight. The polymer was analyzed by HT-GPC.

Polypropylene: The polymeric material was poured into ca. 100 mL of stirring ethanol and the solvents were removed under reduced pressure. The polymer was analyzed by HT-GPC and ¹³C-{¹H} NMR spectroscopy. Typical NMR analysis of the samples showed that the polypropylene obtained is atactic.

General Procedure for 1-Hexene Polymerization: A solution of precatalyst (0.5 mL, 0.01 M in bromobenzene) was dissolved in 1-hexene (9 mL) at room temperature under nitrogen and then a solution of B(C₆F₅)₃ (0.5 mL, 0.01 M in bromobenzene) was added. The reaction mixture was stirred for 30 min. The solvent and remaining monomer were removed under reduced pressure to yield poly(1-hexene) as a colourless sticky oil. The polymer was analyzed by HT-GPC and ¹³C-{¹H} NMR spectroscopy. ¹³C-{¹H} NMR (500 MHz, CD₂Cl₂CD₂Cl₂, ppm): δ = 40.4 (br., CH₂), 34.3 (br., CH₂), 32.4 (CH), 28.7 (CH₂), 28.4 (CH₂), 23.5 (CH₂), 14.5 (CH₃) ppm.

General Procedures for X-ray Crystallography: Colourless crystals of **H₂L¹** and **H₂L²** were obtained from methanol solutions at room temperature. Crystals of **3** (orange), **6** (colourless) and **8** (yellow) were grown from toluene solutions -37 °C. Crystallographic data were collected at *Instituto Superior Técnico* and at the *University of Groningen*. Crystals of air/moisture sensitive compounds were selected inside the glovebox, covered with polyfluoroether oil and mounted on a nylon loop. The data were collected using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) with Bruker AXS-KAPPA APEX II and Bruker SMART APEX CCD diffractometers equipped with an Oxford Cryosystem open-flow nitrogen cryostat. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed

Table 4. Selected crystallographic experimental data and structure refinement parameters for **H₂L¹**, **H₂L²**, **3**, **6** and **8**.

	H₂L¹	H₂L²	3	6	8
Empirical formula	C ₃₅ H ₅₈ N ₂ O ₂	C ₃₇ H ₆₀ N ₂ O ₂	C ₄₀ H ₆₅ ClN ₂ O ₃ Ti·(C ₇ H ₈)	C ₃₅ H ₅₆ Cl ₂ N ₂ O ₂ Zr	C ₄₉ H ₁₀ N ₂ O ₂ Zr·(C ₇ H ₈)
Formula weight	538.83	564.87	797.43	697.93	902.47
Temperature [K]	150(2)	150(2)	100(1)	150(2)	100(1)
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic
Space group	<i>Pbca</i>	<i>P2₁</i>	<i>P1</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> [Å]	29.284(4)	15.2340(15)	9.669(3)	15.7740(11)	10.5347(15)
<i>b</i> [Å]	14.6150(17)	29.903(3)	11.044(4)	16.1970(11)	24.979(4)
<i>c</i> [Å]	31.861(4)	15.4060(18)	11.694(4)	18.4740(13)	18.993(3)
<i>α</i> [°]	90	90	99.800(5)	90	90
<i>β</i> [°]	90	95.267(6)	109.598(4)	99.864(3)	90.602(2)
<i>γ</i> [°]	90	90	93.657(4)	90	90
<i>V</i> [Å ³]	13636(3)	6988.5(13)	1149.4(7)	4650.2(6)	4997.7(13)
<i>Z</i> , ρ _{calc} [g cm ⁻³]	16, 1.050	8, 1.074	1, 1.152	4, 0.997	4, 1.199
μ [mm ⁻¹]	0.064	0.065	0.284	0.376	0.261
Crystal size	0.40 × 0.30 × 0.20	0.30 × 0.25 × 0.25	0.38 × 0.32 × 0.23	0.40 × 0.20 × 0.05	0.53 × 0.44 × 0.35
Crystal colour	colourless	colourless	orange	colourless	yellow
Crystal shape	block	block	block	plate	block
Reflections collected	131094	97609	7448	68995	40092
Unique refl. [<i>R</i> (int)]	12088 [0.1741]	23828 [0.0783]	5928 [0.0390]	8138 [0.0743]	10518 [0.0390]
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0567	0.0577	0.1014	0.1073	0.0422
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.1142	0.1247	0.3063	0.2484	0.0996
GooF	0.941	0.999	1.802	1.317	1.048
Flack's parameter		0.6(9)	0.04(8)		

reflections. Absorption corrections were applied using SADABS.^[22] The structures were solved and refined using direct methods with programs SIR97,^[23] SIR2004^[24] or SHELXS-97.^[25] All programs are included in the package of programs WINGX-Version 1.80.01^[26] SHELXL.^[27] Unless stated otherwise, all non-hydrogen atoms were refined anisotropically and the hydrogen atoms were inserted in idealized positions and allowed to refine riding on the parent carbon atom. Molecular diagrams were drawn with ORTEP-3 for Windows^[28] or Mercury 1.4.2,^[29] included in the software package. Compound **3** crystallizes in a noncentrosymmetric space group and the refinement of the Flack^[30] parameter x resulted in a value of 0.04(8). **H₂L²** crystallizes in a noncentrosymmetric space group but the absolute configuration could not be confirmed as the Friedel pairs were not measured, furthermore as there were no heavy atoms in the molecule, no significant anomalous dispersion could be obtained using Mo radiation. The poor quality of the crystals of **3** and **6** led to low quality data. The structures are included, as they are good enough to confirm the connectivity. Crystallographic data for **H₂L¹**, **H₂L²**, **3**, **6** and **8** are presented in Table 4.

CCDC-823660 (for **H₂L¹**), -823661 (for **H₂L²**), -823662 (for **6**), -821180 (for **8**) and -821181 (for **3**) 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.

Supporting Information (see footnote on the first page of this article): Additional information for the molecular structures of **H₂L¹** and **H₂L²**; ¹H NMR spectra of **8** and **9**.

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