

# Synthesis, characterization and reactivity of amido titanium and zirconium complexes

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## Abstract

The polymerization of ethylene and propylene was studied by using a series of mono- and spirocyclic coordinatively unsaturated early transition metal amides as pre-catalysts. Amido complexes were prepared either by metathesis reaction of  $\text{Cp}_2\text{ZrCl}_2$  and the dilithium salt of the bisamido ligand  $(\text{Me}_3\text{SiN}-(\text{CH}_2)_2-\text{NSiMe}_3)^{2-}$ , by transamination reaction of  $\text{Zr}(\text{NMe}_2)_4$  with two equivalents of the diamine ligand  $(\text{Me}_3\text{SiNH}-(\text{CH}_2)_2-\text{NHSiMe}_3)$ , and by metathesis reaction of  $\text{ZrCl}_4 \cdot 2\text{THF}$  or  $\text{TiCl}_4$  with equimolar amounts of the dilithium salt  $(\text{Me}_3\text{SiN}-(\text{CH}_2)_2-\text{NSiMe}_3)^{2-}$ . The complexes obtained were characterized by standard spectroscopic techniques. 'Cationic' polymerization catalysts were generated from the early transition-metal amides with methylalumoxane. Polymerization activity is dependent on catalyst and co-catalyst concentrations.

*Keywords:* Group 4; Metallocenes; Titanium; Zirconium; Polymerization;  $\alpha$ -olefins

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## 1. Introduction

Currently, there is considerable interest in cationic  $\text{d}^0$   $\text{Cp}_2\text{M}(\text{R})^+$  ( $\text{M} = \text{Ti, Zr, Hf}$ ) complexes as alternatives to traditional Ziegler–Natta catalysts in olefin polymerization: for recent reviews of olefin polymerization catalysts, see Refs. [1,2]; for representative recent isotactic polypropylene work, see Refs. [2–5]; for representative recent syndiotactic polypropylene work, see Refs. [2,6]; for recent thermoplastic elastomers work, see Refs. [2,7]; for recent theoretical studies, see Refs. [8–11]; for recent metallocene ion pairing studies, see Refs. [1,2,4,5,12,13]; for recent polyethylene work, see Refs. [14,15]; for other recent metallocene studies, see Ref. [16]. These species are highly reactive due to (i) the electrophilicity of the  $\text{d}^0$  cationic center, (ii) the highly polarized  $\text{M}-\text{C}$  bonds, which are innately reactive, (iii) the structural bent metallocene, which restricts coordination of substrates cis to the  $\text{M}-\text{R}$  group, and (iv) the steric, electronic and chiral properties of the metal center, which may be tailored by modifying the Cp ligands. These properties lead to a rich insertion and  $\sigma$ -bond metathesis chemistry. Kaminsky et al. [17], have

pioneered a new generation of bridged cationic Group (IV) metallocenes **A** (Fig. 1), that can be used to produce high-density polyethylene and both, isotactic and syndiotactic polyolefins. Uniformity of the active sites in these metallocene-based systems leads to greater uniformity of the polymer microstructure, allowing incorporation of co-monomers with regularity, as well as producing narrow molecular weight distribution plastics. Recently, the constrained geometry catalyst of the half-sandwich metallocene, **B** (Fig. 1)—for theoretical studies see Refs. [9–11,18], produced polymers with side branches well beyond the traditional  $\text{C}_3$  to  $\text{C}_8$   $\alpha$ -olefins. This long chain branching and the narrow molecular weight of the polymers, that is characteristic for metallocene-catalyzed reactions, allows the production of polymers which possess highly desirable performance properties with acceptable processability [19].

In conventional catalytic systems, methylalumoxane (MAO) is typically used as the activator of metallocene dihalides. Alternatively, the reaction of the dialkyl metallocenes with triphenylcarbenium salts of weakly coordinating anions, as  $\text{B}(\text{C}_6\text{F}_5)_4^-$  or  $\text{B}(\text{C}_6\text{F}_5)_3$ , in non-coordinative solvents leads quantitatively to cationic complexes [1,2,4,5,12,13]. Thus, the cationic  $\text{Cp}_2\text{M}(\text{R})^+$  may be expected to establish a series of equilibria by interacting with any available nucleophile, such as the

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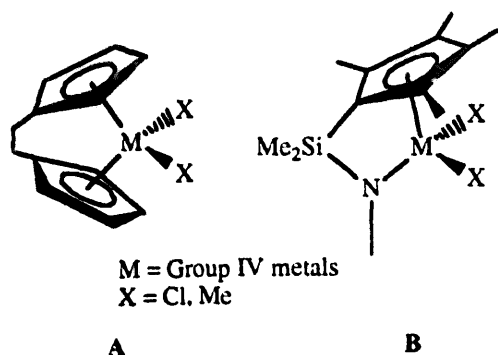


Fig. 1. Uniform site pre-catalysts for olefin polymerization.

solvent, the anion, neutral metal alkyls, or the olefin substrate prior to polymerization [20]. In the absence of a coordinating solvent the cation–anion interactions are the most important of these interactions and have a dramatic influence on the catalytic activity. Pioneering work by Arnold and co-workers, Floriani and co-workers and Jordan and co-workers has shown the analogy between  $\text{Cp}_2\text{M}$  and  $(\text{N}_4\text{-macrocycle})\text{M}$ - and  $(\text{N}_2\text{O}_2\text{-macrocycle})\text{M}$ -compounds: for  $(\text{N}_4\text{-macrocycle})\text{MR}'_2$  and  $(\text{N}_4\text{-macrocycle})\text{M}(\text{R}')^+$  ( $\text{M} = \text{Group 4}$ ) complexes, see Ref. [21]; for  $(\text{N}_2\text{O}_2\text{-chelate})\text{MR}_2$  ( $\text{M} = \text{Group 4}$  and  $\text{N}_2\text{O}_2\text{-chelate} = \text{acen, salen, salophen}$ ) complexes, see Ref. [22]. Despite the fact that cationic complexes of the macrocycles can be achieved in good yields, the reactivity of these complexes toward the polymerization of olefins is not observed.

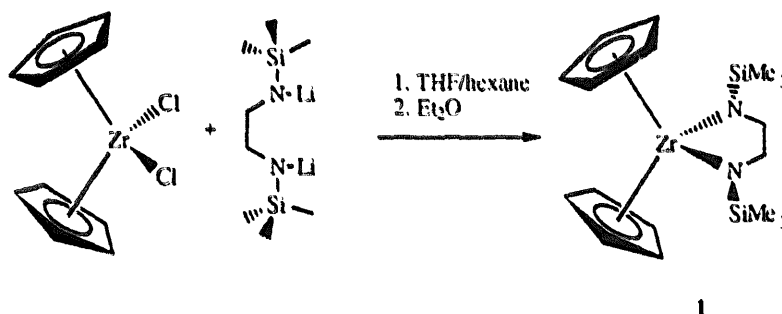
Our efforts are aimed to improved the catalytic polymerization performance of the cationic Group (IV) complexes by the incorporation of alternative  $\sigma$ -donor ligands, focusing on the steric congestion and enhancing the Lewis acidity at the cationic metal center. Thus, the possibility of changing the chlorine or the cyclopentadienyl ancillary ligands in early transition metal complexes by amido ligands ( $\text{R}_2\text{N}^-$ ) provides a way to change the electron-donating anionic equivalents and a possibility for tailoring steric hindrance. In this contribution, we report the preparation of a series of soluble mono- and spirocyclic amido zirconium complexes that constitute a new class of homogeneous polymerization catalysts. The complexes prepared allow us to compare

the effect of the amido ligand either as a counterion or as a spectator group when these amido complexes are reacted in polymerizations in the presence of MAO. These new catalytic precursors differ from the known metallocene complexes in the electron density around the metal center influencing the catalytic activity in the polymerization of  $\alpha$ -olefins.

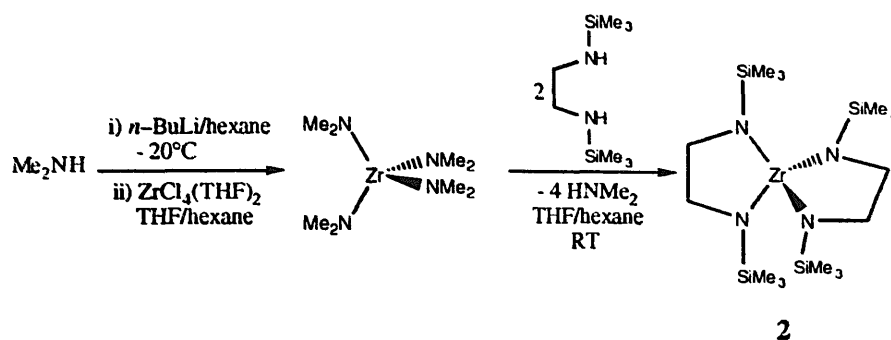
## 2. Results and discussion

Bisamido monocyclic zirconium metallocene complex **1** was obtained by the reaction of equimolar amounts of  $(\text{Me}_3\text{SiN}(\text{CH}_2)_2\text{NSiMe}_3)\text{Li}_2$ , obtained by the double deprotonation of the  $N,N'$ -bis(trimethylsilyl)ethylenediamine with  $n\text{-BuLi}$  in hexane, with zirconocenedichloride ( $\text{Cp}_2\text{ZrCl}_2$ ) in THF. This yielded a yellowish slurry and afforded, after evaporation, extraction into  $\text{Et}_2\text{O}$  and cooling to  $-50^\circ\text{C}$ , orange crystals of the corresponding bis(amido)bis( $\eta^5$ -cyclopentadienyl)zirconium chelating complex **1** in 75% yield, as shown in Scheme 1.

The  $^1\text{H}$  NMR spectrum of complex **1** in benzene- $d_6$  at  $25^\circ\text{C}$  exhibits a resonance Cp singlet at  $\delta = 6.14$  ppm compared with the Cp resonance  $\delta = 6.47$  ppm of zirconocene dichloride at the same temperature in the same solvent. A similar shift pattern is also observed for the  $^{13}\text{C}(\text{H})$  NMR resonances of the Cp groups (**1**: 112.9,  $\text{Cp}_2\text{ZrCl}_2$ : 116.0 ppm). These shifts to higher field values in **1** are a consequence of the increased electron density at the Cp ancillary ligands due to the electron donor capacity of the chelating bis(amido) ligand compared with the two chlorine atoms in zirconocene dichloride. Thus, we can expect the Zr–N bond to be less strong than the Zr–Cl bond, due to this ionic character (vide infra), and should allows us to activate the metallocene amido complex in the presence of Lewis acids. The  $^1\text{H}$  and  $^{13}\text{C}(\text{H})$  NMR resonances related to the ethylene bridge of the bisamido ligand in **1** appear as singlets at  $\delta = 3.29$  ppm and  $\delta = 54.5$  ppm respectively. Comparison with the corresponding ethylene singlet shifts  $^1\text{H}$   $\delta = 2.48$  and  $^{13}\text{C}(\text{H})$   $\delta = 45.4$  ppm off the free diamine ( $\text{Me}_3\text{SiNH}(\text{CH}_2)_2\text{CH}_2\text{NHSiMe}_3$ )



Scheme 1. Synthesis route to the monocyclic bisamido zirconocene complex **1**.



Scheme 2. Synthesis pathway to complex 2.

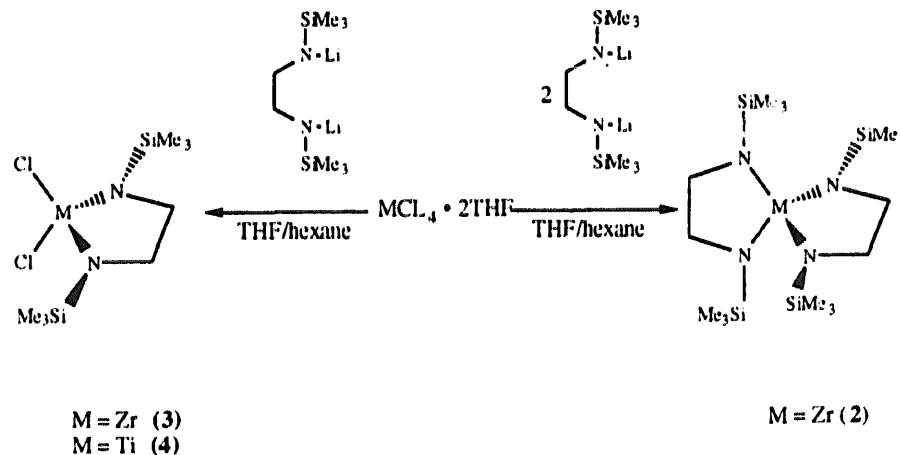
shows the expected lower field shifts in **1** caused by the attachment of the bisamido ligand to the Lewis acid zirconium atom. The  $^1\text{H}$  and  $^{13}\text{C}$ (H) NMR signals of the methyl resonances of the two  $\text{Me}_3\text{Si}$  groups in **1** appear at  $\delta = 0.07$  ppm and  $\delta = 1.0$  ppm respectively with a similar downfield trend, compared with the corresponding signals,  $\delta = -0.14$  ppm and  $\delta = -0.2$  ppm, of the free diamine; (recently, a similar cyclic tetraphenyl bisamido zirconium complex was obtained from Zr(II), see Ref. [23]). Furthermore, structural data for early transition-metal amides show that the nitrogen atom of the amido ligand generally has a planar three-coordinate environment with short M–N distances due to possible  $p_\pi \rightarrow d_\pi$  electronic interactions [24].

The spirocyclic tetraamido zirconium complex **2** was synthesized in 82% yield at room temperature via the transamination reaction of *N,N'*-bis(trimethylsilyl)ethylenediamine with  $\text{Zr}(\text{NMe}_2)_4$  in THF, the latter obtained by the metathesis reaction of  $\text{ZrCl}_4 \cdot 2\text{THF}$  with four equivalents of  $\text{LiNMe}_2$ , as shown in Scheme 2. Recrystallization of complex **2** in hexane at  $-75^\circ\text{C}$  afforded the analytically pure crystalline product; for the analogous Ti complex, see Ref. [25].

The electron density transfer from the two bisamido ligands towards the electrophilic zirconium atom in complex **2** is ascertained by the chemical shifts of the

ethylene groups which appear at  $\delta = 3.74$  ppm and  $\delta = 54.1$  ppm in the  $^1\text{H}$  and  $^{13}\text{C}$ (H) NMR spectra respectively. A similar trend for the  $\text{Me}_3\text{Si}$  groups in complex **2** ( $\delta ^1\text{H} = 0.07$ ,  $\delta ^{13}\text{C} = 0.3$  ppm) is observed. These results, compared with those obtained for complex **1**, show a similar electronic environment between the Cp and the bisamido ancillary ligands. Thus, if activation of the amido ligands in complex **2** with Lewis acids yielding the active cationic complexes is possible, the complexes obtained are expected to have a similar reactivity to complex **1** [20]. Alternatively, complex **2** is also accessible by treatment of two equivalents of the dilithiated *N,N'*-disilylated ethylenediamine with  $\text{ZrCl}_4 \cdot 2\text{THF}$  in THF and recrystallization from hexane at  $-40^\circ\text{C}$  with an overall yield of 54%, as shown in Scheme 3.

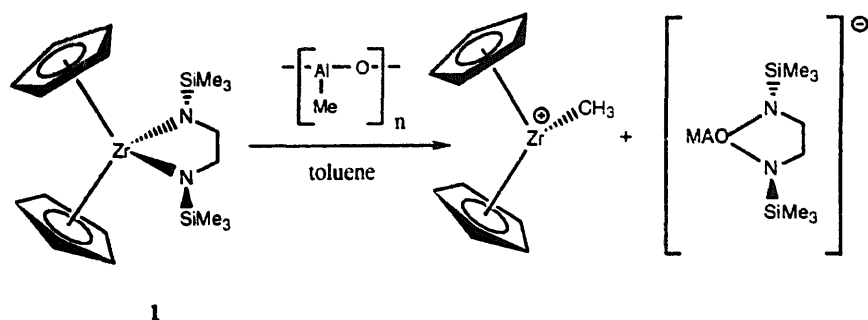
Metathesis reaction of one equivalent of the dilithiated diamine with  $\text{ZrCl}_4 \cdot 2\text{THF}$  or  $\text{TiCl}_4$  forms the monocyclic complexes **3** or **4** respectively. Fractional crystallization from cold hexane affords colorless microcrystals of **3** and orange microcrystals of **4** in 42% and 58% yield accordingly. Complex **3** shows a large electron density transfer from the bisamido ligand towards the metal atom, as indicated by the NMR spectra ( $\delta ^1\text{H} = 3.61$ ,  $\delta ^{13}\text{CH} = 69.3$ ). For the Ti analog **4**, the NMR signals are in agreement with the electrophilicity



M = Zr (**3**)  
M = Ti (**4**)

M = Zr (**2**)

Scheme 3. Synthesis route to complexes **2**, **3** and **4**.



Scheme 4. Formation of the active cationic complex of 1

of the metal, inducing a downfield shift for both methylene and TMS groups respectively ( $\delta^1\text{H} = 4.53, 0.25$ ;  $^{13}\text{C}\{\text{H}\} = 53.8, -1.6$  ppm). Although purification of metal amides by sublimation is a well-known experimental procedure [24,25], intended purification of complex **2** by sublimation at  $60^\circ\text{C}/10^{-3}$  Torr from the reaction mixture leads to colorless decomposition crystals of the bis( $\mu$ -bis(trimethylsilyl)amido)dilithium compound  $[(\text{TMS})_2\text{NLi} \cdot \text{THF}]_2$ , as confirmed by X-ray crystallography [26] (for the similar diethyl ether adduct, see Ref. [27]).

Comparison of the thermodynamic bond disruption energies in metallocene zirconium dichloride and complex **1** ( $D_{(\text{Zr}-\text{Cl})} = 491 \text{ kJ mol}^{-1}$ ,  $D_{(\text{Zr}-\text{N})} = 355 \text{ kJ mol}^{-1}$ ) and our previous observation that early-late phosphido- and arsenido-bridged heterobimetallic complexes can be activated by strong Lewis acids to produce the methyl 'cationic' complexes [28], suggests that, in a similar fashion, it would be possible to heterolytically activate complexes **1–4** by MAO and obtain active species for the polymerization of  $\alpha$ -olefins.

The activation of complex **1** with MAO (Scheme 4)

leads to the active catalyst for the polymerization of  $\alpha$ -olefins and according to the  $^{13}\text{C}\{\text{H}\}$  NMR spectra, to  $\text{Cp}_2\text{ZrMe}^+$  [1,2,4,5,12,13]. Presumably, the formation of the cationic complex is formed by the double metathesis of the amido ligands and the methyl groups of the MAO in a similar way as found for metallocene phosphido ligands [29].

Comparison of the activity of the  $\text{Cp}_2\text{ZrCl}_2$ -MAO system with the **1**-MAO system shows a slight increase in the activity by using the amido ancillary ligand instead of the chlorine ligands under the same conditions [30]. The catalytic activity of complex **1**, with ethylene (Table 1), shows the same trend as found for the analog  $\text{Cp}_2\text{ZrCH}_3^+$ -MAO. For polypropylene, the proton and carbon spectroscopic analysis of the polymers reveal only vinyl/*iso*-propyl end-groups with no vinylidene/*n*-propyl end-groups. Polymers containing these end-groups may be formed from at least three different theoretical mechanisms. The first, involves an allylic C-H activation of propylene [13], the second, involves a  $\beta$ -methyl elimination [13], and thirdly, a  $\beta$ -hydrogen elimination from a polymer chain in which

Table 1

Activity data for the polymerization of ethylene and propylene with amido complexes **1–4**

Run	Catalyst	<b>1</b> <sup>a</sup> (mmol)	<i>T</i> (°C)	Olefin <sup>b</sup>	MAO <sup>c</sup> (mmol)	Polymer (mg)	Cat/MAO ratio	Activity <sup>d</sup>
1	<b>1</b>	3.54	25	ethylene	0.186	269	1:1000	$2.28 \times 10^6$
2	<b>1</b>	3.54	25	ethylene	0.373	888	1:2000	$7.53 \times 10^6$
3	<b>1</b>	3.54	25	ethylene	0.559	769	1:3000	$6.52 \times 10^6$
4	<b>1</b>	3.54	60	ethylene	0.186	320	1:1000	$2.71 \times 10^6$
5	<b>1</b>	3.54	60	ethylene	0.373	377	1:2000	$3.20 \times 10^6$
6	<b>2</b>	3.02	25	ethylene	0.175	131	1:1000	$3.61 \times 10^5$
7	<b>2</b>	3.02	25	ethylene	0.350	45	1:2000	$1.24 \times 10^5$
8	<b>2</b>	3.02	25	ethylene	0.525	39	1:3000	$1.08 \times 10^5$
9	<b>3</b>	5.49	25	ethylene	0.318	476	1:1000	$7.23 \times 10^5$
10	<b>3</b>	5.49	25	ethylene	0.636	381	1:2000	$5.78 \times 10^5$
11	<b>3</b>	5.49	25	ethylene	0.954	374	1:3000	$5.68 \times 10^5$
12	<b>4</b>	4.67	25	ethylene	0.270	695	1:1000	$1.24 \times 10^5$
13	<b>4</b>	4.67	25	ethylene	0.541	577	1:2000	$1.03 \times 10^5$
14	<b>4</b>	4.67	25	ethylene	0.811	536	1:3000	$9.56 \times 10^5$
15	<b>1</b>	3.54	25	propene	0.186	322	1:1000	$1.09 \times 10^6$
16	<b>1</b>	3.54	25	propene	0.373	588	1:2000	$1.99 \times 10^6$
17	<b>1</b>	3.54	25	propene	0.559	361	1:3000	$1.22 \times 10^6$

<sup>a</sup> In 50 ml toluene. <sup>b</sup> Atmospheric pressure. <sup>c</sup> MAO, solvent removed from a 20 wt.% solution in toluene (Witco) at  $25^\circ\text{C}/10^{-6}$  Torr. <sup>d</sup> Grams total polymer/(mol Zr(mol<sup>-1</sup> h atm).

the last inserted monomer inserts in a '2-1' fashion. The last mechanism in our case can be rejected since no vinylidene/*n*-propyl end-groups are observed.

The activation of the spirocycle zirconium complex **2** by MAO also leads to the formation of an active catalyst for the polymerization of ethylene, presumably the ten-electron cationic monocyclic zirconium methyl complex. In addition, the activation of complex **3** by MAO affords the same intermediate complex, despite the bond disruption energies, as shown by the  $^{13}\text{C}\{\text{H}\}$  NMR spectroscopy. The cationic complexes show signals at 50.1 ppm, 69.2 ppm (broad), and a multiplet between 0–3 ppm for the  $\text{Zr}-\text{CH}_3^+$ ,  $(\text{N}-\text{CH}_2)_2$ , and  $\text{Al}-\text{CH}_3/\text{TMS}$  groups respectively. It is important to point out that similar chemical shifts appear for the  $\text{Zr}-\text{CH}_3$  signal in other metallocene cationic systems [1,2,4,5,12,13].

Table 1 shows the similarity in activity of complexes **2** and **3** (entries 6–11) for the polymerization of ethylene, with a slightly higher activity towards the chloride ancillary ligand. In addition, complexes **2** and **3** were found to be less reactive than complex **1** (entries 1–3). Furthermore, comparison of the relationship between activity and co-catalyst concentration shows that, in contrast to complex **1** and other metallocene complexes, in which higher activity is found with large catalyst:MAO ratios [14], complexes **2–4** show the opposite trend. Thus, higher MAO concentrations lowered the activity. This behavior is similar to that found in benzamidinate zirconium complexes [31] and in early-late heterobimetallic phosphine- and arsenide-bridged complexes [29]. This activity/MAO behavior is believed to be a result of the large coordinative unsaturation and electrophilicity of the metal center which drives the active 'cationic' complexes to coordinate with the solvent or MAO [2]. The analogous Ti complex **4** shows slightly higher polymerization activity and a less pronounced effect with MAO.

We have shown that, in addition to the known methyl and chloride ancillary ligands in metallocene complexes, amido ligands can also be activated by strong Lewis acids, such as MAO, to produce similarly active cationic complexes. Furthermore, highly coordinative unsaturated monocyclic and spirocyclic amido complexes can also be activated for the polymerization of ethylene, as with the metallocenes although with lower activity. Albeit the use of  $\text{B}(\text{C}_6\text{F}_5)_3$  as co-catalyst with complex **1** has shown no polymerization activity, the reactivity of complex **1** with other Lewis acid borane salts is currently being investigated.

### 3. Experimental section

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and mois-

ture in flamed Schlenk-type glassware on a dual manifold Schlenk line, or interfaced to a high vacuum ( $10^{-5}$  Torr) line, or in a nitrogen-filled 'Vacuum Atmospheres' glove box with a medium capacity recirculator ( $1-2$  ppm  $\text{O}_2$ ). Argon, ethylene, propylene and nitrogen gases were purified by passage through an  $\text{MnO}$  oxygen-removal column and a Davison 4 Å molecular sieve column. Ether solvents ( $\text{THF}-d_8$ ) were distilled under argon from sodium benzophenone ketyl. Hydrocarbon solvents (toluene- $d_8$ , benzene- $d_6$ ) were distilled under nitrogen from Na–K alloy. All solvents for vacuum-line manipulations were stored in vacuo over Na–K alloy in resealable bulbs. NMR spectra were recorded on Bruker AM 200 and Bruker AM 400 spectrometers. Chemical shifts for  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR are referenced to internal solvent resonances and are reported relative to tetramethylsilane. The NMR experiments were conducted in Teflon valve-sealed tubes (J-Young) after vacuum transfer of the liquids in a high-vacuum line. *n*-BuLi (solution in hexane),  $\text{Cp}_2\text{ZrCl}_2$  and the ethylenediamine were purchased from Aldrich and used as-received. The dilithiated amine  $\text{Me}_3\text{SiNLi}-(\text{CH}_2)_2-\text{NLiSiMe}_3$  was prepared from the freshly distilled respective diamine with *n*-BuLi in hexane [32].  $\text{LiNMe}_2$  was prepared from the corresponding condensed amine and *n*-BuLi and used without further purification.  $\text{Zr}(\text{NMe}_2)_4$  [32] was prepared by published procedures.

#### 3.1. Synthesis of $\text{Cp}_2\text{Zr}[\text{NSiMe}_3-(\text{CH}_2)_2-\text{NSiMe}_3]_1$

Into a glove-box, a 100 ml glass vessel was charged with 1.46 g (5.0 mmol) of  $\text{Cp}_2\text{ZrCl}_2$  and 1.08 g (5.0 mmol) of  $\text{Me}_3\text{SiNLi}-(\text{CH}_2)_2-\text{NLiSiMe}_3$ . 50 ml of THF were vacuum transferred into the vessel at  $-78^\circ\text{C}$  on a high vacuum line; the temperature was slowly raised to ambient temperature and the solution stirred for 48 h. The THF was then removed and 30 ml of  $\text{Et}_2\text{O}$  were added. After 24 h stirring, the precipitated LiCl was filtered off through a C4 frit and the pale orange filtrate was kept overnight at  $-50^\circ\text{C}$ . Orange crystals were isolated while cold in 75% yield (1.59 g, 3.8 mmol,  $M = 423.86$ ) and dried under high vacuum. Anal. Found: C, 51.04; H, 7.42; N, 6.12.  $\text{C}_{18}\text{H}_{32}\text{N}_2\text{Si}_2\text{Zr}$ . Calc.: C, 50.60; H, 7.55; N, 6.60%.  $^1\text{H}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  ppm): 6.14 (s, 10H, Cp), 3.29 (s, 4H,  $\text{CH}_2-\text{CH}_2$ ), 0.07 (s, 18H,  $\text{Si}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  ppm): 112.9 (Cp), 54.5 ( $\text{CH}_2-\text{CH}_2$ ), 1.0 ( $\text{Si}(\text{CH}_3)_3$ ).

#### 3.2. Synthesis of $\text{Zr}[\text{NSiMe}_3-(\text{CH}_2)_2-\text{NSiMe}_3]_2$

(a) Into a glove-box, a 100 ml glass vessel was charged with 1.89 g (5.0 mmol) of  $\text{ZrCl}_4 \cdot 2\text{THF}$  and 2.16 g (10.0 mmol) of  $\text{Me}_3\text{SiNLi}-(\text{CH}_2)_2-\text{NLiSiMe}_3$ . 50 ml of THF were vacuum transferred into the vessel at  $-78^\circ\text{C}$  on a high vacuum line; the temperature was slowly raised to ambient temperature and the solution

stirred for 24h. The solvent was then removed and 30 ml of hexane was added. After 24h stirring, the precipitated LiCl was filtered off through a C4 frit and the colorless filtrate was kept overnight at  $-50^{\circ}\text{C}$ . Colorless crystals were isolated while cold in 54% yield (1.34 g, 2.7 mmol,  $M = 496.12$ ) and dried under high vacuum. Anal. Found: C, 40.96; H, 8.89; N, 10.77.  $\text{C}_{16}\text{H}_{44}\text{N}_4\text{Si}_4\text{Zr}$ . Calc.: C, 38.74; H, 8.94; N, 11.29%.  $^1\text{H}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  ppm): 3.74 (s, 8H,  $\text{CH}_2\text{-CH}_2$ ), 0.07 (s, 36H,  $\text{Si}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  ppm): 54.1 ( $\text{CH}_2\text{-CH}_2$ ), 0.0 ( $\text{Si}(\text{CH}_3)_3$ ).

(b) Into a glove-box, 1.34 g (5.0 mmol) of  $\text{Zr}(\text{NMe}_2)_4$  were weighed in a 100 ml glass vessel. 50 ml of THF and 2.04 g (10.0 mmol) of  $\text{Me}_3\text{SiNH}(\text{CH}_2)_2\text{-NHSiMe}_3$  were transferred into the vessel at  $-78^{\circ}\text{C}$  on a high vacuum line. The temperature was slowly raised to ambient temperature and the solution stirred for 24h. After reflux for 1h the solvents were removed and 30 ml of hexane was added. Cooling to  $-50^{\circ}\text{C}$ , colorless crystals were formed which were filtered off while cold (82% yield) and dried under high vacuum.

### 3.3. Synthesis of $\text{Cl}_2\text{Zr}[\text{NSiMe}_3(\text{CH}_2)_2\text{-NSiMe}_3]_3$

In a procedure similar to that used for 2, 1.89 g (5.0 mmol) of  $\text{ZrCl}_4 \cdot 2\text{THF}$  were treated with 1.08 g (5.0 mmol) of  $\text{Me}_3\text{SiNLi}(\text{CH}_2)_2\text{-NLSiMe}_3$ , to give 0.77 g (2.1 mmol, 42%) of colorless complex 3 ( $M = 364.57$ ). Anal. Found: C, 22.56; H, 5.79; N, 7.28.  $\text{C}_8\text{H}_{22}\text{Cl}_2\text{N}_2\text{Si}_2\text{Zr}$ . Calc.: C, 21.97; H, 6.04; N, 7.68%.  $^1\text{H}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  ppm): 3.61 (s, 4H,  $\text{CH}_2\text{-CH}_2$ ), 0.09 (s, 18H,  $\text{Si}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  ppm): 69.3 ( $\text{CH}_2\text{-CH}_2$ ), 0.3 ( $\text{Si}(\text{CH}_3)_3$ ).

### 3.4. Synthesis of $\text{Cl}_2\text{Ti}[\text{NSiMe}_3(\text{CH}_2)_2\text{-NSiMe}_3]_4$

In a procedure similar to that used for 3, 2.20 ml (20.0 mmol) of  $\text{TiCl}_4$  were treated with 4.32 g (20.0 mmol) of  $\text{Me}_3\text{SiNLi}(\text{CH}_2)_2\text{-NLSiMe}_3$ , to give 3.7 g (11.6 mmol, 58%) of orange complex 4 ( $M = 321.23$ ). Anal. Found: C, 29.28; H, 6.90; N, 8.72.  $\text{C}_8\text{H}_{22}\text{Cl}_2\text{N}_2\text{Si}_2\text{Ti}$ . Calc.: C, 29.91; H, 6.90; N, 8.70%.  $^1\text{H}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  ppm): 4.53 (s, 4H,  $\text{CH}_2\text{-CH}_2$ ), 0.25 (s, 18H,  $\text{Si}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  ppm): 53.8 ( $\text{CH}_2\text{-CH}_2$ ), -1.6 ( $\text{Si}(\text{CH}_3)_3$ ).

### 3.5. Ethylene polymerization experiments

These experiments were conducted in a 100 ml flamed round-bottom reaction flask attached to a high-vacuum line. In a typical experiment, 1.5 mg of the catalyst 1 and 205 mg of MAO (Zr:Al = 1:1000) were charged into the flask containing a magnetic stir bar. The reaction vessel was connected to a high-vacuum line, pumped down and back-filled three times with argon. Then the flask was re-evacuated and a measured quan-

tity of toluene (40 ml) was vacuum transferred into the reaction flask from Na-K. After temperature equilibration, the gaseous ethylene was admitted to the vessel through a gas purification column. The gas pressure was continuously maintained at 1.0 atm with a mercury manometer. Rapid stirring of the solution was initiated and after a measured time interval (2 min) the polymerization was quenched by injecting a mixture of methanol-HCl. The polymeric product was collected by filtration, washed with hexane and acetone and dried under vacuum for several hours.

### 3.6. Propylene polymerization experiments

This was performed in a similar manner to the ethylene polymerization. The polymerization was quenched after 5 min by adding a mixture of methanol-HCl. The resulting oil was removed from the vessel, washed three times with  $\text{CH}_2\text{Cl}_2$  and then the combined organic phases were dried over  $\text{MgCl}_2$  for several hours. After filtration, the organic solvents were removed under vacuum and the remaining colorless, viscous oil was dried under vacuum for 12h.

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