

Chelating diamide complexes of titanium: new catalyst precursors for the highly active and living polymerization of α -olefins

John D. Scollard^a, David H. McConville^{a,*}, Jagadese J. Vittal^b, Nicholas C. Payne^b

^a University of British Columbia, Department of Chemistry, 2036 Main Mall, Vancouver, B.C., Canada V6T 1Z1

^b University of Western Ontario, Department of Chemistry, London, Ont., Canada N6A 5B7

Abstract

The reaction of $\text{RHN}(\text{CH}_2)_3\text{NHR}$ (**1a,b**) (**a**, $\text{R} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$; **b**, $\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) with 2 equiv of BuLi followed by 2 equiv of ClSiMe_3 yields the silylated diamines $\text{R}(\text{Me}_3\text{Si})\text{N}(\text{CH}_2)_3\text{N}(\text{SiMe}_3)\text{R}$ (**3a,b**). The reaction of **3a,b** with TiCl_4 yields the dichloride complexes $[\text{RN}(\text{CH}_2)_3\text{NR}]\text{TiCl}_2$ (**4a,b**) and two equiv of ClSiMe_3 . An X-ray study of **4a** ($P2_1/n$, $a = 9.771(1)$ Å, $b = 14.189(1)$ Å, $c = 21.081(2)$ Å, $\beta = 96.27(1)^\circ$, $V = 2905.2(5)$ Å³, $Z = 4$, $T = 25^\circ\text{C}$, $R = 0.0701$, $R_w = 0.1495$) revealed a distorted tetrahedral geometry about titanium with the aryl groups lying perpendicular to the TiN_2 -plane. Compounds **4a,b** react with 2 equiv of MeMgBr to give the dimethyl derivatives $[\text{RN}(\text{CH}_2)_3\text{NR}]\text{TiMe}_2$ (**5a,b**). An X-ray study of **5b** ($P2_12_12_1$, $a = 8.0955(10)$ Å, $b = 15.288(4)$ Å, $c = 16.909(3)$ Å, $V = 2092.8(7)$ Å³, $Z = 4$, $T = 23^\circ\text{C}$, $R = 0.0759$, $R_w = 0.1458$) again revealed a distorted tetrahedral geometry about titanium with titanium–methyl bond lengths of 2.100(9) Å and 2.077(9) Å. These titanium dimethyl complexes are active catalysts for the polymerization of 1-hexene, when activated with methylaluminoxane (MAO). Activities up to 350,000 g of poly(1-hexene)/mmol catalyst · h were obtained in neat 1-hexene. These systems actively engage in chain transfer to aluminum. Equimolar amounts of **5a** or **5b** and $\text{B}(\text{C}_6\text{F}_5)_3$ catalyze the living aspecific polymerization 1-hexene. Polydispersities (M_w/M_n) as low as 1.05 were measured. Highly active living systems are obtained when **5a** is activated with $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$. A primary insertion mode (1,2 insertion) has been assigned based on both the initiation of the polymer chain and its purposeful termination with iodine. © 1998 Elsevier Science B.V.

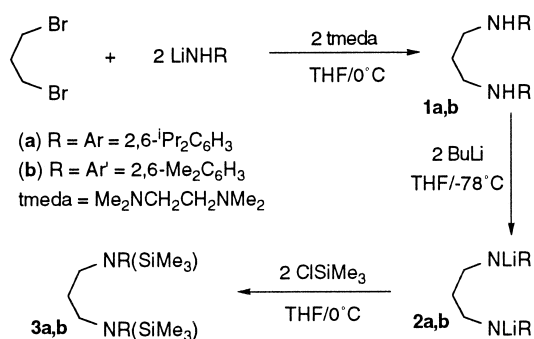
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1. Introduction

Homogeneous single site olefin polymerization catalysts have developed rapidly in the last few decades with the group 4 cyclopentadienyl compounds (e.g., Cp_2ZrX_2 where $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, X = alkyl, halide) receiving considerable attention [1–3]. The research efforts in this area

have been concerned with the way in which the catalytic activity, stereoregularity, and comonomer incorporation can be altered with changes to the ancillary ligands. For example, although the catalyst precursor Cp_2ZrCl_2 will polymerize ethylene with high activity, the homopolymerization of α -olefins is relatively slow. In contrast, linked Cp-amide derivatives such as $[(\eta^5\text{-C}_5\text{Me}_4)\text{SiMe}_2(\text{NCMe}_3)]\text{TiCl}_2$ readily incorporate α -olefins [4,5]. The success of the Cp-amide class of compounds prompted

* Corresponding author. Fax: +1-604-8222847; e-mail: mcconvil@chem.ubc.ca



Scheme 1.

us to investigate the polymerization chemistry of group 4 chelating diamide complexes [6–12]. Previously, we reported that chelating diamide complexes serve as precursors for the highly active [13] and living [14] polymerization of α -olefins. Herein we present the full details of this investigation including the pronounced anion effect operative in these systems.

2. Catalyst precursor synthesis

The reaction of two equiv of LiNHR (prepared from H₂NR and BuLi at -78°C , R = Ar = 2,6-ⁱPr₂C₆H₃, Ar' = 2,6-Me₂C₆H₃) with 1,3-dibromopropane affords after work up the diamine ligands **1a,b** (Scheme 1).

The diamine ligands are formed in a 1:1 ratio with the elimination product RHNCH₂CH=CH₂ (**A**, identified by ¹H NMR spectroscopy). The facile formation of **A** necessitates the use of tetramethylethylenediamine (tmeda) since reactions performed without tmeda contain about 80% **A**. The diamine ligand **1a** is easily separated from **A** via formation of the insoluble salt [ArH₂N(CH₂)₃NH₂Ar]²⁺{2Cl⁻} (47% yield), while **1b** can be crystallized readily from hexanes in 36% yield.

The diamines **1a,b** can be deprotonated in THF at -78°C to give the dilithio diamides

Table 1
Crystal data and experimental details for compounds **4a** and **5b**

	4a	5b
Empirical formula	C ₂₇ H ₄₀ Cl ₂ N ₂ Ti	C ₂₁ H ₃₀ N ₂ Ti
Formula weight	511.41	358.38
Temperature (°C)	25	23
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	P2 ₁ /n	P2 ₁ 2 ₁ 2
Unit cell dimensions	<i>a</i> = 9.771(1) Å <i>b</i> = 14.189(1) Å <i>c</i> = 21.081(2) Å β = 96.27(1) ^o	<i>a</i> = 8.0955(10) Å <i>b</i> = 15.288(4) Å <i>c</i> = 16.909(3) Å
Volume (Å ³)	2905.2(5)	2092.8(7)
Z	4	4
Density, calcd (g cm ⁻³)	1.169	1.137
Absorption coefficient (mm ⁻¹)	0.494	0.413
F(000) electrons	1088	768
Reflections collected	4724	2785
Independent reflections	3754 [<i>R</i> (int) = 0.0371]	2597 [<i>R</i> (int) = 0.024]
Refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3754/73/217	2597/0/133
Goodness-of-fit (GooF)	1.081	0.947
Final <i>R</i> indices [<i>I</i> > 2 sigma(<i>I</i>)]	<i>R</i> 1 = 0.0701, <i>wR</i> 2 = 0.1495	<i>R</i> 1 = 0.0759, <i>wR</i> 2 = 0.1458
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1454, <i>wR</i> 2 = 0.1800	<i>R</i> 1 = 0.1438, <i>wR</i> 2 = 0.1693

$R1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)_2 / \Sigma wF_o^4]^{1/2}$; GooF = $[\Sigma w(F_o^2 - F_c^2)_2 / (n - p)]^{1/2}$ (where *n* is the number of reflections and *p* is the number of parameters refined).

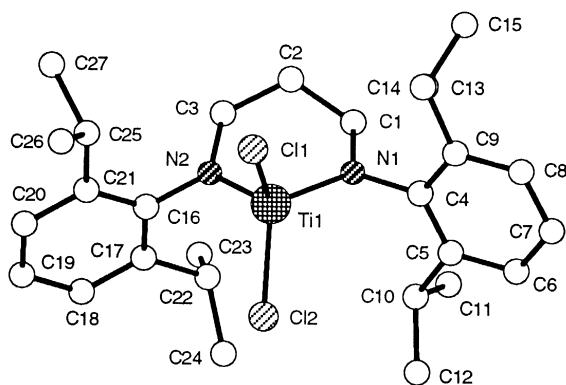
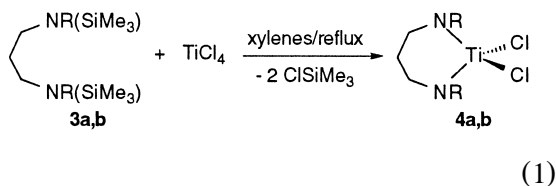


Fig. 1. Chem3D plus representation of the molecular structure of **4a**.

2a,b. Compounds **2a,b** react with 2 equiv of ClSiMe_3 at 0°C to give the silylated diamines **3a,b** in excellent yield. Compound **3a** is a crystalline solid while **3b** is an oil. The silylated diamines **3a,b** react with TiCl_4 in refluxing xylenes to afford two equiv of ClSiMe_3 and the orange dichloride complexes **4a,b** in 75–81% yield (Eq. (1)).



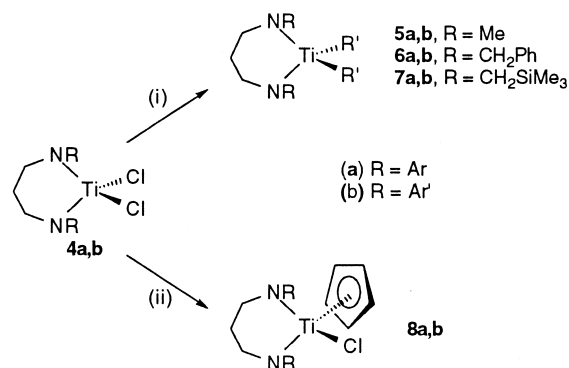
We have found that the elimination of ClSiMe_3 is a convenient, high yield route to bulky diamide complexes of groups 4 and 5 [15,16]. In contrast, the reaction of the dilithio diamides **2a,b** with $\text{TiCl}_4(\text{THF})_2$ gives very low yields (< 10%) of complexes **4a,b** and are difficult to isolate. The proton NMR spectra of complexes **4a,b** display characteristic second-order patterns for the methylene protons (NCH_2 and NCH_2CH_2) of the coordinated ligands. In addition, the isopropyl methyl groups of complex **4a** are diastereotopic which we interpret as a consequence of restricted rotation about the $\text{N}-\text{C}_{\text{ipso}}$ bond. In other words, the aryl groups lie perpendicular to the N_2Ti plane necessarily protecting the metal above and below this plane.

Table 2
Selected bond lengths (Å) and angles ($^\circ$) for **4a**

Bond distances			
Ti(1)–N(1)	1.839(5)	Ti(1)–N(2)	1.856(5)
Ti(1)–Cl(1)	2.240(2)	Ti(1)–Cl(2)	2.257(2)
N(1)–C(4)	1.439(5)	N(2)–C(16)	1.429(6)
N(1)–C(1)	1.465(8)	N(2)–C(3)	1.469(8)
Bond angles			
N(1)–Ti(1)–N(2)	99.2(2)	N(1)–Ti(1)–Cl(1)	108.8(2)
N(1)–Ti(1)–Cl(2)	116.8(2)	N(2)–Ti(1)–Cl(1)	110.1(2)
N(2)–Ti(1)–Cl(2)	113.9(2)	Cl(1)–Ti(1)–Cl(2)	107.77(9)
Ti(1)–N(1)–C(4)	123.2(4)	C(4)–N(1)–C(1)	114.8(5)
C(1)–N(1)–Ti(1)	122.0(4)	Ti(1)–N(2)–C(16)	122.5(4)
C(16)–N(2)–C(3)	114.2(5)	C(3)–N(2)–Ti(1)	123.2(4)

The solid state structure of **4a** was determined by X-ray crystallography (Table 1). The molecular structure of complex **4a** can be found in Fig. 1 and relevant bond distances and angles in Table 2. The structure is best described as a distorted tetrahedron with Ti–N distances comparable to other titanium–amido complexes [17–20]. Each amide is sp^2 -hybridized as evidenced by the sum of the angles about each nitrogen ($\text{N}(1) = 360.0^\circ$ and $\text{N}(2) = 359.9^\circ$) and the aryl rings lie perpendicular to the N_2Ti plane with dihedral angles of 89° and 86° .

With the aim of preparing titanium alkyl derivatives, the reaction of compounds **4a,b** with various alkylating reagents has been investigated (Scheme 2).



Scheme 2. Alkylation of compounds **4a,b**. Reagents and conditions. (i) 2 equiv MeMgBr , or 2 equiv PhCH_2MgCl , or 2 equiv $\text{LiCH}_2\text{SiMe}_3$, Et_2O , -20°C ; (ii) 1 equiv $\text{NaCp} \cdot \text{DME}$, THF , 25°C .

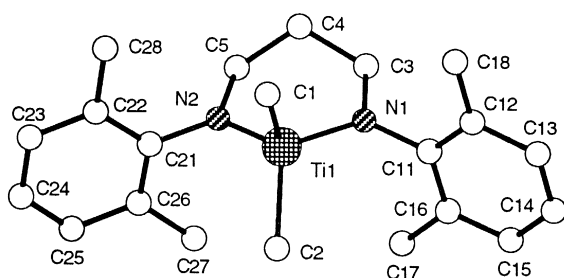


Fig. 2. Chem3D plus representation of the molecular structure of **5b**.

Compounds **4a,b** react with 2 equiv of methyl Grignard to afford the crystalline, thermally stable, yellow dimethyl derivatives **5a,b** in good yield. The proton and carbon NMR spectra of **5b** display Ti–CH₃ and Ti–CH₃ resonances at 0.70 and 51.1 ppm, respectively. Similar shifts are observed for **5a**. These resonances are comparable to other known bis(amide)TiMe₂ species [7,11,18,19,21]. The solid state structure of **5b** was determined by X-ray crystallography (Table 1). The molecular structure of complex **5b** can be found in Fig. 2 and relevant bond distances and angles in Table 3. In addition to the dimethyl complexes, it is possible to prepare bis(benzyl) (**6a,b**), bis(trimethylsilylmethyl) (**7a,b**), and monocyclopentadienyl (**8a,b**) derivatives in good yield. The proton and carbon NMR spectra of compounds **6** and **7** are consistent with local C_{2v}-symmetry while the spectra of complexes **8a,b** are consistent with C_s-symmetric species.

Table 3
Selected bond lengths (Å) and angles (°) for **5b**

Bond distances			
Ti(1)–N(1)	1.858(6)	Ti(1)–N(2)	1.867(6)
Ti(1)–C(1)	2.100(9)	Ti(1)–C(2)	2.077(9)
N(1)–C(3)	1.480(9)	N(2)–C(5)	1.470(9)
N(1)–C(11)	1.470(9)	N(2)–C(21)	1.436(9)
Bond angles			
N(1)–Ti(1)–N(2)	102.6(3)	N(1)–Ti(1)–C(1)	110.3(3)
N(1)–Ti(1)–C(2)	116.7(3)	N(2)–Ti(1)–C(1)	109.2(3)
N(2)–Ti(1)–C(2)	115.4(3)	C(1)–Ti(1)–C(2)	102.7(4)
Ti(1)–N(1)–C(3)	120.6(5)	C(11)–N(1)–C(3)	112.9(6)
C(11)–N(1)–Ti(1)	126.4(5)	Ti(1)–N(2)–C(5)	120.3(5)
C(5)–N(2)–C(21)	113.8(6)	C(21)–N(2)–Ti(1)	125.9(5)

3. Polymerization studies

3.1. Activation with methylaluminumoxane

We have previously reported the 1-hexene polymerization chemistry of compounds **5a,b** with the activator methylaluminumoxane (MAO) [13] (Table 4, entries 1 and 2). The catalyst systems **5a,b**/MAO generate high molecular weight atactic poly(1-hexene) with activities as high as 350 000 g poly(1-hexene)/mmol catalyst · h in neat 1-hexene at 68°C. By comparison, the bis(amide) complex [(Me₃Si)₂N]₂ZrCl₂ shows an activity of 62 g polymer/mmol catalyst · h for the polymerization of propylene under similar conditions [22]. The only chain termination process operative in the **5a,b**/MAO system is transfer to aluminum [23], as we have been unable to detect olefinic resonances in the poly(1-hexene) samples. In fact, the MAO cocatalyst, which is insoluble in 1-hexene, slowly ‘dissolves’ over the course of the polymerization. Replacing the methyl groups in MAO with poly(1-hexene) units would certainly lead to a more soluble aluminumoxane (note the marked difference in heptane solubility of isobutyl modified methylaluminumoxane (MMAO) versus MAO¹). In addition, the polymerization of 1-hexene in the presence of increasing amounts of MAO leads to a decrease in *M_n* (number average molecular weight) due to an increase in the concentration of the transfer reagent (Fig. 3). A corresponding increase in activity is also observed with increasing equivalents of MAO.

A pronounced decrease in activity has been observed [13,14] for these titanium diamide systems when polymerizations are performed in the presence of small amounts of toluene as opposed to neat 1-hexene. It was not clear, how-

¹ MMAO is sold as a heptane solution while MAO, which is insoluble in heptane, is sold as a toluene solution. Both aluminumoxanes are available from Akzo Nobel.

Table 4
Polymerization of 1-hexene

Entry	Catalyst system and conditions	Yield (g)	Time	M_w^a	M_n^a	M_w/M_n	Activity ^b	Source
1	5a /MAO, 68°C	2.96	30 s	81500	47000	1.73	350000	[13]
2	5b /MAO, 68°C	2.42	30 s	54000	30400	1.78	290000	[13]
3	5a /MAO, 68°C ^{c,d}	1.50	10 s	9100	5100	1.78	51000	this work
4	5a /MAO, 68°C ^{c,e}	3.68	10 s	27600	15700	1.76	125000	this work
5	5a /B(C ₆ F ₅) ₃ , 23°C	0.05	10 min	4300	4100	1.05	40	[14]
6	5b /B(C ₆ F ₅) ₃ , 23°C	0.09	30 min	12800	12100	1.06	30	[14]
7	5a /B(C ₆ F ₅) ₃ , 68°C ^f	0.32	1 min	19300	16700	1.15	1800	this work
8	5a /TB, 68°C ^{g,h}	3.05	10 s	239100	177500	1.35	104000	this work
9	5a /MAO, 68°C ^{g,i}	4.53	10 s	23900	11900	2.01	153000	this work
10	5a /TB, 68°C ^{g,h,j}	2.89	10 s	190100	130900	1.45	98000	this work
11	5a /TB, 68°C ^{g,h,k}	3.58	10 s	60200	29000	2.08	122000	this work

MAO = methylaluminoxane and TB = {Ph₃C}⁺[B(C₆F₅)₄]⁻.

^aBy GPC vs. polystyrene standards.

^bg poly(1-hexene)/mmol catalyst · h.

^c10.6 μmol of catalyst was added to 500 equiv of MAO in 5.0 ml of solvent and 5.0 ml of 1-hexene.

^dSolvent = toluene.

^eSolvent = hexane.

^f10.6 μmol of catalyst and 1 equiv of B(C₆F₅)₃ were added to 10.0 ml of 1-hexene.

^g10.6 μmol of catalyst was mixed with cocatalyst in 1.0 ml toluene and added to 9.0 ml of 1-hexene.

^hCocatalyst = 1 equiv of TB.

ⁱcocatalyst = 500 equiv of MAO.

^j100 equiv Al(^tBu)₃ added.

^k100 equiv MAO added.

ever, whether this decrease was a result of lower monomer concentrations, since rates typically decrease with decreasing monomer con-

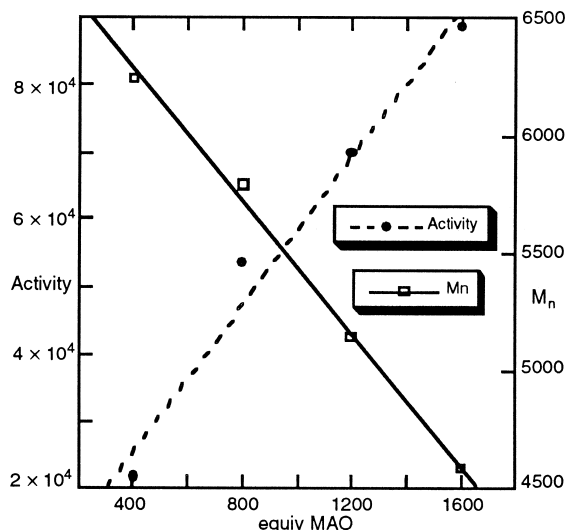
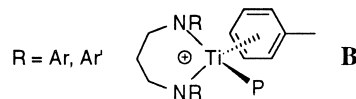


Fig. 3. Plot of activity (g poly(1-hexene)/mmol cat. · h) and M_n versus equivalents of MAO. Conditions: 6.8 μmol of **5a** in 1 ml of pentane was added to MAO (400, 800, 1200, and 1600 equiv) in 9.0 g of 1-hexene and 1.0 g of toluene at 68°C and stirred for 10 s.

centration. Hence, the polymerization of 1-hexene with **5a**/MAO in toluene:1-hexene (1:1) and hexanes:1-hexene (1:1) was attempted (Table 4 entries 3 and 4). The polymerization activity decreases by a factor of 2.5 and the molecular weight of the polymer decreases by a factor of 3 when toluene is present. However, the change in solvent has very little effect on the rate of chain transfer to aluminum (M_w/M_n , 1.78 versus 1.76). Assuming a cationic alkyl as the active species in these systems [24], we interpret these results as competitive binding of toluene to titanium (**B**) which decreases the rate of insertion of 1-hexene.



The preparation of the η^5 -cyclopentadienyl derivatives **8a,b** suggests that the metal can accommodate ligands of this size. Given the low coordination number of these diamide com-

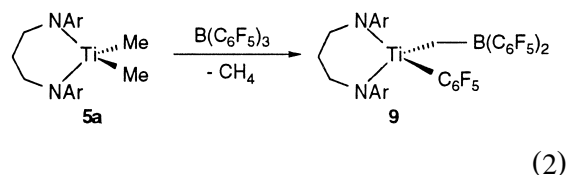
plexes and recent reports of authentic η^6 -toluene complexes of group 4 [25–27], the binding of toluene is plausible.

3.2. Activation with tris(perfluorophenyl) borane

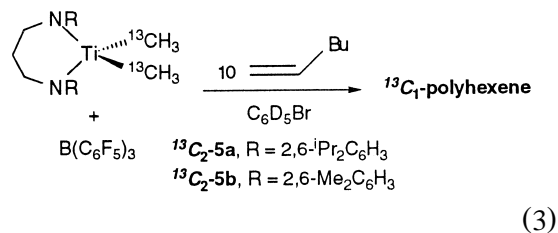
Equimolar amounts of compounds **5a** or **5b** and $B(C_6F_5)_3$ [28] catalyze the living aspecific polymerization of 1-hexene at 23°C [14] (Table 4, entries 5 and 6). Although the measured activities at 23°C are low, higher activities are attainable at higher temperatures (68°C) at the expense of a slight increase in the molecular weight distribution (M_w/M_n) of the polymer (entry 7). Under identical conditions, the borane-activated systems are considerably less active than the MAO-activated systems (compare entries 1 and 7), possibly due to increased charge separation [29–31] in the MAO-activated system relative to the borane-activated system. The inhibitory effect of toluene noted in the MAO-activated systems is equally striking in the borane-activated systems, especially at 23°C. For example, 10 μ mol of **5b** and 1 equiv of $B(C_6F_5)_3$ in a mixture of 5 ml toluene and 5 ml 1-hexene produced no polymer after 15 min at 23°C. Small amounts of narrow molecular weight polymer begin to appear after 20 min.

Attempts to spectroscopically identify the cationic complexes (e.g., $\{[RN(CH_2)_3NR]TiMe\}^+[MeB(C_6F_5)_3]^-$) have been thwarted by the extreme reactivity of these species with chlorinated solvents and their insolubility in aromatic solvents (vide infra). We have noted [32] that mixing pentane solutions of **5a** or **5b** and $B(C_6F_5)_3$ affords the yellow-orange insoluble adducts **5a** · $B(C_6F_5)_3$ and **5b** · $B(C_6F_5)_3$ in nearly quantitative yield. These solids are active for the living polymerization of α -olefins and can be stored for weeks at $-30^\circ C$ with no loss in catalytic activity. Although pentane suspensions of the borane adduct **5b** · $B(C_6F_5)_3$ appear to be indefinitely stable in the absence of monomer, the adduct **5a** · $B(C_6F_5)_3$ slowly evolves methane leading to the formation of the

catalytically *inactive* methylene-bridged derivative **9** [32] (Eq. (2)).

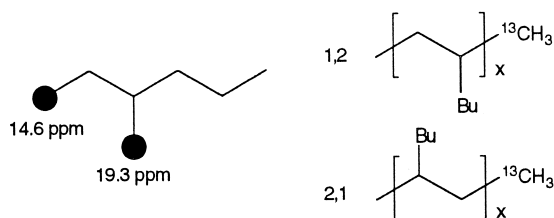


We were interested in determining the mode of α -olefin insertion (1,2 versus 2,1 insertion) in the above catalytic systems (**5a**/ $B(C_6F_5)_3$ and **5b**/ $B(C_6F_5)_3$). To show this, the isotopically labeled complexes $[ArN(CH_2)_3NAr]Ti(^{13}CH_3)_2(^{13}C_2\text{-5a})$ and $[Ar'N(CH_2)_3NAr']Ti(^{13}CH_3)_2(^{13}C_2\text{-5b})$ were prepared from **4a,b** and 2 equiv of $^{13}CH_3MgI$ in ether at $-20^\circ C$. In separate experiments, compounds $^{13}C_2\text{-5a}$ and $^{13}C_2\text{-5b}$ were mixed with 1 equivalent $B(C_6F_5)_3$ and 10 equiv of 1-hexene in d_5 -bromobenzene to yield $^{13}C_1$ -polyhexene (Eq. (3)).



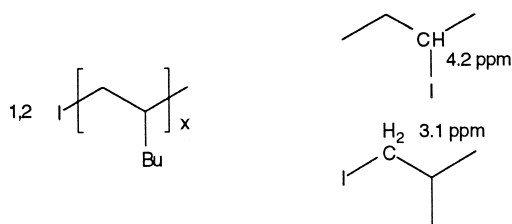
Bromobenzene is sufficiently polar to solubilize catalytic amounts of the titanium–borane complex and is unreactive. In contrast, CD_2Cl_2 reacts with the titanium–borate complex to give the dichlorides **4a,b** while relatively non-polar aromatic solvents such as toluene and benzene yield insoluble red oils. These red oils are, however, active catalysts when exposed to neat 1-hexene. Proton NMR spectroscopy confirmed that all monomer had been consumed (Eq. (3)). The carbon NMR spectra of the $^{13}C_1$ -polyhexene samples are dominated by resonances attributable to the borate anion $[^{13}CH_3B(C_6F_5)_3]^-$ and the isotopically labeled methyl group (average 20.4 ppm) which initiated the polymer chain. In addition, weak resonances are

observed for atactic poly(1-hexene) and in the case of the polymer derived from $^{13}\text{C}_2$ -**5a**, a small resonance at 109 ppm is assigned to the methylene derivative **9** (vide supra). Using 3-methylhexane as a model complex, we ascribe the pattern at 20.4 ppm to a methyl group bound to a tertiary carbon, in other words, to 1,2-inserted 1-hexene.



The pattern at 20.4 ppm is broad which we attribute to the stereochemistry of the first few inserted monomer units (note: the poly(1-hexene) is atactic). The above chemical shift assignment is consistent with chain end studies reported for poly(propylene) [33].

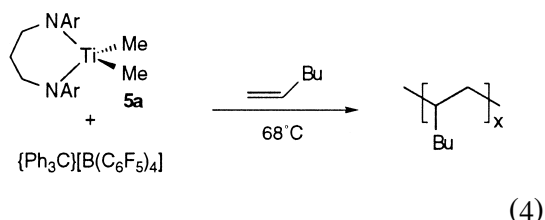
Additional evidence for the 1,2-insertion of 1-hexene is obtained from iodine quenching reactions [34]. For example, 10 equiv of 1-hexene was polymerized with **5b**/ $\text{B}(\text{C}_6\text{F}_5)_3$ in bromobenzene- d_5 followed by quenching with excess I_2 . The proton NMR spectrum of this solution shows resonances for $[\text{Ar}'\text{N}(\text{CH}_2)_3\text{NAr}']\text{TiI}_2$ [35], the typical broad resonances associated with atactic poly(1-hexene), and a broad multiplet at 3.10 ppm which integrates 1:1 with the resonances of $[\text{Ar}'\text{N}(\text{CH}_2)_3\text{NAr}']\text{TiI}_2$. Using 2-iodobutane and 1-iodo-2-methylpropane as model compounds [34], we assign the multiplet at 3.10 ppm to methylene protons located adjacent to an iodide.



A similar study has been used to assign a secondary insertion mode to vanadium living polymerization systems [34].

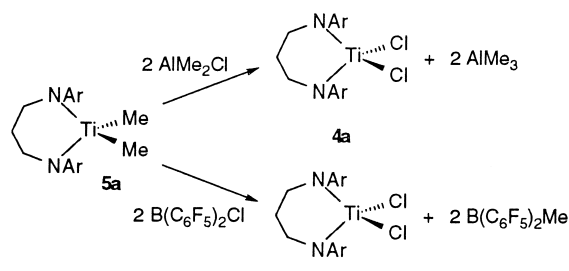
3.3. Activation with trityl tetrakis(perfluorophenyl) borate

In addition to the above mentioned activators, it is also possible to generate highly active living polymerization systems with $\{\text{Ph}_3\text{C}\}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (TB) [36] (Eq. (4)).



Under identical conditions, the TB-activated systems (entry 8) are about 1/3 less active than the MAO-activated systems (entry 9) and at least two orders of magnitude more active than the borane-activated compounds (note that the measured activity in entry 8 is suppressed by toluene relative to entry 7). Less pronounced anion effects of this type have been noted in metallocene systems [37,38]. The molecular weight distribution measured for the TB-activated polymerization is higher than that observed in the less active borane-activated complexes. We believe that this increase in the polydispersity is the result of a change in the relative rates of initiation (k_i) and propagation (k_p), as compared to the borane-activated system, since we see no evidence of β -hydride elimination in low molecular weight polymers (by NMR spectroscopy). In addition, the GPC traces of **5a**/TB generated poly(1-hexene) samples are unimodal confirming that no chain termination is operative in these systems.

The **5a**/TB catalyst system offers an opportunity to confirm our notion that cationic diamide titanium complexes readily engage in



chain transfer to aluminum [23]. For example, when 1-hexene is polymerized with **5a**/TB in the presence of 100 equiv of $\text{Al}(^i\text{Bu})_3$ an increase in the molecular weight distribution is observed along with a corresponding decrease in molecular weight of the polymer (compare entries 8 and 10). Chain transfer to aluminum is even greater when MAO is present (entry 11). The molecular weight distribution increases to 2.08 while the number average molecular weight of poly(1-hexene) drops from 177 500 to 29 000.

3.4. Other potential activators

We have explored other aluminum-based activators and although no active systems were found, some interesting chemistry was noted. Compound **5a** is inactive for the polymerization of neat 1-hexene when activated with $\text{Al}(^i\text{Bu})_3$ (100 equiv) or AlEt_3 (100 equiv) at 68°C. Interestingly, **5a** reacts with 2 equiv of AlMe_2Cl or $\text{B}(\text{C}_6\text{F}_5)_2\text{Cl}$ [39] to give the known dichloride **4a** along with AlMe_3 and $\text{B}(\text{C}_6\text{F}_5)_2\text{Me}$ [40], respectively (Scheme 3).

Analogous reactions of this type have been noted for metallocene derivatives [41].

4. Conclusions

Chelating diamide complexes of titanium serve as catalyst precursors for the polymerization of 1-hexene and other α -olefins [14]. A variety of cocatalysts can be used to activate the complexes, however, these appear to be limited to highly electrophilic Lewis acids that do not

bear halide groups. A pronounced difference in activity is noted between the borane-activated complexes and the MAO- and TB-activated systems. This marked variation in activity is assigned to the nature of the counter ion and its ability to interact with the metal center. Chain transfer to aluminum has been identified as the sole chain termination step in the MAO-activated system. In contrast, the borane- and TB-activated diamide complexes are living catalysts as no chain termination is operative in these systems; however, these systems will engage in chain transfer if aluminum reagents are added. A primary insertion mode (1,2 insertion) has been assigned based on both the initiation of the polymer chain and its purposeful termination with iodine. New ligand variations and polymerization studies will be reported shortly.

5. Experimental details

5.1. General details

All experiments were performed under an atmosphere of dry dinitrogen using standard Schlenk techniques or in an Innovative Technology dry box. Solvents were distilled from sodium/benzophenone ketyl (THF, hexanes, pentane and diethylether) or molten sodium (toluene) and molten potassium (benzene) under argon and stored over activated 4 Å molecular sieves. TiCl_4 , 1,3-dibromopropane, butyl lithium (2.50 M), methyl lithium (1.48 M), and MeMgBr (3.0 M in Et_2O) were obtained from Aldrich Chemicals and used as received. *N,N,N',N'*-tetramethylethylenediamine (tmeda), 2,6-diisopropylaniline, chlorotrimethylsilane and 1-hexene were obtained from Aldrich Chemicals and distilled prior to use. Methylaluminoxane (MAO) and $\{\text{Ph}_3\text{C}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ were obtained from Akzo Nobel. $\text{Me}_3\text{SiCH}_2\text{Li}$ [42], $\text{NaCp} \cdot \text{DME}$ [43], $\text{B}(\text{C}_6\text{F}_5)_3$ [28] were prepared according to literature procedures. Toluene, 1-hexene and pentane (treated with 5% HNO_3 in H_2SO_4 to remove

any olefin contaminants prior to distilling) were stored over NaK and filtered through activated basic alumina just prior to use in polymerizations. Proton (300 MHz) and carbon (75.46 MHz) NMR spectra were recorded in C_6D_6 at approximately 23°C on Varian Gemini-300 and Varian XL-300 spectrometers. The proton chemical shifts were referenced to internal C_6D_5H ($\delta = 7.15$ ppm) and the carbon resonances to C_6D_6 ($\delta = 128.0$ ppm). GPC analysis versus polystyrene standards were performed using a Waters GPC equipped with Waters Styragel columns (HR 1, HR 3, HR 4). Mass spectra were performed on a Finnigan MAT model 8230 spectrometer coupled to a Varian 3400 Gas Chromatograph. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY and by Mr. Peter Borda at the University of British Columbia. Ar = 2,6- iPr_2C_6H_3 , Ar' = 2,6-Me $_2C_6H_3$.

5.2. ArHN(CH $_2$) $_3$ NHAr (**1a**)

BuLi (2.50 M, 79.2 ml, 198 mmol) was added dropwise to a stirring solution of 2,6-diisopropylaniline (35.1 g, 198 mmol) in THF (150 ml) at $-78^\circ C$. The solution was warmed to RT where it was kept for 30 min. The solution was cooled to 0°C and tmeda (23.0 g, 198 mmol) was added dropwise followed by 1,3-dibromopropane (20.0 g, 99.1 mmol) dropwise, then stirred overnight at RT. The solution was poured into H $_2$ O (100 ml) and extracted with CH $_2$ Cl $_2$ (3 \times 100 ml). The organic layer was dried over anhydrous Na $_2$ SO $_4$ and the CH $_2$ Cl $_2$ removed in vacuo. The resulting yellow oil was dissolved in diethyl ether (30 ml) and concentrated HCl (20 ml) was added. The resulting precipitate ([ArH $_2$ N(CH $_2$) $_3$ NH $_2$ Ar]Cl $_2$) was filtered, washed with diethyl ether (20 ml), and redissolved in dichloromethane. This solution was poured into aqueous saturated K $_2$ CO $_3$ (100 ml). The organic layer was separated and dried over anhydrous Na $_2$ SO $_4$. Removal of the solvent yielded pure **1a** (18.2 g, 46.1 mmol; 47%). 1H NMR δ 7.10 (m, 6H, Ar), 3.36 (sept,

4H, CHMe $_2$), 3.01 (t, 4H, NCH $_2$), 2.97 (s, 2H, NH), 1.77 (pent, 2H, NCH $_2$ CH $_2$), 1.22 (d, 24H, CHMe $_2$). $^{13}C\{^1H\}$ NMR δ 144.0, 143.7, 123.9, 124.4, 50.8, 32.7, 28.1, 24.5. MS (EI) m/z 394.3342 (M $^+$). Calcd for C $_{27}H_{42}N_2$: 394.3348.

5.3. Ar'HN(CH $_2$) $_3$ NHAr' (**1b**)

BuLi (2.50 M, 73.0 ml, 183 mmol) was added dropwise to a stirring solution of 2,6-dimethylaniline (20.0 g, 165 mmol) in THF (150 ml) at $-78^\circ C$. The solution was warmed to RT where it was kept for 30 min. The solution was cooled to 0°C and tmeda (19.2 g, 165 mmol) was added dropwise followed by 1,3-dibromopropane (16.7 g, 82.5 mmol) dropwise. The solution was stirred overnight at RT. The solution was poured into H $_2$ O (100 ml) and extracted with CH $_2$ Cl $_2$ (3 \times 100 ml). The organic layer was dried over anhydrous Na $_2$ SO $_4$ and the CH $_2$ Cl $_2$ removed in vacuo. The resulting beige solid was recrystallized from hexanes to leave pure **1b** as a white crystalline solid (10.1 g, 35.6 mmol; 36%). 1H NMR δ 6.98 (m, 4H, Ar), 6.86 (m, 2H, Ar), 2.86 (t, 4H, NCH $_2$), 2.79 (s, 2H, NH), 2.14 (s, 12H, ArMe), 1.51 (pent, 2H, NCH $_2$ CH $_2$). $^{13}C\{^1H\}$ NMR δ 146.7, 129.6, 129.2, 122.3, 46.9, 32.9, 18.6. MS (EI) m/z 282.20894 (M $^+$). Calcd. for C $_{19}H_{26}N_2$: 282.20959.

5.4. Ar(Me $_3$ Si)N(CH $_2$) $_3$ N(SiMe $_3$)Ar (**3a**)

MeLi (1.48 M, 35.3 ml, 52.2 mmol) was added dropwise to a stirring solution of compound **1a** (10.0 g, 25.4 mmol) in THF (150 ml) at $-78^\circ C$. The solution was warmed to RT where it was kept for 30 min. The solution was cooled to 0°C and chlorotrimethylsilane (5.67 g, 52.2 mmol) was added dropwise. The solution was stirred overnight at RT. The solvent was removed in vacuo and the resulting slurry dissolved in hexanes. The solution was then filtered through Celite and the solvent removed in vacuo to leave a yellow solid. Recrystallization

from diethylether yields pure **3a** (13.6 g, 25.2 mmol; 99%). ^1H NMR δ 7.04 (m, 6H, Ar), 3.46 (sept, 4H, CHMe_2), 3.01 (t, 4H, NCH_2), 1.77 (m, 2H, NCH_2CH_2), 1.20 (d, 12H, CHMe_2), 1.17 (d, 12H, CHMe_2), 0.09 (s, 18H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR δ 148.6, 143.8, 126.2, 124.2, 51.0, 32.3, 28.0, 25.3, 24.9, 0.5. MS (EI) m/z 538.41368 (M^+). Calcd. for $\text{C}_{33}\text{H}_{58}\text{N}_2\text{Si}_2$: 538.41385.

5.5. $\text{Ar}'(\text{Me}_3\text{Si})\text{N}(\text{CH}_2)_3\text{N}(\text{SiMe}_3)\text{Ar}'$ (**3b**)

MeLi (1.56 M, 11.4 ml, 17.8 mmol) was added dropwise to a stirring solution of compound **1b** (2.52 g, 8.92 mmol) in THF (50 ml) at -78°C . The solution was warmed to RT where it was kept for 30 min. The solution was cooled to 0°C and chlorotrimethylsilane (1.94 g, 17.8 mmol) was added dropwise. The solution was stirred overnight at RT. The solvent was removed in vacuo and the resulting slurry dissolved in hexanes. The solution was then filtered through Celite and the solvent removed in vacuo to leave pure **3b** as a clear colorless oil (3.54 g, 8.30 mmol; 93%). ^1H NMR δ 6.96 (m, 4H, Ar), 6.89 (m, 2H, Ar), 2.84 (t, 4H, NCH_2), 2.19 (s, 12H, ArMe), 1.55 (m, 2H, NCH_2CH_2), 0.04 (s, 18H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR δ 146.5, 137.9, 128.7, 125.0, 48.7, 32.9, 19.6, 0.4. MS (EI) m/z 426.28798 (M^+). Calcd. for $\text{C}_{25}\text{H}_{42}\text{N}_2\text{Si}_2$: 426.28760.

5.6. $[\text{Ar}'\text{N}(\text{CH}_2)_3\text{NAr}']\text{TiCl}_2$ (**4a**)

Compound **3a** (3.09 g, 5.73 mmol) and TiCl_4 (1.09 g, 5.75 mmol) were refluxed in xylenes for 12 h. The resulting deep red solution was filtered through Celite, the volume of the filtrate was reduced until a slurry formed to which hexanes was added to complete the precipitation. Recrystallization from a toluene/hexanes mixture yields pure complex **4a** as deep red crystals (2.20 g, 4.30 mmol, 75%). ^1H NMR δ 7.09 (m, 6H, Ar), 3.75 (m, 4H, NCH_2), 3.53 (sept, 4H, CHMe_2), 2.48 (m, 2H, NCH_2CH_2),

1.44 (d, 12H, CHMe_2), 1.18 (d, 12H, CHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR δ 144.5, 143.3, 129.2, 125.0, 64.4, 31.1, 28.9, 26.2, 24.4. Anal. Calcd. for $\text{C}_{27}\text{H}_{40}\text{Cl}_2\text{N}_2\text{Ti}$: C, 63.41; H, 7.88; N, 5.48. Found: C, 63.05; H, 8.12; N, 5.27.

5.7. $[\text{Ar}'\text{N}(\text{CH}_2)_3\text{NAr}']\text{TiCl}_2$ (**4b**)

Prepared as per **4a** above. **3b** (2.85 g, 6.68 mmol) and TiCl_4 (1.27 g, 6.70 mmol) yields pure **4b** as dark orange-red crystals (2.16 g, 5.41 mmol, 81%). ^1H NMR δ 6.93 (m, 6H, Ar), 3.46 (m, 4H, NCH_2), 2.34 (s, 12H, ArMe), 2.34 (m, 2H, NCH_2CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR δ 144.2, 133.3, 129.4, 128.5, 62.1, 32.4, 19.0. Anal. Calcd. for $\text{C}_{19}\text{H}_{24}\text{Cl}_2\text{N}_2\text{Ti}$: C, 57.16; H, 6.06; N, 7.02. Found: C, 57.28; H, 6.19; N, 6.89.

5.8. $[\text{Ar}'\text{N}(\text{CH}_2)_3\text{NAr}']\text{TiMe}_2$ (**5a**)

MeMgBr (2.4 M, 0.83 ml, 2.0 mmol) was added dropwise to a stirring solution of **4a** (0.50 g, 0.98 mmol) in Et_2O (50 ml) at -20°C . The solution was allowed to warm to RT and stirred overnight. The solvent was removed in vacuo and the resulting solid extracted with hexanes and filtered through Celite. The solution was concentrated and cooled to -30°C to yield complex **5a** as a yellow crystalline solid (0.27 g, 0.57 mmol, 58%). ^1H NMR δ 7.21 (m, 6H, Ar), 3.72 (sept, 4H, CHMe_2), 3.58 (m, 4H, NCH_2), 2.12 (m, 2H, NCH_2CH_2), 1.39 (d, 12H, CHMe_2), 1.28 (d, 12H, CHMe_2), 0.86 (s, 6H, TiMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR δ 145.3, 144.7, 127.4, 124.6, 61.5, 52.0 ($\text{Ti}-\text{CH}_3$), 31.2, 28.5, 26.4, 24.9. Anal. Calcd. for $\text{C}_{29}\text{H}_{46}\text{N}_2\text{Ti}$: C, 74.02; H, 9.85; N, 5.95. Found: C, 74.32; H, 9.91; N, 5.85.

5.9. $[\text{Ar}'\text{N}(\text{CH}_2)_3\text{NAr}']\text{TiMe}_2$ (**5b**)

Prepared as per **5a** above. MeMgBr (2.4 M, 2.1 ml, 5.0 mmol) and **4b** (1.00 g, 2.50 mmol) in Et_2O (50 ml) yield yellow crystalline **5b** (0.65 g, 1.81 mmol, 73%). ^1H NMR δ 7.11 (m, 4H, Ar), 7.0₂ (m, 2H, Ar), 3.40 (m, 4H, NCH_2),

2.39 (s, 12H, ArMe), 2.04 (m, 2H, NCH₂CH₂), 0.70 (s, 6H, TiMe₂). ¹³C{¹H} NMR δ 146.6, 134.4, 129.1, 126.6, 58.5, 51.1 (Ti–CH₃), 32.0, 18.7. Anal. Calcd. for C₂₁H₃₀N₂Ti: C, 70.38; H, 8.44; N, 7.82. Found: C, 69.98; H, 8.73; N, 7.56.

5.10. [ArN(CH₂)₃NAr]Ti(CH₂Ph)₂ (**6a**)

PhCH₂MgCl (0.90 M, 2.16 ml, 1.94 mmol) was added dropwise to a stirring solution of complex **4a** (0.49 g, 0.96 mmol) in Et₂O (50 ml) at –20°C. The solution was warmed to RT and stirred overnight. The solvent was removed in vacuo and the solid extracted with hexane and filtered through Celite. The solution was concentrated and cooled to –30°C to yield complex **6a** as an orange crystalline solid (0.38 g, 0.61 mmol, 64%). ¹H NMR δ 7.24 (m, 6H, Ar), 7.02 (tt, 4H, Ph), 6.82 (tt, 2H, Ph), 6.70 (dd, 4H, Ph), 3.77 (sept, 4H, CHMe₂), 3.60 (m, 4H, NCH₂), 2.58 (s, 4H, CH₂Ph), 2.07 (m, 2H, NCH₂CH₂), 1.32 (d, 12H, CHMe₂), 1.23 (d, 12H, CHMe₂). ¹³C{¹H} NMR δ 148.2, 147.3, 144.2, 128.5, 127.4, 126.8, 124.9, 122.6, 82.5 (Ti–CH₂Ph), 60.9, 30.2, 28.4, 26.6, 24.7. Anal. Calcd. for C₄₁H₅₄N₂Ti: C, 79.07; H, 8.74; N, 4.50. Found: C, 78.45; H, 8.98; N, 4.27.

5.11. [Ar'N(CH₂)₃NAr']Ti(CH₂Ph)₂ (**6b**)

Prepared as per **6a** above. PhCH₂MgCl (0.90 M, 5.0 ml, 4.5 mmol) and **4b** (0.900 g, 2.25 mmol) in Et₂O (50 ml) yield orange crystalline **6b** (0.860 g, 1.68 mmol, 75%). ¹H NMR δ 7.04 (m, 6H, Ar), 7.00 (tt, 4H, Ph), 6.82 (tt, 2H, Ph), 6.59 (dd, 4H, Ph), 3.38 (m, 4H, NCH₂), 2.54 (s, 4H, CH₂Ph), 2.25 (s, 12H, ArMe), 2.02 (m, 2H, NCH₂CH₂). ¹³C{¹H} NMR δ 149.4, 146.9, 133.9, 129.2, 128.5, 126.8, 126.6, 122.5, 81.6 (Ti–CH₂Ph), 57.8, 30.3, 19.4. Anal. Calcd. for C₃₃H₃₉N₂Ti: C, 77.63; H, 7.50; N, 5.49. Found: C, 77.68; H, 7.42; N, 5.44.

5.12. [ArN(CH₂)₃NAr]Ti(CH₂SiMe₃)₂ (**7a**)

4a (1.00 g, 1.96 mmol) was dissolved in Et₂O (50 ml) and cooled to –20°C. LiCH₂SiMe₃ (0.376 g 4.00 mmol) dissolved in Et₂O was added dropwise. The resulting solution was allowed to warm to RT and stirred overnight. The solvent was removed in vacuo and the resulting solid dissolved in toluene and filtered through Celite. The toluene was removed in vacuo to leave an orange-yellow solid. Analytically pure **7a**, as yellow crystals, is obtained by recrystallization from toluene at –30°C (0.52 g, 0.84 mmol, 43%). ¹H NMR δ 7.19 (m, 6H, Ar), 3.86 (sept, 4H, CHMe₂), 3.61 (m, 4H, NCH₂), 2.31 (m, 2H, NCH₂CH₂), 1.45 (d, 12H, CHMe₂), 1.34 (s, 4H, CH₂SiMe₃), 1.31 (d, 12H, CHMe₂), 0.04 (s, 18H, SiMe₃). ¹³C{¹H} NMR δ 147.8, 143.9, 127.1, 125.0, 60.0, 30.3, 28.0, 26.6, 25.3, 2.3. Anal. Calcd. for C₃₅H₆₂N₂Si₂Ti: C, 64.51 H, 9.22; N, 5.57. Found: C, 64.78; H, 9.00; N, 5.67.

5.13. [Ar'N(CH₂)₃NAr']Ti(CH₂SiMe₃)₂ (**7b**)

Prepared as per **7a** above. **4b** (1.00 g, 2.50 mmol) and LiCH₂SiMe₃ (0.471 g, 5.00 mmol) yield complex **7b** as a yellow crystalline solid after recrystallization from hexanes (0.942 g, 1.88 mmol, 75%). ¹H NMR δ 7.05 (m, 6H, Ar), 3.41 (m, 4H, NCH₂), 2.46 (s, 12H, ArMe₂), 2.16 (m, 2H, NCH₂CH₂), 1.26 (s, 4H, CH₂SiMe₃), 0.03 (s, 18H, SiMe₃). ¹³C{¹H} NMR δ 148.9, 133.7, 129.3, 126.4, 74.1, 58.0, 31.0, 19.6, 2.7. Anal. Calcd. for C₃₅H₆₂N₂Si₂Ti: C, 64.51 H, 9.22; N, 5.57. Found: C, 64.78; H, 9.00; N, 5.67.

5.14. [ArN(CH₂)₃NAr]Ti(η⁵-C₅H₅)Cl (**8a**)

4a (1.00 g, 1.96 mmol) was dissolved in THF (50 ml). NaCp · DME (0.356 g, 2.00 mmol) was then added as a solid. The solution was stirred overnight at 23°C. The solvent was removed in vacuo and the resulting solid taken up in hexane and filtered through Celite. The hexane was

reduced to cat 2 ml and the solution cooled in a freezer. Analytically pure **8a** formed as orange crystals (0.952 g, 1.76 mmol, 90%). ^1H NMR: δ 7.12 (m, 6H, Ar), 5.92 (s, 5H, C_5H_5), 4.34 (m, 2H, NCH_2), 3.77 (sept, 2H, CHMe_2), 3.36 (sept, 2H, CHMe_2), 3.22 (m, 2H, NCH_2), 2.48 (m, 1H, NCH_2CH_2), 1.99 (m, 1H, NCH_2CH_2), 1.34 (d, 6H, CHMe_2), 1.33 (d, 6H, CHMe_2), 1.22 (d, 6H, CHMe_2), 1.05 (d, 6H, CHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR δ 156.6, 144.6, 140.1, 126.4, 124.8, 123.8, 116.2, 63.1, 32.7, 28.0, 27.6, 26.5, 26.2, 24.0. Anal. calcd. for $\text{C}_{32}\text{H}_{45}\text{ClN}_2\text{Ti}$: C, 71.04; H, 8.38; N, 5.18. Found: C, 71.12; H, 8.51; N, 5.14.

5.15. $[\text{Ar}'\text{N}(\text{CH}_2)_3\text{NAr}']\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}$ (**8b**)

Prepared as per **8a** above. **4b** (1.00 g, 2.50 mmol) and $\text{NaCp} \cdot \text{DME}$ (0.446 g, 2.50 mmol) yield **8b** as orange crystals (0.913 g, 2.13 mmol, 85%). ^1H NMR: δ 6.95 (m, 6H, Ar), 5.73 (s, 5H, C_5H_5), 3.81 (m, 2H, NCH_2), 3.35 (m, 1H, NCH_2CH_2), 3.20 (m, 2H, NCH_2), 2.37 (s, 6H, ArMe_2), 2.10 (s, 6H, ArMe_2), 1.95 (m, 1H, NCH_2CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR δ 157.9, 134.4, 129.3, 129.2, 128.7, 125.5, 116.6, 59.5, 31.5, 20.1, 18.9. Anal. calcd. for $\text{C}_{24}\text{H}_{29}\text{ClN}_2\text{Ti}$: C, 67.22; H, 6.82; N, 6.53. Found: C, 67.46; H, 7.01; N, 6.31.

5.16. X-ray crystallographic analysis (**4a**)

A suitable crystal of compound **4a** was grown from saturated toluene and hexanes at -30°C . Crystal data may be found in Table 1. Data were collected on a Siemens P4 diffractometer with the XSCANS software package [44]. The cell constants were obtained by centering 42 reflections ($11.3^\circ < 2\theta < 24.9^\circ$). The Laue symmetry $2/m$ was determined by merging symmetry equivalent positions. The data were collected in the range of $\theta = 1.90\text{--}22.5^\circ$ ($-1 \leq h \leq 10$, $-1 \leq k \leq 15$, $-22 \leq l \leq 22$) in the ω scan mode at variable scan speeds ($2\text{--}20^\circ/\text{min}$). Four standard reflections monitored at the end of every 297 reflections collected showed no decay

of the crystal. The data processing, solution and refinement were done using SHELXTL-PC programs [45]. The final refinements were performed using SHELXL-93 software programs [46]. An empirical absorption correction was applied to the data using the ψ scans data. Anisotropic thermal parameters were refined for all non-hydrogen atoms in the neutral molecule except for two phenyl ring carbon atoms. Large thermal motions were observed for C(2), C(26), and C(27) carbon atoms. The carbon atom C(2) has positional disorder with an occupancy factor of 0.8/0.2 (derived from electron density ratios). The isotropic temperature factor for atom C(2A) was refined. Two different orientations (0.5/0.5) were found for the methyl carbon atoms C(26) and C(27). Individual isotropic thermal parameters were refined for these carbon atoms in the least-squares cycles. All the C–C bond and C–C–C bond angles in the isopropyl groups were restrained using the option SADI. No attempt was made to locate the hydrogen atoms, however, they were placed in calculated positions. In the final difference Fourier synthesis the electron density fluctuates in the range 0.44(7) to $-0.27(7) \text{ e } \text{\AA}^{-3}$.

5.17. X-ray crystallographic analysis (**5b**)

A suitable crystal of compound **5b** was grown from saturated pentane at -30°C . Crystal data may be found in Table 1. The X-ray diffraction experiments were carried out on a Enraf–Nonius CAD4F diffractometer controlled by the Enraf–Nonius CAD4 software package [47]. The cell constants were obtained by centering 24 reflections ($21.9^\circ \leq 2\theta \leq 24.3^\circ$). The Laue symmetry mmm was confirmed by inspection of reflection intensities. The data were collected in the θ range $1.0\text{--}25.0^\circ$ ($-1 \leq h \leq 9$, $-1 \leq k \leq 18$, $-1 \leq l \leq 20$) in $\theta\text{--}2\theta$ scan mode at variable scan speeds ($2\text{--}20^\circ/\text{min}$). Moving background measurements were made at 25% extensions of the scan range. Four standard reflections were monitored at the end of every 297 reflection collected. The data processing was

carried out using the Enraf–Nonius structure determination package [48], solution and initial refinements were done using SHELXTL-PC [45] programs. The final cycles of refinement were performed using SHELXL-93 [46] software programs. An empirical absorption correction was applied to the data using the ψ scans data. Anisotropic thermal parameters were refined for all of the non-hydrogen atoms in the molecule except for the phenyl ring carbon atoms and the carbon and nitrogen atoms of the chelating ring. Individual isotropic thermal parameters were refined for these atoms in the least-squares cycles. The methyl hydrogen atoms were fit in their idealized positions, while the methylene and phenyl hydrogen atoms were placed in their calculated positions. In the final difference Fourier synthesis the electron density fluctuates in the range 0.27(6) to $-0.30(6)$ e \AA^{-3} .

5.18. General polymerizations conditions

The polymerizations were performed under an atmosphere of dry nitrogen in a 100 ml Schlenk flask using 10.6 μmol or 6.8 μmol of catalyst and 1 equiv of $\{\text{Ph}_3\text{C}\}[\text{B}(\text{C}_6\text{F}_5)_4]$, or 1 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$, or 500 equiv of MAO. Any additional solvent, the reaction time, and the temperature are given in Table 4 or in Fig. 3. For polymerizations performed at 68°C, the reaction flask was immersed in a 68°C oil bath for 10 min prior to injection of the catalyst. The polymerizations were quenched with 1.0 N HCl, the poly(1-hexene) extracted with THF, and dried over Na_2SO_4 . The THF was removed and the polymer dried at 23°C overnight.

5.19. Supplementary material available

Details of the final atomic coordinates and equivalent isotropic thermal parameters, complete tables of bond lengths and angles, hydrogen atom parameters, and anisotropic thermal parameters for **4a** (9 pages) and **5b** (7 pages). Ordering information is given on any current masthead page.

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