

New ethylene bridged monofluorenyl-amido group 4 complexes

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Abstract

9-[(2-*t*-Butylamino)ethyl] fluorene (**1**) was synthesized by the use of (1-chloro-2-*t*-butylamino)ethane (**3**) which provided convenient routes to **1** as well as 3-[(2-*t*-butylamino)ethyl] indene (**7**). Deprotonation of **1** with 2 equivalents of butyllithium followed by addition of ZrCl₄ or HfCl₄ led to [1-(η^1 -*t*-butylamido)-2-(η^5 -9-fluorenyl)ethane] zirconium (**8**) and hafnium (**9**) dichloride, respectively. Complexes **8** and **9** when activated with methylaluminoxane (MAO) are active catalysts for the polymerization of ethylene. © 1997 Elsevier Science B.V.

1. Introduction

Since the discovery by Kaminsky and co-workers [1–4] in 1980 that group 4 metallocene complexes along with methylaluminoxane (MAO) as a cocatalyst were efficient catalysts for olefin polymerization, numerous studies have been reported on these catalytic systems [5–15]; for reviews see [16,17]. A significant number of these papers deal with structural modification of the catalyst precursor in order to elucidate the relationship between catalyst structure and the tacticity of the polymer produced. Bercaw et al. [18–20] showed that non-symmetric *ansa*-metallocene-like complexes of scandium could be synthesized using an amido group in place of one of the pentahapto ligands. This idea was then extended to group 4 transition metals by researchers at Exxon [21–25] and Dow Chemical Co. [26–28]. Dow Chemical Co. refers to precursors of the type B(Me₄Cp)(N-*t*-butyl)MCl₂ (B = SiMe₂ or CH₂CH₂ and M = Ti or Zr) as ‘constrained geometry catalysts’ since the Cp–M–N angle is 107.7° for the titanium complex and 102° for the zirconium analog [27]. Furthermore, they have used these precursors to develop a new class of olefin copolymers which has been trademarked INSITE™ Technology. These catalysts have the ability to copolymerize ethylene along with a number of different α -olefins and diene comonomers.

Stevens et al. [27] have reported that the activity of these catalysts increases in the order Me₄Cp > Cp > Ind as the pentahapto ligand is varied. In addition, several bridged monocyclopentadienyl- or fluorenyl-amido zirconium or titanium complexes have been synthesized by several groups [29–32]; however, no polymerization results were reported. In the present study, we attempted to synthesize some new non-symmetric *ansa*-metallocenes which contained an amido group as one of the hapto ligands bridged by an ethylene linkage, and compare their polymerization behavior to that of the constrained geometry catalysts.

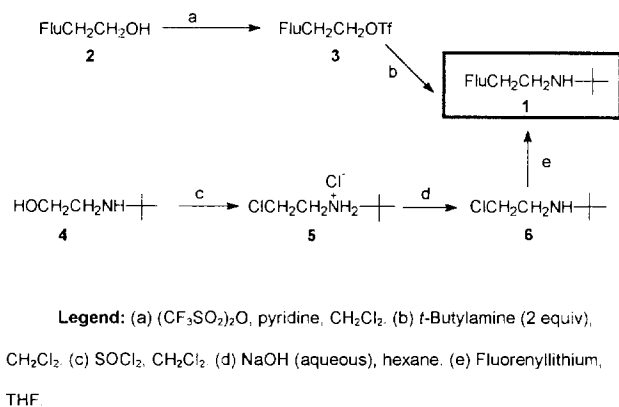
2. Results and discussion

2.1. Synthesis of ligand systems

Two methods were used to synthesize 9-[(2-*t*-butylamino)ethyl]fluorene (**1**) as shown in Scheme 1. The first method involves the use of 2-(9-fluorenyl)ethanol (**2**) which was converted into the triflate derivative (**3**) by reaction with trifluoromethanesulfonic anhydride. A reaction between triflate **3** and 2 equivalents of *t*-butylamine gave **1** in 50% yield. However, by this method the product was contaminated with a small amount of **2** which could not be removed by repeated distillation. Consequently, an alternative method was developed which eliminated the need for **2**.

The second method involves the use of 2-(*t*-butylamino)ethanol (**4**) which was converted into the chlo-

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Scheme 1.

ride hydrochloride (5) by reaction with SOCl_2 . The hydrochloride 5 could then be converted into the free base (6) by reaction with NaOH, and subsequent reaction with fluorenyllithium gave 1 in 67% yield from the chloride 6. 3-[(2-*t*-Butylamino)ethyl] indene (7) was also synthesized following the procedure described for 1. Reaction of 6 with indenyllithium gave the indenyl analog 7 in 61% yield (Scheme 2).

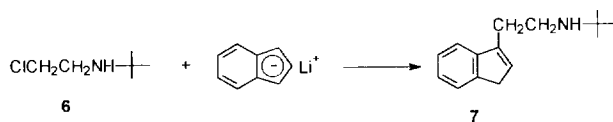
2.2. Synthesis of zirconium and hafnium complexes

Group 4 metal complexes of 1 were synthesized by conversion of 1 into its dianion by reaction with 2 equivalents of butyllithium. Subsequent reaction with either ZrCl_4 or HfCl_4 in diethyl ether gave 8 and 9 in yields of 40% and 37%, respectively (Scheme 3). Attempts to synthesize metal complexes of 7 by the route described for 1 did not lead to the desired product. $^1\text{H-NMR}$ showed that the reaction produced a mixture of products, and that a significant amount of oligomerization took place.

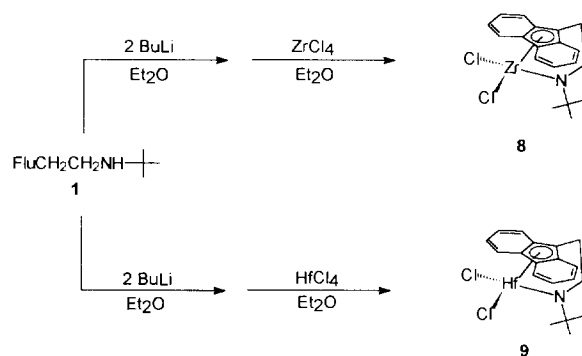
2.3. Stability and catalytic properties

Complexes 8 and 9 are both highly air and moisture sensitive, and decompose readily (ca. 15 min) in toluene under inert atmosphere. However, complexes 8 and 9 are active catalysts for the polymerization of ethylene when activated with MAO (Table 1).

Catalyst 8/MAO exhibited an activity of 2.6×10^5 g of PE/(mol of $\text{Zr} \cdot [\text{C}_2\text{H}_4] \cdot \text{h}$) at 75°C , and activity decreased with a decrease in polymerization tempera-



Scheme 2.



Scheme 3.

ture (T_p). Polyethylene produced by 8/MAO at 0°C had M_r and T_m (determined as in Table 1) of 2.5×10^5 and 132.2°C , respectively. An increase in polymerization temperature caused a decrease in both M_r and T_m of the polymer. A comparison of the catalytic ability of 8/MAO and 9/MAO shows that 8/MAO has a higher activity than 9/MAO at the same T_p , while M_r and T_m of the polymer are higher for 9/MAO under the same conditions. Differences in activity and M_r for analogous zirconium and hafnium complexes were first observed by Ewen et al. [33], and have also been confirmed by other groups.

Stevens et al. [27] reported that $\text{SiMe}_2(\text{Me}_4\text{Cp})(\text{N-}t\text{-butyl})\text{TiCl}_2$ (10) when activated by MAO was active up to $T_p = 130^\circ\text{C}$. The catalyst system 8/MAO was active up to $T_p = 75^\circ\text{C}$, above which the instability of the catalyst resulted in lower polymerization activity. At lower T_p both 8/MAO and 10/MAO have comparable activities; however, when T_p is increased the likelihood of a change from multihapto to monohapto coordination of the fluorenyl ligand is increased. In addition, the longer metal to ligand bond distances observed in zirconium complexes as compared to analogous titanium complexes could combine to decrease the stability of 8/MAO.

Table 1
Polymerization of ethylene with 8 and 9 activated with MAO^a

Compound	T_p ($^\circ\text{C}$)	$A^b \times 10^{-5}$	T_m^c ($^\circ\text{C}$)	$M_r^d \times 10^5$
8	0	0.9	132.2	2.5
8	25	2.0	130.2	1.8
8	75	2.6	129.6	0.9
9	25	0.6	134.3	3.6

^a Polymerization conditions: $[\text{Zr}]$ or $[\text{Hf}] = 50 \mu\text{M}$; Al/Zr or $\text{Hf} = 2000:1$; $\text{P}(\text{C}_2\text{H}_4) = 15 \text{ psi}$; polymerizations were run for 30 min.

^b Activity = g of PE/(mol of Zr or $\text{Hf} \cdot [\text{C}_2\text{H}_4] \cdot \text{h}$).

^c Melting points were determined using a DuPont 2000 DSC.

^d Molecular weights were determined by intrinsic viscosity using decahydronaphthalene as a solvent at 135°C .

3. Experimental section

Reactions were carried out under an argon atmosphere using standard Schlenk techniques. Methylaluminoxane (MAO) was purchased from Akzo, and all other reagents were purchased from Aldrich and used without further purification. 2-(9-Fluorenyl)ethanol (**2**) was synthesized according to literature procedure [34]. Toluene, diethyl ether, tetrahydrofuran (THF), hexane and pentane were distilled with Na/K alloy under argon. Methylene chloride was distilled from CaH₂. ¹H-NMR spectra were recorded on a Varian XL-200 or a Bruker NR-80 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA. The procedure used to polymerize ethylene has previously been reported in detail [35].

3.1. Synthesis of 9-[(2-*t*-butylamino)ethyl]fluorene (**1**)

This compound was prepared by the two methods below.

3.1.1. Method a. Synthesis of 2-*t*-butylaminoethyl chloride hydrochloride (**5**)

2-(*t*-Butylamino)ethanol (25 g, 0.21 mol) was dissolved in CH₂Cl₂ (200 ml) and SOCl₂ (25.4 g, 0.21 mol) was added slowly. The reaction mixture became cloudy upon addition of the SOCl₂ and the resulting suspension was stirred overnight at room temperature. The suspension was filtered and the product washed with hexane (3 × 50 ml) to give **5** (24.2 g, 72%) as a white powder. ¹H-NMR (CDCl₃): δ 9.62 (br s, 2H, NH), 3.98–4.13 (m, 2H, ClCH₂), 3.13–3.40 (m, 2H, CH₂N), 1.50 (s, 9H, *t*-butyl).

3.1.2. Synthesis of (1-chloro-2-*t*-butylamino)ethane (**6**)

To a mixture of **5** (20 g, 0.13 mol) and NaOH (10.1 g, 0.25 mol) was added water (150 ml) and the mixture was stirred for 10 min. The free base was extracted with pentane (2 × 100 ml), the organic layer was dried (Na₂SO₄), and the solvent was evaporated to give **6** (14.1 g, 89%) as a colorless liquid. ¹H-NMR (CDCl₃): δ 3.62 (t, 2H, ClCH₂), 2.85 (t, 2H, CH₂N), 1.21 (br s, 1H, NH), 1.10 (s, 9H, *t*-butyl).

3.1.3. Synthesis of compound **1** from **6**

To a solution of fluorenyllithium, which was prepared from the reaction of fluorene (10 g, 60 mmol) with 1.6 M butyllithium (37.6 ml, 60 mmol) in THF (200 ml), was added a solution of **6** (7.3 g, 60 mmol) in THF (50 ml) at 0°C. After the mixture was stirred overnight at room temperature, water (200 ml) was added and the organic layer was separated. The solvent was removed and the crude product was dissolved in hexane (150 ml). Addition of 0.6 M HCl (150 ml)

caused precipitation of the 1 · HCl which was collected by filtration, washed with hexane (2 × 50 ml), and dried in vacuo. The hydrochloride was then added to a 10% NaOH solution (200 ml) and the mixture was extracted with hexane (2 × 200 ml), dried (Na₂SO₄), and the solvent removed. Vacuum distillation (130–132°C/0.01 mmHg) of the residue gave **1** (10.7 g, 67%) as a colorless oil. ¹H-NMR (CDCl₃): δ 7.25–7.80 (m, 8H, arom H), 4.08 (t, 1H, ring-CH), 2.32–2.54 (m, 2H, FluCH₂), 2.13–2.26 (m, 2H, CH₂N), 0.97 (s, 9H, *t*-butyl), 0.90 (br s, 1H, NH). Anal. Found: C, 85.99; H, 8.65; N, 5.36. C₁₉H₂₃N. Calc.: C, 85.99; H, 8.73; N, 5.28%.

3.1.4. Method b

To a solution of 2-(9-fluorenyl)ethanol (10 g, 48 mmol) and pyridine (3.8 ml, 48 mmol) in CH₂Cl₂ (200 ml) at 0°C was added trifluoromethanesulfonic anhydride (7.8 ml, 48 mmol). The mixture was stirred for 30 min while the temperature was maintained at 0°C. The reaction mixture was washed with ice water (100 ml), and the organic layer was separated and dried (Na₂SO₄). The solution was filtered while the temperature was maintained at 0°C. To the resulting yellow solution was added *t*-butylamine (7.0 g, 95 mmol) and the mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was washed with water (2 × 100 ml) and the organic layer was dried (Na₂SO₄). The solvent was evaporated and the crude product was vacuum distilled (130–132°C/0.01 mmHg) to give **1** (6.4 g, 50%) as a colorless oil. The product had identical physical and spectroscopic properties to those described in Method a.

3.2. Synthesis of 3-[(2-*t*-butylamino)ethyl]indene (**7**)

Following the procedure described for the synthesis of **1** in Method a, indenyllithium was prepared from indene (10.1 g, 58 mmol) and 1.6 M butyllithium (36.3 ml, 58 mmol) in THF (200 ml), and allowed to react with **6** (7.0 g, 58 mmol). Vacuum distillation (87°C/0.01 mmHg) gave **7** (7.6 g, 61%) as a pale, yellow oil. ¹H-NMR (CDCl₃): δ 7.22–7.42 (m, 4H, arom H), 6.27 (m, 1H, sp²-H), 3.34 (d, 2H, ring CH₂), 2.75–2.92 (m, 4H, CH₂CH₂), 1.10 (s, 9H, *t*-butyl), 1.08 (s, 1H, NH). Anal. Found: C, 83.72; H, 9.85; N, 6.60. C₁₅H₂₁N. Calc.: C, 83.67; H, 9.83; N, 6.50%.

3.3. Synthesis of [1-(η¹-*t*-butylamido)-2-(η⁵-9-fluorenyl)ethane]zirconium dichloride (**8**)

A solution of **1** (1.6 g, 6.0 mmol) in Et₂O (50 ml) was cooled to 0°C and 1.6 M butyllithium (7.5 ml, 12 mmol) was added. The mixture was allowed to warm to room temperature and stirred overnight. The resulting suspension was cooled to 0°C, ZrCl₄ (1.4 g, 6.0 mmol)

was added and the solution stirred for 30 min at 0°C and overnight at room temperature. The solution was filtered and the solvent removed in vacuo. The product was extracted with CH₂Cl₂ (40 ml) and filtered. Concentration of the solution to 1/4 its original volume and cooling to –20°C gave **8** (1.02 g, 40%) as yellow-orange needles. ¹H-NMR (CD₂Cl₂): δ 7.32–8.08 (m, 8H, arom H), 4.51 (t, 2H, FluCH₂), 3.63 (t, 2H, CH₂N), 1.21 (s, 9H, *t*-butyl). Anal. Found: C, 53.55; H, 5.07; N, 2.97. C₁₉H₂₁Cl₂NZr. Calc.: C, 53.63; H, 4.97; N, 3.29%.

3.4. Synthesis of [1-(η¹-*t*-butylamido)-2-(η⁵-9-fluorenyl)ethane]hafnium dichloride (**9**)

Following the procedure described for **8**, **1** (3.67 g, 14 mmol), 1.6 M butyllithium (17.3 ml, 28 mmol), and HfCl₄ (2.5 g, 14 mmol) gave **9** (2.6 g, 37%) as yellow-orange needles from CH₂Cl₂. ¹H-NMR (CD₂Cl₂): δ 7.15–8.20 (m, 8H, arom H), 4.60 (t, 2H, FluCH₂), 3.59 (t, 2H, CH₂N), 1.15 (s, 9H, *t*-butyl). Anal. Found: C, 44.05; H, 4.27; N, 2.42. C₁₉H₂₁Cl₂NHf. Calc.: C, 44.50; H, 4.13; N, 2.73%.

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