

Dendritic β -diketiminato titanium and zirconium complexes: synthesis and ethylene polymerisation

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Abstract

The cyclopentadienyl(β -diketiminato)titanium and zirconium chlorides (η^5 -C₅H₅)MCl₂(CH(C(NC₆H₄-4-OR)CH₃)₂) (M = Ti (**4-dend**), Zr (**5-dend**)), where R corresponds to the first generation carbosilane dendron (dendritic wedge) Si(CH₂CH₂SiMePh₂)₃, have been synthesised. After activation with methylaluminoxane, the activity of **4-dend** and **5-dend** as catalysts for ethylene polymerisation has been determined and compared with that of the non-dendritic counterpart (η^5 -C₅H₅)MCl₂(CH(C(NC₆H₅)CH₃)₂) (M = Ti (**4**), Zr (**5**)).

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1. Introduction

A large number of reports published on metallo-dendrimers [1] deal with catalysis [2]. The location of the transition metal within the dendritic framework (core, branches, or periphery) is a critical issue in the design of such catalysts. When one or more dendritic wedges are incorporated to ligands, their metal complexes can benefit from the local environment created by the wedges to which focal point are linked. In a previous paper [3], we observed significant modifications on the molecular weight distributions of polymers when titanium metallocenes with dendritic substituents at the cyclopentadienide ligands were used in ethylene polymerisation. This fact, which was accompanied by a decreasing in activity, was interpreted as a result of the space filling produced by the wedges in the vicinity of the metal centres. In this paper, we describe the synthesis and ethylene polymerisation of mixed cyclopentadie-

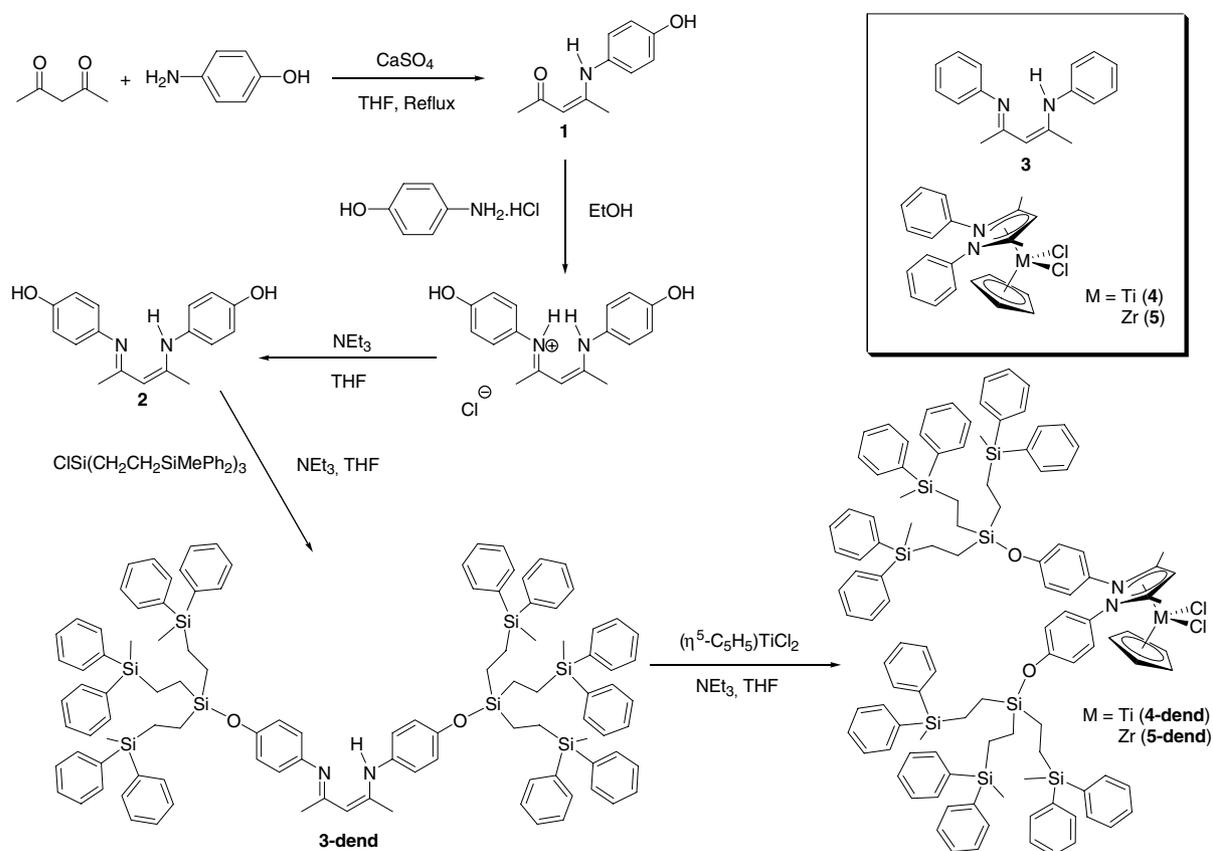
nyl(β -diketiminato) complexes of titanium and zirconium containing carbosilane dendritic wedges of first generation linked to the β -diketiminato ligand [4]. The location of the dendritic wedges in the complexes here described has been chosen in such a way that little steric hindrance should be expected in the close environment of the metal center.

2. Results and discussion

The synthetic route to the metal complexes is depicted in Scheme 1. The hydroxyphenyl β -diketimine **2** was synthesised through the classical method based on the condensation of a primary amine (4-aminophenol) with a β -diketone (2,4-pentanedione) [5], a multistep process involving the enaminoketone intermediate **1**. A carbosilane dendron was attached to the *para* position of each diketimine phenyl ring via phenolysis of Si–Cl bonds at the focal point with the hydroxy protons of **2** in the presence of triethylamine. The protonolysis was quantitative (¹H NMR evidence) but dendritic β -diketimine **3-dend** was isolated as a yellow solid (melting over

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Scheme 1.

15 °C) in only a 48% yield after workup, due to its high solubility in most common organic solvents (see Section 4). Both β -diketiminates **2** and **3-dend**, which are depicted in Scheme 1 with localised bonds for simplicity, are better described by a symmetrically hydrogen-bonded structure consistent with the chemical shift equivalence of the two methyl groups, and the large low-field shift of the N–H proton [6].

Mixed cyclopentadienyl(β -diketiminato) complexes of titanium (**4-dend**) and zirconium (**5-dend**) were obtained by direct reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{MCl}_3$ (M = Ti, Zr) with dendritic β -diketimine **3-dend**, in the presence of triethylamine as Lewis base to promote the protonolysis of the metal–chloride bond. Complexes are isolated in high yield as red (**4-dend**) or pale-yellow (**5-dend**) oily products. Similar procedures have been used for the preparation of related complexes (titanium **4**, and the already reported [7] zirconium **5**), which were synthesised as reference for the ethylene polymerisation studies described below.

β -Diketiminato ligands adopt a diversity of bonding modes in their coordination to metals ranging from $\eta^2\text{-}2\sigma$ (**4e**) to $\eta^5\text{-}\pi$ (**6e**) in mononuclear complexes. The similarity of the NMR chemical shifts for the methine protons [8] in diketiminato complexes **4–5** (5.37 (**4**) and 5.42 (**4-dend**), 5.22 (**5**) and 5.23 ppm (**5-dend**)) may be consistent with the η^5 coordination mode found in

the solid state for the indenyl analogue of **5** [7]. However, the CH shift in **5** is similar to that found in other related complexes with σ coordination, may be indicating a facile $\pi \rightarrow \sigma$ interconversion in solution [7].

The renewed interest in β -diketiminato transition metal complexes is partially due to the ability of this ligand to stabilise coordinatively unsaturated complexes [5] that function as catalysts in, e.g., non-metallocene olefin polymerization [9]. Recent reports have demonstrated that mixed cyclopentadienyl(β -diketiminato)zirconium complexes as **5**, be have as single-site catalyst for the polymerisation of ethylene [10]. Table 1 summarises our results obtained with complexes **4–5** after activation with an excess of methylaluminoxane (MAO). These catalysts are far from the performance of the metallocene complexes $(\eta^5\text{-C}_5\text{H}_5)_2\text{MCl}_2$ (M = Ti, Zr) [3]. However, dendritic catalyst **4-dend** and **5-dend** displayed

Table 1
Ethylene polymerization results with complexes **4–5** and **4–5-dend**^a

Precatalyst	Yield (mg)	Activity (kg _{PE} /mol _M h)
4	22	53
4-dend	76	182
5	4	10
5-dend	10	24

^a Conditions: MAO cocatalyst, Al/M = 1000, 1.25 μmol of catalyst dissolved in 50 ml of toluene, 20 min, 293 K, 1 bar of constant monomer pressure.

slightly higher activities than non dendritic complexes **4** and **5**.

3. Conclusion

A β -diketiminato ligand has been incorporated to the focal point of two carbosilane dendrons, and used for the preparation of the corresponding cyclopentadienyl(β -diketiminato)titanium and zirconium complexes. The dendritic catalysts show an increased activity compared to their non dendritic analogues. Further studies are in progress.

4. Experimental

4.1. Reagents and general techniques

General techniques are described in [3]. (η^5 -C₅H₅)TiCl₃ [11], ClSi(CH₂CH₂SiMePh₂)₃ [3] and **3** [12] were prepared according to literature procedures. Chemical shifts (δ , ppm) are relative to SiMe₄ and were measured by internal referencing to the deuterated solvent (¹³C and residual ¹H resonances), or by the substitution method from the ²⁹Si resonance of SiMe₄.

4.2. Synthesis of MeC(NHC₆H₄-4-OH)CHC(O)Me (**1**)

2,4-Pentanedione (9.0 ml, 88 mmol) was added to a mixture of 4-aminophenol (9.6 g, 88 mmol) and calcium sulphate (5 g) in THF (100 ml). The reaction mixture was refluxed for 24 h. Then, the CaSO₄ was separated by filtration, the solution was concentrated up to 50 ml, and pentane (30 ml) was added. The white solid precipitated was filtered and dried in vacuo to yield 13.3 g (79%) of pure **1**. Anal. Calc. for C₁₁H₁₃NO₂: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.13; H, 6.90; N, 7.37%. ¹H NMR (CDCl₃): δ 12.22 (m, 1H, NH), 8.25 (broad s, 1H, OH), 6.85 (center of an AA'BB' spin system, 4H, C₆H₄), 5.14 (d, 1H, CH, ⁴J = 0.45 Hz), 2.09 (s, 3H, CH₃CO), 1.89 (d, 3H, CH₃NH, ⁴J = 0.36 Hz). ¹³C NMR (CDCl₃): δ 195.6 (CO), 162.9 (CH₃CNH), 155.3 (C₆H₄, C₄), 130.2 (C₆H₄, C₁ (carbon linked to N)), 126.7 (C₆H₄, C_{2,6}), 116.1 (C₆H₄, C_{3,5}), 96.7 (CH), 28.6 (CH₃CO), 19.7 (CH₃CNH).

4.3. Synthesis of MeC(NHC₆H₄-4-OH)CHC(NC₆H₄-4-OH)Me (**2**)

Enaminoketone **1** (5.0 g, 26 mmol), 4-aminophenol hydrochloride (3.8 g, 26 mmol), calcium sulphate (10 g), and dry ethanol (100 ml) were introduced into a 200 ml ampoule fitted with a PTFE stopcock, and heated in an oil bath for 72 h at 90 °C. Subsequently, the solvent was removed in vacuo and the residue

washed with THF (4 \times 50 ml) and reacted with an excess of triethylamine (3 ml) in THF (50 ml). The reaction mixture was stirred overnight and filtered off. The solution was evaporated in vacuo to dryness and the residue was extracted with a mixture of THF/Pentane (ca. 15 ml, 1:5 v/v). After evaporation of solvents, compound **2** (2.5 g, 34%) was obtained as an orange solid, sometimes contaminated by small amounts of 4-aminophenol. Anal. Calc. for C₁₇H₁₈N₂O₂: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.45; H, 6.49; N, 9.89. ¹H NMR (CDCl₃/CD₃OD 5:1 v/v): δ 6.64 (center of an AA'BB' spin system, 8H, C₆H₄), 4.67 (s, 1H, CH), 1.80 (s, 6H, CH₃), NH and OH not observed, probably due to exchange with CD₃OD. ¹³C NMR (CDCl₃/CD₃OD 5:1 v/v): δ 159.9 (CH₃CN), 152.8 (C₆H₄, C₄), 137.5 (C₆H₄, C₁ (carbon linked to N)), 124.0 (C₆H₄, C_{2,3}), 115.0 (C₆H₄, C_{3,5}), 95.7 (CH), 20.1 (CH₃).

4.4. Synthesis of MeC(NHC₆H₄-4-OR)CHC(NC₆H₄-4-OR)Me, R = Si(CH₂CH₂SiMePh₂)₃ (**3-dend**)

An excess of triethylamine (1.0 ml) was added to a solution of β -diketimine **2** (0.382 g, 1.35 mmol) and ClSi(CH₂CH₂SiMePh₂)₃ (2.00 g, 2.70 mmol) in THF (50 ml). After stirring for 2 h, the solvent and the excess of triethylamine were removed by evaporation in vacuo to dryness, and the residue was extracted with cold THF (20 ml, 0 °C). The resulting solution was concentrated up to 2 ml and, after addition of pentane (20 ml), cooled at -30 °C overnight. The yellow oil that separated at the bottom of the Schlenk was dried in vacuo after carefully removal of the supernatant solution with a syringe. The above process (dissolution, cooling, removal and drying) was repeated several times until crystallization of a yellow compound (1.1 g, 48%) that remains permanently solid below its melting point (ca. 15 °C). Anal. Calc. for C₁₀₇H₁₁₈N₂O₂Si₈: C, 76.10; H, 7.04; N, 1.66. Found: C, 76.15; H, 7.10; N, 1.69%. ¹H NMR (C₆D₆): δ 13.12 (s, 1H, NH), 7.47 (m, 24H, SiC₆H₅), 7.15 (two multiplets overlapping, 36H, SiC₆H₅), 6.75 (center of an AA'BB' spin system, 8H, C₆H₄), 4.84 (s, 1H, CH), 1.84 (s, 6H, CH₃CN), 1.09 and 0.86 (m, 24H, SiCH₂H₂Si), 0.46 (s, 18H, SiCH₃). ¹³C NMR (C₆D₆): δ 159.8 (CH₃CN), 152.2 (C₆H₄, C₄), 140.1 (C₆H₄, C₁ (carbon linked to N)), 124.5 (C₆H₄, C_{3,5}), 120.2 (C₆H₄ C_{2,6}), 97.3 (CH), 20.6 (CH₃CNH), 129.4 (C₆H₅, C₄), 137.2 (C₆H₅, C₁ (carbon linked to Si)), 134.9 (C₆H₅, C_{2,6}), 128.2 (C₆H₅, C_{3,5}), 5.9 and 5.2 (SiCH₂CH₂Si), -4.9 (SiCH₃). ²⁹Si NMR (C₆D₆): δ 19.1 (s, 2Si), -5.6 (s, 6Si).

4.5. Synthesis of (η^5 -C₅H₅)MCl₂(CH(C(NC₆H₄-4-OR)-CH₃)₂), R = Si(CH₂CH₂SiMePh₂)₃

4-dend (M = Ti). An excess of triethylamine (0.020 ml, 0.14 mmol) was added to a mixture of β -diketimine **3-dend** (0.100 g, 0.060 mmol) and (η^5 -C₅H₅)TiCl₃ (0.013

g, 0.060 mmol) in toluene (20 ml), and stirred for 8 h. Subsequently, the solution was filtered and evaporated in vacuo to dryness to yield **4-dend** as a spectroscopically pure, red oil (0.095 g, 85%). Anal. Calc. for $C_{112}H_{122}N_2O_2Si_8Cl_2Ti$: C, 71.87; H, 6.57; N, 1.50. Found: C, 71.95; H, 6.60; N, 1.47%. 1H NMR (C_6D_6): δ 7.49 (m, 24H, SiC_6H_5), 7.18 (two multiplets overlapping, 36H, SiC_6H_5), 6.80 (center of an AA'BB' spin system, 8H, C_6H_4), 6.25 (s, 5H, C_5H_5), 5.42 (s, 1H, CH), 1.68 (s, 6H, CH_3CN), 1.10 and 0.92 (m, 24H, $SiCH_2H_2Si$), 0.47 (s, 18H, $SiCH_3$). ^{13}C NMR (C_6D_6): δ 161.4 (CH_3CN) 154.2 (C_6H_4 , C_4), 148.3 (C_6H_4 , C_1 (carbon linked to N)), 125.2 (broad, C_6H_4 , $C_{2,6}$) 120.1 (C_6H_4 , $C_{3,5}$), 122.6 (C_5H_5), 99.9 (CH), 22.7 (C_3 CNH), 129.6 (C_6H_5 , C_4), 137.0 (C_6H_5 , C_1 (carbon linked to Si)), 134.8 (C_6H_5 , $C_{2,6}$), 128.3 (C_6H_5 , $C_{3,5}$), 6.0 and 5.4 ($SiCH_2CH_2Si$), -4.8 ($SiCH_3$). ^{29}Si NMR (C_6D_6): δ 19.9 (s, 2Si), -5.7 (s, 6Si).

5-dend (M = Zr). This complex was obtained as a pale-yellow oil in 90% yield by a similar procedure of that described in detail for **4-dend**. Anal. Calc. for $C_{112}H_{122}N_2O_2Si_8Cl_2Zr$: C, 70.25; H, 6.42; N, 1.46. Found: C, 70.45; H, 6.49; N, 1.43%. 1H NMR (C_6D_6): δ 7.48 (m, 24H, SiC_6H_5), 7.18 (two multiplets overlapping, 36H, SiC_6H_5), 6.80 (center of an AA'BB' spin system, 8H, C_6H_4), 6.23 (s, 5H, C_5H_5), 5.22 (s, 1H, CH), 1.73 (s, 6H, CH_3CN), 1.08 and 0.86 (m, 24H, $SiCH_2H_2Si$), 0.46 (s, 18H, $SiCH_3$). ^{13}C NMR (C_6D_6): δ 164.2 (CH_3CN) 154.1 (C_6H_4 , C_4), 144.1 (C_6H_4 , C_1 (carbon linked to N)), 125.4 (C_6H_4 , $C_{2,6}$), 120.3 (C_6H_4 , $C_{3,5}$), 91.4 (CH), 22.3 (C_3CN), 129.6 (C_6H_5 , C_4), 137.0 (C_6H_5 , C_1 (carbon linked to Si)), 134.8 (C_6H_5 , $C_{2,6}$), 128.2 (C_6H_5 , $C_{3,5}$), 117.3 (C_5H_5), 6.0 and 5.3 ($SiCH_2CH_2Si$), -4.9 ($SiCH_3$). ^{29}Si NMR (C_6D_6): δ 19.8 (s, 2Si), -5.7 (s, 6Si).

4.6. Synthesis of $(\eta^5-C_5H_5)MCl_2(CH(CNC_6H_5)CH_3)_2$

4 (M = Ti). Triethylamine (0.20 ml, 1.4 mmol) was added to a THF solution of β -diketimine **3** (0.200 g, 0.80 mmol) and $(\eta^5-C_5H_5)TiCl_3$ (0.175 g, 0.80 mmol). After stirring for 8 h, the solution was filtered. Toluene was added to the solution until precipitation of a red solid that was filtered and dried in vacuo to yield **4** (0.300 g, 86%). Anal. Calc. for $C_{22}H_{22}N_2Cl_2Ti$: C, 61.00; H, 5.12; N, 6.47. Found: C, 60.85; H, 5.10; N, 6.43%. 1H NMR (C_6D_6): δ 7.10 (m, 4H, C_6H_5), 6.92 (two multiplets overlapping, 6H, C_6H_5), 6.17 (s, 5H, C_5H_5), 5.33 (s, 1H, CH), 1.61 (s, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 161.3 (CH_3CN) 154.4 (C_6H_5 , C_1 (carbon linked to N)), 129.0 (C_6H_5 , $C_{3,5}$), 126.4 (C_6H_5 , C_4), 124.0 (broad, C_6H_5 , $C_{2,6}$), 122.6 (C_5H_5), 99.9 (CH), 22.5 (CH_3).

5 (M = Zr). Complex **5** was prepared by the same procedure above described for **4**, and obtained as a pale-yellow solid in 90% yield. Spectroscopic data are

in agreement with those previously reported by Rahim et al. [7].

4.7. Ethylene polymerisation

A 250 ml flask charged with toluene (50 ml) and equipped with a magnetic stirrer was four times evacuated and refilled with pre-dried ethylene gas. Keeping the flask pressurised with ethylene (1 bar) and stirred at room temperature, a toluene solution of MAO, 0.83 ml, 1.5 M was syringed through a septum. After 5 min, a toluene solution of the catalyst (0.50 ml, 2.5 mM) was injected into the flask with simultaneous starting of a stopwatch. The polymerization was quenched 20 min later by closing the ethylene feeding, release of the overpressure and addition of acidified methanol (4% v/v HCl). The mixture was stirred for 6H and the polymer was filtered, washed with copious amounts of methanol, and dried in an oven to constant weight.

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