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Journal of Organometallic Chemistry 551 (1998) 133–138

Journal of Organometallic Chemistry

Ansa-bridged η-cyclopentadienyl imido and amido derivatives of titanium, zirconium and molybdenum [1]

Pedro T. Gomes [2], Malcolm L.H. Green *, Ana M. Martins [2]

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, USA

Received 19 April 1997; received in revised form 29 June 1997

Abstract

An improved synthesis of the ligand precursor $\{[C_5H_4(SiMe_3)](CH_2)_3N(SiMe_3)_2\}$ is described. It has been used to prepare the compounds $\{Ti[\eta{:}\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)]Cl_2\}$, $\{Ti[\eta\text{-}C_5H_4(CH_2)_3(\mu\text{-}N)]Cl\}_2$, $\{Zr[\eta{:}\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)](SMe_2)Cl_2\}$, $\{Zr[\eta{:}\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)]Cl_2\}$ and $\{Mo[\eta{:}\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)](PMe_3)Cl_2\}$. The zirconium compounds together with methylaluminoxane act as catalysts for ethylene and propylene polymerisation. © 1998 Elsevier Science S.A.

Keywords: Zirconium; Titanium; Molybdenum

1. Introduction

Recently we reported the synthesis of the compound $\{[C_5H_4(SiMe_3)](CH_2)_3N(SiMe_3)_2\}$ and showed that it reacted readily with niobium pentachloride to give the *ansa*-bridged η-cyclopentadienyl-imido derivative $\{Nb[\eta{:}\sigma\text{-}C_5H_4(CH_2)_3N]Cl_2\}$ [1]. In view of the current interest in *ansa*-bridged η-cyclopentadienyl-amido compounds of the group IV metals as catalyst precursors for α-olefin polymerisation [2–12] we have explored further the synthetic potential of the ligand precursor $\{[C_5H_4(SiMe_3)](CH_2)_3N(SiMe_3)_2\}$, as described below. A preliminary report of part of this work has been communicated [13].

2. Results and discussion

Treatment of $[Br(CH_2)_3NH_3]Br$ with three equivalents of $(Me_3Si)SO_3CF_3$ and Et_3N gave $Br(CH_2)_3N(SiMe_3)_2$ **1** which was then reacted with sodium cyclopentadienide giving an isomeric mixture of $[(C_5H_4)(CH_2)_3N(SiMe_3)_2]$ **2**. Addition to **2** of *t*-butyl lithium followed by Me_3SiCl gives the desired compound $\{[C_5H_4(SiMe_3)](CH_2)_3N(SiMe_3)_2]\}$ **3** as a mixture of isomers. The reaction sequence is shown in the Scheme 1. The overall yield of **3** from $[Br(CH_2)_3NH_3]Br$ was reproducibly 50–55%. The compound **3** was stored under dinitrogen at 0°C without noticeable deterioration.

Treatment of $TiCl_4$ in toluene with **3** gave orange crystals for which the analytical and spectroscopic data correspond to the compound $\{Ti[\eta{:}\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)]Cl_2\}$ **4**. The characterising data for **4** and for all the other new compounds described below are given in Table 1 and will only be discussed further where the interpretation is not straightforward.

An attempt to determine the crystal structure of **4** by X-ray diffraction showed the presence of disorder but nonetheless allowed the location of the atoms corresponding to the structure shown in the Scheme 2 [14]. The elimination of $SiMe_3Cl$ from **4** occurs readily in toluene at 60°C to give $\{Ti[\eta\text{-}C_5H_4(CH_2)_3(\mu\text{-}N)]Cl\}_2$ **5**. The dimeric structure of **5** is confirmed by the ^1H NMR spectrum that shows diastereotopic signals for the aliphatic chain protons.

Treatment of $[ZrCl_4(SMe_2)_2]$ [15] with **3** gave white crystals of $\{Zr[\eta{:}\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)](SMe_2)Cl_2\}$ **6**. The ^1H NMR spectrum of this compound shows fluxional behaviour due to sulphur inversion of the

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* Corresponding author.

[1] Dedicated to Prof. Peter Maitlis on the occasion of his 65th birthday and in recognition of his outstanding contributions to organo-transition metal chemistry.

[2] Present address: Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, 1096 Lisboa Codex, Portugal.

SMe_2 group. Thus, at room temperature a broad resonance is observed at δ 2.59, and this sharpens on cooling. At −30°C, a sharp peak is obtained which integrates for 6 protons. The ^1H NMR spectrum shows the molecule has C_s symmetry and the structure proposed for **6** is shown in Scheme 2, i.e., the SMe_2 ligand is coordinated to the Zr atom lying in between the two Cl ligands. The reaction of **3** with $ZrCl_4$ in CH_2Cl_2 led to $\{Zr[\eta:\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)]Cl_2\}$ **7**. The ^1H NMR spectrum of **7** reveals again a C_s symmetry compatible with a monomeric structure, which is further confirmed by the MS data. Attempts to force the elimination of $SiMe_3Cl$ either from **6** or **7** were unsuccessful. We have also explored the reaction of **3** with molybdenum pentachloride in dichloromethane and found that extraction of the reaction mixture with tetrahydrofuran gives a red-brown microcrystalline paramagnetic compound with stoichiometry corresponding to $\{Mo[\eta:\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)](C_4H_8O)Cl_3\}$ **8**. Treatment of **8** with trimethylphosphine causes substitution of the tetrahydrofuran ligand giving orange-brown $\{Mo[\eta:\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)](PMe_3)Cl_3\}$ **9**.

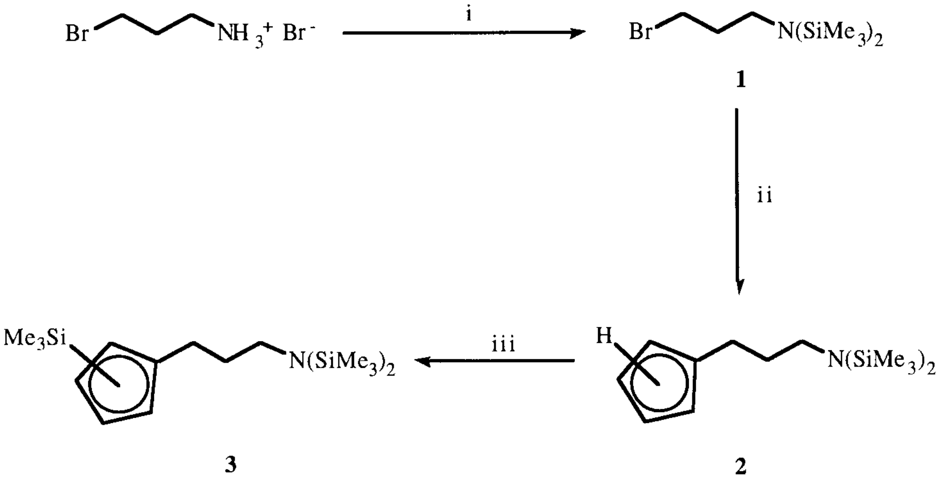
A preliminary study shows that the zirconium amido compound **6** in the presence of methylaluminoxane (Al/Zr ratio ca. 1000) polymerises ethylene (9×10^4 g of polyethylene (mol of Zr)$^{-1}$ h^{-1} atm^{-1}; $N_t = 1.8$ s^{-1}) to highly linear polyethylene ($T_m = 136.9$°C) [16,17]. In the same conditions, it oligomerises propylene (660 g of polypropylene (mol of Zr)$^{-1}$ h^{-1} atm^{-1}; $N_t = 0.5$ min^{-1}) to low molecular weight and highly polydispersed products ($\overline{M}_n = 2100$; $\overline{M}_w/\overline{M}_n = 7.1$). Although much less active than metallocene derivatives [18], this catalytic system has activities of the same order of magnitude of other *ansa*-bridged η-cyclopentadienyl-amido [2,3] or $[Zr(\eta\text{-}C_5H_5)R_3]$ [19,20] based systems.

In conclusion, the new compounds and reactions are shown in the Scheme 2.

3. Experimental

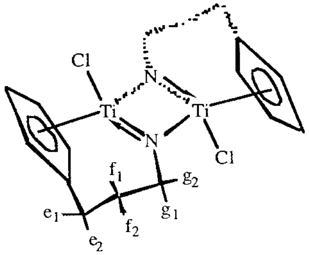
All manipulations and reactions were carried out under an atmosphere of dinitrogen (< 10 ppm oxygen or water) using standard Schlenk vessel and vacuum-line techniques or in a dry-box. Solvents were pre-dried over activated 4 Å molecular sieves and then distilled under an atmosphere of dinitrogen from potassium (tetrahydrofuran), sodium (toluene), sodium-potassium alloy [light petroleum (b.p. 40–60°C) and diethyl ether] or calcium hydride (dichloromethane), and stored under dinitrogen. Deuteriated solvents for NMR samples were stored in ampoules over activated molecular sieves (C_6D_6 and $[^2H_8]$ toluene) or dried using Na/K alloy ($[^2H_8]$ tetrahydrofuran) and calcium hydride (CD_2Cl_2) and transferred by vacuum distillation.

The NMR spectra were recorded on a Brüker AM-300 [^1H, 300 MHz; ^{13}C, 75.43 MHz] and referenced internally using residual ^1H and ^{13}C solvent resonances relative to tetramethylsilane ($\delta = 0$). Low resolution mass spectra were obtained on an AEI MS 302 mass spectrometer, updated by a data-handling system supplied by Mass Spectroscopy Services. Elemental analyses were performed by the Analytical Laboratory in this Department. The differential scanning calorimetry measurements of polyethylene (melting temperature, T_m)



Scheme 1. Synthesis of the ligand precursor **3**. Reagents: (i) $(Me_3Si)SO_3CF_3$ and NEt_3 in diethyl ether, 0°C to room temperature, 4 h; (ii) $Na(C_5H_5)$ in THF, −10°C to room temperature, 12 h; (iii) Li^tBu in hexane, −78 to room temperature, 12 h, then Me_3SiCl, 5 h.

Table 1
Analytical and spectroscopic data of compounds **4**–**9**

Compound[a]	Spectroscopic data[b1]
4 $\{Ti[\eta^5{:}\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)]Cl_2\}$ C, 42.3 (42.5); H, 6.0 (5.8); N, 4.4 (4.5); Cl, 22.3 (22.8)	H r.t.[c]: δ 6.57 (t, 2H, C_5H_4); 6.19 (t, 2H, C_5H_4); 3.52 (c, 2H, CH_2N); 2.67 (t, 2H, $C_5H_4CH_2$); 2.08 (m, 2H, $C_5H_4CH_2CH_2$); 0.46 (s, 9H, $Si(CH_3)_3$).
5 $\{Ti[\eta^5{:}\sigma\text{-}C_5H_4(CH_2)_3(\mu\text{-}N)]Cl\}_2$ C, 47.4 (47.2); H, 5.3 (5.0); N, 6.7 (6.9); Cl, 17.9 (17.4) 	^1H r.t.[c]: δ 6.85 (q, 2H, C_5H_4); 6.38 (q, 2H, C_5H_4); 6.08 (q, 2H, C_5H_4); 5.62 (q, 2H, C_5H_4); 3.71 (m, 2H, H_g); 3.44 (m, 2H, H_g); $^{13}C\{^1H\}$ r.t.[c]: δ 128.9 (C_5H_4 *ipso*); 116.6 (CH of C_5H_4); 115.7 (CH of C_5H_4); 115.3 (CH of C_5H_4); 114.2 (CH of C_5H_4); 59.1 (C_g); 33.7(C_f); 26.2 (C_e)
6 $\{Zr[\eta^5{:}\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)](SMe_2)Cl_2\}$ 1.69 (m, 2H, $C_5H_4CH_2CH_2$); 0.90 (s, 9H, $Si(CH_3)_3$) C, 36.6 (37.4); H, 5.8 (6.0); N, 3.3 (3.3); Cl, 16.2 (17.0)	^1H r.t.[c]: δ 6.66 (t, 2H, C_5H_4); 6.43 (t, 2H, C_5H_4); 2.83 (m, 2H, CH_2N); 2.71 (t, 2H, $C_5H_4CH_2$); 2.59 (br s, $S(CH_3)_2$); ^1H $-30°C$[c]: δ 6.66 (t, 2H, C5H4); 6.44 (t, 2H, C5H4); 2.74 (m, 2H, CH_2N); 2.64 (t, 2H, $C_5H_4CH_2$); 2.56 (s, 6H, $S(CH_3)_2$); 1.60 (m, 2H, $C_5H_4CH_2CH_2$); 0.02 (s, 9H, $Si(CH_3)_3$) ^1H r.t.[d]: δ 6.31 (t, 2H, C_5H_4); 6.21 (t, 2H, C_5H_4); 2.75 (m, 4H, $CH_2N+C_5H_4CH_2$); 2.23 (br s, $S(CH_3)_2$); 1.69 (s, 9H, $Si(CH_3)$) $^{13}C\{^1H\}$ r.t.[c]: δ 139.8 (C_5H_4 *ipso*); 121.5 (CH of C_5H_4); 119.2 (CH of C_5H_4); 45.2 (CH_2N); 36.4 ($C_5H_4CH_2$); 28.6 ($C_5H_4CH_2CH_2$); 21.9 ($S(CH_3)_2$); 1.9 ($Si(CH_3)_3$)
7 $\{Zr[\eta^5{:}\sigma\text{-}C_5H_4(CH_2)_3NSi(Me_3)]Cl_2\}$ C, 36.6 (37.0); H, 6.0 (6.0); N, 3.5 (4.0); Cl, 19.7 (19.95) MS (m/z): 354 $[M]^+$	^1H r.t.[d]: δ 6.18 (t, 2H, C_5H_4); 5.58 (t, 2H, C_5H_4); 2.78 (m, 2H, CH_2N); 2.08 (m, 2H, $C_5H_4CH_2$); 1.41 (m, 2H, $C_5H_4CH_2CH_2$); 0.43 (s, 9H, $Si(CH_3)_3$) $^{13}C\{^1H\}$ r.t.[d]: δ 130.5 (C_5H_4 *ipso*); 116.2 (CH of C_5H_4); 113.5 (CH of C_5H_4); 52.0 (CH_2N); 36.7 ($C_5H_4CH_2$); 26.7 ($C_5H_4CH_2CH_2$); 0.7 ($Si(CH_3)_3$)
8 $\{Mo[\eta^5{:}\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)](OC_4H_8)Cl_3\}$ C, 36.3 (38.5); H, 5.2 (5.8); N, 2.7 (3.0); Cl, 23.6 (22.7)	Paramagnetic
9 $\{Mo[\eta^5{:}\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)](PMe_3)Cl_3\}$ C, 36.0 (35.7); H, 5.9 (6.0); N, 3.2 (3.0); Cl, 22.9 (22.6)	Paramagnetic

[a] Analytical data given as: found (calculated) %. [b1] H NMR at 300 MHz, ^{13}C at 75 MHz. Data given as: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), relative intensity and assignment. [c] In CD_2Cl_2. [d] In $[^2H_6]$ benzene.

were performed on a Setaram TG-DSC 111 (IST-CQE, Portugal), in the range 20–200°C, at a heating rate of 5°C min^{-1}. The molecular weight analysis of polypropylene was performed by gel permeation chromatography at 35°C, on a Waters 150CV (IST-CQE, Portugal), using three Styragel columns (HR 1, HR 3 and HR 4; 30 × 0.78 cm) and THF at a flow rate of 1 cm^3 min^{-1}.

3.1. *N,N-bis-trimethylsilyl-3-bromopropylamine* ***1***

Triethylamine (62.7 cm^3; 449.9 mmol) and trimethylsilyltriflouromethylsulfonate (100.0 g; 449.9 mmol) were added dropwise to a suspension of 3-bromopropylamine hydrobromide (32.8 g; 150.0 mmol) in Et_2O (300 cm^3) at 0°C. The mixture was stirred for 2 h at this temperature and for an additional 4 h at r.t. During the reaction triethylammonium trifluoromethylsulfonate formed as an oil at the bottom of the flask. The volatiles were evaporated under reduced pressure and the residue was extracted with pentane (3 × 60 cm^3) and filtered. Evaporation of the solvent from the filtrate gave **1** as a colourless liquid. Yield, 38.2 g, 90%.

^{1}H NMR ($CDCl_3$): δ 3.34 (t, 2H, $BrCH_2CH_2$); 2.84 (c, 2H, CH_2N); 1.93 (m, 2H, $BrCH_2CH_2$); 0.14 (s, 18H, $Si(CH_3)_3$). MS (m/z): 267 $[M]^+$.

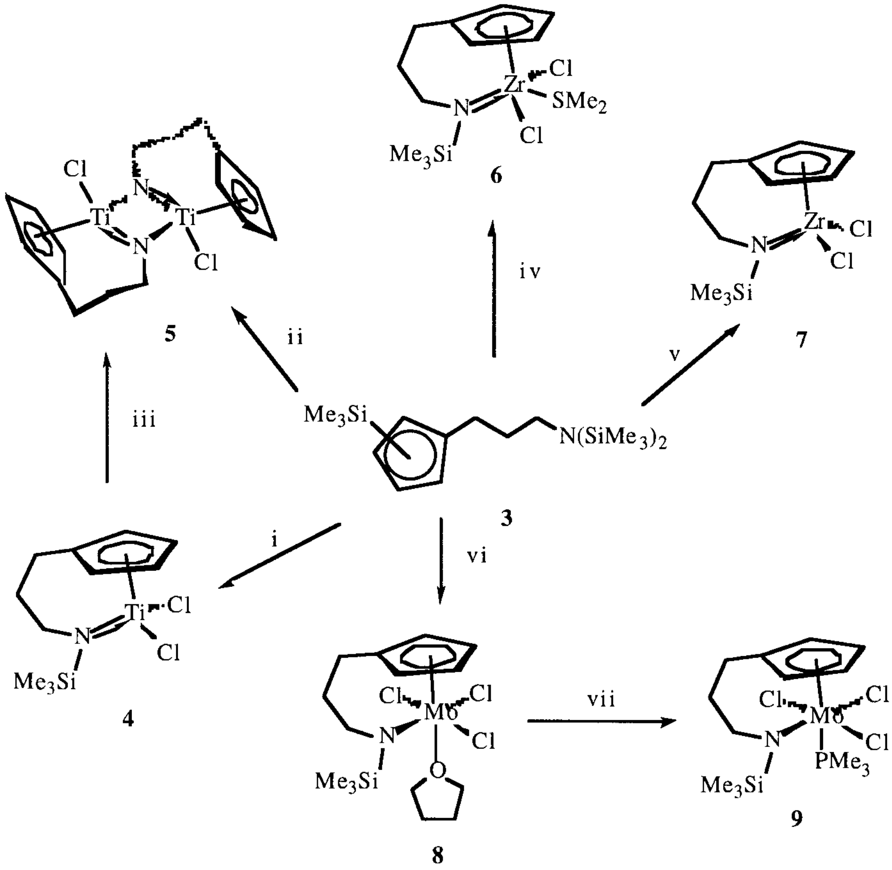
3.2. *N,N-bis-trimethylsilyl-3-cyclopentadienylpropylamine* ***2***

Sodium cyclopentadienide (14.0 g; 158.9 mmol) in THF (200 cm^3) was added dropwise to a solution of *N,N*-bis-trimethylsilyl-3-bromopropylamine (38.5 g; 136.4 mmol) in THF (350 cm^3). The mixture was stirred for 12 h and a white precipitate of NaBr separated. The mixture was filtered and the solvent was removed from the filtrate under reduced pressure. The residue was extracted with pentane and filtered. The filtrate was concentrated under vacuum to give a colourless oil. Yield, 27.4 g, 75%.

^{1}H NMR ($CDCl_3$): δ 6.36, 6.22, 6.06, 5.91 (H_{vinyl} of C_5H_5); 2.86, 2.79 (H_{sat} of C_5H_5); 2.68 (c, 2H, CH_2N); 2.19 (m, 2H, $C_5H_5CH_2CH_2$); 1.50 (m, 2H, $C_5H_5CH_2CH_2$); 0.06 (s, 18H, $NSi(CH_3)_3$). MS (m/z): 283 $[M]^+$.

3.3. *N,N-bis-trimethylsilyl-3-(trimethylsilylcyclopentadienyl)-propylamine* ***3***

A solution of **2** (27.4 g; 102.3 mmol) in THF (300 cm^3) at −78°C was treated with a 1.7 M solution of



Scheme 2. Reactions of the ligand precursor **3**. Reagents: (i) $TiCl_4$ in toluene, −78°C to room temperature, 12 h; (ii) $TiCl_4$ in toluene, −78 to 60°C, 12 h; (iii) in toluene, 60°C, 12 h, (iv) $ZrCl_4(SMe_2)$ in dichloromethane, −10°C to room temperature, 10 h; (v) $ZrCl_4$ in toluene, room temperature, 2 days; (vi) $MoCl_5$ in dichloromethane, −78°C to room temperature, 12 h, then THF; (vii) PMe_3 in THF, room temperature, 12 h.

t-butyl lithium (174.0 cm^3; 102.3 mmol) in hexane in a dropwise manner. The solution was allowed to warm up slowly to r.t. and stirred for a further 4 h. Then, trimethylsilylchloride (18.5 cm^3; 143.2 mmol) was added. After 8–10 h, the solution was filtered and the solvent was evaporated from the filtrate. The residue was extracted with pentane, filtered and the filtrate was concentrated in vacuum to give a pale yellow oil. Yield, 26.1 g, 75%.

Found (%) (calc. for $C_{17}H_{37}NSi_3$(%)): C 59.72 (60.10); H 11.36 (10.98); N 4.28 (4.12). ^1H NMR ($CDCl_3$): δ 6.46, 6.08 (H_{vinyl} of $C_5H_4(SiMe_3)$); 3.28 (H_{sat} of $C_5H_4(SiMe_3)$); 2.79 (m, 2H, CH_2N); 2.33 (m, 2H, $C_5H_4(SiMe_3)CH_2$); 1.62 (m, 2H, $C_5H_4(SiMe_3)CH_2CH_2$); 0.07 (s, 18, $NSi(CH_3)_3$); 0.03 (s, 9H, C_5H_4 $(Si(CH_3)_3)$).

3.4. Synthesis of $\{Ti[\eta:\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)]Cl_2\}$ **4**

A solution of **3** (1.85 g; 5.50 mmol) in toluene was added slowly to a solution of $TiCl_4$ (0.60 cm^3; 5.50 mmol) in toluene (50 cm^3), at −78°C. The mixture was warmed slowly to room temperature and allowed to react for 12 h. The solvent was evaporated to dryness and the orange residue was extracted with petroleum ether (40–60°C). After filtration, the filtrate was concentrated and cooled to −30°C giving orange crystals of **4**. Yield, 0.69 g, 40%.

3.5. Synthesis of $\{Ti[\eta:\sigma\text{-}C_5H_4(CH_2)_3(\mu\text{-}N)]Cl\}_2$ **5**

A toluene solution of **4** (0.35 g; 1.12 mmol) was heated to 60°C for 12 h. After filtration, the solvent was slowly evaporated under vacuum and the concentrated solution was cooled to −80°C. The red-orange crystals of **5** formed were separated by filtration and dried under vacuum. Yield, 0.27 g, 60%.

3.6. Synthesis of $\{Zr[\eta:\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)](SMe_2)Cl_2\}$ **6**

The compound $[ZrCl_4(SMe_2)_2]$ [15] was prepared in situ by treating $ZrCl_4$ (2.33 g; 10.0 mmol) with SMe_2 (15.0 cm^3; 20.4 mmol) in CH_2Cl_2 (60 cm^3) at 0°C. A solution of **3** (3.45 g; 10.0 mmol) in CH_2Cl_2 (20 cm^3) was then added dropwise, at 0°C, and the mixture was allowed to react for 12 h. The solvent was evaporated to dryness and the residue was extracted with toluene and filtered. The solution was concentrated (ca. 5 cm^3) and pentane (10 cm^3) was added. On cooling to −80°C a pale off-white solid formed which was separated and recrystallised from toluene/pentane (1:4) giving white microcrystals of **6**. Yield, 2.70 g, 65%.

3.7. Synthesis of $\{Zr[\eta:\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)]Cl_2\}$ **7**

A solution of $\{[C_5H_4(SiMe_3)](CH_2)_3N(SiMe_3)_2\}$ **3** (2.89 g; 8.5 mmol) in CH_2Cl_2 (15 cm^3) was added dropwise to a suspension of $ZrCl_4$ (1.98 g; 8.5 mmol) in CH_2Cl_2 (100 cm^3) at −30°C. The mixture was allowed to react for 2 days at r.t. and a yellow solution formed. The solvent was evaporated under reduced pressure and the residue was stirred with pentane to give a yellow powder. The suspension was cooled to −50°C and filtered. The residual solid was then extracted with diethylether (2 × 20 cm^3). The solution was filtered and the filtrate was concentrated. On cooling to −80°C a pale-yellow precipitate formed. This was separated and recrystallised from diethyl ether as a white solid. Yield, 0.91 g, 30%.

3.8. Synthesis of $\{Mo[\eta:\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)](OC_4H_8)Cl_3\}$ **8**

The compound $\{[C_5H_4(SiMe_3)](CH_2)_3N(SiMe_3)_2\}$ **3** (3.00 g; 8.83 mmol) in CH_2Cl_2 (15 cm^3) was reacted with a suspension of $MoCl_5$ (2.41 g; 8.83 mmol) in CH_2Cl_2 (200 cm^3) at −78°C for 12 h. A red-brown solid precipitated. This was separated and extracted with THF (3 × 20 cm^3) and the extract was filtered. The filtrate was concentrated and pentane was added, inducing the precipitation of **8** as a red-brown solid. Yield, 2.60 g, 60%.

3.9. Synthesis of $\{Mo[\eta:\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)](PMe_3)Cl_3\}$ **9**

PMe_3 (0.45 cm^3 4.35 mmol) was added to a solution of **8** (1.78 g; 3.81 mmol) in THF and the mixture was stirred for 12 h. The solvent was evaporated to dryness and the residue was extracted with CH_2Cl_2 (3 × 30 cm^3). The filtrate was concentrated and cooled to −80°C. A dark orange solid formed which was separated by filtration and washed with Et_2O. Addition of Et_2O to the mother liquor gave a second crop of **9**. Total yield, 1.43 g, 80%.

3.10. Polymerisation of ethylene and propylene using $\{Zr[\eta:\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)](SMe_2)Cl_2\}$ / MAO catalytic system

Polymerisations were performed in a thermostated and magnetically stirred 300 cm^3 Fischer–Porter appartus.

3.10.1. Ethylene

MAO (1.762 g; 30.4 mmol) was weighed in a glove box and toluene (15 cm^3) was added. The solution was thermostated to 25°C and allowed to equilibrate with ethylene at 2 bar (relative pressure). A colourless toluene solution (5 cm^3) of compound **6** (0.011 g; 0.026 mmol) was transferred into the reaction vessel and the pressure maintained at 2 bar. During the first minutes the solution turned to pale yellow while the polyethylene started precipitating. After 45 min the excess of ethylene was vented and the contents of the reactor treated with 100 cm^3 of a solution containing aliquots of 3 M HCl and methanol, for 1 h. The polyethylene was filtered, washed with acidified methanol and dried under reduced pressure for 4 h, at 60°C. No oligomer fraction was found after evaporation of the toluene layer. Yield, 3.55 g of polyethylene.

3.10.2. Propylene

Compound **6** (0.013 g; 0.031 mmol) and MAO (2.168 g; 37.3 mmol) were weighed and the reaction started using the same procedure as described above (reaction pressure: 2 bar; temperature: 25°C). After 25 h the reaction was stopped by venting the excess of propylene and treating the reaction mixture with acidified methanol. The toluene layer was separated from the aqueous one and dried over $MgSO_4$. After filtration, the toluene was removed under reduced pressure giving oligomeric polypropylene. Yield, 1.06 g.

Acknowledgements

We wish to thank the NATO and Junta Nacional de Investigação Científica e Tecnológica, Portugal, for fellowships (to PTG and AMM, respectively) and Dr. A.C. Fernandes and Mr. A.F. Gomes (IST-CQE, Portugal) for DSC and GPC measurements, respectively.

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