

Olefin polymerisation promoted by monodicarbollide complexes of group 4 metals

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Abstract

The behavior of $(C_2B_9H_{11})M(NEt_2)_2(NHEt_2)$ [$M = Ti$ (**1**), Zr (**2**)] mono-dicarbollide complexes in olefin and styrene polymerisation has been investigated. Compounds **1** and **2**, when activated by MAO ($Al/M = 100$ to 1000), polymerise ethylene with good activity. Surprisingly, **2** can also be activated with small amounts of triisobutylaluminum (TIBA, $Al/Zr = 3$ to 40). The ethylene polymerisation activity of the **2**/TIBA catalyst ($50^\circ C$, 5 atm, toluene–chlorobenzene) is greater than that reported for the $CpZrX_3/MAO$ catalysts but lower by about one or two orders of magnitude than zirconocene–MAO systems (e.g. Cp_2ZrCl_2/MAO , rac -(ethylene-bis-1-idenyl) $ZrCl_2/MAO$). The GPC (gel permeation chromatography) curve of the polyethylene sample obtained with **2**/TIBA catalyst ($50^\circ C$, 5 atm, toluene–chlorobenzene) is bimodal indicating that at least two species are active in this system and one is more active than the other. The **2**/MAO system ($50^\circ C$, 5 atm, toluene–chlorobenzene) slowly polymerises propylene to atactic polymer. Under the same experimental conditions 1-pentene does not polymerise at all. Compounds **1** and **2**, activated with MAO, produce syndiotactic polystyrene (sPS) with very low activity. Attempts to copolymerise styrene with ethylene by the **1**/MAO and **2**/MAO systems afforded a mixture of the two homopolymers. © 1998 Elsevier Science B.V.

Keywords: Group 4 metals; Dicarbollide; Ethylene polymerisation; Styrene polymerisation

1. Introduction

Monocyclopentadienyl $(C_5R_5)MX_3$ derivatives of the group 4 metals, when properly alkylated/activated with ionising agents as MAO, $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$ and $[HNR_3][B(C_6F_5)_4]$ catalyse the polymerisation of several unsaturated monomers including eth-

ylene and α -olefins², styrene [7,8]³ and conjugated dienes⁴. Cationic d^0 dialkyl complexes of general type $Cp'MR_2^+$ ($M = Ti, Zr$; $Cp' = C_5H_5, C_5Me_5$; $R = Me, CH_2Ph$) have been recognised as the active species in olefin poly-

² For MAO activated systems see [1–3]; for $B(C_6F_5)_3$ and $Ph_3CB(C_6F_5)_4$ activated systems see [4–8].

³ For MAO activated systems see [9–14]; for $B(C_6F_5)_3$ or $Ph_3CB(C_6F_5)_4$ activated systems see [15–18].

⁴ For MAO activated systems see [19–26]; for $B(C_6F_5)_3$ activated systems there are some unpublished results from our laboratory.

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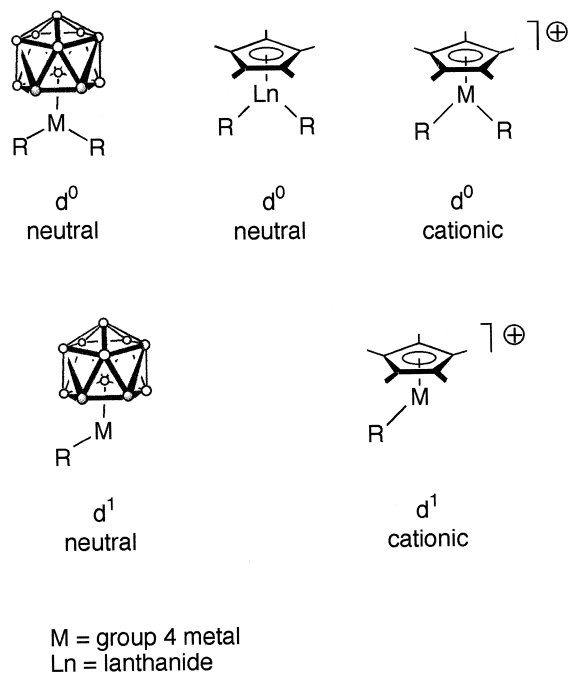
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merisation [6–8] by those systems. However, the identity of the species which are active in syndiospecific styrene polymerisation and conjugated diene polymerisation by $(C_5R_5)MX_3$ -based catalysts is unknown at present. ESR investigations of the catalytic systems based on ‘half-titanocene’ complexes $(C_5Me_5)TiR_3$ [27–30] and the polymerisation activity data of these systems [31] suggest that cationic d^1 complexes, ‘ $(C_5Me_5)TiR^+$ ’ are involved in styrene polymerisation. These Ti(III) species, which are probably stabilised by co-ordinated solvent or monomer, are produced in the polymerisation conditions via reduction of the initially formed $(C_5Me_5)MR_2^+$ ions and produce syndiotactic polystyrene through a metal assisted poly-insertion mechanism [30,32]. On the other hand several lines of experimental evidence suggest that $(C_5Me_5)TiR_2^+$ ions can also initiate the carbocationic polymerisation of styrene to atactic polymer [8,18]. The different activity observed for these two species in styrene polymerisation may reflect differences in Lewis acidity/electrophilicity, backbonding ability, co-ordinative unsaturation and steric properties, all of which are expected to influence the interaction of the metal ions with styrene.

One approach to understanding how steric and electronic factors influence the reactivity of $(C_5R_5)TiR_2^+$ and $(C_5R_5)TiR^+$ cations is to investigate the chemistry of structurally related species which have different charges, electron counts, and/or steric properties. For example, group 3 metal or lanthanide species of general type $(C_5R_5)MR_2$ are neutral isoelectronic analogues of $(C_5R_5)TiR_2^+$ (see Scheme 1).

Schaverein has recently shown that $[(C_5Me_5)Y(\mu-H)(O-2,6-tBu_2-C_6H_3)]_2$ reacts with terminal olefins to yield *trans*- $[(C_5Me_5)Y(O-2,6-tBu_2-C_6H_3)]_2(\mu-H)(\mu-CH_2-CH_2R)$ alkyl complexes, and catalyses the polymerisation of ethylene, 1-hexene and non conjugated dienes [33,34]. The reactivity of these species with styrene has not been reported.

Group 4 metal complexes of general type $(\eta^5-C_2B_9H_{11})MR_2$ and $(\eta^5-C_2B_9H_{11})MR$,



Scheme 1.

which incorporate the dianionic, 6-electron donor, $C_2B_9H_{11}^{2-}$ (dicarbollide, dc) in place of a $C_5R_5^-$ ligand, are also isoelectronic with $(C_5R_5)TiR_2^+$ and $(C_5R_5)TiR^+$ cations, respectively [35–40]. While such species are not yet known, the synthesis of related amide complexes $(\eta^5-C_2B_9H_{11})M(NR_2)_2(NHR_2)$ ($M = Ti, Zr$; $R = Me, Et$) has been reported recently [41]. In other work, it has been shown that $Cp_2Zr(NR_2)_2$ amide complexes can be activated for olefin polymerisation by MAO [42] and that treatment of *rac*-(ethylene-bis-indenyl) $Zr(NR_2)_2$ and *rac*- $Me_2Si(indenyl)_2Zr(NR_2)_2$ with AlR_3 reagents yields the corresponding metallocene dialkyls which can in turn be activated for polymerisation by MAO or cationic activators [43,44]. As an initial approach to studying the olefin polymerisation behavior of group 4 metal mono-dicarbollide complexes, we have investigated the behavior of $(\eta^5-C_2B_9H_{11})M(NEt_2)_2$ ($NHEt_2$) [$M = Ti$ (**1**), Zr (**2**)] complexes in olefin and styrene polymerisation using methylalumoxane (MAO) and triisobutylaluminum (TIBA) as activators.

2. Results

2.1. Olefin polymerisation in the presence of $(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{M}(\text{NEt}_2)_2(\text{NHEt}_2)$ ($\text{M} = \text{Ti}$ (**1**), Zr (**2**))

$(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{M}(\text{NEt}_2)_2(\text{NHEt}_2)$ [$\text{M} = \text{Ti}$ (**1**), Zr (**2**)], TIBA or MAO alone exhibit little if any ethylene polymerisation activity. However, combinations of **1** or **2** with the aluminium activators produce active catalysts (see Tables 1 and 2). Treatment of **1** with several equivalents of TIBA (Al/Ti molar ratio = 4–10) affords a catalyst which exhibits low activity in ethylene polymerisation (entries 1, 2). In contrast treatment of **1** with a large excess of MAO (Al/Ti molar ratio = 400) affords a catalyst which polymerises ethylene with good activity at 50°C and 1 atm of monomer pressure (entry 3). The activity of the **1**/MAO catalyst is comparable to that of $\text{CpTiCl}_3/\text{MAO}$ (entry 4) and superior to that of $\text{Cp}^*\text{TiCl}_3/\text{MAO}$ (entries 6, 7) under the same conditions. For a more realistic comparison, the activity of $\text{CpTiCl}_3/\text{MAO}$ and $\text{Cp}^*\text{TiCl}_3/\text{MAO}$ catalysts poisoned with two equivalents of diethylamine was investigated (entries 5, 8). Inspection of Table 1 shows that **1** is more active than the $(\text{C}_5\text{R}_5)\text{TiX}_3$ complexes after treatment with diethylamine.

Treatment of zirconium complex **2** with MAO affords a catalyst which polymerises ethylene with activity comparable to that of **1** under the same condition described above (Table 2, entries 9–14). The productivity of this catalyst does not depend strongly on MAO level (entries 9–11) and increases almost linearly with polymerisation time (entries 9, 12–14).

Surprisingly, activation of **2** with several equivalents of TIBA (Al/Zr molar ratio = 3–40) also produces catalysts exhibiting good activity for ethylene polymerisation at 50°C and 1 atm of monomer pressure (Table 2, entries 15–17). The productivity of this system does not increase when the Al/Zr molar ratio is increased from 10 to 40/1. Increasing the ethylene pressure from 1 to 5 atm (see entries 18–21) produces an increase of the productivity of both the **2**/MAO and **2**/TIBA catalysts.

The GPC curve of the polyethylene sample obtained with the **1**/MAO catalyst at 1 atm of monomer pressure (entry 3) is bimodal and the two broad components exhibit almost the same intensity. One fraction corresponds to high molecular weight polyethylene (M_w larger than 1×10^6 dalton) while the other corresponds to lower molecular weight material ($M_w = 45\,000$). The GPC curve of the sample obtained with **2**/MAO catalyst under the same condition (en-

Table 1
Polymerisation of ethylene using different titanium complexes as catalyst^a

Entry	Catalyst	Cocatalyst	Al/Ti molar ratio	Time (min)	Yield ^b (mg)
1	(dc)Ti(NEt ₂) ₂ (NHEt ₂)	TIBA	4	45	27
2	(dc)Ti(NEt ₂) ₂ (NHEt ₂)	TIBA	10	45	65
3	(dc)Ti(NEt ₂) ₂ (NHEt ₂)	MAO	400	45	441 ^c
4	CpTiCl ₃	MAO	400	45	335
5	CpTiCl ₃ + 2NHEt ₂	MAO	400	45	230
6	Cp*TiCl ₃	MAO	400	45	90
7	Cp*TiCl ₃	MAO	400	120	346
8	Cp*TiCl ₃ + 2NHEt ₂	MAO	400	45	19

^aPolymerisation conditions: 4.0×10^{-5} mol of the organometallic precursor; solvent = 40 ml of toluene; temperature = 50°C; ethylene pressure = 1 atm.

^bPolymerisation yields are average value of 3 runs and are affected by an error estimated as $\pm 5\%$.

^cThe GPC analysis of this polymer shows a bimodal curve with average molecular weight $M_w = 1\,120\,000$ dalton. The melting point of the polyethylene sample is $T_m = 131^\circ\text{C}$ (determined by DSC).

Table 2
Ethylene polymerisation with (dc)Zr(NEt₂)₂(NH₂Et₂)

Entry	Amount of catalyst (10 ⁵ mol)	Cocatalyst	Al/Zr molar ratio	Time (min)	Ethylene pressure (atm)	Yield (g)	T _m ^s (°C)
9 ^a	4.0	MAO	100	45	1	0.595	128
10 ^a	4.0	MAO	400	45	1	0.477 ^d	130
11 ^a	4.0	MAO	1000	45	1	0.420	127
12 ^a	4.0	MAO	100	20	1	0.298	127
13 ^a	4.0	MAO	100	80	1	0.697	128
14 ^a	4.0	MAO	100	120	1	0.890	130
15 ^a	4.0	TIBA	3	45	1	0.151	130
16 ^a	4.0	TIBA	10	45	1	0.922	131
17 ^a	4.0	TIBA	40	45	1	1.076	123
18 ^b	8.0	MAO	100	5	5	6.392 ^e	133
19 ^b	8.0	TIBA	40	5	5	7.195 ^f	124
20 ^b	4.0	TIBA	40	5	5	6.620	129
21 ^b	1.0	TIBA	40	5	5	3.630	130

^a Polymerisations carried out at 50°C in a 100 ml glass reactor (see Section 4).

^b Polymerisations carried out at 50°C in Buchi glass autoclave (1 l flask) (see Section 4).

^c Determined by DSC analysis.

^d $M_w = 105\,000$ dalton; $M_w/M_n = 50$.

^e $M_w = 94\,000$ dalton; $M_w/M_n = 15$.

^f The GPC analysis of this polymer shows a bimodal behavior and the prevalent component presents $M_w = 2200$ dalton and $M_w/M_n = 3$.

try 10) is very broad ($M_w/M_n = 60$) and the average molecular weight of the polymer is $M_w = 104\,000$ dalton. GPC analysis of the polyethylene sample obtained with the **2**/TIBA catalyst at high ethylene pressure (5 atm) (entry 19) exhibited a bimodal profile with one peak much more abundant than the other one (about 20:1). The largest peak corresponds to low molecular weight polyethylene with a narrow polydispersity ($M_w = 2200$ dalton; $M_w/M_n = 3.3$) whereas the latter corresponds to a polymer

with a higher molecular weight and a very broad polydispersity ($M_w/M_n = 20$ and $M_w = 100\,000$ dalton). The GPC curve of the sample obtained by **2**/MAO catalyst (entry 18) presents $M_w/M_n = 15$ and $M_w = 94\,000$ dalton.

These results suggest that several active species are formed in these catalytic systems. However, in the **2**/TIBA catalyst (50°C, 5 atm of ethylene) one of these species appears to be much more active than the others and mainly produces low molecular weight polyethylene.

Table 3
Polymerisation of styrene using (dc)M(NEt₂)₂(NH₂Et₂) (M = Ti(**1**), Zr(**2**)) as the catalyst^a

Entry	Catalyst	Cocatalyst	Al/M molar ratio	T (°C)	Time (h)	Yield (mg)	% sPs ^b
22	(dc)Ti(NEt ₂) ₂ (NH ₂ Et ₂)	TIBA	4	50	18	238	—
23	(dc)Zr(NEt ₂) ₂ (NH ₂ Et ₂)	TIBA	4	50	18	—	—
24	(dc)Ti(NEt ₂) ₂ (NH ₂ Et ₂) ^c	MAO	800	80	67	216	8
25	(dc)Zr(NEt ₂) ₂ (NH ₂ Et ₂) ^c	MAO	800	80	67	113	12
27 ^d	CpTiCl ₃	MAO	1000	90	0.2	3170	89

^a Polymerisation conditions: 4.0×10^{-5} mol. of catalyst, toluene (30 ml), styrene (10 ml).

^b Evaluated by w/w % after extraction of the raw polymer with 2-butanone.

^c The toluene solution of the organometallic precursor was treated with TIBA at room temperature before the injection into the reactor (see Section 4).

^d This run was reported for comparison (see Macromol. Chem. Phys 196 (1995) 3015).

The melting points of the polymers obtained by **2**/MAO and **2**/TIBA catalysts (Table 2) are lower than that reported for linear high molecular weight polyethylene (134°C). This finding can be explained considering the low molecular weight of the polymer products obtained by these catalysts.

We also explored the polymerisation of higher olefins in the presence of **2** activated with TIBA or MAO. Propene was polymerised to atactic polymer with low activity while 1-pentene does not polymerise at all under the same conditions (see Section 4).

2.2. Styrene polymerisation in the presence of **1** and **2**

Mixtures of either **1** and **2** with TIBA (Al/M molar ratio = 4) do not polymerise styrene at all (Table 3, entries 22, 23). On the contrary, when the same organometallic precursors were treated with TIBA (Al/M molar ratio = 20) at room temperature and then injected in the reactor containing the mixture of styrene and the proper amount of MAO thermostated at 80°C, the polymer recovered contained traces of syndiotactic polystyrene identified by DSC analysis and ¹H NMR spectroscopy (entries 24, 25). Attempts to copolymerise styrene with ethylene afforded a mixture of the two homopolymers (see Section 4).

3. Discussion

The group 4 metal mono-dicarbollide complexes **1** and **2**, when activated with MAO, polymerise ethylene with good activity at 1 atm of monomer pressure and 50°C. Despite the presence of co-ordinated amine the productivity of the dicarbollide-Ti catalyst is comparable with that of the corresponding base-free cyclopentadienyl catalysts CpTiCl₃/MAO and (C₅Me₅)TiCl₃/MAO. Under the same experimental conditions, the **1**/MAO and **2**/MAO systems exhibit similar ethylene polymerisation

activity but the former produces polymers with higher average molecular weights (compare entries 3 and 10).

On the contrary, **2**/TIBA is much more active than **1**/TIBA at 1 atm of ethylene pressure. Interestingly, at 5 atm of ethylene pressure the **2**/TIBA catalyst exhibits a polymerisation activity ($A = 20$ kg polymer/g Zr × h) which is higher than those observed for CpZrR₃-MAO ($A = 4$ kg polymer/g Zr × h) and CpZrR₃-B(C₆F₅)₃ systems ($A = 6$ kg polymer/g Zr × h) under the same conditions [6]. However, the activities of these half-sandwich catalysts are significantly lower than those of metallocene catalysts, e.g. Cp₂ZrCl₂/MAO ($A = 600$ kg polymer/g Zr × h); rac-(ethylene-bis-1-indenyl)₂ZrCl₂/MAO ($A = 420$ kg polymer/g Zr × h) [45–47].

As described in the previous section, GPC analysis of the polyethylene samples produced by dicarbollide complexes **1** and **2** indicates that these catalysts contain several active species. Interestingly, in the **2**-based systems one species is much more active than the other ones and produces a low molecular weight polyethylene fraction. The structure of this species is unknown at present.

Both **1** and **2**, when activated with MAO and TIBA, are poorly active in syndiospecific styrene polymerisation (sPS). Only traces of sPS were obtained in some cases by these systems (Table 3) most probably arising from the decomposition of the catalysts to minor species. One possible reason for this lack of activity is that reductive decomposition to Ti(III) may be disfavoured by the dicarbollide ligand. This result suggests that electronic requirements, namely d¹ electronic configuration of the metal centre, could be determining the activity of the catalysts in sPS polymerisation.

The failure to copolymerise styrene with ethylene by dicarbollide catalysts also confirms that the active species for styrene and olefin polymerisation are different in the catalytic systems based on group 4 metal complexes [48,49].

4. Experimental

4.1. General procedures and materials

All manipulations were performed under nitrogen atmosphere using standard Schlenk type techniques or a Braun dry box. Solvents were distilled from the appropriate drying/deoxygenating agents and stored under nitrogen prior to use. Toluene (Carlo Erba) was treated with concentrated sulphuric acid, followed by washing with saturated bicarbonate solution and distilled water to remove thiophene. It was dried over calcium chloride and finally distilled from sodium-benzophenone before the use. Polymerisation grade ethylene was purchased from Società Ossigeno Napoli (S.O.N.) and used without any further purification. Styrene (Aldrich) was purified by distillation at reduced pressure from calcium hydride. Al(*i*-but)₃ (TIBA) purchased from Aldrich, was checked for the purity by ¹H NMR before use. MAO, purchased from Witco as 30% w/w toluene solution, was dried under vacuum at 50°C to remove toluene and AlMe₃ and used as white solid. CpTiCl₃ [50], Cp*TiCl₃ [51], (η⁵-C₂B₉H₁₁)Ti(NEt₂)₂(NH₂) [41] and (η⁵-C₂B₉H₁₁)Zr(NEt₂)₂(NH₂) [41] were prepared according to the literature.

Gel Permeation Chromatography (GPC) measurements were performed at 135°C on a Waters 150-C equipped with Progel TSK columns using *o*-dichlorobenzene as solvent. The calibration was based on standard polystyrene samples with narrow molecular weights distributions.

Differential Scanning Calorimetric measurements (DSC) were carried out on Du Pont calorimeter using a heating rate of 10°C/min.

4.2. Polymerisation procedures

Polymerisation runs 1–17 were carried out with the following general procedure. Toluene (35 ml) and the proper amount of MAO or TIBA were introduced into a 100 ml glass flask equipped with a magnetic stirrer and thermostated at the polymerisation temperature. The

flask was evacuated and the nitrogen atmosphere was replaced with ethylene. The polymerisations were started by introducing the organometallic precursor dissolved in 5 ml of chlorobenzene. Polymerisation runs were stopped with 5 ml of ethanol acidified with HCl, and the polymer product was coagulated with a large excess of acidified ethanol, recovered by filtration, washed with fresh ethanol and dried in vacuo at 70°C.

For runs 18–21, 65 ml of a toluene containing the proper amount of MAO or TIBA were introduced into a Buchi glass autoclave equipped with a mechanical stirrer and thermostated at 50°C in nitrogen atmosphere. The proper amount of (η⁵-C₂B₉H₁₁)Zr(NEt₂)₂(NH₂) dissolved in 15 ml of chlorobenzene was introduced into the autoclave and ethylene was fed at 5 atm. The monomer pressure was kept constant over the polymerisation runs. After coagulation with ethanol acidified with HCl, the polymers were filtrated, washed with methanol and dried in vacuo at 70°C.

Propylene polymerisation was carried out following the procedure described for runs 17–20. The autoclave was charged with MAO (1.856 g, 32 mmol) and toluene (65 ml) and thermostated at 50°C. (η⁵-C₂B₉H₁₁)Zr(NEt₂)₂(NH₂) (36 mg, 4 μmol) in chlorobenzene (15 ml) was added into the reactor. Propylene was fed at 5 atm to start the polymerisation and the monomer pressure was kept constant for the polymerisation time (2 h). Yield 100 mg of atactic polypropylene.

1-Pentene polymerisation was carried out in a 100 ml glass flask equipped with a magnetic stirrer. The flask was charged with MAO (928 g, 16 mmol), toluene (3 ml) and 1-pentene (5 ml) and thermostated at 25°C. The polymerisation was started by introducing a solution of (η⁵-C₂B₉H₁₁)Zr(NEt₂)₂(NH₂) (18 mg, 4 μmol, Al/Zr molar ratio = 400) in chlorobenzene (5 ml) and run for 12 h. No polymer or oligomers were recovered from the solution after treatment with acidified methanol and removal of the polymerisation solvent.

Styrene polymerisation experiments (runs 22–26) were carried out in a 100 ml glass flask equipped with a magnetic stirrer. For runs 22–23, the flask was charged with toluene (30 ml), the proper amount of TIBA and styrene (5 ml) in the order and the solution was thermostated at 50°C. The polymerisation was started by injecting a slurry of **1** or **2** (40 μ mol) in toluene (5 ml). The polymer was coagulated with ethanol acidified with HCl, isolated by filtration and dried in vacuo at 80°C. For runs 25–26 the flask was charged with toluene (30 ml), the proper amount of solid MAO and styrene (5 ml) in the order and the mixture was thermostated at 80°C. The polymerisation was started by injecting a slurry of **1** or **2** (40 μ mol) in toluene (5 ml) precontacted with TIBA (Al/M molar ratio = 20) for 10 minutes at room temperature. The polymer was coagulated with ethanol acidified with HCl, isolated by filtration and dried in vacuo at 80°C. sPS was isolated by extraction of the raw polymer with 2-butanone.

4.3. Styrene–ethylene copolymerisation

A 100 ml glass reactor was charged with toluene (30 ml), styrene (10 ml) and solid MAO (928 g, 16 mmoles). The flask was evacuated, ethylene was fed at 1 atm and the solution was thermostated at 50°C. Polymerisation was started by injecting a solution of (η^5 -C₂B₉H₁₁)Ti(NEt₂)₂(NH₂Et₂) (16 mg, 40 μ mol, Al/Ti molar ratio = 400) in toluene (5 ml) and run for 4 hours. The reaction was stopped by adding 2 ml of methanol acidified with HCl and the polymer product coagulated in large excess of methanol, recovered by filtration, washed with methanol and dried in vacuo at 80°C (Yield 81 mg). The polymer was fractionated with 2-butanone in a Kumagawa extractor. Polyethylene (16 mg) and atactic polystyrene (57 mg) were identified by ¹H NMR spectroscopy and DSC analysis in the insoluble and soluble fractions respectively.

Styrene and ethylene copolymerisation carried out in the same experimental conditions

using (η^5 -C₂B₉H₁₁)Zr(NEt₂)₂(NH₂Et₂) produced 197 mg of polymer which was shown to consist of polyethylene (90 mg) and of atactic polystyrene (107 mg).

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