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The versatile chemistry of metallocene polymerisation catalysts: new developments in half-sandwich complexes and catalyst heterogenisation

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Abstract

Metallocene complexes of Group 4 metals are playing an increasingly important role in olefin polymerisation catalysis. This contribution surveys several aspects of the chemistry of metallocene catalysts that are being pursued in our laboratory at present, namely the application of half-sandwich complexes as catalysts for high-molecular weight elastomeric polypropene, unusual C–H activation reactions of zirconium half-sandwich complexes, the development of 14-electron borole complexes as neutral analogues of cationic $[Cp_2ZrR]^+$ catalysts, and the heterogenisation of MAO-free zirconocene catalysts on borate-functionalised silica. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Polypropene; Polyethylene; Polymerisation catalysis; Half-sandwich complex; Catalyst deactivation; Catalyst heterogenisation; Silica support; Zirconocene catalysts

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1. Introduction

The advent of catalysts based on metallocene complexes of titanium, zirconium, and hafnium is the most significant development in olefin polymerisation catalysis over the last two decades [1–3]. Numerous lines of evidence suggest that the active species are electron-deficient cationic alkyl complexes of the type $[Cp_2M–R]^+$ [4,5]. These species can be generated either by activating a metallocene dihalide Cp_2MCl_2 with an aluminium alkyl, notably with methylaluminoxane (MAO) [6], or more directly by reacting metallocene dialkyls Cp_2MR_2 with a cation generating agent, i.e., $B(C_6F_5)_3$, $[CPh_3][B(C_6F_5)_4]$ or $[HNMe_2Ph][B(C_6F_5)_4]$. Our research has been almost exclusively concerned with these MAO-free 'well-defined' catalysts. The chemistry of bis-Cp catalyst, the mode of olefin insertion and the nature of resting states, i.e. now reasonably well-understood. Related mono-Cp half-sandwich complexes have been much less investigated. This article summarises some recent results on the reactivity of half-sandwich complexes, including the synthesis of elastomeric polypropene, the contribution of C–H activation reactions to catalyst deactivation and, unusually, catalyst self-reactivation, before describing preliminary results on the heterogenisation of MAO-free metallocene catalysts on silica supports.

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1.1. Half-sandwich complexes

We have become interested in comparing the catalytic behaviour of bis-Cp metallocene complexes with related mono-Cp half-sandwich compounds. Although it is tempting to extrapolate the chemistry of metallocene complexes to that of half-sandwich complexes, there are significant and sometimes surprising differences.

Whereas, as stated above, the active species in metallocene catalysts is the 14-electron cation $[Cp_2MR]^+$, the replacement of a cyclopentadienyl ligand by an alkyl group in a half-sandwich complex affords the 10-electron complex $[CpMR_2]^+$ [7,8]. Such a species is even more electron-deficient, sterically less hindered and possesses two rather than one vacant coordination sites for monomer binding. We were particularly interested in the question whether these properties would enhance chain growth through more facile access by the monomer or might lead to more frequent chain termination (and hence, allow control of the polymer molecular weight) and chose to explore propene polymerisations with the system $Cp^*TiMe_3/B(C_6F_5)_3$ [9]. This catalyst was first studied by Quyoum et al. [10,11] who reported facile ethylene polymerisation even at very low temperatures but found only low propene polymerisation activity in dichloromethane to give polymers of modest molecular weight ($M_w \approx 15{,}000$).

In our hands, Cp^*TiMe_3 activated with $B(C_6F_5)_3$ in either toluene or liquid propene proved to be highly active for the polymerisation of propene over the examined temperature range of −70°C to 20°C, to give atactic polypropene (a-PP) of unusually high molecular weight [9]. Whereas a-PPs of the type obtained as by-products of the stereospecific propene polymerisation with conventional Ziegler catalysts are typically waxes or oils, the polymers resulting from $Cp^*TiMe_3/B(C_6F_5)_3$ are tough, non-sticky elastomers with M_w values in the range of 4×10^5 to 4×10^6 (Table 1). Elastomeric a-PP with similar properties but lower molecular weight ($M_w \approx 2\text{–}4 \times 10^5$) has recently been reported by Resconi et al. using a $Me_2Si(Flu)_2ZrCl_2/MAO$ catalyst [12]. The $Cp^*TiMe_3/B(C_6F_5)_3$ catalyst gives particularly high molecular weights in liquid propene at −45°C. The M_w values of the a-PP obtained under these conditions are almost linearly proportional to the duration of the experiment and increase from ca. 1×10^6 after 40 s to 4×10^6 after 4 min (Fig. 1). The polydispersity remains very narrow, $M_w/M_n = 1.7\text{–}2.0$. In toluene at −20°C, polymer with an even narrower polydispersity was obtained ($M_w = 1.1 \times 10^6$, $M_w/M_n = 1.43$). Polymers with similar M_w and M_n values are obtained at 20°C in hexane, where the reaction is slower and easier to control due to the limited extent of ionisation of $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$. It appears that a substantial

Table 1
Propene polymerisations with $Cp^*TiMe_3/B(C_6F_5)_3$

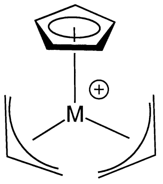
Ti [μmol]	B [μmol]	Propene	Solvent	Temperature [°C]	Time [s]	Yield PP [g]	Productivity[a] ($\times 10^{-6}$)	M_w ($\times 10^{-3}$)	M_w/M_n
40	40	1 bar	toluene	70	60	0.134	0.69	32	4.0
20	20	1 bar	toluene	0	60	1.366	2.76	518	2.9
20	20	1 bar	toluene	−20	45	1.520	2.69	1103	1.4
20	20	40 ml	–	−45	40	0.913	4.1[b]	1079	1.7
20	20	100 ml	–	−45	120	3.47	5.2[b]	2275	2.0
120	120	500 ml	–	−45	240	42.0	5.25[b]	3966	2.0

[a] In g PP $(mol\ Ti)^{-1}\ [C_3H_6]^{-1}\ h^{-1}$.
[b] In g PP $(mol\ Ti)^{-1}\ h^{-1}$.

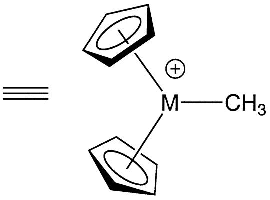
fraction of active centres has living characteristics under these conditions. Living propene polymerization has previously been found for heterogeneous vanadium catalysts, which polymerise propene very slowly at -78°C [13,14], and more recently with $Me_2Si(Flu)(NBu^t)TiCl_2$ catalysts which give low molecular weight polymers [15].

Surprisingly, although 1-alkene polymerizations with $CpTiCl_3/MAO$ and Cp^*TiCl_3/MAO have been reported at 50–60°C [16–18], $Cp^*TiMe_3/B(C_6F_5)_3$ is poisoned by $AlMe_3$ or $AlBu^i_3$ under mild conditions, even if significantly less than one AlR_3 per metal centre is present [9]. Both the catalytic activity and the polymer molecular weight are drastically reduced, and instead of the very narrow polydispersities of the AlR_3-free system, very broad and even bimodal distributions are found. The origins of this unexpected behaviour are as yet unexplained; whereas bis-Cp complexes form stable but catalytically highly active $AlMe_3$ adducts of the type $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+$ [19], NMR investigations have so far failed to provide evidence for the formation of analogous adducts $[Cp^*TiMe(\mu\text{-}Me)_2AlMe_2]^+$ that might reasonably have been expected.

The bis(allyl) half-sandwich cations $[CpM(\eta\text{-allyl})_2]^+$ (**A**) (M = Zr or Hf) are isoelectronic with the metallocene cations $[Cp_2MR]^+$ (**B**), and similar reactivity patterns might be expected. We have prepared zwitterionic bis(allyl) complexes of zirconium and hafnium by adding $B(C_6F_5)_3$ to the diene complexes $(Cp'')M(\eta^3\text{-allyl})(\eta^4\text{-diene})$ [**1**, $Cp'' = 1,3\text{-}C_5H_3(SiMe_3)_2$] on addition of $B(C_6F_5)_3$ (Eq. (1)) [20,21]. The borane attacks exclusively one of the terminal carbon atoms of the diene unit to give **2**; the metal centre is stabilised by two agostic interactions with the B–CH_2 hydrogen atoms. The crystal structure of the zirconium complex is shown in Fig. 2.



A



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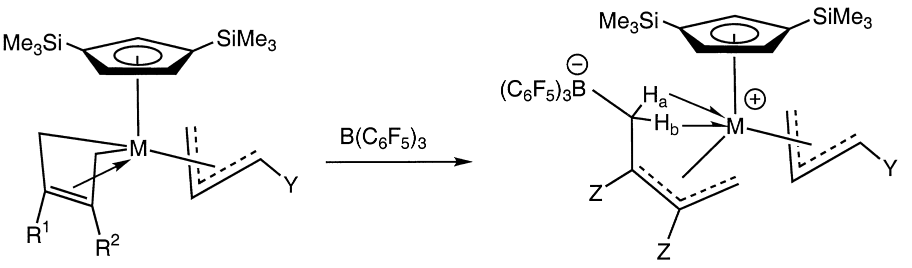


(1)

2a - c

M = Zr, Hf
1a, $R^1 = R^2 = Me$, Y = H
1b, $R^1 = Me$, $R^2 = H$, Y = H
1c, $R^1 = R^2 = H$, Y = Me

Complexes **2a** (M = Zr, Hf) readily polymerise ethylene (M_w up to ca. 3×10^5) but do not react with propene. In this case, too, the catalyst is poisoned by aluminium alkyls. Mixtures of **1** and

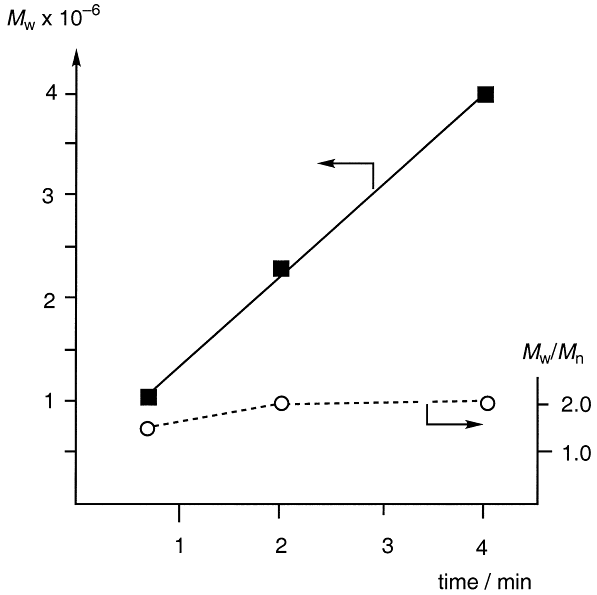


Fig. 1. Dependence of the molecular weight of a-PP obtained with Cp* $TiMe_3/B(C_6F_5)_3$ on the reaction times (liquid propene, −45°C).

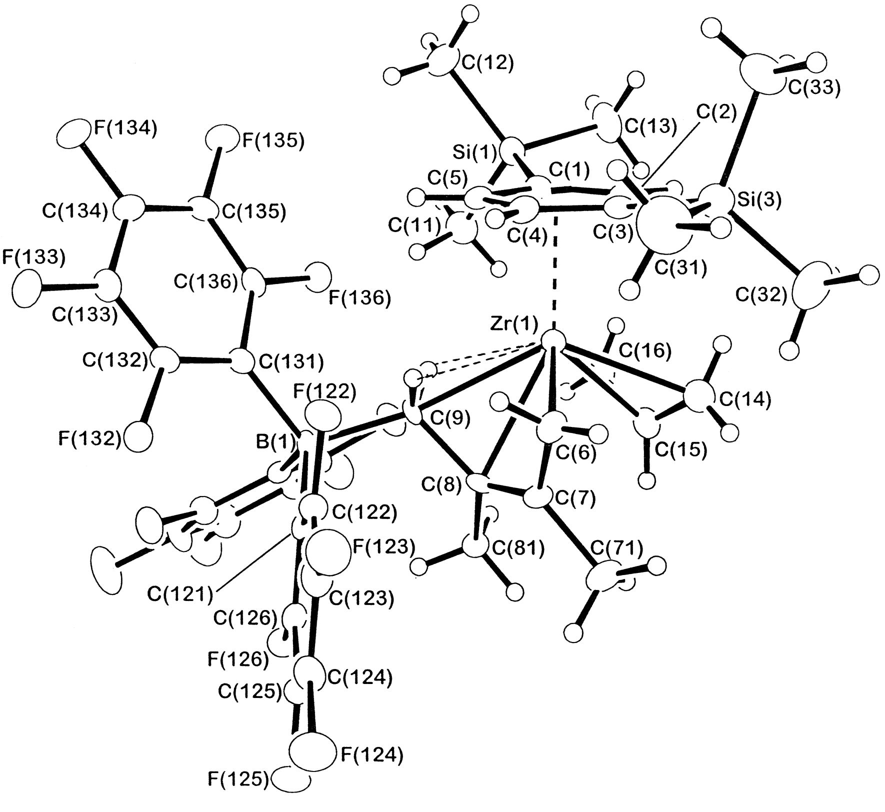


Fig. 2. Molecular structure of **2a**.

$[CPh_3][B(C_6F_5)_4]$ give high molecular weight polyethylene (M_w for the soluble fraction $\approx 1.2 \times 10^6$) with very broad polydispersities [21]. By contrast, the cationic hafnium analogue $[Cp^*Hf(\eta^3\text{-}CH_2CMeCH_2)_2][B(C_6F_5)_4]$, which is formed on treatment of $Cp^*Hf(C_4H_7)_3$ with $[HNMe_2Ph][B(C_6F_5)_4]$, reacts with propene to give atactic oligomers ($M_w \approx 5000$) [22].

The productivity of catalysts of type **2** is limited by their thermal instability, which depends strongly on the degree of substitution of the dienyl moiety. While **2a** ($R^1 = R^2 = Me$) is stable at room temperature, **2b** decomposes slowly above 0°C, and **2c** ($R^1 = R^2 = H$) undergoes a deactivation reaction to **3c** which is about 40% complete even at −60°C (Eq. (2)). These deactivation reactions of **2** are of a type not seen in bis(cyclopentadienyl) chemistry; they involve C–H activation of a $B\text{–}CH_2$ methylene group and loss of the allyl ligand as alkene, accompanied by the migration of a C_6F_5 substituent from boron to zirconium to give the boryldiene complexes **3**. Although $B(C_6F_5)_3$ is widely used as a catalyst activator because of its remarkable chemical stability, suitably electrophilic metal centres evidently mediate its facile degradation via fast C_6F_5 boron-to-metal transfer even under very mild conditions. The boryldiene complexes **3** are fluxional; the *o*-F atom of one C_6F_5 group of the $B(C_6F_5)_2$ moiety is coordinated to the metal centre. The crystal structure of **3b** is shown in Fig. 3.

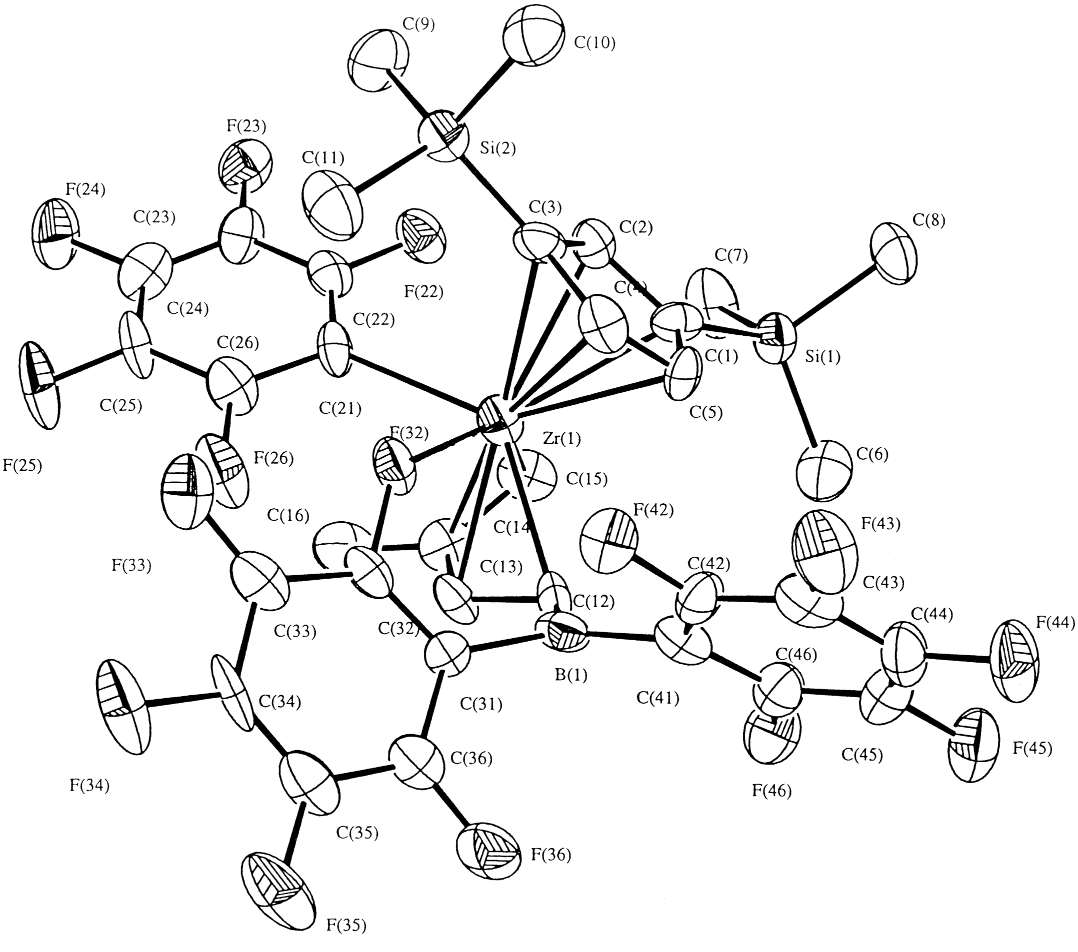
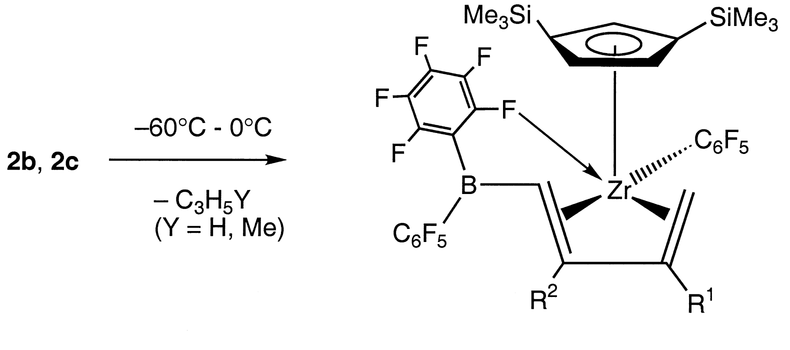


Fig. 3. Molecular structure of the catalyst deacivation product **3b**. Selected bond lengths (Å): Zr–C(21) 2.342(10), Zr–C(12) 2.327(10), Zr–C(13) 2.405(10), Zr–C(14) 2.498(10), Zr–C(15) 2.292(9), C(12)–B(1) 1.514(15).

These boryldiene complexes are catalytically inactive and are not reactivated by the addition of aluminium alkyls. Remarkably, the transformation of **2** to **3** is specific to zirconium and was not detected for the hafnium compounds **2** (M = Hf) which decompose via as yet unknown pathways.



(2)

3b, 3c

The formation of metal-C_6F_5 species such as **3** does not, however, represent irreversible catalyst deactivation. While initial polymerisation attempts with **3b** under an ethene atmosphere in the presence of 28 equivalents of $AlMe_3$ indicated no activity, prolonged exposure to 6 bar ethylene pressure at 60°C showed a slowly increasing activity after an induction period of ca. 10 min (Fig. 4a). NMR studies confirmed that the complexes **3b** and **3c** undergo a further C–H activation process generating C_6F_5H, accompanied by metal-mediated ring closure of the $C_4B(C_6F_5)$ fragment to give complexes of type **4** which contain the novel borole ligand $C_4H_4B(C_6F_5)$ (Eq. (3)) [23]. These

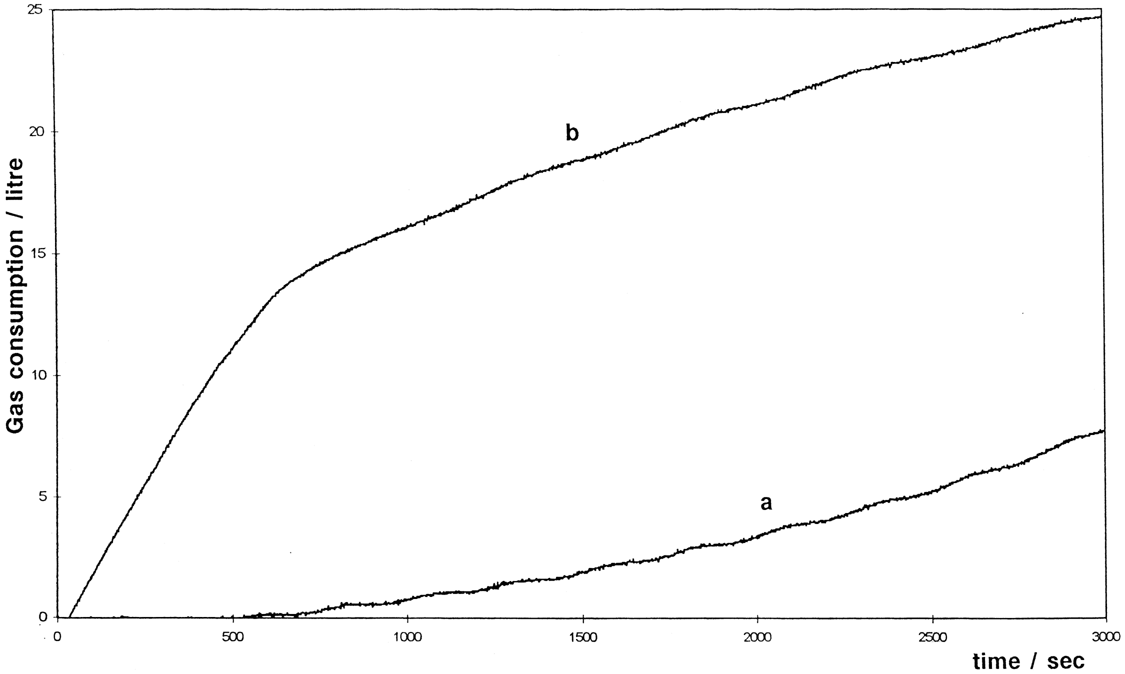


Fig. 4. Ethylene polymerisations with (a) complex **3b**/28 $AlMe_3$; (b) complex **4b** · Et_2O/26 $AlMe_3$, showing the time dependence of gas consumption at 50°C under 6 bar ethylene pressure.

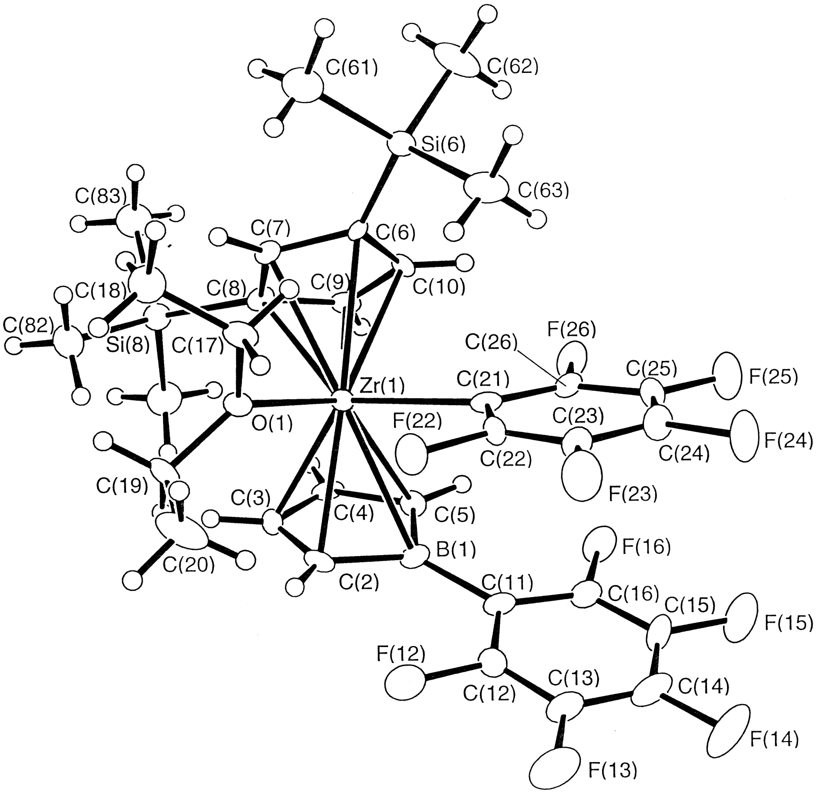
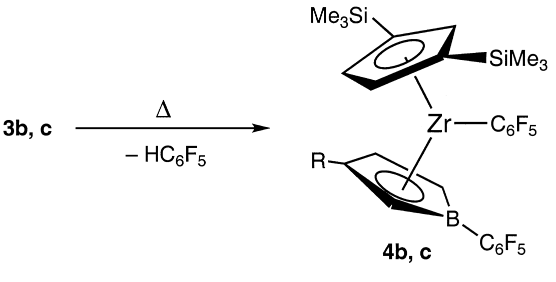


Fig. 5. Molecular structure of **4c** · Et_2O.

compounds are isolated as the crystalline ether adducts **4** · Et_2O. Similar complexes can be conveniently synthesised in a one-pot procedure by mixing $Cp''Zr(\eta^3\text{-}C_4H_7)(\eta^4\text{-}C_4H_6)$ (made from $Cp''ZrCl_3$ and $MeCH{=}CHCH_2MgCl$) with $B(C_6F_5)_3$ for several days at room temperature. The crystal structure of **4c** · Et_2O is shown in Fig. 5. Interestingly, the bonding of the metal to the borole ring, as judged from the zirconium–carbon distances, is stronger than to the $C_5H_3(SiMe_3)_2$ ligand.



(3)

Complex **4** is a 14-electron neutral compound and isoelectronic with the catalytically active cation $[Cp_2ZrR]^+$. It should, therefore, be an active catalyst once the metal-bound C_6F_5 ligand is exchanged for alkyl group. Such a ligand exchange is indeed observed when **4** · Et_2O is mixed with $AlMe_3$; these mixtures polymerise ethylene with good activities and *without* an induction period (Fig. 4b).

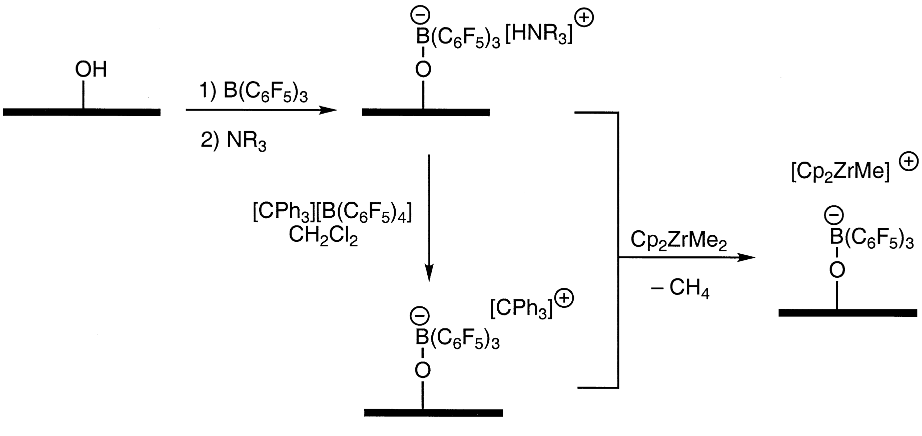
Essentially identical activities are observed with MAO as the activator, and increasing the MAO:Zr ratio from 25:1 to 500:1 does not lead to a significant activity enhancement. It appears that since **4** is already a 14-electron compound, the usual role of MAO as a Lewis acid to generate such a 14-electron metallocene species is not required.

The transformations depicted in Eqs. (1)–(3) represent, to our knowledge, a unique example where the conversion of an active catalyst (**2**) to a deactivation product (**3**) is followed by a subsequent rearrangement to a new catalyst precursor (**4**), a case of *catalyst self-reactivation.*

1.2. Heterogenisation of metallocene catalysts

Heterogenisation of soluble metallocene catalysts is essential if the advantages these catalysts offer are to be harnessed in gas phase or slurry polymerisation processes. Heterogenisation enables the morphology of the polymer particles to be controlled, to give free flowing polymer resins with minimal reactor fouling. The process usually involves the treatment of silica, alumina or zeolites with MAO followed by impregnation with the required metallocene dihalide [24–26]. An alternative strategy for the preparation of heterogenised metallocenes involves the intercalation of metallocene cations into phyllosilicates by ion-exchange with the interlamellar cations, however, these materials still require activating with MAO [27]. We have developed methods for catalyst heterogenisation utilising amorphous silica which involve the conversion of surface OH groups into -$OB(C_6F_5)_3$ anions to generate a polyanionic support for active $[Cp_2ZrMe]^+$ species. This method of heterogenisation has the advantage that the active cationic species remains attracted to the support by electrostatic forces and does not require anchoring via a covalent tether. Furthermore, although normal heterogenisation methods may permit the use of less MAO than the homogeneous system [24], our catalysts are active in the absence of MAO.

High surface area silica was dehydroxylated in vacuo at 450°C for a period of 5–8 h. Initial attempts to generate catalysts directly by treating silica with a light petroleum solution of $B(C_6F_5)_3$ followed by an excess of Cp_2ZrMe_2 and $AlMe_3$ were not successful (Scheme 1). However, treatment of silica with $B(C_6F_5)_3$ followed by dimethylaniline gave a substrate which on contact with toluene solutions of either $Cp_2ZrMe_2/AlMe_3$ mixtures or with Cp_2ZrMe_2 on its own generated catalysts



Scheme 1.

which showed good activity for the polymerisation of ethylene at 1 bar pressure. Elemental analysis indicated that this material contains ca. 8% carbon. The substrate is therefore formulated as approximately $[B(C_6F_5)_3(SiO_2)_{50}]^-[PhNMe_2H]^+$ and this formulation has been used in subsequent calculation of catalyst productivities. Preliminary TEM indicates that the activator particles are approximately 15 μm in diameter and essentially spherical. Early EDX results suggest even distribution of borate functions over the substrate. Further, more detailed studies are planned with SEM, TEM/PEELS and XPS. Other bases, such as 2,6-di-*t*-butylpyridine or proton sponge, also lead to ammonium salts of surface-bound $[\text{-OB}(C_6F_5)_3]^-$ but do not react efficiently with Cp_2ZrMe_2 and give materials of low catalytic activity. Representative polymerisation data are collected in Table 2.

As is not unusual for heterogenised catalysts [25], the activities are lower than those of homogeneous catalysts under comparable conditions. The polymer samples were obtained as free-flowing grains of apparently much higher bulk density than material produced by homogeneous catalysts. TEM studies of the polymer particles indicated that although of similar shape to the treated silica particles, they were much larger at 80 μm in diameter.

Initial results gave polymers with rather broad polydispersities. Typical GPC diagrams are shown in Fig. 6. It was suspected that broad molecular weight distributions could arise if some homogeneous catalyst was present in the slurry and therefore, a fraction of the isolated polymer was due to polymerisation in the solution phase. Such a situation can, for example, occur if excess $B(C_6F_5)_3$ is present which may not be removed completely by washing with hexane, so that reaction with excess Cp_2ZrMe_2 gives catalytically active $Cp_2ZrMe(\mu\text{-Me})B(C_6F_5)_3$. Indeed, suspending the hexane washed catalyst in toluene and allowing the solids to precipitate, gave a supernatant which produced a polymer of comparatively low molecular weight and narrow polydispersity typical for a homogeneous reaction, while the precipitate gave much higher molecular weight polyethylene (cf. Table 2, entries 3 and 4).

The activities and molecular weights obtained with the ansa-metallocene *rac*-$Me_2Si(Ind)_2ZrMe_2$ are comparable to Cp_2ZrMe_2 (Table 2, entries 9 and 10).

Supports containing $[CPh_3]^+$ as the activator are prepared by ion exchange of $[(SiO_2)_{50}B(C_6F_5)_3]^-[HNMe_2Ph]^+$ with $[CPh_3][B(C_6F_5)_4]$ in dichloromethane (Scheme 1). The yellow colour is indicative of $[CPh_3]^+$ cations and colour loss provides a visual indication of reaction

Table 2
Ethylene polymerizations with $[(SiO_2)_{50}B(C_6F_5)_3][HNMe_2Ph]/Cp_2ZrMe_2$ and $Me_2Si(Ind)_2ZrMe_2$ in the presence and absence of $AlMe_3$

Run	Metallocene	Supported activator [μmol]	Zr [μmol]	$AlMe_3$ [μmol]	Temperature [°C]	Polymer yield [g]	Productivity[a]	M_w	M_w/M_n
1	Cp_2ZrMe_2	8.4	100	500	50	0.495	0.36	94,000	45
2	Cp_2ZrMe_2	42	500	2500	50	1.243	0.18	78,000	50
3	Cp_2ZrMe_2	supernatant	500	2500	60	0.515	0.07	1900	1.8
4	Cp_2ZrMe_2	precipitate of run 3			60	1.518	0.21	105,000	14
5	Cp_2ZrMe_2	8.4	100	–	30	0.646	0.15	477,000	9.5
6	Cp_2ZrMe_2	8.4	100	–	60	1.529	0.37	164,000	6.2
7	Cp_2ZrMe_2	8.4	100	–	80	0.818	0.19	122,000	9.3
8	Cp_2ZrMe_2	42	100	–	60	3.235	0.15	174,000	6.6
9	$Me_2Si(Ind)_2ZrMe_2$	8.4	100	–	60	2.64	0.63	75,000	12
10	$Me_2Si(Ind)_2ZrMe_2$	8.4	50	–	60	2.68	0.64	110,000	11

[a] In 10^6 g PE $(\text{mol Zr})^{-1}$ h^{-1} bar^{-1}.

Conditions: 40 ml toluene, 1 bar ethene pressure, 30 min reaction time.

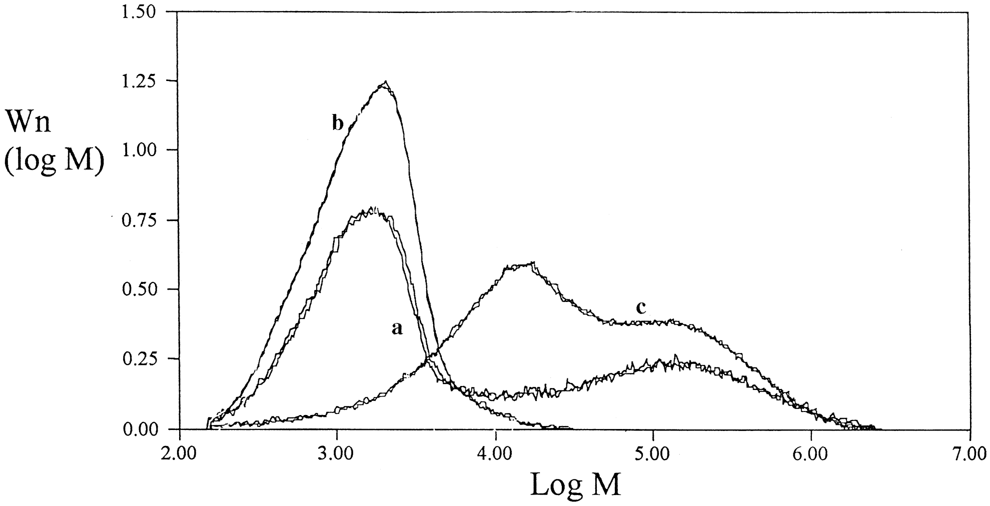


Fig. 6. Gel permeation diagrams of polyethylenes obtained with $[(SiO_2)_{50}B(C_6F_5)_3][HNMe_2Ph]/Cp_2ZrMe_2/AlMe_3$. (a) Product of as-prepared hexane-washed catalyst. (b) Product obtained from the supernatant of a toluene suspension. (c) Polymer resulting from the precipitate of (b).

with Cp_2ZrMe_2. The $[CPh_3]^+$ containing support leads to polyethylene with significantly higher molecular weight than the anilinium-activated catalyst (Table 3).

2. Experimental section

All manipulations were carried out using Schlenk, vacuum-line and glove box techniques. Light petroleum (bp 40–60°C), toluene and diethyl ether were distilled under nitrogen from sodium–potassium alloy. Deuterated solvents were dried over 4 Å molecular sieves and deoxygenated via several freeze–thaw cycles. $AlMe_3$ (97%, Aldrich) was used as purchased. The compounds Cp_2ZrMe_2 [28], $B(C_6F_5)_3$ [29] and $[CPh_3][B(C_6F_5)_4]$ [30,31] were prepared by literature methods. NMR spectra were recorded on a Bruker DPX300 instrument. Polymer molecular weights were determined by gel permeation chromatography (PL gel column; 1,2-dichlorobenzene, 140°C). Powders were dispersed in solvent and pipetted onto holey carbon grids for transmission electron microscopy in a Philips CM20 operated at 200 keV equipped with a Super ATW light element EDX detector (Oxford Instruments).

Table 3
Ethylene polymerizations with $[(SiO_2)_{50}B(C_6F_5)_3][CPh_3]/Cp_2ZrMe_2$

Run	Metallocene	Supported activator [μmol]	Zr [μmol]	Temperature [°C]	Polymer yield [g]	Productivity[a]	M_w	M_w/M_n
11	Cp_2ZrMe_2	8.4	50	60	0.555	0.13	296,000	16
12	Cp_2ZrMe_2	8.4	100	60	0.605	0.14	263,000	14

[a] In 10^6 g PE (mol Zr)$^{-1}$ h^{-1} bar^{-1}.

Conditions: 40 mL toluene, 1 bar ethene pressure, 30 min reaction time.

2.1. Synthesis of $[(SiO_2)_{50}B(C_6F_5)_3]^-[HNMe_2Ph]^+$

To a suspension of 3.46 g (57 mmol) SiO_2 and 0.74 g (1.44 mmol) $B(C_6F_5)_3$ in 200 ml hexanes 0.19 ml (1.44 mmol) dimethylaniline was added. The suspension was stirred at room temperature for 4 h and allowed to settle overnight before filtering off the supernatant and washing with a further 200 ml hexane. The solid was dried at 0.1 Torr/20°C for 4 h.

2.2. Synthesis of $[(SiO_2)_{50}B(C_6F_5)_3]^-[CPh_3]^+$

A suspension of 7 g $[(SiO_2)_{50}B(C_6F_5)_3]^-[HNMe_2Ph]^+$ in 200 ml dichloromethane was stirred at room temperature, in the dark, with a solution of 2.3 g (2.5 mmol) $[CPh_3][B(C_6F_5)_4]$ for 6 h. The solid was allowed to settle and the supernatant filtered off. The process was then repeated with a second 200 ml aliquot of dichloromethane and 2.3 g $[CPh_3][B(C_6F_5)_4]$. After filtration the yellow residue was washed with 3×400 ml dichloromethane before drying at 0.1 Torr/20°C for 4 h.

2.3. Ethylene polymerisations

Stock solutions of 0.1 M Cp_2ZrMe_2, 0.1 M Cp_2ZrMe_2/0.5 M $AlMe_3$ and 0.05 M *rac*-$Me_2Si(Ind)_2ZrMe_2$ in toluene were prepared. The heterogeneous activators were suspended in toluene and stirred rapidly. An all glass reactor vessel was flame dried and charged with 40 ml dry low-sulfur toluene. The toluene was saturated with ethylene at the desired temperature. An aliquot of the metallocene stock solution was introduced using a gas-tight syringe. The polymerisation was initiated by injection of an aliquot of the heterogeneous activator suspension. Polymerisations were terminated by injection of 2 ml methanol. Polymer samples were washed with acidified methanol and dried at 80°C overnight.

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