Zirconium(IV) benzyl complexes that contain chelating diamido ligands: synthesis, fluxionality and ethylene polymerization activity

Régis M. Gauvin[1], Jacky Kress*

*Laboratoire de Chimie des Métaux de Transition et de Catalyse, UMR 7513 CNRS,
Institut Le Bel, 4 Rue Blaise Pascal, 67000 Strasbourg, France*

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Abstract

The synthesis of chelating diamidodibenzyl complexes of the type $Zr(ABA^n)(CH_2Ph)_2$ [$ABA^1 = N, N'$-bis(trimethylsilyl)-2-amidobenzylamido (**1**), $ABA^2 = N, N'$-(methyldiphenylsilyl)(trimethylsilyl)-2-amidobenzylamido (**2**)] is described. The fluxionality of these complexes in solution has been studied by means of variable-temperature NMR. In the presence of one equivalent of a suitable alkyl abstractor, these compounds proved to behave as moderately active ethylene polymerization catalysts. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Dibenzyl complexes; Diamido ligands; Zirconium; Fluxionality; Olefin polymerization

1. Introduction

In the field of the transition metal-catalysed polymerization of olefins, recent attention has focused on non-metallocene systems [1], and more particularly on group 4 amido complexes [2–4]. Metal chloride derivatives have been commonly used as catalyst precursors, in combination with methylaluminoxane (MAO) in large excess, but metal-alkyls have also attracted much attention. These indeed can be activated with stoichiometric amounts of co-catalysts such as $B(C_6F_5)_3$ or $[CPh_3][B(C_6F_5)_4]$, which has led in some instances to improved performances [5,6]. The synthesis and the fluxionality of a series of Zr(IV) dichlorides bearing disymmetric diamido ligands based on the 2-aminobenzylamine framework have been recently reported [7,8]. In the presence of excess of MAO, these compounds display moderate olefin polymerization activity. We now wish to report the synthesis and the fluxional behaviour of two corresponding dibenzyl derivatives, as well as their catalytic polymerization properties in the presence of one equivalent of the classical alkyl abstractors mentioned above.

2. Experimental

2.1. General procedures

All experiments were carried out under an inert atmosphere in a Vacuum Atmosphere drybox or by

* Corresponding author. Tel.: +49-3-90-24-13-32;
fax: +49-3-90-24-13-29.
E-mail address: jkress@chimie.u-strasbg.fr (J. Kress).
[1] Present address: Laboratoire de Chimie Organométallique de Surface, CPE, UMR 9986 CNRS, 69616 Villeurbanne Cedex, France.

Schlenk techniques. Prior to use, solvents were re-fluxed over an appropriate dehydrating agent [9], distilled under argon and stored under argon over acti-vated 4 Å molecular sieves. Deuterated solvents were dried over activated 4 Å molecular sieves. Polymer-ization studies were carried out in classical glassware connected to an ethylene- or propylene-line and the monomer pressure was controlled and monitored with use of a mercury column. Polymerization runs were quenched by addition of methanol. The polymers were filtered off, washed with acetone and dried under vac-uum. NMR spectra were recorded on Bruker AC-300 or AM-400 spectrometers. Chemical shifts are given in ppm, with tetramethylsilane as the reference. Cou-pling constants are given in Hz. Energy barriers were calculated using the Eyring equation [10].

2.2. Complexes **1** and **2**

To a suspension of 300 mg of $Zr(ABA^1)Cl_2$ (7.03×10^{-4} mol) [7] or 500 mg of $Zr(ABA^2)Cl_2$ (9.08×10^{-4} mol) [7] in 15 ml of pentane at $-78\,^\circ$C (or $-55\,^\circ$C) were added 1.45 ml (or 1.86 ml) of a 1.0 M solution of $Mg(CH_2Ph)Br$ in diethylether (1.45×10^{-3} or 1.86×10^{-3} mol, respectively) [$ABA^1 =$ N, N'-bis(trimethylsilyl)-2-amidobenzylamido (**1**), $ABA^2 = N, N'$-(methyldiphenylsilyl)(trimethylsilyl)-2-amidobenzylamido (**2**)]. The reaction mixture was let to warm up to room temperature. After overnight stirring, the white precipitate was centrifuged and the yellow solution was evaporated to dryness. The turbid residual oil was then re-dissolved in pentane in order to separate the remaining magnesium salts. Filtra-tion and evaporation to dryness afforded 302 mg, or 599 mg, of an orange oil which solidified in the case of **2** upon prolonged exposure to high vacuum (yield: ca. 80% for both products).

Compound **1**: ^{1}H NMR (CD_2Cl_2, 300 MHz, 298 K): δ 7.17 (d, 1H, Ar ABA), 7.15 (t, 4H, H_m $ZrCH_2Ph$), 7.08 (dt, 1H, Ar ABA), 6.97 (t, 2H, H_p $ZrCH_2Ph$), 6.76 (dt, 1H, Ar ABA), 6.73 (d, 4H, H_o $ZrCH_2Ph$), 6.71 (d, 1H, Ar ABA), 4.73 (s, 2H, CH_2 ABA), 1.88 (d, $^2J_{H-H} = 10.4$ Hz, 2H, ZrCHH'Ph), 1.82 (d, $^2J_{H-H} = 10.4$ Hz, 2H, ZrCHH'Ph), 0.07 (s, 9H, ArNSiMe_3), 0.03 (s, 9H, CH_2NSiMe_3). ^{13}C NMR (C_7D_8, 75 MHz, 298 K): δ 153.09 (C^2 ABA), 144.68 (C_{ipso} $ZrCH_2Ph$), 131.09 ($C_{o/m}$ $ZrCH_2Ph$), 129.98 (C^1 ABA), 128.91 (Ar ABA),

128.83 (Ar ABA), 127.92 ($C_{o/m}$ $ZrCH_2Ph$), 123.75 (C_p $ZrCH_2Ph$), 120.82 (Ar ABA), 120.32 (Ar ABA), 63.22 (ZrCH_2Ph), 46.90 (CH_2 ABA), 1.64 (SiMe_3), 1.21 (SiMe_3).

Compound **2**: ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 7.58 (m, 4H, H_o SiPh), 7.15 (m, 7H, $H_m + H_p$ SiPh + H^3 or H^6 ABA), 7.07 (t, 4H, H_m $ZrCH_2Ph$), 6.94 (d, 1H, H^3 or H^6 ABA), 6.89 (t, 2H, H_p $ZrCH_2Ph$), 6.81 (dt, 1H, H^4 or H^5 ABA), 6.70 (dt, 1H, H^4 or H^5 ABA), 6.63 (d, 4H, H_o $ZrCH_2Ph$), 4.68 (s, 2H, CH_2 ABA), 2.13 (d, $^2J_{H-H} = 10.7$ Hz, 2H, ZrCHH'Ph), 1.46 (d, $^2J_{H-H} = 10.7$ Hz, 2H, ZrCHH'Ph), 0.60 (s, 3H, SiMePh$_2$), 0.01 (s, 9H, SiMe_3). ^{13}C NMR (C_6D_6, 75 MHz, 298 K): δ 151.27 (C^2 ABA), 144.34 (C_{ipso} $ZrCH_2Ph$), 136.25 (C_o SiPh), 135.62 (C_{ipso} SiPh), 130.63 (C_p SiPh), 129.95 ($C_{o/m}$ $ZrCH_2Ph$), 129.30 (C^1 ABA), 128.78 (C_m SiPh), 128.59 (Ar ABA), 128.46 (Ar ABA), 127.33 ($C_{m/o}$ $ZrCH_2Ph$), 122.93 (C_p $ZrCH_2Ph$ + Ar ABA), 121.63 (Ar ABA), 65.54 (ZrCH_2Ph), 47.85 (CH_2 ABA), 0.71 (SiMe_3), -1.47 (SiMePh$_2$).

3. Results and discussion

3.1. Synthesis

The dibenzyl complexes $Zr(ABA^n)(CH_2Ph)_2$, that differ in the nature of the anilinic substituent of the ABA^n ligand, were synthesized by reaction of the cor-responding dichlorides [7] with two equivalents of the benzyl Grignard reagent (Fig. 1).

After filtration of magnesium chloride and evapo-ration of the filtrate to dryness, **1** and **2** were obtained in good yield as thick orange oils that solidify upon prolonged exposure to vacuum. Both compounds are highly soluble in hydrocarbons, and crystallization at-tempts were unsuccessful. Protonolysis of tetraben-zylzirconium [11] by the diamines $(ABA^n)H_2$ ($n =$

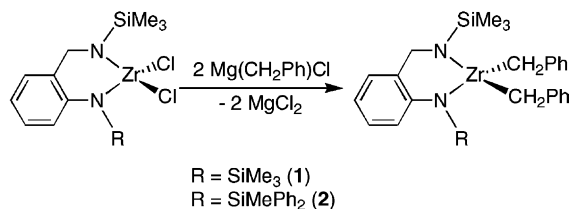R = SiMe$_3$ (**1**)
R = SiMePh$_2$ (**2**)
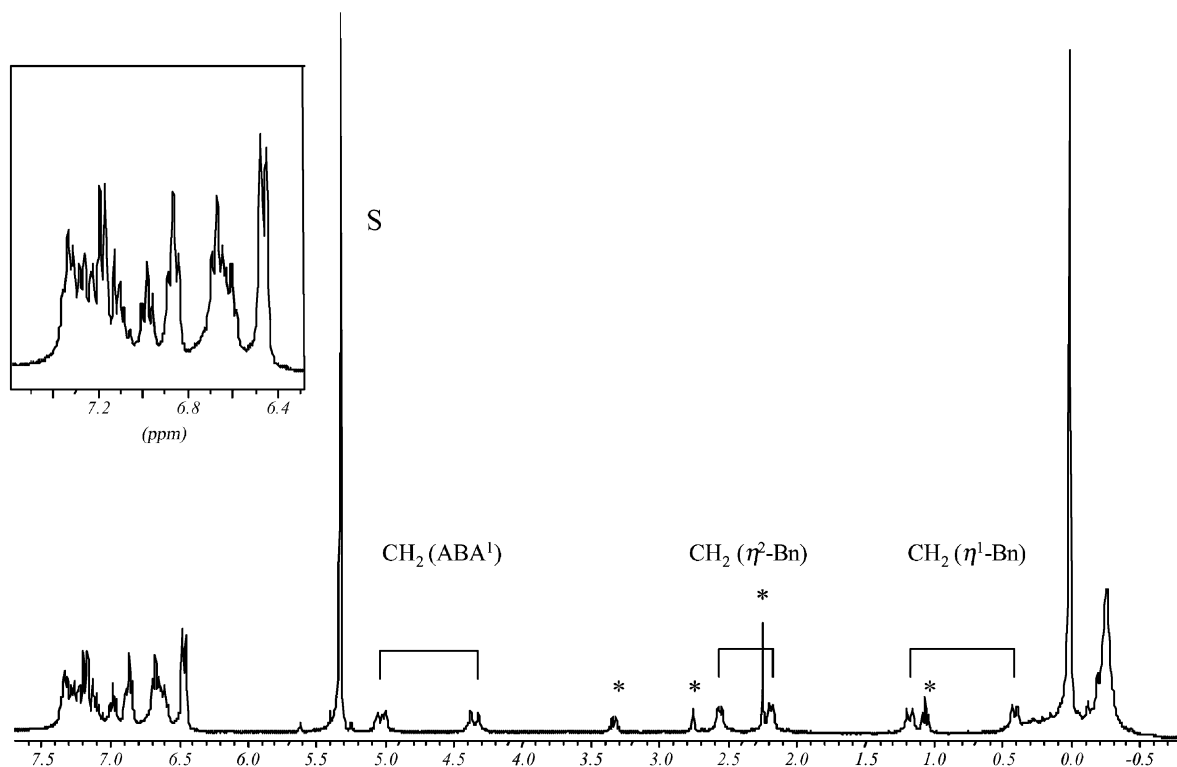
Fig. 1. Synthesis of **1** and **2**.

Fig. 2. ^{1}H NMR spectrum of **1** at 185 K (CD$_2$Cl$_2$, 300 MHz, Bn = CH$_2$Ph, S = CDHCl$_2$; * = organic impurities).

1, 2) [7] also afforded complexes **1** and **2**, but only as unseparable mixtures with the known bis-diamido species Zr(ABA^n)$_2$ [7,8]. Obviously, reaction of the diamines with Zr(CH$_2$Ph)$_4$ first and **1** or **2** in a second stage occurs at comparable rates.

Low-temperature ^{1}H NMR spectra of the two compounds in CD$_2$Cl$_2$ reveal similar features. The spectrum of **1** at 185 K is presented in Fig. 2. For both **1** and **2**, relative integrations are in agreement with the expected stoichiometry of one diamido ligand for two benzyl groups. The latter are non-equivalent. The three methylenic groups give rise to three AB systems, the characteristics of which are reported in Table 1. In both complexes, geminal coupling constants within the benzylic methylene groups are indicative of the presence of one η^1-coordinated ($^2J_{H–H}$ = ca. 11 Hz) and one η^2-coordinated ($^2J_{H–H}$ = ca. 8.5 Hz) benzyl ligand. A value lower than 10 Hz is indeed commonly considered as characteristic of a dihapto benzyl ligand in which the *ipso*-carbon of the phenyl ring is

interacting with the metal centre [12–14]. The gate-decoupled ^{13}C NMR spectrum of **2** in CD$_2$Cl$_2$ at 180 K confirms these conclusions. The η^1- and η^2-coordination modes lead for the CH$_2$Ph carbons of the two benzyl ligands to $^1J_{C–H}$ coupling constants of 115 Hz (at 65.43 ppm) and 137 Hz (at 58.10 ppm), respectively, whereas the C$_{ipso}$ signal of the η^2-benzyl group appears at higher field than that of the η^1-benzyl one (137.4 ppm vs. 148.1 ppm).

It may be noticed further that two types of benzyl *ortho*-protons could be localized at 6.77 ppm (poorly

Table 1
^{1}H NMR characteristics of the different AB spin systems shown by **1** and **2** in CD$_2$Cl$_2$ at 185 K (δ in ppm; $^2J_{H–H}$ in Hz)

	1	**2**
CH$_2$ $_{ABA^n}$	5.03 + 4.35 (16.7)	5.29 + 4.41 (16.4)
CH$_2$ $_{\eta^2\text{-Bn}}$	2.59 + 2.19 (8.2)	1.34 + 0.88 (8.7)
CH$_2$ $_{\eta^1\text{-Bn}}$	1.18 + 0.42 (11.4)	2.56 + 1.28 (11.0)

resolved doublet, 2H) and 5.82 ppm (broad peak, 2H) on the low-temperature ^{1}H NMR spectrum of **2**, on the basis of the variable-temperature studies described below. The high field shift of the latter is not formally assignable to the η^2-benzyl ligand since no such tendency has been established in the literature. It most probably results from a shielding anisotropy effect of the methyldiphenylsilyl group. The chemical shift of the corresponding protons in **1**, in which this group is absent, is indeed unremarkable.

These spectroscopic features, together with the solid-state structures found for related Zr and Ti complexes [7,8], are consistent with the two diastereomeric molecular structures shown in Fig. 3. The relative position of the η^1- and η^2-benzyl ligands with respect to the puckered 6-membered ring formed by the ABA^n ligands and Zr remains unfortunately unknown. The presence of a dihapto benzyl group emphasizes the unsaturation of the metal centre in these compounds.
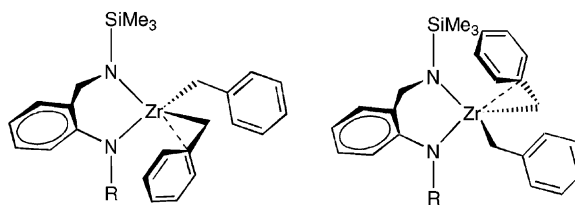

Fig. 3. Possible molecular structures for **1** and **2**.

3.2. Fluxionality

Variable-temperature ^{1}H NMR studies have been carried out on **1** (Fig. 4) and **2** in CD$_2$Cl$_2$. On gradual rising of the sample temperature, the three AB systems of both compounds can be seen to coalesce into new signals. That due to the ABA^n methylenic protons merges into a singlet at 4.73 and 4.78 ppm at room temperature for **1** and **2**, respectively. Those due to the CH$_2$ protons of the two benzyl groups
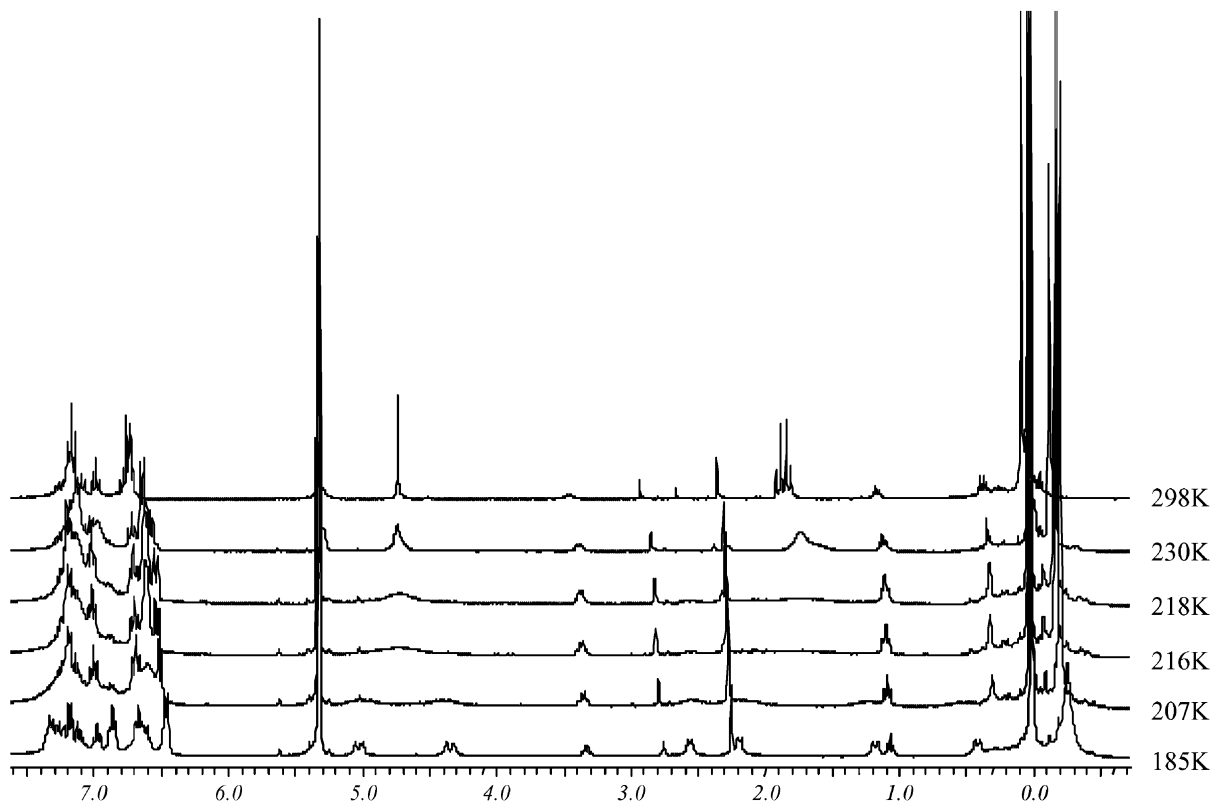

Fig. 4. Variable-temperature ^{1}H NMR spectra of **1** (CD$_2$Cl$_2$, 300 MHz).

Table 2
Coalescence temperature (T_c), chemical shift difference between the coalescing signals ($\Delta\nu$) and calculated activation energies ($\Delta G^{\neq}$) for the coalescing systems in **1** and **2**

	1			**2**		
	T_c (K)	$\Delta\nu$ (Hz)	$\Delta G^{\neq}$ (kJ mol^{-1})	T_c (K)	$\Delta\nu$ (Hz)	$\Delta G^{\neq}$ (kJ mol^{-1})
CH$_2$ (ABA)	213 ± 1	204	40.7 ± 0.2	205 ± 2	352	38.2 ± 0.4
Pair 1 (Bn)	$230 > T_c > 215^a$	651	–	211 ± 2	488	38.8 ± 0.4
Pair 2 (Bn)	215 ± 2	303	40.4 ± 0.3	198 ± 5	160	38.1 ± 1
H$_{ortho}$ (Bn)	–	–	–	205 ± 2	380	38.1 ± 0.4

[a] The coalescence plateau is masked by the resonances of pair 2.

of each compound coalesce pairwise to form a new doublet of doublets centred at 1.88 and 1.82 ppm for **1** ($^2J_{H-H} = 10.4$ Hz) and 1.96 and 1.25 ppm for **2** ($^2J_{H-H} = 10.6$ Hz). The coalescing pairs were shown to be 2.59/0.42 ppm (pair 1) and 2.19/1.18 ppm (pair 2) for **1**, and 2.56/1.34 ppm (pair 1) and 1.28/0.88 ppm (pair 2) for **2**. Furthermore, raising the temperature of **2** from 180 to 193 K leads to slight but significant sharpening of the broad signal at 5.82 ppm, that we assign to the *ortho*-protons of one of the benzyl ligands. Further temperature increase causes this peak to broaden again, before it eventually coalesces with the *ortho*-protons signal of the other benzyl group to yield a sharp doublet centred at 6.48 ppm at room temperature. The final room-temperature spectra of **1** and **2** in CD$_2$Cl$_2$ as well as in C$_6$D$_6$ correspond to molecules with apparent C$_s$ symmetry, i.e. with two equivalent benzyl groups and a planar ABA^n ligand.

The activation energies calculated from these data with use of the Eyring equation [10], along with relevant parameters are presented in Table 2. The narrow range of values for a given compound shows that only one dynamic process is operative in each case. The average energy barriers are 40.7 ± 0.4 kJ mol^{-1} for **1** and 38.2 ± 0.4 kJ mol^{-1} for **2**. Hence, the dynamic

rocking process of the ABA^n framework about the ZrN$_2$ plane already investigated earlier [7] takes also place in the present benzyl complexes. In this case, it is combined with the exchange between the η^1- and the η^2-benzyl ligands, as illustrated in Fig. 5, probably through a bis(η^1-benzyl) transition state (vide infra). This reversibly inverses the chirality of complexes **1** and **2**. The activation energies are close to those found for the preceding examples [7], in which an interaction between the zirconium centre and the aryl *ipso*-carbon of the ABA^n ligands was shown to be involved. Its strength is probably similar in **1** and **2**. Further, the activation energy is again lower for the ABA^2 than for the ABA^1 complex, which could tentatively be explained by the difference in steric hindrance between the SiMePh$_2$ and the SiMe$_3$ substituents of the anilinic nitrogen. The more voluminous SiMePh$_2$ group would reduce the $\Delta G^{\neq}$ value by raising the ground-state energy level.

The second dynamic process that is suspected for **2** on the basis of the behaviour of the signal at 5.82 ppm between 180 and 193 K may correspond to the reversible dissociation of the C$_{ipso}$ atom of the η^2-benzyl ligand from the zirconium centre (Fig. 6). This would exchange the two *ortho*-protons of this
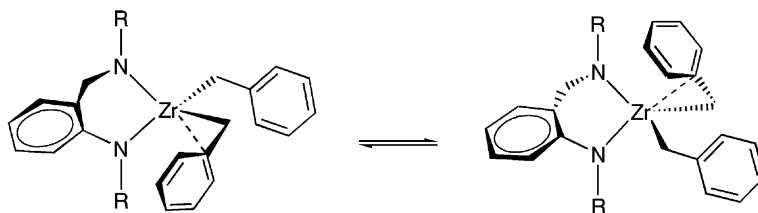
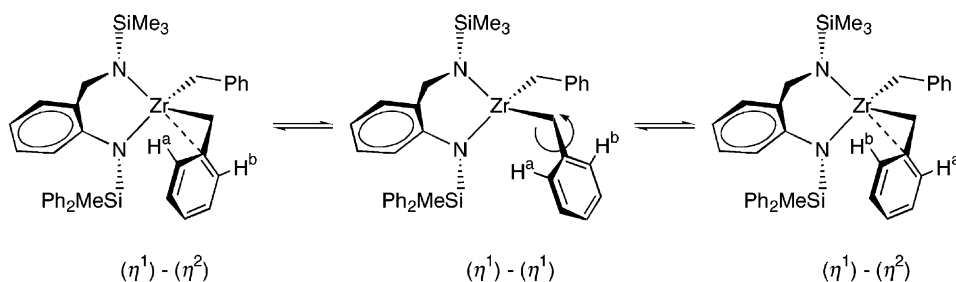Fig. 5. Dynamic rocking process in Zr(ABA^n)(CH$_2$Ph)$_2$.

Fig. 6. Proposal for the low-energy exchange phenomenon observed for **2**.

benzyl group through rotation of the phenyl ring about the CH_2–Ph bond axis, and would be of lower activation energy than the ABA^n rocking process.

3.3. Ethylene polymerization activity

The reactivity of complexes **1** and **2** toward olefins in the presence of one equivalent of an alkyl abstractor has been studied. Addition of $B(C_6F_5)_3$ [15] to a dichloromethane solution of **1** or **2** at −30 °C leads to an immediate colour change from yellow to intense orange. When this reaction was performed on **1** (36.9 μmol) under 1 bar of ethylene pressure, solid polyethylene was produced as a fibrous polymer. Formation of 20 mg of polymer within 25 min corresponds to the modest activity of 1.3 kg (mol bar h)$^{-1}$. The catalyst system **2**/$B(C_6F_5)_3$ is even less productive and yields only traces of polyethylene under comparable conditions.

On the other hand, addition of 1 equiv. of $[CPh_3][B(C_6F_5)_4]$ [16,17] to dichloromethane solutions of **1** has also been shown to afford a catalyst system that is active in the polymerization of ethylene (Table 3). At 21 °C, for instance, exposure of this mixture (37.2 μmol of each) to an atmosphere of ethylene (1 bar) for 5 min leads to the formation of 12 mg of solid polyethylene (entry 1). The activity of 3.9 kg (mol bar h)$^{-1}$ is close to the one observed for the MAO activated complex $Zr(ABA^1)Cl_2$ [7], but remains modest compared with metallocene-based systems. Following-up monomer consumption shows moreover that the system is rapidly deactivated. Slower deactivation is obtained at lower temperature, as shown by the observation that the activity is halved in 15 min at −30 °C (entries 3 and 6), but is only

little modified over 60 min at −80 °C (entries 5 and 9), where the catalytically active cationic species seems to be fairly stable. Simultaneously, the polymerization rate also slows down at lower temperature so that the activity reaches a maximum of 12.5 kg (mol bar h)$^{-1}$ at −30 °C (entries 1–5). Entries 6 and 7 show that use of a less dissociating solvent such as chlorobenzene has an inhibiting effect on the catalytic system. The resulting polymers were not soluble enough for SEC analysis (dichlorobenzene, 145 °C). However, ^{1}H NMR spectra could be recorded that reveal the quasi-absence of methyl groups in the polymer chains, confirming the linearity and the large molecular masses hinted by their poor solubility. Further experiments have shown that these catalyst systems were inactive, under similar conditions, for the polymerization of α-olefins such as propene and hex-1-ene.

Table 3
Ethylene polymerization in the presence of the catalyst system **1**/$[CPh_3][B(C_6F_5)_4]$ (conditions: 20 mg (37.2 μmol) of **1** in 7 ml of CH_2Cl_2; 1 equiv. of $[CPh_3][B(C_6F_5)_4]$ in 3 ml of CH_2Cl_2; 1 bar ethylene pressure)

Run number	T (°C)	t (min)	Yield (mg)	A (kg (mol bar h)$^{-1}$)
1	21	5[a]	12	3.9
2	0	5	31	10.0
3	−30	5	39	12.5
4	−50	5	22	7.1
5	−80	5	4	1.3
6	−30	20	65	5.2
7[b]	−30	20	49	4.0
8	0	60	151	4.1
9	−80	60	38	1.0

[a] Monomer consumption had stopped after a few minutes.
[b] Solvent C_6H_5Cl.

4. Conclusion

New dibenzyl-zirconium compounds that contain chelating diamido ligands have been synthesized and their fluxional behaviour analysed by low-temperature NMR. In the presence of 1 equiv. of an alkyl abstractor, these compounds behave as moderately active catalysts for the polymerization of ethylene. The catalytically active cationic species probably generated by the reaction of **1** with $[CPh_3][B(C_6F_5)_4]$ is able to polymerize ethylene at $-80\,^\circ$C, but is not stable enough at higher temperatures to produce substantial amounts of polymer. The polyethylenes seem to consist of linear high molecular weight chains.

Acknowledgements

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