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Solution structure and decomposition pathway of zwitterionic zirconium (IV) benzyl complexes

Régis M. Gauvin [a,b,1], C. Mazet [a,c,2], Jacky Kress [a,*]

[a] Laboratoire de Chimie des Métaux de Transition et de Catalyse, UMR 7513 CNRS, Institut Le Bel, 4, rue Blaise Pascal, 67000 Strasbourg, France
[b] Laboratoire de Chimie Organométallique de Surface, CPE, UMR 9986 CNRS, 69616 Villeurbanne Cédex, France
[c] Laboratoire de Chimie Organométallique et de Catalyse, UMR 7513 CNRS, Institut Le Bel, 4, rue Blaise Pascal, 67000 Strasbourg, France

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Abstract

Reaction of the chelating diamido complexes $Zr(ABA^n)(CH_2Ph)_2$ [$ABA^1 = N,N'$-$(SiMe_3)_2$-2-amidobenzylamido, $ABA^2 = N,N'$-$(SiMePh_2)(SiMe_3)$-2-amidobenzylamido] with $B(C_6F_5)_3$ leads to formation of the unstable zwitterionic adducts $[Zr(ABA^n)(CH_2Ph)][(\eta^6\text{-}PhCH_2)B(C_6F_5)_3]$ **1** ($n = 1$) and **2** ($n = 2$), as shown by low temperature NMR experiments that, moreover, enabled an insight into the molecular structure of these compounds in solution. Two intermediates of the decomposition of **1** and **2**, that leads to complexes $Zr(ABA^n)(C_6F_5)_2$, were identified. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Zwitterionic complexes; Diamido ligands; Zirconium; Benzylborate anion; Ethylene polymerization

1. Introduction

The search for well-defined molecular catalysts is a standing goal in the field of homogeneous catalysis. Most often, these may not only allow thorough insight into the activation or deactivation mechanism of the catalytic reactions, but also provide superior activities. In particular, cationic alkyl complexes of zirconium (IV) that catalyze the polymerization of olefins have been studied [1]. Most of them are obtained by alkyl abstraction from neutral dialkyl complexes and are associated with fluoro substituted arylborate counter anions of the type $RB(C_6F_5)_3^-$ or $B(C_6F_5)_4^-$, that interact more or less strongly with the cationic centers [1–3].

In the course of our studies on the use of zirconium complexes of diamido ligands as catalysts for the polymerization of ethylene [4], we have shown that compound $Zr(ABA^1)(CH_2Ph)_2$ [$ABA^1 = N,N'$-$(SiMe_3)_2$-2-amidobenzylamido] becomes active on addition of one equivalent of $B(C_6F_5)_3$, although it remains short-lived at room temperature, whereas $Zr(ABA^2)(CH_2Ph)_2$ [$ABA^2 = N,N'$-$(SiMePh_2)(SiMe_3)$-2-amidobenzylamido] is essentially inactive under identical conditions [4b]. We now report that these observations are related to the formation and properties of the well-defined zwitterionic complexes $[Zr(ABA^n)(CH_2Ph)][(\eta^6\text{-}PhCH_2)B(C_6F_5)_3]$ [**1** ($n = 1$) and **2** ($n = 2$)].

2. Results and discussion

2.1. Formation and characterization of *1* and *2*

The dibenzyl Zr(IV) complexes $Zr(ABA^n)(CH_2Ph)_2$ ($n = 1$, 2) react straightforwardly with a stoichiometric amount of $B(C_6F_5)_3$, even at −80 °C, to yield the zwitterionic zirconium–monoalkyl complexes $[Zr(ABA^n)(CH_2Ph)][(\eta^6\text{-}PhCH_2)B(C_6F_5)_3]$ **1** ($n = 1$) and **2** ($n = 2$) as bright orange solutions. These species rapidly revealed too unstable to be isolated at room temperature and were hence only produced in situ in CD_2Cl_2, C_6D_6 or C_7D_8. As discussed below, the NMR spectra show

* Corresponding author. Tel.: +33-390-241-332; fax: +33-390-241-329

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 Cédex, France.

[2] Present address: Laboratoire de Chimie Organométallique et de Catalyse, UMR 7513 CNRS, Institut Le Bel, 4, rue Blaise Pascal, 67000 Strasbourg, France.

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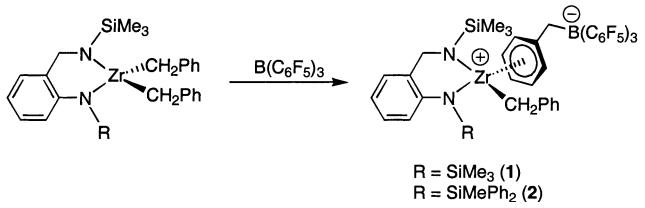


Scheme 1. Formation of **1** and **2**.

that the benzylborate anion is tightly coordinated to the cationic zirconium center through the π system of its benzyl group (Scheme 1), as observed in analogous complexes [3,5]. This is at the origin of the solubility of these compounds in non-polar solvents.

The detailed assignment of the ^{1}H-NMR spectrum of **1** in CD_2Cl_2 (Fig. 1) has been achieved with the help of a ^{1}H–^{1}H COSY correlation and is presented in Scheme 2. The distinction between H_{Ao2} and H_{Ao1} in the ABA^1 ligand has needed, however, the ROESY data described latter on. Due to the lack of symmetry, the five aromatic protons of the coordinated anion are non-equivalent and the three methylene groups give rise to AX or AB quartets, the signal of the one linked to the boron atom being significantly broadened. The geminal coupling constant of 11.4 Hz found for the benzyl ligand is in agreement with a monohapto coordination mode. It may be noticed that replacing dichloromethane-d_2 by toluene-d_8 leads to a significant shift of the ^{1}H-NMR spectrum of **1**. In particular, four resonances assigned to aromatic protons of the benzylborate anion are observed at unexpectedly high-fields, between 5.5 and 6 ppm [3c].

The ^{13}C-NMR spectrum of **1** (CD_2Cl_2, 183 K) confirms these observations. The $ZrCH_2Ph$ *ipso* carbon is located at 145.80 ppm, as expected for the η^1-coordination mode [1]. The C_6F_5 groups of the $(PhCH_2)B(C_6F_5)_3^-$ anion give rise to three doublets [$^1J(^{13}C-^{19}F) = 235–247$ Hz] and the BCH_2Ph *ipso* carbon to a singlet at 156.94 ppm. The latter is deshielded with respect to the free anion (δ 148 ppm), as expected in case of η^6-coordination of this anion to the metal [5]. The two quaternary carbon signals of the ABA^1 ligand are observed at 135.52 and 135.30 ppm. Hence, the C–N carbon is considerably shielded in **1** with respect to neutral ABA^1 complexes [4]. The interaction between the metal and this *ipso* carbon (see Fig. 2), whose existence in these preceding examples was established by X-ray diffraction, is thus strengthened in **1**, showing that the metal center in **1** is more electron deficient than in $Zr(ABA^1)Cl_2$ [4] for instance. Similar effects were found in related complexes [6].

The ^{1}H–^{1}H ROESY NMR spectrum of **1** (CD_2Cl_2, 183 K) enables to determine spatial proximity between the protons and to define more precisely the molecular structure of **1** in solution. In Table 1 are presented the most significant NOE interactions other than those existing within the CH_2 groups or between adjacent aromatic protons. It is shown, in particular, that both -$NSiMe_3$ and -$B(C_6F_5)_3$ substituents of the ABA^1 and (η^6-$PhCH_2$)$B(C_6F_5)_3$ ligands, respectively, are oriented

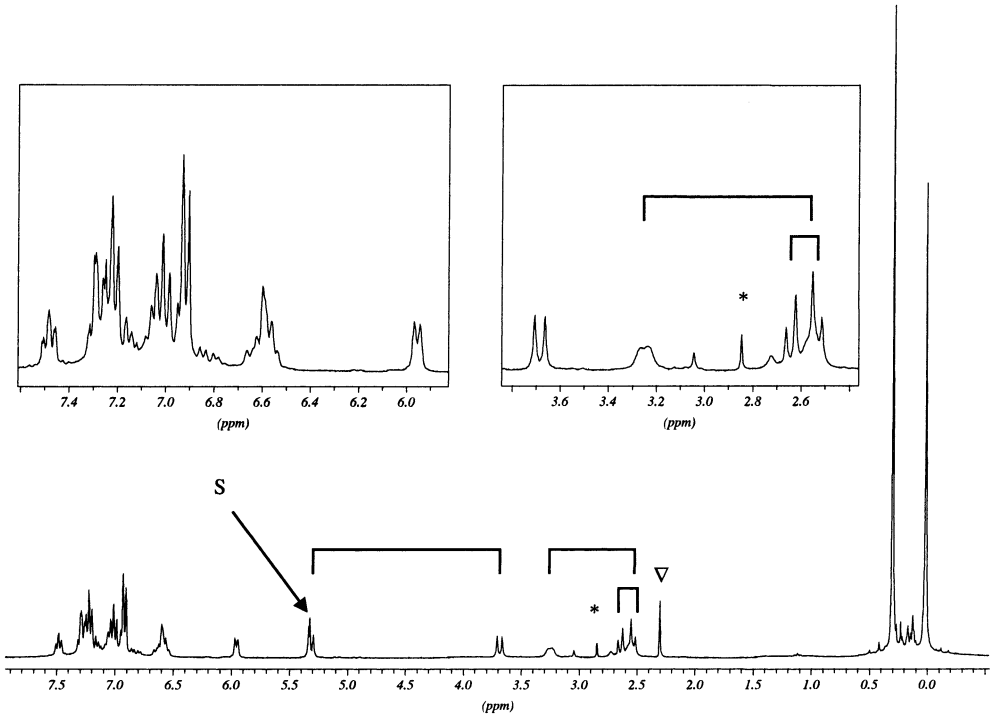
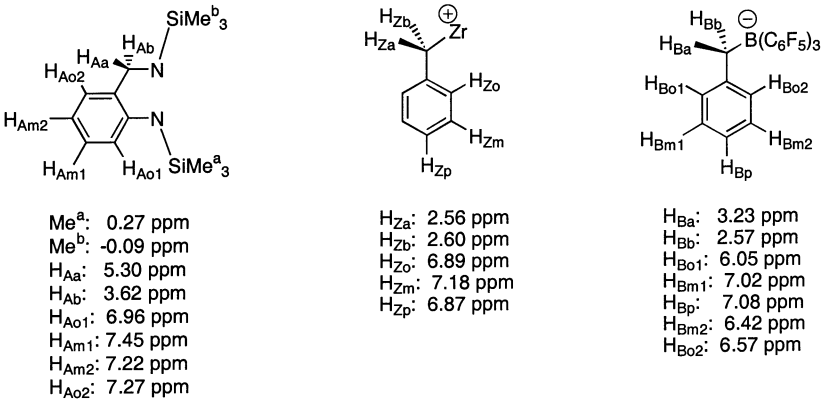


Fig. 1. ^{1}H-NMR spectrum of **1** (CD_2Cl_2, 230 K, 300 MHz; ∇, toluene; *, bibenzyl; S, $CHDCl_2$).



Scheme 2. Assignment of the ^{1}H-NMR signals of **1** (CD_2Cl_2, 183 K).

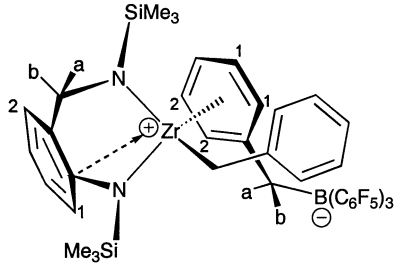


Fig. 2. Schematic representation of the structure of complex **1** in solution (suffixes A, B, o and m defined in Scheme 2 are omitted here).

Table 1
Significant NOE interactions of each proton, by decreasing intensity

	NOE interactions
Me^b	H_{Zo}, H_{Bp}, H_{Bm1}, H_{Zm}, H_{Ao2}, H_{Bo2}, H_{Ab}, H_{Aa}, H_{Bm2}
Me^a	H_{Ao1}, H_{Zo}, H_{Aa}
H_{Aa}	Me^b, Me^a
H_{Ab}	H_{Ao2}; Me^b
H_{Ao1}	H_{Bo2}, H_{Ba}; Me^a
H_{Ao2}	H_{Ab}, H_{Bm2}; Me^b
H_{Ba}	H_{Bo2}, H_{Ao1}
H_{Bb}	H_{Bo1}
H_{Zo}	$H_{Za,b}$, H_{Bo1}, H_{Bm2}, H_{Bo2}; Me^b, Me^a

more or less perpendicularly to the aromatic planes of the corresponding benzyl group. This is based on the differences in the correlation observed for H_{Aa} and H_{Ab} (Scheme 2) on one hand, and for H_{Ba} and H_{Bb} on the other hand (Table 1). Further, correlation between protons of distinct ligands allow us to get a more precise idea of the relative arrangement of the three ligands around zirconium. For instance, the $SiMe_3$ substituent of the benzylic nitrogen atom is close to four aromatic protons of the ligand (η^6-$PhCH_2$)$B(C_6F_5)_3^-$ ligand ($H_{Bp} > H_{Bm1} > H_{Bo2} > H_{Bm2}$), while that of the anilinic nitrogen atom is too far from them to give a significant effect. Moreover, one side of the benzylic ring of the borate anion is found close to both ortho protons of the ABA[1] ligand, as shown by the correlation H_{Ao1}/H_{Bo2} and H_{Ao2}/H_{Bm2}, and one of its methylenic protons (H_{Ba}) is also correlated with H_{Ao1}. The ortho protons of the benzyl ligand, finally, are in proximity of both $SiMe_3$ substituents of the ABA[1] ligand, as well as of several aromatic protons of the borate anion.

A molecular structure consistent with these NMR observations and including the partial designation of some key protons is presented in Fig. 2. One can see that the conformation of the ABA[1] ligand is analogous to that found in the solid state for similar but neutral complexes [4], and that its aromatic plane is ca. parallel to that of the borate anion one and directed toward its side. The orientation of the latter is such that the bulky $B(C_6F_5)_3$ group points away from the other ligands to minimize steric interactions [7].

The ^{1}H and ^{13}C-NMR spectra of **2** at room temperature in toluene-d_8 and C_6D_6, respectively, are similar to those of **1** in the same solvents. The diastereotopic protons of the methylene groups of the ABA[2], CH_2Ph and (η^6-$PhCH_2$)$B(C_6F_5)_3^-$ ligands, in particular, give rise to pairs of doublets at 4.79/3.56 ppm ($^2J_{HH} = 14$ Hz), 2.05/1.47 ppm ($^2J_{HH} = 11.9$ Hz) and 3.49/2.83 ppm (broad), respectively. The two phenyl groups of the -$SiMePh_2$ substituent of the anilinic nitrogen atom are also non-equivalent, as shown by the presence of two multiplets centered at 7.28 (3H) and 7.16 (3H) ppm, assigned each to the meta and para protons of a given phenyl group. The five multiplets due to the aromatic protons of the borate anion are found between 6.5 and 5.4 ppm.

At low temperature, however, the ^{1}H-NMR spectrum of **2** in tol-d_8 is markedly different and much more complex (Fig. 3). At 225 K, it comprises two sets of resonances whose integration ratio are ca. 7/1. This is most evident for the $SiMe_3$ singlet: while observed at 0.03 ppm at room temperature, it is split at 225 K into two singlets at 0.11 (strong) and −0.20 (weak) ppm. Two distinct species are thus present in solution. Although poorly resolved, the spectrum of the major one is clearly similar to (but significantly shifted from) that observed at room temperature. Three pairs of

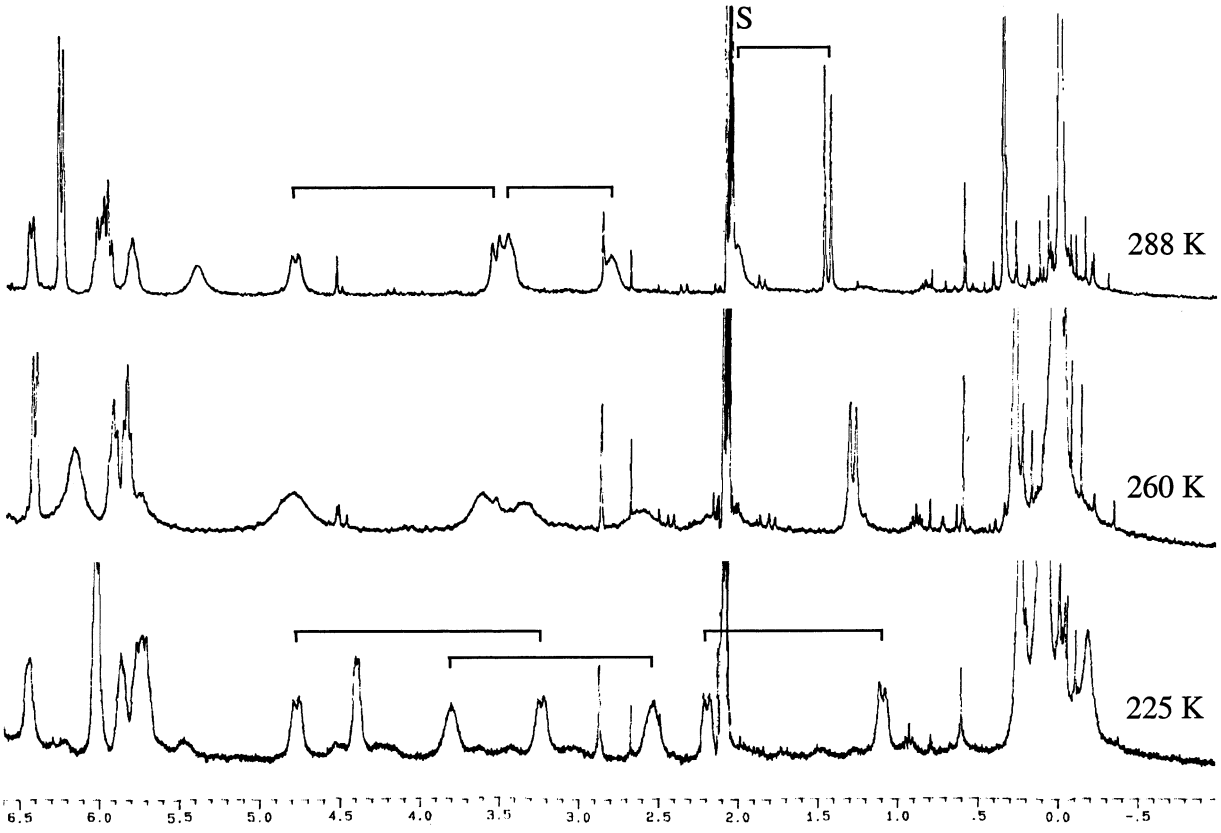


Fig. 3. ^{1}H VT-NMR spectra of **2** (C_7D_8, 300 MHz; S, solvent).

doublets assigned to the CH_2 groups of the ABA^2, $(\eta^6\text{-}PhCH_2)B(C_6F_5)_3^-$ and CH_2Ph ligands are distinguished, respectively, at 4.78/3.20, 3.82/2.59 and 2.18/1.09 ppm, and the chemical shifts of the five aromatic protons of the borate anion are lower than 6.5 ppm. In particular, one ortho proton resonance is found at 4.37 ppm (Fig. 3). The spectrum of the minor species is too ill-defined to allow a similar conclusion. However, it seems plausible that the two species consist of two conformational isomers of **2**. To the major one may correspond the molecular structure found for **1** (Fig. 2), to the other the opposite orientation of the ABA^2 aryl group (Fig. 4).

On raising the temperature, the two spectra coalesce progressively to yield the single spectrum observed at room temperature (Fig. 3). This exchange process would correspond to the interconversion of the two isomers and involve the rocking motion of the diamido framework already shown to occur in the neutral precursors

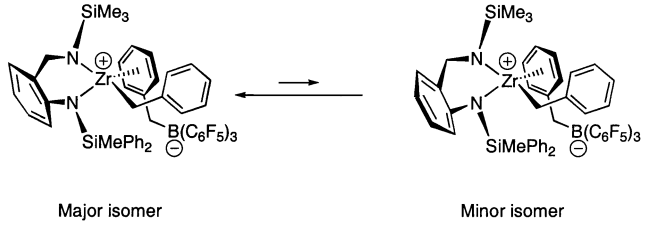


Fig. 4. Postulated structures for the two isomers of **2**.

of **2** [4]. The two singlets due to the $SiMe_3$ group coalesce at 245 K, which corresponds to activation energies of 52.7 and 48.7 ($\pm$1) kJ mol^{-1} for the two isomers [8]. These values are much larger than the one found for the dibenzyl precursor ($\Delta G^{\neq} = 38.3$ kJ mol^{-1}) [4b], as expected from the very different nature of the benzyl and the borate ligands. The fact that this process is not detected for **1** in the same temperature range results probably from a larger difference in energy between the corresponding two isomers of **1**, although a lower $\Delta G^{\neq}$ value cannot be strictly excluded. In any case, it reflects the influence of the nature of the anilinic substituent on the energy levels of these zwitterionic compounds.

2.2. Thermal decomposition studies

At higher temperatures, the ^{1}H-NMR spectra show that complexes **1** and **2** decompose cleanly into stoichiometric amounts of $B(C_6F_5)(CH_2Ph)_2$ and $Zr(ABA^n)(C_6F_5)_2$ **3** ($n = 1$) or **4** ($n = 2$), respectively. The borane was identified by a characteristic signal at 2.88 ppm [3c]. Complex **4** was synthesized independently as a pale yellow highly soluble solid from $Zr(ABA^2)Cl_2$ [4a] and two equivalents of C_6F_5Li, and characterized by ^{1}H and ^{19}F-NMR. Complex **3** was identified by comparison with **4**.

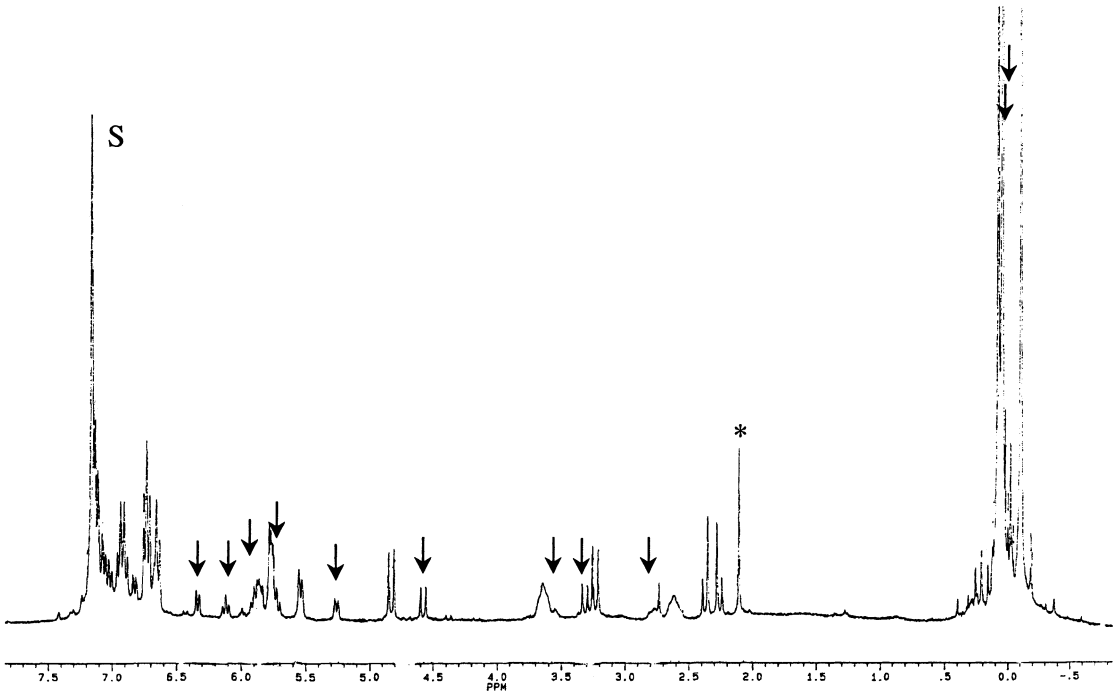
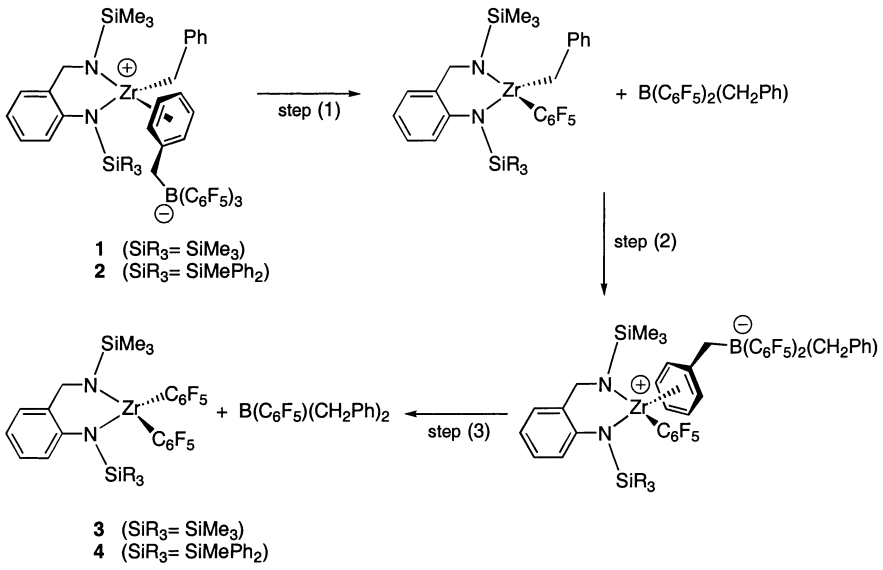


Fig. 5. ^{1}H-NMR spectrum of a solution of **1** in C_6D_6 after few minutes at 298 K (300 MHz; S, C_6D_5H; *, toluene). The arrows designate the decomposition intermediate.

Decomposition of **1** was followed at room temperature in C_6D_6. After a few minutes, one third of **1** had converted into a single new compound that is probably the zwitterionic zirconium-aryl complex $Zr(ABA^1)(C_6F_5)[(\eta^6\text{-}PhCH_2)B(C_6F_5)_2(CH_2Ph)]$ (Fig. 5). Its non-symmetric ABA^1 ligand is characterized by an AX quartet for the methylene group (4.57/3.32 ppm, $^2J_{H-H} = 12.4$ Hz), as well as by two $SiMe_3$ singlets at 0.06 and 0.04 ppm. The aromatic protons of the η^6-bound benzyl substituent of the borate anion give rise to two doublets and three triplets between 6.40 and 5.20 ppm, the connectivity of which was established by simple decoupling experiments, and the corresponding CH_2 protons to two broad signals at 3.53 and 2.78 ppm. The aromatic and CH_2 protons of the second benzyl group linked to the boron atom are probably masked, respectively, by the other multiplets of the lower field aromatic region and by the signal at 3.64 ppm due to residual **1**. After 72 h at room temperature, this complex was still present in high amounts (ca. 45%) in the reaction mixture, but **1** had disappeared in favor of the final decomposition products $B(C_6F_5)(CH_2Ph)_2$ and **3**. It disappeared in turn after few more days at room temperature.

Complex **2** being more stable than **1**, its decomposition was followed at slightly higher temperatures. After a few minutes at 310 K in deuterated toluene, ca. 20% of **2** had converted into $B(C_6F_5)(CH_2Ph)_2$ and **4**, but also into 5% of a new compound that is probably the neutral zirconium-aryl–benzyl complex $Zr(ABA^2)(C_6F_5)(CH_2Ph)$. The ^{1}H-NMR spectrum of the latter comprises two AB systems at 4.27/3.98 ppm (1H each, $^2J_{H-H} = 14$ Hz) and 2.34/1.93 ppm (1H each, $^2J_{H-H} = 11$ Hz), that can be assigned to the CH_2 protons of non-symmetric ABA^2 and η^1-benzyl ligands, respectively. Two sharp singlets at 0.02 (9H) and 0.36 ppm (3H) correspond to the $SiMe_3$ and $SiMePh_2$ groups of this ABA^2 ligand. No third ligand could be detected for this complex, suggesting again the presence of the ^{1}H-NMR-silent C_6F_5 group bound to zirconium. The borane $B(C_6F_5)_2(CH_2Ph)$ is probably generated concomitantly but its spectrum, in particular the broad CH_2 singlet expected at 3.41 ppm [3c], is hidden by other signals. Rising the temperature up to 340 K changes the relative proportions of the four compounds in favor of $Zr[ABA^2](C_6F_5)(CH_2Ph)$ and more especially of the two final decomposition products $B(C_6F_5)(CH_2Ph)_2$ and **4**, that remain alone after 15 min at this temperature.

It must be pointed out, furthermore, that the pairs of resonance observed at 6.46/5.41 ppm, 6.07/5.81 ppm and 3.49/2.83 ppm (25 °C, 1H each) and due, respectively, to the *ortho*, *meta* and CH_2 protons of the η^6-benzyl group of the borate anion in **2** coalesce at 340 K into broad signals at 6.22 (4H) and 3.15 (2H) ppm. This shows that anion exchange occurs in these zwitterionic complexes, for which an activation energy of $\Delta G^{\neq} = 63.8\ (\pm 1)$ kJ mol^{-1} was estimated from the coalescence temperatures of 330, 315 and 330 K, respectively [9]. Similar observations have been reported for closely related systems involving the same anion [5b,10] or the tetraphenylborate one [11].



Scheme 3. Decomposition pathway for **1** and **2**.

Although the intermediates involved in the decomposition of **1** and **2** are different, we propose for these reactions a three steps mechanism that is common to both compounds (Scheme 3). In the first and last steps, the cationic center of the zwitterions is electrophilic enough to pull off a $C_6F_5^-$ substituent of the coordinated borate anions and liberate the resulting boranes. In the second step, the benzyl–borane $B(C_6F_5)_2(CH_2Ph)$ reacts with the neutral monobenzyl–zirconium intermediates in the same way as $B(C_6F_5)_3$ reacts with the zirconium dibenzyl complexes $Zr[ABA^n](CH_2Ph)_2$ ($n = 1, 2$) (Scheme 1). Similar steps were found to occur for other cationic benzyl complexes [3c,12]. In the present case, it appears that the relative rates of these three steps are very dependent on the nature of the anilido substituent. In particular, step (1) is faster for **1** than for **2**, step (2) is rate-determining for $R = SiMePh_2$ but becomes the fastest one for $R = SiMe_3$, and step (3) is rate-determining for $R = SiMe_3$. These differences result most probably from the lower steric bulk of the $SiMe_3$ group with respect to $SiMePh_2$ that restricts steric protection around the electrophilic zirconium centers. However, electronic effects are certainly involved as well, especially in the second step in which the more electron withdrawing $SiMePh_2$ group should make the benzyl ligand of the zirconium-aryl–benzyl intermediate less nucleophilic and thereby disfavor even more its abstraction by $B(C_6F_5)_2(CH_2Ph)$.

3. Conclusion

It can now be assumed that the zwitterionic complexes **1** and **2** are the molecular catalysts that are operating in the polymerization of ethylene in the presence of $Zr[ABA^n](CH_2Ph)_2$ and one equivalent of $B(C_6F_5)_3$ [4b]. The low activity of these catalytic systems is consistent with the strength of the interaction between the cationic centers and the benzyl–borate anions, that disfavors displacement of these anions by ethylene. Evidence for reversible dissociation of **2** in the absence of ethylene indicates, however, that such a displacement is plausible. The highly non-symmetric structure of **1** and **2** does not impede the existence of conformational isomers that can inter convert slowly on the NMR time scale, probably through the ABA^n rocking process detailed earlier for neutral complexes [4]. Studies of the consequences of these properties on the stereoselectivity of the polymerization processes unfortunately aborted owing to the inactivity of these catalysts toward α olefins [4].

On the other hand, the short life-time of the catalytic systems $Zr[ABA^n](CH_2Ph)_2/B(C_6F_5)_3$ is consistent with the low stability of **1** and **2**, that was shown to result essentially from the ability of the cationic zirconium centers to pull off $C_6F_5^-$ groups from the η^6-bound benzyl–borate anions. Comparison of the properties of **1** and **2** illustrates, furthermore, how much the nature of the substituents of the nitrogen atoms of diamido ligands influences not only the activity and the stability of the catalytic species, but also the relative energy level of conformational isomers and the relative rate of the elemental decomposition steps.

4. Experimental

4.1. General procedures

All experiments were carried out under an inert atmosphere in a Vacuum Atmosphere dry box or by Schlenk techniques. Prior to use, solvents were refluxed

over an appropriate dehydrating agent, distilled under argon and stored under argon over activated 4 Å molecular sieves. Deuterated solvents were dried over activated 4 Å molecular sieves. NMR spectra were recorded on Bruker AC-300 or ARX-500 spectrometers. Chemical shifts are given in ppm, with tetramethylsilane as the reference. Coupling constants are given in Hz. Activation energies were calculated using the Eyring equation [9] or by the graphical method derivated from it [8].

4.2. $[Zr(ABA^1)(CH_2Ph)][(\eta^6\text{-}PhCH_2)B(C_6F_5)_3]$ (**1**)

In the glove-box, a solution of 20 mg of Zr(ABA^1)(CH_2Ph)$_2$ (0.037 mmol) in 0.4 ml of CD_2Cl_2 was introduced into an NMR tube, which was then placed in an almost horizontal position. At the top of the NMR tube were deposited 19 mg of $B(C_6F_5)_3$ (0.037 mmol) [13]. While still kept in the same position, the tube was sealed with a rubber septum and cooled in dry ice. It was then set upright again, vigorously shaken to ensure efficient mixing of the reagents, and introduced in the precooled NMR probe. NMR spectroscopy showed that **1** had formed in quantitative yield. ^{1}H-NMR (CD_2Cl_2, 300 MHz, 230 K): δ 7.48 (dt, 1H, H^4 ABA), 7.27 (m, 2H, H^5+H^6 ABA), 7.22 (t, 2H, H_m $ZrCH_2Ph$), 7.05 (m, 2H, H_p + H_{m1} BCH_2Ph), 7.00 (d, 1H, H^3 ABA), 6.94 (t, 1H, H_p $ZrCH_2Ph$), 6.92 (d, 2H, H_o $ZrCH_2Ph$), 6.60 (m, 2H, H_{m2}+H_{o2} BCH_2Ph), 5.96 (d, 1H, H_{o1} BCH_2Ph), 5.31 (d, ^2J = 12.6 Hz, 1H, CHH′ ABA), 3.67 (d, ^2J = 12.6 Hz, 1H, CHH′ ABA), 3.25 (d, broad, ^2J = 8.8 Hz, 1H, BCHH′Ph), 2.62 (d, ^2J = 11.4 Hz, 1H, ZrCHH′Ph), 2.55 (broad, 1H, BCHH′Ph), 2.54 (d, ^2J = 11.4 Hz, 1H, ZrCHH′Ph), 0.29 (s, 9H, $ArNSiMe_3$), −0.01 (s, 9H, CH_2NSiMe_3). Labeling follows Scheme 2. ^{13}C-NMR (CD_2Cl_2, 125 MHz, 183 K): δ 156.94 (C_{ipso} BCH_2Ph), 146.82 (d, $^1J_{CF}$ = 235 Hz, C_o C_6F_5), 145.80 (C_{ipso} $ZrCH_2Ph$), 137.22 (d, $^1J_{CF}$ = 246 Hz, C_p C_6F_5), 135.71 (d, $^1J_{CF}$ = 247 Hz, C_m C_6F_5), 135.52 (C^1 or C^2 ABA), 135.30 (C^1 or C^2 ABA), 131.53, 131.27, 131.11, 130.25, 130.09, 129.89, 129.48 (CH Ar), 128.57 (2C, $C_{o/m}$ $ZrCH_2Ph$), 127.94, 127.88, 126.23 (CH Ar), 124.78 (2C, $C_{o/m}$ $ZrCH_2Ph$), 123.71, 122.22 (CH Ar ABA), 122.04 (broad, C_{ipso} C_6F_5), 73.17 ($ZrCH_2Ph$), 51.98 (CH_2 ABA), 34.35 (broad, BCH_2Ph), 1.27 ($SiMe_3$), −1.39 ($SiMe_3$).

4.3. $[Zr(ABA^2)(CH_2Ph)][(\eta^6\text{-}PhCH_2)B(C_6F_5)_3]$ (**2**)

A solution of 24 mg of Zr(ABA^2)(CH_2Ph)$_2$ (0.036 mmol) in 0.4 ml of C_7D_8 was introduced into an NMR tube. Addition of 18 mg of $B(C_6F_5)_3$ (0.035 mmol) was followed by instantaneous color change to deep orange. NMR spectroscopy showed that **2** had formed in quantitative yield. ^{1}H-NMR (C_7D_8, 300 MHz): δ 7.50 (m, 4H, H_o SiPh), 7.28 (m, 3H, H_m + H_p SiPhPh′), 7.16 (m, 3H, H_m + H_p SiPhPh′), 7.00 (m, 2H, Ar ABA), 6.98 (t, 2H, H_m $ZrCH_2Ph$), 6.84 (d, 1H, H^3 ou H^6 ABA), 6.82 (t, 1H, H_p $ZrCH_2Ph$), 6.46 (d, broad, 1H, H_o BCH_2Ph), 6.27 (d, 2H, H_o $ZrCH_2Ph$), 6.07 (t, broad, 1H, H_m BCH_2Ph), 5.97 (broad, 1H, H_p BCH_2Ph), 5.81 (t, broad, 1H, H_m BCH_2Ph), 5.41 (broad, 1H, H_o BCH_2Ph), 4.79 (d, broad, 1H, ^2J = 14 Hz, 1H, CHH′ ABA), 3.56 (d, broad, ^2J = 14 Hz, 1H, CHH′ ABA), 3.49 (broad, 1H, BCHH′Ph), 2.83 (broad, 1H, BCHH′Ph), 2.05 (broad, 1H, ZrCHH′Ph), 1.47 (d, ^2J = 11.9 Hz, 1H, ZrCHH′Ph), 0.37 (s, 3H, $SiMePh_2$), 0.03 (s, 9H, $SiMe_3$). ^{13}C DEPT-135 NMR (C_6D_6, 75 MHz): δ 135.33, 135.14, 135.05, 132.55, 131.74, 131.20, 131.09, 130.92, 129.14, 128.95, 128.69, 128.54, 128.31, 127.84, 125.86, 125.10, 123.63 (CH Ar), 71.1 ($ZrCH_2Ph$), 53.48 (CH_2 ABA), 35.8 (broad, BCH_2Ph), −0.23 ($SiMe_3$), −0.32 ($SiMePh_2$).

4.4. $Zr(ABA^2)(C_6F_5)_2$ (**4**)

A 1.6 M solution (0.115 ml) of *n*-BuLi (0.184 mmol) in hexane was added to 0.023 ml of C_6F_5Br (0.184 mmol) in 10 ml of diethylether at −78 °C. A white precipitate of C_6F_5Li built up rapidly [13]. After 1 h stirring, 50 mg of Zr(ABA^2)Cl_2 (0.091 mmol) [4a] in 5 ml of diethylether were added and the reaction mixture was allowed to warm to room temperature (r.t.). After one night, the mixture was centrifuged and the clear solution was evaporated to dryness to yield 40 mg of a pale yellow solid (54% yield). ^{1}H-NMR (C_6D_6, 300 MHz): δ 7.61 (m, 4H, H_o SiPh), 6.90 (m, 8H, H_m + H_p SiPh and Ar ABA), 6.79 and 6.72 (dt, 1H, H^4+H^5 ABA), 4.54 (s, 2H, CH_2 ABA), 0.81 (s, 3H, $SiMePh_2$), −0.12 (s, 9H, $SiMe_3$). ^{19}F-NMR (C_6D_6, 376 MHz): δ −122.92 (d, ^3J = 18.6 Hz, 4F, F_o C_6F_5), −155.83 (t, 2F, ^3J = 19.5 Hz, F_p C_6F_5), −164.40 (t, 4F, ^3J = 18.6 Hz, F_m C_6F_5). Anal. Calc. for $C_{35}H_{28}F_{10}N_2Si_2Zr$: C, 51.64; H,3.47; N, 3.44. Found: C, 51.29; H, 3.44; N, 3.31%.

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