NMR evidence for $B(C_6F_5)_3$ attack on the inward position of a highly hindered *meso ansa*-zirconocene

Daniela Maggioni [a], Tiziana Beringhelli [a,*], Giuseppe D'Alfonso [a], Luigi Resconi [b]

[a] *Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Facoltà di Farmacia, Università degli Studi di Milano, Via Venezian 21, 20133 Milano, Italy*
[b] *Basell Poliolefine Italia S.p.A., P.le Privato G. Donegani 12, 44100 Ferrara, Italy*

Abstract

The reaction of the *ansa*-zirconocene *meso*-[$C_2H_4(4,7$-$Me_2Indenyl)_2$]$ZrMe_2$ with $B(C_6F_5)_3$ afforded, besides the expected ion pair with outward $MeB(C_6F_5)_3^-$ anion, also a minor isomer (molar fraction 0.043) with the bulky methylborate anion in the inward site. 2D ^1H EXSY experiments revealed exchange between the two isomers, at $T > 320$ K, through the migration of the $MeB(C_6F_5)_3^-$ anion between outward and inward sites. The presence of free $B(C_6F_5)_3$ fastened the exchange, suggesting $B(C_6F_5)_3$ attack on the zirconium bound methyl ligand of the two ion pairs.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Ansa-zirconocenes; Perfluoroarylboranes; Meso-isomers; Ion-pair; NMR; Dynamics

1. Introduction

Group 4 chiral *ansa*-bisindenyl metallocenes have been the object of intense research activity, since the pioneer reports [1,2] of their high catalytic activity for olefins polymerization [3,4], upon activation with suitable Lewis acids [5]. Differently from C_2-symmetric *ansa-rac*-bisindenyl metallocenes, which afford with good selectivity isotactic polypropylene, the C_S *meso* isomers produce atactic polypropylene [3]. However, these isomers allow efficient synthesis of ethylene-based polymers with high molecular weights and narrow molecular weight distributions [6]. Therefore, also these isomers can have important technological uses [7–9], and the mechanisms responsible for the growth of the polymer chain on the metal site have been investigated [10,11].

In these *meso ansa*-bisindenyl metallocenes the ethylenic loop forces the two indenyl ligands in an "eclipsed" conformation and generates two, achiral, diastereotopic

sites, usually described as "inward" and "outward" with respect to the bisindenyl pocket (Chart 1). As expected, sterically demanding ligands are preferentially coordinated in the less encumbered outward position. Theoretical studies have previously shown that the inward coordination was disfavored by ca. 5–6 kcal/mol, both in the case of propene compared with methyl [10] and in the case of isobutyl vs. propene [11]. Such energy
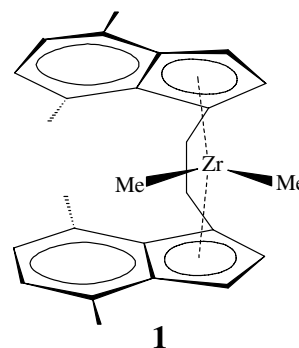

1

Chart 1.

* Corresponding author. Tel.: 39 02 503 14350; fax: 39 02 503 14405.
E-mail address: tiziana.beringhelli@unimi.it (T. Beringhelli).

difference implies (at least for these species, that contain slightly but not negligibly different ligand sets with respect to our ones) that the relative amount of a derivative containing the bulkier ligand in the inward position should be much lower that 0.001.

The reactivity of the recently synthesized *ansa*-zirconocene *meso*-[$C_2H_4(4,7-Me_2Ind)_2$]$Zr(Me)_2$ (**1**, Chart 1) [12] was in line with the above expectations: the reaction with 2 equiv of *t*-BuOH gave the outward mono-*tert*-butoxy derivative only, and the attack of $B(C_6F_5)_3$ on the same compound was found to occur on the outward methyl group, affording the ion pair [$C_2H_4(4,7-Me_2Ind)_2ZrMe_{inw}$]$^+$ [$MeB(C_6F_5)_3$]$^-$ [12].

A careful NMR analysis of these reaction mixtures has now revealed the formation also of another, very minor species, which has been identified as the isomer in which the [$MeB(C_6F_5)_3$]$^-$ anion is in the inward position. We discuss here the characterization of this complex and some aspects of its dynamics, showing that the inward position of this *meso* form is more accessible for $B(C_6F_5)_3$ than expected.

2. Results and discussion

The addition of 1 equiv of $B(C_6F_5)_3$ to a toluene solution of **1** resulted in the formation of one main species,

which has been unambiguously identified as the contact ion pair **2a**, with $B(C_6F_5)_3$ bound in the outward position (Chart 2) on the basis of the dipolar correlations shown by the methyl group bound to the boron atom (Me–B, easily identified from the broadening due to the quadrupolar boron isotopes) and by the zirconium bound methyl group (Me–Zr).

Indeed on the basis of the assignment of the indenylic resonances (Fig. 1), performed as detailed in the Experimental section, in Fig. 2 we observe that Me–B displays correlations with Me9 and H3 (and to a lesser extent with H2), while Me–Zr correlates with both Me9 and Me10, as well as with both the protons H5 and H6.

In these *ansa-meso* species a further evidence assists in the identification of the inward or outward coordination of methyl ligands, namely the chemical shift of the methyl resonances, the inward one being shifted to high field by the shielding effect of the aromatic π-electrons (for instance δ −2.12 vs. 0.02 in **1** [12]). In **2a** the sharp signal of Me–Zr is observed at −1.82 ppm (in agreement with its inward position) and the broad Me–B resonance is at 0.12 ppm.

However, a detailed analysis of dipolar and exchange correlations in experiments at 320 K suggested the presence in solution also of a second very minor isomer (**2b**, ratio about 4.5/100 with respect to **2a**), in slow exchange with **2a**. Even if most of the signals of this species were
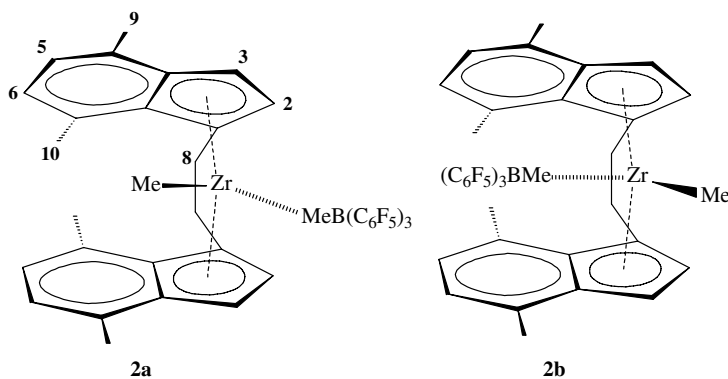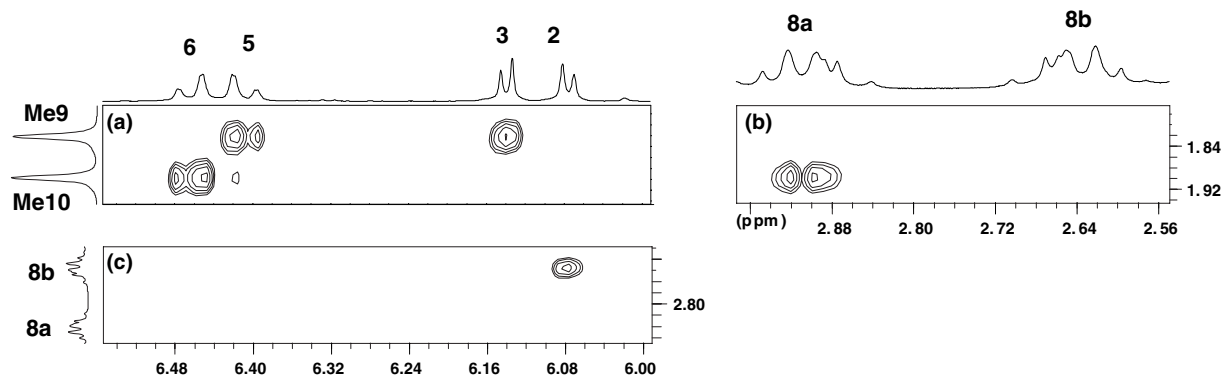

Chart 2.

Fig. 1. Selected regions of a 2D ^1H NOESY of **2a** (toluene-d_8, 273 K, τ_m = 0.5 s) showing the correlations between the indenylic signals.
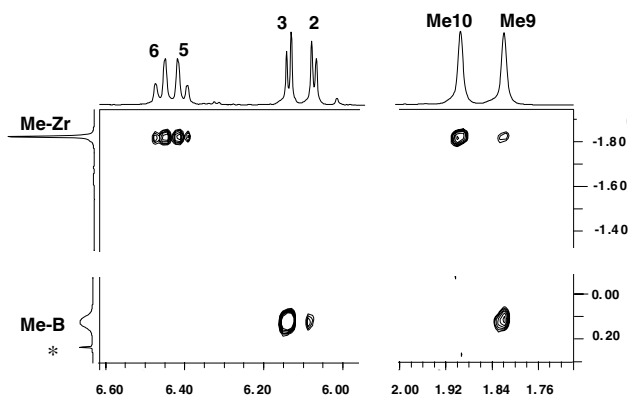
Fig. 2. Selected regions of the same ^{1}H experiment in Fig. 1 showing the correlations between the protons of the indenyl moiety and the Me–Zr and Me–B signals. The asterisk indicates CH$_4$ arising from some decomposition [13].

barely detectable (see the spectra in Figs. 3 and 4), they could be clearly identified by the exchange cross peaks with the resonances of the major isomer **2a**. In particular Fig. 3 shows that Me–Zr of **2a** exchanges with the Me–Zr group of the minor species **2b** (Me–Zr′) and that the Me–B signal of **2a** correlates with the Me–B signal of **2b** (Me–B′). The exchange correlations between the indenylic protons of the two species (as well as some mutual n.O.e. correlation between the signals of the minor species **2b**) are shown in Fig. 4.

These data, and the notably constancy of the **2b/2a** ratio in different samples, allowed to rule out the hypothesis that **2b** was merely an accidental impurity. Attempts to isolate as a pure solid any of the two isomers failed.

Further evidence supports the hypothesis that **2b** was the ion pair in which the [MeB(C$_6$F$_5$)$_3$]$^-$ anion is in the inward site of the *ansa meso*-zirconocene. In particular Me–Zr′, in **2b**, exhibits the same n.O.e correlations shown by Me–B in the major species **2a** (i.e., it correlates with Me9 and with H3) [14]. Moreover, the exchange of the inward and outward position of Me–Zr and Me–B with respect to **2a** is confirmed by the inversion of their

chemical shifts (see the spectrum of Fig. 3): Me–B′ in **2b** lies at negative chemical shift, as observed for Me–Zr of the major isomer **2a** and for the inward methyl groups of the free zirconocene **1**.

Isomer interconversion might occur by two different pathways, involving: (a) dissociation of B(C$_6$F$_5$)$_3$ from one methyl, followed by attack on the other one, or (b) separation of the whole MeB(C$_6$F$_5$)$_3^-$ anion, reorganization of the cationic part of the ion pair and then recombination with the novel stereochemistry. These two processes correspond to the two types of dynamic processes that have been observed in [Cp$_2'$ZrMe]$^+$ [MeB(Ar$_F$)$_3$]$^-$ ion pairs (Cp′ = cyclopentadienyl like ligand, Ar$_F$ = aryl group with fluorine substituents) [5,15–17], as shown in Chart 3 for the prototypal [(Me$_2$Cp)$_2$ZrMe]$^+$[MeB(Ar$_F$)$_3$]$^-$ ion pairs [15]. The terms dissociation-recombination (d–r) and ion pair separation (ips) have been used to indicate the borane or the anion exchange, respectively [15]. In the [Cp$_2'$ZrMe]$^+$[MeB(Ar$_F$)$_3$]$^-$ ion pairs the two methyl sites are equivalent and therefore both the processes are degenerate (mutual exchanges). By contrast, in the present case, due to the C$_s$ symmetry of the rigid *meso* form, the methyl sites are diastereotopic and the d–r and ips dynamic processes become isomerization reactions.

The consequences of the two dynamic processes are depicted in Fig. 5. The "ips" motion would bring the outward Me–B of **2a** into the inward position in **2b**, resulting in the following exchange pattern (the primes refer to the minor isomer): (Me–B) ↔ (Me–B)′, (Me–Zr) ↔ (Me–Zr)′. By contrast, the migration of B(C$_6$F$_5$)$_3$ from the outward to the inward methyl (according to the "d–r" mechanism) would result in the (Me–B) ↔ (Me–Zr)′ and (Me–Zr) ↔ (Me–B)′ exchanges.

Fig. 3 clearly shows that the exchange pattern observed at $T \geqslant 320$ K agrees with the ips and not with the d–r process. No evidence of the exchange pattern expected from the d–r process was obtained up to 340 K. Therefore in the temperature range 320–340 K the anion exchange ("ips") mechanism was the only process active
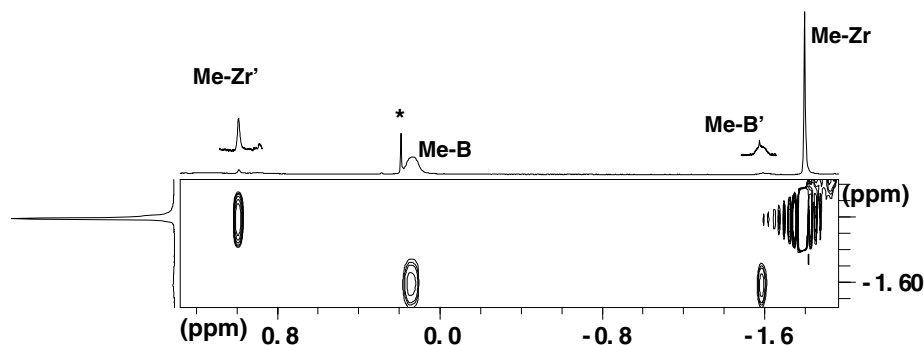

Fig. 3. Selected region of a 2D ^{1}H EXSY spectrum (toluene-d$_8$, 320 K, $\tau_m = 0.5$ s) showing exchange cross peaks between Me–Zr and Me–B of **2a** and the corresponding signals of **2b** (magnified 12× in the insets). The asterisk indicates CH$_4$ arising from some decomposition. The sharp weak signal overlapping the broad resonance of Me–B of **2b** is the low-field ^{13}C satellite of the Me–Zr signal of the main isomer **2a**.
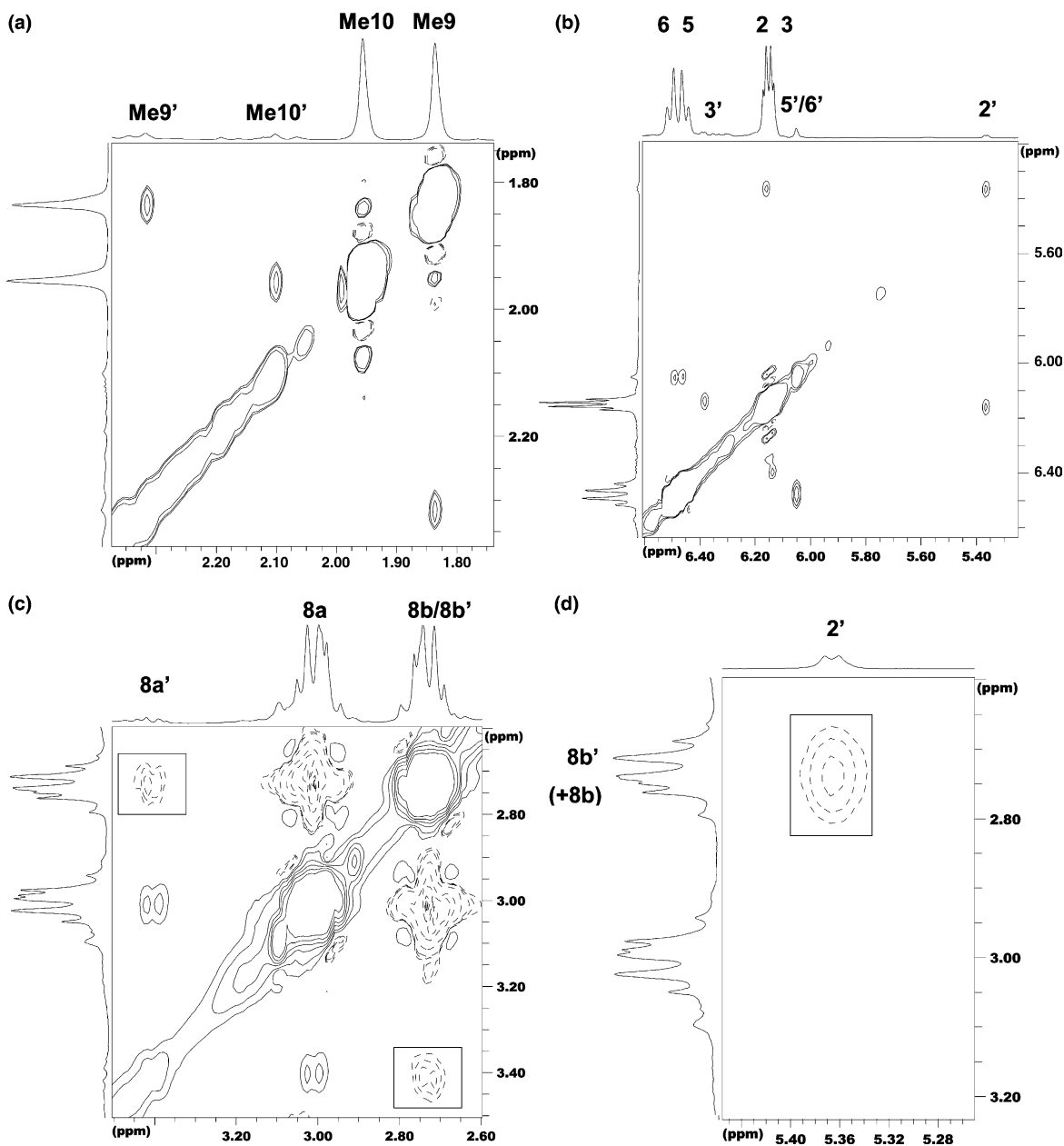
Fig. 4. Selected regions of a 2D ^{1}H EXSY (full line cross peaks)/NOESY (dotted line cross peaks) spectrum (toluene-d_8, 300 K, τ_m = 0.3 s), showing the correlation between the indenyl resonances of the major isomer (**2a**) with the corresponding ones of the minor isomer **2b**: the latter are identified by a prime after the number. The F2 projection of panel d has been magnified. Please note also the inversion of the chemical shifts of protons 2 and 3 (**2a**) with respect to 273 K (Figs. 1 and 2) due to their different temperature dependence. The n.O.e cross-peaks are indicated by boxes.

in the time scale of the EXSY experiments. This is attributable to the fact that $B(C_6F_5)_3$ is a very strong Lewis acid: this favors methyl abstraction and hampers the cleavage of the Me–B interaction (d–r). For a series of related $[Cp'_2ZrMe]^+[MeB(Ar_F)_3]^-$ ion pairs containing different $B(Ar_F)_3$ acids, the *ips* process resulted kinetically favored with respect to the d–r mechanism only with the most strongly bound borane, i.e., $B(C_6F_5)_3$ [15c].

The low intensity of the resonances of **2b** prevented reliable estimation of the kinetic parameters. Anyway,

it can be safely stated that the rates of both the *ips* and d–r processes are much slower than in the corresponding bis-indenyl derivative without the *ansa* bridge, i.e., $[(4,7\text{-}Me_2Ind)_2ZrMe]^+[MeB(C_6F_5)_3]^-$, which adopts a *rac*-like conformation in solution [18]. Indeed, in the latter species the rate of the *ips* process was measurable at a temperature as low as 254 K and at room temperature both the *ips* and d–r processes were simultaneously operating [18].

In principle, the detection of the minor isomer does not imply necessarily that $B(C_6F_5)_3$ is able to attack
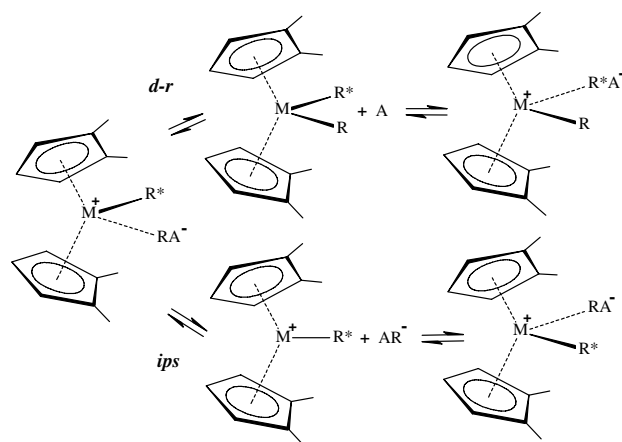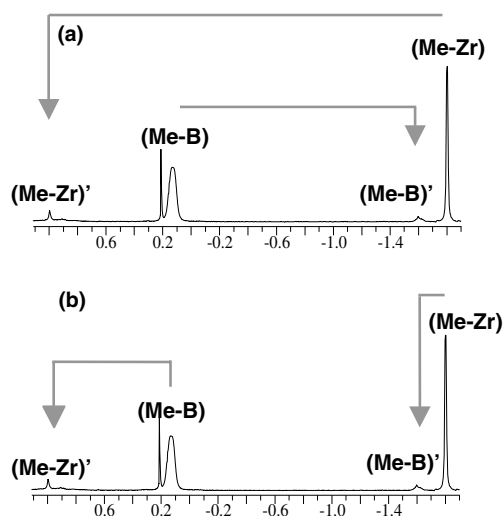
Chart 3.

Fig. 5. A picture of the exchange pattern between the methyl resonances of **2a** and **2b**, according to (a) the *ips* or (b) the *d–r* mechanism.

the inward position: indeed the fact that isomers equilibration occur via anion migration and not $B(C_6F_5)_3$ dissociation would be compatible with the hypothesis that borane attacks the outward site only. However, in the presence of free $B(C_6F_5)_3$, the otherwise undetectable (Me–B) ↔ (Me–Zr)′ and (Me–Zr) ↔ (Me–B)′ exchange pattern, characteristic of the *d–r* process, was observed at a temperature as low as 283 K (Fig. 6) [19]. Since the presence of free $B(C_6F_5)_3$ cannot affect the rate of a truly dissociative process such as the *d–r* one, the observed exchange pattern must arise from a bimolecular process, whose results mimic those of the *d–r* mechanism. We have therefore to admit that, in spite of the steric hindrance, $B(C_6F_5)_3$ is able to attack the (inward) methyl site of **2a**, leading to isomer interconversion through a S_E2-like mechanism, i.e., formation of an unstable *ansa*-(Ind)$_2$Zr^{2+}. 2[MeB(C$_6$F$_5$)$_3$]$^-$ ion pair, followed by $B(C_6F_5)_3$ extrusion from one methyl site.

3. Conclusions

This work indicates that the inward position in *ansa-meso*-bisindenyl zirconocenes is relatively accessible, even for bulky reactants like $B(C_6F_5)_3$. Indeed the species in which the [MeB(C$_6$F$_5$)$_3$]$^-$ anion is into the inward site of the *meso* complex has been found less unfavored than expected (ca. 1.9 Kcal mol^{-1}, on the basis of the measured ratio between isomers **2a** and **2b**). Migration of the [MeB(C$_6$F$_5$)$_3$]$^-$ anion from the outward to the inward position (the *ips* process) also occurs, even if with a rate smaller than that of the migration of the [MeB(C$_6$F$_5$)$_3$]$^-$ anion in the related bisindenyl ion pair without the *ansa* bridge. Moreover, the exchange pattern of the methyl resonances in the 2D ^{1}H EXSY/NOESY maps recorded at 283 K in the presence of free $B(C_6F_5)_3$ suggests that $B(C_6F_5)_3$ is able to attack even the inward position of the *ansa*-bis(indenyl)ZrMe$^+$ cation in ion pair **2a**. This finding contrasts with previous reports concerning related bis(cyclopentadienyl)-dimethyl metallocenes [15a,20], for which the rate of the *d–r* process resulted unaffected by an excess of $B(C_6F_5)_3$. Most likely, the occurrence of electrophilic attack on this (and other ones [18]) (indenyl)$_2$ZrMe$^+$ cations is a consequence of the higher donor power of the indenyl groups that makes these species softer with respect to Cp$_2$ZrMe$^+$.

4. Experimental

All manipulations were performed under nitrogen in oven dried Schlenk-type glassware. $B(C_6F_5)_3$ (Boulder Scientific) was purified by extractions with refluxing *n*-pentane. Deuterated toluene (C.I.L.) was dried on activated molecular sieves (4 Å). The NMR spectra were acquired on Bruker AVANCE DRX-300. ^{19}F NMR spectra were referenced to external CFCl$_3$ ($\delta = 0$ ppm) and ^{11}B NMR spectra to external Et$_2$O · BF$_3$ ($\delta = 0$ ppm). *meso*-[C$_2$H$_4$(4,7-Me$_2$Ind)$_2$ZrMe$_2$] was prepared as previously described [12].

The samples of *meso*-[C$_2$H$_4$(4,7-Me$_2$Ind)$_2$ZrMe]$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$ were prepared in situ, as follows: equimolar amounts of $B(C_6F_5)_3$ and *meso*-[C$_2$H$_4$(4,7-Me$_2$Ind)$_2$ZrMe$_2$] (ca. 20 mg, 0.046 mmol) were separately weighted under N$_2$ in two NMR tubes and dissolved in weighted amounts of dried toluene-d$_8$; then the solution of $B(C_6F_5)_3$ was added to that of the zirconocene.

4.1. meso-[C$_2$H$_4$(4,7-Me$_2$Ind)$_2$ZrMe]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (2a, major isomer)

Panel (b) of the 2D ^{1}H NOESY experiment in Fig. 1 shows the correlation of indenyl methyl resonance at 1.91 ppm with one of the multiplets (centered at 2.83
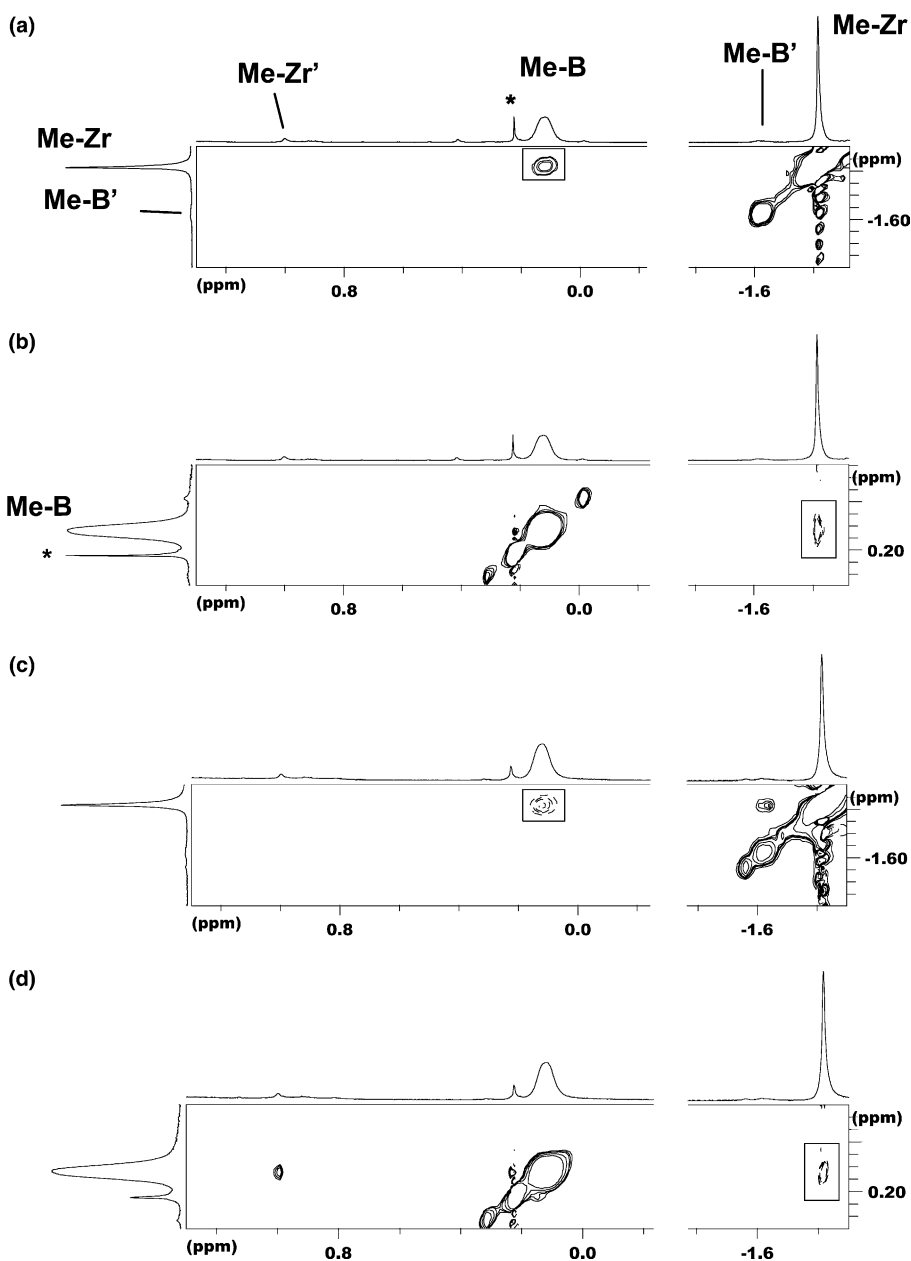
Fig. 6. Selected regions of 2D ^{1}H EXSY (full line cross peaks)/NOESY (dotted line cross peaks) spectra (toluene-d$_8$, 283 K, τ_m = 0.5 s) of ion pair 2, in the absence (panels a and b), or in the presence (c and d) of free B(C$_6$F$_5$)$_3$. Panels a and b: n.O.e. peaks between Me–Zr and Me–B of **2a** only, no exchange with **2b**. Panels c and d: n.O.e. peaks between Me–Zr and Me–B of **2a**, but also exchange with **2b** according to a "d–r like" exchange pathway (see Fig. 5(b)). The n.O.e cross-peaks are indicated by boxes.

ppm) of the ethylene *ansa*, so these resonances are assigned to Me10 and H8a (i.e., the methylenic proton pointing the inward position), respectively. The low-field component (6.50 ppm) of the AB system of the six membered ring is identified as H6 for its cross peak with Me10, while the resonance at 6.14 ppm is assigned to H3 for its correlation with Me9 at 1.83 ppm (Fig. 1(a)). The assignment of the doublet centred at 6.10 ppm to H2 is straightforward for its cross peak with the *ansa* proton H8b, at ca. 2.65 ppm, (i.e., the methylenic proton pointing the outward position) (Fig. 1(c)).

^{1}H NMR: δ 6.54 (d, H6), 6.32 (d, H5), 6.17 (d, H3), 6.05 (d, H2), 3.0–2.8 (m, H8a-inward), 2.73–2.56 (m, H8b-outward), 1.90 (s, Me10), 1.82 (s, Me9), 0.120 (s br, MeB), −1.82 (s, MeZr). ^{13}C NMR: the attributions were performed through 2D^{1}H–^{13}C HMQC and HMBC experiments (300 K, toluene-d$_8$ 7.1 T). Some ambiguities have been resolved by recording the experiments at different temperatures (273 and 300 K): (^{13}C{^{1}H}, 300 K): δ 148.6 (m, $^1J_{C-F}$ = 243 Hz, CF *ortho* or *meta*), 137.6 (m, $^1J_{C-F}$ = 251 Hz, CF *meta* or *ortho*), 139.5 (m, $^1J_{C-F}$ = 249 Hz, CF *para*), 124.2 (C1), 115.9 (C2), 103.4 (C3),

132.2 (C4), 127.1 (C5), 129.9 (C6), 133.4 (C7), 31.59 (C8), 17.28 (C9), 20.25 (C10), 128.7 (C3a), 126.2 (C7a), 51.69 (Me–Zr), 17.64 (Me–B). ^{11}B NMR: δ −13.6 ($\Delta\nu_{1/2}$ = 23 Hz). ^{19}F NMR: (297 K) δ −132.85 (m, F-*ortho*), −159.55 (*pseudo* t, F-*para*), −164.35 (m, F-*meta*).

4.2. meso-[C₂H₄(4,7-Me₂Ind)₂ZrMe]⁺[MeB(C₆F₅)₃]⁻ (2b, minor isomer)

^{1}H NMR: (300 K) δ 6.38 (d, H3), 6.05 (*pseudo*:s H5 and H6), 5.37 (d, H2), 3.40 (m, H8a-inward), 2.73 (m, H8b-outward), 2.32 (s, Me9), 2.10 (s, Me10), 1.00 (s, MeZr), −1.61 (s br, MeB). The accidental overlap of the 8b *ansa* resonances for **2a** and **2b** is confirmed by the n.O.e. correlations with the related 8a and 2 hydrogens (Figs. 4(c) and (d)).

Acknowledgements

References

[1] J. Ewen, J. Am. Chem. Soc. 106 (1984) 6355.

[2] W. Kaminsky, K. Külper, H.H. Brintzinger, F.R.W. Wild, Angew. Chem., Int. Ed. Engl. 24 (1985) 507.

[3] L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, Chem. Rev. 100 (2000) 1253.

[4] See H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem., Int. Ed. Engl. 34 (1995) 1143, and refs therein.

[5] E.Y.-X. Chen, T.J. Marks, Chem. Rev. 100 (2000) 1391.

[6] L. Resconi, F. Piemontesi, M. Galimberti, US Patent 5,585,448 to Montell Tech. Company.

[7] P. Galli, G. Collina, P. Sgarzi, G. Baruzzi, E. Marchetti, J. Appl. Polym. Sci. 66 (1997) 1831.

[8] L. Resconi, U. Giannini, T. Dall'Occo, in: W. Kaminsky, J. Scheirs (Eds.), Metallocene Catalysts, Wiley–Weinheim, New York, 1999, p. 69.

[9] T. Uozomi, K. Miyazawa, T. Sano, K. Soga, Macromol. Rapid Commun. 18 (1997) 883.

[10] L.A. Castoguay, A.K. Rappé, J. Am. Chem. Soc. 114 (1992) 5832.

[11] G. Guerra, L. Cavallo, G. Moscardi, M. Vacatello, P. Corradini, Macromolecules 29 (1996) 4834.

[12] D. Balboni, I. Camurati, G. Prini, L. Resconi, S. Galli, P. Mercandelli, A. Sironi, Inorg. Chem. 40 (2001) 6588.

[13] We suppose that the weak methane signal usually observed in our reaction mixtures arises from methyl protonation by the B(C₆F₅)₃ · H₂O adduct, which is a strong Brønsted acid, formed from adventitious water, present also after careful solvent anhydrification. The hypothesis that methane arises from some slow decomposition pathway can be ruled out, since its signal was already observed immediately after B(C₆F₅)₃ addition to the zirconocene solution.

[14] No correlation could be found for Me–B because its signal, besides being weak, was also very broad.

[15] (a) X. Yang, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10015;
(b) P.A. Deck, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 6128;
(c) P.A. Deck, C.L. Beswick, T.J. Marks, J. Am. Chem. Soc. 120 (1998) 1772.

[16] A.R. Siedle, R.A. Newmark, J. Organomet. Chem. 497 (1995) 119.

[17] S. Beck, S. Lieber, F. Schaper, A. Geyer, H.H. Brintzinger, J. Am. Chem. Soc. 123 (2001) 1483.

[18] T. Beringhelli, G. D'Alfonso, D. Maggioni, P. Mercandelli, A. Sironi, Chem. Eur. J., in press.

[19] The presence of free B(C₆F₅)₃ did not affect the rate of the *ips* process, since the exchange pattern typical of this mechanism became detectable only at 320 K, as in the absence of B(C₆F₅)₃ excess. In Fig. 4 the **2a** ← → **2b** isomer exchange is observable at T = 300 K because of the presence of free B(C₆F₅)₃ in the sample used for this experiment. The same correlations albeit with a worse S/N, due to the poor stability of the mixture at high temperature [12], are observable at 320 K without free B(C₆F₅)₃.

[20] X. Yang, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 113 (1991) 3623.