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Hydrosilane-B(C_6F_5)₃ adducts as activators in zirconocene catalyzed ethylene polymerization[†]

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Hydrosilane-B(C₆F₅)₃ adducts were found to activate zirconocene dihalides and generate ternary catalytic systems possessing moderate to high activity in ethylene polymerization to high density polyethylene (HDPE). The activation efficacy of the adducts increased with increasing hydride donor ability and decreased with steric crowding of the particular hydrosilane used. NMR investigation of the HSiEt₃/ $B(C_6F_5)_3/Cp^*_2ZrF_2$ system (Cp* = η^5 -C₅Me₅) revealed the formation of a stable intermediate [Cp*_2ZrF(FSiEt_3- κ F)]⁺[HB(C₆F₅)₃]⁻, whereas a crucial role of the [HB(C₆F₅)₃]⁻ anion as a hydride donor for generation of an active cationic zirconium hydride center was elucidated.

Introduction

Activation of the Si-H bond in hydrosilanes by the strong Lewis acid $B(C_6F_5)_3$ has found widespread utilization in catalysis during the last 15 years.^{1,2} The formation of the hydrosilane-borane adduct R₃SiH·B(C₆F₅)₃ enhancing the polarization of the hydrosilane moiety and boosting its reactivity towards various substrates has been accepted as a key step. Although the adduct was suggested by DFT calculations to be energetically feasible, both its isolation and spectroscopic characterization have remained elusive until recently.3 An enhanced electropositivity of the silicon atom in the hydrosilane-B(C₆F₅)₃ adduct facilitates abstraction of an anionic σ -ligand X from early transition metal complexes (M = Zr, Sc) vielding a cationic metal center and the corresponding Si-X silane, as depicted schematically in eqn (1). The reaction involves a hydride transfer from the hydrosilane to give rise to the borate counteranion $[HB(C_6F_5)_3]^-$.

$$\{M\}-X+R_3SiH+B(C_6F_5)_3 \to \{M\}^+[HB(C_6F_5)_3]^-+R_3SiX \quad (1)$$

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Activation of the intramolecular β-hydrogen Si-H bond in $[Cp_2Zr{N(SiMe_2H)_2}X]$ complexes (where $Cp = \eta^5 - C_5H_5$, X = Cl, OTf, OMe) with $B(C_6F_5)_3$ led to zwitterionic complexes $[Cp_2Zr]$ $\{N(SiMe_2H)(XSiMe_2-\kappa X)\}^+[HB(C_6F_5)_3]^-$, where the $XSiMe_2$ group stabilized the cationic zirconium center via coordination of X.4 Similarly, the intramolecular activation of the Sc-N bond in the $[{PhC(N-2,6-iPr_2C_6H_4)_2}Sc{N(SiMe_2H)_2}_2]/[Ph_3C]^+[B(C_6F_5)_4]^$ system generating the cationic complex [{PhC(N-2,6 $iPr_2C_6H_4)_2$ ScN{(SiMe_2H)(SiMe_2N(SiMe_2H)_2)}]⁺ has been established.5 Recently, the formation of the zwitterionic $[Cp*_2Sc]^+[HB(C_6F_5)_3]^-$ complex $(Cp* = \eta^5 - C_5Me_5)$ obtained by reacting $[Cp*_2ScCl]$ with one equivalent of $B(C_6F_5)_3$ in the presence of a slight excess of HSiEt3 was published by Piers et al.^{6,7} The X-ray analysis of the complex revealed its stabilization by coordinating ortho and meta fluorine atoms of one perfluorophenyl group of the $[HB(C_6F_5)_3]^-$ anion to the scandium cation. Despite the close cation-anion contact, the hydride transfer from boron to scandium did not occur since the zwitterionic complex failed to react with either propene or deuterium gas.⁶ On the other hand, we have found evidence for an effective intramolecular hydride transfer in titanocene dichloride $[Cp(\eta^5-C_5H_4CH_2SiMe_2H)_2]$ TiCl₂] from the pendant SiMe₂H group to the titanium center, catalyzed by $B(C_6F_5)_3$ giving transient titanocene hydrido chloride. The transient species further reacted to give $[Cp(\eta^5-C_5H_4CH_2SiMe_2Cl)_2TiCl_2]$ in chlorinating solvents or decomposed into paramagnetic Ti(m) species in toluene.⁸ Based on these results we suggested that cationic group 4 hydrides should be accessible via the intermolecular reaction of hydrosilane-B(C₆F₅)₃ adducts with group 4 dihalides. As the zwitterionic complex $[Cp_{2}^{*}ZrH]^{+}[HB(C_{6}F_{5})_{3}]^{-}$ is known to be highly active (A = 3200 kg_{PE} (mol_{Zr} h bar)⁻¹) in ethylene polymerization,⁹ we anticipated a large potential of such in situ formed species in catalysis. Herein, we report on polymerization of ethylene by ternary zirconocene dihalide/hydrosilane/B(C₆F₅)₃ systems, which represent the first catalytic systems based on group 4 halide complexes activated with a non-aluminium cocatalyst or activator.

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Results and discussion

To test the concept, we initially screened ethylene polymerization using ternary catalytic systems [Cp'2TrCl2]/HSiEt3/ $B(C_6F_5)_3$ (where $Cp' = Cp, Cp^*$) at various zirconocene concentrations (5-300 µM) and Zr/Si/B ratios. The results obtained are summarized in Table S1 in the ESI.† At low zirconocene concentrations up to 200 μ M, a large excess of B(C₆F₅)₃ and HSiEt₃ was necessary to achieve a high activity of the catalytic systems (*i.e.* >10³ kg_{PE} (mol_{Zr} h bar)⁻¹; see entries 1–6 for $[Cp_2ZrCl_2]$ and entries 10-12 for [Cp*₂ZrCl₂] in Table S1[†]). We suggest that the hydrosilane-B(C_6F_5)₃ adduct is a less efficient impurity scavenger than aluminium alkyls (e.g. Al(i-Bu)₃) and the catalytic systems must be considered as "naked" ones, where a partial decomposition of active species by trace impurities typically occurs. Indeed, at a high Zr concentration (300 μ M) the systems [Cp₂ZrCl₂]/HSiEt₃/B(C₆F₅)₃ and [Cp*₂ZrCl₂]/HSiEt₃/ $B(C_6F_5)_3$ afforded average activities of 1070 and 200 kg_{PE} $(mol_{Zr} h bar)^{-1}$, respectively, whereas the Zr/Si/B ratio could be reduced to an optimal value of 1/1000/1 (entries 7-9, 13 and 14 in Table S1[†]). Both catalytic systems showed good reproducibility, although the latter one possessed milder polymerization progress (e.g. better temperature control). Therefore, the $[Cp*_2ZrCl_2]/hydrosilane/B(C_6F_5)_3$ systems (Si/Zr = 1000; B/Zr = 1, 2, and 10) were tested further in ethylene polymerization to evaluate the effect of hydrosilane on the catalytic performance. The results are summarized in Fig. 1 and Table S2.†

The activity of the particular system depended strongly on the nature of hydrosilane and followed roughly the order tertiary > secondary > primary. Generally, increasing the B/Zr ratio led to an activity improvement in almost all studied systems, probably as a result of increased concentration of the hydrosilane-B(C_6F_5)₃ adduct leading to faster generation of active species (as could be seen from the ethylene consumption profile in Fig. S1†). Similarly, the consumption profiles showed a direct influence of the particular hydrosilane on the generation of active species (Fig. S2†), whereas the activation process was considerably slower (typically within minutes) in comparison to MAO (methylaluminoxane) activation.¹⁰ To



Fig. 1 The dependence of ethylene polymerization activity of $[Cp*_2ZrCl_2]/hydrosilane/B(C_6F_5)_3$ systems on the nature of the hydrosilane and the Zr/B ratio. Conditions: ethylene pressure 3 bar, 25 °C, 50 mL of toluene, 15 μ mol Zr (* denotes 5 μ mol Zr used), Zr/Si = 1/1000.

understand the hydrosilane effect on system activity, we have expressed the hydride donor ability of hydrosilanes as the nucleophilicity parameter N adapted from the literature.¹¹ Fig. 2 displays the dependence of system activity on the parameter N of the hydrosilane at different Zr/B ratios. Obviously, the activity of the system could not be ascribed exclusively to the silane nucleophilicity, as steric factors seem to play a significant role also. A lower steric crowding around the silicon atom increased the activity for hydrosilanes of similar nucleophilicity (e.g. the activity for tertiary hydrosilanes decreased in the order: $HSiEt_3 > HSiMe_2Ph \gg HSiPh_3 \sim HSi(i-Pr)_3$, whereas for similar silane steric parameters the higher nucleophilicity enhanced the system activity (e.g. the activity decreases in the order: $HSiEt_3 > H_2SiEt_2$; $HSiMe_2Ph > H_2SiMePh$). One can assume that the best hydrosilane for activation should be the one possessing high nucleophilicity and low steric hindrance (i.e. HSiEt₃). In addition to molecular hydrosilanes we have tested polymethylhydrosiloxane (PMHS) as a cheap and readily available hydride source (entries 6 and 7 in Table S2[†]). The system showed sufficient activity (30 kg_{PE} (mol_{Zr} h bar)⁻¹ at B/ Zr = 1/1 ratio; 50 kg_{PE} (mol_{Zr} h bar)⁻¹ at B/Zr = 2/1 ratio), despite the presence of siloxane units which could compete with ethylene for coordination to the active site. Both bulky hydrosilanes, HSi(i-Pr)₃ and HSiPh₃, led to inactive systems under all conditions studied (B/Zr = 1, 2, 10), regardless of their high nucleophilicity. Accordingly, the former one is known to be unreactive in other $B(C_6F_5)_3$ catalyzed reactions due to steric hindrance which precludes the formation of a $(i-Pr)_3SiH \cdot B(C_6F_5)_3$ adduct.^{12,13} In contrast, the Ph₃SiH \cdot B(C_6F_5)_3 adduct forms efficiently as it was shown by its activity in alcohol,¹² carbonyl, or aldehyde^{14,15} reduction. The inability of the bulky Ph₃SiH·B(C₆F₅)₃ adduct to activate the Zr-Cl bond crowded by two bulky Cp* ligands led us to the conclusion that an associative mechanism is to be involved (see below for the mechanism). In addition, a preliminary experiment also



Fig. 2 Dependence of the polymerization activity of the $[Cp*_2ZrCl_2]/hydrosilane/B(C_6F_5)_3$ system on hydrosilane nucleophilicity (blue – tertiary, green – secondary, red – primary hydrosilane) at various Zr/B ratios.

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showed a substantial effect of the σ-ligand bonded to the zirconium atom, since the system $[Cp_2Tr_2]/HSiEt_3/B(C_6F_5)_3$ (entry 22 in Table S2†) displayed about 10-times higher activity in comparison with the system based on $[Cp_2TCl_2]$ ($A = 1840 \nu s$. 160 kg_{PE} (mol_{Zr} h bar)⁻¹).

The polyethylene materials produced by these systems have melting points in the range typical for HDPE (134–137 °C) and narrow dispersity (D = 1.4-2.4). Hydrosilanes are known as chain-transfer agents in early transition metal-catalyzed olefin polymerization producing silyl caped polyolefins,¹⁶ however, catalytic systems comprising zirconocenes exhibit this behavior only rarely.¹⁷ In the present case, IR spectra of the prepared PE samples are devoid of signals characteristic for the silane caps (the spectra are almost identical with the spectra of polymers prepared by the [Cp₂ZrCl₂]/MAO system, see Fig. S5†). Moreover, the M_n values of the polymers are in the range 66–262 kDa, which is comparable to the value for PE produced by [Cp*₂ZrH]⁺[HB(C₆F₅)₃]⁻ ($M_n = 154$ kDa).⁹ Therefore, we suggest that the chain-transfer by hydrosilane and/or hydrosilylation of PE end groups is only negligible, if any.

In order to shed light on the activation process we have performed an NMR investigation of the system. $[Cp^*_2ZrF_2]$ was used instead of $[Cp^*_2ZrCl_2]$ to gain sufficient reactivity and to benefit from the ¹⁹F nucleus visibility in NMR. The reaction of $[Cp^*_2ZrF_2]$ with HSiEt₃ and B(C₆F₅)₃ (in a 1/2/1 molar ratio) in toluene- d_8 (eqn (2)) resulted in an immediate formation of an intensely yellow oily product, analysis of which by a multinuclear NMR showed the presence of cationic complexes $[Cp^*_2ZrF(FSiEt_3-\kappa F)]^+$ ([1]) and $[\{Cp^*_2ZrF\}_2(\mu-F)]^+$ ([2]) in a ratio 74/26, both being stabilized with the $[HB(C_6F_5)_3]^-$ counteranion.



The coordination of FSiEt₃ to the cationic zirconocene moiety in [1] was supported by its high-field shift in the ¹⁹F NMR spectrum (-181.3 ppm) in comparison with the free one (-175.0 ppm) (Fig. S10†) and by the 1D NOESY spectrum (Fig. S11†). Signals for the terminal Zr–F bond appeared at 107.9 ppm for [1] and at 86.8 ppm for [2], while the bridging Zr–F–Zr fluorine in [2] appeared at –109.3 ppm. The anion [HB(C₆F₅)₃][–] is characterized by the broad singlet at 4.15 ppm in ¹H NMR (Fig. S12†), three broad signals centered at –167.3 (s), –164.3 (s), and –133.0 (d) ppm in ¹⁹F NMR and a broad singlet at –24 ppm in the undecoupled ¹¹B NMR spectra (Fig. S13†).

Attempts to isolate either $[1][HB(C_6F_5)_3]^-$ or $[2][HB(C_6F_5)_3]^$ in pure form failed, giving only a mixture of products (for details see the ESI[†]). However, the DFT optimized model of $[1][HB(C_6F_5)_3]^-$ (Fig. 3) supported the structure proposed on the basis of NMR experiments (for details and model of $[2][HB-(C_6F_5)_3]^-$ see the ESI[†]). Geometric parameters as well as Mayer bond orders (Zr–F 0.86; Zr–F(Si) 0.29; Si–F 0.48) show that the



Fig. 3 DFT optimized molecule of $[1][HB(C_6F_5)_3]^-$. Hydrogen atoms (except B–H) are omitted for clarity. Selected atomic distances and angles: Zr–F 1.988 Å; Zr–F(Si) 2.257 Å; Si–F 1.746 Å; B–H 1.214 Å; Zr–F–Si 143.64°; \sum (C–Si–C) 343.23°.

fluorine atom from the Zr–F–Si bridge is closer to the silicon atom than to zirconium.

The reaction of $[Cp_{2}^{*}ZrF_{2}]$ with HSiEt₃ and B(C₆F₅)₃ (in a 1/1/1 molar ratio) conducted in the more polar and coordinating C6D5Br solvent led to the formation of the new species $[Cp*_2ZrF(C_6D_5Br-\kappa Br)]^+[HB(C_6F_5)_3]^ ([3][HB(C_6F_5)_3]^-)$ in addition to [1] and [2] (ratio [1]/[2]/[3] = 76/5/19 at -30 °C), which was determined from a new downfield signal for Zr-F at -124.3 ppm in the ¹⁹F NMR spectrum measured at -30 °C (see Fig. S16[†]). The structure of [3] is consistent with a similar solvent stabilized ion-pair [Cp*₂ZrCl(C₆D₅Cl-κCl)]⁺[B(C₆F₅)₄]⁻ described by Jordan.¹⁸ Variable temperature experiments and an experiment performed at the ratio Zr/Si/B = 2/1/1 implied a mutual equilibrium between [1], [2], and [3] (Scheme S3⁺). Attempts to trap the cationic [Cp*₂ZrF]⁺ fragment by the reaction of in situ generated [1]-[3] with THF yielded [Cp*2ZrF $(THF-\kappa O)$]⁺ $[HB(C_6F_5)_3]^-$ ([4] $[HB(C_6F_5)_3]^-$) as a product of replacing FSiEt₃, [Cp*₂ZrF₂] or C₆D₅Br from the zirconium coordination sphere of [1]-[3]. A B(C₆F₅)₃·THF adduct was also detected in the ¹⁹F NMR spectrum, in addition to the replaced species [Cp*₂ZrF₂] and FSiEt₃ (Fig. S21[†]). The ¹¹B NMR spectrum (Fig. S22[†]) of $[4][HB(C_6F_5)_3]^-$ showed a doublet $({}^1J_{BH} \sim$ 81 Hz) at -25 ppm, which is in contrast to the spectra of the $[HB(C_6F_5)_3]^-$ counteranion in [1]-[3] showing only a broad singlet. These observations led us to a conclusion that certain amounts of B(C₆F₅)₃ remained in the product mixture generated from [Cp*₂ZrF₂]/HSiEt₃/B(C₆F₅)₃ despite the initial Zr/Si/B ratio. Consequently, one could anticipate a reversible formation of the diborohydride $[(C_6F_5)_3B(\mu-H)B(C_6F_5)_3]^-$ anion from B(C₆F₅)₃ and [HB(C₆F₅)₃]⁻ as was described previously.¹⁹

The *in situ* generated C_6D_5Br solutions containing [1]–[3] were found to be highly active (A = 3290 or 1540 kg_{PE} (mol_{Zr} h bar)⁻¹ for initial ratios Zr/Si/B = 1/1/1 or 2/1/1) in ethylene polymerization, however, without any additional HSiEt₃ or $B(C_6F_5)_3$ used (Table S3 in the ESI†). This led us to express our suspicion about the role of the [HB($C_6F_5)_3$]⁻ anion acting as an

additional hydride donor. To support this assumption, we have performed the reaction of $[Cp_2TF_2]$ with HSiEt₃ and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (in a 1/1/1 molar ratio) in C_6D_5Br . The ¹H NMR spectrum (Fig. S24[†]) of the reaction products proved the formation of zirconocene species, FSiEt₃, and Ph₃CH in a 1/1/1 molar ratio, while ¹⁹F NMR (Fig. S25[†]) at -30 °C revealed $[1][B(C_6F_5)_4]^-$ and $[3][B(C_6F_5)_4]^-$ in a *ca.* 70/30 molar ratio as the only zirconocene species (being in equilibrium at higher temperatures). The absence of theoretical $[2][B(C_6F_5)_4]^-$ as well as an equimolar formation of Ph_3CH (with respect to $FSiEt_3$ and [1] + [3]) indicated a gradual formation of an electrophilic silvlium cation, which gave rise to [1] by abstracting one fluorine ligand from $[Cp_{2}^{*}ZrF_{2}]$. The mixture of $[1][B(C_{6}F_{5})_{4}]^{-}$ and $[3][B(C_{6}F_{5})_{4}]^{-}$ was inactive in ethylene polymerization even after addition of 1000 equiv. of HSiEt₃ into the reactor. In contrast, subsequent addition of 1 equiv. of $B(C_6F_5)_3$ resulted in immediate polymer formation and high activity (A = 1470 kg_{PE} (mol_{zr} h bar)⁻¹) was achieved. Similarly, the mixture of $[1][B(C_6F_5)_4]^-$ with $[3][B(C_6F_5)_4]^-$ generated in situ was activated by addition of the hydride $[(t-Bu)_3PH]^+[HB(C_6F_5)_3]^-$ (ref. 20) to obtain a system with high activity (A = 1940 kg_{PE} (mol_{Zr} h bar)⁻¹). These results showed a substantial hydride donor ability of the $[HB(C_6F_5)_3]^-$ anion (about 21 kcal mol⁻¹ stronger hydride donor than HSiEt₃ and only 15 kcal mol⁻¹ weaker hydride donor than borohydride $[BH_4]^-$ – a common hydride source)²¹ and its role in the formation of zirconocene-hydride species.

The formation of zirconocene-hydride within the activation process was proved indirectly based on its reactivity. The reaction of the $[Cp*_2ZrF_2]/HSiEt_3/B(C_6F_5)_3$ system at the 1/2/1 molar ratio in CDCl₃ generated [Cp*₂ZrCl₂], 2 equiv. FSiEt₃, and CDHCl₂ while B(C₆F₅)₃ remained virtually unaffected (Fig. S30 and S31[†]). This composition of products implies that a species containing the Zr-H bond was effectively formed, further reacting *in situ* with $CDCl_3$ to give rise to $[Cp_2ZrCl_2]$ and CDHCl₂ as products of CDCl₃ dechlorination. The exclusive formation of FSiEt₃ over ClSiEt₃ also excluded the silvlium $[SiEt_3]^+$ formation within the reaction course. Similarly, the Zr-D bond generated by using the $[Cp_2ZrF_2]/DSiEt_3/B(C_6F_5)_3$ system was trapped in the reaction with 1-hexene. The ¹H and ²H NMR spectra (Fig. S33[†]) of the obtained oligo(1-hexene) revealed an efficient incorporation of deuterium in the oligomer.

Based on the above experiments we have proposed a tentative mechanism for the generation of cationic zirconocene hydride **F** as a catalytically relevant species (Scheme 1).

The initial part of the cycle parallels the $B(C_6F_5)_3$ catalyzed hydrosilylation of the carbonyl group, where the $S_N 2$ mechanism is involved.^{15,22} The formation of the Si–H–B adduct enhanced the Lewis acidity of the silicon atom, which led to its attack by a nucleophilic halide ligand, giving the intermediate **A**. The following dissociation of **A** to give the zwitterionic complex **B** is probably driven by the formation of a strong Si–X bond. A neutral zirconocene hydridohalide **C** is formed by a hydride transfer from the $[HB(C_6F_5)_3]^-$ counterion to zirconium (hydride transfer from another equivalent of the hydrosilane is unlikely as it was shown above in polymeriz-



Scheme 1 Suggested mechanism of generation of zirconocenium hydride species.

ation experiments). We propose that the hydride transfer would be facilitated by an appropriately oriented LUMO orbital in **B**, which has mostly a metallic d-character contribution (as shown in Fig. S34[†] for [1][B(C₆F₅)₄]⁻). It shall be noted that this step is in contrast with the behavior of $[Cp*_2Sc]^+[HB (C_6F_5)_3]^-$ where the hydridoborate does not transfer the hydride to the scandium center.⁶ The second halide ligand is removed from the zirconium center by the same mechanism through the intermediate **D** to give the cationic zirconocenium hydride **E** stabilized by halosilane coordination. The latter is suggested to form an equilibrium with the polymerization active cationic species **F**.

Conclusions

In conclusion, we have developed a simple zirconocene dihalide/hydrosilane/B(C_6F_5)₃ ternary system, which is active in the catalytic polymerization of ethylene to HDPE. The initial step of activation consisted of nucleophilic substitution at the silicon atom, where replacement of hydride with fluoride took place. As a result, cationic zirconium species stabilized with a hydridoborate anion $[HB(C_6F_5)_3]^-$ was generated. The polymerization experiments including sterically demanding HSiPh₃ implied an S_N2 mechanism of the substitution. In the following step, the hydridoborate acted as a hydride donor for the cationic zirconium center and generated a Zr-H bond, the presence of which is considered to be crucial for polymerization. We propose that the hydride transfer from hydrosilane to $B(C_6F_5)_3$ and finally to a transition metal could be applied to other transition metal halide complexes where the formation of a metal-hydride bond is a prerequisite for their catalytic performance (pyridine-bis(imine)Fe catalysts, nickel diimine catalysts).^{23,24} Application of hydrosilane/B(C₆F₅)₃ as a transition metal activator in other catalytic processes (hydrodefluorination) is currently under investigation.

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