Supporting Information

Hydrosilane-B(C₆F₅)₃ adducts as activators in zirconocene catalyzed ethylene polymerization

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Content:	Page
 Experimental NMR data for starting materials and common products NMR experiments (in combination with polymerization) Polymerization results Figures, graphs, and NMR spectra 	S2 S4 S4 S10 S13
6. Results of DFT studies7. Cartesian coordinates8. References	S30 S32 S35

1. Experimental

1.1. General Considerations.

Manipulations of air sensitive compounds were carried out under argon atmosphere using standard Schlenk techniques or under nitrogen atmosphere using an mBraun Labmaster glove-box. For the attempted isolation of cationic species, all-glass devices equipped with breakable seals were used. Unless stated otherwise, ¹H (300.0 MHz), ¹³C (75.4 MHz), ¹¹B (96.3 MHz), ¹⁹F (282.2 MHz) and ²⁹Si (59.6 MHz) NMR spectra were measured on a Varian Mercury 300 spectrometer at 25 °C. ¹H and ¹³C chemical shifts (δ /ppm) are given relative to solvent signals (δ_{H}/δ_{C} : toluene-*d*₈ 2.08 (CD₂*H*)/137.48 (*C*_{ipso}); C₆D₅Br 7.30(C*H*_{ortho})/122.61 (*C*_{ipso}); CDCl₃ 7.26/77.16). ¹¹B, ¹⁹F, ²⁹Si NMR spectra were referenced to an external reference (¹⁹F NMR to C₆H₅CF₃ at -63.72 ppm; ²⁹Si NMR to SiMe₄ at 0.00 ppm; ¹¹B NMR to BF₃·Et₂O at 0.00 ppm). GC-MS analyses was performed with a Thermo Focus DSQ instrument using a capillary column Thermo TR-5MS (15 m × 0.25 mm ID × 0.25 mm). Electrospray mass spectra (ESI-MS) were measured with a Bruker Esquire 3000 instrument on dichloromethane/acetonitrile solutions.

1.1. Chemicals

Liquid silanes (Et₃SiH, PhMe₂SiH, i-Pr₃SiH, Et₂SiH₂, Ph₂SiH₂, PhMeSiH₂, PhSiH₃) were obtained either form Aldrich or Across and dried by refluxing over LiAlH₄, distilled under argon and stored over 3Å molecular sieve. PMHS (poly(methylhydrosiloxane) was obtained from Aldrich, degassed in vacuum for 12 h and stored over 3Å molecular sieve. Ph₃SiH and DSiEt₃ (97 atom % D) were obtained form Aldrich and used as received. $B(C_6F_5)_3$ and $[Ph_3C]^+[B(C_6F_5)_4]^-$ were obtained from Strem and used as received. $[Cp*_2ZrF_2]$ and $[(t-Bu)_3PH]^+[HB(C_6F_5)_3]^-$ were prepared according to literature procedures.¹⁻²

1.2. Computational details.

DFT studies were carried out on the *bose* cluster at the J. Heyrovský Institute of Physical Chemistry, v.v.i. using Gaussian 09.³ Geometry optimizations employed the M06 functional, the 6-311G(d,p) basis set for all atoms with the exception of the zirconium atoms for which the SDD pseudopotential was used. The Hessian needed for the optimization was computed analytically prior the first step of the optimization procedure. Solvent effects were accounted for by using the Polarizable Continuum Model and assuming toluene as solvent. Numerical integration was done on a pruned grid having 99 radial shells each of 590 angular points.

1.3. Ethylene polymerization

1.3.1. without preactivation

The polymerization experiments were performed in a semibatch-mode using a 250 mL Büchi glass double-jacketed autoclave equipped with a magnetic stirrer (at 800 rpm). The hot autoclave was three times evacuated and filled with argon, and finally tempered at desired temperature. Under argon atmosphere, the autoclave was charged successively with toluene, particular silane (15 mmol), and B(C₆F₅)₃ (15 µmol, toluene stock solution) and the resulting mixture was stirred for 30 min. Argon was vented and the autoclave was pressurized with ethylene to desired pressure (3 bar) and maintained at this pressure for 10 min. Ethylene was partially released (to a pressure ca. 1.1-1.5 bar), while the polymerization was started by injecting of the desired amount of catalyst precursor in toluene (particular zirconocene dihalide 15 µmol) under a stream of ethylene and the autoclave was immediately pressurized to 3 bar. Final volume of polymerization solution was 50 mL in all experiments. The autoclave temperature was kept constant during the reaction by using the external Pt100 sensor connected to Julabo F31-C bath. The consumption of ethylene was followed in each experiment through a calibrated mass flow meter (Bronkhorst, EL-FLOW) which was controlled by a Bronkhorst High-Tech modular digital readout and control system. After the appropriate time, the reactor was vented and the polymerization was quenched with 80 mL of ethanol. The precipitated polyethylene was stirred for 1 h, collected on a glass frit, rinsed repeatedly with ethanol and acetone, and dried in vacuum to constant weight. Results are summarized in Tables S1 and S2

1.3.2. with preactivation in C_6D_5Br (combination of NMR experiments with polymerization experiments)

The polymer reactor was settled as above and filled with 50 mL of toluene and argon atmosphere was replaced with ethylene. In another Schlenk tube, a reaction mixture comprising particular components (details in experiments below and Table S3) was prepared. A part of the mixture was sealed into a NMR tube and from the rest a volume corresponding to 15 μ mol of Zr was taken by Hamilton syringe and directly injected into the autoclave under a stream of ethylene. The autoclave was pressurized with ethylene and the polymerization followed as above. Detailed description of the particular experiments can be found in sections 3.3.–3.6. and the results are summarized in Table S3.

1.3.3. Polyethylene (PE) analysis.

SEC data were measured on a PL GPC 220 high-temperature chromatograph equipped with PL-220DRI and VISKOTEL 220R detectors. Samples concentration was $1.0 \text{ mg} \cdot \text{mL}^{-1}$ and all samples were filtered (0.45 µm filter) prior to injection. Separation was performed at 160 °C on a set of three PL gel columns (10µm MIXED-B, 300 x 7.5 mm) in 1,2,4-trichlorobenzene (Scharlau) stabilized by 0.025% of Santonox R at flow rate 1 mL·min⁻¹. Polyethylene molecular weights and distributions were evaluated on the basis of PS calibration (16 standards; 1080–13 155 000) and corrected using universal calibration method (Viscotek TriSEC software). All the results are averages of two measurements. Thermal behavior of PE was investigated by DSC (TA Instruments Q100) with both heating and cooling rate 10 °C.min⁻¹ under nitrogen (50 cm³.min⁻¹). Melting temperatures and heats of fusion were obtained from second heating run.

2. NMR data for starting materials and common products

 $[Cp*_2ZrF_2]$: ¹H NMR (C₆D₅Br): 1.83 (s, 30H, C₅Me₅). ¹⁹F NMR (C₆D₅Br): 26.8 (s, 2F, ZrF₂). ¹H NMR (toluene-d₈): 1.82 (s, 30H, C₅Me₅). ¹³C{¹H} NMR (toluene-d₈): 10.4 (C₅Me₅); 121.0 (C₅Me₅). ¹⁹F NMR (toluene-d₈): 26.8 (s, 2F, ZrF₂).

 $[Cp*_2ZrCl_2]$: ¹H NMR (CDCl₃): 1.99 (s, 30H, C₅Me₅). ¹³C{¹H} NMR (CDCl₃): 12.10 (C₅Me₅); 123.80 (C₅Me₅). ¹H NMR (toluene-d₈): 1.83 (s, 30H, C₅Me₅). ¹³C{¹H} NMR (toluene-d₈): 11.98 (C₅Me₅); 123.32 (C₅Me₅).

Et₃SiF: ¹H NMR (C₆D₅Br): 0.54–0.63 (m, 6H, SiCH₂Me); 0.89–0.96 (m, 9H, SiCH₂Me). ¹³C{¹H} NMR (C₆D₅Br): 5.3 (d, ²J_{CF} = 14.0 Hz, SiCH₂Me); 6.6 (d, ³J_{CF} = 2.0 Hz, SiCH₂Me). ¹⁹F NMR (C₆D₅Br): -175.0 (sept, ³J_{HF} = 6.2 Hz, FSiEt₃). ¹H NMR (CDCl₃): 0.62–0.74 (m, 6H, SiCH₂Me); 1.00 (t, ³J_{HH} = 7.9Hz, 18H, CH₂Me). ¹⁹F NMR (CDCl₃): -176.3 (sept, ³J_{HF} = 6.5 Hz, FSiEt₃). ²⁹Si NMR(CDCl₃): 33.2 (d, ¹J_{FSi} = 288 Hz, FS*i*Et₃).

B(C₆F₅)₃: ¹¹B NMR (C₆D₅Br): 60 (br s, 1B, $B(C_6F_5)_3$). ¹⁹F NMR (C₆D₅Br, 282 MHz): -160.9 (m, 6H, *meta-F*); -143.5 (m, 3H, *para-F*); -128.9 (m, 6H, *ortho-F*).

 $[B(C_6F_5)_4]^{-: 11}B$ NMR $(C_6D_5Br): -16.3$ (s, $B(C_6F_5)_4$). ¹⁹F NMR $(C_6D_5Br, 282$ MHz): -166.1 (s, 6F, *m*-C₆F₅); -162.2 (s, 3F, *p*-C₆F₅); -132.4 (s, 6F, *o*-C₆F₅).

3. NMR experiments

3.1. Reaction of [Cp*₂ZrCl₂] with HSiEt₃ and B(C₆F₅)₃ (in a 1/10/1 ratio) in toluene-d₈

To a suspension of $[Cp*_2ZrCl_2]$ (13 mg, 30 µmol) and $B(C_6F_5)_3$ (15 mg, 30 µmol) in toluene- d_8 (0.75 mL) was added an excess of Et₃SiH (48 µL, 300 µmol), which caused a mixture color change from slightly yellow to intense yellow. The mixture was stirred for 20 min and then transferred into NMR tube. The tube was degassed, sealed by flame and analyzed by NMR spectroscopy.

¹H NMR spectrum (Fig. S6) showed only a small peak at 1.70 ppm as the only product, in addition to starting materials. ¹⁹F NMR spectrum (Fig. S7) showed very broad (100 - 170 Hz) signals at -129.2, -142.4 and -160.6 ppm – positions typical for B(C₆F₅)₃. It should be noted that a mixture of HSiEt₃ and B(C₆F₅)₃ in 10/1 ratio showed very narrow well resolved signals of B(C₆F₅)₃ in ¹⁹F NMR spectrum (Fig. S8) as a result of water impurity dehydrogenative silylation.⁴ Therefore, the broadening of B(C₆F₅)₃ signals in ¹⁹F NMR spectrum was tentatively assigned to generation of a small amount of [HB(C₆F₅)₃]⁻ anion, which remained in equilibrium with B(C₆F₅)₃ and [(C₆F₅)₃B- μ -H-B(C₆F₅)₃]⁻ as described in literature.⁵ The peak at 1.70 ppm in ¹H NMR probably corresponds to the cationic [Cp*₂ZrCl(ClSiEt₃- κ Cl)]⁺ analogously to [1].

Opening the NMR tube under argon, followed by replacing argon with ethylene led to an immediate formation of solid PE and heat evolution.

3.2 Generation of [1] and $[2][HB(C_6F_5)_3]^-$ in toluene- d_8



Scheme S1

To a solid mixture of $[Cp_{2}ZrF_{2}]$ (60 mg, 150 µmol) and $B(C_{6}F_{5})_{3}$ (77 mg, 150 µmol) was added toluene- d_{8} (0.75 mL), followed by addition of Et₃SiH (48 µL, 300 µmol) by Hamilton microsyringe. A yellow oil separated on the bottom of the reaction flask within several minutes. The mixture was stirred for additional 5 min and then stirring was stopped. The upper colorless phase was separated by syringe and checked by NMR spectroscopy. ¹H revealed presence of unreacted Et₃SiH and free Et₃SiF (in ca 2:1 ratio), while ¹⁹F NMR revealed mainly free Et₃SiF, $B(C_{6}F_{5})_{3}$, residual $[Cp_{2}ZrF_{2}]$ and some unidentified species. The lower yellow oily phase was washed with toluene- d_{8} (0.5 mL) and transferred to a capillary (prepared from Pasteur pipette - see Fig. S9) under argon. The capillary was sealed by flame, inserted into a 5 mm NMR tube, surrounded by toluene- d_{8} and investigated by a NMR spectroscopy (see Figs. S10–S13). The NMR showed the presence of [1][HB(C₆F₅)₃]⁻ and [2][HB(C₆F₅)₃]⁻ in 74/26 ratio. After collecting all spectra, the NMR tube was opened in vacuum and the volatiles were evaporated in vacuum.

The reaction was also conducted in toluene or neat $HSiEt_3$ at ratios Zr/Si/B = 1/1/1, 1/4/1, 1/22 (i.e. in neat Et_3SiH)/1, which resulted in product mixtures containing **[1]**/**[2]** in ratios 30/70, 88/12, 80/20. A comparison of ¹⁹F NMR spectra of product mixture for different Zr/Si/B is depicted in Fig. S14.



¹H NMR (external toluene- d_8 , 300 MHz): 0.50 (q, ${}^{3}J_{HH} = 7.5$ Hz, 6H, SiCH₂Me); 0.64 (t, ${}^{3}J_{HH} = 7.5$ Hz, 9H, SiCH₂Me); 1.44 (br s, 30H, C₅Me₅); 4.1 (br s, 1H, HB(C₆F₅)₃). ¹³C{¹H} NMR (external toluene- d_8 , 75 MHz): 5.4(d, ${}^{3}J_{CF} = 2.9$ Hz, SiCH₂Me); 5.8 (d, ${}^{2}J_{CF} = 13.2$ Hz, SiCH₂Me); 10.4 (br s, C₅Me₅); C₅Me₅ not found. ¹⁹F (external toluene- d_8 , 282 MHz): -181.3 (s, 1F, ZrFSi); 107.9 (br s, 1F, ZrF). We were not able to detect any signal of coordinated FSiEt₃ in ²⁹Si NMR spectroscopy (for spectrum see Fig. S15.)

Data for [2]



¹H NMR (external toluene- d_8 , 300 MHz): 1.48 (br s, 60H, C₅ Me_5). ¹³C{¹H} NMR (external toluene- d_8 , 75 MHz): 11.0 (br s, C₅ Me_5); 126.4 (br s, C₅Me₅). ¹⁹F (external toluene- d_8 , 282 MHz): -109.3 (s, 1F, ZrFZr); 86.8 (s, 2F, ZrF).

Data for $[HB(C_6F_5)_3]^-$ anion:

¹H NMR (toluene- d_8): 4.15 (br s, 1H, *H*B). ¹¹B (toluene- d_8): -24 (br s). ¹⁹F NMR (toluene- d_8 , 282 MHz): -167.3 (s, 6F, *m*-C₆*F*₅); -164.3 (s, 3F, *p*-C₆*F*₅); -133.0 (d, ³*J*_{FF} = 19.7 Hz, 6F, *o*-C₆*F*₅);

3.3. Generation of [1]–[3][HB(C₆F₅)₃]⁻ in haloaromatic solvents



Scheme S3 Proposed equilibrium of 1-3.

3.3.1. Reaction of [Cp*₂ZrF₂] with HSiEt₃ and B(C₆F₅)₃ in a 1/1/1 ratio in C₆D₅Br

To a solution of $[Cp_2ZrF_2]$ (55 mg, 138 µmol) and $B(C_6F_5)_3$ (70 mg, 137 µmol) in C_6D_5Br (1.00 mL), was added Et₃SiH (22 µL, 138 µmol) by Hamilton microsyringe, which caused an immediate color change from slightly to intense yellow. The mixture was stirred for 5 min and then a part (0.7 mL) of the resulting intense yellow solution was sealed into NMR tube and multinuclear NMR (Figs. S16-18) was acquired showing a ratio [1]/[2]/[3] = 76/5/19 at -30 °C (Fig. S16). In addition to [1]-[3] a small amount (ca 10 mol%) of unreacted HSiEt₃ was detected. ESI-MS spectrum of the mixture showed a peak at m/z 660 of unknown composition in positive mode and a peak at m/z 529 (most probably corresponding to $[HOB(C_6F_5)_3]^-$ as a product of hydrolysis) in negative mode.

POLYMERIZATION: 110 μ L (which corresponds to 15 μ mol of Zr) of the residual solution was directly injected into a polymerization autoclave filled with toluene (50 mL). The polymerization was conducted under 3 bars of ethylene at 25 °C for 30 s. After workup described above, 1.234 g of polyethylene was obtained (system activity A = 3290 kg_{PE} (mol_{Zr}.h.bar)⁻¹).

3.3.2. Reaction of [Cp*₂ZrF₂] with HSiEt₃ and B(C₆F₅)₃ in a 2/1/1 ratio in C₆D₅Br

The experiment was conducted similarly as described in above in section 3.3.1. using $[Cp_2ZrF_2]$ (68 mg, 170 µmol), $B(C_6F_5)_3$ (43 mg, 84 µmol), $HSiEt_3$ (13 µL, 85 µmol) and C_6D_5Br (1 mL). Analysis of the solution (0.7 mL of total volume) by ¹⁹F NMR spectroscopy (Fig. S19) revealed [1]/[2]/[3]/Cp*₂ZrF₂ in a 15/35/3/47 ratio.

POLYMERIZATION: 180 μ L (which corresponds to 30 μ mol of Zr and 15 μ mol of B) of the solution was directly injected into a polymerization autoclave filled with toluene (50 mL). The polymerization was conducted under 3 bars of ethylene at 25 °C for 30 s. After workup

described above, 1.156 g of polyethylene was obtained (system activity A = 1540 kg_{PE} $(mol_{Zr}.h.bar)^{-1}$).

3.3.3. Reaction of [Cp*₂ZrF₂] with HSiEt₃ and B(C₆F₅)₃ in PhCl (preparative scale)

To a solution of $[Cp*_2ZrF_2]$ (165 mg, 414 µmol) and $B(C_6F_5)_3$ (212 mg, 414 µmol) in chlorobenzene (6 mL) was added Et₃SiH (70 µL, 442 µmol). The mixture was stirred for 25 min and then an aliquot (220 µL, 15 µmol Zr) was taken and injected into a polymerization autoclave to induce polymerization (see below). The residual reaction mixture was transferred under argon into a glass apparatus equipped with a J. Young valve and breakable seals. The mixture was degassed and J. Young valve was sealed off by flame. Attempted crystallization of the mixture by slow solvent evaporation led repeatedly to oily products. Isolation of the oil by decantation, followed by volatiles evaporation gave a yellow foam. Its analysis by NMR showed the presence of several unidentified zirconocene species, probably decomposition products.

POLYMERIZATION: 220 μ L (15 μ mol Zr) of the reaction mixture was injected into the autoclave. After workup, 1.078 g of polyethylene was obtained (system activity A = 2880 kg_{PE} (mol_{Zr}.h.bar)⁻¹).

3.3.4. NMR data

Data for [1]: ¹H NMR (C₆D₅Br): 0.59-0.72 (m, 6H, SiCH₂Me); 0.89 (t, ³J_{HH} = 7.5 Hz, 9H, SiCH₂Me); 1.65 (br s, 30H, C₅Me₅). ¹³C{¹H} NMR (C₆D₅Br): 5.80 (d, ²J_{CF} = 13.4 Hz, SiCH₂Me); 6.26 (d, ³J_{CF} = 1.9 Hz, SiCH₂Me); 11.04 (br, C₅Me₅); 127.85 (C₅Me₅). ¹⁹F (C₆D₅Br, -30 °C): -182.6 (s, 1F, ZrFSi); 105.1 (s, 1F, ZrF).

Data for **[2]**: ¹H NMR (C₆D₅Br): 1.65 (br s, 30H, C₅*Me*₅) ¹⁹F (C₆D₅Br, -30 °C): -107.2 (s, 1F, Zr*F*Zr); 84.2 (s, 2F, Zr*F*).

Data for [3]: ¹H NMR (C₆D₅Br): 1.65 (br s, 30H, C₅Me₅) ¹⁹F (C₆D₅Br, -30 °C): 124.3 (s, 1F, Zr*F*).

Data for $[HB(C_6F_5)_3]^{-:}$ ¹H NMR (C₆D₅Br, 25 °C): 4.34 (br s, 1H, *H*B). ¹¹B (C₆D₅Br, 25 °C): -24 (br s). ¹⁹F NMR (C₆D₅Br, -25 °C): -166.4 (m, 6F, *m*-C₆*F*₅); -163.5 (m, 3F, *p*-C₆*F*₅); -132.8 (d, ³*J*_{FF} = 20.9 Hz, 6F, *o*-C₆*F*₅);

3.4. Trapping of [Cp*₂ZrF]⁺ species with THF (formation of [4][HB(C₆F₅)₃]⁻)



Scheme S4

A mixture of [1]–[3] was generated as described above from Cp_2ZrF_2 (51 mg, 128 µmol), $B(C_6F_5)_3$ (65 mg, 127 µmol), and $HSiEt_3$ (20 µL, 128 µmol) in C_6D_5Br (1 mL). An excess of THF (20 mg, 278 µmol) was added and the mixture was stirred for 5 min. A sample (0.55 mL) was transferred into a NMR tube and the tube was partly degassed and sealed by flame. Multinuclear NMR spectroscopy (Figs. S20–23) revealed formation of [4] (NMR yield 36%), in addition to FSiEt₃ (NMR yield 20%), Cp_2ZrF_2 (NMR yield 24%), and $B(C_6F_5)_3$ (THF) adduct (NMR yield 20%). ESI-MS spectrum of the mixture showed an identical characteristic as mentioned in section 3.3.1.

POLYMERIZATION: 117 μ L (which corresponds to 15 μ mol of Zr) of the residual solution was directly injected into a polymerization autoclave filled with toluene (50 mL). The polymerization was conducted under 3 bars of ethylene at 25 °C for 30 min. However, the flowmeter did not show any sign of ethylene consumption and no polymer was obtained after addition of methanol. System activity A = 0 kg_{PE} (mol_{Zr}.h.bar)⁻¹).

Data for [4]:



¹H NMR (C₆D₅Br, -30 °C): 1.26–1.41 (m, 2H, OCH₂CH₂, *THF*); 1.43–1.56 partly overlapped (m, 2H, OCH₂CH₂, *THF*); 1.57 (s, 30H, C₅*Me*₅); 3.23–3.33 (m, 2H, OCH₂CH₂, *THF*); 3.65–3.73 (m, 2H, OCH₂CH₂, *THF*). ¹³C{¹H} NMR (C₆D₅Br, -30 °C): 10.83 (C₅*Me*₅); 19.66, 35.49 (OCH₂CH₂); 62.61, 73.32 (OCH₂CH₂); 126.35 (C₅Me₅). ¹⁹F NMR (C₆D₅Br, -30 °C): 108.6 (s, 1F, ZrF).

The signals for coordinated THF showed a fluxional behavior in ¹H NMR spectroscopy upon heating, probably as a result of increased rate of rotation of THF (as could be seen for OCH_2 group in Fig. S20)

data for $[HB(C_6F_5)_3]^-$

¹H NMR (C₆D₅Br, -30 °C): 4.3 (br s, 1H, *H*B). ¹⁹F NMR (C₆D₅Br, -30 °C): -166.4 (m, 6F, *m*-C₆*F*₅); -163.4 (t, ${}^{3}J_{FF}$ = 21.3 Hz, 3F, *p*-C₆*F*₅); -133.0 (d, ${}^{3}J_{FF}$ = 20.5 Hz, 6F, *o*-C₆*F*₅). ¹¹B (C₆D₅Br): -25 (br d, {}^{1}J_{BH} ~ 81 Hz, 1B, H*B*).

data for $B(C_6F_5)_3$ (THF) adduct: for NMR data of $B(C_6F_5)_3$ (THF) adduct in either C_6D_6 or CD_2Cl_2 solutions see ref.⁶⁻⁷

¹⁹F NMR (C₆D₅Br, -30 °C): -162.5 (m, 6F, *m*-C₆*F*₅); -155.1 (m, 3F, *p*-C₆*F*₅); -133.2 (d, ${}^{3}J_{FF}$ = 20.5 Hz, 6F, *o*-C₆*F*₅).

3.5. Generation of $[1][B(C_6F_5)_4]^-$ and $[3][B(C_6F_5)_4]^-$ in C_5D_5Br



Scheme S5

To a solution of Cp*₂ZrF₂ (51 mg, 128 µmol) and [Ph₃C]⁺[B(C₆F₅)₄]⁻ (118 mg, 128 µmol) in C₆D₅Br (1 mL) was added Et₃SiH (20 µL, 128 µmol). The mixture immediately turn from intense orange to green brown and then to yellow-brown. The mixture was stirred for 5 min and then 0.7 mL was transferred into NMR tube. A content of the tube was degassed, sealed off with flame and analyzed by multinuclear NMR spectroscopy (Figs. S24-26). ¹H NMR(Fig. S24) showed a presence of evolved Ph₃CH (methine proton at 5.45 ppm), while ¹⁹F NMR (Fig. S25) revealed cationic species [1] and [3], having characteristic signals for Zr–*F* fluoride ligand (105.6 ppm for [1] and 125.0 ppm for [3]). The presence of compensating [B(C₆F₅)₄]⁻ anion was evident from ¹⁹F and ¹¹B NMR (Fig. S26) spectra. POLYMERIZATION: From reaction mixture left in Schlenk flask after preparation of NMR sample, an aliquot (120 µL, corresponds to 15 µmol Zr) was taken and injected into polymerization autoclave filled with toluene (50 mL). The autoclave was pressurized to 3 bar

for 15 min. However, no ethylene consumption was detected by ethylene flowmeter. The pressure was vented and HSiEt₃ (2.4 mL, 15 mmol) was added under ethylene flow. The autoclave was pressurized to 3 bars for 15 min, which showed no progress again. Finally, the overpressure was released, and B(C₆F₅)₃ solution in toluene (150 μ L, 0.1 M, 15 μ mol) was added. After autoclave repressurizing to 3 bar, immediate precipitation of polymer was observed. Polymerization was conducted for 1 min and gave 1.100 g of polyethylene (A = 1470 kg_{PE} (mol_{Zr}.h.bar)⁻¹).

3.6. Reaction of [1][B(C₆F₅)₄]⁻ and [3][B(C₆F₅)₄]⁻ with [(*t*-Bu)₃PH]⁺[HB(C₆F₅)₃]⁻

A mixture of $[1][B(C_6F_5)_4]^-$ and $[3][B(C_6F_5)_4]^-$ was prepared as described above in section 3.5. from Cp*₂ZrF₂ (40 mg, 100 µmol), [Ph₃C]⁺[B(C₆F₅)₄]⁻ (93 mg, 100 µmol), and Et₃SiH (16 µL, 100 µmol) in C₆D₅Br (0.5 mL). The green-brown mixture was stirred for 5 min and then injected into a colorless solution of $[(t-Bu)_3PH]^+[HB(C_6F_5)_3]^-$ (72 mg, 100 µmol) in C₆D₅Br (0.5 mL). The mixture was stirred for 10 min, which led to formation of yellow-orange solution. An aliquot of the mixture (0.7 mL) was used for preparation of sample for NMR analysis. ¹H, ¹⁹F and ¹¹B NMR spectra (Figs. S27-29) showed Ph₃CH, FSiEt₃, zirconocene species, $[(t-Bu)_3PH]^+$ and anions $[HB(C_6F_5)_3]^-$, $[B(C_6F_5)_4]^-$.

POLYMERIZATION: 150 μ L (which corresponds to 15 μ mol of Zr) of the residual solution was directly injected into a polymerization autoclave filled with toluene (50 mL), which caused an immediate polymerization. The polymerization was conducted for 40 s and gave 0.969 g of PE. System activity A = 1940 kg_{PE} (mol_{Zr}.h.bar)⁻¹).

3.7 Proofing of the elusive Zr-H species by hydrodechloration of CDCl₃



Scheme S6

In a Schlenk vial, a mixture of Cp_2ZrF_2 (42 mg, 105 µmol) and $B(C_6F_5)_3$ (53 mg, 104 µmol) was dissolved in 0.8 mL CDCl₃. To the formed yellow solution was added HSiEt₃ (33 µL, 208 µmol), the mixture was sealed into NMR tube and analyzed by ¹H and ¹⁹F NMR. ¹H NMR (Fig. S30) showed the presence of 2 eq. FSiEt₃, Cp_2ZrCl_2 and CDHCl₂ (5.28, t, ² J_{HD} = 1.1 Hz). ¹⁹F NMR (Fig. S31) showed B(C₆F₅)₃ and FSiEt₃ in a 1/2 molar ratio.

3.8. 1-hexene oligomerization catalyzed by Cp*₂ZrF₂/DSiEt₃/B(C₆F₅)₃ system



Scheme S7 A proposed reaction pathway leading to an incorporation of deuterium atom from DSiEt₃ into oligo(1-hexene) chain.

To a slightly yellow solution of $Cp_2^2ZrF_2$ (50 mg, 125 µmol) and $B(C_6F_5)_3$ (64 mg, 125 µmol) in PhCl (3 mL) was added DSiEt₃ (22 µL, 137 µmol), which caused an immediate color change to intense yellow. The mixture was stirred for 5 min and 1-hexene (152 mg, 1.81 mmol, 15 eq. with respect to Zr) was added. The red-orange mixture was inserted into bath

preheated to 60 °C and stirred for 20 min. After cooling to room temperature the mixture was passed through a pad of Fluorisil (3×1.5 cm) and eluted with THF. Volatile components of eluate were evaporated in vacuum to leave oligo(1-hexene) as a colorless oil (110 mg, conversion 78%). GC-MS (see Fig. S32) showed trimers and tetramers as the most abundant species. Theoretical products of deuterosilylation of 1-hexene (m/z at 201) were not found. The ¹H and ²H NMR spectra of the oligo(1-hexene) are depicted in Fig.S33.

4. Polymerization results

Table S1: Screening of catalytic systems $Cp'_2ZrCl_2/HSiEt_3/B(C_6F_5)_3$ (where $Cp' = \eta^5-C_5H_5$ (Cp); $\eta^5-C_5Me_5$ (Cp*) for ethylene polymerization.^{*a*}

entry	Complex	Zr	B/Zr	Si/Zr	t	yield	Ab	T _m c	M _n ^d	Đe
	1	[µmol]			[min]	[g]		[°C]		
1	Cp ₂ ZrCl ₂	0.25	10	1000	30	-	-			
2	Cp ₂ ZrCl ₂	0.25	500	5000	10	0.126	1000			
3	Cp ₂ ZrCl ₂	0.25	500	10000	10	0.606	4850			
4	Cp ₂ ZrCl ₂	2.50	50	5000	10	3.046	2440			
5	Cp ₂ ZrCl ₂	5	1	1000	60	trace	trace			
6	Cp ₂ ZrCl ₂	10	1	1000	5	1.461	580			
7	Cp ₂ ZrCl ₂	15	1	1000	3	2.238	1000	135	104	2.4
8	Cp ₂ ZrCl ₂	15	1	1000	3	2.440	1080			
9	Cp ₂ ZrCl ₂	15	1	1000	3	2.540	1130			
10	$Cp*_2ZrCl_2$	0.25	500	5000	15	trace	trace			
11	$Cp*_2ZrCl_2$	1	100	5000	10	2.180	4360	136	231	2.0
12	$Cp*_2ZrCl_2$	5	1	1000	10	trace	trace			
13	$Cp*_2ZrCl_2$	15	1	1000	3	0.365	160	136	129	1.5
14	$Cp*_2ZrCl_2$	15	1	1000	3	0.543	240			

^a Polymerization conditions: ethylene pressure 3 bar, temperature 25 °C, solvent toluene, total volume 50 mL, rpm 800.

^b Activity in [kg_{PE} (mol_{Zr}.h.bar)⁻¹]

^c Melting point (second heat) determined using DSC.

^d Determined using gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 160 °C. in kg/mol

^e Dispersity ($\theta = M_w/M_n$).

entry	B/Zr	Silane	N ^b	ΔG^{c}	t	yield	A ^d	T _m e	$M_n^{\rm f}$	Ðg
-	(mol/mol)			[kcal/mol]	[min]	[g]		[°C]		
1	1	HSiEt ₃	3.58	86	3	0.365	160	136	129	1.5
2	2				2.3	0.870	500			
3 ^h	10				5	1.840	1470	136	262	1.7
4	1	HSiMe ₂ Ph	3.55	85	3	0.132	60	135	86	1.5
5	2				3	0.156	70			
6	1	PMHS	-	-	25	0.537	30	136	66	1.4
7	2				18	0.734	50			
8	1	HSi(<i>i</i> -Pr) ₃	2.93	84	3	0	0			
9	10				30	0	0			
10	1	HSiPh ₃	2.65	85	30	0	0			
11	2				30	0	0			
12	10				30	0	0			
13	1	H ₂ SiEt ₂	2.27 ⁱ	-	20	0.983	70	134		
14	2				15	1.010	90			
15	1	H ₂ SiMePh	2.13	-	10	n.i.	1 ^j			
16	2				30	0.452	20	135		
17	1	H ₂ SiPh ₂	1.52	92	10	n.i.	3 ^j			
18	2				25	0.828	40	137		
19	1	H ₃ SiPh	0.06	96	30	0	0			
20	2				30	0	0			
21	10				10	0.600	80	134		
22 ^k	1	HSiEt ₃	3.58	86	1.5	2.068	1840	136	242	1.7

Table S2 The dependence of ethylene polymerization activity of $[Cp*_2ZrCl_2]/hydrosilane/B(C_6F_5)_3$ systems on the nature of hydrosilane and characterization of obtained PE samples.^a

^a Polymerization conditions: $Zr = 15 \mu mol$, Zr/silane = 1/1000, ethylene pressure 3 bar, temperature 25 °C, solvent toluene, total volume 50 mL, rpm 800.

^b nucleophilic reactivity parameter of the particular hydrosilane. Values taken from ref.⁸

^c Calculated hydride donor abilities of hydridosilanes in MeCN (ΔG [kcal/mol] for reaction MH \rightarrow M⁺ + H⁻). Values taken from ref.⁹

^d Activity in [kg_{PE} (mol_{Zr}.h.bar)⁻¹]

^e Melting point (second heat) determined using DSC.

^f Determined using gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 160 °C. in kg/mol

^g Dispersity ($D = M_w/M_n$).

^h Zr = 5 μ mol

ⁱ value for structurally and electronically similar H₂Si(*n*-Hex)₂ taken from ref.⁸

^j activities calculated from ethylene uptake curve

^k [Cp*₂ZrF₂] used as a zirconocene component

PMHS = polymethylhydrosiloxane,

n.i. = not isolated

entry	Experiment	Reaction mixture	Zr species	B species	time	PE yield	Ab
		(molar ratio)	detected by NMR	detected by		[g]	
				NMR			
1	3.3.1.	$Cp*_2ZrF_2/HSiEt_3/B(C_6F_5)_3$ (1/1/1)	[1]-[3]	$[HB(C_6F_5)_3]^-$	30 s	1.234	3290
2	3.3.3.	$Cp*_2ZrF_2/HSiEt_3/B(C_6F_5)_3$ (1/1/1) ^c	[1]-[3]	$[HB(C_6F_5)_3]^-$	30 s	1.078	2880
3	3.3.2.	$Cp*_2ZrF_2/HSiEt_3/B(C_6F_5)_3$ (2/1/1)	[1]–[3] Cp* ₂ ZrF ₂	$[HB(C_6F_5)_3]^-$	30 s	1.156	1540
4	3.4.	Cp* ₂ ZrF ₂ /HSiEt ₃ /B(C ₆ F ₅) ₃ /THF (1/1/1/2)	$\begin{bmatrix} 4 \\ Cp^*_2 ZrF_2 \end{bmatrix}$	$[HB(C_6F_5)_3]^-$ $B(C_6F_5)_3 \cdot THF$	30 min	0	0
5		$Cp*_2ZrF_2/HSiEt_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ (1/1/1)	[1], [3]	$[B(C_6F_5)_4]^-$	15 min	0	0
6	3.5.	+ 1000 HSiEt ₃	n.m. ^d	n.m. ^d	15 min	0	0
7		+ 1 eq. $B(C_6F_5)_3$	n.m. ^d	n.m. ^d	1 min	1.100	1470
8	3.6.	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	[1], [3]	$[B(C_6F_5)_4]^-$ $[HB(C_6F_5)_3]^-$	40 s	0.969	1940

Table S3	Results	of polyı	nerization	with a	preactivation	in C ₆ D ₅ Br ^a
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^a Polymerization conditions: Zr = 15 µmol for all experiments, ethylene pressure 3 bar, temperature 25 °C, solvent toluene, total volume 50 mL, rpm 800.

^b Activity in [kg_{PE} (mol_{Zr}.h.bar)⁻¹] ^c reaction in PhCl

 d n.m. = not measured by NMR (reactions performed in the autoclave)

5. Figures, graphs, and NMR spectra



Fig S1. Ethylene consumption profiles [mL/min vs time] for $[Cp*_2ZrCl_2]/PMHS/B(C_6F_5)_3$ catalytic system with different B/Zr ratio. Red line corresponds to entry 7 in Table S2 and blue line corresponds to entry 6 in Table S2. Time period up to 1.5 minute corresponds to pressurization of the autoclave to the appropriate pressure (3 bar). Polymerization conditions see Table S2.



Fig S2. Ethylene consumption profiles [mL/min vs time] for $[Cp*_2ZrCl_2]/hydrosilane/B(C_6F_5)_3$ catalytic system with different hydrosilanes used (green line = entry 1, red line = entry 13, blue line = entry 6; all from Table S2). Time period up to 1.5 minute corresponds to pressurization of the autoclave to the appropriate pressure (3 bar). Polymerization conditions see Table S2.



Fig. S3. Activity as a function of nucleophilicity vs. steric factor.



Fig S4. Dependence of activity on nucleophilic reactivity of phenylsilanes. There should be noted an obvious inactivity of strongly nucleophilic $HSiPh_3$ in comparison to less sterically demanding phenylsilanes.



Fig. S5. An expanded region of IR spectra of PE films prepared by $[Cp_2ZrCl_2]/MAO$ (red), $[Cp_2ZrCl_2]/HSiEt_3/B(C_6F_5)_3$ (entry 7 in Table S1, green), $[Cp_2ZrCl_2]/HSiEt_3/B(C_6F_5)_3$ (entry 1 in Table S2, violet) and $[Cp_2ZrCl_2]/H_3SiPh/B(C_6F_5)_3$ (entry 20 in Table S2, blue) systems.



Fig. S6. ¹H NMR (300 MHz) spectrum of a mixture of $[Cp*_2ZrCl_2]$, HSiEt₃, and B(C₆F₅)₃ (1/10/1 ratio) in toluene-*d*₈ at 25 °C. The mixture was generated as described in section 3.1.



Fig. S7. ¹⁹F NMR spectrum of mixture $[Cp*_2ZrCl_2]$, HSiEt₃ and B(C₆F₅)₃ (in 1/10/1 ratio) in toluene-*d*₈ at 25 °C. The mixture was generated as described in section 3.1.



Fig. S8. ¹⁹F NMR spectrum of a mixture of HSiEt₃ and B(C₆F₅)₃ (in a 10/1 ratio) in toluene- d_8 at 25 °C.



Fig. S9. Left side: a "kit" created from a Pasteur pipette for sealing oily products under argon (the silicone septum has O.D. 7.1 mm). Right side: NMR tubes containing a sealed capillary surrounded by toluene- d_8 .



ratio) in toluene- d_8 at 25 °C. The mixture was generated as described in section 3.2.



Fig. S11. 1D NOESY spectrum of a mixture of $[1][HB(C_6F_5)_3]^-$ and $[2][HB(C_6F_5)_3]^-$ (74/26 ratio) in toluene- d_8 at 25 °C with an irradiated Et_3 SiF region (0.4 to 0.7 ppm). The mixture was generated as described in section 3.2.



Fig. S12. ¹H NMR spectrum of a mixture of $[1][HB(C_6F_5)_3]^-$ and $[2][HB(C_6F_5)_3]^-$ (74/26 ratio) in toluene- d_8 at 25 °C. * denotes a residual CD₂H signal of external toluene- d_8 ; the arrow shows a toluene- d_8 coordinated in the second coordination sphere of cationic centers and forming complex-toluene clathrate. As the mixture of $[1][HB(C_6F_5)_3]^-$ and $[2][HB(C_6F_5)_3]^-$ was in a sealed capillary the signals of coordinated and free toluene- d_8 could be distinguished. The mixture was generated as described in section 3.2.



Fig. S13. ¹¹B NMR spectrum of a mixture of $[1][HB(C_6F_5)_3]^-$ and $[2][HB(C_6F_5)_3]^-$ in toluene- d_8 at 25 °C. A borosilicate glass of NMR tube is responsible for unmarked signals as was verified by measuring ¹¹B NMR spectrum of neat toluene- d_8 . The mixture was generated as described in section 3.2.



Fig. S14. ¹⁹F NMR spectra of mixtures of [1][HB(C₆F₅)₃]⁻ and [2][HB(C₆F₅)₃]⁻ in toluene- d_8 or neat HSiEt₃ (where Zr/Si/B = 1/22/1) generated at various Zr/Si/B ratios. The mixtures were generated as described in section 3.2.



Fig. S15. ²⁹Si NMR spectrum of a mixture of [1][HB(C_6F_5)_3]⁻ and [2][HB(C_6F_5)_3]⁻ (74/26 ratio) in toluene- d_8 at 25 °C (d1 = 30, ns = 1550). The broad signal centered at -109 ppm corresponds to SiO₄ units in borosilicate glass of NMR tube. The mixture was generated as described in section 3.2.



Fig. S16. ¹⁹F NMR spectrum of a mixture of $[1][HB(C_6F_5)_3]^-$, $[2][HB(C_6F_5)_3]^-$ and $[3][HB(C_6F_5)_3]^-$ (76/5/19 ratio) in C₆D₅Br at -30 °C. The mixture was generated as described in section 3.3.1.



Fig. S17. ¹⁹F NMR spectra of a mixture of $[1][HB(C_6F_5)_3]^-$, $[2][HB(C_6F_5)_3]^-$, and $[3][HB(C_6F_5)_3]^-$ in C_6D_5Br at temperature range from -30 °C to 65 °C. The mixture was generated as described in section 3.3.1.



Fig. S18. ¹¹B NMR spectrum of a mixture of $[1][HB(C_6F_5)_3]^-$, $[2][HB(C_6F_5)_3]^-$, and $[3][HB(C_6F_5)_3]^-$ in C₆D₅Br at 25 °C. The mixture was generated as described in section 3.3.1.



Fig. S19. ¹⁹F NMR spectrum of a mixture of $[1][HB(C_6F_5)_3]^-$, $[2][HB(C_6F_5)_3]^-$, and $[3][HB(C_6F_5)_3]^-$ and $Cp*_2ZrF_2$ (15/35/3/47 ratio) in C_6D_5Br at -30 °C. The mixture was generated as described in section 3.3.2.

Fig S20. OC H_2 region of THF in ¹H NMR spectra of [4][HB(C₆F₅)₃]⁻ in C₆D₅Br measured in temperature range from -35 to 25 °C. The mixture was generated as described in section 3.4.

Fig. S21. ¹⁹F NMR spectrum of a product mixture in C_6D_5Br at -30 °C. The mixture was generated as described in section 3.4.

Fig. S22. ¹¹B NMR spectrum of [4][HB(C_6F_5)₃]⁻ in C_6D_5Br at 25 °C.

Fig. S23. Comparison of ¹¹B (top) and ¹¹B{¹H} NMR spectra (bottom) of [4][HB(C₆F₅)₃]⁻ in C_6D_5Br at 25 °C.

Fig. S24. ¹H NMR of the mixture prepared in section 3.5. in C_6D_5Br at 45 °C.

Fig. S26. ¹¹B NMR of the mixture prepared in section 3.5. in C_6D_5Br .

Fig. S28. ¹⁹F NMR of the mixture prepared in section 3.6. in C_6D_5Br .

Fig. S29. ¹¹B NMR of the mixture prepared in section 3.6. in C_6D_5Br .

Fig. S30. ¹H NMR spectra of the mixture prepared in section 3.7. (top) and [Cp*₂ZrCl₂] (bottom) in CDCl₃.

Fig. S31. ¹⁹F NMR spectra of the mixture prepared in section 3.7. in CDCl₃.

Fig S32. GC chromatogram for oligo(1-hexene) obtained as described in section 3.8.

Fig. S33. ²H (top) and ¹H (bottom) NMR spectrum of oligo(1-hexene) prepared in section 3.8. in $CHCl_3/CDCl_3$ (ca 100/1, v/v) mixture. The oligo(1-hexene) was prepared as described in section 3.8.. The highlighted area showed a CHD signals of the oligomer resulted from transfer of deuterium from silicon atom to 1-hexene (as depicted in Scheme). * denotes solvent signals; # denotes a transmitter artifact.

6. Results of DFT calculations

Fig. S34. Perspective view of molecular HOMO (left) and LUMO (right) orbitals of $[1][HB(C_6F_5)_3]^-$ depicted at 5% probability. The HOMO contains 7% of s-character contribution from the hydride. The LUMO has 73% d-character contribution from the metal and is generated from mixing the metallic d_z^2 and $d_x^2 - y^2$.

Fig. S35. DFT optimized molecule of $[2][HB(C_6F_5)_3]^-$. Hydrogen atoms (except B–H) are omitted for clarity. Selected atom distances and angles: Zr–F_{terminal} 1.987, 2.004 Å; Zr–F_{bridge} 2.193, 2.209 Å; B–H 1.214 Å; Zr–F–Zr 167.34°.

Fig. S36. DFT optimized molecule of **[3][HB(C₆F₅)₃]**⁻. Hydrogen atoms (except B–H) are omitted for clarity. Selected atom distances and angles: Zr–F 1.982 Å; Zr–Br 2.907 Å; B–H 1.214 Å; Zr–Br–C_{ipso} 108.61°.

7. Cartesian coordinates

[1][HB(C ₆ F ₅) ₃] ⁻			н	2.301370	-2.182593	-1.435810
Zr	2.352253	1.257583	-0.379032	С	3.856790	-3.838731	2.368473
F	1.177770	-0.270631	0.107520	н	4.568941	-1.798051	2.630643
F	3.902785	-0.352244	-0.068221	Н	2.850082	-1.936466	2.247535
Ċ	1,492596	0.631828	-2.681722	н	7.643374	-3.518682	-0.212474
Ċ	0 480460	-0 448703	-2 853413	н	6 696984	-3 432883	1 271438
Ċ	1 169973	2 002861	-2 1/3298		6 1193/8	-1 395/28	-0 002268
Ċ	-0 222440	2.002001	-2.445250	н Ц	2 105580	-4.555420	-0.002200
Ċ	282260	2.352/25	-2.40/3/4	н Ц	1 079021	-4.001202	-2.150515
Ċ	2.303302	1 226072	-2.442475	П Ц	2 7/62/7	- / 992611	-2.332400
Ċ	2.490423	4.220975	2.002328	н Ц	2 520222	2 007094	2 206652
Ċ	1 011047	2 154020	2.501455	н Ц	2 170912	- 3. 997 984 1 11 207	1 726072
Ċ	2 000020	2.134039	2.000003	н Ц	J.1/9015	4.411307	2 276251
Ċ	2.030320	0.550905	-2./33902	П	4.055405	-4.2/5510	2.270351
Ċ	1 061122	2 440061	-3.1/0104	Б	-2.404957	1 022169	1 222700
c	1.301122	3.449901 4.707515	0.034400	C	-1./01202	-1.022100	1.522/99
Ċ	1.293551	4.707515	0.500/04	C C	-3.05/542	0.796085	0.490055
C	1.300589	2.433608	1.5/8098	C	-3.00/054	-1.195903	-1.105059
C	-0.105558	2.31/283	1.821335	C	-3.51/919	-2.500467	-0.970488
C	2.283509	1.568859	2.122436	C	-4.008455	-3.249596	-2.0290/2
C	1.963/0/	0.443692	3.041095	C	-4.0/0/42	-2.691268	-3.292564
C	3.555905	2.024200	1.686515	C	-3.643913	-1.389010	-3.4/4963
C	4.891961	1.480025	2.064974	C F	-3.1/2684	-0.6/4865	-2.386803
C	3.362090	3.188408	0.890800	F	-3.4/9080	-3.119660	0.212970
C	4.4//98/	4.0/5084	0.442513	F	-4.416654	-4.502436	-1.846690
Н	1.339379	0.796534	3.870882	F	-4.532546	-3.397764	-4.318365
Н	1.391050	-0.332483	2.520486	F	-3.688779	-0.840712	-4.687678
Н	2.859682	-0.007010	3.473924	F	-2.790959	0.587705	-2.633948
Н	-0.372919	2.266086	2.897291	C	-4.822377	0.339260	1.093826
Н	-0.715822	3.166886	1.411533	C	-5.884928	1.156205	1.432717
Н	-0.584981	1.408937	1.371279	C	-5.805449	2.512027	1.162925
Н	0.985594	5.278798	1.270774	C	-4.665959	3.015947	0.567120
Н	1.954862	5.347756	-0.197651	C	-3.625460	2.156283	0.244827
Н	0.386228	4.524570	-0.197632	F	-4.938758	-0.957639	1.396239
Н	4.996777	4.492200	1.314344	F	-6.975090	0.664600	2.013838
Н	5.232611	3.543984	-0.148881	F	-6.812540	3.318635	1.477211
Н	4.121355	4.919768	-0.150497	F	-4.578932	4.319672	0.308958
Н	5.371766	2.129578	2.807285	F	-2.556813	2.733896	-0.326958
Н	4.816999	0.480823	2.501596	C	-1.827813	-0.615074	2.647276
Н	5.570602	1.419042	1.205884	C	-1.068582	-1.169697	3.668176
Н	4.143727	-0.442842	-4.170164	C	-0.206482	-2.208554	3.386082
Н	4.566443	-0.818626	-2.508436	C	-0.123083	-2.668919	2.084982
Н	3.134244	-1.557944	-3.251511	C	-0.872302	-2.065195	1.092668
Н	-0.275422	-0.148921	-3.588306	F	-2.608526	0.410540	3.016496
Н	0.938043	-1.377588	-3.205388	F	-1.120355	-0.672765	4.902767
Н	-0.044386	-0.665849	-1.914827	F	0.577282	-2.719134	4.332646
Н	-0.637810	2.583860	-3.422815	F	0.719239	-3.668484	1.803021
Н	-0.888517	1.884073	-1.830487	F	-0.678283	-2.529145	-0.147258
Н	-0.277950	3.539033	-1.983531	Н	-1.560457	0.401325	-0.423580
Н	2.656996	4.447848	-3.665287				
Н	1.590551	4.750392	-2.300837	[2][ŀ	IB(C ₆ F₅)₃] ⁻		
Н	3.344550	4.656397	-2.060689	Zr	-1.416349	2.285130	0.105107
Н	5.289892	1.919829	-3.670573	F	-2.713513	0.499108	0.201254
Н	5.105933	3.213753	-2.485125	F	0.160041	1.076831	0.065670
Н	5.519810	1.574755	-1.959421	С	-1.188511	1.989805	-2.389385
Si	4.118050	-2.063491	0.202381	С	-0.219669	2.958614	-2.024690
С	2.802977	-2.921410	-0.803066	С	-0.904319	4.123465	-1.586114
С	5.891719	-2.235005	-0.361692	С	-2.308052	3.865475	-1.663672
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