Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Preparation of silyl-terminated branched polyethylenes catalyzed by Brookhart's nickel diimine complex activated with hydrosilane/$B(C_6F_5)_3$

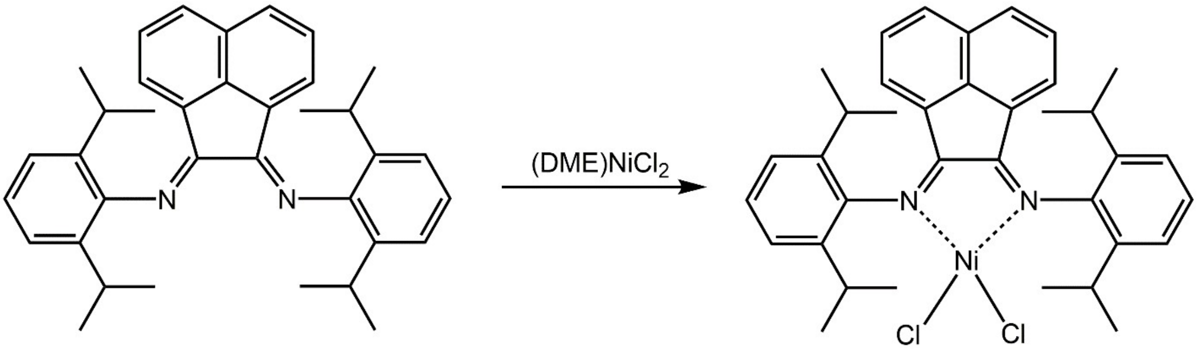
Vojtech Varga, Kristyna Pokorna, Martin Lamac, Michal Horacek, Jiri Pinkas

J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, 182 23 Prague 8, Czech Republic

Experimental details

All syntheses and manipulations with air- and moisture-sensitive compounds were performed either under an argon atmosphere using Schlenk techniques or under purified nitrogen in a Labmaster 130 glovebox (mBraun). Solvents (hexane, toluene, dichloromethane) were purified by a solvent purification system (PureSolv MD 7; Innovative Technology, Inc.). Chemicals were used as received from commercial sources (Aldrich, Strem). IR spectra of samples in KBr pellets were measured in an air-protecting cuvette on a Nicolet Avatar FT IR spectrometer in the range 400−4000 cm^{-1}. KBr pellets were prepared under purified nitrogen in the glove box. NMR spectra were measured on a Bruker neo Avance 500 spectrometer at 293 K. Chemical shifts (δ, ppm) are given relative to solvent signal (CD_2Cl_2: δ_H 5.32; toluene-d_8 δ_H 2.08, δ_C 137.48). EPR spectra were recorded on a CW X-band (9.5 GHz) EPR spectrometer MiniScope MS400 (Magnettech) with 100 kHz modulation equipped with microwave frequency counter FC 400 and temperature controller TC H03.

Preparation of 1



BIAN (BIAN = {Ar-N=Ace=N-Ar}, Ace = acenaphthen-1,2-diyl, and Ar = 2,6-$(iPr)_2$-C_6H_3)) (1.000 g, 2.00 mmol) and 1.98 mmol of $NiCl_2DME$ (where DME = 1,2-dimethoxyethane) (0.435 g, 1.98 mmol), were weighted under nitrogen in the glove box. Flask was connected to an argon/vacuum line and 50 ml of dried CH_2Cl_2 was added. The mixture was stirred (1000 rpm) for 24 h at room temperature. The dark red solution was obtained. All volatiles were evaporated to give brick-red powder. This powder was three times washed with 15 ml of diethyl ether and the solution was filtered off via PTFE capillary. The brick-red powder was dried under a vacuum. The yield was 0.99 g (79 %).

^{1}H NMR ($CDCl_3$) δ: 24.42, 23.88, 16.82, 7.26, 5.82, 3.79, 2.84, 1.47, 1.27, 0.89, 0.07, -13.96. ^{1}H NMR (toluene-d_8) δ: 23.52, 16.17, 7.10, 6.98, 4.52, 1.34, 1.29, 1.26, 1.24, -1.66, -13.96. IR (KBr, cm^{-1}): 3061 (m), 2961 (vs), 2867 (s), 1655 (s), 1623 (s), 1598 (s), 1584 (s), 1488 (m), 1464 (s), 1436 (s), 1419 (m), 1384 (s), 1362 (s), 1327 (m), 1290 (s), 1253 (m), 1223 (m), 1202 (m), 1187 (m), 1130 (m), 1112 (m), 1088 (m), 1043 (m), 952 (m), 937 (m), 834 (s), 801 (s), 780 (vs), 758 (vs), 736 (m), 615 (m), 543 (s), 470 (m), 403 (m).

Polymerization

Polymerization procedure for 1/$B(C_6F_5)_3$/hydrosilane

Ethylene polymerization experiments were performed in a 250 mL Büchi glass double-jacketed laboratory autoclave equipped with a magnetic propeller-like stirrer at constant ethylene pressure. The hot autoclave was three times evacuated and filled with argon, charged successively with a solvent (dichloromethane or toluene), hydrosilane, and $B(C_6F_5)_3$ (toluene stock solution, 3.5×10^{-2} M) and the resulting mixture was stirred at 25 °C under argon for 30 min. The inert gas was vented and the reactor was pressurized with ethylene to the appropriate pressure for 10 min. Then, the ethylene pressure was partially released and the polymerization was started by injecting the desired amount of precatalyst in CH_2Cl_2 under a stream of ethylene and the autoclave was immediately pressurized with ethylene. Final volume of the polymerization solution was 50 mL for all experiments. The autoclave temperature was monitored during the reaction by using an external Pt100 sensor connected to a Julabo F31-C bath. Data collection was performed for temperature changes inside the reactor as well as for ethylene uptake during the polymerization. The consumption of ethylene was followed in each experiment using a calibrated mass flow meter (Bronkhorst, EL-FLOW, 1L/min). After the appropriate time, the reactor was vented and the polymerization was quenched with 80 mL of methanol. The precipitated polymer was stirred for 1 h, filtered off on a glass frit, rinsed repeatedly with methanol and acetone, and dried in a vacuum to constant weight.

Polymerization procedure for 1/$B(C_6F_5)_3$/binary hydrosilane system

A similar polymerization procedure (vide supra) was used for the binary hydrosilane system. The reactor was charged successively with dichloromethane, triethylhydrosilane, and the solution of borane under the stream of argon, and the resulting mixture was stirred at 25

°C for 30 min. The inert gas was displaced with ethylene and the reactor was pressurized 10 min with ethylene gas at 3 × 10^5 Pa. After venting the autoclave, the polymerization was started by consecutive loading of diphenylhydrosilane and the desired volume of Ni precatalyst in CH_2Cl_2. The reactor was immediately repressurized with ethylene to 3 × 10^5 Pa. After the appropriate time, the autoclave was vented and the polymerization was terminated by the addition of 80 mL of methanol. Processing of the precipitated polyethylene was the same as described above.

Polymerization procedure for 1/MMAO system

The polymerization was carried out in the same equipment as above under similar conditions (ethylene pressure 3 × 10^5 Pa, temperature 25 °C, total volume 50 mL, rpm 800). Dichloromethane was loaded into the reactor and pressurized with ethylene for 10 min. Subsequently, the reactor was vented and polymerization was initiated by successive injection of aluminoxane (solution of MMAO, 7 wt% in toluene, molar ratio MMAO/Ni= 1 000), the appropriate amount of precatalyst (1 μmol, solution in CH_2Cl_2) and immediate repressurization of the autoclave. After 10 min the polymerization mixture was quenched with 80 mL of a 10 % solution of HCl in methanol. The precipitated polymer was stirred for 1 h, filtered off on a glass frit, rinsed repeatedly with methanol and acetone, and dried in a vacuum to constant weight. Activity A= 4 070 kg_{PE} $(mol_{Ni}$ h $bar)^{-1}$, M_n= 223 kg mol^{-1}, M_w/M_n= 2.1.

Fig. S1 Ethylene uptake during polymerization catalyzed with **1**/$B(C_6F_5)_3$/Et_3SiH (red line, entry 1 in Table 1) and Cp_2ZrCl_2/$B(C_6F_5)_3$/Et_3SiH (blue line). Both polymerizations were conducted at identical conditions. Time period up to 0,2 min corresponds to the pressurization of the autoclave to an appropriate pressure (3 bar).

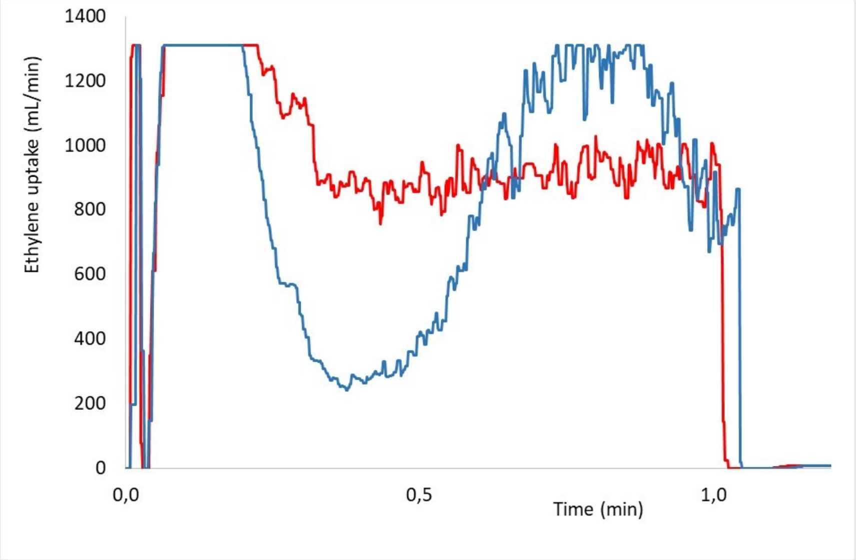


Fig. S2 Selected ethylene uptake profiles for **1**/B(C_6F_5)$_3$/Et_3SiH catalytic system (Table 2), Influence of Si/Ni molar ratio. Time period up to 0,2 min corresponds to the pressurization of the autoclave to an appropriate pressure (3 bar).

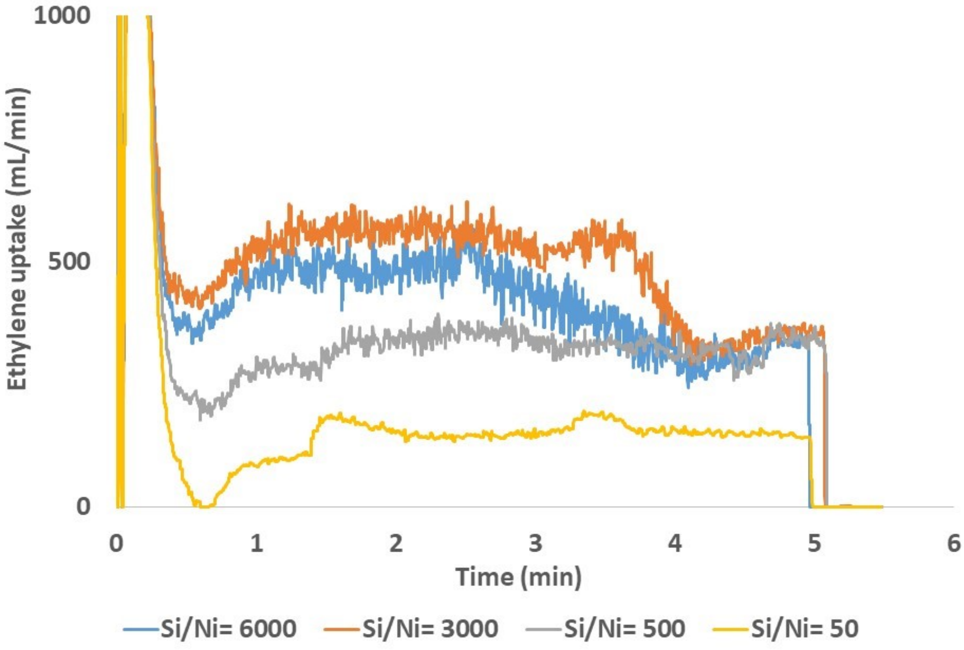
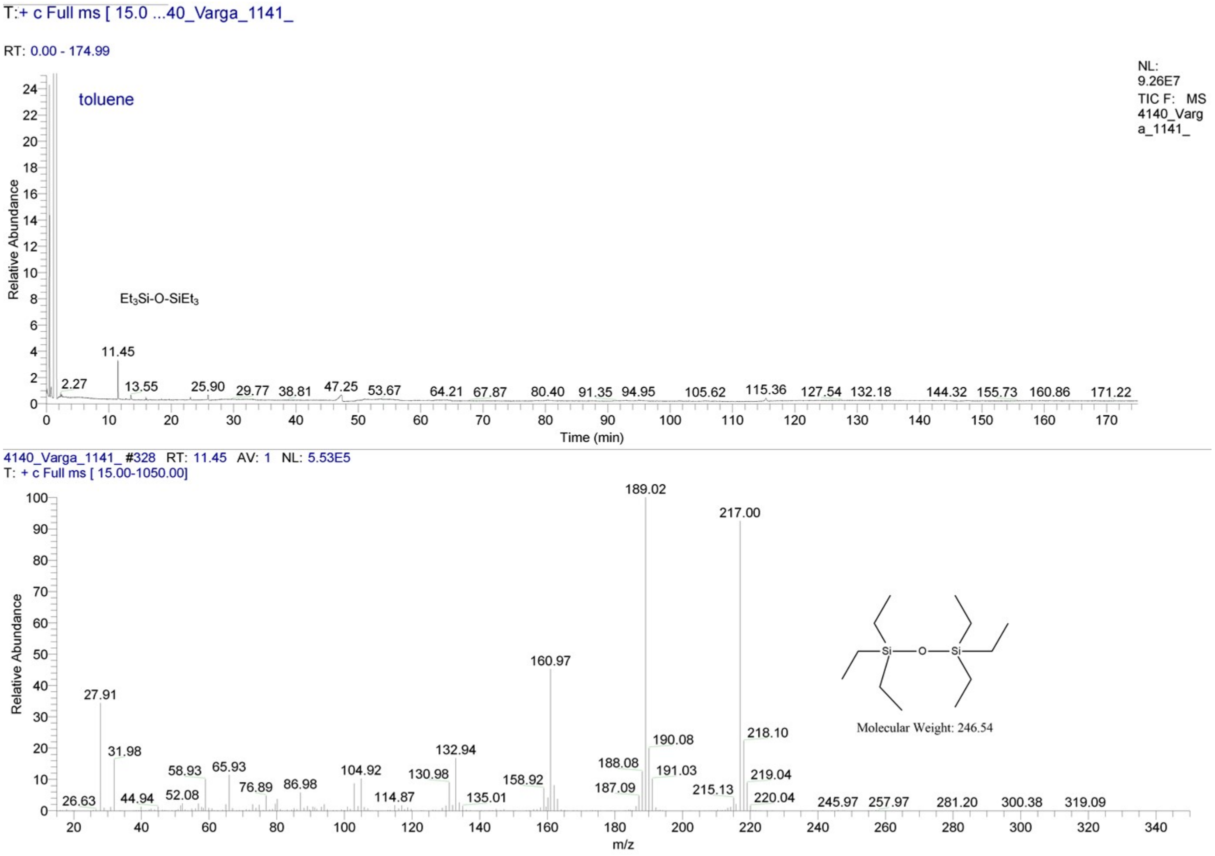


Fig. S3. GC-MS analysis of polymerization mixture (entry 2, Table 4) after polymer isolation and volatile species evaporation. No ethylene oligomers nor products of hydrosilane dehydrocoupling were detected. A siloxane $(Et_3Si)_2O$ (at rt 11.45 min) was the only assigned product.



Polymer characterization

Molar masses and dispersities of polyethylene were determined using an HT SEC chromatograph (Polymer char) with infrared and viscometric detectors. NMR of polymers was measured on a Varian Mercury 300 instrument (^1H at 300 MHz, ^{13}C at 75 MHz, and 29Si at 59 MHz in toluene-d_8 at 100 °C). The branching content of polymers was determined based on ^1H NMR spectra. FTIR of polymer samples were measured on a Nicolet iS10 FT-IR instrument. Transmission spectra were registered in the region 4000 – 400 cm^{-1} using 64 scans at a resolution of 4 cm^{-1}. Solid samples of polymers were pressed on a special press at laboratory temperature into thin foils with a thickness optimally in the range of 150-250 μm and directly analyzed in the transmission mode of the spectrometer. The foil thickness was determined from the average of three measurements using a digital micrometer. For silyl-terminated polymers PE-SiH_2Ph and PE-$SiHPh_2$, the number of silyl groups per 1000 carbons of the polymer chain (N_{Si}= Si/1000C) was calculated from the relation of $N_{Si}= 14\ A\ (\rho\ t\ \epsilon)^{-1}$, where A is the absorbance of the signal at 2134 cm^{-1} or 2117 cm^{-1} (stretching vibrations of SiH_2 and SiH for groups SiH_2Ph and $SiHPh_2$, respectively), ρ is the density of the polymer (0.95 g m L^{-1}), t is the thickness of the PE film (cm) and ϵ denotes the relevant molar absorption coefficient. Coefficients $\epsilon_{2134\ \mathrm{cm-1}}$ = 165 Lmol^{-1}cm^{-1} and $\epsilon_{2117\ \mathrm{cm-1}}$ = 95 Lmol^{-1}cm^{-1} were calculated from a calibration curve by plotting a series of linear silyl-terminated polyethylenes with known silyl content quantified by NMR spectroscopy, against the absorbances of the mentioned IR signals at different thickness of PE foils.

For the quantitative estimation of unsaturated groups in polymer products, the molar absorption coefficients of signals 908 cm^{-1} for the vinyl group in 1-dodecene ($\epsilon_{908\ \mathrm{cm-1}}$ = 110 L mol^{-1} cm^{-1}), 964 $_{\mathrm{cm-1}}$ for *trans*-vinylene ($\epsilon_{964\ \mathrm{cm-1}}$ = 168 L mol^{-1} cm^{-1}), and 888 cm^{-1} for vinylidene in 2,3-dimethylbutadiene ($\epsilon_{888\ \mathrm{cm-1}}$ = 146 L mol^{-1} cm^{-1}) were used.[1] In this case, the absorbances of the mentioned alkene signals obtained by subtracting the spectrum of polyethylene after bromination from the original spectrum of the polymer before halogenation were evaluated. Bromination of polymer samples was carried out at laboratory temperature in liquid bromine for 24 hours. After removal of bromine, the sample was thoroughly rinsed with acetone and dried to constant weight in a vacuum oven at a temperature of 120 °C. ATR spectra of polyethylenes were obtained on the same FT-IR spectrometer using an attenuated total reflectance cell equipped with a ZnSe crystal in the range 650-4000 cm^{-1}.

Fig. S4 ^{1}H NMR spectrum of *br*-PE (entry 6 in Table 2) measured at 100 °C in toluene-d_8. (*) denote residual proton signals of the solvent. The insert spectrum indicates a trace amount of internal double bonds (multiplet centered at 5.40 ppm) and vinyl chain-ends (multiplets centered at 4.95 and 5.76 ppm) in the polymer.

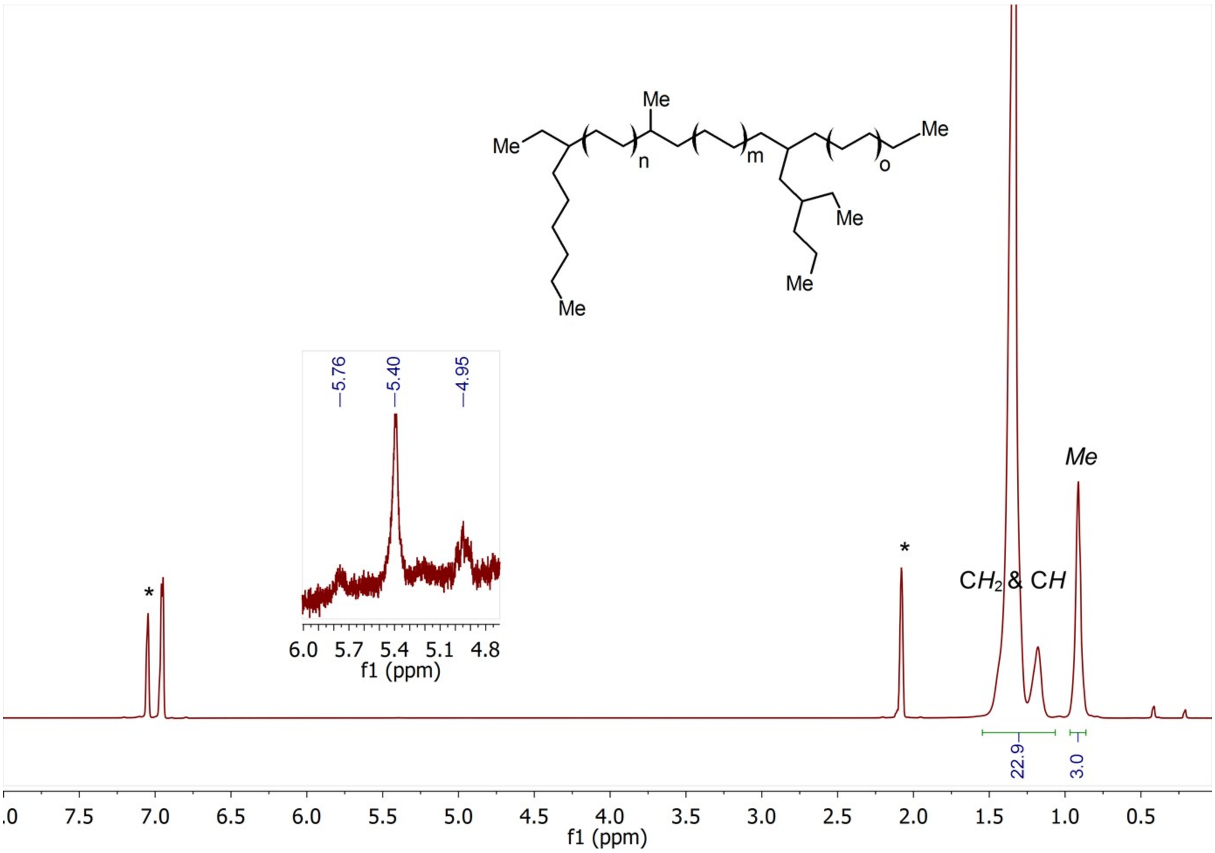


Fig. S5 ^{1}H NMR spectrum of *br*-PE-SiPhH$_2$ (entry 8 in Table 3) measured at 100 °C in toluene-d_8. (*) denote residual proton signals of the solvent. The insert spectrum indicates a trace amount of internal double bonds in the polymer (multiplet centered at 5.39 ppm).

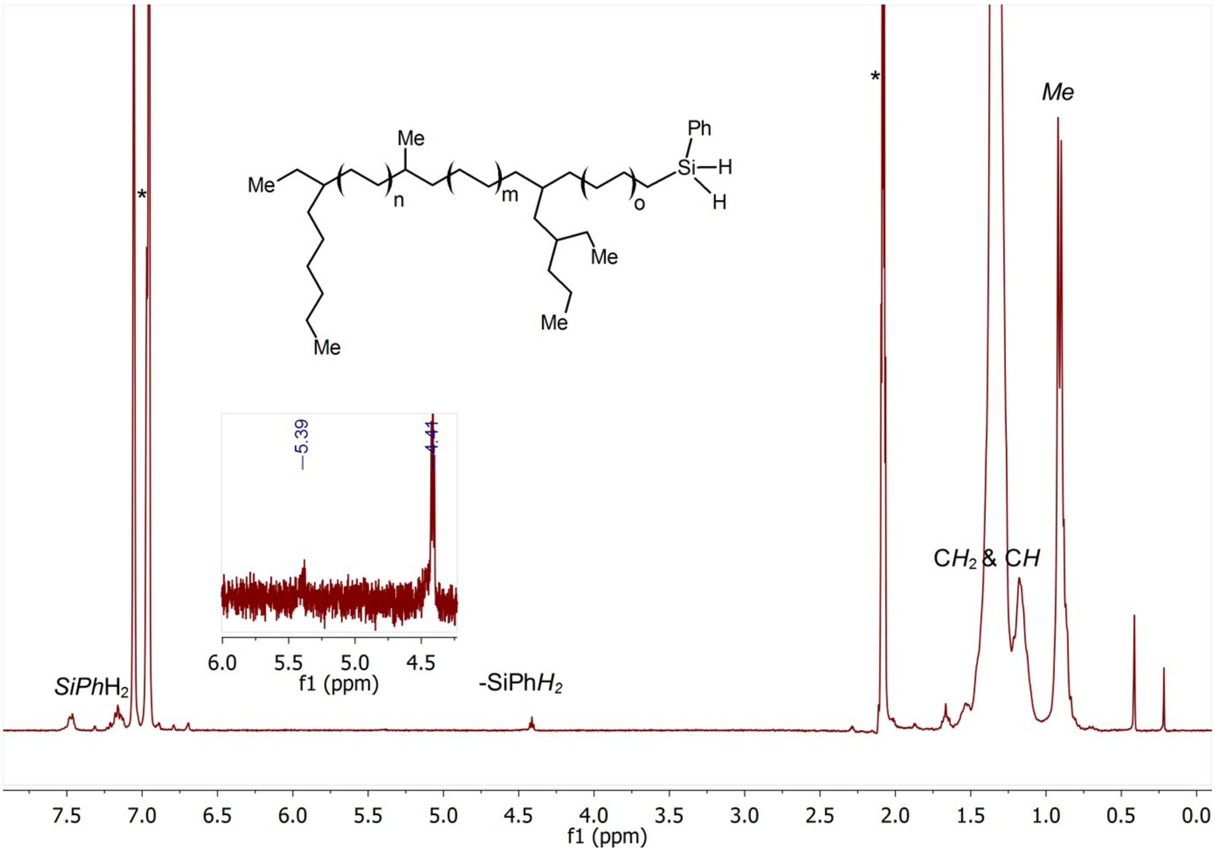


Fig. S6 FT-IR spectra (PE foils, an expanded region) of polymers obtained from **1**/B$(C_6F_5)_3$/Et_3SiH system: red line (entry 1, Table 2), violet line (entry 2, Table 2). For comparison spectra of vinyl-terminated PEs are depicted. The green line shows PE prepared with Cp_2ZrCl_2/B$(C_6F_5)_3$/Et_3SiH system (Mn = 81 000 g/mol, vinyl content 40 mol%). Turquoise line shows PE prepared with bis{N-(3-tert-butylsalicylidene)anilinato}zirconium(IV)dichloride/B$(C_6F_5)_3$/Et_3SiH system (M_n = 5000 g/mol, vinyl content 98 mol%). Bands at 908 and 990 cm^{-1} are characteristic of vinyl vibrations, while the band at 964 cm^{-1} is suggested to be characteristic of internal double bonds.

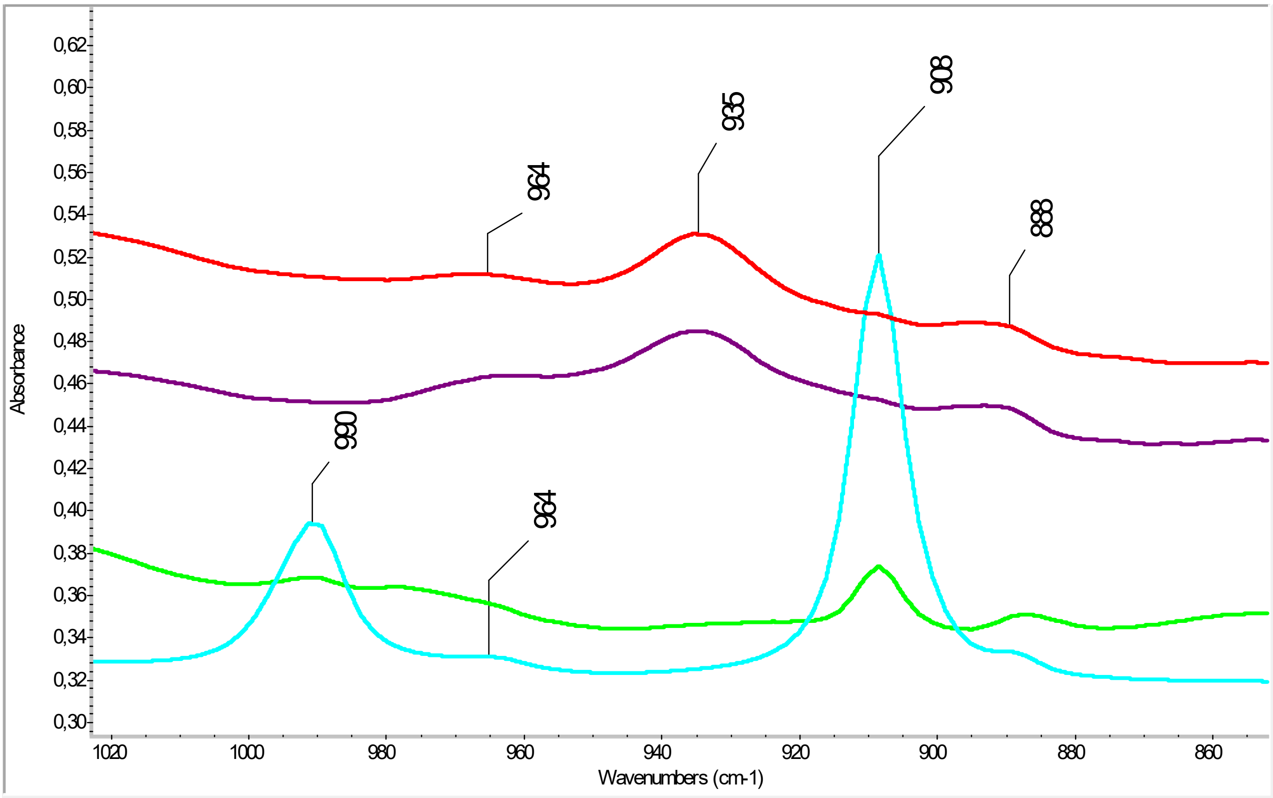
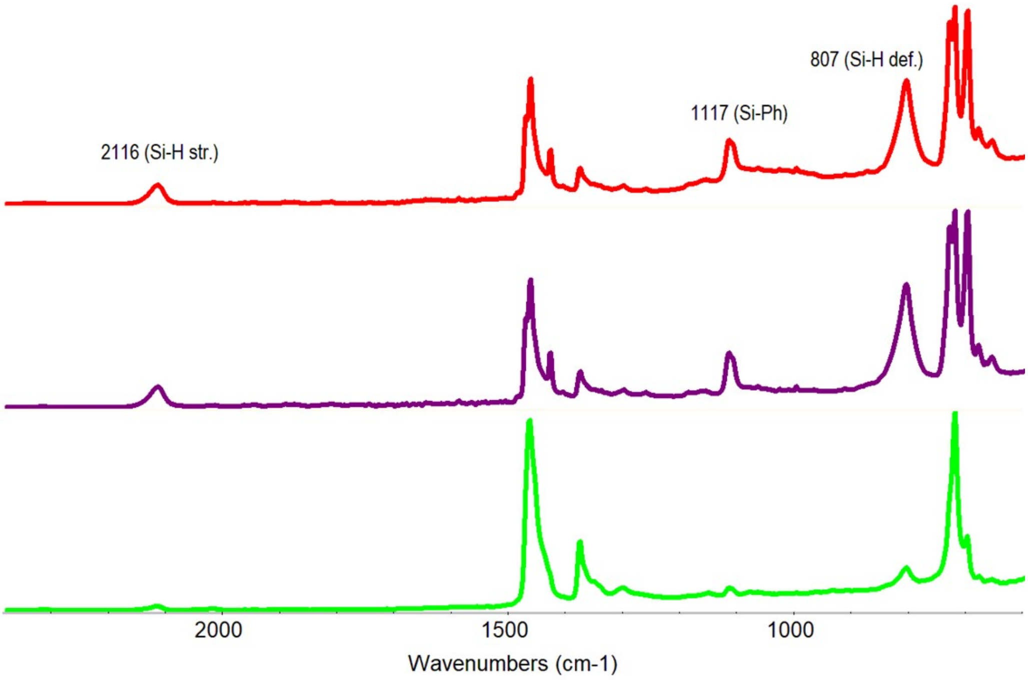


Fig.S7 ATR-ZnSe spectra (an expanded region) of PEs obtained from binary hydrosilane system activation of **1**: Et_3SiH/Ph_2SiH_2 = 60/1 (entry 1 in Table 4, bottom), Et_3SiH/Ph_2SiH_2 = 1/1 (entry 2 in Table 4, middle) and from activation using sole Ph_2SiH_2 (entry 5 in Table 3, top). For clarity, only vibrations of the terminal silyl group are assigned.



NMR experiments

1/B(C_6F_5)$_3$/10 eq. Et_3SiH in CD_2Cl_2

In a glovebox B(C_6F_5)$_3$ (20 mg, 0.039 mmol), and **1** (24 mg, 0.039 mmol) were weighed into a flask equipped with a Young valve and then connected to an argon-vacuum line. 1 ml of CD_2Cl_2 was added to dissolve all components. To the orange solution, Et_3SiH (65 μl, 0.407 mmol) was added. The solution was transferred by gastight syringe to an NMR cuvette equipped with a Young valve and sealed off under a vacuum. The evolution of the reaction mixture was followed by multinuclear NMR spectroscopy.

1/B(C_6F_5)$_3$/20 eq. 1-hexene/10 eq. Et_3SiH in CD_2Cl_2

The initial mixture was prepared as described above from B(C_6F_5)$_3$ (20 mg, 0.039 mmol) and **1** (24 mg, 0.039 mmol). To the orange solution, 1-hexene (120 μl, 0.970 mmol) was added (no color change was observed). Finally, Et_3SiH (65 μl, 0.407 mmol) was added and the solution was transferred by gastight syringe to an NMR cuvette equipped with a Young valve and sealed off under a vacuum. The evolution of the reaction mixture was followed by multinuclear NMR spectroscopy.

1/B(C_6F_5)$_3$/200 eq. 1-hexene/100 eq. Et_3SiH in tolueneD$_8$

Stock solutions of **1** (2.4 μmol, 3 ml of 0.8 mM) and B(C_6F_5)$_3$ (2.4 μmol, 3 ml of 0.8 mM) in toluene were transferred into a flask equipped with a Young valve by a gastight syringe, and then connected to an argon-vacuum line. The toluene was evaporated under a vacuum and 1 ml of deuterated toluene was added to dissolve all components. To the orange solution, 1-hexene (60 μl, 0.480 mmol) was added (no color change was observed). Finally, Et_3SiH (38 μl, 0.240 mmol) was added and the solution was transferred by gastight syringe to an NMR cuvette equipped with a Young valve and sealed off under a vacuum. The evolution of the reaction mixture was followed by multinuclear NMR spectroscopy.

Fig. S8 ^1H NMR spectra of **1**/$B(C_6F_5)_3$/10 eq. Et_3SiH/1-hexene in CD_2Cl_2 measured after 15 min, 75 min, 1 day, and 2 days. The inserts showed APT spectrum of the mixture measured 1 day after mixing.

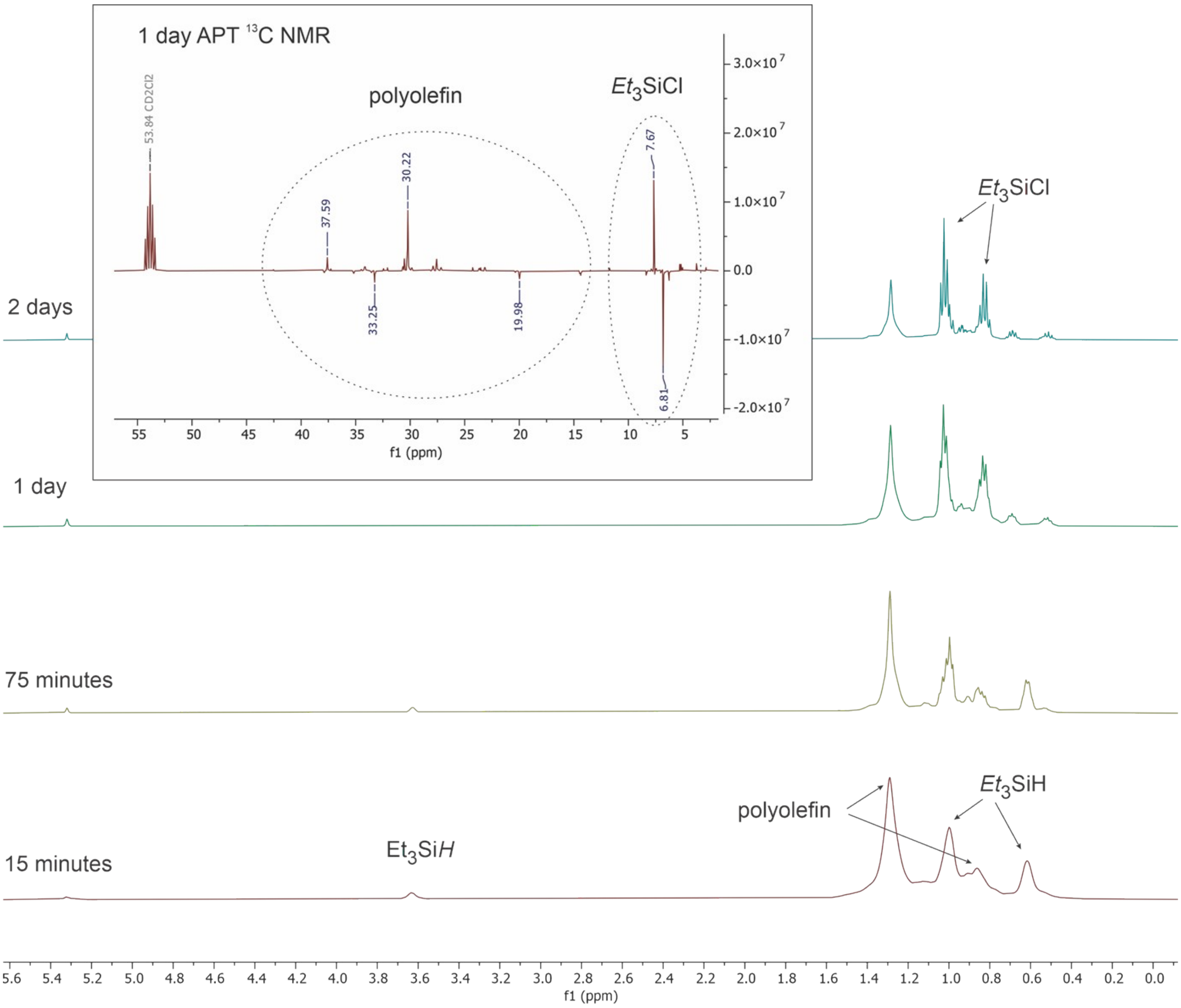


Fig. S9 $^{29}Si\{^1H\}$ NMR spectra of **1**/$B(C_6F_5)_3$/10 eq. Et_3SiH in CD_2Cl_2 measured after 1h, 9h, 2 days, and 7 days.

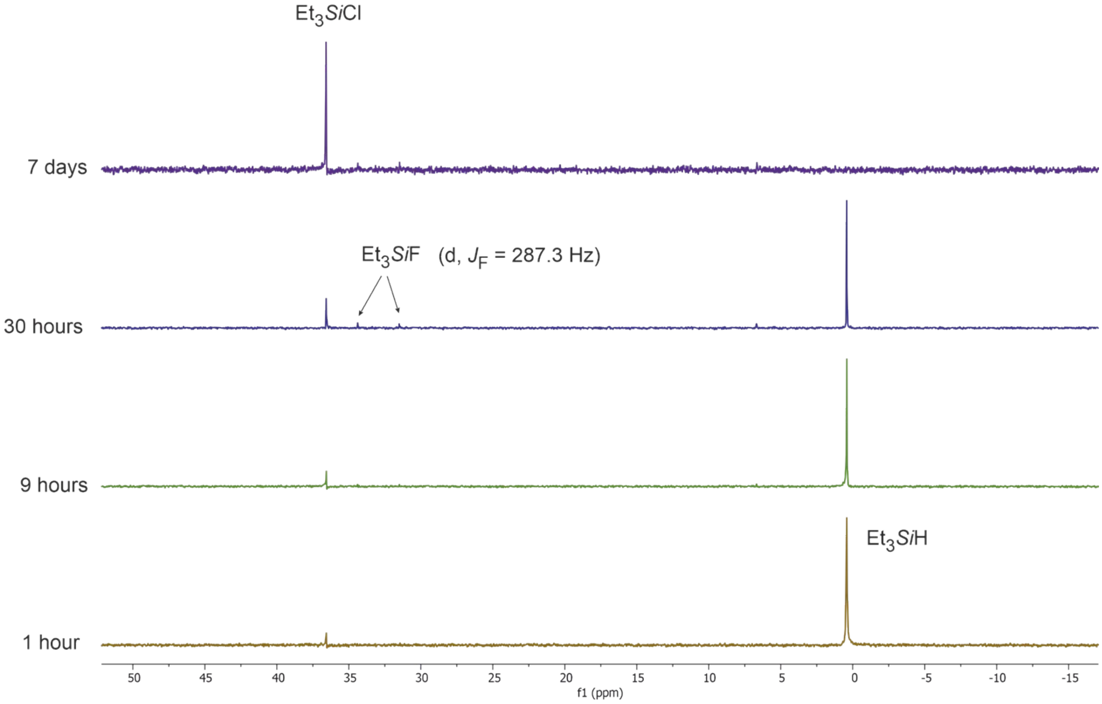


Fig. S10 ^{1}H NMR spectra of **1**/$B(C_6F_5)_3$/10 eq. Et_3SiH in CD_2Cl_2 measured after 35 min, 9h, 2 days, and 7 days. The inserts showed the formation of CD_2HCl (δ_H centered at 2.99 ppm) and CD_2H_2 δ_H centered at 0.19 ppm).

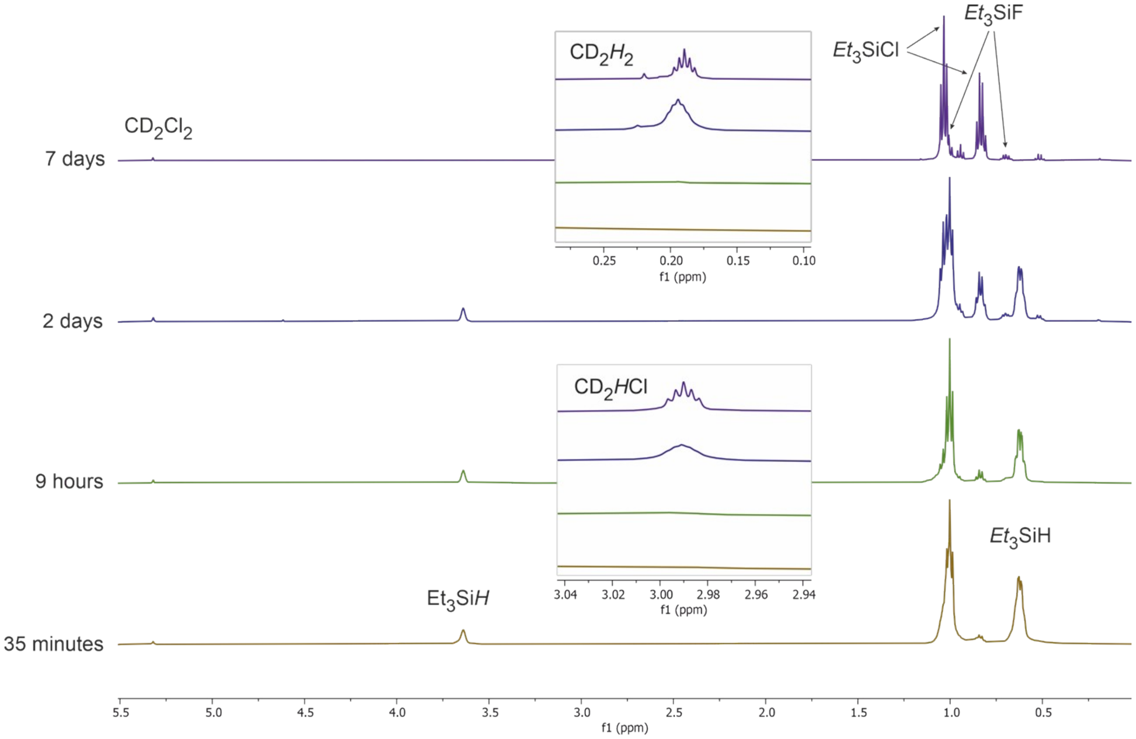


Fig.S11 $^{29}Si\{^{1}H\}$ NMR spectra of **1**/$B(C_6F_5)_3$/100 eq. Et_3SiH/200 eq. 1-hexene in toluene-d_8 (NS= 20 000) measured 2 months after the mixture preparation.

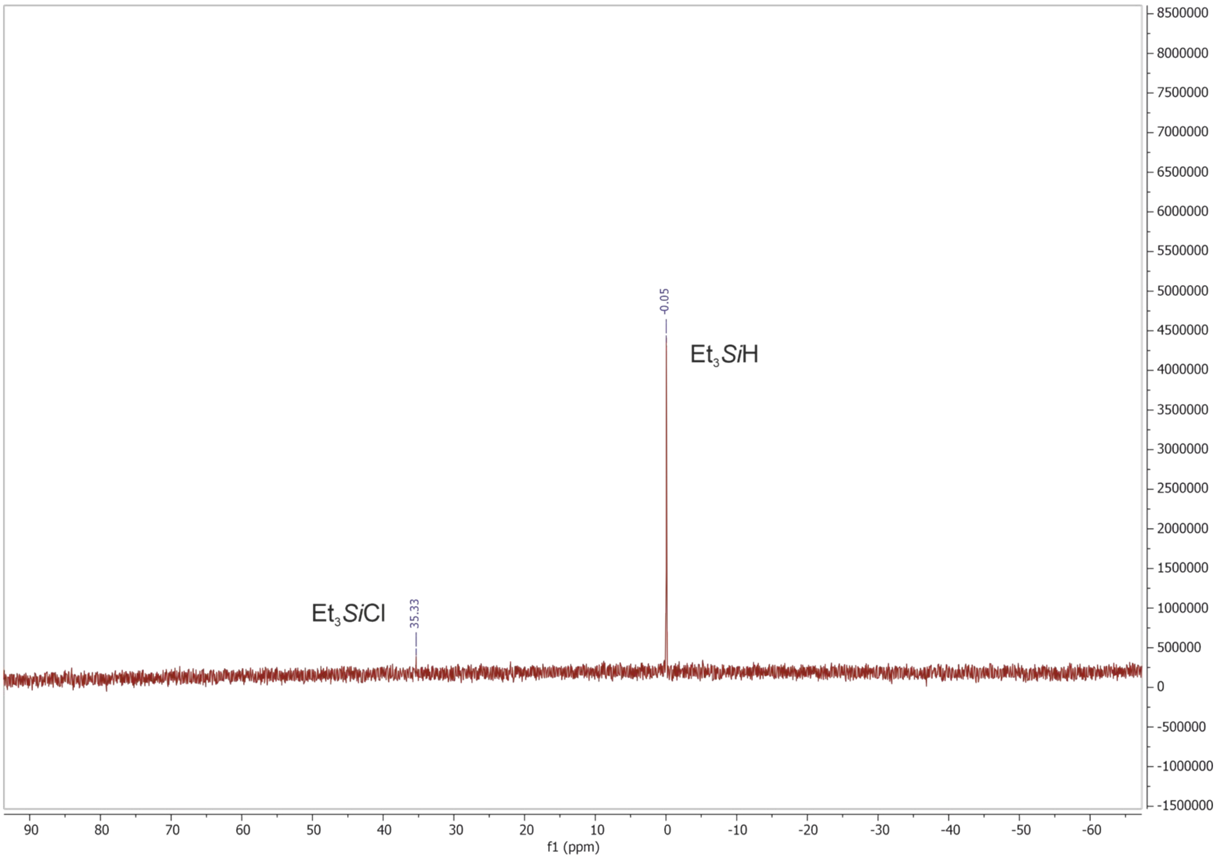
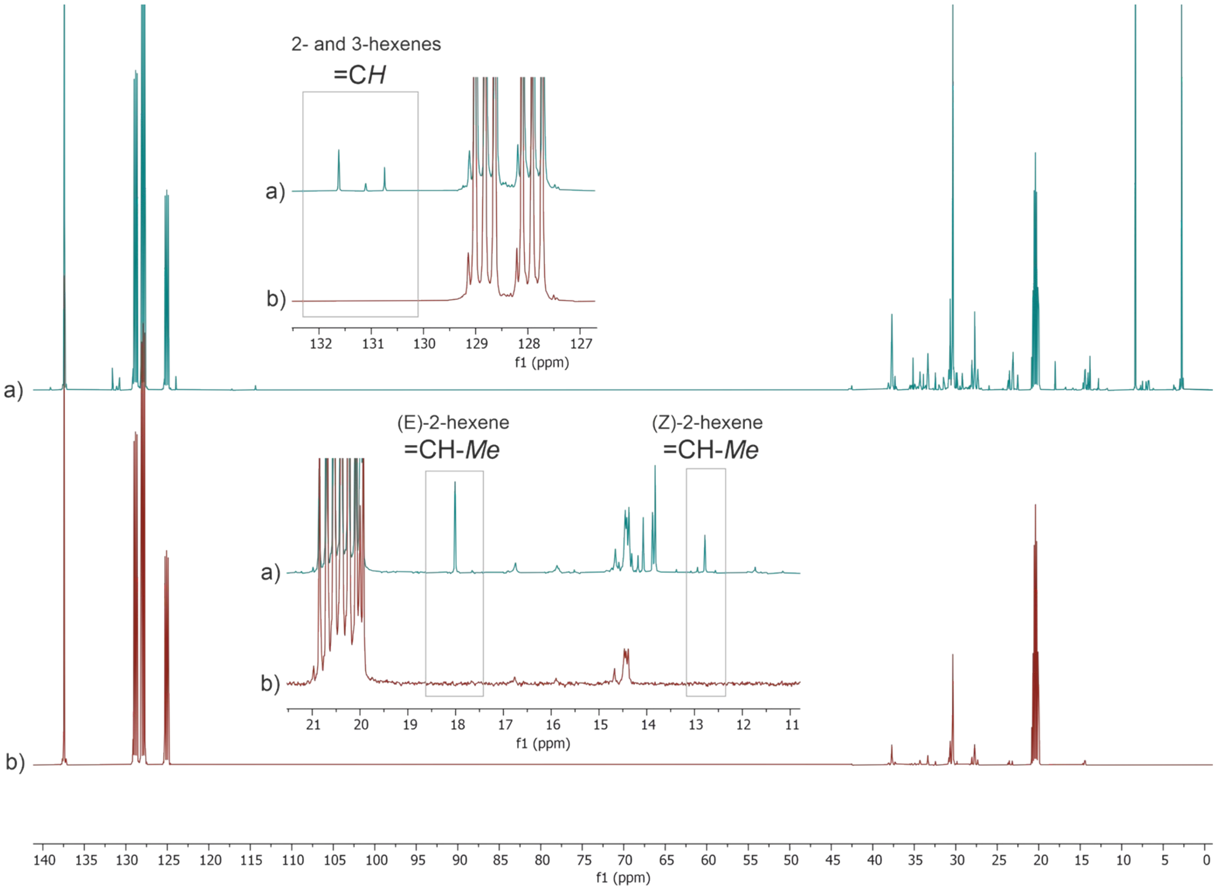


Fig. S12. $^{13}C\{^1H\}$ NMR spectrum of mixture **1**/B(C_6F_5)$_3$/100 eq. Et_3SiH/200 eq. 1-hexene in toluene-d_8 measured 2 months aftef mixing (a) and $^{13}C\{^1H\}$ NMR spectrum of poly(1-hexene) isolated thereof mixture (b).



EPR experiments

1/B(C_6F_5)$_3$/hydrosilane

B(C_6F_5)$_3$ (20 mg, 0.039 mmol) and **1** (24 mg, 0.039 mmol) were weighed into a flask equipped with a Young valve in the glove box and moved to the argon-vacuum line. 5 ml of dichloromethane was added to dissolve all components. The orange solution was then transferred by gastight syringe to an EPR cuvette equipped with a Young valve. All volatiles were evaporated by the vacuum and 6 ml of toluene was added. EPR spectra were collected (no signal was observed in the absence of hydrosilane). An EPR cuvette was then connected to the argon-vacuum line and a hydrosilane (0.405 mmol) was added. In dependence on a hydrosilane nature, the color of the mixture remained yellow (Et_3SiH) or changed steadily/immediately to green/turquoise (Ph_2SiH_2/$PhSiH_3$). EPR spectra were collected at room and low temperatures (in the range 293-113 K). In addition, the time evolution of Ni(I) signal was monitored for several hours.

1/Et_3SiH /B(C_6F_5)$_3$ /1-hexene

1 (4 mg, 6 μmol) was weighted in the glovebox into the Schlenk flask. 5.5 ml of toluene was added by syringe to form an orange solution, all solid was dissolved. The solution was transferred to an ampoule equipped with an EPR cuvette. 0.313 mmol of Et_3SiH (0.05 ml, 313 μmol) was added. No change of color was observed. No EPR signal was observed for 4 days. B(C_6F_5)$_3$ (10 mg, 19 μmol) was weighed in the glove box and dissolved in 2 ml of toluene. The colorless solution was transferred into the reaction mixture by syringe. The color of the solution was changed to bright yellow. EPR measurements show signals of Ni(I) and radical (7 lines) at a g-value of 2.002 immediately after mixing. After 24 h only the signal of Ni(I) remains in the EPR spectrum. 1-hexene (10 μl, 80 μmol) were added. EPR spectra without change also at low temperatures were obtained. No color change was observed. After 24 h another 0.5 ml of 1-hexene was added and stirred. After one week of stirring, the ampoule contains a viscous solution (mead consistency). EPR measurement did not show any changes in the EPR spectra of Ni(I) species (measured at low temperatures too). The solution was opened and poured into a mixture of methanol with HCl. The gel was immediately observed together with a color change into pink. The polymer was separated and left stirred in methanol. The yield of polyhexene was 122 mg.

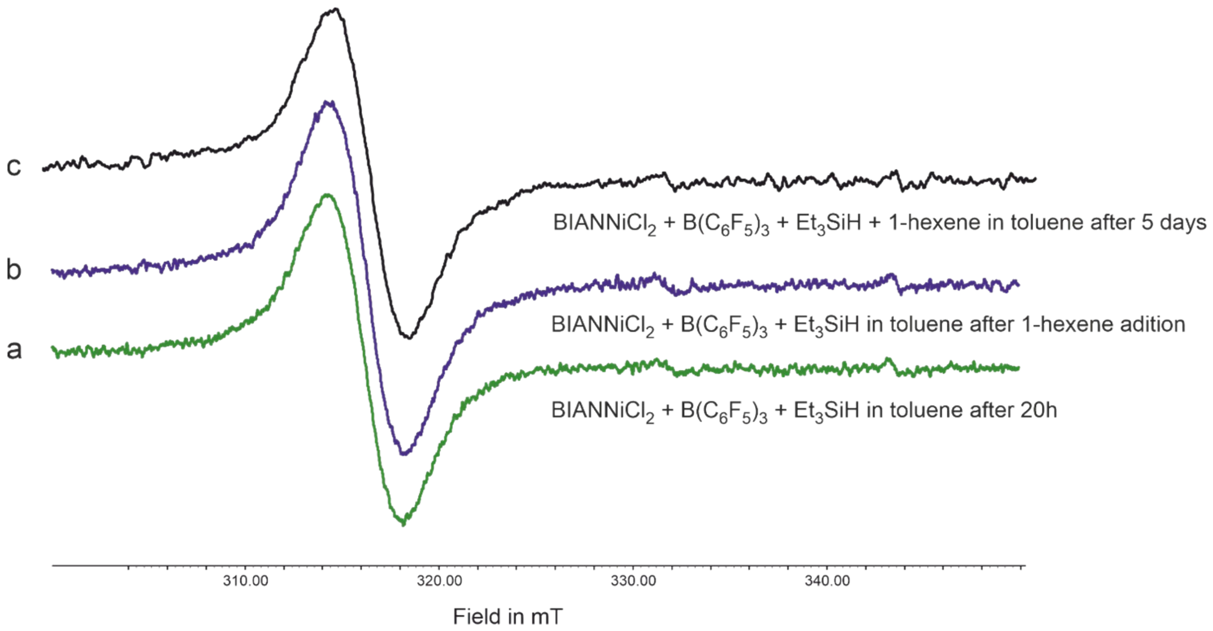
1/$B(C_6F_5)_3$/Et_3SiH

$B(C_6F_5)_3$ (6 mg, 12 μmol) and **1** (5 mg, 8 μmol) were weighted in the glovebox into the Schlenk flask. 2 ml of dichloromethane were added, and all compounds were dissolved formed a yellow solution. The solution was transferred by syringe to the next ampoule equipped with an EPR cuvette (quartz tube 5 mm). All volatiles were evaporated to vacuum and toluene (6 ml) was added. The yellow solution was obtained and EPR spectra were collected without any signal. After 24 h new small signal (7 lines) was found in the solution at g = 2.002 and its intensity was increased with time. 0.313 mmol of Et_3SiH (0.05 ml, Mw = 116.28) was added and the mixture was stirred, and immediately measured on an EPR spectrometer. Continuous measurement proved the rising signal of Ni(I) and the increased signal of radical too. The next day dark blue-grey solution shows a signal of Ni(I) only. Radical disappeared. All volatiles were evaporated off and measured on GC-MS.

BIAN / $B(C_6F_5)_3$

$B(C_6F_5)$ (7 mg, 14 μmol) and BIAN (5 mg, 12 μmol) were weighted in the glovebox into the Schlenk flask. 5 ml of toluene was added by syringe. The reaction followed by the color change was observed. All solids were dissolved and the dark yellow solution was transferred to an ampoule equipped with a quartz cuvette for EPR measurement. EPR spectrum shows one signal with splitting (7 lines). Measurements were repeated several times till no change in signal intensity was observed.

Fig. S13 Comparison of X-band EPR spectra of Ni(I) species in the reaction mixture **1**, $B(C_6F_5)_3$, Et_3SiH and 1-hexene in toluene solution at room temperature



Discussion concerning the formation of organic ligand (g = 2.001) generated in 1/$B(C_6F_5)_3$/10 eq. hydrosilane system.

A second signal detected in the EPR spectrum of mixture **1**/$B(C_6F_5)_3$/hydrosilane was the signal of an organic radical with hyperfine splitting. The radical displayed a 7-lined signal at g value 2.002 with hyperfine splitting a = 0.51 mT (Figure 3A). This signal suggests the presence of a radical formed by the interaction of $B(C_6F_5)_3$ with the π-system of BIAN. The splitting of the signal may come from the coupling of the unpaired electron with two ^{14}N (I=1) and two ^{1}H (I=1/2) nuclei.

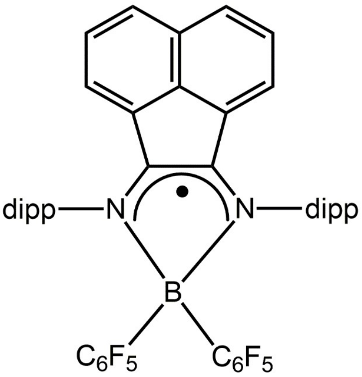
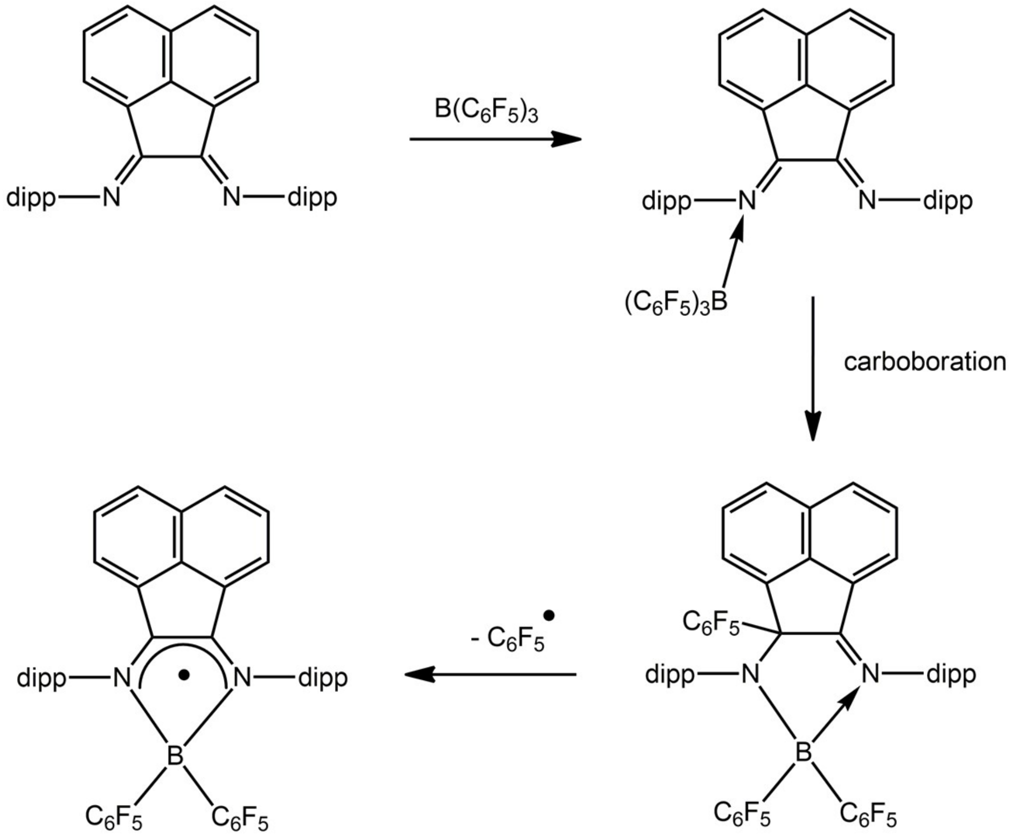


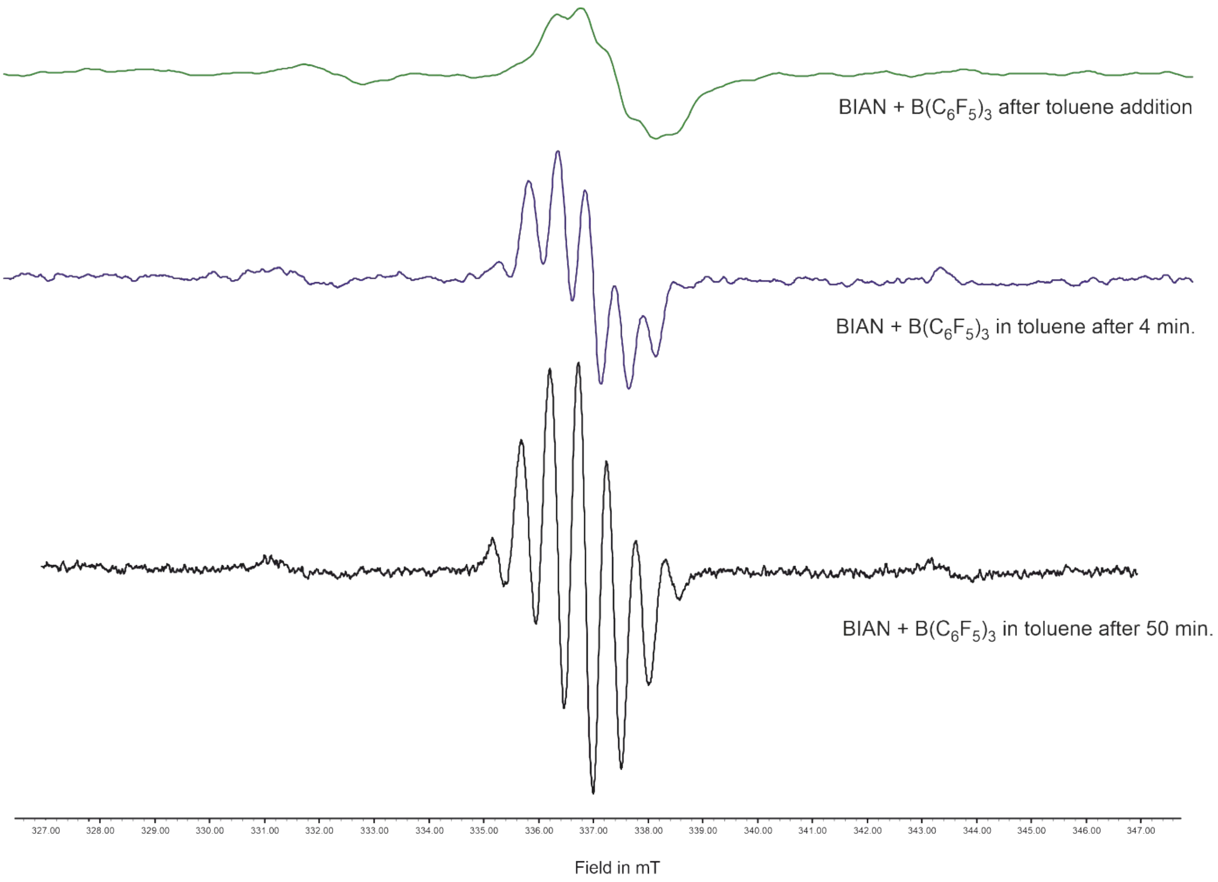
Chart S1

The exact structure of the radical cannot be unequivocally determined from our experiments, however, we tentatively propose a formation of boron species with ligand based radical [(BIAN)B(C_6F_5)$_2$] depicted in Chart S1. The splitting from ^{11}B and ^{10}B nuclei was not observed in the experimental spectrum and is suppressed by more significant splitting from two ^{14}N and two ^{1}H nuclei, as was reported for [DPP-DAB]$^-$BF$_2^+$ radical.[2] The formation of the radical [(BIAN)B(C_6F_5)$_2$] could be explained as a carboboration of BIAN with B(C_6F_5)$_3$, followed by C_6F_5 elimination (see Scheme S1), similarly as was described by Stephan for carboboration of dione $O_2C_{14}H_8$ with B(C_6F_5)$_3$.[3-4] Notably, a reaction of free diimine BIAN ligand with B(C_6F_5)$_3$ generated an identical signal at g 2.002 (see Fig. S14), which supported that its formation did not involve any Ni species derived from **1**.



Scheme S1: Proposed mechanism of the reaction of BIAN with B(C_6F_5)$_3$ leading to the paramagnetic species.

Fig. S14 EPR spectrum of mixture BIAN molecule with $B(C_6F_5)_3$



References

1. a) R. Blom, A. Follestad, O. Noel, *Journal of Molecular Catalysis*, 1994, **91**, 237-249. b) K. Thorshaug, J. A. Stovneng, E. Rytter, M. Ystenes, *Macromolecules*, 1998, **31**, 7149-7165.
2. N. S. Gurinovich, S. K. Petrovsky, I. V. Saliy and V. V. Saraev, *Res. Chem. Intermediat.*, 2018, **44**, 1935.
3. K. L. Bamford, L. E. Longobardi, L. Liu, S. Grimme and D. W. Stephan, *Dalton Trans.*, 2017, **46**, 5308.
4. A. Bodach, K. L. Bamford, L. E. Longobardi, M. Felderhoff and D. W. Stephan, *Dalton Trans.*, 2020, **49**, 11689.