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Kinetic and mechanistic studies of the transformation of the catalyst, tris (pentafluorophenyl)borane, in the presence of silyl and germyl hydrides



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ABSTRACT

Tris(pentafluorophenyl)borane catalyzed Si-H bond activation opens the door to numerous transitionmetal-free reduction processes and is widely used in organic and polymer chemistry. However, chemical stability of $B(C_6F_5)_3$ in the presence of silyl hydrides is limited, which can strongly affect its catalytic activity. Transformations of $B(C_6F_5)_3$ in the presence of phenyldimethylsilane, triethylsilane and triethylgermane were studied by ¹⁹F NMR and UV spectroscopy, GC/MS and quantum-mechanical calculations. The observed exchange of pentafluorophenyl group attached to boron to hydrogen results in the formation of bis(pentafluorophenyl)borane, which has a strongly reduced ability to activate the Si-H bond. The substitution kinetics were studied by following the disappearance of absorption of the $B(C_6F_5)_3$ charge transfer peak in the UV spectrum. Complementary quantum mechanical calculations allowed us to propose a mechanism of the ligand exchange reaction, which involves electrophilic substitution of the pentafluorophenyl group through a four-center transition state.

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1. Introduction

Catalysis by tris(pentafluorophenyl)borane (TPFPB) of various reactions with the participation of silyl hydrides has been widely practiced in organic chemistry and organosilicon chemistry. TPFPB is strong Lewis acid, which effectively activates the Si-H bond in processes involving hydride ion transfer [1,2]. It is very effective in promoting the reduction of many functional organic compounds, such as alcohols, ketones, aldehydes, amides, acyl chlorides, imines, carboxylic acids and esters, by hydrosilanes [3–6]. It also promotes rearrangement processes such as reductive carbocyclization [7]. Many silvl derivatives may be obtained by TPFPB catalyzed hydrosilylation of various organic functions [8-10]. Recent advances in frustrated Lewis pairs open up a new area in organic synthesis involving Si-H bond activation by TPFBP [2,11]. Silanol and alcohol silvlation by SiH functional reagents catalyzed by this borane are important processes in polysiloxane chemistry [12,13], which are used for modification of silica, silicon and carbon nanotubes surfaces [14-16]. The catalysis of dehydrocarbonative condensation by TPFPB, known as the Piers-Rubinsztajn reaction, found broad application in polysiloxane chemistry [17-19]. It is practiced in syntheses of siloxane copolymers [20], oligomers [21], branched polymers [22], cyclic polymers [23], and in the modification of polysiloxanes [24]. TPFPB is used as an initiator of the ring-opening polymerization of cyclic siloxanes by hydride transfer mechanism [25], and in oligomerization processes of hydrosiloxanes [26]. The dehydrocarbonative condensation of hydrosilanes with alkyl esters of boric acid promoted by TPFBP was also reported [27].

Reactions involving germanium hydrogen bond activation by B $(C_6F_5)_3$ are known, although they are not so common as those with the Si-H bond activation. Gevorgian et al. reported selective germylation of alkyne with trialkylgermanes and triphenylgermane, which is a promising route to germylated olefins [28]. An interesting feature of this reaction is that it proceeds in the presence of carboxyl and ether groups in alkyne reagents leaving them untouched. This observation proves much lower oxophilicity of germanium as compared with silicon. Olefin hydrogermylation has recently been reported using cyclohexa-2,5-dien-1-yl-substitu ted germanes. These compounds under the action of TPFPB and in the presence of an olefin, liberated hydrogermanes, which in situ hydrogermylated the olefin [29]. It was shown that the dehydrocarbonative condensation between trialkylgermanium hydrides and alkoxysilanes catalyzed by TPFPB occurs analogously to the Piers-Rubinsztajn process and leads to products with SiOGe bonds [30]. The condensation of trialkylsilanes with some alkoxygermanes occurred as well, but with very low yields. By contrast, it



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has recently been found that the reaction of phenyldimethylsilane with tetrabutoxygermane in the presence of TPFPB leads exclusively to the reactive group exchange i.e. to the substitution of alkoxy group at germanium with hydrogen [31].

The rapid increase in the use of hydrosilanes and hydrogermanes in combination with catalytic amounts of $B(C_6F_5)_3$ in synthetic chemistry poses the question about the chemical stability of these systems. In our experimental works, we observed that the catalytic ability of TPFPB is decreasing over time in the presence of reagents containing SiH and GeH moieties. Synthetic chemists should be conscious of the reactions of the borane with hydrosilanes and hydrogermanes and should know to what extent they affect catalytic activity of TPFPB. The knowledge on the reactions between TPFPB and SiH functional compounds is scarce. It is known that the reaction leads to the exchange of one of the aromatic groups attached to boron to hydrogen. This reaction was used for the generation of $HB(C_6F_5)_2$, which was applied further as hydroboration agent [32]. Theoretical calculation gave the free energy barrier to this reaction of 27.8 kcal/mol [33]. To the best of our knowledge, kinetic studies of reactions of $B(C_6F_5)_3$ with Si-H reagents and any studies of the interaction of TPFPB with GeH reagents have not yet been reported. The aim of our research was to gain more knowledge about reactions of $B(C_6F_5)_3$ with hydrosilanes and hydrogermanes, which result in a strong reduction of its catalytic activity.

2. Experimental section

2.1. Materials

Triethylsilane and dimethylphenylsilane were products of Aldrich, declared purities were 99% and \geq 98% respectively. Triethylgermane, declared purity 97%, 1,1,3,3-tetramethyldisiloxane, declared purity 99%, were purchased from ABCR. Their purity was checked by gas chromatography and were used as received. Poly(methylhydrosiloxane), Catalog #: AB112087, viscosity 15-25cSt, molecular weight about 2000 g/mol, was purchased from ABCR. Tris(pentafluorophenyl)borane was a product of TCI, declared purity > 97%. Its purity was confirmed by ¹⁹F NMR spectroscopy. Toluene HPLC Plus, a product of JT Baker, purity 99.9%, was additionally dried on column system NBSPS of dry-box MBRAVN model UNILAB. Toluene *d*₈, a product of Deutero GmbH of declared purity 99.5%, was stored over 3 Å molecular sieves.

2.2. Analytical methods

 ^{19}F NMR spectra were registered on a Bruker AV III 500 MHz spectrometer working at 470.54 MHz. Gas chromatography-mass spectrometry GC/MS analysis was carried out using a Shimadzu QP2010 ultra apparatus equipped with Zebron ZB-5MSi Capillary GC column (30 m \times 0.25 mm \times 0.25 μ m). Carrier gas was helium. Temperature program was: hold at 50 °C for 3 min, heating to 250 °C at a rate 10 °C /min, hold at 250 °C for 20 min. Quadrupole mass spectrometer, Shimadzu QP2010 Ultra, with electron ionization was connected to the GC system. UV spectra were recorded using a UV–VIS spectrometer, Specord S600 Zeiss Jena, Analytik Jena AG, Jena Germany, equipped with Peltier temperature-controlled 8-cell changer. A 1 mm quartz cuvette with a Rotaflo stopcock was used.

2.3. Studies by ¹⁹F NMR

The solutions of the borane in toluene d_8 were prepared in drybox and were placed in an NMR tube purged with dry nitrogen. Small excess of 1,1,3,3-tetramethyldisiloxane was added to the sample to remove traces of water. The presence of dry borane was confirmed by recording ¹⁹F NMR spectra. The desired amount of silicon or germanium reagent was then introduced, typically about a 50-fold molar excess, compared to the borane. The NMR tube was sealed and ¹⁹F NMR spectra were taken at desired time intervals. The chemical shifts were reported relative to the CFCl₃ standard.

2.4. Kinetic studies by UV spectroscopy

A mother solution of tris(pentafluorophenyl)borane in dry toluene 0.033 mol/L was prepared and stored in dry box. A suitable amount of this solution was diluted with dry toluene to obtain the final B(C₆F₅)₃ solution at a concentration of about 5.5×10^{-4} mol/L. 0.3 mL of the final solution was transferred to 1 mm thick UV quartz cuvette. In the case of the germanium reagent, an excess of dimethylphenylsilane was introduced to remove borane-bound water. The presence of water-free $B(C_6F_5)_3$ was confirmed by the appearance of a strong UV band with a maximum at 305 nm. The desired amounts of PhMe₂SiH. Et₃SiH or Et₃GeH were then added using a Hamilton syringe. The cuvette was closed with stopcock, removed from dry box and placed in the Peltier temperaturecontrolled changer set at a constant temperature. UV spectra were recorded in a desired time interval using a UV-VIS spectrometer, Specord S600 Zeiss Jena, Analytik Jena AG, Jena Germany, equipped with Peltier temperature-controlled 8-cell changer.

2.5. Theoretical calculations

All quantum mechanical calculations were performed using the Gaussian 16 suite of programs [34]. Geometries of the reagents and complexes were optimized using the hybrid B3LYP density functional [35] corrected for dispersion interactions using Grimme GD3 empirical term [36], with Def2-SVP basis set [37] in the gas phase. All stationary points were identified as stable minima by frequency calculations. The vibrational analysis provided thermal enthalpy and entropy corrections at 298 K within the rigid rotor/harmonic oscillator/ideal gas approximation [34]. Thermochemical corrections were scaled by a factor of 0.985 [38]. More accurate single point electronic energies were obtained using the B3LYP functional, including Grimme GD3 dispersion correction [36], with the larger Def2-TZVP basis set for the Def2-SVP optimized geometries [39]. This level of theory is denoted as B3LYP-GD3/Def2TZVP//Def2SVP. Integration grid was set to ultrafine. The basis set superposition error (BSSE) has been neglected since it is small (<0.5 kcal/mol) and the method of its estimation [40] is not accurate enough to precisely calculate weak interactions.

3. Results and discussions

3.1. Studies by ¹⁹F NMR spectroscopy

Studies of $B(C_6F_5)_3$ reaction with silyl and germyl hydrides were carried out using dimethylphenylsilane, triethylsilane and triethylgermane as model reagents and toluene as solvent. ¹⁹F NMR spectroscopy is an effective method for the investigation of the chemical transformation of fluoroarylboranes [41–43]. The reactions between borane and PhMe₂SiH, Et₃SiH and Et₃GeH were followed directly in an NMR tube at a constant temperature. It is known that the presence of water strongly reduces the catalytic activity of TPFPB in various reactions, such as dehydrocarbonate condensation, ring-opening polymerization of cyclic siloxanes by a hydride transfer mechanism, and oligomerization of SiH functional siloxanes due to the formation of strong hydrates [44,45]. Commercial TPFPB usually contains water in the form of strong hydrates. Traces of water at the level of $10^{-4} - 10^{-3}$ mol/L always remain even after very careful purification of the solvent and can form these hydrates. It has been found that both free water and borane-bound water are efficiently and rapidly removed by a SiH reagent such as triethylsilane or phenyldimethylhydrosilane, producing a small amount of disiloxane and hydrogen in the reaction [44]. Thus, water is simply removed after mixing the borane with PhMe₂SiH or Et₃SiH substrates, which are added in a large excess to $B(C_6F_5)_3$. The problem arises in reaction studies with Et_3GeH_1 . which reacts slowly with water and produces additional byproducts revealed by GC-MS. To obtain reproducible results in experiments with Et₃GeH, traces of water were removed by introducing a small amount of SiH-containing compound into the borane solution before adding Et₃GeH. ¹⁹F NMR spectrum of the mixture of 55 mol eq. of PhMe₂SiH with 1 mol eq. of TPFPB in toluene at 30 °C was collected just after mixing both reagents. Fig. S1A. Three sets of signals at $\delta = -128.66 \text{ ppm} (2F_{\text{ortho}})$, δ = -142.67 ppm (F_{para}) and δ = -160.20 ppm (2F_{meta}) were observed, which is consistent with the ¹⁹F NMR spectrum of pure TPFPB [42]. The ¹⁹F NMR cumulative spectra of the same mixture collected during the reaction, zoomed to the Fortho region, are shown in Fig. 1.

The intensity of the F_{ortho} signal of TPFPB at δ = -128.66 ppm decreases as the reaction proceeds. There are two sets of new sig-

nals, and their intensity increases over time, indicating the formation of two products containing pentafluorophenyl groups. The signal at $\delta = -126.61$ ppm is attributed to F_{ortho} of PhMe₂Si(C₆F₅). Corresponding F_{para} and F_{meta} signals are located at $\delta = -149.7$ ppm and $\delta = -161.27$ ppm respectively, Fig. S1B. GC/MS analysis of the final mixture confirmed the presence of $PhMe_2Si(C_6F_5)$ as the main product containing silicon and pentafluorophenyl group, Figs. S2 and S3. The F_{ortho} signals with chemical shift from $\delta = -130.8$ ppm to -132.9 ppm belong to bis(pentafluorophenyl)borane, HB(C₆F₅)₂. The formation of $H_2B(C_6F_5)$ may also take place in the reaction mixture as a result of the subsequent exchange process (Eqs. (1) and (2)). Bis(pentafluorophenyl)borane appears as a mixture of its monomer, dimer $(C_6F_5)_2B(\mu-H)_2B(C_6F_5)_2$ [46] and mixed complex $(C_6F_5)_2B(\mu-H)_2B(H)(C_6F_5)$ formed through an interaction of B-H moieties [32]. The formation of an additional mixed complex of HB(C_6F_5)₂ with an excess of PhMe₂SiH can also occur in the reaction mixture, which would explain a larger number of signals in this region of the spectrum. Quantum-mechanical calculations of thermodynamics of these processes confirm the possibility of occurrence of these interactions, Table 1.

Based on these results, it can be concluded that exchange of pentafluorophenyl group for hydrogen occurs between the TPFPB and PhMe₂SiH according to Eq. (1). The subsequent replacement of the pentafluorophenyl group in the just formed $HB(C_6F_5)_2$ with hydrogen is carried out according to Eq. (2).



Fig. 1. ¹⁹F NMR spectra (F_{ortho} region) of the reaction mixture of Me₂PhSiH [2.36 mol/L] and B(C₆F₅)₃ [0.043 mol/L] in deuterated toluene at 30 °C.

Table 1

Enthalpies and Gibbs free energies [kcal/mol], entropies [cal/mol K], and approximate K_{eq} of complex formation at 298 K of model silvl and germyl hydrides with $B(C_6F_5)_3$ and HB (C_6F_5)₂ calculated by B3LYP-GD3/Def2TZVP//Def2SVP in the gas phase.

Reaction	ΔH	ΔG	ΔS	K _{eq}
$Et_3SiH + B(C_6F_5)_3 \rightarrow Et_3SiH \cdots B(C_6F_5)_3$	-10.2	4.9	-50.6	$2.5\cdot 10^{-4}$
PhMe ₂ SiH + B(C ₆ F ₅) ₃ → PhMe ₂ SiH···B(C ₆ F ₅) ₃	-11.2	3.6	-49.5	$2.4 \cdot 10^{-3}$
$Et_3GeH + B(C_6F_5)_3 \rightarrow Et_3GeH \cdots B(C_6F_5)_3$	-12.2	3.5	-52.5	$3.0 \cdot 10^{-3}$
$Me_3SiH + HB(C_6F_5)_2 \rightarrow Me_3SiH \cdots HB(C_6F_5)_2$	-7.9	3.3	-37.5	$4\cdot 10^{-3}$
$Me_3GeH + HB(C_6F_5)_2 \rightarrow Me_3GeH \cdots HB(C_6F_5)_2$	-8.9	2.4	-38.1	$1.6 \cdot 10^{-2}$
$2 \operatorname{HB}(C_6F_5)_2 \rightarrow (C_6F_5)_2 BH \cdots HB(C_6F_5)_2$	-19.7	-6.2	-41.8	$3.4\cdot10^4$
$(C_6F_5)_2BH + H_2B(C_6F_5) \rightarrow (C_6F_5)_2BH \cdots H_2B(C_6F_5)$	-20.0	-7.8	-40.9	$5\cdot 10^5$

 $PhMe_2SiH + B(C_6F_5)_3 \rightarrow PhMe_2Si(C_6F_5) + HB(C_6F_5)_2$ (1)

$$PhMe_2SiH + HB(C_6F_5)_2 \rightarrow PhMe_2Si(C_6F_5) + H_2B(C_6F_5)$$
(2)

Conversion of the borane and formation of both primary products according to Eq. (1) are shown in Fig. 2. Their concentrations are calculated from integrations of respective F_{ortho} signals. The borane substrate is fully converted via exchange of pentafluorophenyl group of the borane with hydrogen at silicon, which results in the formation of bis(pentafluorophenyl)borane and PhMe₂SiC₆F₅. The concentration of HB(C₆F₅)₂ reaches a plateau, suggesting that this compound may undergo the subsequent reaction of pentafluorophenyl group exchange according to Eq. (2).

An analogous reaction between TPFPB and Et₃SiH at 60 °C leading to the formation of $Et_3SiC_6F_5$ and $HB(C_6F_5)_2$ was previously reported [32]. However, kinetics of this reaction have never been investigated. The course of the reaction between Et_3SiH and TPFPB is illustrated by ¹⁹F NMR cumulative spectra, Fig. 3.

The formation of $Et_3SiC_6F_5$ as the main product of the pentafluorophenyl group exchange process was confirmed by GC/MS, Figs. S4 and S5. Conversion of substrate and formation of Et₃SiC₆F₅ are shown in Fig. 4. The reaction proceeds in analogous way to that with PhMe₂SiH, however the rate of the group exchange is much lower. It was not until after 10 h of maintaining the reaction mixture at 30 °C that distinct signals of the C₆F₅ group exchange product appeared with chemical shifts at $\delta = -127.3$, -151.98 and -161.52 ppm, Fig. 3.

The approximate values of the specific rate of the boron substrate disappearance for reactions of PhMe₂SiH and Et₃SiH with TPFPB at 30 °C estimated from plots in Figs. 2 and 4, assuming second order kinetics, were $6.08 \cdot 10^{-5}$ and $1.84 \cdot 10^{-6}$ L/mol·s respectively, Figs. S6 and S7. These results show that the rate of the group exchange reaction between TPFPB and silyl hydride depends much on substituents at the silicon atom. In addition, the reaction of TPFPB with Et₃SiH is more complex than the analogous reaction with PhMe₂SiH. Unexpectedly, a sharp multiplet appeared at a very high field, $\delta = -175.66$ ppm, J_{Si-F} = 290 Hz, Fig. S8. This signal was assigned to triethylfluorosilane because the observed chemical shift and spin–spin coupling values fit well with the literature data for this compound [47,48]. The triethylfluorosilane is formed in



Fig. 2. Substrate conversion and products concentrations vs. time for reaction of Me₂PhSiH [2.36 mol/l] with B(C₆F₅)₃ [0.043 mol/L] in deuterated toluene at 30 °C. B (C₆F₅)₃ – (\diamond), PhMe₂SiC₆F₅ – (\bigcirc), HB(C₆F₅)₂ – (\square).



Fig. 4. Substrate and products concentrations vs. time for reaction of Et₃SiH [2.32 mol/L] with $B(C_6F_5)_3$ [0.047 mol/L] in deuterated toluene at 30 °C. Substrate – (\diamond), $Et_3SiC_6F_5$ – (\bigcirc); Et_3SiF – (\square).



Fig. 3. ¹⁹F NMR spectra of the reaction mixture of Et₃SiH [2.32 mol/L] and B(C₆F₅)₃ [0.047 mol/L] in deuterated toluene at 30 °C.

parallel with the pentafluorophenyl group exchange product, Fig. 4. The competitive cleavage of fluorine from the TPFPB occurs according to the reaction shown in Eq. (3). This competitive reaction results in a more complex form of the ¹⁹F NMR spectrum of the reaction mixture at high TPFPB conversion, Fig. 3. However, the fluorine cleavage is significantly slower than the exchange of pentafluorophenyl group with hydrogen between TPFPB and Et₃SiH, which occurs in an analogous way as shown in Eq. (1).

$$Et_{3}SiH + B(C_{6}F_{5})_{3} \rightarrow Et_{3}SiF + B(C_{6}F_{5})_{2}(C_{6}F_{4}H)$$
(3)

Comparative studies on the reaction of SiH and GeH reagents with TPFPB were carried out using triethylsilane and triethylgermane as model compounds. The reactions of Et₃SiH and Et₃GeH with TPFPB are somewhat similar to each other, however the reaction of the germanium reagent is much faster than the reaction of the silicon analogue. The cumulative spectra illustrating the reaction of Et₃GeH performed at the 50:1 of the Ge/B molar ratio, together with the spectrum of the borane solution after removal of water by reaction with 1,1,3,3-tetramethyldisiloxane, are displayed in Fig. 5 and Fig. S9. Addition of Et₃GeH to the borane solution in deuterated toluene at 30 °C causes a noticeable upfield shift of all the three signals of pentafluorophenyl group; Fortho from δ = -128.7 to -130.3 ppm, F_{para} from δ = -142.0 to -148 ppm, F_{meta} from $\delta = -160.1$ to -161.6 ppm. These shifts reflect a strong interaction between the borane and germanium reagents thus giving evidence of a partial transfer of hydride ion to boron, Eq. (4).

$$Et_{3}GeH + B(C_{6}F_{5})_{3} \rightarrow Et_{3}Ge^{\delta + \dots}H^{\delta - \dots}B(C_{6}F_{5})_{3}$$

$$\tag{4}$$

This observation agrees with our theoretical calculations of thermodynamic parameters for these processes, Table 1.

The intensity of ¹⁹F NMR signals associated with TPFPB decreases as the reaction with Et₃GeH progresses and two sets of new signals appear indicating the formation of two main products containing pentafluorophenyl groups, Fig. 5. The obtained results revealed that the predominant germanium containing product of this reaction giving signals at F_{ortho} $\delta = -126.8$ ppm, $F_{para} \ \delta = -153.1$ ppm, and $F_{meta} \ \delta = -161.6$ ppm is triethyl(penta fluorophenyl)germane. The presence of this product was confirmed by GCMS analysis, Figs. S10 and S11. ¹⁹F NMR signals of the other fluorine product, $F_{ortho} \ \delta = -131.5$ to -133.5 ppm, point to the formation of bis(pentafluorophenyl)borane, Fig. 5. As discussed earlier, this compound exists as a mixture of its monomer, dimer and a complex with Et₃GeH. At least in the first stage, the exchange of pentafluorophenyl group for hydrogen between the boron and germanium reagents is carried out according to Eq. (5).

$$Et_3GeH + B(C_6F_5)_3 \rightarrow Et_3Ge(C_6F_5) + HB(C_6F_5)_2$$
(5)

Quantum mechanical calculation of the thermodynamics of this reaction confirmed the feasibility of this process, Table 2. The calculated Gibbs free energies values of the exchange reactions suggest only partial conversion of $B(C_6F_5)_3$ if monomeric $HB(C_6F_5)_2$ product is assumed. However, it should be remembered that monomeric $HB(C_6F_5)_2$ shows a strong tendency to form a dimer and may also participate in the formation of adducts with an excess of silyl or germyl hydrides, Table 1. Due to free $HB(C_6F_5)_2$ consumption, the equilibrium of ligand exchange reaction is continuously shifting towards the group exchange products.

Based on the calculated free energy barriers, Table 2, it can be concluded that the reactivity in the exchange process decreases in order $Et_3GeH > PhMe_2SiH > Et_3SiH$, which is consistent with



Fig. 5. ¹⁹F NMR spectra (Fortho region) of the reaction mixture of Et₃GeH [1.96 mol/L], B(C₆F₅)₃ [0.039 mol/L] in deuterated toluene at 30 °C.

Table 2

Enthalpies [kcal/mol], Gibbs free energies [kcal/mol], entropies [cal/mol·K], and approximate equilibrium constants K_{eq} at 298 K for the exchange reactions of model silyl and germyl hydrides with $B(C_6F_5)_3$ calculated at B3LYP-GD3/Def2TZVP//Def2SVP level in the gas phase.

Reaction	ΔH	ΔG	ΔS	K _{eq}	ΔH^{\ddagger}	ΔG^\ddagger	ΔS^{\ddagger}
$Et_3SiH + B(C_6F_5)_3 \rightarrow Et_3SiC_6F_5 + HB(C_6F_5)_2$	0.0	-0.6	2.0	2.8	17.1	32.8	-52.6
$PhMe_2SiH + B(C_6F_5)_3 \rightarrow PhMe_2SiC_6F_5 + HB(C_6F_5)_2$	1.3	0.8	1.8	0.3	13.2	29.2	-53.5
$Et_{3}GeH + B(C_{6}F_{5})_{3} \rightarrow Et_{3}GeC_{6}F_{5} + HB(C_{6}F_{5})_{2}$	1.9	1.3	2.1	0.1	12.7	28.4	-52.5

Table 3

Specific rates, k [L/mol·s] and activation parameters ΔG^{\ddagger} [kcal/mol], ΔH^{\ddagger} [kcal/mol] and ΔS^{\ddagger} [cal/mol·K] at 298 K of the reactions of B(C₆F₅)₃ with Et₃SiH, Et₃GeH and PhMe₂SiH in toluene determined by UV measurements.

Reaction	k	ΔG^{\ddagger}	ΔH^{\ddagger}	ΔS^{\ddagger}
$\begin{array}{l} Et_3SiH+B(C_6F_5)_3\rightarrow Et_3SiC_6F_5+HB(C_6F_5)_2\\ PhMe_2SiH+B(C_6F_5)_3\rightarrow PhMe_2SiC_6F_5+HB(C_6F_5)_2\\ Et_3GeH+B(C_6F_5)_3\rightarrow Et_3GeC_6F_5+HB(C_6F_5)_2 \end{array}$	$\begin{array}{c} 1.36\cdot 10^{-6} \\ 6.98\cdot 10^{-5} \\ 1.97\cdot 10^{-4} \end{array}$	25.4 23.1 22.4	14.4 10.8 12.1	-36.9 -41.3 -34.7



Fig. 6. Substrate conversion and product concentration vs. time for the reaction of $B(C_6F_5)_3$ [0.039 mol/L] with Et_3GeH [1.96 mol/L] in deuterated toluene at 30 °C. Substrate – (\diamond), ($Et_3GeC_6F_5$) – (\bigcirc).

kinetic measurements. The calculated values of entropy of activation are much lower than the values obtained from kinetic studies, Table 3, mainly because the calculations were made for the gas phase and the solvation effects were omitted.

The high intensity of signals of $Et_3Ge(C_6F_5)$ persists after 22 h while signals of $HB(C_6F_5)_2$ become much smaller, Fig. S9. This indicates that $HB(C_6F_5)_2$ is not stable in the reaction system as was previously observed for silyl hydrides.

Conversion of TPFPB and concentrations of the major germanium product containing C_6F_5 group calculated based on integration of F_{ortho} signals of relevant C_6F_5 group as a function of time are shown in Fig. 6. The approximate value of the rate constant for the reaction according to Eq. (5) and assuming its simple second order kinetics is $1.46 \cdot 10^{-4}$ L/mol·s at 30 °C, Fig. S12.

3.2. Studies by UV spectroscopy

The UV spectrum of $B(C_6F_5)_3$ in a toluene solution shows an intensive charge transfer band with a maximum located at 305 nm resulting from the interaction of pentafluorophenyl π -electrons with an empty boron p orbital [44]. The absorbance at the maximum of this band is directly related to the concentration of free TPFPB. The kinetics of the TPFPB reactions with PhSiMe₂H, Et₃SiH and Et₃GeH were studied by following changes in this absorbance, Fig. S13. A large excess of SiH and GeH reagents over borane was used to observe the reactions as pseudo first order processes. Indeed, for all studied reagents, conversion-time curves adhere well to the first order kinetics, although in some cases the



Fig. 7. Pseudo 1st order kinetic plots for reaction the pentafluorophenyl group exchange of $B(C_6F_5)_3$ with SiH and GeH reagents: $Et_3SiH - (\blacksquare)$, $PhMe_2SiH - (O)$, $Et_3GeH - (\Delta)$, in toluene at 60 °C.



Fig. 8. Dependences of the experimental pseudo 1st order rate constant (k') of reaction of the pentafluorophenyl group exchange of $B(C_6F_5)_3$ on the initial concentration of SiH and GeH reagents (C_o) in toluene: $Et_3SiH - (\blacksquare)$ at 80 °C and PhMe₂SiH - (O), $Et_3GeH - (\Delta)$ at 60 °C.





Table 4

Specific rates of conversion of TPFPB (k') and its half-life ($t_{0.5}$) in the presence of various SiH reagents in toluene at 60 °C. Initial concentration of SiH was 0.5 mol/L and $[SiH]_0/[TPFPB]_0 = 7 \cdot 10^2$.

Reagent	k'/s^{-1}	t _{0.5} /h
(HMe ₂ Si) ₂ O	$5.5\cdot10^{-4}$	0.35
PhMe ₂ SiH	$2.82\cdot10^{-4}$	0.68
Me ₃ Si(OSiHMe) _n OSiMe ₃ ^a	$1.55 \cdot 10^{-5}$	12.4
Et₃SiH	$1.00\cdot 10^{-5}$	19.2

^a Poly(hydromethylsiloxane) (PHMS), viscosity = 15-25cSt, molecular weight about 2000 g/mol.

reactions were followed to over 80% conversion. Representative first-order kinetic graphs of TPFPB conversion in the presence of Et_3SiH , PhMe₂SiH and Et_3GeH at 60 °C are shown in Fig. 7.

The dependence of the borane conversion rate on the initial concentration of SiH and GeH reagents indicates that in these cases the reaction rate may be well approximated by the second order kinetics law expressed by Eq. (6), Fig. 8.

$$d[B(C_6F_5)_3]/dt = k[Mt-H][B(C_6F_5)_3], (k = k_1 + k_2 + ...)$$
(6)

where [Mt-H] is concentration of SiH and GeH reagents and k_1 is the rate constant of the pentafluorophenyl group exchange. The specific rate constant (k) includes also rate constants of competing reactions, such as fluorine cleavage. However, these competitive reactions are much slower than the exchange of ligands between SiH or GeH and TPFPB and have been neglected in our kinetic analysis. The measurement of specific rates of the reactions studied at variable temperatures allowed us to create corresponding Arrhenius plots, Fig. 9, and assess the value of their activation parameters, Table 3.

The borane reaction with PhMe₂SiH proceeds faster than with Et₃SiH under the same conditions by a factor of about 30. The observed difference in the rate of TPFPB conversion is due to the higher activation energy of the borane reaction with of Et₃SiH. This observation shows that the stability of tris(pentafluorophenyl)borane mixed with the silyl hydride depends to a large extent on the structure of the hydrosilane reagent. We also measured the initial conversion rates and half-life of TPFPB in the presence of selected silyl hydrides and hydrosiloxanes. Currently, these systems are commonly used in organic and organosilicon chemistry. The obtained data may be useful for synthetic chemists interested in using TPFPB / SiH system as a mild reducing reagent in the syn-



Fig. 10. Four-center transition state for the reaction of ligand exchange between $B(C_6F_5)_3$ and Et_3GeH ; dashed lines mark forming/breaking bonds to germanium. Calculated at B3LYP-GD3/Def2TZVP//Def2SVP. Interatomic distances: r(Ge-H) = 2.115 Å, r(H-B) = 1.229 Å. For comparison, in $Et_3Ge-H-B(C_6F_5)_3$ complex the corresponding bonding parameters are r(Ge-H) = 1.637 Å, r(H-B) = 1.514 Å, Fig. S15.



Fig. 11. Intermediate arenium ion complex for the reaction of ligand exchange between $B(C_6F_5)_3$ and Et_3GeH . Calculated at B3LYP-GD3/Def2TZVP//Def2SVP. Interatomic distances r(Ge-C) = 2.202 Å, r(C-B) = 1.775 Å (compared to the regular $B-C_6F_5$ bond of 1.633 Å).

thesis, Table 4.

3.3. Reaction mechanism

From the mechanistic point of view, the exchange of ligand between $B(C_6F_5)_3$ and SiH or GeH reagents proceeds through electrophilic aromatic substitutions. Support of this statement was obtained using quantum-mechanical calculations. The proposed mechanism involves a coordination of the borane to hydrogen, Table 1, which causes a weakening of the Mt-H bond, where Mt = Si or Ge, Figs. S14 and S15. As a result of such interaction, the partial positive charge on the metal atom increases. The proposed borane-hydrosilane adduct have been recently isolated and characterized for 1,2,3-tris(pentafluorophenyl)-4,5,6,7-tetrafluoro-1-boraindene and triethylsilane system [49]. At these conditions, the electrophilic substitution in the pentafluorophenyl ring becomes possible through a four-center transition state, as shown for Et₃GeH in Fig. 10, which leads to the intermediate arenium ion complex, Fig. 11.

The developing positive charge is delocalized throughout the aromatic ring. In a situation of high electron deficiency, the fluorine substituents, which are generally considered electronwithdrawing, can stabilize the aromatic cation by means of electron donation via resonance. Decomposition of the intermediate complex results in the aryl group migration from boron to germanium center. An analogous four-center transition state for the TPFPB reaction with Et₃SiH is shown in Fig. S16. However, the intermediate complex could not be located in the case of Et₃SiH. It is probably due to a very flat potential energy surface, which



Fig. 12. Four-center transition state for ligand exchange between PhMe₂SiH and B(C₆F₅)₃. Dashed lines mark forming/breaking bonds to silicon. Phenyl ring and one of C₆F₅ rings at boron are roughly parallel, which suggests some π-π interaction. Calculated at B3LYP-GD3/Def2TZVP//Def2SVP.

makes the optimization difficult. The rate of Et_3GeH reaction with TPFPB is two orders of magnitude higher than its silicon analogue, Et_3SiH . Such a significant difference in the rate of these reactions results from the difference of their energy barriers, Table 3. The quantum mechanical calculations lead to a similar conclusion, Table 2.

Since germanium is more electropositive than silicon, the hydrogen transfer to borane in the complex is more advanced and therefore the substitution reaction proceeds more easily. Entropy of activation for TPFPB reactions with ethyl substituted silicon and germanium reagents are similar. The slightly higher entropy for the germanium substrate results from the less compact structure of the transition state, which leads to easier rotational movements, Fig. 10.

The reaction of phenyldimethylsilane with TPFPB shows a lower enthalpy of activation as compared to the same reaction of triethylsilane, and a much lower entropy of activation. These results can be explained by the interaction between the phenyl group and the pentafluorophenyl ligand in the complex of $B(C_6F_5)_3$ with PhMe₂SiH, Fig. S17, which lowers the energy barrier for the ligand exchange reaction, but at the same time reduces the freedom of movement in the proposed transition state. Indeed, the calculated optimal transition state structure, Fig. 12 and the intermediate complex, Fig. S18, for the reaction of TPFPB with PhMe₂SiH shows that one of the pentafluorophenyl groups of the borane adopts roughly parallel position to the phenyl group of the PhMe₂SiH thus making possible the π - π interaction between both phenyl rings.

4. Conclusions

The chemical stability of tris(pentafluorophenyl)borane is reduced in the presence of Si-H and Ge-H reagents. Undesirable transformations of TPFPB via metathetic exchange of hydrogen at silicon or germanium with pentafluorophenyl group of the borane result in the formation of bis(pentafluorophenyl)borane. Kinetic studies confirmed by theoretical calculations showed that these reactions strongly affect catalytic activity of the borane. The TPFPB decomposition reactions studied for selected silvl hydrides (triethylsilane and phenyldimethylsilane) and triethylgermane occur according to the second order kinetic law. Their mechanism involves electrophilic substitution in the pentafluorophenyl group via four-centered transition state. The experimentally determined reactivity order is $Et_3GeH > PhMe_2SiH \gg Et_3SiH$. The same order is deduced from the theoretical calculations made for these reactions in the gas phase. Substituents at silicon have considerable impact on the reactivity. Significantly lower entropy of activation for the TPFPB reaction with PhMe₂SiH results from stacking interaction between the phenyl group of the silane reagent and the pentafluorophenyl group of the borane in the transition state. This interaction lowers the energy barrier and limits the freedom of movement within the transition state structure. Currently, various SiH functional silanes in combination with catalytic amounts of TPFPB are frequently used as transition-metal-free reducing systems in the organic and polymer chemistry. The obtained rates of decomposition of TPFPB in the presence of various SiH reagents may be helpful for synthetic chemists.

Declaration of Competing Interest

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. The authors declare no competing financial interest.

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Appendix A. Supplementary material

Supplementary materials, which include ¹⁹F NMR spectra, GC/ MS data, kinetic plots, UV Spectra of the reaction mixture B (C_6F_5)₃ and Et₃GeH. Calculated structures of complexes between B(C_6F_5)₃ and Et₃GeH. Calculated structures of complexes between B(C_6F_5)₃ and Et₃SiH, B(C_6F_5)₃ and Et₃GeH, B(C_6F_5)₃ and PhMe₂SiH. Calculated structure of four-center transition state for the reaction of ligand exchange between B(C_6F_5)₃ and Et₃SiH. Calculated structure of the complex between B(C_6F_5)₃ and PhMe₂SiH via Si···H···B interaction. Cartesian coordinates of the SiH and GeH reagents, and the Si and Ge adducts with B(C_6F_5)₃ and transition states for the exchange reactions. Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.09.023.

References

- [1] W. Piers, A. Marwitz, L. Mercier, Mechanistic aspects of bond activation with perfluoroarylboranes, Inorg. Chem. 50 (2011) 12252–12262.
- [2] M. Oestreich, J. Hermeke, J. Mohr, A unified survey of Si-H and H-H bond activation catalysed by electron-deficient boranes, Chem. Soc. Rev. 44 (2015) 2202–2220.
- [3] V. Gevorgyan, M. Rubin, S. Benson, J. Liu, Y. Yamamoto, A novel B(C₆F₅)₃catalyzed reduction of alcohols and cleavage of aryl and alkyl ethers with hydrosilanes, J. Org. Chem. 65 (2000) 6179–6186.
- [4] V. Gevorgyan, M. Rubin, J. Liu, Y. Yamamoto, A direct reduction of aliphatic aldehyde, acyl chloride, ester, and carboxylic functions into a methyl group, J. Org. Chem. 66 (2001) 1672–1675.
- [5] R. Chadwick, V. Kardelis, P. Lim, A. Adronov, Metal-free reduction of secondary and tertiary N-phenyl amides by tris(pentafluorophenyl)boron-catalyzed hydrosilylation, J. Org. Chem. 79 (2014) 7728–7733.
- [6] V. Fasano, J. Radcliffe, M. Ingleson, B(C₆F₅)₃-catalyzed reductive amination using hydrosilanes, ACS Catal. 6 (2016) 1793–1798.
- [7] T.A. Bender, J.A. Dabrowski, H. Zhong, M.R. Gagne, Diastereoselective B(C₆F₅)₃catalyzed reductive carbocyclization of unsaturated carbohydrates, Org. Lett. 18 (2016) 4120–4123.
- [8] D. Parks, W. Piers, Tris(pentafluorophenyl)boron-catalyzed hydrosilation of aromatic aldehydes, ketones, and esters, J. Am. Chem. Soc. 118 (1996) 9440– 9441.
- [9] D. Parks, J. Blackwell, W. Piers, Studies on the mechanism of B(C₆F₅)₃-catalyzed hydrosilation of carbonyl functions, J. Org. Chem. 65 (2000) 3090–3098.
- [10] Y. Ma, B. Wang, L. Zhang, Z. Hou, Boron-catalyzed aromatic C-H bond silylation with hydrosilanes, J. Am. Chem. Soc. 138 (2016) 3663–3666.
- [11] V. Fasano, J. Radcliffe, L. Curless, M. Ingleson, N-methyl-benzothiazolium salts as carbon lewis acids for Si-H sigma-bond activation and catalytic (De) hydrosilylation, Chem. Eur. J. 23 (2017) 187–193.
- [12] D. Zhou, Y. Kawakami, Tris(pentafluorophenyl)borane as a superior catalyst in the synthesis of optically active SiO-containing polymers, Macromolecules 38 (2005) 6902–6908.
- [13] J. Cella, S. Rubinsztajn, Preparation of polyaryloxysilanes and polyaryloxysiloxanes by B(C₆F₅)₃ catalyzed polyetherification of dihydrosilanes and bis-phenols, Macromolecules 41 (2008) 6965–6971.
- [14] D.H. Flagg, T.J. McCarthy, Rapid and clean covalent attachment of methylsiloxane polymers and oligomers to silica using B(C₆F₅)₃ catalysis, Langmuir 33 (2017) 8129–8139.
- [15] J. Escorihuela, S. Pujari, H. Zuilhof, Organic monolayers by B(C₆F₅₎₃-catalyzed siloxanation of oxidized silicon surfaces, Langmuir 33 (2017) 2185–2193.
- [16] R. Chadwick, J. Grande, M. Brook, A. Adronov, Functionalization of singlewalled carbon nanotubes via the Piers-Rubinsztajn reaction, Macromolecules 47 (2014) 6527–6530.
- [17] M.A. Brook, J.B. Grande, F. Ganachaud, New synthetic strategies for structured silicones using B(C₆F₅)₃, Adv. Polym. Sci. 235 (2010) 161–183.
- [18] M. Brook, New control over silicone synthesis using SiH chemistry: the Piers-Rubinsztajn reaction, Chem. Eur. J. 24 (2018) 8458–8469.
- [19] F. Vidal, F. Jäkle, Functional polymeric materials based on main-group elements, Angew. Chem. Int. Ed. Engl. 58 (2019) 5846–5870.
- [20] S. Rubinsztajn, J. Cella, A new polycondensation process for the preparation of polysiloxane copolymers, Macromolecules 38 (2005) 1061–1063.
- [21] D. Thompson, M. Brook, Rapid assembly of complex 3D siloxane architectures, J. Am. Chem. Soc. 130 (2008) 32–33.
- [22] J. Chojnowski, S. Rubinsztajn, W. Fortuniak, J. Kurjata, Synthesis of highly branched alkoxsiloxane-dimethylsiloxane copolymers by nonhydrolytic

dehydrocarbon polycondensation catalyzed by tris(pentafluorophenyl)borane, Macromolecules 41 (2008) 7352–7358.

- [23] J. Yu, Y. Liu, Cyclic polysiloxanes with linked cyclotetrasiloxane subunits, Angew. Chem. Int. Ed. Engl. 56 (2017) 8706–8710.
- [24] M. Gretton, B. Kamino, M. Brook, T. Bender, The use of Piers-Rubinsztajn conditions for the placement of triarylamines pendant to silicone polymers, Macromolecules 45 (2012) 723–728.
- [25] J. Chojnowski, J. Kurjata, W. Fortuniak, S. Rubinsztajn, B. Trzebicka, Hydride transfer ring-opening polymerization of a cyclic oligomethylhydrosiloxane. Route to a polymer of closed multicyclic structure, Macromolecules 45 (2012) 2654–2661.
- [26] J. Chojnowski, W. Fortuniak, J. Kurjata, S. Rubinsztajn, J. Cella, Oligomerization of hydrosiloxanes in the presence of tris(pentafluorophenyl) borane, Macromolecules 39 (2006) 3802–3807.
- [27] S. Rubinsztajn, New facile process for synthesis of borosiloxane resins, J. Inorg. Organomet. Polym. Mater. 24 (2014) 1092–1095.
- [28] T. Schwier, V. Gevorgyan, Trans- and cis-selective Lewis acid catalyzed hydrogermylation of alkynes, Org. Lett. 7 (2005) 5191–5194.
- [29] S. Keess, M. Oestreich, Access to fully alkylated germanes by B(C₆F₅)₃catalyzed transfer hydrogermylation of alkenes, Org. Lett. 19 (2017) 1898– 1901.
- [30] L. Ignatovich, V. Muravenko, S. Grinberga, E. Lukevics, New reactions of the Si-O-Ge group formation, Khim. Geterotsikl. Soedin. 299–302 (2006).
- [31] S. Rubinsztajn, M. Cypryk, J. Chojnowski, W. Fortuniak, U. Mizerska, P. Pospiech, Reaction of silyl hydrides with tetrabutoxygermanium in the Presence of B(C₆F₅)₃: difference between silicon and germanium chemistries and easy route to GeH₄, Organometallics 37 (2018) 1585–1590.
- [32] D.J. Parks, W.E. Piers, G.P.A. Yap, Synthesis, properties, and hydroboration activity of the highly electrophilic borane Bis(pentafluorophenyl)borane, HB (C₆F₅)₂, Organometallics 17 (1998) 5492–5503.
- [33] G. Nikonov, S. Vyboishchikov, O. Shirobokov, Facile activation of H-H and Si-H bonds by boranes, J. Am. Chem. Soc. 134 (2012) 5488–5491.
- [34] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A.V. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M.J. Bearpark, J.J. Heyd, E. N. Brothers, K.N. Kudin, V.N. Staroverov, T.A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A.P. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam, M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas, J.B. Foresman, D.J. Fox, Gaussian 16 Rev. B.01, Wallingford, CT, 2016.
- [35] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. 98 (1993) 5648–5652.

- [36] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, J. Chem. Phys. 132 (2010), 154104/154101-154104/154119.
- [37] F. Weigend, R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: design and assessment of accuracy, Phys. Chem. Chem. Phys. 7 (2005) 3297–3305.
- [38] J.L. Bao, J. Zheng, I.M. Alecu, B.J. Lynch, Y. Zhao, D.G. Truhlar, Database of Fequency Scale Factors for Electronic Model Chemistries, https://comp.chem. umn.edu/freqscale/version3b2.htm.
- [39] J. Kreutzer, P. Blaha, U. Schubert, Assessment of different basis sets and DFT functionals for the calculation of structural parameters, vibrational modes and ligand binding energies of Zr₄O₂(carboxylate)₁₂ clusters, Comput. Theor. Chem. 1084 (2016) 162–168.
- [40] S.F. Boys, F. Bernardi, The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors, Mol. Phys. 19 (1970) 553–566.
- [41] H.J. Frohn, H. Franke, P. Fritzen, V.V. Bardin, (Fluoroorgano)fluoroboranes and fluoroborates. I. Synthesis and spectroscopic characterization of potassium fluoroaryltrifluoroborates and fluoroaryldifluoroboranes, J. Organomet. Chem. 598 (2000) 127–135.
- [42] T. Beringhelli, D. Maggioni, G. D'Alfonso, ¹H and ¹⁹F NMR investigation of the reaction of B(C₆F₅)₃ with water in toluene solution, Organometallics 20 (2001) 4927–4938.
- [43] A. Di Saverio, F. Focante, I. Camurati, L. Resconi, T. Beringhelli, G. D'Alfonso, D. Donghi, D. Maggioni, P. Mercandelli, A. Sironi, Oxygen-bridged borate anions from tris(pentafluorophenyl)borane: synthesis, NMR characterization, and reactivity, Inorg. Chem. 44 (2005) 5030–5041.
- [44] J. Chojnowski, S. Rubinsztajn, J. Cella, W. Fortuniak, M. Cypryk, J. Kurjata, K. Kazmierski, Mechanism of the B(C₆F₅)₃-catalyzed reaction of silyl hydrides with alkoxysilanes. Kinetic and spectroscopic studies, Organometallics 24 (2005) 6077–6084.
- [45] A. Schneider, Y. Chen, M.A. Brook, Trace water affects tris (pentafluorophenyl) borane catalytic activity in the Piers-Rubinsztajn reaction, Dalton Trans. (2019), https://doi.org/10.1039/C9DT02756D.
- [46] D.J. Parks, R.E. von H. Spence, W.E. Piers, Bis(pentafluorophenyl)borane: synthesis, properties, and hydroboration chemistry of a highly electrophilic borane reagent, Angew. Chem., Int. Ed. Engl. 34 (1995) 809–811.
- [47] R. Panisch, M. Bolte, T. Mueller, Hydrogen- and fluorine-bridged disilyl cations and their use in catalytic C-F activation, J. Am. Chem. Soc. 128 (2006) 9676– 9682.
- [48] W. Piers, T. Chivers, Pentafluorophenylboranes: from obscurity to applications, Chem. Soc. Rev. 26 (1997) 345–354.
- [49] A.Y. Houghton, J. Hurmalainen, A. Mansikkamaki, W.E. Piers, H.M. Tuononen, Direct observation of a borane-silane complex involved in frustrated Lewispair-mediated hydrosilylations, Nat. Chem. 6 (2014) 983–988.