Surface Organometallic Chemistry of Main Group Elements: Selective Synthesis of Silica Supported $[\equiv Si{-}OB(C_6F_5)_3]^-[HNEt_2Ph]^+$

Nicolas Millot, Andrew Cox, Catherine C. Santini,* Yann Molard, and Jean-Marie Basset*[a]

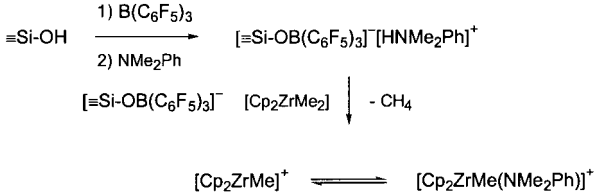
Abstract: The reaction of the Lewis acid $B(C_6F_5)_3$ with silanol groups of silica surfaces, dehydroxylated at different temperatures (300, 500, 700, and 800 °C), has been investigated in presence of the Brønsted base NEt_2Ph. The structure of the resulting modified silica supports $[\equiv Si{-}OB(C_6F_5)_3]^-[HNEt_2Ph]^+$ (**1**) has been carefully identified by IR and multinuclear solid-state NMR spectroscopies, isotopic ^2H and ^{18}O labeling, elemental analysis, molecular modeling, and comparison with synthesized molecular models. Highly dehydroxylated silica surfaces were required to transform selectively each silanol group into *unique* $[\equiv Si{-}OB(C_6F_5)_3]^-[HNEt_2Ph]^+$ fragments. For lower dehydroxylation temperatures, two sorts of surface sites were coexisting on silica: the free silanol groups [≡SiOH] and the ionic species **1**.

Keywords: supported ammonium · supported borate · ion pairs · silica · surface chemistry

Introduction

The reaction of organometallic compounds with surfaces of silica leads in most cases to organometallic fragments that are sigma bonded to the surface through one, two, or three oxygen–metal bonds.[1] This kind of bonding can stabilize well-defined and highly electrophilic fragments capable of catalytically activating the C–H and C–C bonds of alkanes (alkane hydrogenolysis,[2] alkane metathesis[3]), or polyolefins (Ziegler–Natta depolymerization).[4] These surface species usually have no real molecular analogues that could exhibit similar catalytic properties.

In some cases it is necessary to avoid covalent bonding with the surface and to immobilize a "cationic" complex directly on silica through specific reactions. Under these conditions, the support should play the role of a "noncoordinating" heterogeneous anion which stabilizes the molecular cation "floating" above the surface. In such cases the silica is treated first with a strong alkylating agent and/or Lewis acid (such as AlR_3,[5, 6] methylaluminoxane (MAO),[6, 7] BF_3,[8] $B(C_6F_5)_3$,[9] etc…). Then, such a grafted Lewis acid/alkylating agent is attached to a suitable organometallic complex to give the cationic complex by several possible routes. The resulting silica-supported compounds are unfortunately poorly defined and characterized both at the first and the second stage of the process. In this regard, a huge amount of work has been devoted to the immobilization of cationic metallocenes for Ziegler–Natta polymerization.[10, 7f] One particularly elegant strategy consists of modifying a silica surface with $B(C_6F_5)_3$ in the presence of a tertiary amine and reacting the resulting support with a metallocene such as $[Cp_2ZrMe_2]$ to yield, by an irreversible process of alkane elimination, the cationic complex $[Cp_2ZrMe^+]$ (Scheme 1).[9b–e]



Scheme 1. Activation of $[Cp_2ZrMe_2]$ on modified silica.

However all the surface intermediates in the process are incompletely characterized, although it would be of great interest if this could be acheived. Herein we demonstrate that it is possible to effectively isolate on silica the well-defined surface organometallic fragment $[\equiv Si{-}OB(C_6F_5)_3]^-[HNEt_2Ph]^+$ (**1**), which can be obtained selectively only under the very specific conditions described. This surface fragment can be used as a very promising building block in surface organometallic chemistry.

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Results and Discussion

We have used a flame aerosil silica from Degussa dehydroxylated at increasing temperatures (T°C) that we refer to as $SiO_{2\text{-}(T)}$. The specific surface areas were 200 m^2g^{-1} for $SiO_{2\text{-}(300)}$ and $SiO_{2\text{-}(500)}$, and 180 m^2g^{-1} for $SiO_{2\text{-}(700)}$ and $SiO_{2\text{-}(800)}$. The amount of silanol groups, determined by quantitative solid-state ^1H NMR spectroscopy and by reaction with CH_3Li, decreases from 1.7 OH nm^{-2} for $SiO_{2\text{-}(300)}$ to 0.6 OH nm^{-2} for $SiO_{2\text{-}(800)}$.[11]

Infrared studies: When an excess of $[B(C_6F_5)_3 + NEt_2Ph]$ (1:1 molar ratio) is chemisorbed on various silicas ($SiO_{2\text{-}(300,500,800)}$), the IR band ascribed to isolated silanols at 3747 cm^{-1} disappears totally (Figure 1) and is replaced by broad bands at 3681 and 3624 cm^{-1} (ν(OH) of interacting silanols) and by a sharp band at 3232 cm^{-1}. The intensity of the bands at 3681 and 3624 cm^{-1} decreases inversely with the dehydroxylation temperature; simultaneously that of the band at 3232 cm^{-1} increases. To tentatively assign the band at 3232 cm^{-1}, deuterated silica $SiO_{2\text{-}(500d)}$ (94% ≡Si–OD) and partially labeled $Si^{18}O_{2\text{-}(700)}$ (35% ≡Si–^{18}OH) were used. After reaction with $[B(C_6F_5)_3 + NEt_2Ph]$, a shift of the band at 3232 cm^{-1} to 2402 cm^{-1} was observed on $SiO_{2\text{-}(500D)}$.[12] With $Si^{18}O_{2\text{-}(700)}$, no shift or broadening was observed. These results taken together support the fact that the band at 3232 cm^{-1} was not due to a ν(O–H) vibration but likely to a ν(N–H) vibration.

Confirmation of all IR bands was achieved by comparison with the spectra of molecular analogues of **1** (Table 1). The synthesis of the following molecular complexes $[HNEt_2Ph]^+[(C_6F_5)_3BOR]^-$ (R = H (**2**), $SiPh_3$ (**3**), and $Si_8O_{12}(c\text{-}C_5H_9)_7$ (**4**)) was performed according to known procedures.[13] The band at 3232 cm^{-1} was also observed in the IR spectra of the model compounds **2**–**4** but not in the IR spectrum of NEt_2Ph, confirming the assignment of the band at 3232 cm^{-1} to a ν(N–H) vibration. Other bands observed in the 1700–1300 cm^{-1} region were ascribed to ν(C–H), ν(C=C),[14] and δ(C–H) vibrations of organic groups (Table 1). These data are consistent with the expected surface complex: $[\equiv Si{-}OB(C_6F_5)_3]^-[HNEt_2Ph]^+$ (**1**).

Table 1. Selection of characteristic IR data [cm^{-1}] for compounds **1**–**4**.

$B(C_6F_5)_3$[a]	NEt_2Ph[b]	**2**[a]	**3**[a]	**4**[a]	**1**[c]	Assignment
		3234 (w)	3226 (vw)	3228 (w)	3232 (m)	ν(N–H$^+$)
	3061 (w)	3070 (w)	3072 (w)		3071 (w)	$\nu(C{-}H)_{arom.}$
	2971 (vs)	2999 (m)	2999 (vw)		2996 (w)	$\nu_{as}(CH_3)$
	2892 (m)	2880 (m)			2887 (w)	$\nu_s(CH_3)$
1650 (s)		1645 (s)	1642 (m)	1643 (w)	1645 (s)	C_6F_5
1589 (w)	1598 (vs)	1602 (m)	1588 (vw)	1593 (vw)	1599 (w)	ν(C=C)
1525 (s)	1507 (vs)	1517 (vs)	1515 (s)	1512 (m)	1517 (vs)	ν(C=C)
1474 (vs)	1468 (m)	1465 (vs)	1459 (vs)	1464 (s)	1461 (vs)	ν(C=C)
	1396 (s)	1392 (m)	1394 (w)		1396 (m)	$\delta_s(CH_3)$
1381 (s)	1374 (s)	1382 (m)	1379 (w)	1382 (vw)	1383 (m)	C_6F_5
	1354 (vs)	1365 (m)			1369 (m)	$\delta_s(CH_3)$
	1266 (vs)	1278 (s)	1273 (m)	1274 (w)	n.o.[d]	$\delta_i(C{-}H)_{arom.}$
973 (vs)		974 (vs)	971 (s)	976 (m)	n.o.[d]	C_6F_5

[a] KBr pellets of solid compounds. [b] Neat liquid in KBr windows. [c] Compacted silica pellets. [d] n.o. = not observed.

Solid-state NMR studies: The solid-state CP-MAS ^{13}C NMR spectra of **1** (Figure 2) and molecular models **2** and **4** are very similar. Note that the deshielding of the anilinium methylene carbon atom (observed for **1** at $\delta = 51$ and for physisorbed NEt_2Ph at $\delta = 47$) with respect to the free amine is typical of the normal behavior when an amine is protonated (Table 2). The solid-state ^{11}B NMR spectra of **1** exhibit a single peak at $\delta = -8$ in agreement with the ^{11}B chemical shift (solid state) of **2** and **4** ($\delta = -6.9$ and -7), or literature data.[9b] These data support the presence of an anionic borato fragment, that is, $[\equiv Si{-}OB(C_6F_5)_3]^-$, in which the boron atom is tetracoordinate, anionic, and with a similar sphere of coordination.

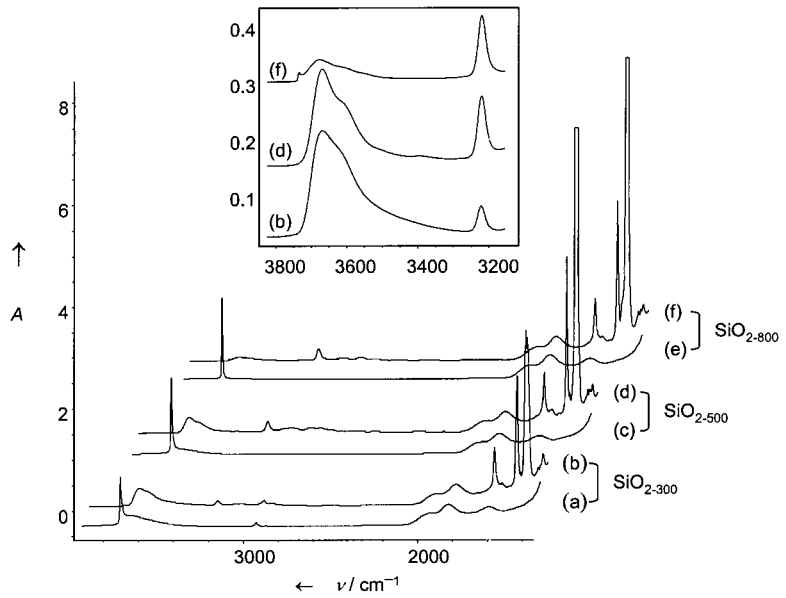


Figure 1. IR spectra of a) $SiO_{2\text{-}(300)}$; b) $SiO_{2\text{-}(300)}$ after reaction with M (M = $B(C_6F_5)_3$ + NEt_2Ph, 1:1, 5 equivalents); c) $SiO_{2\text{-}(500)}$; d) $SiO_{2\text{-}(500)}$ after reaction with M; e) $SiO_{2\text{-}(800)}$; f) $SiO_{2\text{-}(800)}$ after reaction with M; and expended 3800–3200 cm^{-1} region.

Stoichiometry of reaction: Elemental analyses of **1**/$SiO_{2\text{-}(300,500,700,800)}$ (Table 3) indicate a slight decrease in the weight percentage of boron, from 0.23 to 0.17%, when the dehydroxylation temperature of the silica is increased from 300 to 800 °C. For all silica, the boron/nitrogen molar ratio of the surface species **1** in several experiments is found close to 1. The values of fluorine/boron (F/B > 10) and carbon/(boron + nitrogen) (12 < C/(B+N) < 15) molar ratios confirm that there was no B–C (from C_6F_5) bond cleavage. Note that no C_6F_5H was detected during the impregnation work-up.

An accumulating body of analytic and spectroscopic evidence as well as their similar-

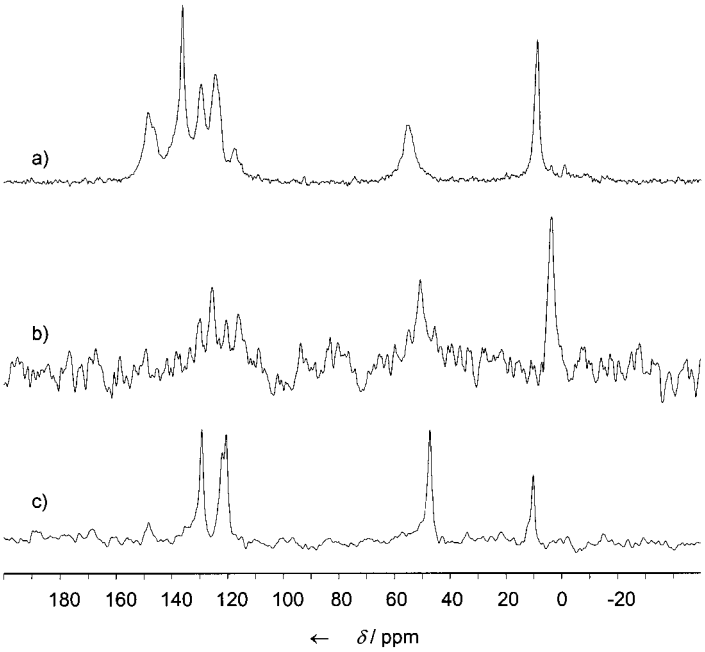


Figure 2. Solid-state CP-MAS ^{13}C NMR spectra of a) $[(C_6F_5)_3BOH]^-[HNEt_2Ph]^+$ salt (**2**); b) $[\equiv SiO_{500}\text{-}B(C_6F_5)_3]^-[HNEt_2Ph]^+$ (**1**); c) $SiO_{2\text{-}(500)} + NEt_2Ph$.

Table 2. Comparison of solid-state ^{13}C and ^{11}B NMR data[a] of **1** and related compounds **2** and **4**.

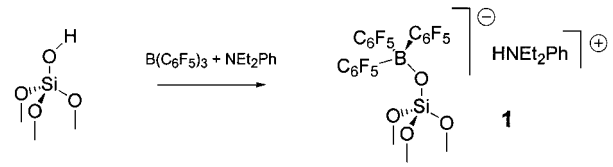
$NEt_2Ph/\equiv SiO_{2\text{-}(500)}$	**1**	**2**	**4**	Assignment
10	3.9	8.9	9.7	δCH_3
47	51	55	57	δCH_2
120	115	124		δC_{ortho}
122	121	129	134	δC_{para}
129	125	136	137	δC_{meta}
148	130	148		δC_{ipso}
	−8	−6.9	−7	$\delta(^{11}B)$

[a] 75.47 MHz for ^{13}C, 96.31 MHz for ^{11}B.

Table 3. Results of elemental analysis of **1** as a function of the dehydroxylation temperature of the silica.

T [°C]	OH [nm^2]	B [%][a]	N [%][a]	B/N[b]	F/B[b,c]	C/(B + N)[b]	B/OH [d]	N/OH [d]
300	1.7	0.23	0.30	0.99	10.6	12.1	0.38	0.38
500	1.2	0.21	0.27	1.01	13.6	14.3	0.49	0.48
500	1.2	0.22	0.29	1	12	13	0.51	0.52
700	0.7	0.16	0.18	1.15	12.3	15.6	0.71	0.61
800	0.6	0.16	0.21	0.99	16.2	16.4	0.82	0.84
800	0.6	0.17	0.24	0.92	12.1	15.2	0.88	0.96
theory				1	15	14		

[a] Weight %. [b] Molar ratios. [c] Titration values obtained by conductimetry for fluorine in presence of boron were lowered by formation of BF_4^- ion. [d] Calculated from respective weight percentages of boron and nitrogen.



Scheme 2. Reaction of silica surface with $B(C_6F_5)_3$ and NEt_2Ph.

temperature of the silica was increased from 300 to 800 °C (Table 3). These results indicate that the bulkiness of the grafted $[B(C_6F_5)_3 + NEt_2Ph]$ fragment prevents the reaction of all the silanols with $B(C_6F_5)_3$. *On highly dehydroxylated surfaces ($SiO_{2\text{-}(800)}$), the silanol groups are sufficiently isolated to be almost entirely transformed in anionic sites.* In contrast, on moderately dehydroxylated silica ($SiO_{2\text{-}(300)}$), a large number of the silanol groups are unreactive towards further modification as soon as the maximum loading (0.23 %) is achieved. This has been confirmed by analysis of the ν(O–H) IR region (Figure 1): the area of the bands at 3681 and 3624 cm^{-1} (interacting silanols) decreases as the dehydroxylation temperature of the silica decreases.

To check if the experimental weight percentage of boron corresponded to the highest loading achievable on the surface, a molecular modeling of **1** was performed by using the Sybyl computer modeling program. The molecular fragment $[HOB(C_6F_5)_3]^-[HNEt_2Ph]^+$ was attached to a silanol group of a modeled silica particle $SiO_{2\text{-}(500)}$, by replacing the hydrogen atom with [≡SiO], and minimized by using the molecular mechanics Tripos force field.[15] The calculated value obtained for the length of the B–O bond (1.567 Å) in the modeled complex was in the range of those reported for related silsesquioxane compounds (1.505 – 1.495 Å).[14] The projected area of such a complex on the silica particle was estimated to be 1.27 nm^2 (Figure 3). According to the specific

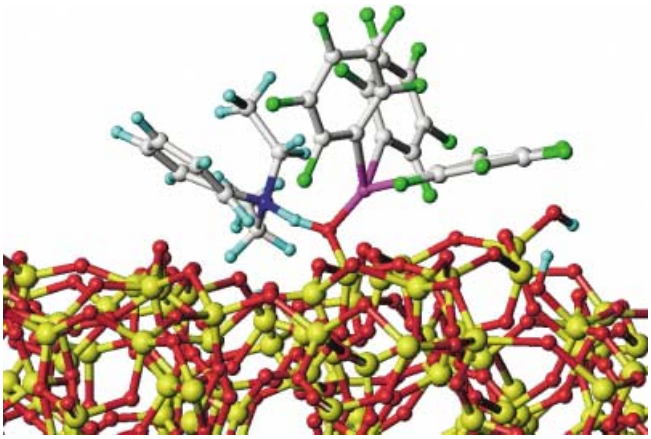


Figure 3. Molecular model of $[\equiv SiO\text{-}B(C_6F_5)_3]^-[HNEt_2Ph]^+$ (**1**), grafted onto $SiO_{2\text{-}(500)}$. H: blue, B: magenta, C: white, F: green, N: dark blue, O: red, Si: yellow.

ities with those of molecular compounds **2** – **4** confirm the proposed structure[9b–e] for **1** (Scheme 2).

It must be emphasized, however, that IR spectra and elemental analysis demonstrated unambiguously that all silica did not afford a unique surface species. Indeed, the weight percentage of boron corresponds to a proportion of modified silanols ranging from 38 to 88 % when the pretreatment area on silica (Aerosil 200 m^2 g^{-1}), this projection corresponds to a theoretical value of 0.24 wt % of boron on a saturated surface. This result is in good agreement with the experimental percentages obtained on $SiO_{2\text{-}(500)}$ (0.21 – 0.22 %).

In conclusion, we have found experimental conditions in which each surface silanol group is transformed into a *unique* and well-defined ionic entity $[\equiv Si{-}OB(C_6F_5)_3]^-[HNEt_2Ph]^+$.

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Experimental Section

General: Solid-state NMR spectra were recorded on Bruker DSX-300 equipped with a standard 4 mm double-bearing probe head and operating at 75.47, 96.31, and 300.18 MHz for ^{13}C, ^{11}B, and ^{1}H, respectively. Chemical shifts are given with respect to TMS by using adamantane as an external reference ($\delta = 37.7$ for the highest chemical shift). The ^{11}B chemical shifts were given relative to $BF_3 \cdot OEt_2$ ($\delta = 0$). Solution NMR spectra were recorded on Bruker AC 200 MHz (^{19}F), AC 300 MHz (^{1}H, ^{13}C), and DRX 300 MHz (^{11}B) spectrometers. Chemical shifts were reported in ppm and referenced to residual solvent resonances (C_6D_6: 7.15 for ^{1}H, 128 for ^{13}C; CD_2Cl_2: 5.32 for ^{1}H, 53.8 for ^{13}C), or external standards (^{19}F, $CFCl_3$ at 0; ^{11}B, $BF_3 \cdot OEt_2$ at 0). IR spectra were recorded under vacuum on a Nicolet 550 FT spectrometer by using an IR cell equipped with CaF_2 windows. Elemental analyses were performed by the Central Analysis Service of the CNRS at Solaize.

All operations were performed in the strict absence of oxygen and water under a purified argon atmosphere by using gloveboxes (Jacomex, MBraun) or vacuum-line techniques. Toluene was distilled under argon from Na/K alloy, degassed, and stored under argon over Na. C_6D_6 (SDS 99.6 %) and CD_2Cl_2 (SDS 99.6 %) were degassed by three "freeze-pump-thaw" cycles and dried over freshly regenerated 3 Å molecular sieves. NEt_2Ph (Aldrich Chemicals, 98 %) was dried over KOH, distilled under vacuum, and used immediately. $B(C_6F_5)_3$ (Merck Chemicals, > 97 %) was dried over $MeSiCl_3$[16] and purified by vacuum sublimation before use. (c-$C_5H_9)_7O_{12}Si_8(OH)$ and Ph_3SiOH were purchased from Aldrich Chemical and dried under vacuum before use. The silica support (Aerosil, Degussa, 200 $m^2 g^{-1}$) was compacted to a disk (30 mg) for IR studies or was hydrated, dried (80 °C), and crushed to prepare large quantities (1–2 g) for NMR studies and elemental analyses. Before reaction silica was calcined at 300 or 400 °C in air for 4 h and dehydroxylated at the desired temperature (300, 500, 700, or 800 °C) under high vacuum (10^{-5} Torr) for 12 h (referred to as $SiO_{2\text{-}(300)}$, $SiO_{2\text{-}(500)}$, $SiO_{2\text{-}(700)}$, and $SiO_{2\text{-}(800)}$, respectively). Deuterated ($SiO_{2\text{-}(500D)}$) and ^{18}O-labeled ($Si\text{-}^{18}O_{2\text{-}(500)}$) silica were obtained as already described.[17]

1: A pink solution of $B(C_6F_5)_3$ (260 mg, 0.51 mmol) and NEt_2Ph (80 μL, 0.50 mmol) in dry toluene (25 mL) was filtered under argon on $SiO_{2\text{-}(800)}$ (2 g). After the mixture had been stirred for 4 h at room temperature, the solution was filtered. The solid was washed four times with dry toluene (20 mL), dried under vacuum (10^{-5} mbar) for 4 h at ambient temperature, and stored under argon. Solid-state ^{1}H NMR (300.18 MHz, 25 °C): $\delta = 7.2$ (s, m-C_6H_5), 3.4 (br, CH_2), 1.0 (s, CH_3); elemental analysis calcd (wt %): B 0.16, N 0.21, C 5.87 (see also Table 3). For IR experiments, a solution of $B(C_6F_5)_3$ (16 mg, 0.03 mmol) and NEt_2Ph (5 μL, 0.03 mmol) in dry toluene (10 mL) was brought into contact in a glovebox with a pellet (30 mg) of $SiO_{2\text{-}(800)}$ over four hours at room temperature. The white disk was then washed with three fractions (10 mL) of dry toluene and dried under vacuum (10^{-5} mbar) for 1 h. IR: $\tilde{\nu} = 3685$ (w, br), 3619 (w, br), 3232 (m), 3095 (w), 3071 (w), 2996 (w), 2930 (w), 2887 (w), 2863 (w), 1645 (s), 1599 (w), 1559 (w), 1517 (vs), 1461 (vs), 1406 (m), 1396 (m), 1383 (m), 1369 (m), 1322 (w) cm^{-1}. The same procedure was used for $SiO_{2\text{-}(300)}$, $SiO_{2\text{-}(500)}$, and $SiO_{2\text{-}(700)}$.

2: Distilled water (7.5 μL, 0.49 mmol) and NEt_2Ph (62 μL, 0.51 mmol) were added to a solution of $B(C_6F_5)_3$ (207 mg, 0.40 mmol) in dry toluene (5 mL). After the mixture had been stirred for two hours at room temperature, the solution was concentrated under vacuum to give a pale yellow oil. Addition of dry pentane (10 mL) led to the precipitation of a white solid which was washed, filtered, and dried under high vacuum (10^{-5} mbar) for 2 h and at ambient temperature. Yield: 258 mg (97 %); ^{1}H NMR (300.13 MHz, C_6D_6, 25 °C): $\delta = 7.9$ (br s, 1H; NH), 6.82 (m, 3H; p- and m-C_6H_5), 6.52 (d, $^{3}J(H,H) = 7.2$ Hz, 2H; o-C_6H_5), 2.80 (br s, 1H; BOH), 2.25 (br q, 4H; CH_2), 0.36 (t, $^{3}J(H,H) = 6.9$ Hz, 6H; CH_3); $^{13}C\{^{1}H\}$ NMR (75.47 MHz, C_6D_6, 25 °C): $\delta = 148.7$ (d, $^{1}J(C,F) = 238$ Hz; o-C_6F_5), 139.5 (d, $^{1}J(C,F) = 250$ Hz; p-C_6F_5), 137.9 (s; i-C_6H_5), 137.3 (d, $^{1}J(C,F) = 239$ Hz; m-C_6F_5), 130.2 (s; p- and m-C_6H_5), 120.2 (s; o-C_6H_5), 51.5 (s; CH_2), 9.5 (s; CH_3); $^{19}F\{^{1}H\}$ NMR (188.31 MHz, C_6D_6, 25 °C): $\delta = -135.4$ (d, $^{3}J(F,F) = 21$ Hz, 6F; o-C_6F_5), −159.4 (t, $^{3}J(F,F) = 20$ Hz, 3F; p-C_6F_5), −164.4 (m, 6F; m-C_6F_5); $^{11}B\{^{1}H\}$ NMR (96.31 MHz, C_6D_6, 25 °C): $\delta = -3.5$ (s; $[(C_6F_5)_3BOH]^-$); IR (KBr): $\tilde{\nu} = 3665$ (s), 3234 (w), 3070 (w), 3020 (m), 3008 (m), 2999 (m), 2990 (m), 2969 (m), 2880 (m), 2726 (m), 2672 (m), 2652 (s), 2603 (m), 2585 (s), 2527 (s), 2500 (m), 2401 (m), 1645 (s), 1602 (m), 1517 (vs), 1465 (vs), 1392 (m), 1382 (m), 1365 (m), 1278 (s), 1155 (m), 1083 (vs), 974 (vs), 937 (s), 920 (s), 894 (m), 843 (m) cm^{-1}.

3: Same experimental procedure as for **2** with $B(C_6F_5)_3$ (400 mg, 0.78 mmol), triphenylsilanol (220 mg, 0.79 mmol), and NEt_2Ph (125 μL, 0.78 mmol) in dry toluene (5 mL) afforded white crystals on cooling at −25 °C. Yield: 0.71 g (97 %); ^{1}H NMR (300.13 MHz, CD_2Cl_2, 25 °C): $\delta =$ 7.6 (m, 2H; m-C_6H_5 aniline), 7.5 (d, $^{3}J(H,H) = 7.2$ Hz, 6H; o-C_6H_5 silanol), 7.3 (t, $^{3}J(H,H) = 7.6$ Hz, 3H; p-C_6H_5 silanol), 7.2 (m, 7H; p-C_6H_5 aniline and m-C_6H_5 silanol), 7.0 (dd, $^{3}J(H,H) = 8.0$ Hz, $^{4}J(H,H) = 1.1$ Hz, 2H; o-C_6H_5 aniline), 5.6 (br s, 1H; N−H), 3.2 (qua, $^{3}J(H,H) = 7.1$ Hz, 4H; CH_2), 0.94 (t, $^{3}J(H,H) = 6.9$ Hz, 6H; CH_3); $^{13}C\{^{1}H\}$ NMR (75.47 MHz, CD_2Cl_2, 25 °C): $\delta = 148.3$ (d, $^{1}J(C,F) = 252$ Hz; o-C_6F_5), 139.8 (s; i-C_6H_5 silanol), 138.3 (d, $^{1}J(C,F) = 242$ Hz; p-C_6F_5), 136.7 (d, $^{1}J(C,F) = 234$ Hz; m-C_6F_5), 135.6 (s, o-C_6H_5 silanol), 135.0 (s, i-C_6H_5 aniline), 132.2 (s, p-C_6H_5 aniline), 131.8 (s, m-C_6H_5 aniline), 128.7 (s, p-C_6H_5 silanol), 127.2 (s, m-C_6H_5 silanol), 121.2 (s, o-C_6H_5 aniline), 56.0 (s, CH_2), 10.9 (s, CH_3); $^{19}F\{^{1}H\}$ NMR (188.31 MHz, CD_2Cl_2, 25 °C): $\delta = -131.2$ (d, $^{3}J(F,F) = 18.3$ Hz, 6F; o-C_6F_5), −161.5 (t, $^{3}J(F,F) = 19.3$ Hz, 3F; p-C_6F_5), −165.2 (pseudo t, $^{3}J(F,F) = 19.3$ Hz, 6F; m-C_6F_5); $^{11}B\{^{1}H\}$ NMR (96.31 MHz, C_6D_6, 25 °C): $\delta = -4.5$ (s, $[Ph_3SiOB(C_6F_5)_3]^-$); IR (KBr): $\tilde{\nu} = 3226$ (vw), 3146 (m), 3072 (w), 3050 (vw), 3012 (vw), 2999 (vw), 1642 (m), 1588 (vw), 1515 (s), 1459 (vs), 1452 (vs), 1429 (m), 1394 (w), 1379 (w), 1273 (m), 1148 (w), 1112 (s), 1090 (vs), 971 (s) cm^{-1}; elemental analysis calcd (%) for $C_{46}H_{31}ONBF_{15}Si$: C 59.93, N 1.49, B 1.15, F 30.39, Si 3.00; found: C 59.13, N 1.47, B 1.21, F 24.77, Si 2.32.

4: Same experimental procedure as for **2** with $B(C_6F_5)_3$ (165 mg, 0.32 mmol), 3,5,7,9,11,13,15-heptacyclopentylpentacyclooctasiloxan-1-ol (297 mg, 0.32 mmol), and NEt_2Ph (53 μL, 0.33 mmol) in dry toluene (10 mL) afforded white crystals on cooling at −25 °C. Yield: 0.30 mg (59 %); ^{1}H NMR (500.13 MHz, C_6D_6, 25 °C): $\delta = 7.08$ (m, 3H; p- and m-C_6H_5), 6.37 (d, $^{3}J(H,H) = 7.1$ Hz, 2H; o-C_6H_5), 4.89 (br s, 1H; NH), 2.54 (qua, $^{3}J(H,H) = 7.2$ Hz, 4H; CH_2 aniline), 2.03 (m, 14H; CH_2 C_5H_9), 1.87 (m, 28H; CH_2 C_5H_9), 1.66 (m, 14H; CH_2 C_5H_9), 1.30 (m, 4H; CH C_5H_9), 1.23 (m, 3H; CH C_5H_9), 0.43 (t, $^{3}J(H,H) = 7.2$ Hz, 6H; CH_3); $^{13}C\{^{1}H\}$ NMR (75.47 MHz, C_6D_6, 25 °C): $\delta = 148.8$ (d, $^{1}J(C,F) = 249$ Hz; o-C_6F_5), 138.9 (d, $^{1}J(C,F) = 245$ Hz; p-C_6F_5), 137.1 (d, $^{1}J(C,F) = 239$ Hz; m-C_6F_5), 134.3 (s, i-C_6H_5), 131.4 (s, p-C_6H_5), 131.0 (s, m-C_6H_5), 120.5 (s, o-C_6H_5), 54.8 (s, CH_2 aniline), 27.8, 27.4, 27.3 (s, CH_2 C_5H_9), 23.2, 22.8 (s, CH C_5H_9), 9.8 (s, CH_3 aniline); $^{19}F\{^{1}H\}$ NMR (188.31 MHz, C_6D_6, 25 °C): $\delta = -133.1$ (d, $^{3}J(F,F) =$ 18.4 Hz, 6F; o-C_6F_5), −162.7 (t, $^{3}J(F,F) = 21$ Hz, 3F; p-C_6F_5), −166.3 (pseudo t, $^{3}J(F,F) = 19.5$ Hz, 6F; m-C_6F_5); $^{11}B\{^{1}H\}$ NMR (96.31 MHz, C_6D_6, 25 °C): $\delta = -5.0$ (s, $[(C_6F_5)_3BOSi_8O_{12}(c\text{-}C_5H_9)_7]^-$); IR (KBr): $\tilde{\nu} = 3228$ (w), 2951 (s), 2911 (w.sh), 2866 (m), 1643 (w), 1593 (vw), 1512 (m), 1464 (s), 1382 (vw), 1274 (w), 1250 (w), 1107 (vs), 976 (m) cm^{-1}; elemental analysis calcd (%) for $C_{63}H_{79}O_{13}NBF_{15}Si_8$: C 47.93, N 0.89, B 0.68, F 18.05, Si 14.23; found: C 47.74, N 1.06, B 0.94, F 17.34, Si 15.36.

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