

# Functionalized borazines as precursors for new silica gels

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Trialkynylborazines have been prepared in excellent yields by reacting alkynyl-bis(diisopropylamino)borane with powdered ammonium chloride in toluene. These were subsequently used in hydrosilylations with trichlorosilane and trialkoxysilanes using platinum on charcoal as heterogeneous catalyst. This reaction is stereoselective and gives the  $\beta$ -isomers as major product. The tris( $\beta$ -trichlorosilylvinyl)-substituted derivative ( $\text{Cl}_3\text{SiCH}=\text{CH}$ )<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub> was isolated in pure form and transformed into a highly functionalized silica gel by a sol-gel process. This gel has a specific surface of about 315 m<sup>2</sup> g<sup>-1</sup> and is the first containing intact borazine rings. The structures of (*i*Pr<sub>2</sub>N)<sub>2</sub>B-C≡CH, *B*,*B'*,*B''*-(HC≡CH)<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub>, *B*,*B'*,*B''*-(Me<sub>3</sub>SiC≡CH)<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub> and *B*,*B'*,*B''*-(Cl<sub>3</sub>Si-CH=CH)<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub> were determined by X-ray structure analyses and are reported.

## 1 Introduction

Borazines have a long standing history as inorganic heterocycles with aromatic character (*i.e.* B<sub>3</sub>N<sub>3</sub>H<sub>6</sub> is referred to as “inorganic benzene”).<sup>1</sup> Being relatively robust when compared to other boron nitrogen compounds, they became interesting as precursor molecules in boron nitride (BN) material science and some selected applications are cited in the following. The parent compound, B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>, has been intensively studied especially as a precursor for the formation of pre-polymers (poly-borazylene [B<sub>3</sub>N<sub>3</sub>H<sub>4</sub>]<sub>*n*</sub>) for boron nitride based polymers.<sup>2–6</sup> Efficient routes to boron nitride (BN) fibers<sup>7–10</sup> and porous BN supports<sup>11</sup> based on *B*-amino borazines were developed recently. Also a very short time ago, borazines of the type {[B(CH<sub>2</sub>SiCl<sub>2</sub>R)]<sub>3</sub>(NH)<sub>3</sub>} were recognized as suitable single-source precursors for the formation of multinary non-oxide inorganic materials such as amorphous network ceramics.<sup>12</sup> The reaction of the *B*-silyl substituted borazine [B{Si(SiMe<sub>3</sub>)<sub>3</sub>}(BCl<sub>2</sub>(NH)<sub>3</sub>)] with HN(SiMe<sub>3</sub>)<sub>2</sub> gave a pre-polymer which could be used for an amorphous BN/Si<sub>*x*</sub>N<sub>*y*</sub>C<sub>*z*</sub> composite material.<sup>13</sup> In a different approach, *B*-vinyl substituted borazines have been used for the synthesis of polymers with pendant borazine groups.<sup>14</sup> Elegantly, the homogeneously catalyzed reaction of poly(vinyl siloxanes), PVS, with *B*,*B'*-diethylborazine gave siloxane polymers with pendant borazine groups which served as pre-polymers for the formation of SiOCB ceramics.<sup>15</sup> In a patent, Vaultier and co-workers described the use of symmetrically boron-substituted alkynyl and vinyl borazines as precursors for ceramics.<sup>16</sup> This research group also developed a very convenient route for the synthesis of trialkynylborazine by ammonolysis of bis(diisopropylamino)alkynylborane.<sup>17–19</sup> The trivinyl derivative was subsequently obtained by a Pd catalysed hydrogenation of trialkynylborazine.<sup>16</sup>

In this article we describe our efforts to synthesize trialkynylborazines which were subsequently hydrosilylated to give  $\alpha$ - and  $\beta$ -tri(silylvinyl)borazines. These can be transformed into highly functionalized silica gels with large surface areas containing intact borazine rings and C=C–Si units. Furthermore we report the X-ray crystal structures of various products which served as intermediates for the silica gel production.

## 2 Results and discussion

For our syntheses of trialkynylborazines, we have chosen the Vaultier-method<sup>17–19</sup> which we slightly optimized to give

the desired compounds in three simple steps starting from BCl<sub>3</sub> in high yield (Scheme 1).

The preparation of the chloro-bis(diisopropylamino)borane (**2**) from BCl<sub>3</sub> (**1**) and diisopropylamine is documented [eqn. (1) in Scheme 1].<sup>19,20</sup> A change of the solvent from *n*-hexane to toluene increases the yield of **2** up to 90%. We ascribe this increase under our conditions as due to the microcrystalline form of the ammonium salt [NH<sub>2</sub>*i*Pr<sub>2</sub>]Cl which adsorbs less of the product (*i*Pr<sub>2</sub>N)<sub>2</sub>BCl (**2**). The synthesis of the alkynyl-bis(diisopropylamino)boranes **3a**,**b** was performed according to published procedures<sup>16–19</sup> and the reaction of **2** with LiC≡CR (R = H, SiMe<sub>3</sub>) in the presence of catalytic amounts of 12-crown-4 proceeds in almost quantitative yield. Single crystals of **3a** were obtained by sublimation (0.1 mbar, 45 °C) as orthorhombic crystals up to 5 mm edge length.

In the published method, *B*,*B'*,*B''*triethynylborazine (**4a**) is obtained in 76% yield when **3a** is reacted with gaseous ammonia in toluene at 95 °C.<sup>19,21</sup> We found that, even more conveniently, **4a** can be prepared in 92% yield by reacting **3a** with an excess of powdered solid ammonium chloride at 120 °C in toluene for 12 h [eqn. (2) in Scheme 1]. In an analogous manner, *B*,*B'*,*B''*tris(trimethylsilylethynyl)borazine (**4b**) is obtained in 83% yield. From both compounds, single crystals were prepared and subjected to X-ray structure analyses (*vide infra*).

Subsequently we studied the possibility of performing platinum catalyzed hydrosilylations of the C≡C triple bonds in **4a**. The regioselectivity of the addition of chlorosilanes to terminal alkynes with platinum on charcoal as heterogeneous catalyst was studied recently and a high selectivity for the formation of  $\beta$ -*trans* vinylsilanes was observed.<sup>22</sup> In our experiments, we used trichlorosilane, HSiCl<sub>3</sub>, and trialkoxysilanes, HSi(OR)<sub>3</sub> (R<sup>1</sup> = Me, Et, *i*Pr) as reagents and the triethynylborazine **4a** as substrate [eqn. (3) in Scheme 2].

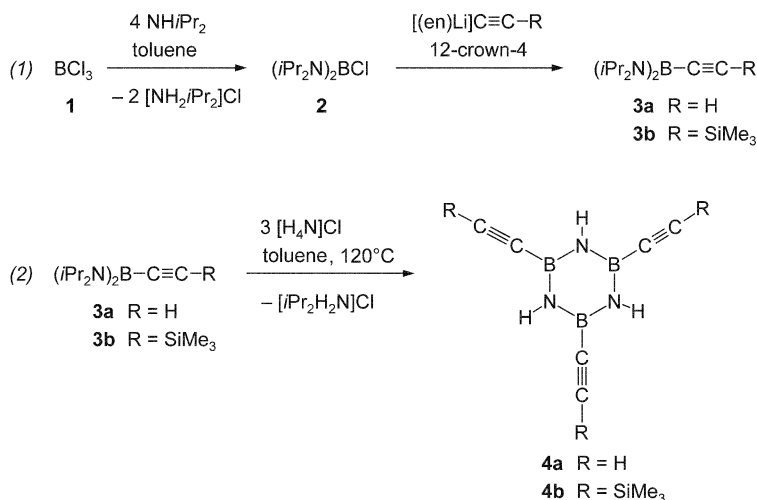
After 36–48 h at *T* = 120 °C in toluene the hydrosilylation of **4a** was almost complete; in experiments with the alkoxy-silanes less than 5% of non-hydrosilylated C≡C triple bond units were detected by <sup>13</sup>C NMR spectroscopy. The addition of the silane to the C≡C triple bond proceeds with *cis*-stereoselectivity and the major products were the tri- $\beta$ -*trans* isomers  $\beta$ -**5–8** in all cases. With HSiCl<sub>3</sub> more than 80% of this isomer,  $\beta$ -**5**, was formed. By fractional crystallisation, we were able to obtain the tris(trichlorosilyl) derivative  $\beta$ -**5** in pure form in good yields. The result of an X-ray structure analysis is reported below.

The remaining part contains a mixture of isomers hydro-silylated in both  $\alpha$ - and  $\beta$ -positions, which was not analyzed in

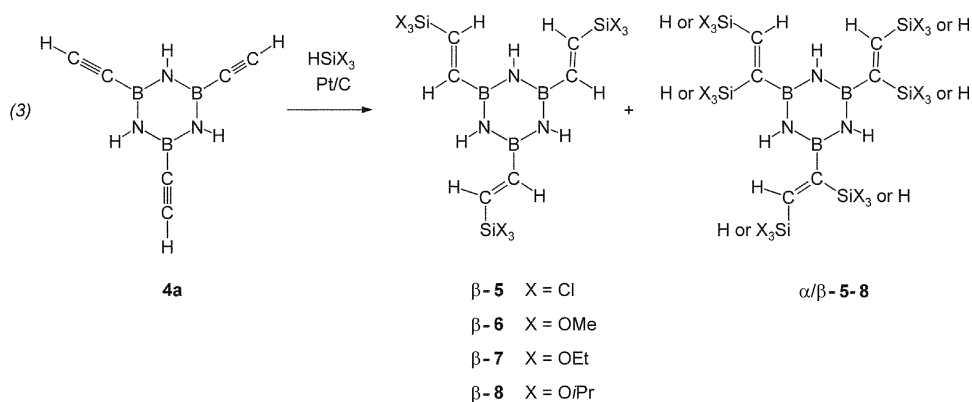
**Table 1** Selected NMR shifts for **3a**, **4a**, **6**, **7**, **8** in CDCl<sub>3</sub> and **3b**, **4b**,  $\beta$ -**5** in C<sub>6</sub>D<sub>6</sub> ( $\delta$  in ppm). <sup>13</sup>C shifts of  $\beta$ -**6**–**8** are mean values of isomer mixtures. Further NMR data are given in the Experimental section

Compound	$\delta$ ( <sup>11</sup> B)	$\delta$ ( <sup>13</sup> C) B–C $\alpha$ C	$\delta$ ( <sup>13</sup> C) B–CC $\beta$
( <i>i</i> Pr <sub>2</sub> N) <sub>2</sub> B–C≡CH <b>3a</b>	28.4	95.5	93.6
( <i>i</i> Pr <sub>2</sub> N) <sub>2</sub> B–C≡C–SiMe <sub>3</sub> <b>3b</b>	25.1	n.d.	n.d.
(N <sub>3</sub> B <sub>3</sub> H <sub>3</sub> )(C≡CH) <sub>3</sub> <b>4a</b>	28.1	86 (br)	90.2
(N <sub>3</sub> B <sub>3</sub> H <sub>3</sub> )(C≡C(SiMe <sub>3</sub> )) <sub>3</sub> <b>4b</b>	24.5	110.2 (br)	129.3
(N <sub>3</sub> B <sub>3</sub> H <sub>3</sub> )(CH=CH(SiCl <sub>3</sub> )) <sub>3</sub> $\beta$ - <b>5</b>	34.0	153.6 (br)	137.4
(N <sub>3</sub> B <sub>3</sub> H <sub>3</sub> )(CH=CH(Si(OMe) <sub>3</sub> )) <sub>3</sub> $\beta$ - <b>6</b>	34.7	152.4 (br)	135.5
(N <sub>3</sub> B <sub>3</sub> H <sub>3</sub> )(CH=CH(Si(OEt) <sub>3</sub> )) <sub>3</sub> $\beta$ - <b>7</b>	34.4	152.1 (br)	138.3
(N <sub>3</sub> B <sub>3</sub> H <sub>3</sub> )(CH=CH(Si(O <i>i</i> Pr) <sub>3</sub> )) <sub>3</sub> $\beta$ - <b>8</b>	34.7	151.7 (br)	140.4

n.d. = Not detected.



**Scheme 1** Synthesis of the bis(diisopropylamino)alkynylboranes **3a,b** and the triethynylborazines **4a,b**.



**Scheme 2** Synthesis of the *B,B',B''*-tri(silylvinyl)borazines **5–9** via catalytic hydrosilylation of **4a**.

detail. With the alkoxy silanes, HSi(OR)<sub>3</sub>, the reactions were less regioselective and complex product mixtures with  $\alpha$ - and  $\beta$ -silylated vinyl groups were obtained. From an integration of the <sup>13</sup>C NMR resonances we estimated that approximately 60% of the C≡C triple bond units were hydrosilylated in the  $\beta$ -position independently of the nature of the substituents (R = Me, Et, *i*Pr).

### NMR spectroscopy

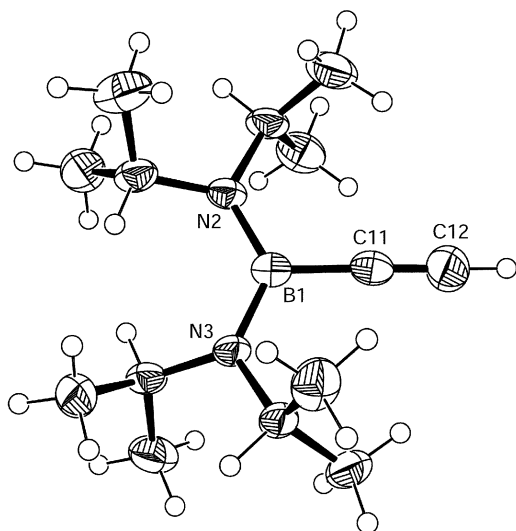
All compounds were characterized by <sup>1</sup>H, <sup>11</sup>B and <sup>13</sup>C NMR spectroscopy. Selected <sup>11</sup>B and <sup>13</sup>C NMR spectroscopic data are given in Table 1.

Quaternary C atoms attached to the boron fragments are difficult to observe because of the low intensity caused by the quadrupole moment of the boron nucleus.<sup>23</sup> As a consequence, the <sup>13</sup>C NMR shift of these nuclei were measured with long relaxation times *T*<sub>1</sub> up to 60 s. In the diaminoalkynylborane **3a**, we observe the <sup>13</sup>C NMR signal for the  $\alpha$ -C atom of the

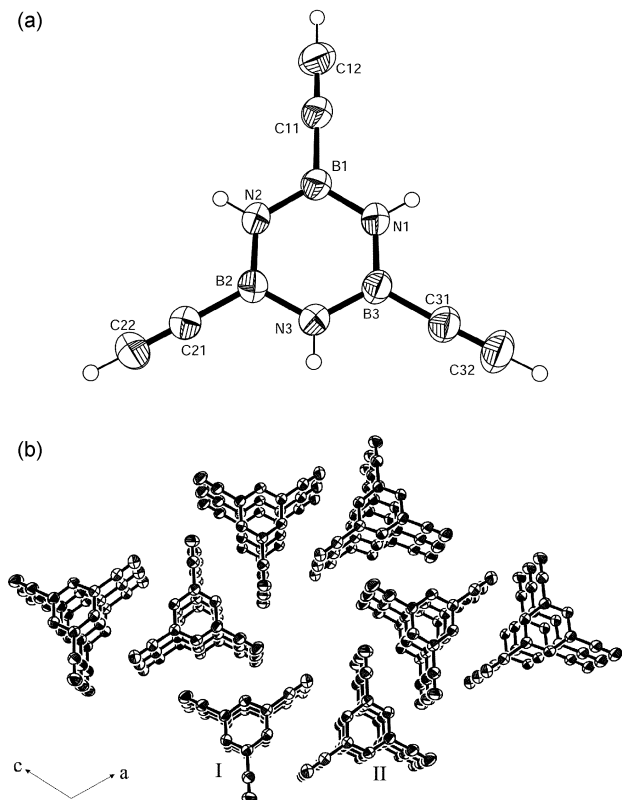
alkynyl groups at 95.5 ppm in contrast to the data reported in the literature.<sup>16,19</sup> No signals for the alkynyl carbons, B–C≡C, were detected for **3b**. In the spectrum of the triethynylborazine **4**, the corresponding <sup>13</sup>C NMR resonance is also very broad (*w*<sub>1/2</sub> ≈ 300 Hz) and the signal is shifted to lower frequencies ( $\delta$  = 86 ppm). DEPT-NMR spectroscopy was applied to assign the <sup>13</sup>C NMR shifts of the different isomers ( $\alpha$ ,  $\beta$ ) of the hydrosilylated products **5–8**. For the trialkoxysilyl substituted vinyl borazines  $\beta$ -**6–8**, the <sup>13</sup>C NMR shifts (mean values) of the CH units appear at  $\delta$  ≈ 138 ± 2 ppm for =CH–Si and  $\delta$  ≈ 152 ± 1 ppm for B–CH=. The isomers carrying Si(OR)<sub>3</sub> groups in  $\alpha$ -position to the borazine ring, reveal a resonance at  $\delta$  ≈ 143 ± 1 ppm for the terminal =CH<sub>2</sub> groups. The carbon atoms of the =CH groups attached to boron are observed at  $\delta$  ≈ 142 ± 2 ppm (folded to the opposite side with respect to the CH<sub>2</sub> groups in the DEPT-NMR spectrum). Due to the non-symmetric substituent pattern, all <sup>11</sup>B NMR signals are broadened (*w*<sub>1/2</sub> ≈ 390 Hz) and the chemical shifts range from 25 to 34 ppm.<sup>23</sup>

### X-Ray structure analyses of 3a, 4a,b and $\beta$ -5

The molecular structures of ethynyl-bis(diisopropylamino)-borane **3a**, trialkynyl substituted borazines **4a** and **4b**, and of the tris( $\beta$ -trichlorosilylvinyl)borazine  $\beta$ -5 have been determined by X-ray single crystal structure analyses. Plots of the molecular structures are shown in Figs. 1–4. For each of the borazines **4a,b** and  $\beta$ -5, the packing in the crystal is shown in Figs. 2(b), 3(b) and 4(b), respectively.

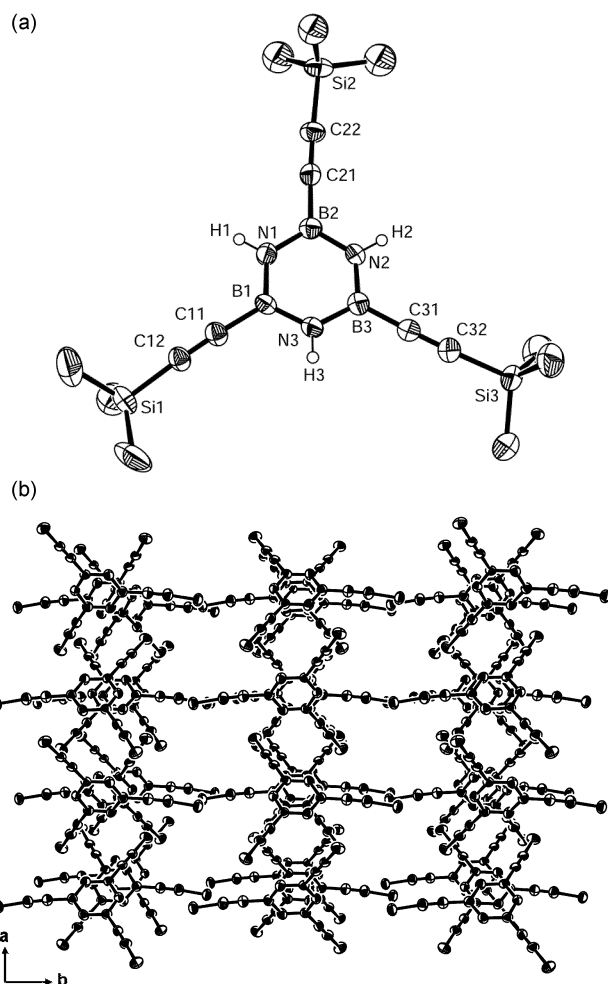


**Fig. 1** Molecular structure of **3a**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths and angles are given in Table 2.



**Fig. 2** Molecular structure and crystal packing of **4a**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths and angles are given in Table 2.

A summary of selected bond lengths and angles is given in Table 2. Details concerning the data collection and refinement are given in Table 3 in the Experimental section. Most of the structural features are as expected for borazine compounds.<sup>1</sup>



**Fig. 3** Molecular structure and crystal packing of **4b**. The methyl substituents of the trimethylsilyl groups at Si1 and Si2 are distorted, only one position is shown. Thermal ellipsoids are drawn at the 50% probability level. Methyl substituents were omitted for clarity in Fig. 3(b). Selected bond lengths and angles are given in Table 2.

The boron and nitrogen centers are strictly trigonal planar coordinated and the  $B_3N_3$  rings in **4a,b** and  $\beta$ -5 are planar within experimental error. As expected, the  $B-C\equiv C-R$  ( $R = H, SiMe_3$ ) units in the acyclic compound **3a** and in the borazines **4a,b** are almost linear. In tris( $\beta$ -trichlorosilylvinyl)borazine  $\beta$ -5, one vinylidene substituent [ $C31=C32$  in Fig. 4(a)] is rotated by  $180^\circ$  with respect to the molecular plane likely due to stacking effects (*vide infra*). Therefore a paddle-wheel arrangement of the three alkenylidene substituents is not observed in this case.

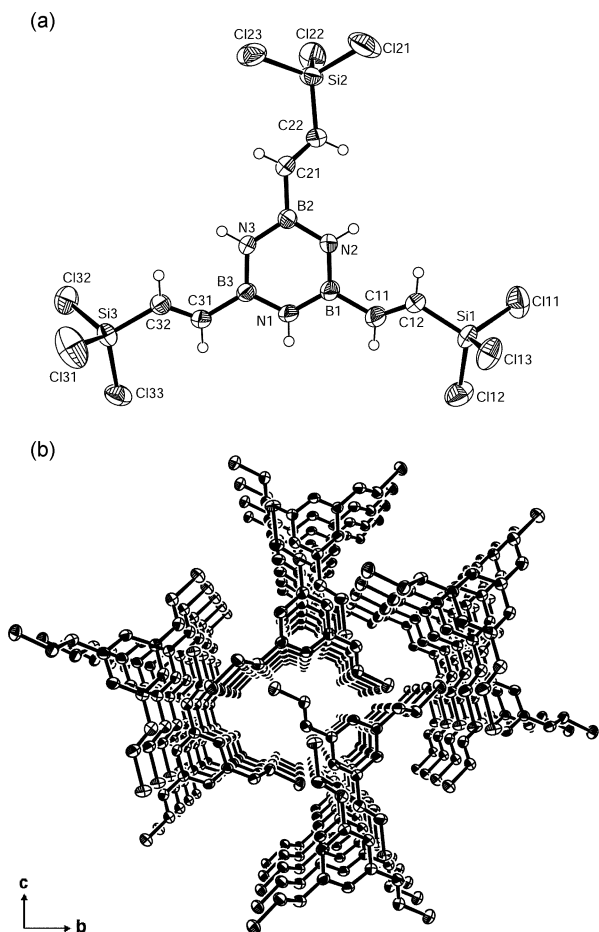
The arrangement of the individual molecules **4a** in the crystal is shown in Fig. 2(b). Columns of borazine rings are aligned along the crystallographic  $b$ -axis. Within each column, the  $B_3N_3$  rings are exclusively co-planar and in eclipsed positions. The intermolecular  $B \cdots B$  and  $N \cdots N$  distances are 393.4 pm, respectively. The two different types of columns I and II formed by the molecules [see Fig. 2(b)] are tilted by  $46.9^\circ$  with respect to each other.

In the silyl-substituted derivative **4b**, such an alignment of the borazine rings along the crystallographic  $a$ -axis is also observed [Fig. 3(b)]. However, the bulky  $SiMe_3$  groups prevent close intermolecular interactions under 800 pm and furthermore the individual molecules within each column are rotated by approximately  $60^\circ$  with respect to each other such that a boron atom lies above and beyond a nitrogen atom of the neighbouring borazine molecule. The borazines in one column form a  $82.7^\circ$  angle with the borazines in a neighbouring column such that sheets of borazine molecules in a zigzag conformation are formed in the crystallographic  $a,b$ -plane.

**Table 2** Selected interatomic distances (pm) and angles ( $^{\circ}$ ), averaged values are given for the borazine derivatives

Compound	B–N	B–C $_{\alpha}$	C $_{\alpha}$ –C $_{\beta}$	N–B–N	B–N–B	C $_{\beta}$ –C $_{\alpha}$ –B
( <i>i</i> Pr $_2$ N) $_2$ B–C $\equiv$ CH <b>3a</b>	143.1(2)	156.2(3)	118.6(3)	125.8(2)	n.a.	177.9(2)
(N $_3$ B $_3$ H $_3$ )(C $\equiv$ CH) $_3$ <b>4a</b>	141.9(5)	154.5(2)	117.9(2)	117.4(1)	122.6(1)	179.4(1)
(N $_3$ B $_3$ H $_3$ )(C=C(SiMe $_3$ ) $_3$ ) <b>3</b>	142.3(4)	154.6(4)	120.4(4)	117.0(2)	122.9(2)	175.3(3)
(N $_3$ B $_3$ H $_3$ )(CH=CH(SiCl $_3$ ) $_3$ ) <b><math>\beta</math>-5</b>	141(2)	157(2)	127(1)	117(1)	123(1)	129(1)

n.a. = Not available.

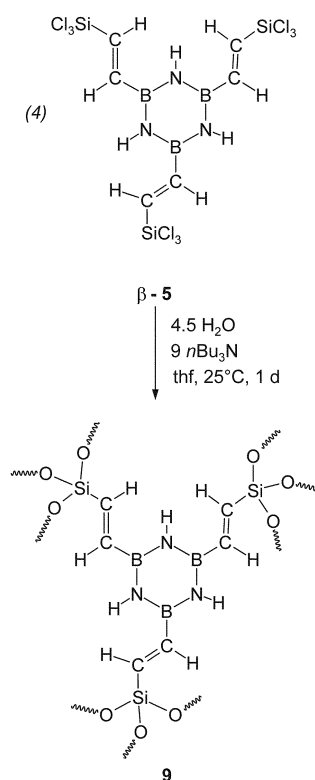
**Fig. 4** Molecular structure and crystal packing of  $\beta$ -5. Thermal ellipsoids are drawn at the 50% probability level. The chloro substituents were omitted for clarity in Fig. 4(b). Selected bond lengths and angles are given in Table 2.

The chlorosilyl-substituted derivative  $\beta$ -5 is stacked in the crystal along the *a*-axis [Fig. 4(b)]. The silylvinyl group which shows a different orientation [see C31=C32 of the molecular structure shown in Fig. 4(a)] at a borazine ring of one column is intercalated by two borazine rings of the neighbouring column. As a consequence, the stacking period of each column is shifted by half of the inter-ring distances (1327 pm) vs. that of the neighbouring columns.

### Silica gel formation

Evidently, the *B,B',B''*-tri(silylvinyl)borazines **5–8** are attractive reagents for sol–gel processes to give highly functionalised silica gels which contain Lewis-acidic (the boron centers) and Lewis-basic (the nitrogen and olefinic) sites. This property would make these borazines interesting supports. To our knowledge, silica gels comparable to the ones we targeted have not been described in the literature. Related composite materials formed from cyclo/poly-phosphazenes and metal oxides (*e.g.* SiO $_2$ , TiO $_2$ , ZrO $_2$ , Al $_2$ O $_3$ ) *via* a sol–gel process were described in the literature.<sup>24</sup> As mentioned above, borazines are comparatively stable, however, they are sensitive towards

hydrolysis upon prolonged exposure to moisture. Therefore we have chosen the borazine  $\beta$ -5 containing highly reactive trichlorosilyl groups for our experiments. In this compound, which was also obtained in a stereochemically well-defined form, the chloro substituents should be hydrolysed much more rapidly than the B $_3$ N $_3$  ring. Indeed, when a solution of  $\beta$ -5 in tetrahydrofuran (thf) containing tri(*n*-butyl)amine as HCl binding reagent was reacted with an equimolar amount of water under classical sol–gel-conditions, a colourless clear gel was formed within about one day [eqn. (4) in Scheme 3]. After extraction with thf to remove the ammonium chloride [*n*Bu $_3$ HN]Cl and drying in vacuum a yellow amorphous silica gel was obtained (see Fig. 5).

**Scheme 3** Synthesis of the silica gel **9** from *B,B',B''*-tris[(trichlorosilyl)vinyl]borazine ( $\beta$ -5).**Fig. 5** Photograph of silica gel **9** after purification.

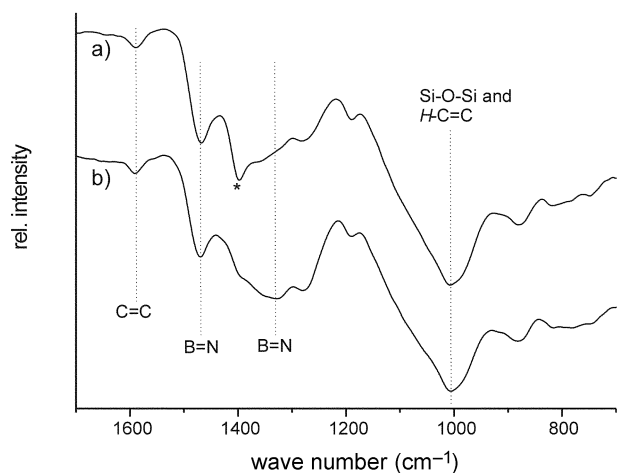
**Table 3** Crystal data and structure refinement<sup>a</sup> parameters for compounds **3a**, **4a,b** and **β-5**; Mo-Kα, graphite monochromator

	<b>3a</b>	<b>4a</b>	<b>4b</b>	<b>β-5</b>
Empirical formula	C <sub>14</sub> H <sub>29</sub> BN <sub>2</sub>	C <sub>6</sub> H <sub>6</sub> B <sub>3</sub> N <sub>3</sub>	C <sub>15</sub> H <sub>30</sub> B <sub>3</sub> N <sub>3</sub> Si <sub>3</sub>	C <sub>6</sub> H <sub>9</sub> B <sub>3</sub> Cl <sub>9</sub> N <sub>3</sub> Si <sub>3</sub>
Formula weight	236.21	152.57	369.11	558.92
<i>T</i> /K	233	293	293	233
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>Pbca</i>	<i>C2/c</i>	<i>Iba2</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> /pm	789.4(1)	2279.2(3)	1673.9(1)	1326.8(2)
<i>b</i> /pm	1774.5(3)	393.45(5)	2386.3(1)	1117.3(1)
<i>c</i> /pm	2293.8(4)	2367.1(3)	1234.5(1)	1567.4(2)
$\beta$ /°		116.641(2)		92.250(4)
10 <sup>30</sup> <i>V</i> /m <sup>3</sup>	3213.1(1)	1897.3(4)	4931.1(5)	2321.7(5)
<i>Z</i>	8	8	8	4
$\mu$ /mm <sup>-1</sup>	0.056	0.064	0.195	1.238
<i>F</i> (000)	1056	624	1584	1104
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	0.977	1.068	0.994	1.60
Crystal size/mm	0.9 × 0.64 × 0.34	0.61 × 0.13 × 0.12	0.42 × 0.27 × 0.15	1.80 × 0.80 × 0.12
Diffractometer	Siemens SMART PLATFORM with CCD	Siemens SMART PLATFORM with CCD	STOE IPDS	Siemens SMART PLATFORM with CCD
$\theta_{\max}$ /°	24.71	32.89	24.93	30.51
Index ranges	-9 ≤ <i>h</i> ≤ 9 -20 ≤ <i>k</i> ≤ 20 -26 ≤ <i>l</i> ≤ 26	-34 ≤ <i>h</i> ≤ 33 -6 ≤ <i>k</i> ≤ 5 -34 ≤ <i>l</i> ≤ 26	-19 ≤ <i>h</i> ≤ 19 -28 ≤ <i>k</i> ≤ 28 -14 ≤ <i>l</i> ≤ 14	-18 ≤ <i>h</i> ≤ 14 -15 ≤ <i>k</i> ≤ 15 -22 ≤ <i>l</i> ≤ 19
Reflections collected	23005	8798	21962	22017
Independent reflections	2739	3156	4273	7068
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.953	1.067	1.053	0.938
Final <i>R</i> indices ( <i>I</i> > 2σ( <i>I</i> ))	<i>R</i> <sub>1</sub> = 0.0453, <i>wR</i> <sub>2</sub> = 0.0992	<i>R</i> <sub>1</sub> = 0.0525, <i>wR</i> <sub>2</sub> = 0.1495	<i>R</i> <sub>1</sub> = 0.0350, <i>wR</i> <sub>2</sub> = 0.1024	<i>R</i> <sub>1</sub> = 0.0434, <i>wR</i> <sub>2</sub> = 0.1119
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0802, <i>wR</i> <sub>2</sub> = 0.1113	<i>R</i> <sub>1</sub> = 0.0761, <i>wR</i> <sub>2</sub> = 0.1641	<i>R</i> <sub>1</sub> = 0.0371, <i>wR</i> <sub>2</sub> = 0.1042	<i>R</i> <sub>1</sub> = 0.0854, <i>wR</i> <sub>2</sub> = 0.1251
Largest diff. peak, hole/10 <sup>30</sup> e m <sup>-3</sup>	0.101, -0.136	0.242, -0.243	0.426, -0.258	0.706, -0.533

<sup>a</sup> Programs: SHELXTL-Plus, SHELXL-97;<sup>28</sup> solutions by direct methods, full matrix refinement with all independent structure factors.

We characterized this material by IR spectroscopy, <sup>11</sup>B and <sup>29</sup>Si MAS NMR, <sup>13</sup>C CP-MAS NMR, thermogravimetry (TG) and BET measurements. The IR spectrum of the crude silica gel (**9**) after purification is displayed in Fig. 6(a).

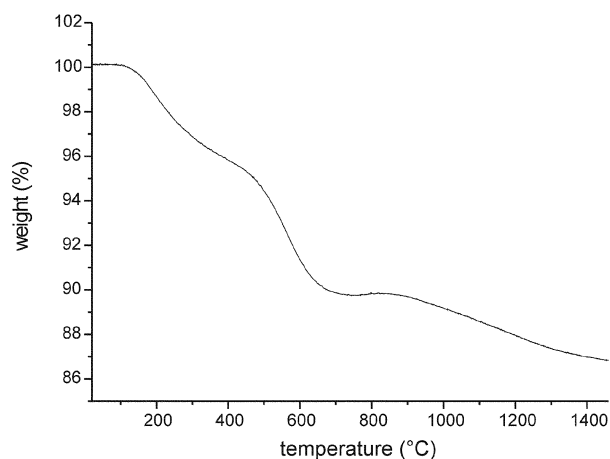
For comparison, the spectrum obtained after heating of **9** to 200 °C under vacuum for 24 h is shown in Fig. 6(b). Clearly, no major changes appear and only the evaporation of residual thf is observed. The IR spectra reveals for the borazines typical E' N–B–N vibration modes of the B<sub>3</sub>N<sub>3</sub> ring at about 1470 and 1320 cm<sup>-1</sup>.<sup>1</sup> Furthermore, the C=C stretching vibration is observed at about 1590 cm<sup>-1</sup>, and the H–C=C bending mode is observed together with the intense Si–O–Si stretching modes at about 1000 cm<sup>-1</sup>. These data indicate that all functional groups, especially the borazine rings, have been retained during silica gel formation. This assumption is further supported by the solid-state NMR data. In the <sup>11</sup>B MAS NMR spectrum, a signal at about 24 ppm indicates the presence of intact borazine rings in the silica gel in accordance with the precursor mole-



**Fig. 6** IR spectra of the silica gel, (a) as obtained after purification and (b) after heating the same sample at 200 °C for 24 h in vacuum. \* denotes modes from residual thf.

cules **4a** and **β-5**. For the latter, <sup>11</sup>B MAS NMR signals at ~20 ppm (**β-5**) and 24 ppm (**4a**)<sup>25</sup> were measured. In the <sup>29</sup>Si MAS NMR spectrum of the silica gel **9**, only one signal at -72 ppm is observed which is very typical for a SiO<sub>2</sub>/C environment around the silicon nucleus<sup>26</sup> and demonstrates that within the detection limits the chloro substituents in **β-5** have been replaced by oxygen substituents. The presence of the Si–C=C vinyl groups is indicated by a signal in the cross-polarized <sup>13</sup>C MAS NMR spectrum at  $\delta \approx 143$  ppm with a half-width of 1200 Hz.

The thermal stability of the silica gel was investigated by a TG measurement. As the curve in Fig. 7 shows, a first weight loss occurs at about 200 °C and amounts to 5% at about 400 °C. In a second step, another 5.4% of the weight is lost between 400 and 800 °C. Finally, at a temperature of 1500 °C a total of about 13.5% of the starting weight has been lost. The remaining residue is a black ceramic material which has not yet been investigated in detail. Repeated BET measurements of the purified and dried silica gel give a specific surface area of about ~315 m<sup>2</sup> g<sup>-1</sup> which is in the typical range for such materials.<sup>27</sup>



**Fig. 7** TG curve of the silica gel **9** under a dynamic Ar atmosphere.

We tested also silica gel formation using the trialkoxy-substituted *B,B',B''*-tri(silylvinyl)borazines **6–8**. As anticipated (*vide supra*) the gel formation was much slower (4–5 d) and not complete, *i.e.* residual alkoxy groups were detected by IR spectroscopy. Also, these materials had a significantly lower specific surface area ( $\sim 230 \text{ m}^2 \text{ g}^{-1}$ ).

### 3 Conclusion

We showed in this work that trialkynylborazines can be easily functionalised by a heterogeneously catalysed hydrosilylation reaction. The resulting *B,B',B''*-tri( $\beta$ -silylvinyl)borazines are suitable precursors for the formation of silica gels which are highly functionalised. Especially, the trichlorosilyl derivative where the Si–Cl bonds are more rapidly hydrolysed than the  $\text{B}_3\text{N}_3$  ring, allow the preparation of a silica gel with intact borazine moieties. Remarkably, stirring a suspension of the silica gel in water for several hours did not lead to a colour change and notable decomposition indicating that the borazine rings are quite stable against hydrolysis when immobilised in the gel. The vinyl groups are additional functional groups to which transition metals may be bonded and this aspect is currently being investigated in our laboratories.

### 4 Experimental

#### General techniques

All syntheses were performed in carefully dried glassware under an argon atmosphere which was passed through the Oxisorb<sup>®</sup>-gas purification system of Messer–Griesheim to remove the last traces of oxygen and moisture. All solvents were dried and purified using standard procedures and were freshly distilled under argon from sodium/benzophenone (thf, toluene) or from sodium/diglyme/benzophenone (heptane, hexane, pentane) prior to use. Air-sensitive compounds were stored and weighed in a glove-box (Braun MB 150 B–G system) and reactions on small scale were performed directly in the glove-box. NMR spectra were taken on the AMX-500, Avance DRX-400, Avance DPX-300 or Avance DPX-250 system. The chemical shifts are reported on the  $\delta$  scale in ppm relative to residual non-deuterated solvent signals ( $^1\text{H}$ ) or the signals of the deuterated solvent ( $^{13}\text{C}$ ) as internal standards, or relative to tetramethylsilane ( $^{29}\text{Si}$ ) or  $\text{BF}_3 \cdot \text{OEt}_2$  ( $^{11}\text{B}$ ) as an external standard.  $^{29}\text{Si}$  and  $^{13}\text{C}$  chemical shifts of the solid samples were determined relative to the external standard  $\text{Q}_8\text{M}_8$ . Values were then expressed relative to the reference compound TMS (0 ppm).  $^{11}\text{B}$  MAS NMR spectra were determined relative to an aqueous solution of boric acid, which has a chemical shift of 19.6 ppm relative to the  $^{11}\text{B}$  reference compound  $\text{BF}_3 \cdot \text{OEt}_2$  (0 ppm). Coupling constants,  $J$ , are given in Hertz (Hz) and as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as s, d, t for singlets, doublets, triplets, respectively. Broadened resonances are indicated as br.

Mass spectra were either taken on a Finnigan MAT SSG 7000 or a Varian MAT CH-7A in the EI (70 eV) mode. Melting points were determined in sealed capillaries in an apparatus fabricated by Büchi according to Dr Tottoli and are uncorrected. IR spectra were recorded with a Perkin-Elmer Spectrum 2000 NIR-FT-Raman spectrometer. Energy values are given in  $\text{cm}^{-1}$ . Thermal analyses were taken on a NETZSCH STA 409. BET measurements were taken on a Micromeritics ASAP 2010 at  $-196^\circ\text{C}$ . The samples were degassed at 0.1 mbar and  $200^\circ\text{C}$  for 6 h prior to measurements.

#### Chemicals

Commercial chemicals were purchased from Fluka or Aldrich and used as delivered.

### Syntheses

**Chloro-bis(diisopropylamino)borane (2).** A mixture of a 1 M solution of  $\text{BCl}_3$  in heptane (400 mL, 0.4 mol  $\text{BCl}_3$ ) and 400 mL toluene was first cooled at  $0^\circ\text{C}$ . Subsequently  $i\text{Pr}_2\text{NH}$  (167 g, 1.65 mol) was added dropwise over 2 h under strong stirring. The reaction mixture was allowed to warm to room temp. and stirred for 12 h. The solution was separated by filtration and the residue was carefully washed with  $3 \times 100 \text{ mL}$  heptane. After removing the solvents the product was distilled at 0.1 mbar at  $80^\circ\text{C}$  to give a colourless liquid. Yield: 88.5 g (0.36 mol, 90%). NMR ( $\text{CDCl}_3$ ):  $^1\text{H}$ :  $\delta$  1.34 [d,  $^3J(\text{HH}) = 6.9 \text{ Hz}$ , 6 H,  $\text{CH}_3$ ], 3.59 [sept.,  $^3J(\text{HH}) = 6.9 \text{ Hz}$ , 1 H, CH];  $^{11}\text{B}$ :  $\delta$  33.6;  $^{13}\text{C}$ :  $\delta$  23.0 ( $\text{CH}_3$ ), 46.6 (CH). MS:  $m/z$  (% ion) = 247 (26, M), 232 (100,  $\text{M} - \text{CH}_3$ ).

**Ethynyl-bis(diisopropylamino)borane (3a).** To a suspension of  $[(\text{en})\text{Li}]\text{C}\equiv\text{CH}$  (6.9 g, 0.075 mol) in 80 mL THF a solution of **2** (12.3 g, 0.05 mol) in 80 mL THF was added with a catalytic amount of 12-crown-4. The reaction mixture was heated for several hours and checked by  $^{11}\text{B}$  NMR spectroscopy to monitor the completeness of the reaction. The suspension was filtered over Celite. Subsequently, the solvents were removed in vacuum and the remaining product sublimed at 0.1 mbar,  $45^\circ\text{C}$  to obtain colourless crystals. Mp  $40^\circ\text{C}$ . Yield: 11.6 g (0.049 mol, 98%). NMR ( $\text{CDCl}_3$ ):  $^1\text{H}$ :  $\delta$  1.34 [d,  $^3J(\text{HH}) = 4.1 \text{ Hz}$ , 12 H,  $\text{CH}_3$ ], 3.53 [sept.,  $^3J(\text{HH}) = 4.1 \text{ Hz}$ , 2 H, CH], 2.9 (br, 1 H,  $\text{C}\equiv\text{CH}$ );  $^{11}\text{B}$ :  $\delta$  28.4;  $^{13}\text{C}$ :  $\delta$  23.7 ( $\text{CH}_3$ ), 46.3 (CH), 93.6 ( $\text{B}-\text{C}\equiv\text{C}$ ), 95.5 ( $\text{B}-\text{C}\equiv\text{C}$ ). IR: 2056 ( $\text{C}\equiv\text{C}$ ). MS:  $m/z$  (% ion) = 236 (98, M), 220 (99,  $\text{M} - \text{CH}_4$ ), 192 (100,  $\text{M} - \text{C}_3\text{H}_8$ ).

**(Trimethylsilyl)ethynyl-bis(diisopropylamino)borane (3b).** A solution of trimethylsilylacetylene (8.3 mL, 0.06 mol) in 100 mL toluene was cooled to  $0^\circ\text{C}$  and 37.5 mL  $n\text{-BuLi}$  (1.6 M in pentane, 0.06 mol) were added. After 1.5 h at room temp. 9.87 g (0.04 mol) **2** and a catalytic amount of 12-crown-4 were added. The reaction mixture was heated for 1.5 h at  $80^\circ\text{C}$  and stirred for 72 h. After filtration and removing the solvent the crude product was distilled at 0.03 mbar,  $50^\circ\text{C}$ . Yield: 10.9 g (0.0355 mol, 89%). NMR ( $\text{C}_6\text{D}_6$ ):  $^1\text{H}$ :  $\delta$  0.33 (s, 9 H,  $\text{Si}-\text{CH}_3$ ), 1.44 (d,  $^3J(\text{HH}) = 6.6 \text{ Hz}$ , 12 H,  $\text{C}-\text{CH}_3$ ), 3.54 (sept.,  $^3J(\text{HH}) = 6.6 \text{ Hz}$ , 2 H, CH);  $^{11}\text{B}$ :  $\delta$  25.1;  $^{13}\text{C}$ :  $\delta$   $-0.4$  ( $\text{Si}-\text{CH}_3$ ), 24.2 ( $\text{C}-\text{CH}_3$ ), 47.0 ( $\text{C}-\text{CH}_3$ ). MS:  $m/z$  (% ion) = 308 (1,  $\text{M}^+$ ), 293 (15,  $\text{M}^+ - \text{CH}_3$ ), 44 (100).

***B,B',B''*-Triethynylborazine (4a).** To a solution of **3a** (70.8 g, 0.3 mol) in toluene (400 mL), freshly crushed  $\text{NH}_4\text{Cl}$  (64.2 g, 1.2 mol) was added under stirring and refluxed for 12 h. After filtration and removing the solvent, the crude product was sublimed at  $90^\circ\text{C}$ , 0.1 mbar to form small white needles. Mp  $132^\circ\text{C}$ . Yield: 42.1 g (0.276 mol, 92%). NMR ( $\text{CDCl}_3$ ):  $^1\text{H}$ :  $\delta$  2.70 (s, 1H,  $\text{C}\equiv\text{CH}$ ), 5.63 (s, 1H, N–H);  $^{11}\text{B}$ :  $\delta$  28.1;  $^{13}\text{C}$ :  $\delta$  86 ( $\text{C}\equiv\text{CH}$ ), 90.2 ( $\text{C}\equiv\text{CH}$ ).  $^{11}\text{B}$  MAS (solid state):  $\delta$   $\sim 24$  ppm (quadrupole coupling constant  $c_{\text{qcc}} = 2.8 \text{ MHz}$ ). IR/ $\text{cm}^{-1}$ : 2073 ( $\text{C}\equiv\text{C}$ ); 1461, 1332 (B–N). MS:  $m/z$  (% ion) = 153 (100, M).

***B,B',B''*-Tris(trimethylsilylethynyl)borazine (4b).** 9.8 g (0.18 mol)  $\text{NH}_4\text{Cl}$  were suspended in 200 mL toluene and heated to  $80^\circ\text{C}$ . Subsequently a solution of **3b** (4.63 g, 0.015 mol) in 100 mL toluene was added. After refluxing for 24 h, the solution was filtered hot and the solvents removed under vacuum. Recrystallization from  $n$ -pentane at  $-30^\circ\text{C}$  leads to colorless crystals of **4b**. Yield: 1.53 g (0.004 mol, 83%). NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$   $^1\text{H}$ : 0.28 (s, 3 H,  $\text{CH}_3$ ), 5.35 (s, 1 H, NH);  $^{11}\text{B}$ :  $\delta$  24.5;  $^{13}\text{C}$ :  $\delta$   $-0.27$  ( $\text{CH}_3$ ), 110.2 ( $\text{B}-\text{C}\equiv\text{C}$ ), 129.3 ( $\text{B}-\text{C}\equiv\text{C}$ ). MS:  $m/z$  (% ion) = 369 (11, M), 354 (100,  $\text{M} - \text{CH}_3$ ).

***B,B',B''*-Tris(*E*-trichlorosilylvinyl)borazine ( $\beta$ -5).** To a solution of **4a** (5.03 g, 33 mmol) in toluene, 500 mg Pt/C

(1% wt, 0.026 mmol Pt) and  $\text{HSiCl}_3$  (30.3 mL, 0.3 mol) were added. After refluxing over 36 h, the Pt/C catalyst was removed by filtration and residual  $\text{HSiCl}_3$  and toluene removed under vacuum. The colourless oil was dried under vacuum (<0.1 mbar) for several hours to give the crude product as a mixture of isomers in quantitative yield. The main product  $\beta$ -**5** was obtained by fractional crystallization from hexane at  $-30^\circ\text{C}$  as colourless crystals. Yield: 14.7 g (26.4 mmol, 80%). NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$   $^1\text{H}$ : 4.60 (s, 1H, NH), 6.22 [d, 1H,  $\text{CH}=\text{CH}-\text{Si}$ ,  $^3J(\text{H,H}) = 21.3$  Hz], 6.85 [d, 1H,  $\text{CH}=\text{CH}-\text{Si}$ ,  $^3J(\text{H,H}) = 21.3$  Hz];  $^{11}\text{B}$ :  $\delta$  34.0;  $^{13}\text{C}$ :  $\delta$  137.4 ( $\text{CH}=\text{CH}-\text{Si}$ ), 153.6 ( $\text{CH}=\text{CH}-\text{Si}$ );  $^{29}\text{Si}$ :  $\delta$   $-3.2$ .  $^{11}\text{B}$  MAS (solid state):  $\delta$   $\sim 20$  ( $c_{\text{qcc}} = 1.9$  MHz). IR/ $\text{cm}^{-1}$ : 1582 (C=C); 1452, 1353 (B-N); 1000 (C=C-H). MS:  $m/z$  (% ion) = 559 (15, M), 524 (2, M - Cl), 424 (100, M -  $\text{SiCl}_3$ ), 398 (9, M-CH=CH-SiCl<sub>3</sub>).

**B,B',B''-Tris[tri(alkoxy)silylvinyl]borazines 6–8 via hydrosilylation of 4a with HSi(OR)<sub>3</sub>.** To a solution of **4a** (33 mmol) in toluene, 800 mg Pt/C (1% wt, 0.042 mmol Pt) and  $\text{HSi(OR)}_3$  (0.3 mol) were added. After refluxing over 48 h, the Pt/C catalyst was removed by filtration and residual  $\text{HSi(OR)}_3$  and toluene were removed under vacuum. The light yellow oil was dried under vacuum (<0.1 mbar) over several hours to give the products as a mixture of different isomers in quantitative yields.  $^{29}\text{Si}$  NMR shifts ( $\text{CDCl}_3$ ,  $\alpha/\beta$  isomer): **6**:  $\delta$   $-53.3/-56.2$ ; **7**:  $\delta$   $-55.5/-59.5$ ; **8**:  $\delta$   $-59.5/-63.0$ . IR/ $\text{cm}^{-1}$  (mixture of isomers): **6**: 1587 (C=C); 1474, 1344 (B-N); **7**: 1587 (C=C); 1471, 1390 (B-N); **8**: 1587 (C=C); 1470, 1378 (B-N). MS: **6**:  $m/z$  (% ion) = 519 (32, M), 397 [100, M -  $\text{HSi(OCH}_3)_3$ ]; **7**:  $m/z$  (% ion) = 645 (15, M), 616 (34, M -  $\text{C}_2\text{H}_5$ ), 481 [100, M -  $\text{HSi(OC}_2\text{H}_5)_3$ ]; **8**:  $m/z$  (% ion) = 771 (3, M), 756 (2, M -  $\text{CH}_3$ ), 565 [12, M -  $\text{HSi(OC}_2\text{H}_7)_3$ ] 258 (100).

**Silica gel (9).** 0.5 g (0.895 mmol) of **5** are dissolved in 10 mL thf and 2 mL (8.1 mmol)  $n\text{Bu}_3\text{N}$  were added. 26.9 mL of a 1.5 M  $\text{H}_2\text{O}$  in thf (4.03 mmol) were added dropwise at  $-10^\circ\text{C}$  under strong stirring. The reaction mixture was warmed to room temp. and stirred for 24 h whereby a colourless gel separated from the mixture. The solvent was removed and the gel was dried under vacuum (< 0.1 mbar). Subsequently, the solid was grounded with a pestle and transferred to an extraction apparatus. The material was extracted with thf for 15 h under inert atmosphere until all  $[n\text{Bu}_3\text{NH}]\text{Cl}$  was removed (monitored by IR). Drying at  $200^\circ\text{C}$  under high vacuum leads to a yellow powder of the silica gel (see photograph in Fig. 5). This material contains <0.1% Cl indicating complete substitution of the trichlorosilyl groups.

MAS NMR:  $^{11}\text{B}$ :  $\delta$   $\sim 24$  ( $c_{\text{qcc}} = 2.2$  MHz);  $^{13}\text{C}$ :  $\delta$  143 ( $w_{1/2} = 1200$  Hz);  $^{29}\text{Si}$ :  $\delta$   $-72$  ( $w_{1/2} = 1600$  Hz). Specific surface area (BET):  $315\text{ m}^2\text{ g}^{-1}$ . IR/ $\text{cm}^{-1}$ : 1590 (C=C); 1490, 1400 (B-N); 1000 (C=C-H and Si-O-Si).

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