DOI: 10.1002/adsc.200900029

Reaction of Bis(alkynyl)silanes with Tris(pentafluorophenyl)-borane: Synthesis of Bulky Silole Derivatives by Means of 1,1-Carboboration under Mild Reaction Conditions

Gereon Dierker,[a] Juri Ugolotti,[a] Gerald Kehr,[a] Roland Fröhlich,[a,b] and Gerhard Erker[a,*]

[a] Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, 48149 Münster, Germany
Fax: (+49)-251-833-6503; e-mail: erker@uni-muenster.de
[b] Address for correspondence concerning the X-ray crystal structure analyses.

Received: January 14, 2009; Revised: March 18, 2009; Published online: April 30, 2009

Dedicated to Professor Armin de Meijere on the occasion of his 70th birthday.

Supporting information for this article is available on the WWW under
http://dx.doi.org/10.1002/adsc.200900029.

Abstract: The strong Lewis acid tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] reacts rapidly with dimethylbis(phenylethynyl)silane (**1c**) at room temperature in toluene by shift of a pentafluorophenyl (C_6F_5) group and formation of a new carbon-bis(pentafluorophenyl)boron linkage [$C-B(C_6F_5)_2$] in a sequence of 1,1-carboboration reactions to yield the 4-bis(pentafluorophenyl)boryl/3-pentafluorophenyl-substituted 1,1-dimethyl-2,5-diphenylsilole derivative **7c**. The analogous reaction of bis(trimethylsilylethynyl)diphenylsilane (**1d**) with tris(pentafluorophenyl)borane gave the corresponding boryl-substituted silole derivative (**7d**) featuring six bulky substituents attached at the central heterocyclic framework. Both the starting materials (**1c**, **1d**) and the products (**7c**, **7d**) were characterized by X-ray crystal structure analyses.

Keywords: boranes; 1,1-carboboration; Lewis acids; siloles

Introduction

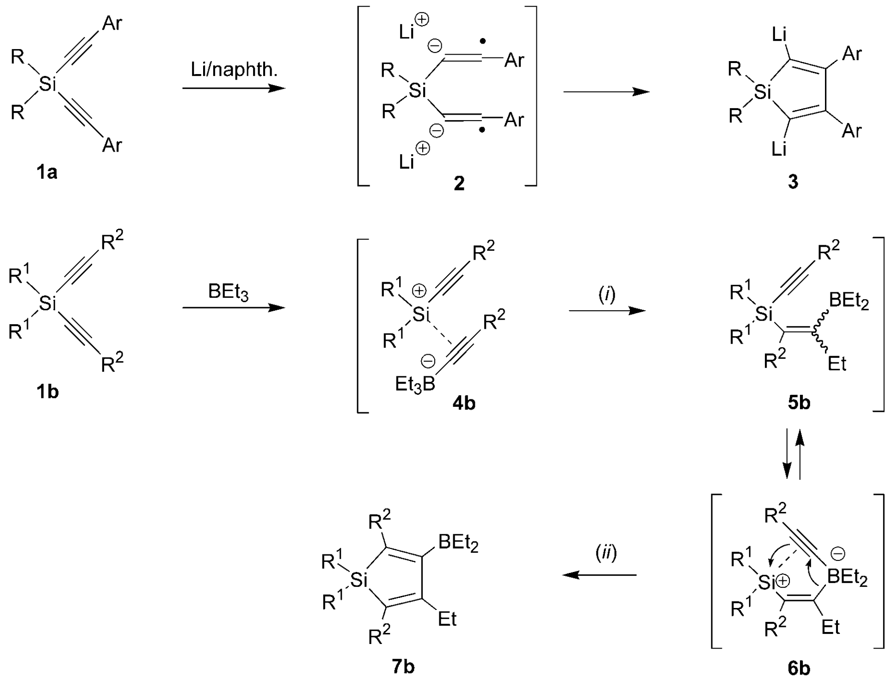
The synthetic chemistry of siloles has found increased interest lately.[1,2] This is mostly due to their use in modern materials chemistry. Suitably substituted silole derivatives have found extensive use due to their photoluminescent properties.[1b,c,3–7] Some derivatives were used as sensor materials.[8]

Early synthetic entries to siloles[9] include salt metathesis routes, e.g., by reacting substituted 1,4-dilithiobutadiene reagents with R_2SiCl_2 substrates.[10,11] A related route was used more recently to prepare lithiosiloles.[12] Other work reported in the last 15 years makes use of the ready formation of the group 4 metallacyclopentadienes[13] and related complexes[14] followed by direct or indirect transmetallation from titanium or zirconium to silicon.[15]

Tamao et al. developed an ingenious method of silole formation from bis(alkynyl)silanes (**1a**) by treatment with Li/naphthalene.[16] The formation of the silole products (**3**) probably takes place by means of an intramolecular ring closure of a bis-radical anion intermediate (**2**) (see Scheme 1). This route has extensively been applied for the preparation of novel silole-based electronic materials.[6,7a,b,d–f,h]

In this context, boron- and silicon-containing systems have become of interest, and easy accesses to specifically functionalized boryl-substituted siloles or similar compounds are becoming increasingly important.[17] Wrackmeyer et al. have developed and described a fascinating one-pot procedure for the preparation of boryl-substituted silole derivatives (**7b**) by treatment of a bis(alkynyl)silane (**1b**) with, for example, triethylborane.[1a,2a,18,19] The unique reaction sequence involves alkynyl abstraction/1,1-carboboration followed by a 1,1-alkenylboration step to directly lead to the boryl-functionalized silole derivative (see Scheme 1).[20] Unfortunately, the reaction with simple alkylboranes often requires elevated temperatures (*ca.* 100 °C).

When more reactive boranes were used (e.g., triallylborane, 1-boraadamantane) the reaction conditions



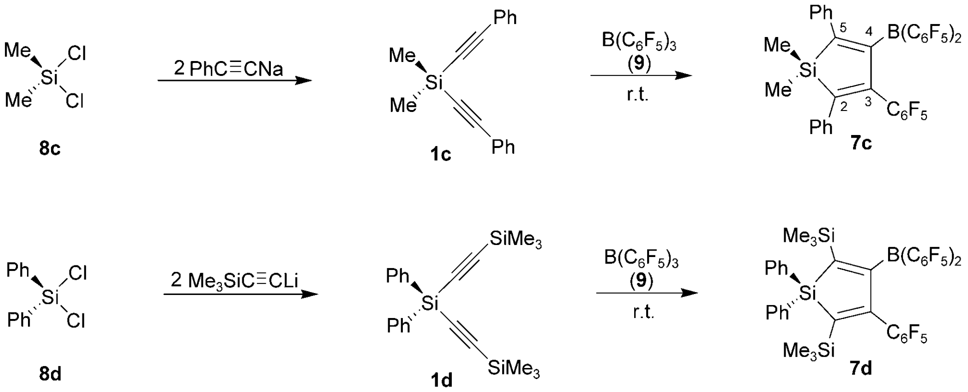
Scheme 1. (*i*): 1,1-ethylboration, (*ii*): 1,1-alkenylboration.

of the 1,1-organoboration reactions were milder but sometimes the formation of side products took place.[21] We have now found that this general reaction sequence can very favourably be used for the synthesis of substituted siloles containing a combination of C_6F_5 and $B(C_6F_5)_2$ groups that are probably of great advantage in the respective areas of silole-derived materials science. We describe two representative examples in this article.

Results and Discussion

Following procedures reported in the literature, we have prepared the known dimethylbis(phenylethynyl)silane (**1c**)[22] by treatment of Me_2SiCl_2 (**8c**) with the phenylethynylsodium reagent in tetrahydrofuran. After filtering off the precipitated sodium chloride, the product (**1c**) was obtained as a colorless solid in *ca.* 40% yield. The more bulky bis(trimethylsilylethynyl)diphenylsilane[23] (**1d**, see Scheme 2) was prepared analogously by treatment of trimethylsilylethynyllithium with Ph_2SiCl_2 (**8d**). The product (**1d**) was obtained as an oil which solidified upon standing at ambient temperature. It was isolated in 77% yield.

The identity of the known compounds **1c** and **1d** was confirmed spectroscopically. In addition, the two compounds were characterized by X-ray diffraction. Single crystals of both compounds suitable for the X-ray crystal structure analysis were obtained from diethyl ether. Compound **1c** features a pseudotetrahe-



Scheme 2.

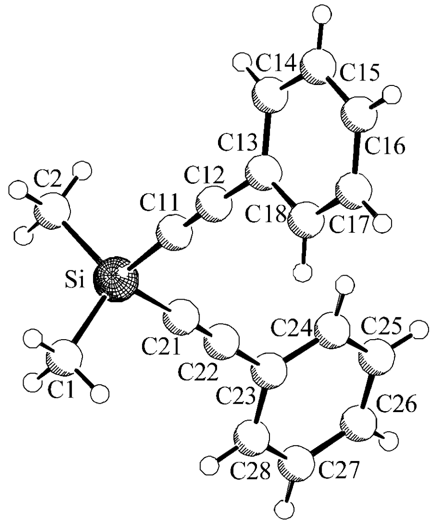


Figure 1. A view of the bis(phenylethynyl)dimethylsilane compound **1c**. Selected bond lengths (Å) and angles (°): Si–C1 1.843(2), Si–C2 1.848(2), Si–C11 1.830(2), Si–C21 1.835(2), C11–C12 1.201(3), C21–C22 1.204(2), C11–Si–C21 106.4(1), C1–Si–C2 112.4(1), C12–C11–Si 177.7(2), C11–C12–C13 177.7(2).

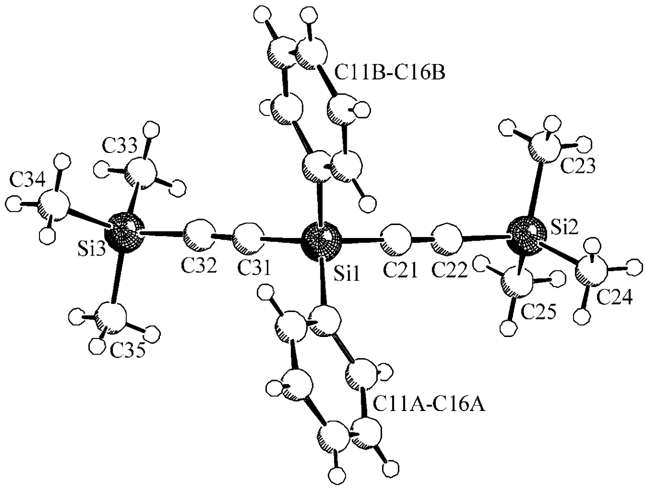


Figure 2. Molecular structure of **1d**. Selected bond lengths (Å) and angles (°): Si1–C21 1.831(2), Si1–C31 1.831(2), C21–C22 1.208(2), C31–C32 1.203(2), Si2–C22 1.846(2), Si3–C32 1.847(2), Si1–C11A 1.867(2), Si1–C11B 1.870(2), C21–Si1–C31 108.0(1), C22–C21–Si1 176.6(2), C21–C22–Si2 177.2(2).

dral coordination geometry around the central silicon atom (see Figure 1). The Si–C(*sp*^{3}) bond lengths are slightly longer than the Si–C(*sp*) bond lengths, as expected. The C1–Si–C2 angle between the methyl–Si vectors is markedly larger than the C11–Si–C21 angle of the acetylide substituents at silicon. Compound **1c** exhibits short C≡C bonds. The acetylide units are nearly linear, as expected. The planes of the terminal phenyl substituents form an angle of 92.6°. The phenyl groups are located close to in-plane with their respective Si–CH_3 vectors [dihedral angles C1–Si···C23–C28: 26.6°, C2–Si···C13–C14: −10.4°)].

Compound **1d** has a very similar structure (see Figure 2). The Si–C(*sp*) σ-bond lengths of **1d** are almost the same as found for **1c** (see above). The corresponding C21–Si1–C31 angle amounts to 108.0(1)°. The C≡C triple bonds again are short, and the terminal C(*sp*)–Si bonds are slightly longer than the internal ones. The Si–C≡C–Si units are nearly linear. The situation around the central silicon atom Si1 is rather crowded. This leads to rather long Si–C(*sp*^{2}, aryl) bond lengths. The angle between the phenyl planes in **1d** amounts to 50.6°.

The reaction of compound **1c** with one molar equivalent of tris(pentafluorophenyl)borane (**9**)[24] was performed in toluene at room temperature. In contrast to the reactions of bis(alkynyl)silanes with the much less Lewis acidic trialkylboranes (see above) rapid silole formation takes place with the strong Lewis acid B(C_6F_5)$_3$[25] at ambient conditions. After work-up and crystallization from pentane the product **7c** was isolated in 36% yield.

Silole formation also takes place readily upon treatment of the sterically more congested bis(trimethylsilylethynyl)diphenylsilane substrate (**1d**) with the tris(pentafluorophenyl)borane reagent (**9**) at ambient temperature. After work-up and crystallization from pentane the B(C_6F_5)$_2$/C_6F_5-substituted silole derivative **7d** was isolated in 35% yield (see Scheme 2).

Both products **7c** and **7d** were characterized spectroscopically and by X-ray diffraction (single crystals from pentane). The silole **7c** shows a ^{29}Si NMR signal at $\delta = +9.8$, which occurs downfield from the corresponding ^{29}Si NMR resonance of the starting material **1c** ($\delta = -39.4$).[26] It features two sets of *o*-, *p*- and *m*-C_6F_5 ^{19}F NMR signals in a 2:1 ratio, namely of the Lewis acidic -B(C_6F_5)$_2$ substituent, with a typically rather large $\Delta\delta(m/p)$ separation[27] and the signals of the single carbon bound C_6F_5 group. The ^{13}C NMR signals of the four "quarternary" ring carbon atoms C2 to C5 were located at $\delta = 152.3$, 136.7, 161.9 (adjacent to B), and 165.5. The UV/Vis spectrum of compound **7c** shows absorptions at λ_{max} (log ε) = 305 (4.41) and 231 (4.27) nm and a corresponding feature at $\lambda_{max} = 390$ nm in the emission spectrum. The more bulky compound **7d** features overlapping UV/Vis absorptions at λ_{max} (log ε) = 234 (4.73), 262 (4.47) and 274 (4.50) nm and emission bands at $\lambda_{max} = 402$ and 390 nm. The absorption data are similar to results observed previously in siloles carrying perfluorinated aryl groups in positions 2 and 5,[4c] whereas the emission spectra show a shift to the ultraviolet region when compared to related systems.[6,7] Compound **7d** shows three characteristic ^{29}Si NMR resonances, namely that of the ring silicon atom at $\delta = +17.6$ and a pair of resonances at $\delta = -9.0/-8.3$ attributed to the

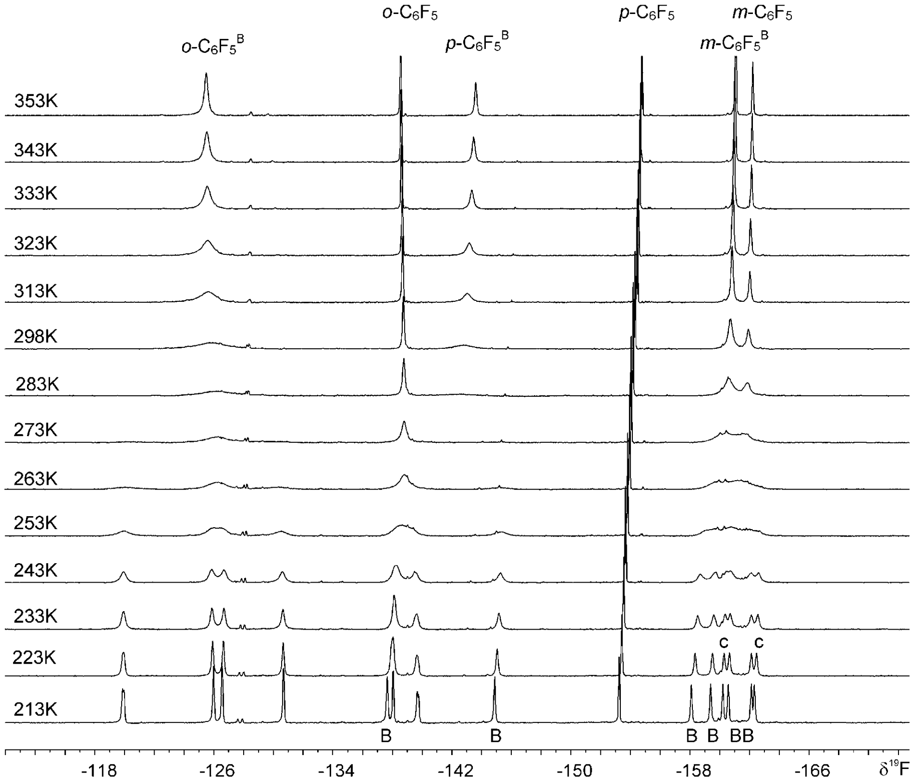


Figure 3. ^{19}F NMR spectra (470 MHz, C_7D_8, $CFCl_3$) of **7d** at various temperatures.

chemically inequivalent $SiMe_3$ substituents. The ^{13}C NMR signals of the ring carbon atoms C2–C5 of **7d** occur at $\delta = 154.9$, 150.2, 176.8 and 161.5. At 298 K there is one set of broad ^{19}F NMR resonances of the C_6F_5 substituent [$\delta = -138.7$ (2F, *o*), -154.3 (1F, *p*), -161.9 (2F, *m*)], as well as another for the $B(C_6F_5)_2$ group [$\delta = -126.0$ (4F, *o*), $\delta = -142.8$ (2F, *p*), $\delta = -160.7$ (4F, *m*)]. Due to the steric congestion caused by the presence of bulky vicinal $SiMe_3$ and $B(C_6F_5)_2$ substituents at the planar five-membered framework the silole **7d** features hindered rotation around the C4–B vector[28] [$\Delta G^{\neq} \approx 11.3 \pm 0.2$ kcal mol^{-1}], the B–$C_{ipso}(C_6F_5)$ vectors [$\Delta G^{\neq} \approx 11.5 \pm 0.2$ kcal mol^{-1}] and the C3–$C_{ipso}(C_6F_5)$ vector [$\Delta G^{\neq} \approx 11.4 \pm 0.2$ kcal mol^{-1}]. Consequently, pairwise decoalescence of all *o*- and *m*-F ^{19}F NMR signals, as well as the $B(C_6F_5)_2$ *p*-F ^{19}F NMR signals was observed upon monitoring the ^{19}F NMR spectrum of **7d** in toluene-d_8 at 213 K (see Figure 3, for details see the Supporting Information).

The X-ray crystal structure analysis of compound **7c** (see Figure 4) has revealed the presence of a planar five-membered silole framework with an alternating unsaturated C_4 section. The Me_2Si unit completes the silole framework. The C11A–Si1–C11B angle of the germinal dimethylsilylene unit is much larger and the respective Si–CH_3 bonds are slightly shorter compared to the endocyclic $Si(C_2)$ unit. The phenyl substituents attached at carbon atoms C2 and

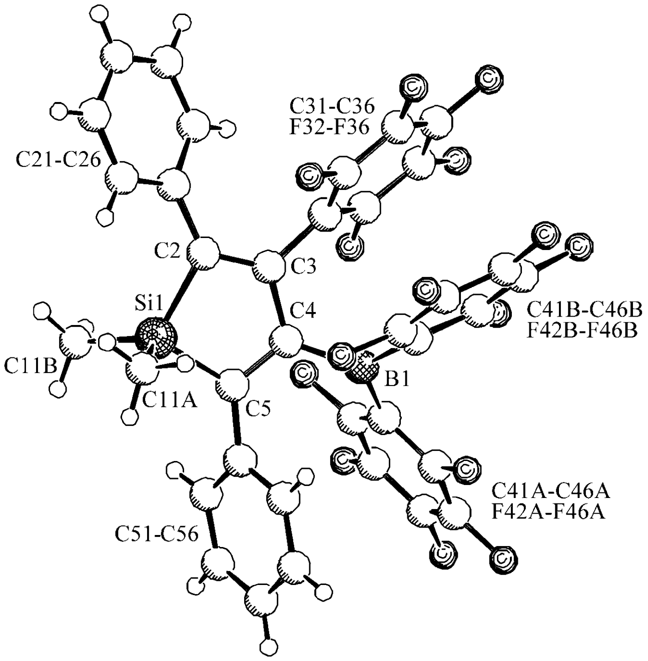


Figure 4. Molecular geometry of compound **7c**. Selected bond lengths (Å) and angles (°): C2–C3 1.353(3), C3–C4 1.508(3), C4–C5 1.358(3), Si–C2 1.888(3), Si–C5 1.874(2), Si–C11A 1.866(3), Si–C11B 1.851(3), C3–C31 1.497(3), C4–B1 1.554(4), C2–Si1–C5 91.5(1), C11A–Si1–C11B 111.5(2), B1–C4–C3 122.6(2), C4–C3–C31 118.2(2), C4–B1–C41A 122.6(2), C4–B1–C41B 116.8(2), C41A–B1–C41B 120.6(2).

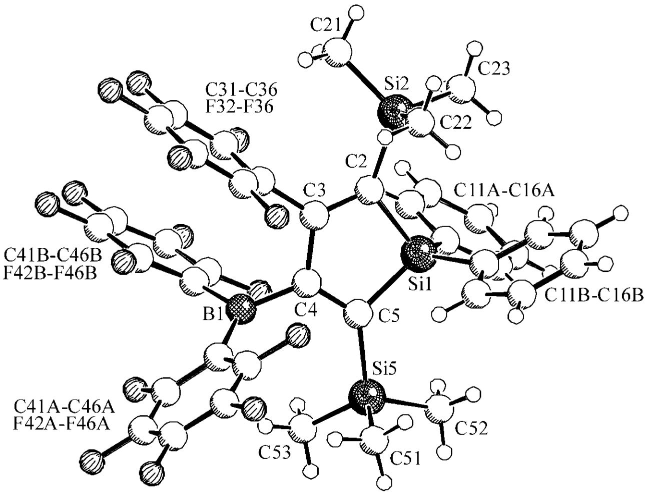


Figure 5. A projection of the molecular structure of compound **7d** in the crystal. Selected bond lengths (Å) and angles (°): C2–C3 1.345(3), C3–C4 1.515(3), C4–C5 1.368(3), Si1–C2 1.879(2), Si1–C5 1.891(2), Si1–C11A 1.874(2), Si1–C11B 1.871(2), Si2–C2 1.885(2), Si5–C5 1.879(2), C3–C31 1.506(3), C4–B1 1.561(3), C2–Si1–C5 94.6(1), C11A–Si1–C11B 112.4(1), C3–C2–Si2 128.6(2), C4–C5–Si5 128.5(1).

C5 are found markedly rotated from the central SiC_4 ring plane [dihedral angles: C3–C2–C21–C22 −147.3(3)°, C4–C5–C51–C52: 57.2(4)°]. A single C_6F_5 substituent is attached at C3. It is rotated markedly relative to the central silole plane [θ C4–C3–C31–C32: −122.9(2)°]. The bulky $B(C_6F_5)_2$ group is attached at the adjacent ring carbon atom C4 [dihedral angle C31–C3–C4–B1: 11.9(3)°]. The electron-deficient boron center is planar-tricoordinate (sum of bond angles at boron: 360.0°). The $B(C_6F_5)_2$ unit is rotated markedly relative to the central silole plane [θ C5–C4–B1–C41A: 52.3(4)°, C5–C4–B1–C41B: −128.7(2)°] and the individual C_6F_5 groups are found in a propeller-like conformation [θ C4–B1–C41A–C42A: 31.7(4)°, C4–B1–C41B–C42B: 40.9(3)°].

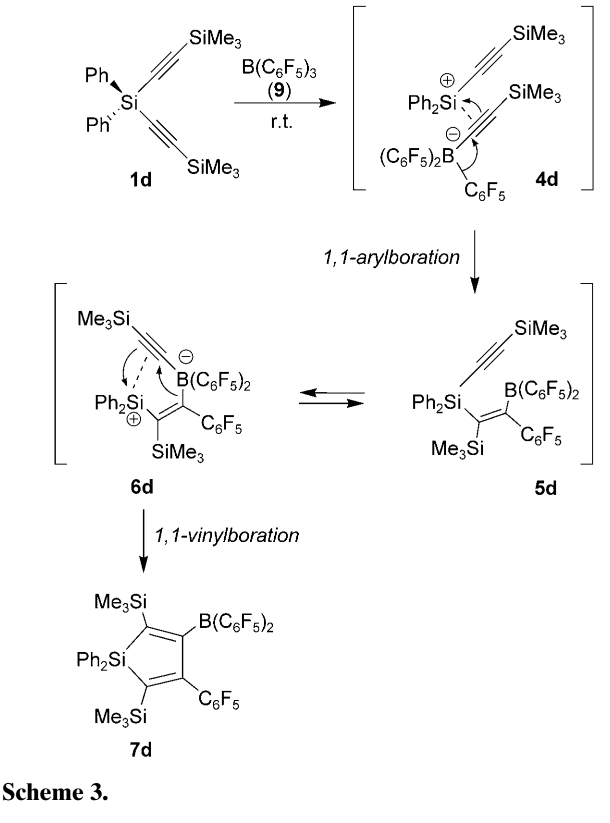
In the crystal, compound **7d** features a rather crowded periphery of substituents around the central five-membered ring core (see Figure 5). The framework again shows bond alternation among the carbon-carbon linkages, which is supplemented by a pair of long Si1–C2/C5 endocyclic bonds. The exocyclic Si1–C(aryl) bonds are only slightly shorter. The steric bulk appears in rather large C3–C2–Si2 [128.6(2)°] and C4–C5–Si5 [128.5(1)°] bond angles. The single C_6F_5 substituent at C3 is rotated toward a perpendicular orientation to the central silole ring [θ C2–C3–C31–C32: −97.2(2)°] as is the coordination plane of the $B(C_6F_5)_2$ substituent at C4 [sum of bond angles at B1: 359.8(2)°, θ C5–C4–B1–C41A: 70.0(3)°, C5–C4–B1–C41B: −115.7(2)°].

Conclusions

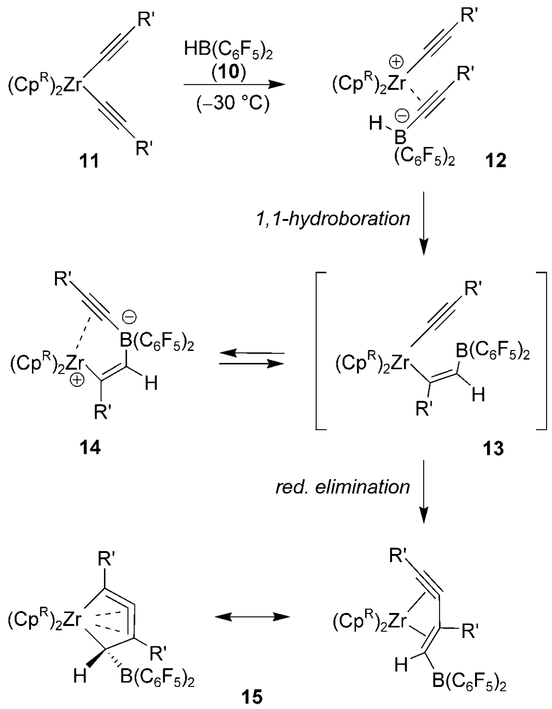
Our new variant of the "Wrackmeyer reaction"[1a,c,2a,18] can apparently be used to construct highly substituted and functionalized boryl-silole systems under mild reaction conditions. Even the formation of the highly sterically crowded derivative **7d** proved to be unproblematic. It is remarkable how easily these reactions proceed to form products with an accumulation of very bulky substituents all around the periphery of the central five-membered silole framework.

We assume that the products **7c** and **7d** are formed by means of a reaction pathway as it is schematically depicted in Scheme 3. The rate enhancement upon employing $B(C_6F_5)_3$ instead of, for example, Et_3B may be due to the markedly increased Lewis acidity of this boron reagent,[25,29] resulting in a lowering of the barrier of acetylide abstraction in the initial 1,1-carboboration step – actually an intermediate (**12**, see Scheme 4) conceptually related to **4c**/**4d** was recently isolated by us from the reaction of a bis(acetylide)zirconocene complex (**11**) with $HB(C_6F_5)_2$ (**10**).[30]

The X-ray crystal structure analyses and the NMR spectra have revealed that there is no significant C-(sp^2)–B conjugation present in **7c** or **7d**, quite different from remotely related five-membered group 4 metallacyclic compounds (e.g., **15**, see Scheme 4) that were recently prepared by similar reaction sequences.[31,32]



Scheme 3.



Scheme 4.

The use of boranes of enhanced Lewis acidities seems to help carrying out the synthetic sequences under mild conditions that include variants of the unusual 1,1-carboboration reaction. It might be worthwhile to investigate advanced variations of this interesting reaction type for the preparation of new heterocyclic systems, for example of interest for applications in materials chemistry on a broader scale.

Experimental Section

In all preparations, the air- and moisture-sensitive compounds were synthesized and handled under an argon atmosphere using standard glove-box and Schlenk techniques. Anhydrous solvents were used in all the preparations. The solvents were passed through alumina columns under an argon atmosphere, the deuterated solvents were distilled from drying agents and stored under argon. For the NMR experiments, C_6D_6 (room temperature measurements) and toluene-d_8 (variable temperature) were used. The physical characterization of the products was performed using the following instruments: NMR: Bruker AC 200 P-FT (^{11}B: 64 MHz), Bruker ARX 300 (^{11}B: 96 MHz), Varian Inova 500 (^{1}H: 500 MHz; ^{13}C: 126 MHz; ^{11}B: 161 MHz; ^{19}F: 470 MHz; ^{29}Si: 99 MHz), Varian Unity Plus 600 (^{1}H: 600 MHz; ^{13}C: 151 MHz; ^{19}F: 564). References: TMS for ^{1}H, ^{13}C and ^{29}Si NMR, $BF_3{\cdot}OEt_2$ for ^{11}B NMR, $CFCl_3$ for ^{19}F NMR. Most NMR assignments were supported by additional 2D experiments. IR spectra: Varian 3100 FT-IR (EXCALIBUR Series) spectrometer. Elemental analyses: Foss-Heraeus CHN-O-Rapid instrument. Exact mass determination: GTC Waters Micromass (Manchester, UK). UV/Vis: UV double-ray spectrometer Uvikon 923 (Kontron Instruments, Zürich, Switzerland), using SUPRASIL Quarz glass (200–2500 nm). Fluorescence spectra: spectrofluorometer AMINCO-Bowman Series 2 (AB2) (Thermo Fischer Scientific Inc., Waltham, USA), with excitation at 350 nm, using SUPRASIL Quarz glass cuvette (200–2500 nm). $B(C_6F_5)_3$[23b] was prepared according to procedures reported in the literature (***caution:*** *the intermediate involved is explosive*). X-ray crystal structure analyses: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN,[33] absorption correction Denzo,[34] structure solution SHELXS-97,[35] structure refinement SHELXL-97,[36] graphics SCHAKAL (E. Keller, Univ. Freiburg, 1997).

CCDC 715065, 715066, 715067 and 715068 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-(1223)-336-033, E-mail: deposit@ccdc.cam.ac.uk].

Dimethylbis(phenylethynyl)silane[22] (1c) and Bis(trimethylsilylethynyl)diphenylsilane[23] (1d)

These compounds were prepared analogously as described in the literature (for details see the Supporting Information).

X-ray crystal structure analysis of 1c (single crystals were obtained from a diethyl ether solution): formula $C_{18}H_{16}Si$, $M=260.40$, colourless crystal $0.55\times0.15\times0.10$ mm, $a=14.709(1)$, $b=11.454(1)$, $c=18.613(1)$ Å, $V=3135.9(4)$ Å^3, $\rho_{calcd.}=1.103$ g cm^{-3}, $\mu=1.173$ mm^{-1}, empirical absorption correction ($0.565\leq T\leq0.892$), $Z=8$, orthorhombic, space group *Pbca* (No. 61), $\lambda=1.54178$ Å, $T=223$ K, ω and ϕ scans, 12740 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]=0.58$ Å^{-1}, 2475 independent ($R_{int}=0.041$) and 2179 observed reflections [$I\geq2\ \sigma(I)$], 174 refined parameters, $R=0.040$, $wR^2=0.109$, max. residual electron density 0.22 (–0.19) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

X-ray crystal structure analysis of 1d (single crystals were obtained from a diethyl ether solution): formula $C_{22}H_{28}Si_3$, $M=376.71$, colourless crystal $0.50\times0.45\times0.40$ mm, $a=18.706(1)$, $b=10.077(1)$, $c=12.444(1)$ Å, $\beta=90.78(1)°$, $V=2345.5(3)$ Å^3, $\rho_{calcd.}=1.067$ g cm^{-3}, $\mu=1.860$ mm^{-1}, empirical absorption correction ($0.457\leq T\leq0.523$), $Z=4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda=1.54178$ Å, $T=293$ K, ω and ϕ scans, 19157 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]=0.60$ Å^{-1}, 4111 independent ($R_{int}=0.035$) and 3823 observed reflections [$I\geq2\ \sigma(I)$], 232 refined parameters, $R=0.040$, $wR^2=0.109$, max. residual electron density 0.26 (–0.20) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

4-[Bis(pentafluorophenyl)boryl]-3-pentafluorophenyl-1,1-dimethyl-2,5-diphenylsilole (7c).

Dimethylbis(phenylethynyl)silane (**1c**) (100 mg, 0.384 mmol) and tris(pentafluorophenyl)borane (**9**) (197 mg, 0.384 mmol) were weighed in an argon-filled glove-box and put into a 100-mL Schlenk flask under argon. Toluene (70 mL) was added to the flask at room temperature by cannula and the resulting bright yellow solution was stirred overnight. The volatiles were removed under vacuum, leaving a yellow oily product. The product was crystallised at −30 °C from pentane (2 mL) (107 mg, 36%). Crystals suitable for single-crystal X-ray diffraction were obtained in a NMR tube by slow evaporation of C_6D_6. ^{1}H NMR (500 MHz, C_6D_6, 298 K): $\delta=$ 7.00 (m, 4-H, *o*,*m*-Ph^{2}), 6.97 (m, 2H, *o*-Ph^{5}), 6.93 (m, 1H, *p*-Ph^{2}), 6.85 (m, 2H, *m*-Ph^{5}), 6.74 (m, 1H, *p*-Ph^{5}), 0.22 (s, $^{2}J_{\mathrm{Si,H}}=7.0$ Hz, 6H, SiMe$_2$); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): $\delta=165.5$ (C5), 161.9 (br, C4), 152.3 (C2), 147.9 (dm, $^{1}J_{\mathrm{F,C}}\approx252$ Hz, $C_6F_5{}^{B}$), 143.8 (dm, $^{1}J_{\mathrm{F,C}}\approx$ 248 Hz, $C_6F_5{}^{B}$), 143.8 (dm, $^{1}J_{\mathrm{F,C}}\approx248$ Hz, C_6F_5), 141.4 (*i*-Ph^{5}), 140.7 (dm, $^{1}J_{\mathrm{F,C}}\approx257$ Hz, C_6F_5), 138.7 (*i*-Ph^{2}), 137.6 (dm, $^{1}J_{\mathrm{F,C}}\approx253$ Hz, C_6F_5), 137.4 (dm, $^{1}J_{\mathrm{F,C}}\approx253$ Hz, $C_6F_5{}^{B}$), 136.7 (C3), 129.0 (*m*-Ph^{2}), 128.5 (*m*-Ph^{5}), 128.5 (*p*-Ph^{5}), 128.1 (*o*-Ph^{5}), 127.6 (*p*-Ph^{2}), 127.1 (*o*-Ph^{2}), 115.4 (*i*-C_6F_5), 114.5 (br, *i*-$C_6F_5{}^{B}$), −5.4 ($^{1}J_{\mathrm{Si,C}}=51.5$ Hz, SiMe$_2$) [tentative assignment for positions 2 and 5]; ^{19}F NMR (470 MHz, C_6D_6, 298 K, CFCl$_3$): $\delta=-128.2$ (br, 4 F, *o*-F), −145.7 (tt, $^{3}J_{\mathrm{F,F}}=20.7$ Hz, $^{4}J_{\mathrm{F,F}}=5.7$ Hz, 2F, *p*-F), −161.5 (br, 41F, *m*-F) [B(C_6F_5)$_2$], −138.3 (m, 2F, *o*-F), −154.4 (t, $^{3}J_{\mathrm{F,F}}=20.9$ Hz, 1F, *p*-F), −161.9 (m, 2F, *m*-F) (C_6F_5).; ^{29}Si{DEPT} NMR (99 MHz, C_6D_6, 298 K): $\delta=9.8$; UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (ε) = 305 (25700), 231 (18620) nm; fluorescence (CH$_2$Cl$_2$); $\lambda_{\max}=390$ nm; anal. calcd. for $C_{36}H_{16}BF_{15}Si$ (772.4): C 55.98, H 2.09; found: C 55.73, H 1.93%.

X-ray crystal structure analysis of 7c: formula $C_{36}H_{16}BF_{15}Si$, $M=772.39$, yellow crystal 0.20×0.15×0.03 mm, $a=15.928(1)$, $b=9.076(1)$, $c=23.222(1)$ Å, $\beta=104.03(1)°$, $V=3256.9(4)$ Å^3, $\rho_{\mathrm{calcd.}}=1.575$ g cm^{-3}, $\mu=1.686$ mm^{-1}, empirical absorption correction ($0.729\le T\le0.951$), $Z=4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda=1.54178$ Å, $T=223$ K, ω and ϕ scans, 46761 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 5811 independent ($R_{\mathrm{int}}=0.081$) and 4504 observed reflections [$I\ge2\,\sigma(I)$], 480 refined parameters, $R=0.046$, $wR^2=0.107$, max. residual electron density 0.31 (−0.26) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

4-[Bis(pentafluorophenyl)boryl]-3-pentafluorophenyl-2,5-bis(trimethylsilyl)-1,1-diphenylsilole (7d)

Bis(trimethylsilylethynyl)diphenylsilane (**1d**) (0.88 g, 2.34 mmol) and tris(pentafluorophenyl)borane (**9**) (1.20 g, 2.34 mmol) were weighed in an argon-filled glove-box and placed into a 100-mL Schlenk flask. Toluene (30 mL) was added at room temperature and the yellow solution was stirred overnight. Then the volatiles were removed under vacuum, leaving a yellow glue-like product. Pentane (4 mL) was added, and the product dissolved completely with stirring under argon. After 30 min, the volume was reduced to 2 mL by reduced pressure, and the resulting yellow solution was stored at −30 °C. Part of the product crystallised overnight and was filtered off while kept at −30 °C, to avoid redissolution. The filtrate was stored again at −30 °C, affording more crystalline product in 14 days; total yield: 0.721 g (35%). Crystals suitable for single-crystal X-ray diffraction were obtained at −30 °C from a concentrated pentane solution. ^{1}H NMR (500 MHz, C_6D_6, 298 K): $\delta=7.93$ (m, 4H, *o*-Ph), 7.22 (m, 4H, *m*-Ph), 7.19 (m, 2H, *p*-Ph), −0.25 (s, $^{2}J_{\mathrm{Si,H}}=6.5$ Hz, 9H, 5-SiMe$_3$), −0.30 (s, 9H, $^{2}J_{\mathrm{Si,H}}=6.6$ Hz, 2-SiMe$_3$); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): $\delta=176.8$ (C4), 161.5 (C5), 154.9 (C2), 150.2 (C3), 148.9 (dm, $^{1}J_{\mathrm{F,C}}\approx254$ Hz, 4×CF), 145.1 (dm, $^{1}J_{\mathrm{F,C}}\approx260$ Hz, 2×CF), 143.6 (dm, $^{1}J_{\mathrm{F,C}}\approx245$ Hz, 2×CF), 141.0 (dm, $^{1}J_{\mathrm{F,C}}\approx256$ Hz, CF), 137.7 (dm, $^{1}J_{\mathrm{F,C}}\approx254$ Hz, 6×CF) (C_6F_5), 135.7 (*o*-Ph), 131.0 (*p*-Ph), 130.6 (*i*-Ph), 128.8 (*m*-Ph), 118.7 (*i*-C_6F_5), 113.9 (br, *i*-$C_6F_5{}^{B}$), 1.5 [$^{1}J_{\mathrm{Si,C}}=52.3$ Hz, 5-Si(CH$_3$)$_3$], −0.3 [$^{1}J_{\mathrm{Si,C}}=52.7$ Hz, 2-Si(CH$_3$)$_3$]; ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 298 K): $\delta=17.6$ (SiPh$_2$), −8.3 (2-Si), −9.0 (5-Si) [tentative assignment for positions 2 and 5]; ^{19}F NMR (470 MHz, C_7D_8, 298 K, CFCl$_3$): $\delta=-126.0$ (br, 4F, *o*-F), −142.8 (br, 2F, *p*-F), −160.7 (br, 4F, *m*-F) [B(C_6F_5)$_2$], −138.7 (br, 2F, *o*-F), −154.3 (t, $^{3}J_{\mathrm{F,F}}=20.8$ Hz, 1F, *p*-F), −161.9 (br, 2F, *m*-F) (C_6F_5); ^{19}F NMR (470 MHz, C_7D_8, 213 K, CFCl$_3$): $\delta=$ −119.9, −126.0 (each m, each 1F, *o*-F), −137.7 (br, 1F, *p*-F), −159.4, −160.6 (each br, each 1F, *m*-F), −126.6, −130.7 (each m, each 1F, *o*-F), −144.9 (br, 1F, *p*-F), −158.1, −162.1 (each br, each 1F, *m*-F) [B(C_6F_5)$_2$], −138.1, −139.8 (each m, each 1F, *o*-F), −153.2 (br, 1F, *p*-F), −160.2, −162.3 (each br, each 1F, *m*-F) (C_6F_5); ^{19}F NMR (470 MHz, C_7D_8, 353 K, CFCl$_3$): $\delta=-125.4$ (br, 4F, *o*-F), −143.6 (br, 2F, *p*-F), −161.1 (m, 4F, *m*-F) [B(C_6F_5)$_2$], −138.5 (m, 2F, *o*-F), −154.8 (t, $^{3}J_{\mathrm{F,F}}=20.3$ Hz, 1F, *p*-F), −162.2 (m, 2F, *m*-F) (C_6F_5). UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (ε) = 274 (31620), 262 (29500), 234 (53700) nm; fluorescence (CH$_2$Cl$_2$); $\lambda_{\max}=390$, 402 (sh) nm; anal. calcd. for $C_{40}H_{28}BF_{15}Si_3$ (888.7): C 54.06, H 3.17; found: C 53.99, H 3.37%.

X-ray crystal structure analysis of 7d: formula $C_{40}H_{28}BF_{15}Si_3$, $M=888.70$, colourless crystal 0.30×0.25×0.25 mm, $a=11.7473(3)$, $b=37.8490(8)$, $c=9.1945(2)$ Å, $\beta=92.531(1)°$, $V=4084.1(2)$ Å^3, $\rho_{\mathrm{calcd.}}=1.445$ g cm^{-3}, $\mu=1.962$ mm^{-1}, empirical absorption correction ($0.591\le T\le0.640$), $Z=4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda=1.54178$ Å, $T=223$ K, ω and ϕ scans, 39467 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 7242 independent ($R_{\mathrm{int}}=0.044$) and 6708 observed reflections [$I\ge2\,\sigma(I)$], 538 refined parameters, $R=0.043$, $wR^2=0.118$, max. residual electron density 0.30 (−0.25) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

References

[1] For recent reviews, see: a) S. Yamaguchi, K. Tamao, *J. Chem. Soc. Dalton Trans.* **1998**, 3693–3702, and references therein; b) M. Hissler, P. W. Dyer, R. Réau, *Coord. Chem. Rev.* **2003**, *244*, 1–44; c) B. Wrackmeyer, *Heteroat. Chem.* **2006**, *17*, 188–208.

[2] See also: a) J. Dubac, A. Laporterie, G. Manuel, *Chem. Rev.* **1990**, *90*, 215–263; b) E. Colomer, R. J. P. Corriu, M. Lheureux, *Chem. Rev.* **1990**, *90*, 265–282; c) B. Wrackmeyer, *Coord. Chem. Rev.* **1995**, *145*, 125–156.

[3] a) S. Yamaguchi, Y. Itami, K. Tamao, *Organometallics* **1998**, *17*, 4910 – 4916; b) S. Yamaguchi, T. Endo, M. Uchida, T. Izumizawa, K. Furukawa, K. Tamao, *Chem. Eur. J.* **2000**, *6*, 1683 – 1692; c) S. Yamaguchi, K. Tamao, *Chem. Lett.* **2005**, *34*, 2 – 7.

[4] a) X. Zhan, C. Risko, F. Amy, C. Chan, W. Zhao, S. Barlow, A. Kahn, J.-L. Brédas, S. R. Marder, *J. Am. Chem. Soc.* **2005**, *127*, 9021 – 9029; b) M. M. Sartin, A. J. Boydston, B. L. Pagenkopf, A. J. Bard, *J. Am. Chem. Soc.* **2006**, *128*, 10163 – 10170; c) K. Geramita, J. McBee, Y. Shen, N. Radu, T. D. Tilley, *Chem. Mater.* **2006**, *18*, 3261 – 3269; d) C. Booker, X. Wang, S. Haroun, J. Zhou, M. Jennings, B. L. Pagenkopf, Z. Ding, *Angew. Chem.* **2008**, *120*, 7845 – 7849; *Angew. Chem. Int. Ed.* **2008**, *47*, 7731 – 7735.

[5] V. N. Khabashesku, V. Balaji, S. E. Boganov, O. M. Nefedov, J. Michl, *J. Am. Chem. Soc.* **1994**, *116*, 320 – 329.

[6] a) K. Tamao, S. Yamaguchi, Y. Ito, Y. Matsuzaki, T. Yamabe, M. Fukushima, S. Mori, *Macromolecules* **1995**, *28*, 8668 – 8675; b) S. Yamaguchi, K. Tamao, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2327 – 2334; c) K. Tamao, S. Ohno, S. Yamaguchi, *Chem. Commun.* **1996**, 1873 – 1874.

[7] See also: a) K. Tamao, M. Uchida, T. Izumizawa, K. Furukawa, S. Yamaguchi, *J. Am. Chem. Soc.* **1996**, *118*, 11974 – 11975; b) S. Yamaguchi, K. Tamao, *J. Organomet. Chem.* **2002**, *653*, 223 – 228; c) J. Chen, C. C. W. Law, J. W. Y. Lam, Y. Dong, S. M. F. Lo, I. D. Williams, D. Zhu, B. Z. Tang, *Chem. Mater.* **2003**, *15*, 1535 – 1546; d) J. Lee, Q.-D. Liu, M. Motala, J. Dane, J. Gao, Y. Kang, S. Wang, *Chem. Mater.* **2004**, *16*, 1869 – 1877; e) J. Lee, Q.-D. Liu, D.-R. Bai, Y. Kang, Y. Tao, S. Wang, *Organometallics* **2004**, *23*, 6205 – 6213; f) H. J. Tracy, J. L. Mullin, W. T. Klooster, J. A. Martin, J. Haug, S. Wallace, I. Rudloe, K. Watts, *Inorg. Chem.* **2005**, *44*, 2003 – 2011; g) J. Lee, Y.-Y. Yuan, Y. Kang, W.-L. Jia, Z.-H. Lu, S. Wang, *Adv. Funct. Mater.* **2006**, *16*, 681 – 686; h) G. Yu, S. Yin, Y. Liu, J. Chen, X. Xu, X. Sun, D. Ma, X. Zhan, Q. Peng, Z. Shuai, B. Tang, D. Zhu, W. Fang, Y. Luo, *J. Am. Chem. Soc.* **2005**, *127*, 6335 – 6346. See also: i) C.-H. Zao, A. Wakamiya, Y. Inukai, S. Yamaguchi, *J. Am. Chem. Soc.* **2006**, *128*, 15934 – 15935; j) H.-J. Son, W.-S. Han, J.-Y. Chun, C.-J. Lee, J.-I. Han, J. Ko, S. O. Kang, *Organometallics* **2007**, *26*, 519 – 526; k) H.-J. Son, W.-S. Han, J.-Y. Chun, S.-N. Kwon, J. Ko, S. O. Kang, *Organometallics* **2008**, *27*, 2464 – 2473; l) S.-i. Otsuka, H. Fukumoto, T. Yamamoto, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 536 – 538.

[8] a) H. Sohn, M. J. Sailor, D. Magde, W. C. Trogler, *J. Am. Chem. Soc.* **2003**, *125*, 3821 – 3830; b) S. J. Toal, W. C. Trogler, *J. Mater. Chem.* **2006**, *16*, 2871 – 2883; c) J. C. Sanchez, A. G. DiPasquale, A. L. Rheingold, W. C. Trogler, *Chem. Mater.* **2007**, *19*, 6459 – 6470.

[9] a) E. H. Braye, W. Hübel, *Chem. Ind. (London)* **1959**, 1250 – 1251; b) E. H. Braye, W. Hübel, I. Caplier, *J. Am. Chem. Soc.* **1961**, *83*, 4406 – 4413.

[10] a) P. Jutzi, A. Karl, *J. Organomet. Chem.* **1981**, *214*, 289 – 302; b) U. Losehand, N. W. Mitzel, *J. Chem. Soc. Dalton Trans.* **2000**, 1049 – 1052.

[11] a) T. Hiiro, N. Kambe, A. Ogawa, N. Miyoshi, S. Murai, N. Sonoda, *Angew. Chem.* **1987**, *99*, 1221 – 1222; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1187 – 1188; b) M. Katkevics, S. Yamaguchi, A. Toshimitsu, K. Tamao, *Organometallics* **1998**, *17*, 5796 – 5800.

[12] C. Wang, Q. Luo, H. Sun, X. Guo, Z. Xi, *J. Am. Chem. Soc.* **2007**, *129*, 3094 – 3095.

[13] a) K.-i. Kanno, M. Kira, *Chem. Lett.* **1999**, 1127 – 1128; see also: b) P. J. Fagan, W. A. Nugent, J. C. Calabrese, *J. Am. Chem. Soc.* **1994**, *116*, 1880 – 1889; c) Y. Ura, Y. Li, Z. Xi, T. Takahashi, *Tetrahedron Lett.* **1998**, *39*, 2787 – 2790; d) Z. Xi, Z. Li, *Top. Organomet. Chem.* **2004**, *8*, 27 – 56; and references cited therein.

[14] a) S. Yamaguchi, R.-Z. Jin, S. Ohno, K. Tamao, *Organometallics* **1998**, *17*, 5133 – 5138; b) S. Yamaguchi, R.-Z. Jin, K. Tamao, F. Sato, *J. Org. Chem.* **1998**, *63*, 10060 – 10062; c) J. Braddock-Wilking, Y. Zhang, J. Y. Corey, N. P. Rath, *J. Organomet. Chem.* **2008**, *693*, 1233 – 1242; d) T. Matsuda, Y. Yamaguchi, M. Murakami, *Synlett* **2008**, 561 – 564.

[15] See, for example: a) M. Horáček, N. Bazyakina, P. Štěpnička, R. Gyepes, I. Císařová, S. Bredeau, P. Meunier, J. Kubišta, K. Mach, *J. Organomet. Chem.* **2001**, *628*, 30 – 38; b) T. Yu, X. Sun, C. Wang, L. Deng, Z. Xi, *Chem. Eur. J.* **2005**, *11*, 1895 – 1902; c) C. K. Jin, T. Yamada, S. Sano, M. Shiro, Y. Nagao, *Tetrahedron Lett.* **2007**, *48*, 3671 – 3675; d) J. Liu, W.-X. Zhang, X. Guo, Z. Hou, Z. Xi, *Organometallics* **2007**, *26*, 6812 – 6820; e) J. Liu, S. Zhang, W.-X. Zhang, Z. Xi, *Organometallics* **2009**, *28*, 413 – 417, and references cited therein.

[16] K. Tamao, S. Yamaguchi, M. Shiro, *J. Am. Chem. Soc.* **1994**, *116*, 11715 – 11722.

[17] a) A. Sundararaman, M. Victor, R. Varughese, F. Jäkle, *J. Am. Chem. Soc.* **2005**, *127*, 13748 – 13749; b) A. Wakamiya, T. Taniguchi, S. Yamaguchi, *Angew. Chem.* **2006**, *118*, 3242 – 3245; *Angew. Chem. Int. Ed.* **2006**, *45*, 3170 – 3173; c) A. Sundararaman, R. Varughese, H. Li, L. N. Zakharov, A. L. Rheingold, F. Jäkle, *Organometallics* **2007**, *26*, 6126 – 6131; d) H. Li, A. Sundararaman, K. Venkatasubbaiah, F. Jäkle, *J. Am. Chem. Soc.* **2007**, *129*, 5792 – 5793; e) A. Wakamiya, K. Mori, S. Yamaguchi, *Angew. Chem.* **2007**, *119*, 4351 – 4354; *Angew. Chem. Int. Ed.* **2007**, *46*, 4273 – 4276; f) C.-H. Zao, A. Wakamiya, S. Yamaguchi, *Macromolecules* **2007**, *40*, 3898 – 3900; g) S. L. Hellstrom, J. Ugolotti, G. J. P. Britovsek, T. S. Jones, A. J. P. White, *New J. Chem.* **2008**, *32*, 1379 – 1387; h) A. Fukazawa, H. Yamada, S. Yamaguchi, *Angew. Chem.* **2008**, *120*, 5664 – 5667; *Angew. Chem. Int. Ed.* **2008**, *47*, 5582 – 5585; i) M. Elbing, G. Bazan, *Angew. Chem.* **2008**, *120*, 846 – 850; *Angew. Chem. Int. Ed.* **2008**, *47*, 834 – 838; j) C.-W. So, D. Watanabe, A. Wakamiya, S. Yamaguchi, *Organometallics* **2008**, *27*, 3496 – 3501.

[18] a) B. Wrackmeyer, *J. Chem. Soc. Chem. Commun.* **1986**, 397 – 399; b) A. Sebald, P. Seiberlich, B. Wrackmeyer, *J. Organomet. Chem.* **1986**, *303*, 73 – 81.

[19] a) L. Killian, B. Wrackemeyer, *J. Organomet. Chem.* **1977**, *132*, 213 – 221; b) A. Sebald, B. Wrackmeyer, *J. Chem. Soc. Chem. Commun.* **1983**, 1293 – 1294.

[20] a) B. Wrackmeyer, C. Bihlmayer, *J. Chem. Soc. Chem. Commun.* **1981**, 1093 – 1094; b) B. Wrackmeyer, *Rev. Silicon, Germanium, Tin, Lead Compd.* **1982**, *6*, 75 – 148; c) B. Wrackmeyer, G. Kehr, J. Süß, *Chem. Ber.* **1993**, *126*, 2221 – 2226; d) R. Köster, G. Seidel, J. Süß, B. Wrackmeyer, *Chem. Ber.* **1993**, *126*, 1107 – 1114;

e) B. Wrackmeyer, G. Kehr, J. Süß, E. Molla, *J. Organomet. Chem.* **1998**, *562*, 207–215; f) B. Wrackmeyer, O. L. Tok, K. Shahid, S. Ali, *Inorg. Chim. Acta* **2004**, *357*, 1103–1110.

[21] a) B. Wrackmeyer, W. Milius, E. V. Klimkina, Y. N. Bubnov, *Chem. Eur. J.* **2001**, *7*, 775–782; b) B. Wrackmeyer, W. Milius, O. L. Tok, Y. N. Bubnov, *Chem. Eur. J.* **2002**, *8*, 1537–1543; c) B. Wrackmeyer, M. H. Bhatti, S. Ali, O. L. Tok, Y. N. Bubnov, *J. Organomet. Chem.* **2002**, *657*, 146–154.

[22] a) V. V. Korshak, A. M. Sladkov, L. K. Luneva, *Russ. Chem. Bull.* **1962**, *11*, 677; b) S. D. Ibekwe, M. J. Newlands, *J. Chem. Soc.* **1965**, 4608–4610.

[23] a) U. Krüerke, *J. Organomet. Chem.* **1970**, *21*, 83–90; b) W.-Y. Wong, A. W.-M. Lee, C.-K. Wong, G.-L. Lu, H. Zhang, T. Mo, K.-T. Lam, *New J. Chem.* **2002**, *26*, 354–360; c) M. Horáček, P. Štěpnička, R. Gyepes, I. Císařová, J. Kubišta, L. Lukešová, P. Meunier, K. Mach, *Organometallics* **2005**, *24*, 6094–6103.

[24] a) A. G. Massey, A. J. Park, F. G. A. Stone, *Proc. Chem. Soc.* **1963**, 212; b) A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1964**, *2*, 245–250; c) G. Erker, *Dalton Trans.* **2005**, 1883–1890.

[25] For an estimation of the Lewis acidity of $B(C_6F_5)_3$ see for example: a) M. A. Beckett, G. C. Strickland, J. R. Holland, K. S. Varma, *Polym. Commun.* **1996**, *37*, 4629–4631; b) M. A. Beckett, D. S. Brassington, S. J. Coles, M. B. Hursthouse, *Inorg. Chem. Commun.* **2000**, *3*, 530–533; c) G. J. P. Britovsek, J. Ugolotti, A. J. P. White, *Organometallics* **2005**, *24*, 1685–1691.

[26] See for a comparison: B. Wrackmeyer, *Annual Reports on NMR Spectroscopy* **2006**, *57*, 1–49.

[27] a) B. Wrackmeyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds Containing Two-, Three- and Four-Coordinated Boron*, in: *Annual Reports on NMR Spectroscopy*, (Ed.: G. A. Webb), Academic Press, London, **1988**, Vol. 20, pp 61–203; b) D. Vagedes, G. Erker, R. Fröhlich, *Angew. Chem.* **1999**, *111*, 3561–3565; *Angew. Chem. Int. Ed.* **1999**, *38*, 3362–3364; c) G. Erker, S. Venne-Dunker, G. Kehr, N. Kleigrewe, R. Fröhlich, C. Mück-Lichtenfeld, S. Grimme, *Organometallics* **2004**, *23*, 4391–4395; d) C. Herrmann, G. Kehr, R. Fröhlich, G. Erker, *Organometallics* **2008**, *27*, 2328–2336; e) P. Spies, R. Fröhlich, G. Kehr, G. Erker, S. Grimme, *Chem. Eur. J.* **2008**, *14*, 333–343; *Chem. Eur. J.* **2008**, *14*, 779; f) T. Beringhelli, D. Donghi, D. Maggioni, G. D′Alfonso, *Coord. Chem. Rev.* **2008**, *252*, 2292–2313.

[28] See for a comparison: a) W. Ahlers, B. Temme, G. Erker, R. Fröhlich, T. Fox, *J. Organomet. Chem.* **1997**, *527*, 191–201; b) D. Vagedes, G. Erker, G. Kehr, K. Bergander, O. Kataeva, R. Fröhlich, S. Grimme, C. Mück-Lichtenfeld, *Dalton Trans.* **2003**, 1337–1344.

[29] a) D. C. Bradley, I. S. Harding, A. D. Keefe, M. Motevalli, D. H. Zheng, *J. Chem. Soc. Dalton Trans.* **1996**, 3931–3936; b) H. Jacobsen, H. Berke, S. Döring, G. Kehr, G. Erker, R. Fröhlich, O. Meyer, *Organometallics* **1999**, *18*, 1724–1735; c) T. Beringhelli, D. Maggioni, G. D’Alfonso, *Organometallics* **2001**, *20*, 4927–4938.

[30] J. Ugolotti, G. Kehr, R. Fröhlich, S. Grimme, G. Erker, *J. Am. Chem. Soc.* **2009**, *131*, 1996–2007.

[31] M. M. Corradi, G. Jimenez Pindado, M. J. Sarsfield, M. Thornton-Pett, M. Bochmann, *Organometallics* **2000**, *19*, 1150–1159.

[32] J. Ugolotti, G. Dierker, G. Kehr, R. Fröhlich, S. Grimme, G. Erker, *Angew. Chem.* **2008**, *120*, 2662–2665; *Angew. Chem. Int. Ed.* **2008**, *47*, 2622–2625.

[33] Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307–326.

[34] Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr.* **2003**, *A59*, 228–234.

[35] G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467–473.

[36] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.