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Synthesis and reactions of a novel bulky aryllithium†

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A novel bulky aryllithium, 2,6-bis{2,5-bis[bis(trimethylsilyl)methyl]phenyl}phenyllithium (BbspLi), was synthesized. Reactions of BbspLi 5 with Group 14 electrophiles, such as stannous chloride, with carbon tetrachloride or tetrachlorometallanes gave fluorene 6. Reaction of BbspLi with carbon tetrachloride gave benzyl chloride 8, which converted to 6 under acidic conditions. BbspLi 5 isomerized to the corresponding benzyl anion 10, which underwent halophilic reactions with Group 14 electrophiles to give fluorene 6 via the benzyl chloride intermediate 8. Copyright © 2007 John Wiley & Sons, Ltd.

INTRODUCTION

Since the first isolation of silene (Si=C)[1] and disilene (Si=Si)[2] by taking advantage of bulky ligands to prevent their dimerization, protecting a reactive center by appropriate bulky ligands has made it possible to synthesize stable low-coordinated compounds of heavier Group 14 elements,[3–18]* and even stable derivatives of heavier congeners of alkyne have been reported recently.[19–24] However, as for heavier analogs of nitrile having a triple bond between a heavier Group 14 element and nitrogen, no examples of stable derivatives have so far appeared. Stabilization of such species is extremely difficult because they can have only one substituent on the Group 14 element to sterically protect the reactive center. Thus, there is a continuing need to develop new types of sterically encumbered ligands.

Among a wide variety of steric protection groups, *m*-terphenyl ligands have been applied to the stabilization of reactive species of Group 14 elements because bulkiness of the ligand can be easily modified by including flanking ligands on the 2,6-positions.[25–27] *m*-Terphenyl ligands with flanking ligands having bulky substituents on the 2,6-positions (*o*,*o*-type) can protect a central reactive site on the near site (for recent examples of the synthesis of reactive species using *o*,*o*-type *m*-terphenyl ligands, see References[28–40]), while those with flanking ligands having bulky substituents on the 3,5-positions (*m*,*m*-type) can protect a central reactive site from remote site (for recent examples of the synthesis of reactive species using *m*,*m*-type *m*-terphenyl ligands, see References[41–45]). We became interested in a novel concept of steric protection, that is, surrounding a reactive center from remote and near sites to prevent its dimerization by the sole bulky substituent. We report herein the synthesis of a novel bulky aryllithium, 2,6-bis{2,5-bis[bis(trimethylsilyl)methyl]phenyl}phenyllithium (**5**, BbspLi) having bulky substituents at the *o*,*m*-positions of the flanking ligands and its reactivity.

RESULTS AND DISCUSSION

Synthesis of BbspI (1)

The starting material for the flanking ligand, 2-bromo-1,4-bis[bis(trimethylsilyl)methyl]benzene (**2**), was synthesized by the reaction of 1,4-bis[bis(trimethylsilyl)methyl]benzene (**3**)[46] with bromine in a mixture of carbon tetrachloride and dimethyl formamide in 81% yield. Although dimethyl formamide is a very efficient solvent for the synthesis of bulky bromobenzenes from the corresponding benzenes,[47] this synthetic method is unsuitable for a large-scale preparation of **2** because **3** is sparingly soluble in dimethyl formamide. Next, the large-scale bromination of **3** was carried out in carbon tetrachloride in the presence of a catalytic amount of iodine to give **2** in 66% yield (Scheme 1).[48] The targeted 2,6-bis{2,5-bis[bis(trimethylsilyl)methyl]phenyl}iodobenzene (BbspI) (**1**)

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†Dedicated to the memory of the late Professor Des Cunningham.

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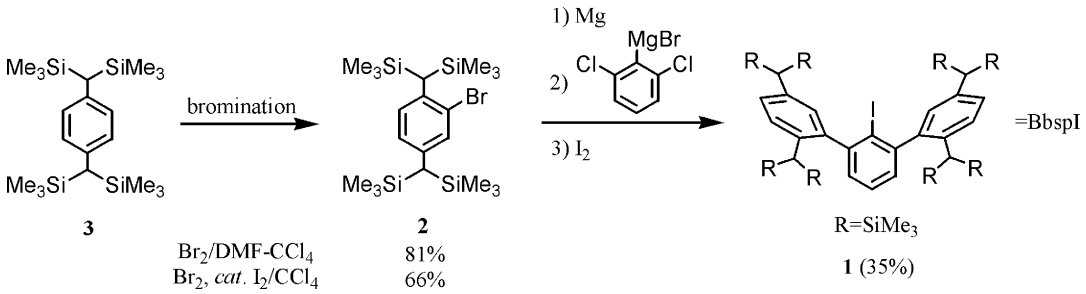
* Although the first stable compound having a formal Sn=Sn bond had been already reported by Lappert in 1976 before the breakthrough,[1,2] it should be described as bis(stannylene) because of its long Sn–Sn bond and large folded angles, see Goldberg *et al*.[18]



Scheme 1. Synthesis of bulky iodobenzene **1**.

was prepared by the established procedure.[25,26] The Grignard reagent prepared from **2** was coupled with the Grignard reagent prepared from 2,6-dichloroiodobenzene[49] to give the targeted **1** in 35% yield (Scheme 1).

X-ray crystallographic analysis of BbspI (1)

Single crystals of **1** suitable for X-ray crystallographic analysis were obtained by recrystallization from a hexane and ethanol mixture of **1**. The molecular structure, which has crystallographically imposed 2-fold symmetry bisecting the central aromatic ring and containing the iodide atom, is shown in Fig. 1, while in most related systems, the flanking ligands are perpendicular to the central aromatic ring and hence *m*-terphenyl systems tend to form bowl-type shapes. However, in the present case, the flanking ligands cross each other, located symmetrically to the central aromatic ring. For estimating steric congestion of **1**, space filling models of **1** and 2,6-bis(2,4,6-triisopropylphenyl)iodobenzene (**4**)[50] are shown in Fig. 2. As expected, the central iodide atom is more recessed under four steric congested bis[(trimethylsilyl)methyl] groups more deeply in **1** compared with that of **4**.

Reactions of BbspLi (5) with Group 14 electrophiles

In order to introduce Group 14 element functionalities into a Bbsp group, reaction of 2,6-bis{2,5-bis[bis(trimethylsilyl)methyl]phenyl}phenyllithium (BbspLi, **5**) with stannous chloride was first carried out because the formation of the expected chlorostannylene [Bbsp(Cl)Sn:] could be easily determined by a lowfield resonance characteristic of chlorostannylenes in the ^{119}Sn NMR spectrum.[51,52] After treatment of BbspLi **5**, prepared from **1** and *t*-butyllithium in THF (tetrahydrofuran), with stannous chloride, the ^{119}Sn NMR spectrum of the reaction mixture did not reveal any signals characteristic of chlorostannylenes.[51,52] In order to confirm the formation of chlorostannylene Bbsp(Cl)Sn:, the resulting mixture was treated with carbon tetrachloride because stannylenes were reported to react with carbon tetrachloride to give the corresponding dichloro derivatives.[53,54] After column chromatography of the reaction mixture, **6** was unexpectedly obtained in 32% yield and trichlorostannane BbspSnCl$_3$ was not obtained (Scheme 2). The structure of **6** was established by X-ray crystallographic analysis (Fig. 3).

Next, reactions of BbspLi **5** with other Group 14 electrophiles were carried out. Reactions of BbspLi **5** with

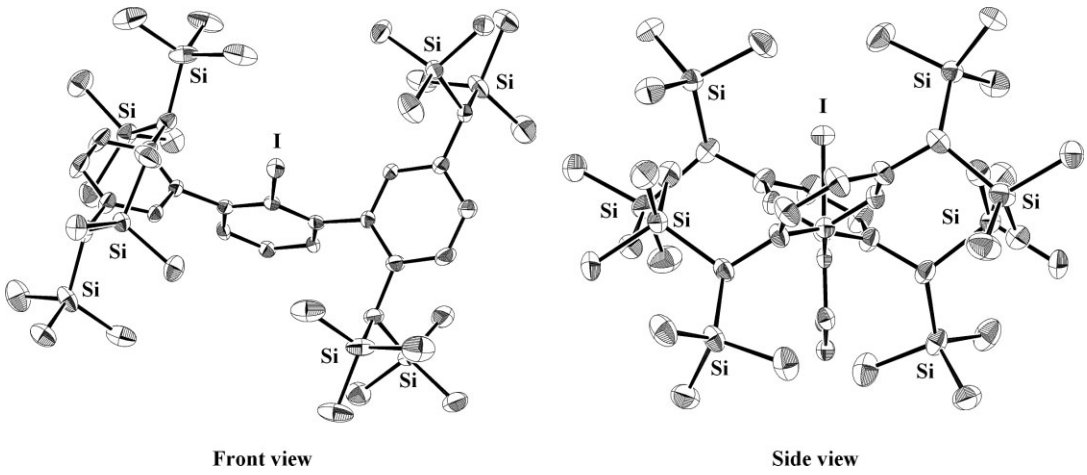


Figure 1. ORTEP drawing of BbspI **1** with thermal ellipsoids plots (40% probability for non-hydrogen atoms). All hydrogen atoms were omitted for clarity.

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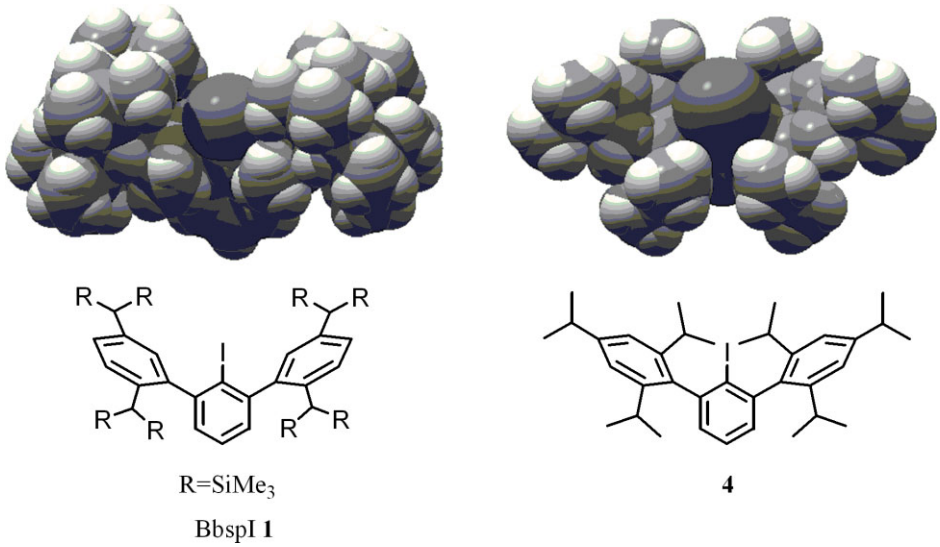
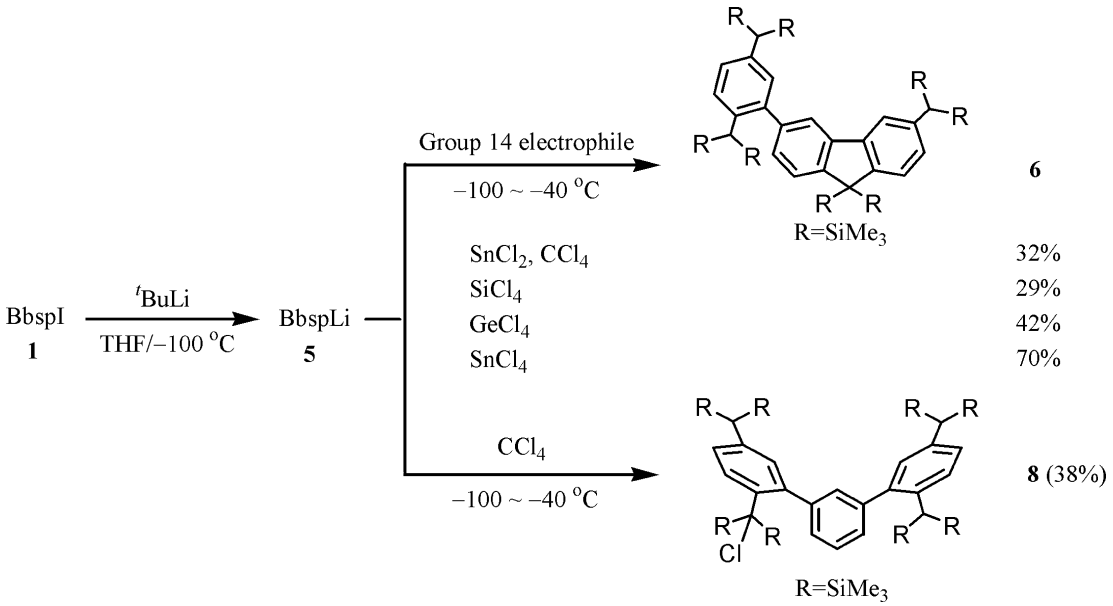
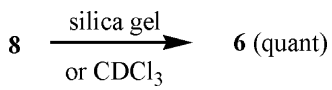


Figure 2. Space filling model of **1** and **4**.[50] This figure is available in colour online at www.interscience.wiley.com/AOC.



Scheme 2. Reactions of BbspLi **5** with Group 14 electrophiles.



Scheme 3. Conversion of **8** to **6**.

tetrachloro-silane, -germane or -stannane gave a mixture containing fluorene **6** (30–70% yields) together with BbspH **7** (BbspH **7** was alternatively synthesized by the reaction of BbspLi **5** with methanol, see Experimental section), while the corresponding trichlorides $BbspMCl_3$ (M═Si, Ge or Sn) were not obtained.

Reaction of BbspLi **5** with carbon tetrachloride was also carried out. Contrary to the reactions of **5** with heavier Group 14 tetrachlorides, recrystallization of the reaction mixture gave benzyl chloride **8** in 38% yield (Scheme 2), the structure of which was established by X-ray crystallographic analysis (Fig. 4). On the other hand, purification of the crude product by column chromatography gave fluorene **6** (39%) together with BbspH **7** (13%), suggesting that benzyl chloride **8** should convert to fluorene **6** during the purification on silica gel (Scheme 3), as was reported in the conversion of 2-biphenyldiphenylchloromethane to 9,9-diphenylfluorene under acidic conditions.[55] Moreover,

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benzyl chloride **8** in chloroform-*d* quantitatively converted to fluorene **6** over 6 days because of a trace amount of acid in chloroform-*d*. Thus, the formation of **6** in the reactions of **5** with tetrachlorometallanes is caused by involvement of hydrochloric acid generated from tetrachlorometallanes during workup.

Behavior of BbspLi 5: mechanism for the formation of 8

Since the reaction of BbspLi **5** with carbon tetrachloride unexpectedly provided benzyl chloride **8**, the behavior of BbspLi **5** was investigated. After treatment of **1** with *t*-butyllithium in THF at −100 °C, the reaction was quenched by D_2O. Surprisingly, compound **9** bearing a deuterium atom on the benzyl carbon at the 2-position of the flanking ligand was obtained in 67% yield (D content: 100%), suggesting the formation of benzyl anion **10** from BbspLi **5** even at low temperature (Scheme 4). Hence, the benzyl anion **10** underwent halophilic reaction with each of Group 14 electrophiles to give benzyl chloride **8**, which converted to fluorene **6** under acidic conditions. In the cyclization of **8**, a less congested moiety of the central aromatic ring of **8** attacks the benzyl carbon atom with the elimination of a chloride ion to give cationic intermediate **11**, which is attacked by the chloride ion to give fluorene **6** (Scheme 5). The conversion of BbspLi **5** to the benzyl anion **10** is probably caused for the steric reason that a benzyl proton of **5** can be located near to the anionic center of BbspLi **5** as well as the electronic reason that the anion **10** thus formed can be stabilized by two silyl groups at the benzyl position. To the best of our knowledge, such an isomerization of *m*-terphenyllithium to the corresponding benzyl anion is unprecedented.

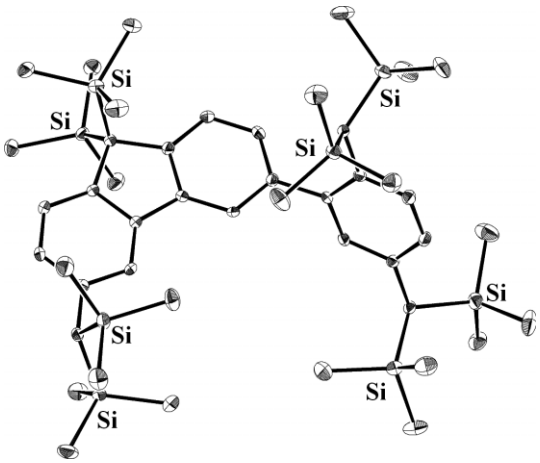


Figure 3. ORTEP drawing of **6** with thermal ellipsoids plots (40% probability for non-hydrogen atoms). All hydrogen atoms were omitted for clarity.

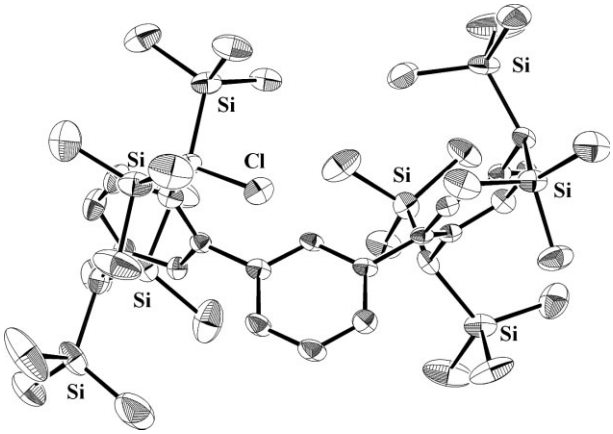
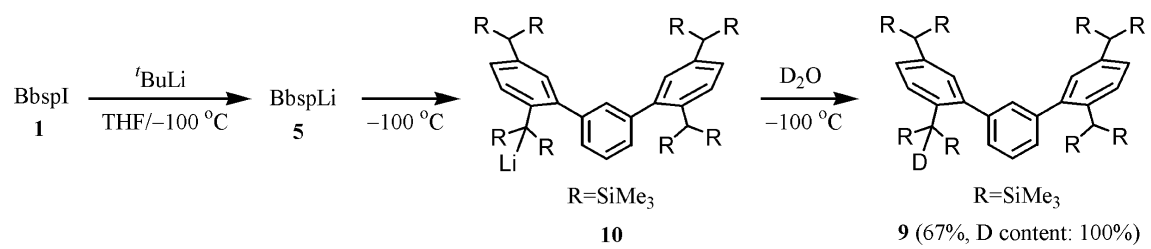


Figure 4. ORTEP drawing of **8** with thermal ellipsoids plots (40% probability for non-hydrogen atoms). All hydrogen atoms and minor disordered parts were omitted for clarity.

EXPERIMENTAL SECTION

General procedures

All experiments were performed under an argon atmosphere using the usual glass apparatus. THF, diethyl ether, benzene and benzene-d_6 were distilled over sodium/benzophenone. ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{119}Sn NMR (149 MHz) spectra were recorded on a Bruker DRX-400, a Bruker DPX-400 or a Bruker AM-400 spectrometer in $CDCl_3$ or benzene-d_6. The multiplicities of signals in ^{13}C NMR given in parentheses were deduced from DEPT spectra. Wet column chromatography (WCC) was carried out with Kanto silica gel 60N. Preparative gel permeation chromatography (GPC) was carried out on an LC-918 (Japan Analytical Ind. Co. Ltd) with Jaigel-1H and -2H columns with chlorform as the



Scheme 4. Formation of benzyllithium **10**.

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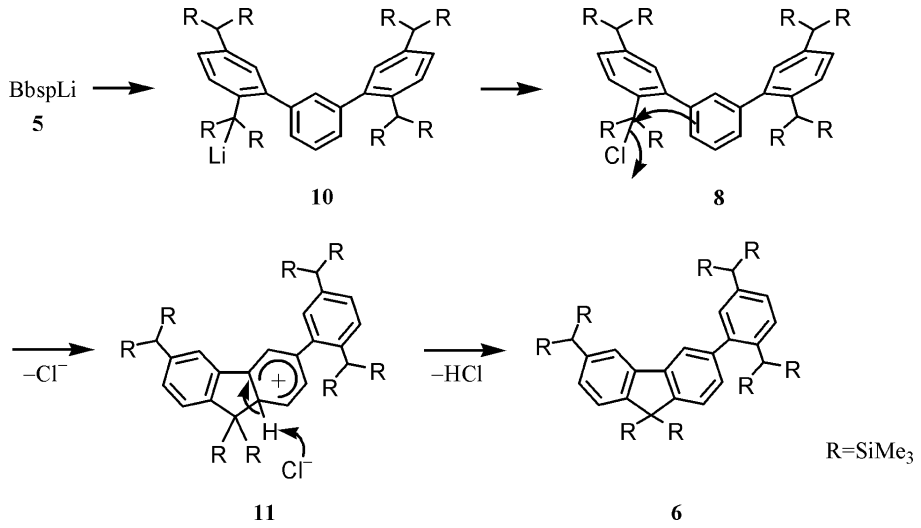

Scheme 5. Mechanism for the formation of **6**.

eluant. All the melting points were determined on a Mitamura Riken Kogyo MEL-TEMP apparatus and were uncorrected. Elemental analyses were carried out at the Microanalytical Laboratry of Molecular Analysis and Life Science Center, Saitama University.

Preparation of 2-bromo-1,4-[bis(trimethylsilyl)methyl]benzene (2) in dimethyl formamide and carbon tetrachloride

To a carbon tetrachloride (70 ml) and dimethyl formamide (140 ml) solution of 1,4-[bis(trimethylsilyl)methyl]benzene (**3**)[46] (4.967 g, 2.59 mmol) was added a dimethyl formamide (54 ml) solution of bromine (1.8 ml, 35.9 mmol) at room temperature and the mixture was stirred for 18 h at the same temperature. After treatment of the resulting mixture with aqueous sodium sulfite, the organic layer was extracted with hexane and dried over anhydrous magnesium sulfate. After removal of volatile substances, the residue was recrystallized from dichloromethane and ethanol to give 2-bromo-1,4-bis[bis(trimethylsilyl)methyl]benzene (**2**) (4.837 g, 81%). **2**: mp 67–68 °C (dichloromethane + ethanol). ^{1}H NMR($CDCl_3$): δ 0.01(s, 18H), 0.02(S, 18H), 1.36(s, 1H), 6.73(dd, $J = 2$, 8 Hz, 1H), 6.87(d, $J = 8$ Hz, 1H), 7.11(d, $J = 2$ Hz, 1H); ^{13}C NMR($CDCl_3$): δ 0.09(q), 0.13(q), 26.56(d), 28.49(d), 125.24(s), 127.34(d), 128.24(d), 132.63(d), 137.47(s), 139.87(s). Anal. calcd for $C_{20}H_{41}BrSi_4$: C, 50.70; H, 8.72. Found: C, 50.62; H, 8.82.

Preparation of 2-bromo-1,4-[bis(trimethylsilyl)methyl]benzene (2) in carbon tetrachloride in the presence of catalytic amount of iodine

To a carbon tetrachloride (70 ml) solution of **3**[46] (10.07 g, 25.5 mmol) and iodine (340 mg, 1.34 mmol) was added a carbon tetrachloride (20 ml) solution of bromine (1.28 ml, 25.5 mmol) at 0 °C and the mixture was stirred at the same temperature. After treatment of the resulting mixture with aqueous sodium sulfite, the organic layer was extracted with hexane and dried over anhydrous magnesium sulfate. After removal of volatile substances, the residue was recrystallized from dichloromethane and ethanol to give **2** (7.974 g, 66%).

Preparation of 2,6-bis{2,5-bis[bis(trimethylsilyl)methyl]phenyl}iodobenzene (1)

To a THF (9 ml) solution of ethylmagnesium bromide prepared from bromoethane (0.53 ml, 7.11 mmol) and magnesium powder (171 mg, 7.02 mmol) was added a THF (9 ml) solution of 2,6-dichloroiodobenzene[49] (1.904 g, 6.98 mmol) and the mixture was stirred for 1 h at room temperature. The resulting solution of 2,6-dichlorophenylmagnesium iodide was added to a THF (19 ml) solution of 2,5-bis[bis(trimethylsilyl)methyl]phenylmagnesium bromide prepared from **2** (7.247 g, 15.3 mmol), magnesium powder (397 mg, 16.3 mmol) and 1,2-dibromoethane (0.02 ml, 0.24 mmol). After heating of the mixture at reflux for 18 h, the resulting mixture was treated with a THF (16 ml) solution of iodine (5.929 g, 23.4 mmol) at room temperature. After being stirred for 6 h at room temperature, the mixture was treated with aqueous sodium sulfite and the organic layer was extracted with ether and dried over anhydrous magnesium sulfate. After removal of volatile substances, the crude product (7.718 g) was subjected to column chromatorgraphy (hexane) to give 2,6-bis{2,5-bis[bis(trimethylsilyl)methyl]phenyl}iodobenzene (**1**) (2.386 g, 35%). **1**: m.p. 174 °C (dec) (hexane + ethanol). ^{1}H NMR($CDCl_3$): δ 0.03(s, 18H), 0.04(S, 54H), 1.43(s, 2H), 1.66(s, 2H), 6.73(d, $J = 2$ Hz, 2H), 6.81(dd, $J = 2$, 8 Hz, 2H), 6.92(d, $J = 8$ Hz, 2H), 7.09(d, $J = 7$ Hz, 2H), 7.28(t, $J = 7$ Hz, 1H); ^{13}C NMR($CDCl_3$): δ 0.38(q), 0.47(q), 1.14(q), 1.90(q), 23.06(d), 28.59(d), 106.64(s), 125.83(d), 127.67(br d), 128.50(d), 129.78(d), 132.04(br d), 135.55(s), 137.09(s), 143.33(s), 148.07(s). Anal. calcd for $C_{46}H_{85}Isi_8$: C, 55.82; H, 8.66. Found: C, 55.54; H, 8.93.

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Reaction of BbspLi 5 with stannous chloride and carbon tetrachloride

After treatment of a THF (2 ml) solution of BbspI **1** (202 mg, 0.20 mmol) with *t*-butyllithium (1.49 N in pentane; 0.30 ml, 0.45 mmol) at −100 °C, the mixture was stirred at below −50 °C for 1 h. To the resulting solution of BbspLi **5** was added a THF (1.5 ml) solution of stannous chloride (49 mg, 0.26 mmol) and the mixture was stirred at below −40 °C for 30 min. To the resulting reaction mixture was added carbon tetrachloride (1 ml, 10.3 mmol) and the mixture was warmed to room temperature. After removal of volatile substances and insoluble materials in dichloromethane, the crude product (267 mg) was obtained. Recrystallization of the crude product from dichloromethane and ethanol gave 3-bis(trimethylsilyl)methyl-6-{2,5-bis[bis(trimethylsilyl)methyl]phenyl}-9,9-bis(trimethylsilyl)fluorene (**6**) (70 mg, 32%). **6**: m.p. 180–182 °C(dichloromethane + ethanol). ^{1}H NMR ($CDCl_3$): δ − 0.10(br s, 36H), 0.02(s, 18H), 0.05(s, 18H), 1.45(s, 1H), 1.57(s, 1H), 1.74(s, 1H), 6.80(dd, J = 2, 8 Hz, 1H), 6.87(s, 1H), 6.89–6.90(m, 2H), 7.08(dd, J = 2, 8 Hz, 1H), 7.38(d, J = 8 Hz, 1H), 7.42(d, J = 1 Hz, 1H), 7.53(d, J = 8 Hz, 1H), 7.64(d, J = 1 Hz, 1H); ^{13}C NMR($CDCl_3$): δ − 1.04(q), 0.25(q), 0.28(q), 0.45(q), 22.61(d), 28.54(d), 29.27(d), 42.87(s), 119.43(br d), 120.90(d), 123.95(d), 124.04(d), 127.06(br d), 127.50(d), 127.71(d), 130.63(br d), 135.89(s), 137.15(s), 139.07(s), 140.03(s), 140.50(s), 141.71(s), 143.06(s), 145.84(s). Anal. calcd for $C_{46}H_{84}Si_8$: C, 64.11; H, 9.82. Found: C, 64.21; H, 10.09.

Monitoring of reaction of BbspLi 5 with stannous chloride

After treatment of a THF (1 ml) solution of BbspI **1** (105 mg, 0.11 mmol) with *t*-butyllithium (1.49 M in pentane; 0.15 ml, 0.22 mmol) at −100 °C, the mixture was stirred at below −50 °C for 1 h. To the resulting solution of BbspLi **5** was added a THF (1 ml) solution of stannous chloride (27 mg, 0.14 mmol) and the mixture was stirred at below −40 °C for 30 min. After removel of volatile substances, to the residue was added benzene-d_6 (1 ml) and the mixture was placed in an NMR tube. The tube was degassed by freeze–pump–thaw cycles and sealed. No signals were observed in the ^{119}Sn NMR spectroscopy.

Preparation of 1,3-bis{2,5-bis[bis(trimethylsilyl)methyl]phenyl}benzene (7)

After treatment of a THF (2.5 ml) solution of BbspI **1** (250 mg, 0.25 mmol) with *t*-butyllithium (1.43 M in pentane; 0.40 ml, 0.57 mmol) at −100 °C, the mixture was stirred at below −80 °C for 1 h. To the resulting solution of BbspLi **5** was added methanol (1 ml, 24.7 mmol) at −80 °C and the reaction mixture was warmed to room temperature. After removal of volatile substances and insoluble materials in dichloromethane, the residue (251 mg) was subjected to GPC to afford 1,3-bis{2,5-bis[bis(trimethylsilyl)methyl]phenyl}benzene (**7**) (150 mg, 70%). **7**: m.p. 116–118 C (hexane + ethanol). ^{1}H NMR($CDCl_3$): δ − 0.05(s, 36H), 0.00(s, 36H), 1.39(s, 2H), 1.90(s, 2H), 6.74(d, J = 2 Hz, 2H), 6.77(dd, J = 2, 8 Hz, 2H), 6.88(d, J = 8 Hz, 2H), 7.06(br s, 1H), 7.13(dd, J = 2, 8 Hz, 2H), 7.35(t, J = 8 Hz, 1H); ^{13}C NMR($CDCl_3$): δ 0.19(q), 0.55(q), 22.61(d), 28.45(d), 126.90(d), 127.25(d), 127.72(d), 128.11(d), 130.91(d), 131.40(d), 135.12(s), 137.32(s), 140.95(s), 142.98(s). Anal. calcd for $C_{46}H_{86}Si_8$: C, 63.96; H, 10.03. Found: C, 64.09; H, 10.27.

Reaction of BbspLi 5 with tetrachlorosilane

After treatment of a THF (2 ml) solution of BbspI **1** (107 mg, 0.11 mmol) with *t*-butyllithium (1.46 M in pentane; 0.20 ml, 0.28 mmol) at −100 °C, the mixture was stirred at below −40 °C for 1.5 h. To the resulting solution of BbspLi **5** was added a THF solution of tetrachlorosilane (0.30 M; 0.4 ml, 0.12 mmol) and the mixture was warmed to room temperature. Removal of volatile substances and insoluble materials in diethyl ether gave a mixture (75 mg) containing fluorene **6** (29%) and BbspH **7** (51%), estimated by ^{1}H NMR spectroscopy.

Reaction of BbspLi 5 with tetrachlorogermane

After treatment of a THF (2 ml) solution of BbspI **1** (99 mg, 0.10 mmol) with *t*-butyllithium (1.42 M in pentane; 0.15 ml, 0.21 mmol) at −100 °C, the mixture was stirred at below −40 °C for 1.5 h. To the resulting solution of BbspLi **5** was added a THF solution of tetrachlorogermane (0.54 M; 0.2 ml, 0.11 mmol) and the mixture was warmed to room temperature. Removal of volatile substances and insoluble materials in diethyl ether gave a mixture (80 mg) containing fluorene **6** (42%) and BbspH **7** (51%), estimated by ^{1}H NMR spectroscopy.

Reaction of BbspLi 5 with tetrachlorostannane

After treatment of a THF (2 ml) solution of BbspI **1** (98 mg, 0.10 mmol) with *t*-butyllithium (1.46 M in pentane; 0.15 ml, 0.22 mmol) at −100 °C, the mixture was stirred at below −40 °C for 1.5 h. To the resulting solution of BbspLi **5** was added tetrachlorostannane (0.013 ml, 0.11 mmol) and the mixture was warmed to room temperature. Removal of volatile substances and insoluble materials in diethyl ether gave a mixture (80 mg) containing fluorene **6** (70%) and BbspH **7** (23%), estimated by ^{1}H NMR spectroscopy.

Reaction of BbspLi 5 with carbon tetrachloride: purification by recrystallization

After treatment of a THF (2 ml) solution of BbspI **1** (89 mg, 0.089 mmol) with *t*-butyllithium (1.46 M in pentane; 0.15 ml, 0.22 mmol) at −100 °C, the mixture was stirred at below −50 °C for 1.5 h. To the resulting solution of BbspLi **5** was added carbon tetrachloride (0.1 ml, 1.03 mmol) at −40 °C and the mixture was warmed to room temperature. After removal of volatile substances and insoluble materials in diethyl ether, the crude product (71 mg) was obtained. Recrystallization of the crude product from diethyl ether and ethanol gave 1-[2-chlorobis(trimethylsilyl)methyl-5-bis(trimethylsilyl)methyl]phenyl-3-{2,5-bis[bis- (trimethylsilyl)methyl]}phenylbenzene (**8**) (31 mg, 38%). **8**: m.p. 141–142 C (diethyl ether + ethanol). ^{1}H NMR(C_6D_6): δ 0.06(s,

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9H), 0.07(s, 9H), 0.103(s, 9H), 0.108(s, 9H), 0.11(s, 9H), 0.13(s, 9H), 0.19(s, 9H), 0.23(s, 9H), 1.35(s, 1H), 1.42(s, 1H), 2.23(br s, 1H), 6.82–6.92(m, 3H), 7.05–7.12(m, 3H), 7.21–7.25(m, 1H), 7.29–7.37(m, 2H), 7.44(br s, 1H); ^{13}C NMR(C_6D_6): δ − 0.30(q), 0.09(q), 0.30(q), 0.37(q), 0.42(q), 0.79(q), 0.95(q), 1.35(q), 23.24(d), 28.55(d), 28.66(d), 56.67(s), 126.10(d), 126.35(d), 126.45(d), 127.66(d), 128.20(d), 128.31(d), 131.69(d), 131.77(d), 134.13(s), 135.24(d), 135.82(s), 137.71(s), 138.39(s), 141.14(s), 141.66(s), 142.12(s), 145.58(s). Anal. calcd for $C_{46}H_{85}ClSi_8$: C, 61.50; H, 9.53. Found: C, 61.15; H, 9.54.

Reaction of BbspLi 5 with carbon tetrachloride: purification by column chromatography

After treatment of a THF (2 ml) solution of BbspI **1** (100 mg, 0.10 mmol) with *t*-butyllithium (1.42 M in pentane; 0.15 ml, 0.21 mmol) at −100 °C, the mixture was stirred at below −50 °C for 1.5 h. To the resulting solution of BbspLi **5** was added carbon tetrachloride (0.1 ml, 1.03 mmol) at −50 °C and the mixture was warmed to room temperature. After removal of volatile substances and insoluble materials in diethyl ether, the crude product (72 mg) was obtained. The crude product was subjected to column chromatography (hexane) to afford a mixture (45 mg) containing fluorene **6** (39%) and BbspH **7** (13%), estimated by ^{1}H NMR spectroscopy.

Behavoir of BbspLi 5: quenched by D_2O at −100 °C

After treatment of a THF (2 ml) solution of BbspI **1** (103 mg, 0.10 mmol) with *t*-butyllithium (1.59 M in pentane; 0.15 ml, 0.24 mmol) at −100 °C, the mixture was stirred at below −100 °C for 1.5 h. The reaction was quenched by a THF (1 ml) solution of D_2O (0.1 ml, 0.55 mmol) at −100 °C. The mixture was stirred for 1 h at the same temperature and gradually warmed to room temperature. After removal of volatile substances, the organic layer was extracted with diethyl ether and dried over anhydrous magnesium sulfate. After removal of the solvent, deuterio derivative **9** (61 mg, 67%, D content: 100%) was obtained.

X-ray crystallography

Data were collected at on Bruker SMART APEX diffractometer fitted with Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97)[56] and refinement {non-hydrogen atoms with anisotropic displacement parameters, H atoms in their calculated positions and with a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$} was solved by full-matrix least-squares procedures on F^2 (SHELXL-97).[57] In **8**, disorder around the chloride atom and three methyl groups of one of the trimethylsilyl units was found and resolved into two separate components. The fractional occupancies were determined from refinement to be 0.541(3):0.459(3) and 0.559(17):0.441(17), respectively. In each of **1** and **6**, the maximum residual electron density peak was located in the vicinity of a Si atom. Crystal data are listed in Table 1 and molecular structures were drawn with ORTEP-II.[58]

Table 1. Crystallographic data and refinement details for BbspI (**1**), fluorene (**6**) and benzyl chloride (**8**)

	1	**6**	**8**
Molecular formula	$C_{46}H_{85}ISi_8$	$C_{46}H_{84}Si_8$	$C_{46}H_{85}ClSi_8$
Formula weight	989.76	861.85	898.31
Temperature, K	123	103	123
Crystal system	monoclinic	triclinic	triclinic
Space group	$C2/c$	$P-1$	$P-1$
a (Å)	16.691(2)	13.1176(7)	12.028(2)
b (Å)	17.090(2)	15.0337(8)	14.750(2)
c (Å)	20.837(3)	15.6554(9)	17.892(3)
α (deg)	90	67.110(1)	72.908(4)
β (deg)	91.867(4)	81.763(1)	76.538(4)
γ (deg)	90	77.040(1)	86.330(3)
V(Å^3)	5940.5(13)	2766.4(3)	2950.7(8)
Z	4	2	2
D_x (g cm^{-3})	1.107	1.035	1.011
μ(mm^{-1})	0.727	0.221	0.254
θ_{max} (deg)	25.3	27.9	25.0
No. unique data	5390	13 267	10 410
No. data with $I \geq 2\sigma(I)$	4361	10 383	6337
R, observed data; all data	0.065, 0.164	0.060, 0.154	0.068, 0.164
a; b in weighting scheme	0.091, 39.000	0.092, 0.843	0.1, 0
R_w, observed data; all data	0.082, 0.180	0.076, 0.165	0.117, 0.194
Largest residual (e Å^{-3})	2.00	1.60	0.58
CCDC deposition number	638 842	638 843	638 844

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