

gem-Silylborylation approach for tri- and tetrametalmethanes: the first synthesis of boryl(germyl)(silyl)(stannyl)methanes

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Abstract

gem-Silylborylation of halomethylolithiums with silylboranes allows us to prepare boryl(silyl)methanes substituted by such heteroatoms as Cl, Br, I, O, S, Si, Ge, and Sn in high yields. With B, Si, and Sn- or B, Ge, and Si-substituted methanes, the first synthesis of B, Ge, Si, and Sn-substituted methanes was achieved via deprotonation of the trimetalated methane followed by germylation with Me₃GeCl or stannylation with Bu₃SnCl, respectively.

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1. Introduction

Di-, tri-, and tetrametalated methanes especially containing silicon and/or boron are versatile C₁ reagents in organic synthesis, because the polymetalated reagents can efficiently perform multiple chemical transformations in one vessel via a single operation or stepwise manipulations and thus can serve as valuable precursors of functionalized organometallic reagents [1,2]. For example, fluorotris(trimethylsilyl)methane reacted with aldehydes in the presence of fluoride ion to give 1,3-disubstituted 2-fluoroallylic alcohols **2o**, **2p**. The reaction involves five events in single operation: generation of naked methyl anion, aldehyde addition, Peterson elimination, generation of naked *sp*² anion, and alde-

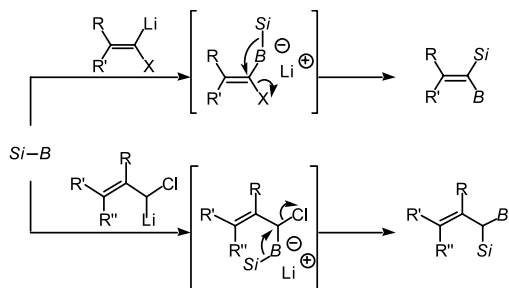
hyde addition. Using (dialkoxyboryl)methylzinc iodide [3], Pd catalyzed-cross coupling reaction with an alkenyl halide and subsequent aldehyde allylation was achieved in one pot [4]. Moreover, functionalized allylic silanes were prepared from tris[(trimethylsilyl)methyl]borane, which can be regarded as both silicon and boron substituted methane, via treatment of the borane with 1-alkynyllithium followed by the addition of an aldehyde [2v].

We recently reported that alkylidene-type lithium carbenoids reacted with silylboranes to generate the corresponding borates in which a silyl group migrated in 1,2-fashion to afford 1-boryl-1-silyl-1-alkenes in good yields (Scheme 1) [5]. This novel *gem*-silylborylation is applicable to *sp*³ carbenoids generated from allylic chlorides, giving rise to 1-boryl-1-silyl-2-alkenes stereospecifically in good yields [6]. Both silylborylated compounds are valuable reagents in organic synthesis.

We envisioned that heteroatom-substituted boryl(silyl)methanes, potentially versatile C₁ organometallic

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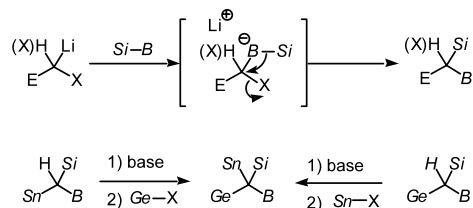
Scheme 1. *gem*-Silylborylation of lithium carbenoids with silylboranes.

reagents in synthetic chemistry, would be synthesized efficiently via *gem*-silylborylation of halomethyl lithium bearing heteroatom(s). Reported herein are facile synthesis of chalcogen, halogen, or metal-substituted boryl(silyl)methanes and their application to the first synthesis of boryl(germyl)(silyl)(stannyl)methanes (Scheme 2).

2. Results and discussion

2.1. Silylborylation of heteroatom-substituted methanes

Since halomethylolithiums were thermodynamically labile [7], generation and reaction of such carbenoids were carried out in the presence of silylborane **1**. Thus, a THF solution of **1** and halomethane **2** was treated with lithium diisopropylamide (LDA) at $-98\text{ }^{\circ}\text{C}$ and the resulting solution was allowed to warm to room temperature before quenching with saturated aqueous NH_4Cl solution (Eq. (1)). The results are summarized in Table 1. Reaction of (dimethylphenylsilyl)(pinacolato)borane (**1a**) and methoxymethyl chloride (**2a**) gave the corresponding product **3aa** in low yield, probably because chloro(methoxy)methyl lithium was extremely unstable under the conditions (entry 1), while chloromethyl lithium generated from (2-methoxyethoxy)methyl chloride (**2b**) reacted with **1a** to afford **3ab** in moderate yield (entry 2). Improvement of the yield may be attributed to the stabilization of the carbenoid intermediate by chelation between two etheral oxygens and a lithium [8]. Similarly, 2-(trimethylsilyl)ethoxymethyl chloride (**2c**) and methylthiomethyl chloride (**2d**) were



Scheme 2. *gem*-Silylborylation approach for tri- and tetrametal-methanes.

Table 1
Silylborylation of halomethanes **2**

Entry	1	2	E	X	3	Yield ^a (%)
1	1a	2a	MeO	Cl	3aa	17
2	1a	2b	MEO ^b	Cl	3ab	37
3	1a	2c	SEO ^c	Cl	3ac	41
4	1a	2d	MeS	Cl	3ad	45
5	1a	2e	Cl	Cl	3ae	20
6	1a	2f	Br	Br	3af	47
7	1a	2g	I	I	3ag	69
8	1a	2h	Me ₃ Si	Cl	3ah	88
9	1a	2i	Me ₃ Ge	Cl	3ai	76
10	1b	2i	Me ₃ Ge	Cl	3bi	59
11	1c	2i	Me ₃ Ge	Cl	3ci	26
12	1a	2j	Bu ₃ Sn	Cl	3aj	51
13	1a	2k	Bu ₃ Sn	I	3aj	67
14	1a	2l	Ph ₃ Pb	I	3al	62

For entries 1–4 and 8–14, a solution of **1** (1.0 mmol), **2** (1.1 mmol) in THF (3 ml) was treated with a solution of LDA (1.1 mmol) in THF (1 ml) at $-98\text{ }^{\circ}\text{C}$ and the resulting mixture was allowed to warm to room temperature. For entries 5–7, a solution of **1a** (1.0 mmol), **2** (1.5 mmol) in THF (3 ml) was treated with a solution of LDA (1.4 mmol) in THF (1.4 ml) at $-98\text{ }^{\circ}\text{C}$ and the resulting mixture was allowed to warm to room temperature.

^a Isolated yields are given.

^b ME: 2-methoxyethyl.

^c SE: 2-(trimethylsilyl)ethyl.

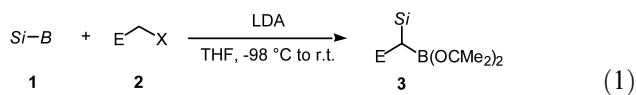
silylborylated in moderate yields, respectively (entries 3 and 4). Silylborylation of such dihalomethanes as dichloro- and dibromo-, and diiodomethanes (**2e–g**) also proceeded to give **3ae**, **3af**, and **3ag** in 20, 47, and 69% yields, respectively (entries 5–7). When halomethanes bearing a metal element were employed, trimetalated methanes were isolated by purification with column chromatography on silica gel in moderate to good yields. Lithiation of chloromethyltrimethylsilyl silane (**2h**) and subsequent silylborylation with **1a** gave bis(silyl)(boryl)methane **3ah** in 88% yield (entry 8). (Dimethylphenylsilyl)(trimethylgermyl)(pinacolato)boronate (**3ai**) was obtained from chloromethyltrimethylgermane (**2i**) and **1a** in 76% yield (entry 9). With **2i**, (methyl)diphenylsilyl(pinacolato)borane (**1b**) and (pinacolato)(triphenylsilyl)borane (**1c**) were also applicable to the present silylborylation albeit the yields were lower than that with **1a** (entries 10 and 11). Tin-substituted boryl(silyl)methane **3aj** was prepared from chloro- and iodomethanes **2j** and **2k** in 51 and 67% yields, respectively (entries 12 and 13), while iodo-methyltriphenylplumbane [9] was transformed to boron, lead, and silicon-substituted methane **3al** in 62% yield (entry 14). On the other hand, reaction of iodo-methyl(pinacolato)borane (**2m**) [10] with **1a** did not take place at all. Since no consumption of **2m** was observed, treatment of **2m** with LDA might cause the formation of the corresponding borate and such complexation would retard the deprotonation, i.e. generation of the carbenoid.

Table 2
Silylborylation of tri- and tetrahalomethanes **2**

Entry	2	Z	X	Method	3	Yield ^a (%)
1	2n	H	Cl	A	3an	70
2	2o	Cl	Cl	B	3an	64
3	2p	H	Br	A	3ap	86
4	2q	Br	Br	B	3ap	93
5	2r	H	I	A	3ar	42
6	2s	I	I	B	3ar	19

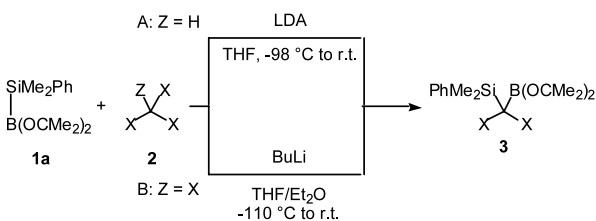
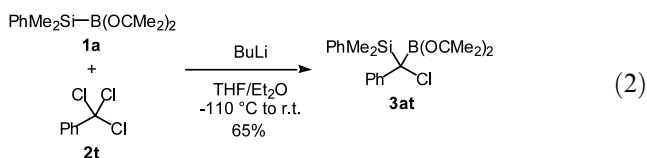
Method A: a solution of **1** (1.0 mmol), **2** (1.1 mmol) in THF (3 ml) was treated with a solution of LDA (1.1 mmol) in THF (1 ml) at $-98\text{ }^{\circ}\text{C}$ and the resulting mixture was allowed to warm to room temperature. Method B: a solution of **1a** (1.0 mmol), **2** (1.2 mmol) in THF (2 ml) in diethyl ether (1 ml) was treated with a solution of BuLi (1.2 mmol) in hexane (1.56 M, 0.77 ml) at $-110\text{ }^{\circ}\text{C}$ and the resulting mixture was allowed to warm to room temperature.

^a Isolated yields are given.



1a: Si = SiMe₂Ph, B = B(OCMe₂)₂, **1b**: Si = SiMePh₂, B = B(OCMe₂)₂,
1c: Si = SiPh₃, B = B(OCMe₂)₂

We next examined silylborylation of tri- and tetrahalomethanes leading to boryl(dihalo)(silyl)methanes (Scheme 3). Trihalomethanes **2n**, **2p**, and **2r** were silylborylated with **1a** under the same conditions for **2a–2l**, while tetrahalomethanes **2o**, **2q**, and **2s** were converted to the corresponding trihalomethylolithiums by halogen–lithium exchange with BuLi in THF/Et₂O at $-110\text{ }^{\circ}\text{C}$, which reacted with coexisting **1a**. Dichloro- and dibromomethanes **3an** and **3ap** were isolated in acceptable to good yields (Table 2, entries 1–4). Especially silylborylation of **2q** proceeded giving rise to **3ap** in 93% yield (entry 4). On the other hand, diiodomethane **3ar** was obtained in low to moderate yields (entries 5 and 6). In all cases, no diboryl(disilyl)methane, double silylborylated product, formed. Silylborylation via chlorine–lithium exchange was applicable to trichloromethylbenzene (**2t**), giving rise to benzyl chloride **3at** in 65% yield (Eq. (2)).

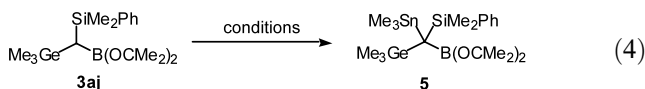
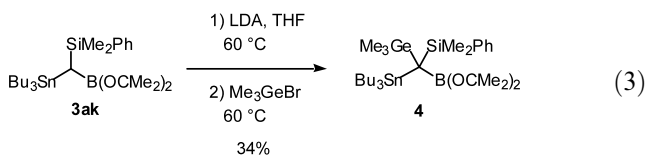


Scheme 3.

2.2. Synthesis of boryl(germyl)(silyl)(stannyl)methanes **4** and **5**

With trimetalated methanes in hand, we scrutinized the synthesis of methanes substituted by such four different kinds of metal elements as B, Ge, Si, and Sn. To our knowledge, no example of the four different metals-substituted methanes was available [11].

At first, deprotonation of **3ak** with BuLi followed by germylation with Me₃GeBr was attempted to synthesize boryl(germyl)(silyl)(stannyl)methane **4**. Tin–lithium exchange, however, took place in preference to the deprotonation and **3aj** was produced in 58% yield. Then, **3ak** was treated with LDA in THF at $60\text{ }^{\circ}\text{C}$ and then the methylolithium was trapped with Me₃GeBr to produce B-, Ge-, Si-, and Sn-substituted methane **4** in 34% yield as a colorless oil (Eq. (3)). Alternatively, lithiation of **3aj** and subsequent stannylation leading to another tetrametalated methane **5** was also examined (Eq. (4)). When **3aj** was lithiated with BuLi or lithium 2,2,6,6-tetramethylpiperidide (LiTMP) and stannylated with Me₃SnCl at $60\text{ }^{\circ}\text{C}$, **5** was isolated in moderate yield (entries 1 and 2). In case of LDA, boron–lithium exchange also occurred in some extent and Ge-, Si-, and Sn-substituted methane **6** was co-produced in 23% yield. On the other hand, a superbases consisting of BuLi and *t*-BuOK was found highly effective for the lithiation and the following stannylation afforded **5** in 81% yield (entry 3). These are the first synthesis of B-, Ge-, Si-, and Sn-substituted methanes.



Entry	Conditions	Yield (%)
1	(1) BuLi, THF, -78 to $0\text{ }^{\circ}\text{C}$ (2) Me ₃ SnCl, $60\text{ }^{\circ}\text{C}$	39
2	(1) LiTMP, TMEDA, THF, $60\text{ }^{\circ}\text{C}$ (2) Me ₃ SnCl, $60\text{ }^{\circ}\text{C}$	30
3	(1) BuLi/ <i>t</i> -BuOK, THF, -78 to $-40\text{ }^{\circ}\text{C}$ (2) Me ₃ SnCl, $-78\text{ }^{\circ}\text{C}$ to r.t.	81

Recrystallization of **5** from methanol, fortunately, afforded single crystals suitable for X-ray diffraction

analysis [12]. ORTEP drawing of **5** is shown in Fig. 1. The bond lengths of C(1)–B(1) and C(1)–Si(1) were 1.558(6) and 1.882(4) Å, both of which were almost the same as normal bond lengths being 1.56 and 1.87 Å [13], respectively. On the other hand, the C(1)–Ge(1) bond being 2.041(4) Å was longer than normal value being 1.94 Å [13], while the distance between C(1) and Sn(1) being 2.132(5) Å was found shortened by comparison with the normal C(1)–Sn bond length (2.17 Å) [13]. The Sn(1)–C(1)–Si(1) (112.2(2)°), B(1)–C(1)–Si(1) (111.7(3)°), and Ge(1)–C(1)–Si(1) (111.8(2)°) bond angles were larger than an ideal angle (109.5°) of a tetrahedral carbon, while the bond angles of B(1)–C(1)–Ge(1) (105.1(3)°) and B(1)–C(1)–Sn(1) (106.4(3)°) were smaller than the typical angle. These observations indicate that steric repulsions between the boryl and the silyl groups, and the silyl and the stannyl groups are larger than those between the boryl and the germyl groups, and the germyl and the stannyl groups presumably due to the bulkier substituents on boron and silicon atoms.

3. Experimental

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere (deoxygenated by passing through BASF-Catalyst R3-11 column at 80 °C). ¹H-NMR spectra were measured on a Varian Mercury 200 (¹H, 200 MHz) spectrometer. Chemical shifts of ¹H-NMR are expressed in parts per million downfield relative to an internal tetramethylsilane ($\delta = 0$ ppm) or chloroform ($\delta = 7.26$ ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; brs, broad singlet. ¹³C-NMR spectra were measured on a Varian Mercury 200 (¹³C, 50 MHz) spectrometer and JEOL JMN ECP-500 (¹³C, 125 MHz) spectrometer with tetramethylsilane as an internal standard ($\delta = 0$ ppm). Infrared spectra (IR) were recorded on a Shimadzu FTIR-8400 spectrometer. GC-MS analyses were obtained with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Kyoto University Elemental Analysis Center. Melting points were determined using a YANAKO MP-500D. TLC analyses were performed by means of Merck Kieselgel 60 F₂₅₄ and *R_f* values were given. Column chromatography was carried out using Wakogel C-200. Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC-908 chromatograph equipped with JAIGEL-1H and -2H columns (chloroform as an eluent). Cooling a reaction vessel at –110 or –98 °C was effected using pentane with liquid nitrogen, or methanol with liquid nitrogen respectively. Ethereal solvents like THF, and

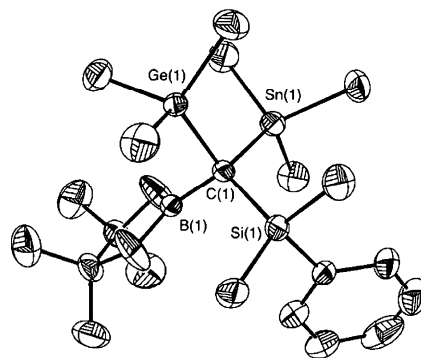


Fig. 1. ORTEP drawing of **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C(1)–B(1), 1.558(6); C(1)–Si(1), 1.882(4); C(1)–Ge(1), 2.041(4); C(1)–Sn(1), 2.132(5). Selected angles (°): B(1)–C(1)–Si(1), 111.7(3); B(1)–C(1)–Sn(1), 106.4(3); B(1)–C(1)–Ge(1), 105.1(3); Si(1)–C(1)–Sn(1), 112.2(2); Si(1)–C(1)–Ge(1), 111.8(2); Ge(1)–C(1)–Sn(1), 109.26(18).

diethyl ether were distilled from benzophenone and sodium under an argon atmosphere. Butyllithium was purchased from Sigma-Aldrich Co. Inc., and titrated with *N*-pivaloyl-*o*-toluidine as an indicator. Silylboranes **1a–c** were prepared by the reported procedure [14].

3.1. Typical procedure for silylborylation of halomethanes: synthesis of (dimethylphenylsilyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(trimethylsilyl)methane (**3ah**)

To a solution of chloromethyltrimethylsilane (**2h**, 0.13 g, 1.10 mmol) and (dimethylphenylsilyl)(pinacolato)borane (**1a**, 0.26 g, 1.00 mmol) in THF (3.0 ml) at –98 °C was added a solution of LDA (1.10 mmol) in THF (1 ml). The reaction mixture was stirred for 10 min at –98 °C and then allowed to gradually warm to room temperature before quenching with saturated aqueous NH₄Cl solution (0.5 ml). The resulting mixture was diluted with diethyl ether (20 ml), and then washed with water (10 ml). The organic layer was dried over anhydrous magnesium sulfate, and concentrated in vacuo. Purification of the crude product by column chromatography on silica gel (hexane/ethyl acetate 9:1) afforded **3ah** (0.31 g, 88% yield) as a colorless oil. *R_f*: 0.48 (hexane/ethyl acetate 9:1). ¹H-NMR: δ –0.01 (s, 9H), 0.15 (s, 1H), 0.35 (s, 3H), 0.38 (s, 3H), 1.07 (s, 6H), 1.12 (s, 6H), 7.27–7.37 (m, 3H), 7.50–7.60 (m, 2H). ¹³C-NMR: δ –0.3, 0.3, 1.5, 24.9, 25.1, 82.6, 127.4, 128.5, 133.7, 141.1. IR: ν_{max} 2975, 1349, 1308, 1245, 1142, 1110, 1023, 848, 732, 699 cm^{–1}. MS: *m/z* 333 [M⁺ – Me], 251, 233, 191, 59, 135, 83. Anal. Calc. for C₁₈H₃₃O₂BSi₂: C, 62.05; H, 9.55. Found: C, 62.12; H, 9.53%.

3.2. Spectral data of 3

3.2.1. (Dimethylphenylsilyl)(methoxy)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (3aa)

Colorless oil. R_f : 0.26 (hexane/ethyl acetate 9:1). $^1\text{H-NMR}$: δ 0.36 (s, 3H), 0.38 (s, 3H), 1.17 (s, 6H), 1.20 (s, 6H), 3.18 (s, 1H), 3.33 (s, 3H), 7.30–7.42 (m, 3H), 7.57–7.67 (m, 2H). $^{13}\text{C-NMR}$: δ -4.1, -3.7, 24.4, 25.1, 62.6, 83.5, 127.5, 129.0, 134.0, 137.7. IR: ν_{max} 3065, 2977, 1455, 1348, 1334, 1239, 1143, 798 cm^{-1} . MS: m/z 306 $[\text{M}^+]$, 291 $[\text{M}^+ - \text{Me}]$, 191, 135, 84. FAB HRMS: m/z Calc. for $\text{C}_{16}\text{H}_{27}\text{BO}_3\text{Si}$ $[\text{M}^+]$: 306.1823. Found 306.1823.

3.2.2. (Dimethylphenylsilyl)(2-methoxyethoxy)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (3ab)

Purified by GPC. Colorless oil. R_f : 0.23 (hexane/ethyl acetate 10:1). $^1\text{H-NMR}$: δ 0.36 (s, 3H), 0.39 (s, 3H), 1.16 (s, 6H), 1.27 (s, 6H), 3.28–3.78 (m, 9H), 7.30–7.65 (m, 5H). $^{13}\text{C-NMR}$: δ -4.1, -3.8, 24.3, 25.2, 58.9, 72.0, 73.7, 83.4, 127.5, 129.0, 134.1, 137.4. IR: ν_{max} 3069, 2978, 1456, 1348, 1330, 1245, 1113, 837 cm^{-1} . MS: m/z 335 $[\text{M}^+ - \text{Me}_2\text{O}]$, 277, 191, 135, 83. FAB HRMS: m/z Calc. for $\text{C}_{17}\text{H}_{28}\text{BO}_4\text{Si}$ $[\text{M}^+]$: 355.1850. Found 355.1845.

3.2.3. (Dimethylphenylsilyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)[2-(triethylsilyl)ethoxy]methane (3ac)

Purified by GPC. Colorless oil. R_f : 0.23 (hexane/ethyl acetate 10:1). $^1\text{H-NMR}$: δ 0.02 (s, 9H), 0.33 (s, 3H), 0.39 (s, 3H), 1.13 (s, 6H), 1.18 (s, 6H), 3.21–3.65 (m, 4H), 4.66 (s, 2H), 7.28–7.62 (m, 5H). $^{13}\text{C-NMR}$: δ -3.9, -1.4, 18.3, 24.3, 25.2, 64.9, 71.7, 83.3, 127.5, 128.9, 134.0, 138.0. IR: ν_{max} 2977, 1427, 1381, 1330, 1247, 1144, 786 cm^{-1} . MS: m/z 377 $[\text{M}^+ - \text{Me}]$, 349, 191, 135, 73. FAB HRMS: m/z Calc. for $\text{C}_{20}\text{H}_{38}\text{BO}_3\text{Si}_2$ $[\text{MH}^+]$: 393.2452. Found 393.2455.

3.2.4. (Dimethylphenylsilyl)(methylthio)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (3ad)

Colorless oil. R_f : 0.30 (hexane/ethyl acetate 9:1). $^1\text{H-NMR}$: δ 0.43 (s, 3H), 0.44 (s, 3H), 1.16 (s, 6H), 1.19 (s, 6H), 1.82 (s, 1H), 2.12 (s, 3H), 7.30–7.42 (m, 3H), 7.55–7.65 (m, 2H). $^{13}\text{C-NMR}$: δ -3.1, -2.8, 19.4, 24.7, 24.9, 83.5, 127.6, 129.2, 133.9, 137.4. IR: ν_{max} 2980, 1373, 1325, 1249, 1146, 1117, 971, 852, 821, 780, 737, 701 cm^{-1} . MS: m/z 324 $[\text{M}^+ + 2]$, 323 $[\text{M}^+ + 1]$, 322 $[\text{M}^+]$, 207, 191, 135. Anal. Calc. for $\text{C}_{16}\text{H}_{27}\text{O}_2\text{BSSi}$: C, 59.62; H, 8.44. Found: C, 59.38; H, 8.63%.

3.2.5. Chloro(dimethylphenylsilyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (3ae)

Colorless oil. R_f : 0.34 (hexane/ethyl acetate 9:1). $^1\text{H-NMR}$: δ 0.46 (s, 3H), 0.47 (s, 3H), 1.18 (s, 12H), 2.90 (s,

1H), 7.30–7.40 (m, 3H), 7.55–7.65 (m, 2H). $^{13}\text{C-NMR}$: δ -4.0, -3.6, 24.7, 24.8, 84.2, 127.7, 129.6, 134.1, 136.2. IR: ν_{max} 2978, 1379, 1339, 1250, 1140, 1115, 968, 846, 820, 785, 733, 700 cm^{-1} . MS: m/z 313 $[\text{M}^+ + 3]$, 312 $[\text{M}^+ + 2]$, 311 $[\text{M}^+ + 1]$, 310 $[\text{M}^+]$, 309 $[\text{M}^+ - 1]$, 135. Anal. Calc. for $\text{C}_{15}\text{H}_{24}\text{O}_2\text{BClSi}$: C, 57.99; H, 7.79. Found: C, 57.82; H, 7.84%.

3.2.6. Bromo(dimethylphenylsilyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (3af)

Colorless oil. R_f : 0.48 (hexane/ethyl acetate 9:1). $^1\text{H-NMR}$: δ 0.48 (s, 6H), 1.16 (s, 6H), 1.18 (s, 6H), 2.54 (s, 1H), 7.30–7.40 (m, 3H), 7.52–7.62 (m, 2H). $^{13}\text{C-NMR}$: δ -3.5, -3.4, 24.5, 24.6, 84.0, 127.6, 129.4, 133.9, 136.4. IR: ν_{max} 2977, 1381, 1330, 1247, 1144, 786 cm^{-1} . MS: m/z 339 $[\text{M}^+ - \text{Me}]$, 275, 135, 83. Anal. Calc. for $\text{C}_{15}\text{H}_{24}\text{O}_2\text{BBrSi}$: C, 50.73; H, 6.81. Found: C, 50.91; H, 7.09%.

3.2.7. (Dimethylphenylsilyl)(iodo)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (3ag)

Colorless oil. R_f : 0.42 (hexane/ethyl acetate 9:1). $^1\text{H-NMR}$: δ 0.49 (s, 3H), 0.51 (s, 3H), 1.12 (s, 6H), 1.16 (s, 6H), 2.05 (s, 1H), 7.28–7.40 (m, 3H), 7.50–7.60 (m, 2H). $^{13}\text{C-NMR}$: δ -2.8, -2.2, 24.3, 24.4, 83.8, 127.7, 129.4, 133.9, 137.0. IR: ν_{max} 2965, 1366, 1153, 1111, 781 cm^{-1} . MS: m/z 402 $[\text{M}^+]$, 387 $[\text{M}^+ - \text{Me}]$, 207, 135, 84. Anal. Calc. for $\text{C}_{15}\text{H}_{24}\text{O}_2\text{BISi}$: C, 44.80; H, 6.02. Found: C, 44.81; H, 6.14%.

3.2.8. (Dimethylphenylsilyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(trimethylgermyl)methane (3ai)

Colorless oil. R_f : 0.53 (hexane/ethyl acetate 9:1). $^1\text{H-NMR}$: δ 0.13 (s, 9H), 0.33 (s, 3H), 0.35 (s, 3H), 1.09 (s, 6H), 1.12 (s, 6H), 7.27–7.37 (m, 3H), 7.52–7.62 (m, 2H). $^{13}\text{C-NMR}$: δ -0.3, 0.5, 1.0, 25.0, 25.1, 82.5, 127.4, 128.5, 133.6, 141.2. IR: ν_{max} 2985, 1357, 1316, 1267, 1250, 1148, 1115, 852, 816, 734, 701 cm^{-1} . MS: m/z 379 $[\text{M}^+ - \text{Me}]$, 281, 279, 278, 277, 275. Anal. Calc. for $\text{C}_{18}\text{H}_{33}\text{O}_2\text{BGeSi}$: C, 55.02; H, 8.46. Found: C, 55.32; H, 8.24%.

3.2.9. (Methylphenylsilyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(trimethylgermyl)methane (3bi)

Colorless needles. M.p. 48.8 °C (dec.). R_f : 0.42 (hexane/ethyl acetate 10:1). $^1\text{H-NMR}$: δ 0.08 (s, 9H), 0.73 (s, 3H), 1.03 (s, 12H), 7.31–7.65 (m, 10H). $^{13}\text{C-NMR}$: δ -2.4, 1.1, 25.0, 25.1, 82.6, 127.3, 127.4, 128.6, 128.6, 134.1, 134.5, 139.0, 139.3. IR: ν_{max} 2976, 2906, 1427, 1313, 1252, 1144, 1109, 849, 799, 698 cm^{-1} . MS: m/z 441 $[\text{M}^+ - \text{Me}]$, 341, 237, 135, 83, 73. FAB HRMS: m/z Calc. for $\text{C}_{22}\text{H}_{32}\text{BGeO}_2\text{Si}$ $[\text{M}^+ - \text{Me}]$: 441.1476. Found 441.1474.

3.2.10. (4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)(trimethylgermyl)(triphenylsilyl)methane (**3ci**)

Colorless needles. M.p. 65.6 °C (dec.). R_f : 0.39 (hexane/ethyl acetate 10:1). $^1\text{H-NMR}$: δ 0.01 (s, 9H), 0.93 (s, 6H), 1.03 (s, 6H), 7.31–7.67 (m, 15H). $^{13}\text{C-NMR}$: δ 1.1, 24.9, 25.0, 82.8, 127.4, 128.9, 136.0, 136.8. IR: ν_{max} 2976, 2908, 1427, 1310, 1264, 1143, 1113, 849, 788, 700 cm^{-1} . FAB MS: m/z 518 [M^+], 503 [$\text{M}^+ - \text{Me}$], 135, 83. FAB HRMS: m/z Calc. for $\text{C}_{28}\text{H}_{37}\text{BGeO}_2\text{Si}$ [M^+]: 518.1868. Found 518.1866.

3.2.11. (Dimethylphenylsilyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(tributylstannyl)methane (**3aj**)

Colorless oil. R_f : 0.53 (hexane/ethyl acetate 9:1). $^1\text{H-NMR}$: δ 0.13 (s, 1H), 0.31 (s, 3H), 0.33 (s, 3H), 0.70–0.88 (m, 6H), 0.85 (t, $J = 7.0$ Hz, 9H), 1.11 (s, 6H), 1.12 (s, 6H), 1.14–1.50 (m, 12H), 7.26–7.35 (m, 3H), 7.50–7.60 (m, 2H). $^{13}\text{C-NMR}$: δ 0.5, 11.0, 13.6, 25.0, 25.1, 27.4, 28.9, 82.3, 127.4, 128.4, 133.5, 141.9. IR: ν_{max} 2957, 2930, 1351, 1311, 1294, 1262, 1247, 1146, 1113, 851, 818, 733, 700 cm^{-1} . FAB MS: m/z 564 [M^+], 549 [$\text{M}^+ - \text{Me}$], 191, 135, 83. Anal. Calc. for $\text{C}_{18}\text{H}_{33}\text{O}_2\text{BSiSn}$: C, 57.37; H, 9.09. Found: C, 57.65; H, 8.79%.

3.2.12. (Dimethylphenylsilyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(triphenylplumbanyl)methane (**3al**)

Colorless oil. R_f : 0.39 (hexane/ethyl acetate 10:1). $^1\text{H-NMR}$: δ 0.39 (s, 3H), 0.51 (s, 3H), 1.09 (s, 12H), 7.43–7.83 (m, 20H). $^{13}\text{C-NMR}$: δ 0.5, 24.6, 25.1, 82.8, 127.4, 128.0, 128.9, 129.5, 129.7, 129.9, 133.6, 136.9, 137.1, 137.4, 137.9, 141.0, 148.2, 150.9, 151.3, 154.5. IR: ν_{max} 3047, 2976, 1429, 1313, 1263, 1143, 849 cm^{-1} . FAB MS: m/z 714 [M^+], 191, 135, 83. FAB HRMS: m/z Calc. for $\text{C}_{32}\text{H}_{36}\text{BO}_2\text{PbSi}$ [M^+]: 699.2344. Found 699.2343.

3.2.13. Typical procedure of method B for silylborylation of tetrahalomethanes: synthesis of (dimethylphenylsilyl)(diiodo)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**3ar**)

To a solution of tetraiodomethane (**2s**, 0.62 g, 1.20 mmol) and (dimethylphenylsilyl)(pinacolato)borane (**1a**, 0.26 g, 1.00 mmol) in a mixture of THF (5.0 ml) and diethyl ether (2.5 ml) at -110 °C was added BuLi (1.56 M, 0.77 ml, 1.20 mmol). The reaction mixture was stirred for 10 min at -110 °C and then allowed to gradually warm to room temperature before quenching with saturated aqueous NH_4Cl solution (0.5 ml). The resulting mixture was diluted with diethyl ether (25 ml), and then washed with water (10 ml). The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. Purification of the crude product by column chromatography on silica gel (hexane/ethyl acetate 9:1) afforded **3ar** (0.10 g, 19% yield) as a colorless oil.

R_f : 0.47 (hexane/ethyl acetate 10:1). $^1\text{H-NMR}$: δ 0.70 (s, 6H), 1.27 (s, 12H), 7.36–7.81 (m, 5H). $^{13}\text{C-NMR}$: δ

-2.2 , 24.3, 85.1, 127.1, 129.6, 134.8, 135.4. IR: ν_{max} 2976, 1371, 1303, 1267, 1140, 1113, 849 cm^{-1} . FAB MS: m/z 529 [$\text{M}^+ + 1$], 528 [M^+], 527 [$\text{M}^+ - 1$], 135. FAB HRMS: m/z Calc. for $\text{C}_{15}\text{H}_{23}\text{BI}_2\text{O}_2\text{Si}$ [M^+]: 527.9650. Found 527.9655.

3.2.14. Dichloro(dimethylphenylsilyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**3an**)

Pale yellow oil. R_f : 0.51 (hexane/ethyl acetate 10:1). $^1\text{H-NMR}$: δ 0.60 (s, 6H), 1.22 (s, 12H), 7.26–7.70 (m, 5H). $^{13}\text{C-NMR}$: δ -5.0 , 24.5, 24.6, 85.3, 100.5, 127.5, 129.9, 133.6, 135.0. IR: ν_{max} 2978, 1373, 1319, 1251, 1136, 1110, 970 cm^{-1} . MS: m/z 348 [$\text{M}^+ + 4$], 347 [$\text{M}^+ + 3$], 346 [$\text{M}^+ + 2$], 345 [$\text{M}^+ + 1$], 344 [M^+], 343 [$\text{M}^+ - 1$], 229, 135. HRMS: m/z Calc. for $\text{C}_{15}\text{H}_{23}\text{BCl}_2\text{O}_2\text{Si}$ [M^+]: 344.0937. Found 344.0937.

3.2.15. Dibromo(dimethylphenylsilyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**3ap**)

Pale yellow oil. R_f : 0.48 (hexane/ethyl acetate 10:1). $^1\text{H-NMR}$: δ 0.65 (s, 6H), 1.25 (s, 12H), 7.35–7.76 (m, 5H). $^{13}\text{C-NMR}$: δ -3.9 , 24.4, 85.3, 127.4, 129.9, 134.2, 135.3. IR: ν_{max} 2982, 1470, 1390, 1373, 1315, 1248, 1137, 1117, 970 cm^{-1} . MS: m/z 436 [$\text{M}^+ + 4$], 434 [$\text{M}^+ + 2$], 432 [M^+], 421, 419, 417, 334, 253, 135. HRMS: m/z Calc. for $\text{C}_{15}\text{H}_{23}\text{BBr}_2\text{O}_2\text{Si}$ [M^+]: 431.9927. Found 431.9934. Anal. Calc. for $\text{C}_{15}\text{H}_{23}\text{BBr}_2\text{O}_2\text{Si}$: C, 41.51; H, 5.34. Found: C, 41.79; H, 5.30%.

3.2.16. [(Chloro)(dimethylphenylsilyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]benzene (**3at**)

Colorless oil. R_f : 0.42 (hexane/ethyl acetate 10:1). $^1\text{H-NMR}$: δ 0.39 (s, 3H), 0.43 (s, 3H), 1.22 (s, 6H), 1.25 (s, 6H), 7.12–7.44 (m, 10H). $^{13}\text{C-NMR}$: δ -4.7 , -4.5 , 24.5, 24.7, 84.4, 125.3, 126.3, 127.0, 127.5, 129.4, 135.2, 135.3, 139.0, 139.3. IR: ν_{max} 2978, 2931, 1495, 1427, 1373, 1323, 1269, 1141, 1114, 974 cm^{-1} . MS: m/z 388 [$\text{M}^+ + 2$], 387 [$\text{M}^+ + 1$], 386 [M^+], 286, 244, 135. HRMS: m/z Calc. for $\text{C}_{21}\text{H}_{28}\text{BClO}_2\text{Si}$ [M^+]: 386.1640. Found 386.1646. Anal. Calc. for $\text{C}_{21}\text{H}_{28}\text{BClO}_2\text{Si}$: C, 65.21; H, 7.30. Found: C, 64.94; H, 7.23%.

3.3. (Dimethylphenylsilyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(tributylstannyl)(trimethylgermyl)methane (**4**)

To a solution of **3ak** (0.41 g, 0.73 mmol) in THF (5 ml) was added LDA (0.76 mmol) in THF at room temperature and the resulting mixture was heated at 60 °C for 1.5 h. Bromotrimethylgermane (0.21 ml, 1.6 mmol) was added to the mixture at 60 °C and stirred for 1 h at 60 °C before quenching with saturated aqueous NH_4Cl solution. Usual workup followed by purification with silica gel column chromatography (hexane only) gave **4** (0.17 g, 34% yield).

Colorless oil. R_f : 0.28 (hexane). $^1\text{H-NMR}$: δ 0.11 (s, 9H), 0.41 (s, 3H), 0.42 (s, 3H), 0.74–0.96 (m, 6H), 0.87 (t, $J=6.9$ Hz, 9H), 1.23 (s, 12H), 1.2–1.5 (m, 12H), 7.25–7.34 (m, 3H), 7.58–7.68 (m, 2H). $^{13}\text{C-NMR}$: δ 2.4, 2.5, 3.8, 13.2, 13.6, 25.5, 27.7, 29.3, 82.5, 127.2, 128.4, 134.5, 142.5. IR: ν_{max} 2958, 2926, 1284, 1259, 1141, 855, 817 cm^{-1} . Anal. Calc. for $\text{C}_{30}\text{H}_{59}\text{O}_2\text{BGeSiSn}$: C, 52.83; H, 8.72. Found: C, 52.67; H, 8.80%.

3.4. (*Dimethylphenylsilyl*)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(trimethylgermyl)(trimethylstannyl)methane (**5**)

To a suspension of *t*-BuOK (0.25 g, 2.25 mmol) in THF (3 ml) was added BuLi (1.56 M in hexane, 1.44 ml, 2.25 mmol) at -78°C . A solution of **3aj** (0.15 g, 0.45 mmol) in THF (0.5 ml) was added to the solution at -78°C and the resulting mixture was allowed to warm to -40°C over a period of 7 h. The mixture was cooled to -78°C , treated with chlorotrimethylstannane (1 M in THF, 2.25 ml, 2.25 mmol), and allowed to warm to room temperature before quenching with saturated aqueous NH_4Cl solution. Usual workup followed by purification with silica gel column chromatography afforded **5** (0.19 g, 81% yield).

Colorless needles. M.p. 130°C (dec). $^1\text{H-NMR}$: δ 0.03 (s, 9H), 0.14 (s, 9H), 0.42 (s, 3H), 0.43 (s, 3H), 1.23 (s, 12H), 7.26–7.34 (m, 3H), 7.58–7.68 (m, 2H). $^{13}\text{C-NMR}$: δ -4.2 , 1.9, 2.2, 3.5, 25.4, 25.5, 82.5, 127.3, 128.5, 134.4, 142.1. IR: ν_{max} 2928, 2855, 1461, 1379, 1282, 1260, 1141, 857, 820 cm^{-1} . Anal. Calc. for $\text{C}_{21}\text{H}_{41}\text{O}_2\text{BGeSiSn}$: C, 45.38; H, 7.44. Found: C, 45.09; H, 7.17%.

3.5. (*Dimethylphenylsilyl*)(trimethylgermyl)(trimethylstannyl)methane (**6**)

Isolated by column chromatography on silica gel (hexane). Colorless oil. R_f : 0.43 (hexane). $^1\text{H-NMR}$: δ -0.25 (s, 1H), 0.02 (s, 9H), 0.13 (s, 9H), 0.31 (s, 3H), 0.32 (s, 3H), 7.27–7.36 (m, 3H), 7.44–7.53 (m, 2H). $^{13}\text{C-NMR}$: δ -5.9 , -2.9 , 1.2, 1.5, 2.7, 127.6, 128.5, 133.4, 142.3. IR: ν_{max} 2972, 2911, 1428, 1250, 1113, 1012, 959, 813, 769, 733, 700 cm^{-1} . Anal. Calc. for $\text{C}_{15}\text{H}_{30}\text{GeSiSn}$: C, 41.92; H, 7.04. Found: C, 41.66; H, 6.80%.

4. Summary

We have demonstrated that heteroatom-substituted boryl(silyl)methanes could be prepared efficiently by a reaction with silylboranes of halomethylolithiums substituted by such heteroatoms as chalcogens, halogens, germanium, lead, silicon, and tin. Moreover, we have synthesized B-, Ge-, Si-, and Sn-substituted methanes for the first time, which may act as a versatile C_1

organotetrametallic reagent for asymmetric synthesis of a quaternary carbon.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 207409 for compound **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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