

Synthesis and Reactions of Cyclic Silylboranes

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Five-membered cyclic silylboranes, 2-(diisopropylamino)-1,1-diorgano-1-sila-2-boracyclopentanes, were synthesized via intramolecular reductive B–Si bond formation with 3-[chloro(diisopropylamino)boryl]-1-(chlorodiorganosilyl)-propane. The cyclic silylboranes were thermally stable and could be distilled under a vacuum. The reaction of the cyclic silylboranes with alcohols resulted in a cleavage of the Si–B bond, whereas a reaction with *sec*-amines led to an amino group exchange on the boron atom. The insertion of alkynes into the Si–B bond of the cyclic silylborane was effectively catalyzed by palladium catalysts, leading to a regioselective formation of seven-membered cyclic alkenes in high yields.

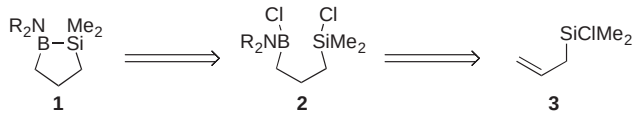
Organometallic compounds possessing inter-element linkages have gained much attention in organometallic chemistry, because they exhibit interesting properties and serve as useful reagents for organic synthesis.[1] Particular attention has been paid to the reactivities of the inter-element linkages between such group 13 and 14 elements as boron, silicon, and tin.[2,3] The activation of such inter-element linkages by a transition metal permits a variety of catalytic reactions. Indeed, catalytic bis-metallation reactions using bimetallic compounds containing B–B, Si–Si, Si–B, and Si–Sn are recognized as highly efficient methods for the synthesis of functionalized organic molecules.

The inter-element bonds of cyclic derivatives often exhibit characteristic reactivities that are inaccessible with acyclic derivatives. For example, in the addition of the silicon–silicon bond to alkynes, a five-membered cyclic disilane, 1,1,2,2-tetramethyl-1,2-disilacyclopentane, showed a much higher reactivity than the corresponding acyclic disilane, e.g., hexamethyldisilane.[4] Furthermore, the five-membered disilane undergoes unique cyclodimerization,[5] cyclooligomerization,[6,7] and ring-opening polymerization[6,8] via σ-bond metathesis in the presence of palladium catalysts. The synthesis and unique reactivities of a five-membered cyclic diboron derivative were also reported.[9]

We have been involved in the development of new transition metal-catalyzed reactions of silylboranes.[10–12] The synthetic potential of silylboranes was demonstrated by a variety of addition reactions to unsaturated organic compounds. In the course of the study, we became interested in the reactivity of cyclic silylboranes. We expected that the cyclic derivatives might exhibit interesting reactivities, which had never been found for acyclic silylboranes. Herein, we report on the first synthesis of five-membered cyclic silylboranes, starting from easily available starting materials. The reactivities of the cyclic silylboranes are also described.

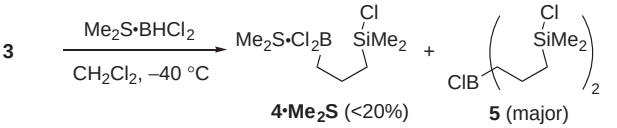
Results and Discussion

Retrosynthetic analysis of the target silylborane **1** is shown in Eq. 1. A silicon–boron bond is formed in the final step by a Wurtz-type reductive cyclization of dichloride **2**. The dichloride is prepared from allylsilane **3** via hydroboration. This retrosynthesis is based upon the successful synthesis of a five-membered cyclic disilane via hydrosilylation of **3**, followed by the reductive formation of a Si–Si bond.[13] A five-membered cyclic diboron was also prepared via reductive B–B bond formation.[9]



(1)

Our synthetic work started with seeking an efficient hydroboration system for introducing a chloro(dialkylamino)boryl group into allylsilane **3**. Because no practical hydroboration system using chloro(dialkylamino)borane [$(R_2N)ClBH$] could be found in the literature, we initially attempted a two-step sequence in which hydroboration with dichloroborane was followed by selective monoamination on the boron atom. The reaction of **3** with $Me_2S\cdot BHCl_2$, freshly prepared by disproportionation of $Me_2S\cdot BCl_3$ and $Me_2S\cdot BH_3$,[14] however, afforded dialkylchloroborane **5** as a major product with the formation of a dimethyl sulfide complex of the desired monoalkyldichloroborane **4** in less than 20% yield (Eq. 2). The formation of the undesired **5** may be attributed to rapid and reversible disproportionation of the dichloroborane to monochloroborane and trichloroborane.[15] The thus-formed monochloroborane reacts with two equivalents of **3** more rapidly than does the dichloroborane. Although we could isolate a dimethyl sulfide complex of **4** by recrystallization in hexane at −30 °C under a nitrogen atmosphere, a more practical method to prepare **4** was desired.



(2)

We then applied a reported protocol for the conversion of tri-

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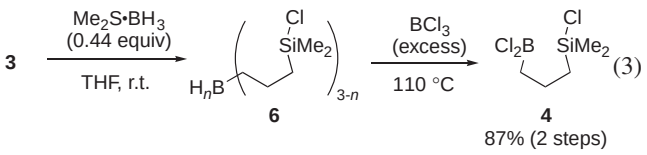
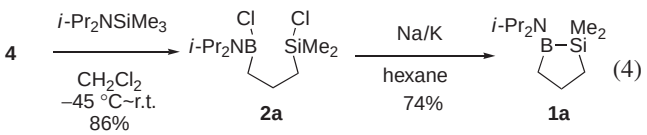
alkylborane to monoalkyldichloroborane via disproportionation with BCl_3.[16] A mixture of mono-, di-, and trialkylboranes **6**, which was prepared by the hydroboration of **3** with borane (0.44 equiv), was subsequently treated with BCl_3 (excess) at 110 °C (Eq. 3). Clean disproportionation took place to afford **4** in 87% yield.



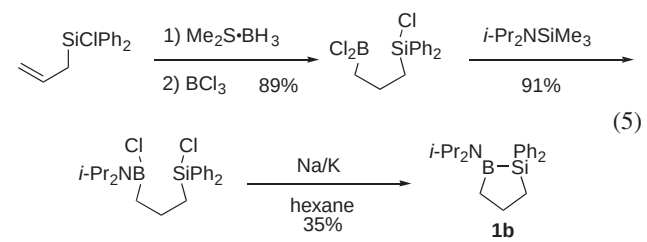
(3)

The 3-(dichloroboryl)propylsilane **4** was reacted with *N*-trimethylsilyldiisopropylamine, resulting in highly selective monoamination on the boron atom (Eq. 4). Thus, the desired 3-[chloro(diisopropylamino)boryl]propylsilane **2a** was obtained. Finally, **2a** was treated with Na/K alloy at room temperature in hexane. The Wurtz-type reductive coupling took place to give five-membered cyclic silylborane **1a** in 74% yield. The cyclic silylborane **1a** was thermally stable, allowing isolation by distillation. Although the cyclic silylborane gradually decomposed upon exposure to air, it could be handled in air for a short period.



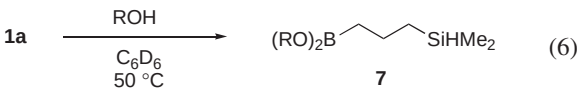
(4)

The established route to cyclic silylborane was successfully applied to the synthesis of derivative **1b** carrying phenyl groups on the silicon atom (Eq. 5).



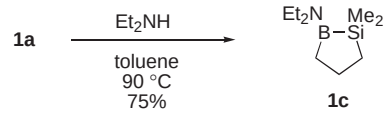
(5)

With the cyclic silylboranes in hand, substitution of the diisopropylamino group with alkoxy or other amino groups was attempted for the synthesis of related cyclic silylboranes bearing various functionalities on the boron atom. The reaction of **1a** with alcohols, however, resulted in the formation of ring-opening product **7** with the incorporation of two molecules of alcohol in the product (Eq. 6). Notably, only the dialkoxyborane derivatives were obtained in high yields with either methanol, isopropyl alcohol, or phenol. We presume that the diisopropylamino group of **1a** is initially substituted by an alkoxy group, giving an alkoxy-substituted cyclic silylborane. Subsequent alcoholysis of the silylborane may take place quickly, resulting in the formation of the ring-opening product **7**.



(6)

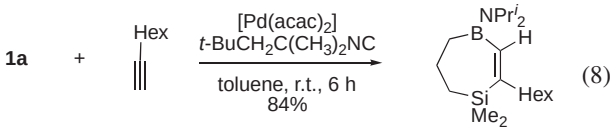
Unlike the reaction with alcohols, successful substitution of the diisopropylamino group of **1a** with a diethylamino group took place in a reaction with diethylamine in toluene at 90 °C (Eq. 7). The diethylamino-substituted cyclic silylborane **1c** was isolated by distillation. Although similar amino exchange reactions took place in the reaction of **1a** with morpholine or pyrrolidine, isolation of the corresponding products by distillation failed due to thermal decomposition.



(7)

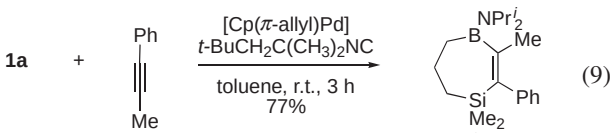
Our interest was then focused on the reactivity of the cyclic silylborane toward transition metal catalysts. It has been established that acyclic silylboranes are activated by group 10 metal catalysts, i.e., nickel, palladium, and platinum complexes, leading to the catalytic silaboration and silaborative C–C bond-forming reactions.[10–12] To demonstrate the potential utility of the cyclic silylborane in the transition metal catalysis, we tested some simple insertion reactions of alkynes into the Si–B bond.[11a,b]

1-Octyne reacted with **1a** in the presence of a palladium catalyst having isocyanide ligands at room temperature (Eq. 8).[17] The reaction selectively afforded one of the two possible regioisomers **8** in which the boron atom is attached to the terminal alkyne carbon atom selectively.



(8)

The silaboration was also examined with an internal alkyne, 1-phenylpropyne. Only the single regioisomer **9** was formed after 3 h at room temperature in the reaction using cyclic silylborane **1a**. It should be noted that the cyclic silylborane gives a better regioselectivity than the acyclic one (93:7), which requires a higher temperature of 110 °C (Eq. 9),[11a,b] although it seems to be difficult to assume the effect of the cyclic structure on the reactivity and selectivity because of the significant difference in the substitution pattern.



(9)

Conclusion

We have synthesized the first five-membered cyclic silylboranes, starting from easily available starting materials, i.e., chlorodiorganoallylsilane and dimethyl sulfide–borane complex, via reductive silicon–boron bond formation with Na/K alloy. The cyclic silylboranes were thermally stable and could be distilled under an inert atmosphere. The cyclic silylboranes added to alkynes in the presence of palladium catalysts. The silaboration reactions proceeded with higher regioselectivity under milder reaction conditions than the acyclic silylboranes used in previous studies. The successful activation of the silicon–boron bond of the cyclic silylborane may open new possibilities to the transition metal catalysis of silylborane.

Experimental

General. ^{1}H, ^{11}B, and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 spectrometer (7.0 T magnet) at ambient temperature. ^{29}Si NMR spectra were recorded on a JEOL JNM-GX400 spectrometer (9.3 T magnet) at ambient temperature. ^{1}H NMR data are reported as follows: chemical shift in ppm downfield from tetramethylsilane (δ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), and integration. ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). All ^{13}C NMR spectra were obtained with complete proton decoupling. ^{11}B NMR chemical shifts are reported in ppm downfield from $Et_2O{\cdot}BF_3$ (δ scale). ^{29}Si NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). High resolution mass spectra (HRMS) were recorded on a JEOL JMS-SX102A spectrometer.

All reactions were carried out under an argon or nitrogen atmosphere. $Me_2S{\cdot}BH_3$ and BCl_3 were purchased from commercial sources, and used without further purification. Allylchlorodimethylsilane, trimethylsilyldiisopropylamine, and 1,1,3,3-tetramethylbutyl isocyanide were purchased from commercial sources and purified by distillation before use. All solvents were distilled under an argon atmosphere from appropriate drying agents before use.

Synthesis of Chloro(3-dichloroborylpropyl)dimethylsilane (4). To a solution of dimethyl sulfide–borane (6.2 mL, 66 mmol) in dichloromethane (24 mL) placed in a three-necked flask was added a solution of allylchlorodimethylsilane (**3**) (20 g, 149 mmol) in dichloromethane (24 mL) dropwise over 40 min at room temperature. The mixture was stirred for 10 h at room temperature. The solution was then transferred to a three-necked flask fitted with a dry-ice condenser and a gas inlet. The volatile materials were evaporated under a vacuum at room temperature. Into the residue heated at 110 °C was introduced BCl_3 (21 mL, 250 mmol) over 45 min via a gas-inlet tube with vigorous stirring. The mixture was heated at 110 °C for 2 h, and then 1-hexene (27 mmol) was added while still heating. The mixture was further stirred at 110 °C for 30 min and then cooled to room temperature. The volatile materials were evaporated under a vacuum. Distillation under a vacuum (79–93 °C/15 mmHg) afforded **4** (28 g, 87% for 2 steps) as a colorless liquid.

^{1}H NMR (C_6D_6) δ 0.12 (s, 6H), 0.42 (m, 2H), 1.11 (t, 2H), 1.37 (m, 2H); ^{13}C NMR (C_6D_6) δ 2.7, 20.2, 22.5, 34.0 (br); ^{11}B NMR (C_6D_6) δ 62.1; ^{29}Si NMR (C_6D_6) δ 30.2.

Synthesis of Chloro{3-[chloro(diisopropylamino)boryl]propyl}dimethylsilane (2). To a solution of **4** (2.38 g, 11.0 mmol) in dichloromethane (6.4 mL) was added dropwise a solution *N*-trimethylsilyldiisopropylamine (1.59 g, 11.0 mmol) in dichloromethane (6.4 mL) over 5 min at −40 °C. The solution was stirred for 10 h while gradually raising the bath temperature (−40 °C to room temperature). After concentration of the reaction mixture under a vacuum, **2** (2.65 g, 86%) was isolated by bulb-to-bulb distillation (100 °C/0.2 mmHg (bath temperature)). ^{1}H NMR (C_6D_6) δ 0.20 (s, 6H), 0.75–0.79 (m, 2H), 0.91 (d, J = 6.8 Hz, 6H), 1.00–1.13 (br, 6H), 1.18 (t, J = 8.0 Hz, 2H), 1.73 (m, 2H), 3.24–3.43 (bs, 2H); ^{13}C NMR (C_6D_6) δ 1.8, 20.2, 22.5, 23.2, 26.6 (br), 48.2 (br); ^{11}B NMR (C_6D_6) δ 38.6; ^{29}Si NMR (C_6D_6) δ 30.7.

Synthesis of 2-Diisopropylamino-1,1-dimethyl-1-sila-2-boracyclopentane (1a). To a suspension of Na/K alloy, prepared from Na (2.54 g, 66 mmol) and K (7.7 g, 198 mmol), in hexane (90 mL) was added **2** (15.5 g, 55 mmol) in hexane (90 mL) at room temperature over 20 min. The resultant blue-purple suspension was vigorously stirred for 3 days at room temperature. Under a nitrogen atmosphere, the supernatant solution was decanted and the remaining precipitates were centrifuged to allow separation of the precipitates. The precipitates were washed with hexane. The combined hexane solution was evaporated in vacuo. Bulb-to-bulb distillation (90 °C/10 mmHg (bath temperature)) afforded **1a** (8.5 g, 74%). ^{1}H NMR (C_6D_6) δ 0.22 (s, 6H), 0.81 (t, J = 7.2 Hz, 2H), 1.00 (d, J = 6.8 Hz, 6H), 1.02 (d, J = 6.8 Hz, 6H), 1.20 (t, J = 6.8 Hz, 2H), 1.91 (m, 2H), 3.29 (septet, J = 6.8 Hz, 1H), 3.47 (septet, J = 6.8 Hz, 1H); ^{13}C NMR (C_6D_6) δ 1.1, 18.5, 24.0, 25.2, 25.6, 27.2 (br), 49.5, 57.5 (br); ^{11}B NMR (C_6D_6) δ 53.2; ^{29}Si NMR (C_6D_6) δ −15.2 (broad). HRMS Calcd for $C_{11}H_{26}BNSi$ (M^+): 211.1927. Found: 211.1922.

Synthesis of 2-Diisopropylamino-1,1-diphenyl-1-sila-2-boracyclopentane (1b). According to a procedure similar to that for the synthesis of **1a**, **1b** was prepared from chloro{3-[chloro(diisopropylamino)boryl]propyl}diphenylsilane (2.1 g, 5.2 mmol) over 2 days at room temperature. **1b** (0.60 g, 35%) was isolated by bulb-to-bulb distillation (160–190 °C/0.4 mmHg (bath temperature)). **1b**: ^{1}H NMR (C_6D_6) δ 0.83 (d, J = 6.8 Hz, 6H), 1.07 (d, J = 6.8 Hz, 6H), 1.26 (t, J = 6.8 Hz, 2H), 1.37 (t, J = 6.8 Hz, 2H), 2.00 (m, 2H), 3.06 (septet, J = 6.8 Hz, 1H), 3.90 (septet, J = 6.8 Hz, 1H), 7.14–7.22 (m, 6H), 7.63–7.66 (m, 4H); ^{13}C NMR (C_6D_6) δ 16.6, 22.5, 24.4, 24.7, 26.9, 47.0, 60.9, 128.5, 129.2, 136.4, 138.9; ^{11}B NMR (C_6D_6) δ 53.3; ^{29}Si NMR (C_6D_6) δ −13.0. HRMS Calcd for $C_{21}H_{30}BNSi$ (M^+): 335.2241. Found: 335.2240.

Reaction of 1a with Alcohols: A Representative Reaction of 1a with Isopropyl Alcohol. A mixture of **1a** (0.10 g, 0.47 mmol) and isopropyl alcohol (0.11 mL, 1.42 mmol) in C_6D_6 (4 mL) was heated at 50 °C. Periodically, a small portion of the sample was taken out, and the extent of the reaction was checked by ^{1}H NMR. No intermediary species, such as 2-isopropoxy-1,1-dimethyl-1-sila-2-boracyclopentane, were detected by the ^{1}H NMR observation. After 24 h, the volatile materials were evaporated under a vacuum. Quick bulb-to-bulb distillation (90 °C/10 mmHg (bath temperature)) of the residue gave 1-dimethylsilyl-3-(diisopropylboryl)propane (90 mg, 83%). An attempt at further purification of the material by distillation was accompanied by slight decomposition. The material did not give a satisfactory mass spectrum under EI or FAB ionization conditions. ^{1}H NMR (C_6D_6) δ 0.05 (d, J = 2.8 Hz, 6H), 0.69 (m, 2H), 0.88 (t, J = 7.6 Hz, 2H), 1.09 (d, J = 6.0 Hz, 12H), 1.69 (m, 2H), 4.16 (m, 1H), 4.35 (septet, J = 6.0 Hz, 2H); ^{13}C NMR (C_6D_6) δ −13.8, 17 (br), 18.2, 20.2, 25.2, 65.5; ^{11}B NMR (C_6D_6) δ 29.8; ^{29}Si NMR (C_6D_6) δ 13.9.

Reaction of 1a with Diethylamine: Amino Group Exchange. To a 0.5 M solution of **1a** (1.0 g, 4.7 mmol) in toluene was added diethylamine (3.0 mL, 29 mmol) at room temperature. The mixture was stirred at 90 °C for one week. Evaporation of the volatile materials and bulb-to-bulb distillation under a vacuum (85 °C/8 mmHg (bath temperature)) afforded 2-diethylamino-1,1-dimethyl-1-sila-2-boracyclopentane (0.65 g, 75%). ^{1}H NMR (C_6D_6) δ 0.23 (s, 6H), 0.887 (t, J = 7.2 Hz, 3H), 0.892 (t, J = 7.2 Hz, 2H), 0.96 (t, J = 7.2 Hz, 3H), 1.05 (t, J = 7.2 Hz, 2H), 1.94 (quintet, J = 7.2 Hz, 2H), 2.91 (q, J = 7.2 Hz, 2H), 3.06 (q, J = 7.2 Hz, 2H); ^{13}C NMR (C_6D_6) δ 2.9, 16.1, 17.0, 18.2, 24.2, 44.3, 50.5; ^{11}B NMR (C_6D_6) δ 54.3; ^{29}Si NMR (C_6D_6) δ −17.2. HRMS Calcd for $C_9H_{22}BNSi$ (M^+): 183.1615. Found: 183.1617.

Reaction of 1a with 1-Octyne. To a mixture of **1a** (21.1 mg, 0.10 mmol) and 1-octyne (30 μL, 0.20 mmol) in C_6D_6 (0.5 mL) was added a solution of [Pd(acac)$_2$] (0.61 mg, 2.0 μmol) and

1,1,3,3-tetramethylbutyl isocyanide (1.1 mg, 8.0 μmol) in C_6D_6 (10 μL). The mixture was allowed to react at room temperature for 6 h. Evaporation of the volatile material, followed by bulb-to-bulb distillation (150 °C/2.0 mmHg (bath temperature)), afforded 7-diisopropylamino-2-hexyl-3,3-dimethyl-3-sila-7-boracycloheptene (**8**) (27 mg, 84%): ^{1}H NMR (C_6D_6) δ 0.25 (s, 6H), 0.80 (t, $J = 6.4$ Hz, 2H), 0.87 (t, $J = 7.2$ Hz, 3H), 1.03 (d, $J = 6.0$ Hz, 6H), 1.12 (d, $J = 6.0$ Hz, 6H), 1.20–1.30 (m, 6H), 1.30–1.40 (m, 2H), 1.51–1.59 (m, 2H), 1.87–1.93 (m, 2H), 2.34–2.38 (m, 2H), 3.85–3.70 (brs, 2H), 6.85–7.04 (brs, 1H); ^{13}C NMR (C_6D_6) δ −0.83, 14.5, 17.1, 20.1, 22.3, 23.3, 23.7, 29.9, 30.0, 30.5, 32.4, 41.2, 47.6, 149.0, 153.5. HRMS Calcd for $C_{19}H_{39}BNSi$ (MH^+): 320.2945. Found: 320.2934.

Reaction of 1a with 1-Phenylpropyne. A mixture of π-allyl(cyclopentadienyl)palladium (1.1 mg, 5.0 μmol), 1,1,3,3-tetramethylbutyl isocyanide (14 mg, 10 μmol), and 1-phenylpropyne in toluene (0.5 mL) was stirred for 30 min at room temperature. To the mixture was added **1a** (21.1 mg, 0.10 mmol), and the resulting mixture was stirred at room temperature for 1 h. Evaporation of the volatile material, followed by bulb-to-bulb distillation (150 °C/2.0 mmHg (bath temperature)), afforded 7-diisopropylamino-1,3,3-trimethyl-2-phenyl-3-sila-7-boracycloheptene (**9**) (60 mg, 77%): ^{1}H NMR (C_6D_6) δ −0.55 (s, 3H), 0.28 (s, 3H), 0.67–0.74 (m, 1H), 0.88–1.00 (m, 1H), 0.93 (d, $J = 6.8$ Hz, 3H), 1.06 (d, $J = 6.4$ Hz, 3H), 1.11–1.17 (m, 1H), 1.19 (d, $J = 6.8$ Hz, 3H), 1.35 (d, $J = 7.2$ Hz, 3H), 1.55–1.67 (m, 1H), 1.71 (s, 3H), 1.86–1.98 (m, 1H), 2.07–2.14 (m, 1H), 3.02–3.12 (septet, $J = 7.2$ Hz, 1H), 3.83–3.93 (septet, $J = 7.2$ Hz, 1H), 7.02–7.05 (m, 2H), 7.07–7.12 (m, 1H), 7.23–7.27 (m, 2H); ^{13}C NMR (C_6D_6) δ 0.2, 1.7, 17.4, 20.8, 21.1, 21.8, 23.1, 23.6, 26.3, 26.6, 33.2, 46.0, 53.2, 126.6, 145.7, 147.3. HRMS Calcd for $C_{20}H_{34}BNSi$ (MH^+): 327.2554. Found: 327.2548.

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