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Toward Multi-Functionalized Organogermaniums: Diastereoselective Transformations of Germacycles Derived from Cheletropic Reactions of Boron-Substituted Butadienes with Ge(II) Salts

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The field of organogermanium in chemistry has recently attracted attention. Thanks to the inherent features of germanium (Ge), introducing Ge-based substituents into organic frameworks has enhanced bioactivity and optoelectronic properties of molecules. Herein, the synthesis of multi-functionalized organogermaniums using Ge(II) salts is reported. The germacycles having an allylboron moiety, which is derived from the (4 + 1) cycloadditions of the butadienes bearing a boronic ester moiety with Ge(II) salts, can be applied to further allylboration of aldehydes with perfect diastereoselectivity. The obtained allylated adducts enable access to π-extended organogermaniums with the retention of the stereocenters.

Introduction

The field of organogermanium in chemistry has recently demonstrated its growing importance. Compared with other widely used Group 14 atoms, Si and Sn, the inherent atomic specificity of Ge is attractive as a component of the functional group of organic frameworks (Figure 1A).[1] Germanium has higher electronegativity than silicon and tin (Pauling: Si: 1.90; Ge: 2.01; Sn: 1.96), and as a result, Ge–C bonds are more covalent.[1] The covalent radius of Ge (121 pm) is slightly larger than that of Si (116 pm) and significantly smaller than that of Sn (140 pm).[2] Even though it is in the 4th period of the periodic table, the relatively smaller atomic size of Ge allows it to readily interact with external ligands and facilitate the incorporation of Ge moieties into organic frameworks. Thanks to these inherent features of Ge, not shared by Si and Sn, introducing Ge-based substituents into organic frameworks has enhanced the bioactivity of pharmacological molecules[3–9] and modulated optoelectronic properties of π-conjugated systems.[10–17] More recently, the Ge–C bond has been applied to the orthogonal cross-coupling reaction in the presence of other readily functionalizable moieties.[18–20]

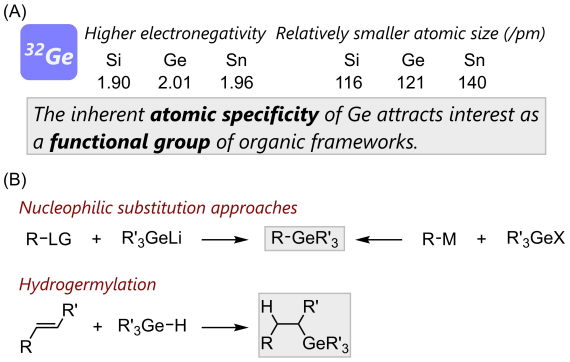

Figure 1. (A) Atomic specificity of Ge. (B) Examples of conventional approaches to the preparation of organogermaniums. LG = leaving group. M = Li and MgX. X = Cl and Br.

Several synthetic approaches have been provided to introduce Ge moieties into organic frameworks (Figure 1B). Nucleophilic substitution of alkyl halides/tosylates with germanium nucleophiles[21–26] or nucleophilic displacement at halogermanes with metallic nucleophiles[27,28] and hydrogermylations of unsaturated bonds with hydrogermanes[29–34] have been well-established as powerful methodologies. Still, inevitable synthetic problems in these traditional approaches, including poor functional group tolerance, chemical instability of reagents, and requirements for excess reagents, hamper the expression and use of organogermaniums, and the development of reliable and versatile synthetic methods for organogermaniums is eagerly anticipated. Recent progresses, including reductive coupling using low-valent metals,[35,36] electrochemical coupling,[37] metal-free germylation with dibenzothiophenium salts,[38] and direct C–H germylation promoted by lithium tetramethylpiperidide (LiTMP),[39] have demonstrated a rich chemistry of organogermaniums. Along with the developments of a variety of synthetic methods of organo organogermaniums,

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recent achievements of transition metal-catalyzed cross-coupling have enhanced the synthetic value of organogermaniums. Thanks to important contributions by Schoenebeck and co-workers, germyl groups are now functional groups that can be transformed through transmetalations and photoredox processes.[40–47]

A promising alternative approach to organogermaniums is to use divalent germanium species, germylenes.[48–50] Germylene, which possesses both reducing ability originating from its low-valent nature and Lewis acidity derived from its vacant *p*-orbital, readily undergoes oxidative addition[51,52] with electrophilic substrates, *i.e.*, alkyl halides and (4+1) cycloaddition[53–55] with unsaturated substrates, *i.e.*, enones. The distinct reactivities of divalent germanium salts have paved the way for the stereoselective synthesis of multi-functionalized molecules.[56–59] The stereoselective allylations[59] or aldol-type reactions[60–63] of carbonyl compounds have been accomplished using low-valent germanium. Our recent studies revealed that the diastereoselective synthesis of oxagermacycles **B** from enones and aldehydes via cyclic germanium enolates **A** resulted in their transformations into triols bearing four diastereo-controlled stereocenters[64] and multisubstituted enones (Figure 2A).[65] Inspired by the reactivity of the oxagermacycle **B**, in which a Ge–O bond plays a crucial role in the stereoselective transformation, we conceive replacing the Ge–O bond of an oxagermacycle with a Ge–C bond by changing the starting substrates from enones to butadienes (Figure 2B). Considering the high covalent character of a Ge–C bond, the corresponding carbon-based germacycles **C** will be a suitable starting material for multi-functionalized organogermaniums. Herein, we demonstrate (4+1) cycloadditions of boron-substituted butadienes with Ge(II) salts, in which the boron-substituents enhanced the reactivity of dienes with Ge(II) salts and assisted further functionalization. The obtained carbon-based germacycles are applicable as a synthon for functionalized organogermaniums.

Results and Discussion

In an initial study, to obtain carbon-based germacycles, we focused on the (4+1) cycloaddition of simple dienes with Ge(II) salts. This protocol was originally employed to trap the reactive Ge(II) species,[16,48,66,67] but the cheletropic reaction with relatively stable Ge(II) salts has only been investigated to a limited extent because of its low reactivity.[51,68,69] Moreover, the transformation of the generated carbon-based germacycles has not been well examined previously.[70–72] As a model study, we first examined the reaction of (2*E*,4*E*)-hexa-2,4-diene **1a** or (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene **1b** with a $GeCl_2$-dioxane complex (Scheme 1A). No reaction occurred, because the steric hindrance of the terminal methyl or phenyl groups and the relatively high LUMO energy level of the dienes may hamper the reaction. To promote the reaction, the diene **2**, in which one of the terminal substituents of **1** was replaced with a boronic acid pinacol ester, was employed. Introducing a boron-based moiety stabilizes the LUMO energy level of the diene (−0.595 eV for **1a** and −1.29 eV for **2a** calculated at the B3LYP/6-311+G(d) level, Figure S6)[73] and extends the diversity of functionalization of the generated germacycle.[58,74,75] The treatment of boron-substituted diene **2a**[76] or **2b**[76] with $GeCl_2$-dioxane in CH_3CN at room temperature stereoselectively gave germacycle **3a**/**b**-Cl with a *cis*-orientation, determined by nuclear Overhauser effect (NOE) of correlation of the protons at the 1- and 4-positions in **3b**-Cl (Scheme 1B). It should be noted that no corresponding cheletropic reaction occurred using $SnCl_2$ instead of $GeCl_2$-dioxane. This result indicates the reducing ability of Ge(II) salt is suitable for the (4+1) cycloaddition. The (4+1) cycloaddition was applicable to several dienes, including substituted dienes at the 1-, 3-, and/or 4-positions, to yield the corresponding germacycle **3c**–**3f** in moderate to good yields (Table 1). $GeBr_2$-dioxane was also applicable to the reactions. The reaction of diene **2g**[77] having a boronic acid pinanediol ester as a chiral auxiliary moiety proceeded stereoselectively, giving the germacycle **3g** as a 1:1 diastereomixture (entry 7).

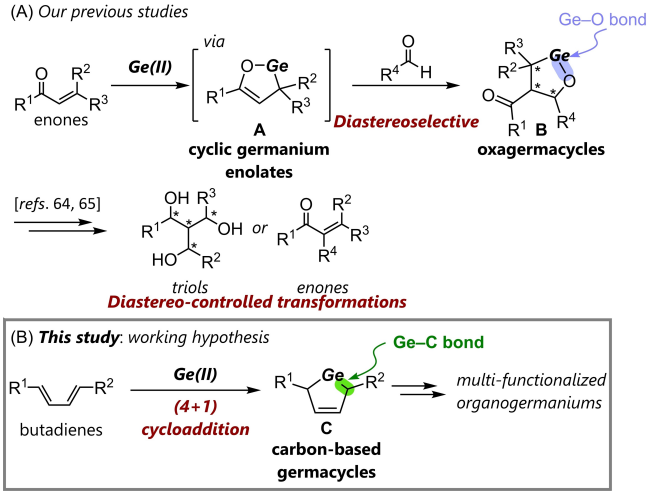
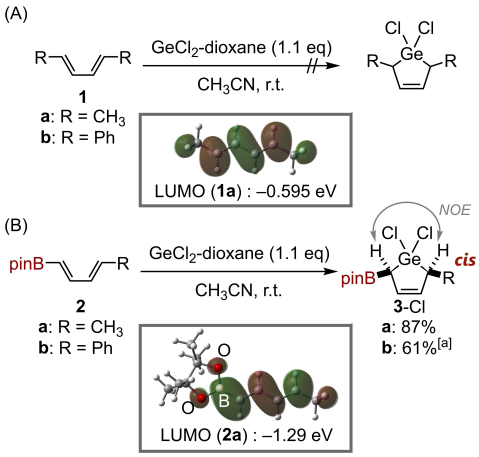


Figure 2. (A) Our previous studies of the transformations of oxagermacycles **B**.[64,65] (B) Synthesis of multi-functionalized organogermaniums from carbon-based germacycles **C** in this work.



Scheme 1. Model trials for the (4+1) cycloaddition of (A) **1** and (B) **2** with $GeCl_2$-dioxane. [a] The yield was estimated by ^{1}H NMR measurement.

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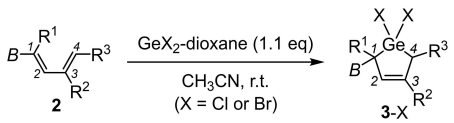
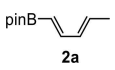
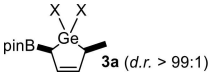
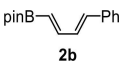
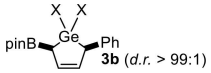
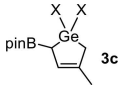
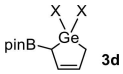
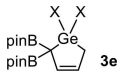
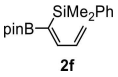
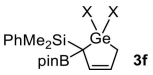
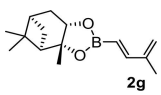
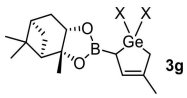
Table 1. (4+1) cycloadditions of boron-substituted butadienes **2** with GeX_2-dioxane.



entry	diene 2	germacycle 3	yield of 3
1	 **2a**	 **3a** (*d.r.* > 99:1)	**3a**-Cl: 87% **3a**-Br: 87%
2	 **2b**	 **3b** (*d.r.* > 99:1)	**3b**-Cl: 61%[a] **3b**-Br: 51%[a]
3	 **2c**	 **3c**	**3c**-Cl: 99% **3c**-Br: 96%
4	 **2d**	 **3d**	**3d**-Cl: 87% **3d**-Br: 89%
5	 **2e**	 **3e**	**3e**-Cl: 66% **3e**-Br: 85%
6	 **2f**	 **3f**	**3f**-Cl: 76% **3f**-Br: 73%
7	 **2g**	 **3g**	**3g**-Cl: 82% **3g**-Br: 67%

[a] The yield was estimated by ^{1}H NMR measurement.

The molecular structures of **3c**-Br, **3e**-Br, and **3f**-Br were confirmed by the X-ray crystallographic analysis (Figure 3A). The germacycle **3** is formally depicted as the superimposition of an allylborane and an allylgermane moiety. The Ortep drawing **3c**-Br revealed that the dihedral angle of the B–C–C=C (67°) is much larger than that of the Ge–C–C=C (8.6°), suggesting that the germacycles have significant character as nucleophilic allylborane species via an effective hyperconjugation between σ(C–B) and π*(C=C) orbitals. Theoretical calculations also supported this idea (Figure S7). Although 1,1-diboryl germacycle **3e**-Br shows an identical geometry to **3c**-Br, 1-boryl-1-silyl germacycle **3f**-Br exhibits a larger dihedral angle between the Si–C–C=C (76°) rather than the B–C–C=C (47°) owing to the effective hyperconjugation of the allylsilane moiety (Figure 3B).

The reaction of germacycle **3c**-Cl with benzaldehyde **4a** nicely gave a sole product of allylboration **5ca**-Cl without any activators. It should be emphasized that extremely high disateroselectivity was observed (Figure 4A). The *syn*-geometry of the product was confirmed by X-ray analysis (Figure 4B, entry 1 in Table 2). The high diastereoselectivity suggests that the allylation was expected to proceed via a chair-like transition state, in which the phenyl group of benzaldehyde is placed at the equatorial position of the six-membered ring due to the steric hindrance between the boronic ester moiety (Figure 4C).[78]

The allylboration of benzaldehyde **4a** with the germacycles **3** is summarized in Table 2. The germacycles **3d**-Cl and **3e**-Cl afforded the corresponding products (**5da**-Cl and **5ea**-Cl, entries 3 and 4). For the germacycles derived from $GeBr_2$-dioxane (**3c**-B, entry 2) or having a bulky boronic ester group (**3g**-Cl, entry 5), the products remained at low yield. The germacycles having a substituent at the 4-position (**3a**, **3b**) or Si-group at the 1-position (**3f**) exhibited no reaction, only to give the starting butadiene (**2a**, **2b**, and **2f**) through retro (4+1) cycloaddition (entries 6–8).

The allylations of several aldehydes were investigated by using the germacycle **3c**-Cl (Table 3). The benzaldehyde derivatives bearing electron-donating (**4c**, entry 1) and electron-withdrawing (**4d**, **4e**, and **4f**, entries 2–4) groups and 2-naphthaldehyde (**4g**, entry 5) and cinnamaldehyde (**4h**, entry 6) were applicable to the reaction, but 4-methoxybenzaldehyde (**4b**, entry 7) possessing a strong electron-donating group suppressed the yield. The allylated adducts were obtained with perfect stereoselectivity in all reactions. Allylations of aliphatic aldehydes, ketones, or imines did not proceed.

The high accessibility of the stereocontrolled allylated adducts, which are carbon-based germacycles, prompted us to transform the adducts into multi-functionalized organogermaniums diastereoselectively (Figure 5). First, the borate ester

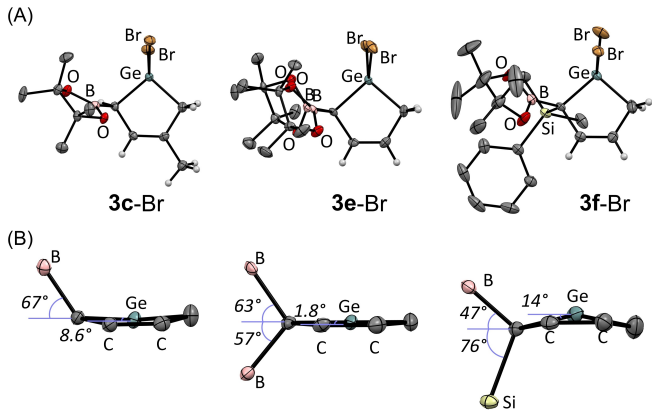


Figure 3. Ortep drawings of **3c**-Br, **3e**-Br, and **3f**-Br with 50% probability ellipsoids. (A) Top view and (B) side view. Some atoms are omitted for clarity.

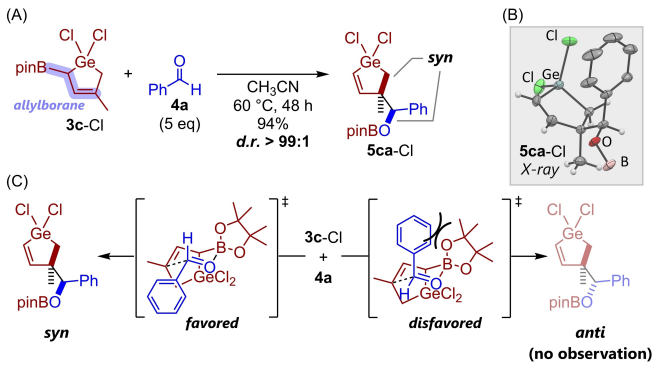


Figure 4. (A) Diastereoselective allylboration of **4a** with **3c**-Cl. (B) Ortep drawings of **5ca**-Cl with 50% probability ellipsoids. Some atoms are omitted for clarity. (C) Plausible transition state structures in the allylation of **4a** with **3c**-Cl.

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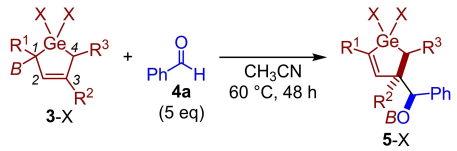
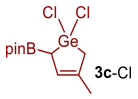
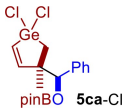
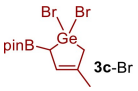
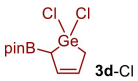
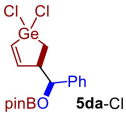
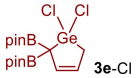
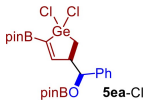
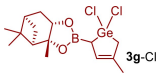
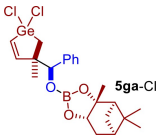
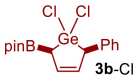
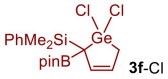
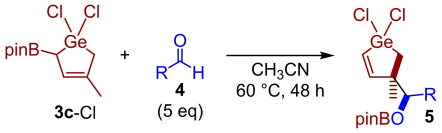
Table 2. Scope of alyllborations of **4a** with germacycles **3**.

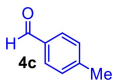
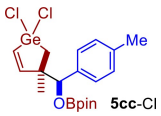
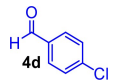
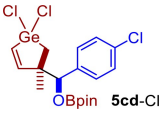
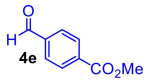
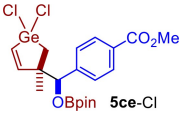
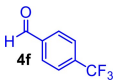
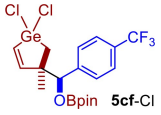
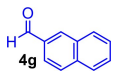
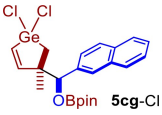
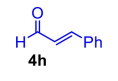
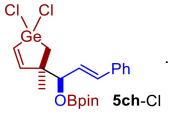
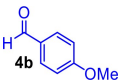
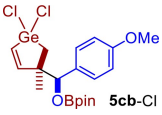


entry	germacycle **3**	allylated adduct **5**	*d.r.*	yield of **5**
1	 **3c**-Cl	 **5ca**-Cl	>99:1	94%
2	 **3c**-Br	 **5ca**-Br	>99:1	42%[a]
3	 **3d**-Cl	 **5da**-Cl	>99:1	79%
4	 **3e**-Cl	 **5ea**-Cl	>99:1	78%
5	 **3g**-Cl	 **5ga**-Cl	>99:1	69%[a]
6	 **3a**-Cl	n.d.	–	–
7	 **3b**-Cl	n.d.	–	–
8	 **3f**-Cl	n.d.	–	–

[a] The yield was estimated by ^{1}H NMR measurement.

Table 3. Substrate scope of aldehyde **4** for the allylboration.



entry	aldehyde **4**	allylated adduct **5**	d.r.	yield of **5**
1	 **4c**	 **5cc**-Cl	>99:1	54%[a]
2	 **4d**	 **5cd**-Cl	>99:1	58%
3	 **4e**	 **5ce**-Cl	>99:1	46%[a]
4	 **4f**	 **5cf**-Cl	>99:1	35%[a]
5	 **4g**	 **5cg**-Cl	>99:1	46%
6	 **4h**	 **5ch**-Cl	>99:1	23%[b]
7	 **4b**	 **5cb**-Cl	–	n.d.

[a] The yield was estimated by ^{1}H NMR measurement. [b] Chlorobenzene was employed as the reaction solvent instead of CH_3CN.

moiety was removed by the treatment of **5** with methanol to give the secondary alcohol **6**. The dichlorogermyl group of **6** was converted into dihydro- (**7**-H), dimethyl- (**7**-Me), and diethylgermyl (**7**-Et) moieties (Figure 5A). Next, the selective functionalization of the C(sp^2)—Ge bond of the germacycles was conducted (Figure 5B). The reaction of **7**-Et with *N*-iodosuccinimide (NIS) afforded the oxagermacyclopentane with iodovinyl moiety **8**-Et via the addition of iodonium to the C=C double bond followed by the nucleophilic attack of the hydroxy group on the Ge center.[79] The X-ray analysis of **8cd**-Et demonstrated that the iodination and the subsequent nucleophilic substitution proceeded with the retention of the stereocenter generated by the allylboration. A similar transformation was accomplished by using a Pd-catalyzed cross-coupling in the presence of Ag(I) salt.[38,42] The reaction of the germacycle **7ca**-Me with iodobenzene in the presence of $Pd_2(dba)_3$ and $AgBF_4$ followed by the treatment of MeMgBr gave the homoallylalcohol **9** having a stereo-controlled germyl group. The ring-opening of **10** derived from methylation of the germacycle **7ca**-Me with I_2[80,81] and the subsequent methylation of **11** with MeMgBr resulted in the iodovinyl derivative **12**. Utilizing the iodovinyl moiety of **12** allowed us to synthesize several π-extended organogermaniums having a stereo-controlled germyl group. Palladium-catalyzed Suzuki-Miyaura, Mizoroki-Heck, and Sonogashira cross-couplings furnished the arylated (**13**), vinylated (**14**), and ethynylated (**15**) products, respectively. The functionalizations of the germyl moieties in the obtained products failed despite a number of attempts using various reported methodologies. Further studies are now ongoing in our laboratory.

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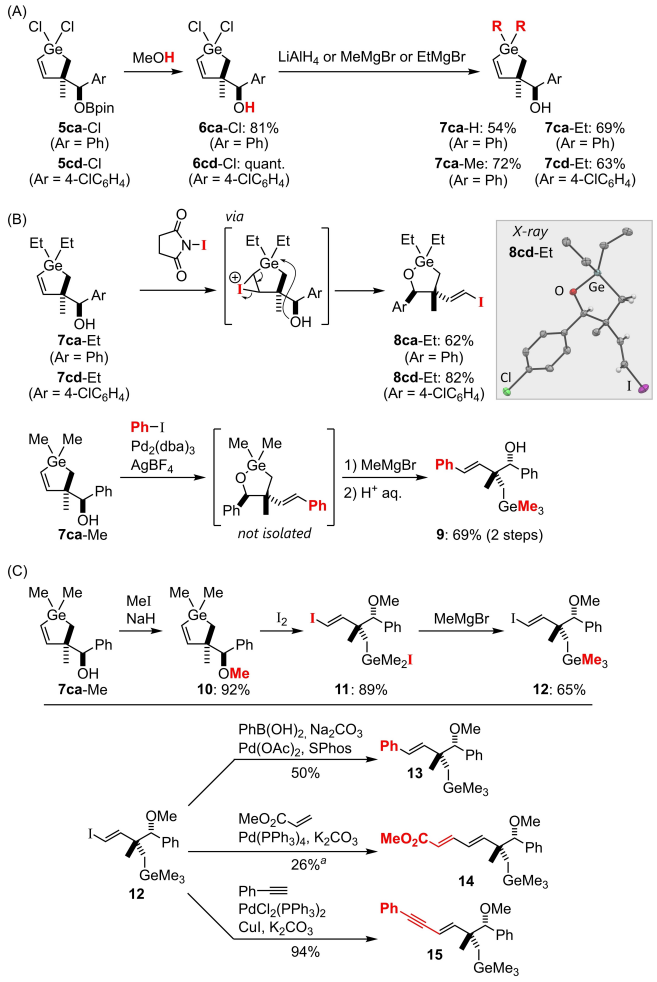

Figure 5. (A) Nucleophilic substitutions on the Ge center of the germacycle **5**. (B) Selective iodinations of the C(sp^2)–Ge bond of **7**, and Ortep drawing of **8cd**-Et with 50 % probability ellipsoids. Some hydrogen atoms are omitted for clarity. (C) Transformations of the iodovinyl **12** into various π-extended organogermaniums having a stereocontrolled germyl group. [a]The yield was estimated by ^{1}H NMR measurement.

Conclusions

In conclusion, we investigated the (4 + 1) cycloaddition of the butadienes bearing a boronic ester moiety with Ge(II) salts. The generated germacycle having an allylboron moiety can be applied to further allylboration of aldehydes with perfect diastereoselectivity. The allylated adducts, which are carbon-based germacycles, enabled access to π-extended organogermaniums with the retention of the stereocenters. The highly diastereo-controlled organogermaniums may potentially be exploited as building blocks for natural products and functional materials. Further studies of other transformations of the germacycles in the allylated adduct are underway in our group.

Experimental Section

All synthetic procedures and characterizations for unknown compounds are provided in the Supporting Information. The data that support the findings of this study are available in the supplementary material of this article.

Deposition numbers 2357801 (for **3c**-Br), 2357802 (for **3e**-Br), 2357803 (for **3f**-Br), 2357804 (for **5ca**-Cl), and 2357805 (for **8cd**-Et) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Allylation · Cheletropic reaction · Diastereoselective · Germacycle · Organogermanium

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