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Preparation, Structural Characterization, and Photochemical Reactions of Silyl- and Germylborates

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Received August 25, 2005

Silylborates (Li[$Ph_nMe_{3-n}SiBPh_3$], $n = 1-3$) and germylborates (Li[$Ph_nMe_{3-n}GeBPh_3$], $n = 1-3$; M[Et_3GeBPh_3], M = Li, Na, K) were prepared by the reaction of the corresponding silyl- and germylalkali metals with triphenylborane in a hexane/benzene mixed solvent. The silyl- and germylborates were fully identified by ^{1}H, ^{13}C, ^{11}B, and ^{7}Li NMR spectroscopic methods. The solid-state structure of germylborates Li[Ph_3GeBPh_3] and M[Et_3GeBPh_3] (M = Li and Na) were determined by X-ray diffraction analyses. The polymeric structure of M[Et_3GeBPh_3] was observed in the solid state and in hydrocarbon solution. The alkali metal atoms were located near the center of the benzene ring of triphenylborane and interacted with the neighboring borate molecules by $Li^+-\pi$ interaction. The polymeric structure was broken by the addition of MeOH. However, M[Et_3GeBPh_3] was coordinated by three MeOH molecules to form a dimeric structure without methanolysis reaction. The primary processes in photochemical reactions of silyl- and germylborates were investigated by chemical trapping experiments and the CIDEP (chemical-induced dynamic electron polarization) method. The cleavage of the Ge−B (or Si−B) bonds of germylborates (or silylborates) was considered most probably to occur from their triplet states.

Introduction

Tetraorganoborate salts have attracted considerable interest in organic chemistry and organic synthesis.[1] While the tetraorganoborate salts have been well studied, far less attention has been devoted to tetracoordinated borates containing group 14 elements (silicon or germanium)−boron bonds. Seyferth et al. pioneered the preparation of aryl-substituted silylborate (Li[Ph_3SiBPh_3]) and germylborate (Li[Ph_3GeBPh_3]) in 1961,[2] and later, alkyl-substituted silylborates (Li[Me_3SiBMe_3]) were introduced by Nöth in 1980.[3,4] Recently, crystal structures of tetraalkylsilylborate (Li[Me_3Si]$_4$B) and trialkyl-substituted silylborate (Li[$(Me_3Si)_3BMe$]) have been determined.[5] However, few reports on the solid-state structure of germylborates or any reactivitity studies of silyl- or germylborates have appeared.[6,7] Very recently, trihydro(triphenylgermyl)borate (Li[Ph_3GeBH_3]) and trihydro(triphenylstannyl)borate (Li[Ph_3SnBH_3]) have been synthesized and characterized by Habereder and Nöth.[8,9] In this paper, we describe the preparation and characterization of silyl- and germylborates. The primary photochemical process of silyl- and germylborates probed by chemical experiments and CIDEP techniques is discussed.

Results and Discussion

Preparation and Characterization of Silyl- and Germylborates. Phenyl-substituted silyllithiums ($Ph_nMe_{3-n}SiLi$, $n = 1-3$) were prepared by reactions of the corresponding disilanes with lithium metal in tetrahydrofuran (THF) under an argon atmosphere.[1010] Treatment of the resulting $Ph_nMe_{3-n}SiLi$ ($n = 1-3$) with 1 equiv of triphenylborane (Ph_3B) in benzene/hexane mixed solvent under argon produced the corresponding phenyl-substituted silylborates ([Li($Ph_nMe_{3-n}SiBPh_3$)], **1**−**3**, $n = 1-3$, respectively) as pale yellow crystals in 60−90% yields (E = Si, eq 1).

$$\begin{gathered} \mathrm{Ph_nMe_{3-n}ELi + Ph_3B \rightarrow} \\ \mathrm{Li[Ph_nMe_{3-n}EBPh_3]} \\ \mathrm{E = Si,\ \mathbf{1-3}\ (n = 1-3);\ Ge,\ \mathbf{4-6}\ (n = 1-3)} \end{gathered} \tag{1}$$

The phenyl-substituted silylborates **1**−**3** were recrystallized from THF at room temperature to give colorless crystals in 48% (**1**), 72% (**2**), and 85% (**3**) isolated yield. The silylborates **1**−**3** were fully characterized by ^{1}H, ^{13}C, ^{11}B, and ^{7}Li NMR spectra. The ^{1}H NMR spectroscopic examination of a CD_3CN solution of the white solid **1** displayed the methyl signal of the dimethylphenylsilyl group (Me_2PhSi) at 0.09 ppm, signals of three coordinated THF molecules at 1.83−1.94 ppm and 3.66−3.80 ppm, and the phenyl groups of Me_2PhSi and Ph_3B at 6.91−7.35 ppm. The ^{11}B NMR signal of **1** in CD_3CN was significantly shifted upfield at $\delta = -11.4$ ppm, due to the anionic nature of the boron atom compared with that of a neutral species. The ^{11}B NMR spectra of C_6D_6 solutions of borates such as lithium tetrahydroborate ($LiBH_4$), lithium isopropyltrihydroborate (Li^{i}PrBH$_3$), and lithium tetraisopropylborate (Li^{i}Pr$_4$B), [Li(Me_3GeBH_3)], and [Li(Ph_3GeBH_3)] have been observed to be in the

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10.1021/om050733y CCC: $33.50

range −43.1 to −15.4 ppm.[8,11,12] On the other hand, the ^{11}B NMR signals of neutral compounds such as Ph_3B in CD_3CN and $^{i}Pr_3B$ in C_6D_6 are seen at 45 and 85 ppm, respectively.[12] The ^{7}Li NMR signal of a CD_3CN solution of **1** was shifted a little upfield at −1.30 ppm. The ^{7}Li NMR resonance of triphenylsilyllithium (Ph_3SiLi) coordinated by THF is observed at −0.1 ppm.[13] The ^{11}B and ^{7}Li NMR spectra of CD_3CN solutions of **2** and **3** displayed trends ($\delta = -11.0$ and −1.30 ppm for **2**, and $\delta = -11.4$ and −1.30 ppm for **3**) similar to the silylborate **1**. The NMR spectra of silylborates **2** and **3** showed the presence of three coordinated THF molecules. The solid silylborates **1**−**3** are stable at 100 °C for 2 days in the absence of air. In contact with air, the silylborates **1**−**3** decomposed gradually to pale yellow pasty crystals. The silylborates **1**−**3** are soluble in methanol or CH_3CN and are insoluble at room temperature in hydrocarbon or aromatic solvents. At higher temperatures (>80 °C), the solubility of silylborates **1**−**3** increased. Solutions of the silylborates **1**−**3** in MeOH or CH_3CN are very stable when heated at reflux for 1 day. However, the silylborates **1**−**3** reacted with acetic acid at room temperature for 6 h to give the corresponding organosilicone hydrides in quantitative yield.

The reactions of phenyl-substituted germyllithiums ($Ph_nMe_{3-n}GeLi$, $n = 1-3$), which were prepared by treatment of the corresponding chlorogermanes with lithium metal in THF,[14,15] with 1 equiv of Ph_3B in a benzene/hexane mixed solvent under argon gave the corresponding phenyl-substituted germylborates ($[Li(Ph_nMe_{3-n}GeBPh_3)]$, **4**−**6**, $n = 1-3$, respectively) as pale yellow crystals in 30−85% yield (E = Ge, eq 1).

The phenyl-substituted germylborates **4**−**6** were isolated as colorless crystals by recrystallization from THF at room temperature in 15% (**4**), 42% (**5**), and 78% (**6**) isolated yield. The germylborates **4**−**6** were identified by ^{1}H, ^{13}C, ^{11}B, and ^{7}Li NMR spectra. The solid-state structure of **5** was determined by X-ray diffraction analysis. The ^{1}H NMR spectrum of a CD_3CN solution of white solid **5** displayed the methyl signal of $MePh_2Ge$ at 0.29 ppm, signals of three THF molecules at 1.75−1.90 ppm and 3.60−3.73 ppm, and the phenyl groups of $MePh_2Ge$ and Ph_3B at 6.88−7.23 ppm. As in the case of $Li[Ph_nMe_{3-n}SiBPh_3]$,[8,11,12] the ^{11}B NMR signal of **5** in CD_3CN was shifted significantly upfield $\delta = -7.2$ ppm due to the anionic nature of the boron atom. The ^{7}Li NMR signal of a CD_3CN solution of **5** was shifted somewhat upfield to −1.4 ppm. For comparison, the ^{7}Li NMR resonances of $PhMe_2GeLi$ coordinated by THF and Ph_3GeLi coordinated by diethyl ether in C_6D_6 were observed at 0.83 and 1.46 ppm, respectively.[8] The ^{11}B and ^{7}Li NMR spectra of CD_3CN solutions of **4** and **6** displayed trends (−8.3 and −1.5 ppm for **4**, and −7.2 and −1.01 ppm for **6**) similar to the germylborate **5**. The ^{1}H NMR spectra of germylborates **4** and **6** also showed them to be coordinated by THF molecules.

The molecular structure of **5**, recrystallized from dimethoxyethane (DME), was analyzed by X-ray diffraction as shown in Figure 1. Selected bond lengths and bond angles for **5** are summarized in Table 1. The crystallographic data are summarized in the Experimental Section.

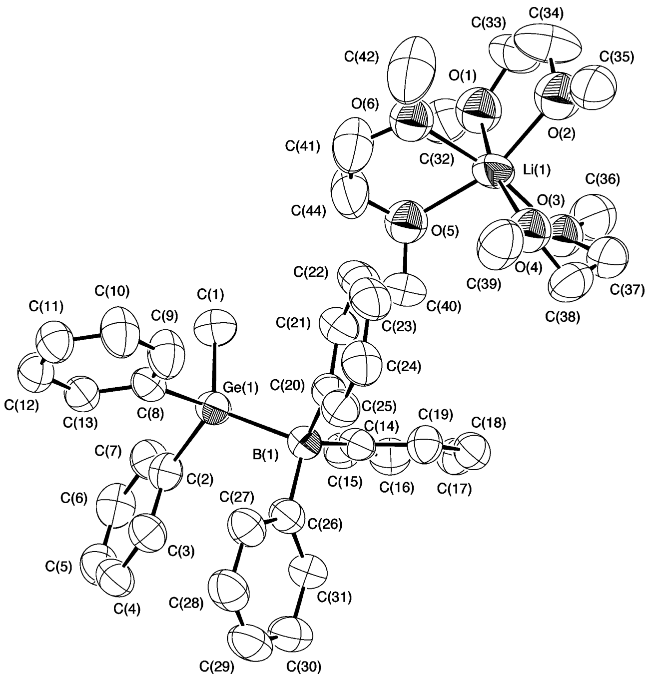

Figure 1. Molecular structure of **5** at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Atomic Distances (Å) and Bond Angles (deg) of 5

Ge(1)−C(1)	1.984(6)	Li(1)−O(1)	2.098(12)
Ge(1)−C(2)	1.992(5)	Li(1)−O(2)	2.069(12)
Ge(1)−C(8)	1.968(6)	Li(1)−O(3)	2.210(14)
Ge(1)−B(1)	2.138(6)	Li(1)−O(4)	2.083(11)
B(1)−C(14)	1.627(8)	Li(1)−O(5)	2.100(12)
B(1)−C(20)	1.646(8)	Li(1)−O(6)	2.412(15)
B(1)−C(26)	1.628(7)		
C(1)−Ge(1)−C(2)	103.6(2)	Ge(1)−B(1)−C(26)	102.9(3)
C(1)−Ge(1)−C(8)	101.6(2)	C(14)−B(1)−C(20)	109.7(4)
C(2)−Ge(1)−C(8)	103.2(2)	C(14)−B(1)−C(26)	111.4(4)
C(1)−Ge(1)−B(1)	117.0(3)	C(20)−B(1)−C(26)	115.9(4)
C(2)−Ge(1)−B(1)	114.1(2)	O(1)−Li(1)−O(2)	77.7(4)
C(8)−Ge(1)−B(1)	115.5(2)	O(3)−Li(1)−O(4)	77.3(4)
Ge(1)−B(1)−C(14)	109.3(3)	O(5)−Li(1)−O(6)	74.0(4)
Ge(1)−B(1)−C(20)	107.2(3)		

The Ge−C bond lengths of 1.968(6)−1.992(5) Å are normal. The Ge−B bond length of 2.138(6) Å is slightly longer compared with that of the neutral germylene-borane adduct, $Ge[C_6H_3(NMe_2)_2\text{-}2,6]_2BH_3$ (2.041 Å).[16] This suggests that the Ge−B bond is essentially covalent with a small ionic contribution. The closest distance between the lithium cation and the phenyl carbon atom of Ph_3B in **5** is over 6 Å, well beyond any significant interaction. The solvent-separated lithium cation is complexed with three DME molecules with Li−O bond lengths of 2.069(12)−2.412(15) Å and Li−O−Li bond angles of 74.0(5)−78.4(4)°. The lithium atom shows an octahedral conformation. The solid germylborates **4**−**6** are very stable (100 °C, 2 days) in the absence of air, but gradually decomposed to pale yellow pasty crystals in air. They are soluble in polar solvents (MeOH and CH_3CN) and insoluble in nonpolar solvents. The solubility of the germylborates in nonpolar solvents increased with increasing temperatures (80 °C). They reacted with MeOH at 50 °C over 6 h to give the corresponding organogermanium hydrides. The formation of $Li[Ph_3SiBPh_3]$ and $Li[Ph_3GeBPh_3]$ was first reported by Seyferth et al.,[2] but their crystal structures were not determined.

Unsolvated triethylgermyl-alkali metal compounds (Et_3GeM, M = Li, Na) were prepared by the metal exchange reaction of

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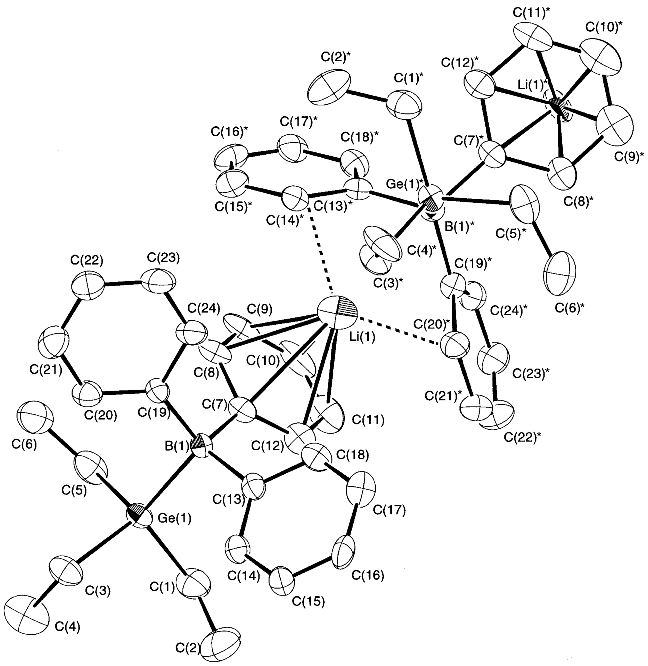

Figure 2. Molecular structure of **7** at the 50% probability level. Hydrogen atoms are omitted for clarity.

$(Et_3Ge)_2Hg$ with alkali metals in benzene using a modified method reported by Vyazankin et al.[17] Treatment of unsolvated Et_3GeM with 1 equiv of Ph_3B in benzene/hexane mixed solvent produced alkali metal (triethylgermyl)triphenylborates ($M[Et_3GeBPh_3]$, M = Li (**7**), Na (**8**), K (**9**)) as colorless crystals in quantitative yield (eq 3). The triethyllgermylborates **7** and **8** were recrystallized from toluene at −20 °C to give colorless needles in 74 and 72% isolated yields, respectively. The germylborates **7** and **8** were fully characterized by spectroscopic and X-ray analyses. However, attempts to obtain X-ray quality crystals of **9** were not unsuccessful.

$$(Et_3Ge)_2Hg + 2M \rightarrow 2Et_3GeM + Hg \qquad (2)$$

$$Et_3GeM + Ph_3B \rightarrow M(Et_3GeBPh_3)$$
$$M = Li\ (\mathbf{7}),\ Na\ (\mathbf{8}),\ K\ (\mathbf{9}) \qquad (3)$$

The ^{1}H NMR spectrum of **7** showed a quartet at 0.51 ppm and a triplet at 0.82 ppm due to the Et_3Ge group, and phenyl resonances at 6.84−7.19 ppm. The triethylgermylborate **7** was not coordinated by solvents. The ^{11}B and ^{7}Li NMR of **7** in CD_3CN showed signals at −8.6 and −1.93 ppm, respectively. The ^{7}Li NMR signal of germylborate **7** depends on the solvent used. In toluene-d_8 at 80 °C it was significantly upfield-shifted at $\delta = -7.0$ ppm due to the shielding effect of the phenyl groups. However, in methanol-d_4 it was observed at $\delta = -0.15$ ppm, indicating that the lithium cation no longer is shielded by the phenyl groups due to complexation with CD_3OD. Indeed, this phenomenon was observed by X-ray diffraction analysis. The molecular structure of **7** was unequivocally confirmed by X-ray diffraction as shown in Figure 2. Selected bond lengths and bond angles of **7** are summarized in Table 2. Crystallographic data are summarized in the Experimental Section.

The Ge−C bond lengths (1.984(3)−1.994(3) Å) are normal compared with that found in tetraphenylgermane. The Ge−B bond length of 2.145(4) Å is slightly longer compared with that of the neutral germylene-borane adduct.[16] This suggests that the Ge−B bond is covalent with a small ionic contribution. The boron atom in germylborate **7** shows a tetrahedral configuration. The Ge(1)−B(1)−C bond angles of 98.4(2)°, 113.9(2)°, and 111.6(2)° are contracted. The structure of germylborate **7** in the solid state is a zigzag polymeric structure. Lithium cations are linked to germylborates by the $Li^{+}-\pi$ interaction, which leads to a linear one-dimensional coordination polymer. Each lithium cation is surrounded by three phenyl groups of BPh_3 and is placed above one side of the three horizontal phenyl planes of BPh_3. The coordination distances between the lithium cation and the three phenyl ring planes in **7** are 2.072(5) Å (intramolecular) and 2.452(6) and 2.532(6) Å (intermolecular). The lithium atom is not located directly over the center of the benzene rings, but is in rather close contact with the *para* and *meta* carbon atoms of the benzene rings. These Li−C distances (Li−C(10) 2.390(7), Li(1)−C(9) 2.405(7), Li−C(11) 2.468(7), Li−C(8) 2.519(6), Li(1)−C(12) 2.590(6), and Li(1)−C(7) 2.679(6) Å) are typical for π-complexed organolithiums.[18] Such interactions apparently are caused by electrostatic attraction between the lithium ion and the benzene rings. The ^{7}Li NMR spectrum of germylborate **7** in toluene-d_8 rather than in CD_3OD suggests that the polymeric structure was broken by the addition of MeOH to the lithium atoms. The dimeric structure of $[\mathbf{7}\cdot(3MeOH)]_2$ was also established by X-ray diffraction analysis (Figure 3). Selected atomic distances and bond lengths are listed in Table 3. Each lithium cation is complexed by three MeOH molecules, and one of three MeOH molecules bridges two lithium cations by μ-oxygen atoms. The two lithium cations and two μ-oxygen atoms constitute a planar four-membered ring with Li−O bond lengths of 2.003(6) and 2.034(6) Å, an Li−O−Li bond angle of 92.4(2)°, and Li−Li distance of 2.79(1) Å. The closest distance between the lithium cation and the phenyl carbon atom is 3.91(0) Å (for C(14)), beyond any significant interaction to form a solvent-separated ion pair. The Ge−B bond length of 2.152(4) Å is slightly longer than that found in the polymeric germylborate. The bond angles of the boron range from 104.8(1)° to 114.0(2)°. The sum of the angles is equal to 656(0)°. The molecular structure of $Na[Et_3GeBPh_3]$ **8** was confirmed by X-ray diffraction, and its selected bond lengths and bond angles are shown in Figure 4 and in Table 4. Crystallographic data of $[\mathbf{7}\cdot(3MeOH)]_2$ and **8** are summarized in the Experimental Section.

Table 2. Selected Atomic Distances (Å) and Bond Angles (deg) of 7

Ge(1)−C(1)	1.987(4)	Li(1)−C(9)	2.405(7)
Ge(1)−C(3)	1.994(3)	Li(1)−C(10)	2.390(7)
Ge(1)−C(5)	1.984(3)	Li(1)−C(11)	2.468(7)
Ge(1)−B(1)	2.145(4)	Li(1)−C(12)*	2.590(6)
B(1)−C(7)	1.642(4)	Li(1)−C(13)*	2.565(6)
B(1)−C(13)	1.642(4)	Li(1)−C(14)*	2.737(7)
B(1)−C(19)	1.630(4)	Li(1)−C(19)*	2.482(6)
Li(1)−C(7)	2.679(6)	Li(1)−C(24)*	2.689(6)
Li(1)−C(8)	2.519(6)		
C(1)−Ge(1)−C(3)	103.8(1)	Ge(1)−B(1)−C(7)	98.4(2)
C(1)−Ge(1)−C(5)	100.5(1)	Ge(1)−B(1)−C(13)	111.6(2)
C(3)−Ge(1)−C(5)	103.8(1)	Ge(1)−B(1)−C(19)	113.9(2)
C(1)−Ge(1)−B(1)	113.6(1)	C(7)−B(1)−C(13)	112.5(2)
C(3)−Ge(1)−B(1)	121.1(1)	C(7)−B(1)−C(19)	111.4(2)
C(5)−Ge(1)−B(1)	111.6(1)	C(13)−B(1)−C(19)	108.8(2)

Compound **8**, recrystallized from toluene, has also a zigzag polymeric structure. The Ge−C and Ge−B bond lengths are 1.984(1)−1.990(2) and 2.137(2) Å, respectively. The Ge−B bond length is similar to that in **5** and **7**. The boron atom in **8**

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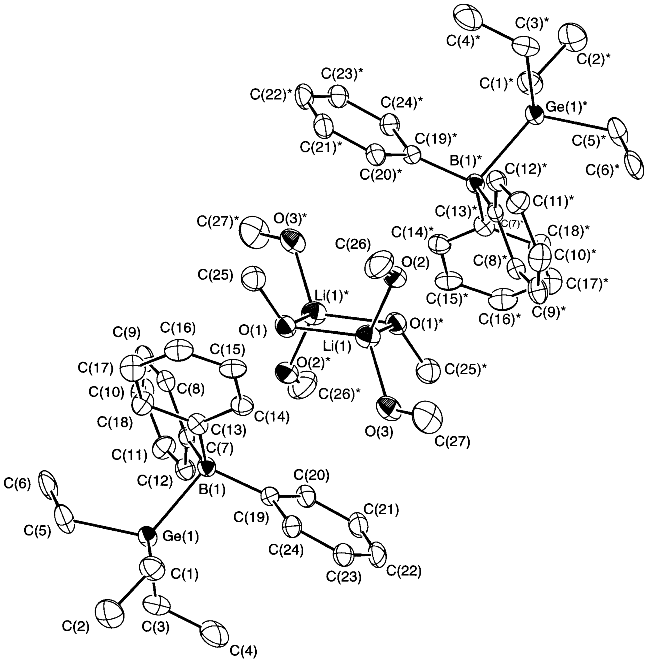

Figure 3. Molecular structure of [**7**·3MeOH]$_2$ at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 3. Selected Atomic Distances (Å) and Bond Angles (deg) of [7·3MeOH]$_2$

Ge(1)−C(1)	1.984(3)	B(1)−C(19)	1.632(4)
Ge(1)−C(3)	1.975(3)	Li(1)−O(1)	2.003(6)
Ge(1)−C(5)	1.986(3)	Li(1)−O(2)	1.887(6)
Ge(1)−B(1)	2.152(3)	Li(1)−O(3)	1.877(6)
B(1)−C(7)	1.624(4)	Li(1)−O(1)*	2.034(6)
B(1)−C(13)	1.642(4)	Li(1)−Li(1)*	2.79(1)
C(1)−Ge(1)−C(3)	103.7(1)	C(7)−B(1)−C(13)	113.1(2)
C(1)−Ge(1)−C(5)	103.5(1)	C(7)−B(1)−C(19)	114.0(2)
C(3)−Ge(1)−C(5)	101.7(1)	C(13)−B(1)−C(19)	112.9(2)
C(1)−Ge(1)−B(1)	112.3(1)	Li(1)−O(1)−Li(1)*	87.6(2)
C(3)−Ge(1)−B(1)	117.1(1)	O(1)−Li(1)−O(2)	112.9(3)
C(5)−Ge(1)−B(1)	116.7(1)	O(1)−Li(1)−O(3)	116.9(3)
Ge(1)−B(1)−C(7)	104.9(1)	O(2)−Li(1)−O(3)	111.9(3)
Ge(1)−B(1)−C(13)	105.3(1)	O(1)−Li(1)−O(1)*	92.4(2)
Ge(1)−B(1)−C(19)	105.7(1)		

also shows a tetrahedral configuration with Ge−B−C bond angles of 99.80(9)°, 111.62(9)°, and 114.4(1)°. The sodium cations are surrounded by three phenyl groups of BPh$_3$ and are placed above one side of the three horiozontal phenyl planes of BPh$_3$. The sodium atom is located almost over the center of the benzene rings. The distances between Na(1) and the phenyl planes [C(7)−C(12), C(13)−C(18), C(19)−C(24)] are 2.648(0), 2.669(0), and 2.469(0) Å, respectively. They are apparently longer than that found in **7** due to the larger size of the ionic radius of sodium.

The triethylgermylborates **7** and **8** were stable under an inert gas atmosphere, but were unstable in air. They are soluble in protic solvents such as water and MeOH, but nearly insoluble in benzene and toluene. Surprisingly, they are very stable at room temperature for 4 days even in degassed water. No alcoholysis by MeOH or EtOH was observed at 50 °C for 10 h.

Photochemical Reactions of Silyl- and Germylborates. The absorption spectra of phenyl-substituted silyl- (**2**, **3**) and germylborates (**5**, **6**) in THF are shown in Figure 5. Each of the borates has an absorption peak at ca. 270 nm, which can be explained in terms of a $\sigma-\sigma^*$ transition from the bonding orbital of the Si (or Ge)−B bond to its antibonding orbital. The THF solutions containing **2**, **5**, or **6** in a quartz photolysis cell were degassed and then irradiated with a xenon lamp at room temperature. The reaction products were analyzed by gas chromatography and GC-MS spectrometry. The main products of this photochemical reaction are the corresponding hydrides.

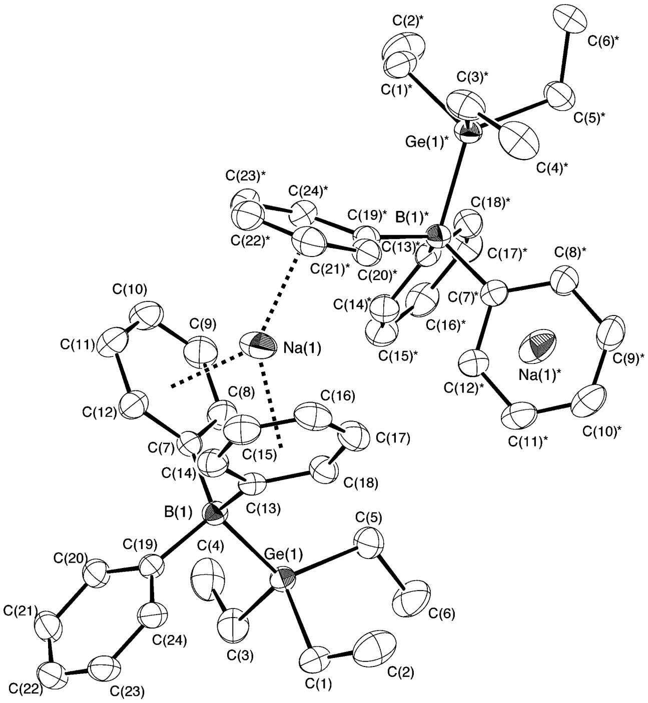

Figure 4. Molecular structure of **8** at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 4. Selected Atomic Distances (Å) and Bond Angles (deg) of 8

Ge(1)−C(1)	1.984(1)	Na(1)−C(12)	2.827(1)
Ge(1)−C(3)	1.987(1)	Na(1)−C(13)	2.774(1)
Ge(1)−C(5)	1.990(2)	Na(1)−C(14)	3.045(1)
Ge(1)−B(1)	2.137(1)	Na(1)−C(19)*	3.004(1)
B(1)−C(7)	1.639(2)	Na(1)−C(20)*	2.876(1)
B(1)−C(13)	1.637(2)	Na(1)−C(21)*	2.779(2)
B(1)−C(19)	1.623(2)	Na(1)−C(22)*	2.748(2)
Na(1)−C(7)	2.742(1)	Na(1)−C(23)*	2.779(1)
Na(1)−C(8)	2.991(2)	Na(1)−C(24)*	2.890(1)
C(1)−Ge(1)−C(3)	100.81(8)	Ge(1)−B(1)−C(7)	114.4(1)
C(1)−Ge(1)−C(5)	104.07(8)	Ge(1)−B(1)−C(13)	111.62(9)
C(3)−Ge(1)−C(5)	104.02(8)	Ge(1)−B(1)−C(19)	99.80(9)
C(1)−Ge(1)−B(1)	112.66(7)	C(7)−B(1)−C(13)	105.1(1)
C(3)−Ge(1)−B(1)	111.58(7)	C(7)−B(1)−C(19)	112.0(1)
C(5)−Ge(1)−B(1)	121.40(7)	C(13)−B(1)−C(19)	105.1(1)

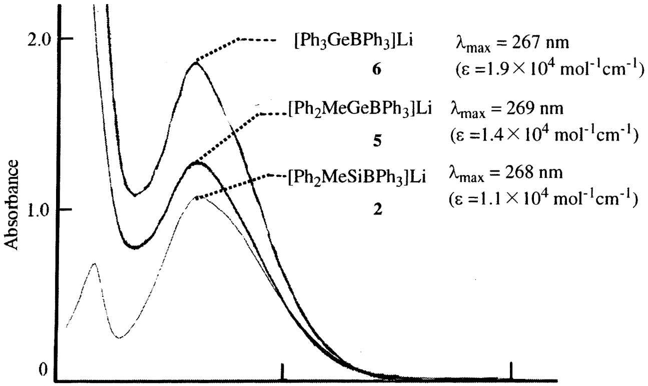

Figure 5. Absorption spectra of phenyl-substituted silyl- and germyl-borates in THF at 23 °C. Optical path length is 1 cm.

Table 5. Photochemical Reactions of Silylborate 2 and Germylborates 5 and 6 at 23 °C for 30 min

borate	quencher	conv/%	products, yields/%
Li($Ph_2MeSiBPh_3$) **2**	none	9	Ph_2MeSiH (4), $(Ph_2MeSi)_2$ (trace)
2	$CHCl_3$ (5 equiv)	84	$Ph_2MeSiCl$ (63), Ph_2MeSiH (6), $(Ph_2MeSi)_2$ (trace) $(CHCl_2)^2$ (23), CH_2Cl_2 (3)
Li($Ph_2MeGeBPh_3$) **5**	none	12	Ph_2MeGeH (3), $(Ph_2MeGe)_2$ (trace)
5	$CHCl_3$ (5 equiv)	35	$Ph_2MeGeCl$ (23), Ph_2MeGeH (trace), $(Ph_2MeGe)_2$ (trace), $(CHCl_2)_2$ (7), CH_2Cl_2 (2)
Li(Ph_3GeBPh_3) **6**	none	10	Ph_3GeH (4)
6	$CHCl_3$ (5 equiv)	35	Ph_3GeCl (20), $(CHCl_2)_2$ (12), CH_2Cl_2 (4)

Dimers, disilane for **2** and digermane for **5** and **6**, were also detected as minor products. These hydrides and dimers are considered to be derived from the silyl and germyl radicals generated by photocleavage of Si−B and Ge−B bonds of silyl- and germylborates, respectively.[19−21] In the presence of chloroform, a trapping agent for group 14 element-centered radicals, photolysis of silyl- and germylborates **2**, **5**, and **6** afforded the corresponding chlorosilane and chlorogermanes, respectively.[19−21] The results of photochemical reactions of **2**, **5**, and **6** at room temperature for 30 min are listed in Table 5.

$$[Ph_nMe_{3-n}E\text{-}BPh_3]^- \xrightarrow{h\nu} Ph_nMe_{3-n}E^\bullet + BPh_3^{\bullet -} \tag{4}$$

$$Ph_nMe_{3-n}E^\bullet \xrightarrow{SH} Ph_nMe_{3-n}EH \tag{5}$$

$$2Ph_nMe_{3-n}E^\bullet \rightarrow (Ph_nMe_{3-n}E)_2 \tag{6}$$

Thus, the phenyl-substituted silyl and germyl radicals are suggested to be generated as shown by reaction 4.

Transient optical absorption measurements were performed on degassed THF solutions containing **6** (5.0×10^{-4} mol/L) at room temperature using the fourth harmonic (266 nm) of an Nd:YAG laser as an exciting light source. We measured the time profiles of the transient absorbance, $A(t)$ curves, in the wavelength region 310−700 nm in the time region 0−35 μs. The curves below 310 nm could not be observed by the absorption of **6**. From the observed $A(t)$ curves in the wavelength region, we could obtain time-resolved optical absorption spectra with the time resolution of about 10 ns. Figure 6 shows the spectrum observed at 500 ns after laser excitation. The spectral shape was almost unchanged in the time region 0−35 μs. As far as the signal intensity is concerned, the signal grew from 0 μs to 1 μs and kept almost constant from 1 μs to 35 μs. The growth rate was found to be 7.7×10^{6} s^{-1}.

As shown in Figure 6, appreciable signals were obtained in the wavelength region 310−400 nm with a peak at 325 nm. Previously, we found the transient absorption peak of the triphenylgermyl radical in THF at 330 nm.[22] In the present study, we synthesized the triphenylboron anion radical by the method of Leffler et al.,[23] finding its peak in THF at 318 nm. Thus, the peak observed at 325 nm in Figure 6 may be ascribed to an overlap of the peak of the triphenylgermyl radical and that of the triphenylboron anion radical. From the above-mentioned time profiles of the signals, the growth rate may be ascribed to the decay rate of their precursor, which will be shown to be the triplet state of **6** from transient ESR measurements. Because the signals did not decay until 35 μs, the lifetimes of both radicals may be longer than 35 μs.

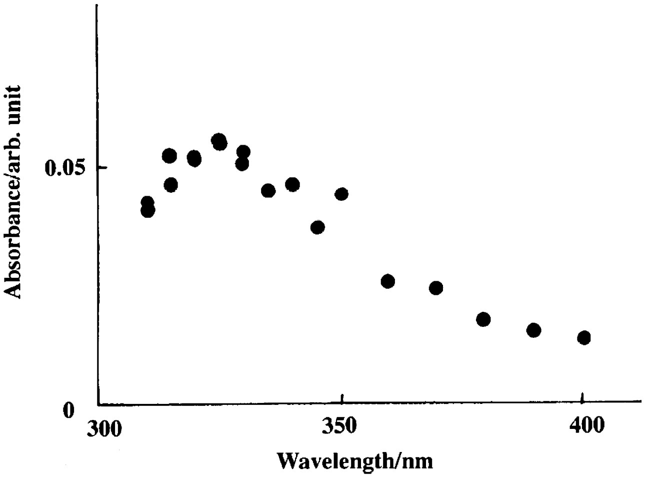

Figure 6. Transient absorption spectrum observed 500 ns after excitation of the THF solution containing **6**.

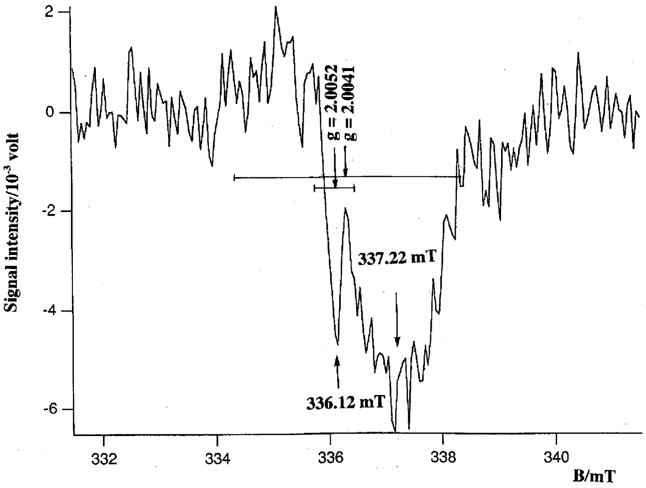

Figure 7. CIDEP spectrum observed with **6**.

Transient ESR measurements were also performed on degassed THF solutions containing **6** (5.0×10^{-4} mol/L) at room temperature using the fourth harmonic (266 nm) of an Nd:YAG laser as an exciting light source. Although the time resolution of our ESR apparatus was about 100 ns, we carried out time integration of the ESR spectra because the spectra had poor S/N ratios. Figure 7 shows the transient ESR spectrum observed during 400−600 ns after laser excitation. As shown in Figure 7, a sharp absorptive signal was observed at a low-field site and a broad absorptive one at a high-field site. The peak position of the sharp signal was $B = 336.12$ mT and that of the broad signal was $B = 337.22$ mT. The g-value of the former and the latter positions correspond to 2.0052 and 1.9987, respectively. Sakurai et al.[24] already observed the g-value of the triphenylgermyl radical in DTBP to be 2.0054 and also found that its spectral width was as small as about 0.5 mT.

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Thus, the sharp signal may be ascribed to the triphenylgermyl radical. The broad signal seems to be due to the triphenylboron anion radical because Leffler et al.[23] found that its spectral width was as large as about 4 mT. On the other hand, they did not obtain its *g*-value. In the present study, we synthesized the triphenylboron anion radical with their method, finding its *g*-value to be 2.0041. Thus, the observed ESR spectrum shown in Figure 7 may be ascribed to be an overlap of the signal of the triphenylgermyl radical and that of the triphenylboron anion radical.

The observed transient ESR signals of **6** in THF decayed within 3 μs after laser excitation, but the transient optical signals of the same system did not decay until 35 μs. Thus, the observed transient ESR signals are not due to those at thermal equilibrium but due to CIDEP. Both the triphenylgermyl radical and the triphenylboron anion radical showed absorptive phase patterns as shown in Figure 7. Such totally absorptive patterns may be explained in terms of the p-type triplet mechanism.[25] Thus, we can safely conclude that the reaction precursor of the cleavage of the Ge$-$B bond is the triplet state of **6**. We also performed transient ESR measurements on degassed THF solutions containing **2** and **5** at room temperature using the fourth harmonic (266 nm) of an Nd:YAG laser as an exciting light source. Although we obtained similar transient ESR signals for **2** and **5**, they were very noisy and had no clear structure. Although we could not analyze their signals, we can speculate that the radical species are probably produced at the initial stages of their photochemical reactions.

Experimental Section

General Procedures. All experiments were performed under an inert atmosphere of argon by standard vacuum line techniques. All solvents were dried by standard methods and freshly distilled prior to use. Column chromatography was performed with Kanto Chemical silica gel 60N. Samplings of air-sensitive compounds were performed in an MBrown Lab Master 130 glovebox under argon atmosphere. Mass spectra were recorded on a JEOL AX505H spectrometer. The product yields were determined by gas$-$liquid chromatography (Shimadzu GC-14A) on a Frontier Laboratories capillary column UA5 (30 m × 0.25 mm) using n-$C_{20}H_{42}$ as an internal standard. ^{1}H (400 MHz), ^{13}C (100 MHz), ^{7}Li (155 MHz), and ^{11}B (128 MHz) NMR spectra were recorded on a Varian Inova 400 spectrometer. ^{1}H and ^{13}C chemical shifts were referenced to Me_4Si as an external standard. The chemical shifts of ^{7}Li NMR spectra were referenced to external LiCl (1.0 M in methanol). ^{11}B chemical shift was referenced to $BF_3 \cdot Et_2O$ as an external standard. CW ESR spectra were recorded on a JEOL JES-FE3XGA spectrometer. X-ray crystallographic data and diffraction intensities were collected on a MacScience DIP2030 diffractometer utilizing graphite-monochromated Mo Kα ($\lambda = 0.71073$Å) radiation. The structures were solved by direct methods using the program system SIR-92[26] and refined with all data on F^2 by means of SHELXL-97.[27] Refinement was performed by a Silicon Graphics O_2 with MaXus.

Materials. BPh_3 was commercially available. $Ph_nMe_{3-n}SiLi$ ($n = 1-3$),[10] $Ph_nMe_{3-n}GeLi$ ($n = 1-3$),[14,15] Et_3GeM (M = Li, Na, K),[17] $Li[Ph_3SiBPh_3]$,[2] and $Li[Ph_3GeBPh_3]$[2] were prepared as described in the cited references.

Preparation of Phenyl-Substituted Silylborates, $Li[Ph_nMe_{3-n}SiBPh_3]$ ($n = 1-3$). As a representative example, preparation of $Li[PhMe_2SiBPh_3]$ ($n = 1$) (**1**) is described. Triphenylborane (2.42 g, 10.0 mmol) was added to a THF solution (15 mL) of dimethylphenylsilyllithium (0.7 N), prepared by the reaction of dimethylphenylchlorosilane with lithium metal.[14] The reaction was exothermic, and the mixture was stirred overnight to give the pale yellow solid as a precipitate. Recrystallization from THF afforded **1**$\cdot$3THF (1.84 g, 4.8 mmol) in 48% yield as colorless crystals. Silylborate **1** in a sealed tube had no sharp melting point; **1** turned yellow and partially melted at 200 °C on heating. ^{1}H NMR (CD_3CN, δ) 0.09 (s, 6 H), 1.83$-$1.94 (m, 12 H, THF), 3.66$-$3.80 (m, 12 H, THF), 6.91 (t, 3 H, $J = 7$ Hz), 7.02$-$7.11 (m, 9 H), 7.25$-$7.35 (m, 8 H); ^{13}C NMR (CD_3CN, δ) -1.2, 23.0 (THF), 65.3 (THF), 119.0, 123.3, 123.4, 132.7, 133.2, 148.3, 160.1 (br); ^{7}Li NMR (CD_3CN, δ) -1.3; ^{11}B NMR (CD_3CN, δ) -11.4. Anal. Calcd for $C_{38}H_{50}O_3SiBLi$: C, 75.99; H, 8.39. Found: C, 76.50; H, 8.42. $Li[Ph_2MeSiBPh_3] \cdot 3THF$ (**2**): colorless crystals, 72% yield. Silylborate **2** in a sealed tube had no sharp melting point; **2** turned yellow and partially melted at 200 °C on heating. ^{1}H NMR (CD_3CN, δ) 0.35 (s, 3 H), 1.80$-$1.95 (m, 12 H, THF), 3.65$-$3.78 (m, 12 H, THF), 6.88$-$6.95 (m, 3 H), 6.97$-$7.07 (m, 10 H), 7.08$-$7.19 (m, 6 H), 7.19$-$7.27 (m, 6 H); ^{13}C NMR (CD_3CN, δ) -3.2, 23.0 (THF), 65.3 (THF), 119.4, 123.3, 123.7, 123.9, 133.5, 133.7, 145.7, 159.3 (br); ^{7}Li NMR (CD_3CN, δ) -1.3; ^{11}B NMR (CD_3CN, δ) -11.0. Anal. Calcd for $C_{43}H_{52}O_3SiBLi$: C, 77.93; H, 7.91. Found: C, 78.30; H, 8.32. $Li[Ph_3SiBPh_3] \cdot 3THF$ (**3**):[2] colorless crystals, 85% yield. ^{1}H NMR (CD_3CN, δ) 1.80$-$1.95 (m, 12 H, THF), 3.65$-$3.78 (m, 12 H, THF), 6.88$-$6.95 (m, 3 H), 6.97$-$7.07 (m, 10 H), 7.08$-$7.19 (m, 6 H), 7.19$-$7.27 (m, 6 H); ^{13}C NMR (CD_3CN, δ) 26.0 (THF), 68.1 (THF), 119.4, 123.3, 123.7, 123.9, 133.5, 133.7, 145.7, 159.3 (br); ^{7}Li NMR (CD_3CN, δ) -1.3; ^{11}B NMR (CD_3CN, δ) -11.0.

Preparation of Phenyl-Substituted Germylborates, $Li[Ph_nMe_{3-n}GeBPh_3]$ ($n = 1-3$). As a representative example, preparation of $Li[PhMe_2GeBPh_3]$ ($n = 1$) (**4**) is described. Triphenylborane (2.42 g, 10.0 mmol) was added to a THF solution (15 mL) of dimethylphenylgermyllithium (0.7 N), prepared by the reaction of dimethylphenylchlorogermane with lithium metal.[14] The mixture was stirred for 4 h to give the crude product as a milky white solid. Recrystallization from THF afforded **4**$\cdot$3THF (0.64 g, 1.5 mmol) in 15% yield as colorless crystals. Germylborate **4** in a sealed tube had no sharp melting point; **4** turned yellow and partially melted at 200 °C on heating. ^{1}H NMR (CD_3CN, δ) 0.06 (s, 6 H), 1.83$-$1.88 (m, 6 H, THF), 3.67$-$3.74 (m, 6 H, THF), 6.88$-$6.93 (m, 3 H), 7.01$-$7.07 (m, 9 H), 7.20$-$7.25 (m, 6 H), 7.26$-$7.30 (m, 2 H); ^{13}C NMR (CD_3CN, δ) -2.9, 23.0 (THF), 65.2 (THF), 119.5, 122.9, 123.5, 124.1, 132.5, 133.0, 151.5 158.8 (br); ^{7}Li NMR (CD_3CN, δ) -1.5; ^{11}B NMR (CD_3CN, δ) -8.3. Anal. Calcd for $C_{38}H_{50}O_3GeBLi$: C, 75.99; H, 8.39. Found: C, 76.50; H, 8.42. $Li[Ph_2MeGeBPh_3] \cdot 3THF$ (**5**): colorless crystals, 42% yield. Germylborate **5** in a sealed tube had no sharp melting point; **5** turned yellow and partially melted at 200 °C on heating. ^{1}H NMR (CD_3CN, δ) 0.29 (s, 3 H), 1.75$-$1.90 (m, 8 H, THF), 3.60$-$3.73 (m, 8 H, THF), 6.88$-$6.93 (m, 3 H), 6.96$-$7.07 (m, 12 H), 7.10$-$7.15 (m, 4 H), 7.17$-$7.23 (m, 6 H); ^{13}C NMR (CD_3CN, δ) -3.5, 23.0 (THF), 65.3 (THF), 119.8, 123.2, 123.5, 124.2, 133.5, 133.7, 149.2, 158.1 (br); ^{7}Li NMR (CD_3CN, δ) -1.5; ^{11}B NMR (CD_3CN, δ) -7.2. Anal. Calcd for $C_{43}H_{52}O_3GeBLi$: C, 77.93; H, 7.91. Found: C, 78.30; H, 8.32. **$Li[Ph_3$**$GeBPh_3] \cdot 3THF$ **(6)**[2]: Colorless crystals, 85% yield. ^{1}H NMR (CD_3CN, δ) 1.83 (m, 12 H, THF), 3.07 (m, 12 H, THF), 6.92$-$7.02 (m, 21 H), 7.08$-$7.12 (m, 21 H), 7.19$-$7.21 (m, 6 H); ^{13}C NMR (CD_3CN, δ) 26.0 (THF), 68.1 (THF), 122.9, 126.3, 126.4, 127.0, 136.5, 137.0, 149.6, 159.7 (br); ^{7}Li NMR (CD_3CN, δ) -1.0; ^{11}B NMR (CD_3CN, δ) -7.2.

Preparation of Triethylgermylborates $E[Et_3GeBPh_3]$ (E = Li, Na, K). As a representative example, preparation of $Li[Et_3GeBPh_3]$

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Table 6. Summary of Crystallographic Data for 5, 7, [7·3MeOH]$_2$, and 8

	5	**7**	[**7**·3MeOH]$_2$	**8**
formula	$C_{43}H_{58}BGeLiO_8$	$C_{24}H_{30}BGeLi$	$C_{27}H_{42}BGeLiO_3$	$C_{24}H_{30}BGeNa$
fw	761.23	408.82	504.99	424.87
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a (Å)	11.661(4)	12.1640(12)	11.1920(9)	12.4970(4)
b (Å)	12.151(2)	11.3280(5)	11.0830(6)	11.6750(4)
c (Å)	16.271(5)	16.1220(14)	11.5370(10)	15.5740(4)
α (deg)	82.807(19)	90	84.692(5)	90
β (deg)	69.852(13)	100.114(4)	84.914(4)	102.449(2)
γ (deg)	84.226(19)	90	86.971(5)	90
V (Å3)	2143.3(11)	2187.0(3)	1417.88(18)	2218.86(12)
Z	2	4	2	4
T (K)	200	200	200	200
ρ_{calcd} (g cm^{-3})	1.180	1.242	1.103	1.272
F(000)	808	856	518	888
no. of unique reflns	6940	3066	3899	5007
no. of reflns used for refinement	4832	2647	3684	4719
no. of refined params	440	275	311	245
R1 ($I > 2\sigma(I)$)	0.0806	0.0362	0.0367	0.0344
wR2 (all data)	0.2325	0.1153	0.1238	0.1221
GOF	1.454	0.945	1.125	1.117
max./min. $\Delta\rho$ (e Å^{-3})	0.604/−0.578	+0.310/−0.573	+0.510/−0.438	+0.504/−0.511

(**7**) is described. A benzene/hexane mixed solution (10 mL) of unsolvated triethylgermyllithium[18] (9.3 mmol) was added to triphenylborane (2.01 g, 8.3 mmol). The mixture was stirred for 2 days to give the crude product as a white solid. Recrystallization from toluene afforded **7** (1.98 g, 5.8 mmol) in 71% yield as colorless crystals. Mp > 200 °C. ^{1}H NMR (C_7D_8, 80 °C, δ) 0.67 (q, 6 H, J = 7.9 Hz), 0.89 (t, 9 H, J = 7.9 Hz), 6.80−6.90 (m, 3 H), 6.94−7.06 (m, 6 H), 7.17−7.32 (m, 6 H); ^{13}C NMR (C_7D_8, 80 °C, δ) 7.1, 10.5, 124.8, 128.4, 135.2, 154.4−156.4 (br); ^{7}Li NMR (C_7D_8, 80 °C, δ) −7.0 ($\nu_{1/2}$ = 26.8 Hz); ^{11}B NMR (C_7D_8, 80 °C, δ) −11.3. Anal. Calcd for $C_{24}H_{30}GeBLi$: C, 71.02; H, 7.45. Found: C, 71.55; H, 7.12. Spectral data for **7** in methanol: ^{1}H NMR (CD^3OD, δ) 0.52 (q, 6 H, J = 8 Hz), 0.79 (t, 9 H, J = 8 Hz), 6.81 (t, 3 H, J = 7 Hz), 6.98 (t, 6 H, J = 7 Hz), 7.26 (d, 6 H, J = 7 Hz); ^{13}C NMR (CD_3OD, δ) 6.0, 9.3, 120.1, 124.5, 135.0, 161.8 (q, J(^{11}B−^{13}C) = 53 Hz); ^{7}Li NMR (CD_3OD, δ) −0.15; ^{11}B NMR (CD_3OD, δ) −8.6. Na[Et_3GeBPh_3] (**8**): colorless crystals, 77% yield. Mp > 200 °C. ^{1}H NMR (CD_3CN, δ) 0.51 (q, 6 H, J = 8 Hz), 0.82 (t, 9 H, J = 8 Hz), 6.84 (t, J = 7 Hz, 3 H), 7.00 (t, J = 7 Hz, 6 H), 7.19 (d, J = 7 Hz, 6 H); ^{13}C NMR (CD_3CN, δ) 4.4, 8.0, 119.1, 123.3, 133.2, 160.0 (q, J(^{11}B−^{13}C) = 50 Hz); ^{11}B NMR (CD_3CN, δ) −8.5. Anal. Calcd for $C_{24}H_{30}GeBNa$: C, 67.84; H, 7.12. Found: C, 68.20; H, 6.95. K[Et_3GeBPh_3] (**9**): colorless crystals, 58% yield. Mp > 200 °C. ^{1}H NMR (CD_3CN, δ) 0.51 (q, 6 H, J = 8 Hz), 0.82 (t, 9 H, J = 8 Hz), 6.84 (t, J = 7 Hz, 3 H), 7.00 (t, J = 7 Hz, 6 H), 7.19 (d, J = 7 Hz, 6 H); ^{13}C NMR (CD_3CN, δ) 4.5, 8.0, 119.1, 123.3, 133.3, 160.0 (q, J(^{11}B−^{13}C) = 50 Hz); ^{11}B NMR (CD_3CN, δ) −8.6.

X-ray Crystal Structure Analyses for 4, 5, 7, and 8. Crystal data for all structures are presented in Table 6. Crystallographic data for **5**, **7**, [**7**·3MeOH]$_2$, and **8** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-244796, -178044, -178043, and -244797, respectively. Copies are available free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code + 44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

Absorption Spectra of the Borates. The silyl- and germylborates are extremely sensitive to oxygen and moisture. A closed absorption cell was used to observe the absorption spectra of the borates. The absorption cell apparatus used in these studies consists of a 1-cm quartz absorption cell sealed to a sidearm of a round-bottomed flask. The apparatus was connected to a high-vacuum system for alternate degassing and flushing with argon. Access to the flask was through a second sidearm closed by a rubber string cap. The borate was quickly placed in throughly degassed THF in a round-bottomed flask.

Photochemical Reactions of the Borates. The THF solution (1 cm^3) containing the borate (30 mmol) was sealed under vacuum in a quartz tube connected to a Pyrex tube at the upper part. The tube was degassed under vacuum and filled with argon. The sample was irradiated with a xenon lamp at room temperature for 30 min. After irradiation, the photoproducts were identified by comparing the retention times on GLC and GC-MS with those of authentic samples.

Photochemical Reactions of the Borates in the Presence of Trapping Agents. The borate (30 mmol) and chloroform (150 mmol) were dissolved in dry THF (1 cm^3) in a quartz tube. The tube was degassed in a vacuum and filled with argon. The sample was irradiated with a xenon lamp at room temperature for 30 min. After irradiation, the photoproducts were identified by GLC and GC-MS.

Transient Optical Absorption Measurements. Laser flash photolysis measurements were performed at 293 K. They were basically the same as described previously.[28] The sample solutions were excited with the fourth harmonic (266 nm) of an Nd:YAG laser (Quanta Ray GCR-3, Spectra-Physics). In the measurements of the profiles of the transient absorbance, $A(t)$ curves, we averaged the data of 5 shots. The time resolution of the apparatus was about 10 ns.

ESR Measurements. Transient ESR measurements were performed at 293 K using an X-band spectrometer (JEOL RSV 2000) without field modulation. They were basically the same as described previously.[29] The sample solutions were excited with the fourth harmonic (266 nm) of an Nd:YAG laser (Quanta Ray GCR-3, Spectra-Physics). We averaged the data of 50 transient ESR spectra. To obtain good S/N ratios, we averaged 5 scans for one spectrum. Conventional ESR measurements were performed at 293 K using an X-band spectrometer with field modulation of 100 kHz.

Acknowledgment. The authors thank Prof. Toshihiro Takahashi of Gakushuin University for the ESR spectrum of the triphenylboron anion radical. The authors also thank Mr. Yuki Watanabe for preliminary experiments of phenyl-substituted germyl borates. This work was supported by a Grant-in-Aid from the Ministry of Education, Culture, Science, Sports, and Technology, Japan (No. 15550041).

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM050733Y

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