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# Syntheses, Structures, and Reactions of Heptacoordinate Trihalogermanes Bearing a Triarylmethyl-Type Tetradentate Ligand

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Trichloro[tris(3-*tert*-butyl-6-methoxyphenyl)methyl]germane (**3**), containing a tetradentate ligand with three methoxy groups as coordinating sites, was synthesized by the reaction of the corresponding (triarylmethyl)lithium species with tetrachlorogermane. In contrast to the case for the previously reported trichlorosilane analogue, **3** slowly decomposed during column chromatography on silica gel, although it was quite stable against moisture. The corresponding trifluoro-, tribromo-, and triiodogermanes **4**−**6** were prepared from the trichlorogermane **3**. X-ray crystallographic analyses of **3**−**6** showed heptacoordinate structures with interatomic distances between the oxygen atom and the central germanium atom shorter than the sum of van der Waals radii. By systematic comparisons of these intramolecular interactions based on the interatomic distances, it was found that they strongly depend on the Lewis acidity of the trihalogenated germanium atom. An Atoms-in-Molecules (AIM) analysis of the model compound **4′**, in which three *tert*-butyl groups of trifluorogermane **4** were omitted, showed the existence of weak and ionic bonding between oxygen and germanium atoms. Reactions of these trihalogermanes with aqueous NaOH, $LiAlH_4$, and $BX_3$ were also investigated. Alkaline hydrolysis of trihalogermanes resulted in the cleavage of the carbon−germanium bond. $LiAlH_4$ also caused the same kind of bond cleavage, together with nucleophilic attack on the germanium atom, giving the trihydrogermane **8**. Reaction of the trihalogermanes with trihaloboranes was found to be an efficient procedure to give other trihalogermanes through a halogen exchange reaction.

## Introduction

Hypercoordinated main-group-element compounds have been extensively studied because of their interesting structures and reactivities and also as models of the transition state or the intermediate of $S_N2$ reactions. Among group 14 element compounds, hypercoordinated organogermanium compounds have been rather less studied, while organosilicon compounds have been investigated intensively and widely used in synthetic applications.[1] Ionic penta-, hexa-, and heptacoordinate group 14 element compounds have been synthesized by nucleophilic attack by anions at a neutral central atom. Bidentate ligands such as the Martin ligand[2] were well-known to stabilize these highly coordinated species. In contrast, the syntheses of neutral group 14 element compounds with high coordination numbers have been achieved by the introduction of intramolecular dative bonds provided by bidentate or tridentate ligands such as van Koten type ligands.[3]

In comparison to the number of penta- and hexacoordinate compounds, neutral heptacoordinate silicon compounds are rare and only a few examples are known of germanium and tin compounds.[4,5] The syntheses of these compounds have been achieved by using more than two multidentate ligands in which coordination sites are connected to the central atom (Figure 1, type I). This type of compound can have only one functional group, and each dative bond is opposite to one of the covalent bonds with the central atom and another ligand. In contrast, compounds using another type of interaction (Figure 1, type II), in which coordination sites are connected to the atom adjacent to the central atom, are rare despite their advantages; more than two functional groups can be introduced, and each coordination site is located at the opposite side of the functional group, which makes possible a direct effect on its coordinating nature by altering the functional groups. We have reported the synthesis of a novel type of heptacoordinate trichlorosilane, **1**, with a type II interaction based on a tris(3-*tert*-butyl-6-

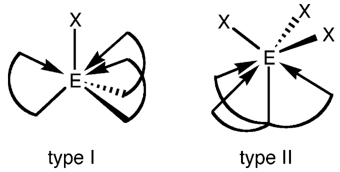

**Figure 1.**

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[†] The University of Tokyo.

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(1) Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds*; Wiley: New York, 1998; Vol. 2, p 1339.

(2) A bidentate ligand (−$(C_6H_4)$-2-$C(CF_3)_2O$−): (a) Martin, J. C.; Perozzi, E. F. *Science* **1976**, *191*, 154. (b) Perozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H., III; Dess, D. B.; Ross, M. R. Martin, J. C. *J. Org. Chem.* **1981**, *46*, 1049. (c) Martin, J. C. *Science* **1983**, *221*, 509.

(3) A bidentate ligand (−$(C_6H_4)$-2-$(CH_2NMe_2)$): van Koten, G.; Schaap, C. A.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *99*, 157. A tridentate ligand (−$(C_6H_3)$-2,6-$(CH_2NMe_2)_2$): van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Spek, A. L.; Schoone, J. C. *J. Organomet. Chem.* **1978**, *148*, 233.

(4) (a) Brelière, C.; Carré, F.; Corriu, R. J. P.; Royo, G. *Organometallics* **1988**, *7*, 1006. (b) Brelière, C.; Carré, F.; Corriu, R. J. P.; Royo, G.; Man, M. W. C. *Organometallics* **1994**, *13*, 307. (c) Carré, F.; Chuit, C.; Corriu, R. J. P.; Fanta, A.; Mehdi, A.; Reyé, C. *Organometallics* **1995**, *14*, 194. (d) Kano, N.; Nakagawa, N.; Kawashima, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 3450.

(5) (a) Kawachi, A.; Tanaka, Y.; Tamao, K. *Organometallics* **1997**, *16*, 5102. (b) Dostal, S.; Stoudt, S. J.; Fanwick, P.; Sereatan, W. F.; Kahr, B.; Jackson, J. E. *Organometallics* **1993**, *12*, 2284.

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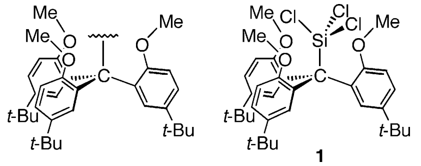


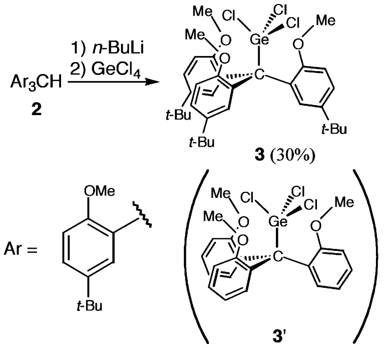
**1**

**Figure 2.**

methoxyphenyl)methyl unit (Figure 2), and found that **1** is unusually stable to nucleophilic substitutions.[6] Despite several reports on syntheses of heptacoordinate compounds with type II interactions,[5−7] there have been few systematic studies on group 14 element compounds with varying functional groups using the same ligand. We report here the syntheses of heptacoordinate trihalogermanes substituted with the tris(3-*tert*-butyl-6-methoxyphenyl)methyl group, and we compare their structures and reactivities.

## Results and Discussion

**Synthesis of the Trichlorogermane 3 and Its Derivatization to the Corresponding Trifluoro-, Tribromo-, and Triiodogermanes.** In a way similar to that previously reported by us and Takeuchi et al. for the trichlorosilane **1**[6] and trichlorogermane **3′**,[7] respectively, the trichlorogermane **3** was synthesized by the lithiation of tris(3-*tert*-butyl-6-methoxyphenyl)methane (**2**) by an excess of *n*-butyllithium followed by reaction of the lithium reagent thus formed with tetrachlorogermane (eq 1). An increase in the yield of **3** was achieved when DME was used as a solvent in the presence of HMPA, which is well-known to activate the lithium reagent by solvation to the lithium cation. Once isolated, **3** was quite stable compared with the usual trichlorogermanes and could be stored in the air. However, **3** was slightly less stable than **1** and slowly decomposed during column chromatography on silica gel, thus resulting in isolation in only low yield (30%).



(1)

The trifluoro-, tribromo-, and triiodogermanes **4**−**6** were obtained by halogen exchange reactions with the trichlorogermane **3** (eqs 2−4; the yields of **5** and **6** were quantitative, as estimated by $^1$H NMR). **3** was allowed to react slowly with an excess of silver(I) fluoride in benzene to give the trifluorogermane **4**. Although the fluorination reaction proceeded more rapidly in polar solvents such as chloroform and acetonitrile, side reactions also occurred, so that a complex mixture of **4** and unidentified products was obtained. The reaction of **3** with 3 equiv of bromotrimethylsilane and iodotrimethylsilane yielded the tribromogermane **5** and the triiodogermane **6**, respectively. **5** was also synthesized by treatment of **3** with an excess of tribromoborane at −78 °C (vide infra). The reaction at higher temperature caused decomposition to give a complex mixture, in marked contrast to the previous report that trichlorosilane **1** underwent demethylation followed by Si−O bond formation.[8] These results indicate that the present halogen exchange reaction on the central atom proceeds more readily than demethylation in the germanium derivative **3** compared to the silicon derivative **1**.

$$\underset{\mathbf{3}}{\mathrm{Ar_3CGeCl_3}} \xrightarrow{\mathrm{AgF}} \underset{\mathbf{4}\ (50\%)}{\mathrm{Ar_3CGeF_3}} \tag{2}$$

$$\underset{\mathbf{3}}{\mathrm{Ar_3CGeCl_3}} \xrightarrow{\mathrm{Me_3SiX}} \underset{\substack{\mathbf{5}\ (\mathrm{X = Br})\\ \mathbf{6}\ (\mathrm{X = I})}}{\mathrm{Ar_3CGeX_3}} \tag{3}$$

$$\underset{\mathbf{3}}{\mathrm{Ar_3CGeCl_3}} \xrightarrow{\mathrm{BBr_3}} \underset{\mathbf{5}\ (98\%)}{\mathrm{Ar_3CGeBr_3}} \tag{4}$$

**X-ray Crystallographic Analyses and Spectroscopic Properties of Trihalogermanes.** Single crystals of **3**−**6** suitable for X-ray analysis were obtained in each case by slow evaporation from a hexane solution for **3**, a hexane/ether solution for **4**, a benzene/THF solution for **5**, and a benzene/$CHCl_3$ solution for **6**, respectively. The crystal structures of **3**−**6** were determined by X-ray crystallographic analysis, and ORTEP drawings of **4** are shown in Figure 3. Selected bond lengths, interatomic distances, and bond angles are given in Table 2. All have approximate $C_3$ symmetrical propeller-like structures, as had been found in the previously reported trichlorosilane **1**[6] and trichlorogermane **3′**.[7] The oxygen ligands adopt positions anti to the halogen atoms (O···Ge−X angles are 170−178°), while the three aryl rings have similar twists out of their common coordination plane with the germanium atom.

Interatomic distances between the oxygen atom and the germanium atom are 16−23% shorter than the sum of van der Waals radii (3.40 Å).[9] The ratio of O···Ge distances to the sum of van der Waals radii is gradually increased as the halogen atom on the germanium atom becomes less electronegative: **4** (2.622 Å; 77%) < **3** (2.769 Å; 81%) < **5** (2.821 Å; 83%) < **6** (2.853 Å; 84%). The averaged X−Ge−X angles also widen with **4** (98.93°) < **3** (101.25°) < **5** (101.78°) < **6** (102.55°), and the averaged torsion angles of the propellers Ge−C1−C2−C3 (see Figure 4) increase except for **6**: **4** (47.8°) < **3** (51.5°) < **5** (55.3°) ≈ **6** (54.7°). Because the Lewis acidity of the germanium atom was generally enhanced by the introduction of more electronegative groups, these results indicate that all of these compounds have a heptacoordinate structure with "tricapped tetrahedral" geometry, by the coordination of three oxygen atoms from the side opposite to the halogen atoms. The Ge−X bond lengths of **3**−**6** are slightly elongated compared to the average Ge−X bond lengths of tetracoordinate organotrihalogermanes without coordination, as shown in the Cambridge Structural Database (CSD).

The changes in the NMR spectra between trihalogermanes can be rationalized by the structural changes. The $^{13}$C NMR chemical shift of the methoxy groups was shifted to lower field with a decrease in the distances between the oxygen atom and the central germanium atom, as shown in the X-ray structures. When the oxygen−germanium interaction is increased, the neighboring carbon atom is more deshielded. When the $^{13}$C NMR chemical shifts of the methoxy group were plotted against the interatomic distances between the oxygen atom and the

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[6] Kobayashi, J.; Ishida, K.; Kawashima, T. *Silicon Chem.* **2002**, *1*, 351.

[7] Takeuchi, Y.; Takase, Y. *J. Organomet. Chem.* **2004**, *689*, 3275.

[8] Kobayashi, J.; Kawaguchi, K.; Kawashima, T. *J. Am. Chem. Soc.* **2004**, *126*, 16318.

[9] For the van der Waals radii of Ge: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

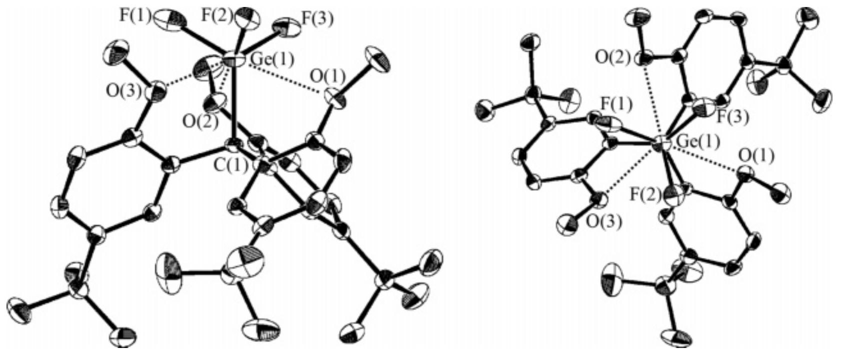
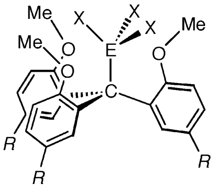


**Figure 3.** ORTEP drawings of **4** (50% probability): (left) side view; (right) top view.

**Table 1. Crystallographic Data for the Trihalo[tris(3-*tert*-butyl-6-methoxyphenyl)methyl]germanes 3−6**

| | 3 | 4 | 5 | 6 |
|---|---|---|---|---|
| formula | $C_{34}H_{45}Cl_3GeO_3$ | $C_{34}H_{45}F_3GeO_3$ | $C_{34}H_{45}Br_3GeO_3$ | $C_{34}H_{45}GeI_3O_3$ |
| temp/K | 153(2) | 120(2) | 120(2) | 120(2) |
| cryst syst | monoclinic | triclinic | cubic | cubic |
| space group | $C2/c$ | $P\bar{1}$ | $Pa3$ | $Pa\bar{3}$ |
| $a$/Å | 35.665(15) | 10.093(3) | 19.7087(5) | 19.9244(5) |
| $b$/Å | 10.282(4) | 11.968(4) | | |
| $c$/Å | 20.270(9) | 14.947(5) | | |
| α/deg | | 97.379(4) | | |
| β/deg | 103.1143(17) | 98.341(4) | | |
| γ/deg | | 105.019(4) | | |
| $V$/Å$^3$ | 7239(5) | 1699.2(10) | 7655.5(3) | 7909.6(3) |
| $Z$ | 8 | 2 | 8 | 8 |
| $D_{calcd}$/g cm$^{-3}$ | 1.249 | 1.234 | 1.742 | 1.670 |
| no. of rflns collected | 19 977 | 9622 | 36 618 | 39 716 |
| no. of unique rflns | 5852 | 5135 | 1894 | 2151 |
| goodness of fit | 1.099 | 1.140 | 1.173 | 1.073 |
| $R_1$ | 0.0734 | 0.0330 | 0.0392 | 0.0536 |
| w$R_2$ | 0.1896 | 0.0866 | 0.0983 | 0.1634 |

**Table 2. Selected Bond Lengths, Interatomic Distances, and Angles**[a]



| | E | X | R | $r_w$/Å[b] | O···E/Å | E−X/Å | E−X in CSD/Å[c] | O···E−X/deg |
|---|---|---|---|---|---|---|---|---|
| **1**[d] | Si | Cl | *t*-Bu | 3.39 | 2.80 (83)[e] | 2.07 | 2.02 (−)[d] | 176 |
| **3** | Ge | Cl | *t*-Bu | 3.40 | 2.77 (81) | 2.16 | 2.13 (18) | 176 |
| **3′** | Ge | Cl | H | 3.40 | 2.78 (81) | 2.16 | 2.13 (18) | |
| **4** | Ge | F | *t*-Bu | 3.40 | 2.62 (77) | 1.78 | *f* | 171 |
| **5** | Ge | Br | *t*-Bu | 3.40 | 2.82 (83) | 2.32 | 2.28 (3) | 177 |
| **6** | Ge | I | *t*-Bu | | 2.85 (84) | 2.52 | 2.52 (2) | 178 |

[a] Values are the average of the symmetric parts of the compounds. [b] The sum of van der Waals radii of O···E. [c] Average E−X bond lengths of trichlorosilane or trihalogermanes without any coordination. Values in parentheses represent the number of compounds from the CSD. [d] Reference 6. [e] Values in parentheses represent (O···E)/(sum of VDW radii) in percent. [f] There are no crystal data for organotrifluorogermanes in the CSD.

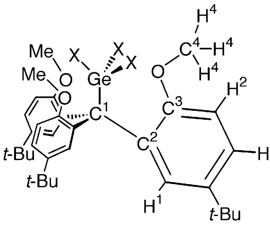


**Figure 4.**

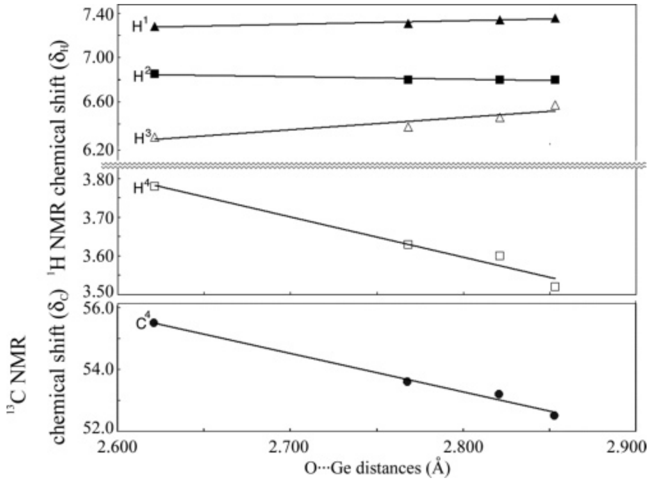


**Figure 5.** Plots of oxygen−germanium interatomic distances vs NMR chemical shifts.

germanium atom, they showed a good linear correlation (Figure 5), and this result indicates that trihalogermanes have a "tricapped tetrahedral" heptacoordinate structure with oxygen−germanium interactions in solution as well as in the solid state.

To clarify the properties of the interatomic interaction of trihalogermanes, AIM analysis[10] of the model compound **4′**, in which three *tert*-butyl groups of trifluorogermane **4** were omitted, was performed at the B3PW91/6-311+G(d)[Ge]:6-31+G(d)[O,F]:6-31G(d)[C,H] level. The optimized geometry of **4′** reproduced well that of **4**, and the O···Ge distance of **4′** (2.638 Å) was close to those (2.521, 2.658, and 2.685 Å) of **4**. As the bond critical points were found on the bond paths between the oxygen atoms and the germanium atom, bonding between oxygen and germanium should be considered to exist. The small value of the electron density ($\rho(\mathbf{r})$: 0.0229 e/$a_o^3$) and the small positive Laplacian value ($\nabla^2\rho(\mathbf{r})$: 0.0598 e/$a_o^5$) at the bond critical point indicate that the corresponding bonds are weak and have ionic character.[11]

**Reactivity of Trihalogermanes.** To obtain further insight into the properties of these trihalogermanes, reactions of **3**−**5** with some reagents were performed. Unfortunately, the reactivities of triiodogermane **6** could not be examined properly

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(10) (a) Bader, R. F. W. *Atoms in Molecules-A Quantum Theory*; Oxford University Press: Oxford, U.K., 1990. (b) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893. (c) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061. (d) Bader, R. F. W. *J. Phys. Chem. A* **1998**, *102*, 7314.

(11) For similar values, see: Yamashita, M.; Yamamoto, Y.; Akiba, K.-y.; Hashizume, D.; Iwasaki, F.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2005**, *127*, 4354.

**Table 3. Ratios of the Products for the Reactions of 3−5 with $\mathbf{LiAlH_4}$[a]**

| | X | **2**[b] | **8**[b] |
|---|---|---|---|
| **3** | Cl | 29 | 16 |
| **4** | F | 0 | 100 |
| **5** | Br | 23 | 77 |

[a] Reactions were carried out for 4 h at room temperature, with 3 equiv of $LiAlH_4$. [b] Estimated by $^1H$ NMR.

because it was difficult to isolate from the byproducts formed in its preparation and also it was relatively unstable compared with the other trihalogermane derivatives.

Alkaline hydrolysis of both the trichlorogermane **3** and the tribromogermane **5** with aqueous NaOH gave the triarylmethanol species **7**[12] (eq 5). This result indicates that these trihalogermanes

$$\underset{\mathbf{3},\ \mathbf{5}}{\mathrm{Ar_3CGeX_3}} \xrightarrow[\text{THF}]{\text{aq NaOH}} \underset{\mathbf{7}}{\mathrm{Ar_3COH}} \tag{5}$$

tend to be attacked by nucleophiles (in this case, $OH^-$) at their triarylmethyl carbon position, resulting in carbon−germanium bond cleavage. For 4 h at room temperature, only 31% of **7** was obtained from trichlorogermane **3**, in contrast to quantitative conversion in the case of tribromogermane **5**. The higher reactivity of **5** may be caused by the great leaving ability of $GeBr_3$, which is bulkier than $GeCl_3$.

Similar reactivity was also observed in the reaction of trichlorogermane **3** with 3 equiv of $LiAlH_4$. The triarylmethane **2** was the major product, and the trihydrogermane **8** was formed in lower yield (eq 6 and Table 3). The origin of the hydrogen

$$\underset{\mathbf{3-5}}{\mathrm{Ar_3CGeX_3}} \xrightarrow[\text{THF}]{\mathrm{LiAlH_4}} \underset{\mathbf{2}}{\mathrm{Ar_3CH}} + \underset{\mathbf{8}}{\mathrm{Ar_3CGeH_3}} \tag{6}$$

atom substituted on the triarylmethyl carbon was confirmed by treatment with $LiAlD_4$; triaryldeuteriomethane (**2**-*d*) was obtained, suggesting direct nucleophilic attack by the hydride (deuteride) anion. The trihydrogermane derivative **8** was very likely formed by nucleophilic displacement of chlorine by hydride. Both **2** and **8** were obtained in the reaction of tribromogermane **5** with $LiAlH_4$, but their ratio was reversed and **8** was the major product. The reaction of trifluorogermane **4** with $LiAlH_4$ yielded **8** quantitatively. These results indicate that the ratio of **2** and **8** in the competing reactions is determined by the difference in the halogen substituents of the trihalogermanes, their leaving abilities and steric factors, as well as the Lewis acidity of the Ge atom in each case.

The reaction of trichlorogermane **3** with an excess (10 equiv) of tribromoborane at −78 °C yielded tribromogermane **5** quantitatively. To obtain further insight, the reactions of trihalogermanes **3**−**5** and $BBr_3$ or $BCl_3$ were investigated (eqs 7 and 8 and Table 4). Treatment with a large excess (10 equiv)

$$\underset{\mathbf{3},\ \mathbf{4}}{\mathrm{Ar_3CGeX_3}} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{BBr_3}} \underset{\mathbf{5}}{\mathrm{Ar_3CGeBr_3}} \tag{7}$$

$$\underset{\mathbf{4},\ \mathbf{5}}{\mathrm{Ar_3CGeX_3}} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{BCl_3}} \underset{\mathbf{3}}{\mathrm{Ar_3CGeCl_3}} \tag{8}$$

of tribromoborane at −78 °C also converted trifluorogermane **4** into tribromogermane **5** quantitatively, whereas reactions carried out at 0 °C resulted in a complex mixture. With trichloroborane, the reactions of trifluoro- and tribromogermanes **4** and **5** gave trichlorogermane **3**. In contrast to the reactions with tribromoborane, the halogen exchange reactions of **4** and **5** with trichloroborane proceeded without formation of byproducts at 0 °C or at room temperature. The desirable halogen exchange reactions of the tribromogermane **5** with trichloroborane proceeded slowly (31% for 17 h at room temperature). On the other hand, the reaction of trifluorogermane **4** proceeded much more quickly. Apparently, the more electronegative fluorine accelerates the halogen exchange reaction. Trifluoroborane etherate did not react with any of these trihalogermanes, and reactions with triiodoborane resulted in a complex decomposition of substrates. To obtain further insight into these reactions, theoretical calculations of the free energy differences of the reaction of trihalomethylgermanes with trihaloboranes were performed at the B3LYP/6-31G*//B3LYP/6-31G* level.[13] Equations 9−11 are energetically favorable, which can be

$$\mathrm{MeGeF_3} + \mathrm{BCl_3} \rightarrow \mathrm{MeGeCl_3} + \mathrm{BF_3} \tag{9}$$

$$\Delta G = -40\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{MeGeF_3} + \mathrm{BBr_3} \rightarrow \mathrm{MeGeBr_3} + \mathrm{BF_3} \tag{10}$$

$$\Delta G = -64\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{MeGeCl_3} + \mathrm{BBr_3} \rightarrow \mathrm{MeGeBr_3} + \mathrm{BCl_3} \tag{11}$$

$$\Delta G = -23\ \mathrm{kcal\ mol^{-1}}$$

rationalized by the quantitative conversion to products in the corresponding reactions of trihalo(triarylmethyl)germanes with trihaloboranes. The reverse reaction of eq 11 is energetically disfavored, reflecting the low conversion yield in the reaction of tribromogermane **5** with trichloroborane. Considering that the reverse reactions of eqs 9 and 10 are thermodynamically more unfavorable and trifluoroborane etherate was used in the real system, it is quite reasonable that **3** and **5** did not react with trifluoroborane etherate at all.

**Table 4. Reaction Conditions and Products for the Reactions of 3−5 with Trihaloboranes**

| | X | reagent (amt/equiv) | conditions | product[a] |
|---|---|---|---|---|
| **3** | Cl | $BBr_3$ (10) | −78 °C, 1 h | **5** (98) |
| **4** | F | $BBr_3$ (10) | −78 °C, 1 h | **5** (quant) |
| **4** | F | $BCl_3$ (6) | 0 °C, 3 h | **3** (quant) |
| **5** | Br | $BCl_3$ (6) | room temp, 17 h | **3** (31)[b] |

[a] Estimated by $^1H$ NMR; percentage yields are given in parentheses. [b] 69% of **5** was observed.

## Experimental Section

**Synthesis of Trichloro[tris(3-*tert*-butyl-6-methoxyphenyl)-methyl]germane (3).** To a solution of tris(3-*tert*-butyl-6-methoxy-

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phenyl)methane[12] (5.00 g, 9.95 mmol) in benzene (250 mL) was added *n*-BuLi (1.67 M hexane solution, 50.1 mmol) at 50 °C. The mixture was stirred at 50 °C for 12 h. After removal of the solvent under reduced pressure, DME (125 mL) and HMPA (6.90 mL, 39.7 mmol) were added to the residue. To the mixture was added tetrachlorogermane (11.3 mL, 99.5 mmol) at 0 °C. The mixture was stirred at 0 °C for 2 h and at room temperature for 12 h. After removal of the solvent, the residue was treated with 200 mL of EtOH and then 100 mL of $H_2O$. The mixture was extracted with $CHCl_3$. After removal of the solvent under reduced pressure, the residue was dissolved in ether and washed with 2% aqueous NaOH. The extracts were combined and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel. Elution with 15/1 hexane/AcOEt gave **3**, which was further purified by recrystallization from hexane/$CHCl_3$ to afford the pure product (2.02 g, 30%). **3**: colorless crystal, mp 265.5−265.7 °C; $^1$H NMR (500 MHz, $CDCl_3$, 27 °C) $\delta$ 1.06 (s, 27H), 3.63 (s, 9H), 6.37 (d, 3H, $J = 2.3$ Hz), 6.80 (d, 3H, $J = 8.5$ Hz), 7.31 (dd, 3H, $J = 2.3$, 8.5 Hz); $^{13}$C NMR (126 MHz, $CDCl_3$, 27 °C) $\delta$ 31.2 (q), 34.0 (s), 53.6 (q), 69.0 (s), 108.7 (d), 125.2 (d), 126.5 (s), 127.8 (d), 143.0 (s), 154.4 (s). Anal. Calcd for $C_{34}H_{45}Cl_3GeO_3$: C, 59.99; H, 6.66. Found: C, 59.74; H, 6.74.

**Synthesis of Trifluoro[tris(3-*tert*-butyl-6-methoxyphenyl)methyl]germane (4).** To a solution of trichlorogermane **3** (500 mg, 735 $\mu$mol) in benzene (5 mL) was added silver(I) fluoride (467 mg, 3.68 mmol), and the mixture was heated at reflux for 4 days. Insoluble silver salts were filtered off, and the solvent was removed under reduced pressure. The residue was purified by recrystallization from hexane to afford **4** (233 mg, 50%). **4**: colorless crystal, mp 263.3−263.7 °C dec; $^1$H NMR (500 MHz, $CDCl_3$, 27 °C) $\delta$ 1.06 (s, 27H), 3.78 (s, 9H), 6.28 (d, 3H, $J = 2.4$ Hz), 6.85 (d, 3H, $J = 8.5$ Hz), 7.28 (dd, 3H, $J = 2.4$, 8.5 Hz); $^{13}$C NMR (126 MHz, $CDCl_3$, 27 °C) $\delta$ 31.2 (q), 34.0 (s), 52.3 (q, $^2J_{CF} = 6.5$ Hz), 55.5 (q), 109.3 (d), 125.1 (d), 126.4 (d), 127.7 (s), 143.5 (s), 153.2 (s); $^{19}$F NMR (376 MHz, $CDCl_3$, 27 °C) $\delta$ −25.45. Anal. Calcd for $C_{34}H_{45}F_3GeO_3$: C, 64.68; H, 7.18. Found: C, 64.52; H, 7.22.

**Synthesis of Tribromo[tris(3-*tert*-butyl-6-methoxyphenyl)methyl]germane (5) by Reaction of 3 with Bromotrimethylsilane.** To a solution of the trichlorogermane **3** (50 mg, 73.5 $\mu$mol) in $CDCl_3$ (0.5 mL) was added bromotrimethylsilane (17.5 $\mu$L, 132 $\mu$mol) at room temperature in a 5 mm o.d. NMR tube. After several freeze−pump−thaw cycles, the tube was evacuated and sealed. The solution was heated at 75 °C for 2 weeks. After the completion of the reaction was confirmed by $^1$H NMR spectroscopy, the sealed tube was opened in a glovebox, and the solvent was removed under reduced pressure. The residue was purified by recrystallization from hexane/$Et_2O$ to afford **5** (31 mg, 53%). **5**: yellow crystal, mp 181.9−182.3 °C dec; $^1$H NMR (500 MHz, $CDCl_3$, 27 °C) $\delta$ 1.08 (s, 27H), 3.60 (s, 9H), 6.46 (d, 3H, $J = 2.3$ Hz), 6.80 (d, 3H, $J = 8.5$ Hz), 7.34 (dd, 3H, $J = 2.3$, 8.5 Hz); $^{13}$C NMR (126 MHz, $CDCl_3$, 27 °C) $\delta$ 31.2 (q), 34.0 (s), 53.2 (q), 72.2 (s), 108.9 (d), 125.3 (d), 126.3 (s), 128.2 (d), 142.9 (s), 154.5 (s). Anal. Calcd for $C_{34}H_{45}Br_3GeO_3$: C, 50.16; H, 5.57. Found: C, 50.14; H, 5.72.

**Synthesis of Tribromo[tris(3-*tert*-butyl-6-methoxyphenyl)methyl]germane (5) by Reaction of 3 with Tribromoborane.** To a solution of the trichlorogermane **3** (68 mg, 0.10 mmol) in $CH_2Cl_2$ (3 mL) was added tribromoborane (1.0 M $CH_2Cl_2$ solution, 1.0 mmol) at −78 °C. The mixture was stirred at −78 °C for 1 h. Subsequently it was treated with EtOH and then $H_2O$ and extracted with $CHCl_3$. The extracts were combined and dried over anhydrous $MgSO_4$, the solvent was removed under reduced pressure, and the residue was purified by recrystallization from hexane to afford **5** (80 mg, 98%).

**Synthesis of Triiodo[tris(3-*tert*-butyl-6-methoxyphenyl)methyl]germane (6).** To a solution of the trichlorogermane **3** (50 mg, 73.5 $\mu$mol) in $CDCl_3$ (0.5 mL) was added iodotrimethylsilane (32 $\mu$L, 220 $\mu$mol) at room temperature in a 5 mm o.d. NMR tube. After several freeze−pump−thaw cycles, the tube was evacuated and sealed. The solution was heated at 75 °C for 8 h. After the completion of the reaction was confirmed by $^1$H NMR spectroscopy, the sealed tube was opened in a glovebox, and the solvent was removed under reduced pressure. The residue was purified by recrystallization from hexane/$Et_2O$ to afford **6** (16 mg, 23%). **6**: yellow crystal, mp 169.5−169.8 °C dec; $^1$H NMR (500 MHz, $CDCl_3$, 27 °C) $\delta$ 1.08 (s, 27H), 3.52 (s, 9H), 6.57 (d, 3H, $J = 1.8$ Hz), 6.80 (d, 3H, $J = 8.5$ Hz), 7.36 (dd, 3H, $J = 1.8$, 8.5 Hz); $^{13}$C NMR (126 MHz, $CDCl_3$, 27 °C) $\delta$ 31.3 (q), 33.9 (s), 52.5 (q), 69.7 (s), 109.8 (d), 125.2 (d), 126.6 (s), 128.4 (d), 143.1 (s), 154.3 (s). Anal. Calcd for $C_{34}H_{45}GeI_3O_3$: C, 42.76; H, 4.75. Found: C, 42.95; H, 5.00.

**X-ray Structural Analysis.** Single crystals of **3**−**6** were grown from the appropriate solution (hexane solution for **3**, hexane/ether solution for **4**, benzene/THF solution for **5**, and benzene/$CHCl_3$ solution for **6**). The intensity data were collected at 120 K (except for **3**, at 153 K) on a Rigaku/MSC Mercury CCD with Mo K$\alpha$ radiation ($\lambda = 0.710\,69$ Å). The structures were solved by direct methods and refined by full-matrix least squares on $F^2$ using SHELXS97.[14] Crystallographic data are given in Table 1. The structures were refined anisotropically, except for hydrogen atoms. Hydrogen atoms were idealized by using the riding models.

**Alkaline Hydrolysis of Trichlorogermane 3.** To a solution of the trichlorogermane **3** (4.8 mg, 7.0 $\mu$mol) in THF (1 mL) was added NaOH (0.7 mM aqueous solution, 0.7 mmol) at room temperature. The mixture was stirred for 6 h and then was extracted with $CHCl_3$. The extracts were combined and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was analyzed by $^1$H NMR spectroscopy to give the ratio of **3** (69%) and tris(3-*tert*-butyl-6-methoxyphenyl)methanol (**7**;[12] 31%).

**Alkaline Hydrolysis of Tribromogermane 5.** To a solution of the tribromogermane **5** (5.7 mg, 7.0 $\mu$mol) in THF (1 mL) was added NaOH (0.7 mM aqueous solution, 0.7 mmol) at room temperature. The mixture was stirred for 6 h and extracted with $CHCl_3$. The extracts were combined and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was analyzed by $^1$H NMR spectroscopy to show the quantitative formation of tris(3-*tert*-butyl-6-methoxyphenyl)methanol (**7**).[12]

**Reaction of Trichlorogermane 3 with Lithium Aluminum Hydride.** To a solution of trichlorogermane **3** (50 mg, 74 $\mu$mol) in THF (3 mL) was added $LiAlH_4$ (9.0 mg, 237 $\mu$mol) at 0 °C. The mixture was warmed to room temperature and stirred for 4 h. The mixture was treated with aqueous $NH_4Cl$ and extracted with $CHCl_3$. The extracts were combined and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was analyzed by $^1$H NMR spectroscopy to show that the ratio of **3** to tris(3-*tert*-butyl-6-methoxyphenyl)methane (**2**) to trihydro[tris(3-*tert*-butyl-6-methoxyphenyl)methyl]germane (**8**) was 55:29:16.

**8**: colorless crystal, mp 189.5−190.0 °C dec; $^1$H NMR (500 MHz, $CDCl_3$, 27 °C) $\delta$ 1.04 (s, 27H), 3.63 (s, 9H), 4.33 (s, 3H), 6.33 (d, 3H, $J = 2.5$ Hz), 6.78 (d, 3H, $J = 8.4$ Hz), 7.15 (dd, 3H, $J = 2.5$, 8.4 Hz); $^{13}$C NMR (126 MHz, $CDCl_3$, 27 °C) $\delta$ 31.3 (q), 33.9 (s), 54.5 (q), 55.9 (s), 109.6 (d), 122.7 (d), 127.2 (d), 134.4 (s), 142.4 (s), 155.1 (s); HR-MS (FAB+) *m*/*z* calcd for $C_{34}H_{47}GeO_3$ ($[M - H]^+$) 577.2737, found 577.2762. Anal. Calcd for $C_{34}H_{48}GeO_3$: C, 70.73; H, 8.38. Found: C, 70.59; H, 8.52.

**Reaction of Tribromogermane 5 with Lithium Aluminum Hydride.** To a solution of the tribromogermane **5** (20 mg, 25 $\mu$mol) in THF (1.5 mL) was added $LiAlH_4$ (3.0 mg, 79 $\mu$mol) at 0 °C. The mixture was warmed to room temperature and stirred for 4 h. The mixture was treated with aqueous $NH_4Cl$ and extracted with

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(14) Sheldrick, G M. SHELXS-97: Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, 1997.

$CHCl_3$. The extracts were combined and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was analyzed by $^1H$ NMR spectroscopy to show that the ratio of tris(3-*tert*-butyl-6-methoxyphenyl)methane (**2**) to the trihydrogermane **8** was 23:77.

**Reaction of Trifluorogermane 4 with Lithium Aluminum Hydride.** To a solution of the trifluorogermane **4** (19 mg, 30 $\mu$mol) in THF (3 mL) was added $LiAlH_4$ (3.4 mg, 90 $\mu$mol) at 0 °C. The mixture was warmed to room temperature and for 4 h. The mixture was treated with aqueous $NH_4Cl$ and extracted with $CHCl_3$. The extracts were combined and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was analyzed by $^1H$ NMR spectroscopy to show the quantitative formation of the trihydrogermane **8**.

**Reaction of Trifluorogermane 4 with Tribromoborane.** To a solution of the trifluorogermane **4** (11 mg, 17 $\mu$mol) in $CH_2Cl_2$ (1.5 mL) was added tribromoborane (1.0 M $CH_2Cl_2$ solution, 170 $\mu$mol) at −78 °C. The mixture was stirred at −78 °C for 1 h. The mixture was treated with EtOH and then $H_2O$ and extracted with $CHCl_3$. The extracts were combined and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was analyzed by $^1H$ NMR spectroscopy to show the quantitative formation of the tribromogermane **5**.

**Reaction of Tribromogermane 5 with Trichloroborane.** To a solution of the tribromogermane **5** (16 mg, 20 $\mu$mol) in $CH_2Cl_2$ (2 mL) was added trichloroborane (1.0 M hexane solution, 120 $\mu$mol) at room temperature. The mixture was stirred at room temperature for 17 h. The mixture was treated with EtOH and then $H_2O$ and extracted with $CHCl_3$. The extracts were combined and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was analyzed by $^1H$ NMR spectroscopy to show that the ratio of **5** to the trichlorogermane **3** was 69:31.

**Reaction of Trifluorogermane 4 with Trichloroborane.** To a solution of the trifluorogermane **4** (14 mg, 22 $\mu$mol) in $CH_2Cl_2$ (2 mL) was added trichloroborane (1.0 M hexane solution, 130 $\mu$mol) at 0 °C. The mixture was stirred at 0 °C for 3 h. The mixture was treated with EtOH and then $H_2O$ and extracted with $CHCl_3$. The extracts were combined and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was analyzed by $^1H$ NMR spectroscopy to show the quantitative formation of the trichlorogermane **3**.

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**Supporting Information Available:** CIF files giving crystallographic data for **3**−**6** and figures giving ORTEP drawings of **3**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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