# SYNTHESIS OF A PENTACOORDINATE GERMANIUM COMPOUND POSSESSING A γ-LACTONE AND A DATIVE-BONDING CARBOXYLIC ACID

**Hiroki Tanimoto,\* Daiki Toumori, Tsumoru Morimoto, and Kiyomi Kakiuchi\***

Division of Materials Science, Graduate School of Science and Technology, Nara Institute of Science and Technology (NAIST), 8916-5 Takayama-cho, Ikoma, Nara 630-0192, Japan; E-mail: tanimoto@ms.naist.jp; kakiuchi@ms.naist.jp

This paper is dedicated to Professor Yasuyuki Kita on the occasion of his 77th birthday.

**Abstract** − A pentacoordinate germanium compound consisting of a spirocyclic dilactone-like structure was synthesized. Both radical and oxidation synthetic routes afforded the diphenylgermanium dicarboxylic acid compound. Then, mono-dearylation by acid treatment successfully delivered a hypercoordinate germane product. X-Ray crystallographic analysis revealed that the product adopted trigonal bipyramidal geometry in which a γ-lactone ring and a dative-bonding carboxylic acid moiety were incorporated.

Currently, there is a strong demand for easy-to-prepare small-molecule drugs that possess novel bioactivity or mode of action. A promising approach in current drug design involves the use of bioisosteres.[1] In many cases, bioisosteres have been found to improve compound stability, solubility, and pharmacokinetic properties. As a new bioisostere replacement strategy, element replacement has become a recent focus.[2] Silicon and germanium are both bioisosteres of carbon, and element replacement from carbon to silicon or germanium in pharmaceutical molecules—the so-called "silicon switch", in the case of silicon—has presented a new approach to drug discovery.[3,4] Although there are many similarities among carbon, silicon, and germanium, differences in their bond length, lipophilicity, electropositivity, and hypercoordination characteristics have been efficiently exploited to improve bioactivities. Specifically, hypercoordinate states,[5] which are never formed in carbon atoms,[6] could have potential for novel bioactivity and new working mechanisms. Within the scope of silicon and germanium,

organogermanium materials have been reported to be less toxic than organosilicon compounds.[7] To date, some bioactive germanium compounds have been reported, including germoxanes such as the marketed drug propagermanium (SEROCION[TM]),[4,8] germylated sugars,[9] and hypercoordinate germanes (Figure 1).[10,11] However, the research on organogermanium compounds is still limited unlike that of silicon.[3,4] Encouraged by our previous works[12] based on element-block organogermanium material chemistry,[13] we have started developing potentially bioactive organogermanium candidates. Herein, we report the synthesis of a novel pentacoordinate organogermanium carboxylic acid compound possessing a γ-lactone moiety in a trigonal bipyramidal geometry.
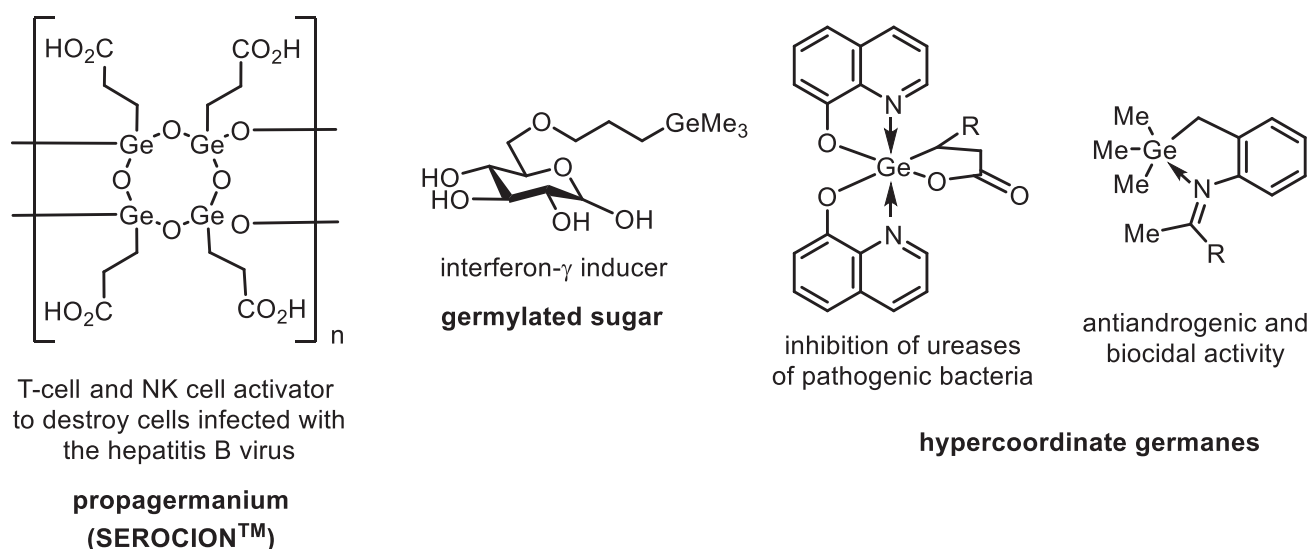


Figure 1. Bioactive organogermanium compounds

Our research commenced with diphenylgermane **1**.[14] By making use of the characteristic features of germanium,[15] we attempted a radical Michael addition of **1** to *tert*-butyl acrylate, and obtained diester **2** (Scheme 1), albeit in low yield. In an attempt to improve the reaction yield, we investigated the effect of both heating and extended reaction times. However, the yield was not improved beyond 35%. The *tert*-butyl groups of **2** were then removed under acidic conditions to give dicarboxylic acid **3** in moderate yield. Although **3** was successfully obtained, unsatisfactory yields prompted us to find a new synthetic route to **3**, starting from commercially available diphenylgermanium dichloride **4**. Following diallylation of **4** in accordance with the reported procedure,[16] hydroboration-oxidation gave the diol **6** in good yield. Next, the oxidation to the dicarboxylic acid **3** from **6** was examined. Although Jones oxidation gave **3**, purification from the chromium residue was extremely challenging. Finally, TEMPO oxidation[17] successfully afforded **3** without difficulty in purification.
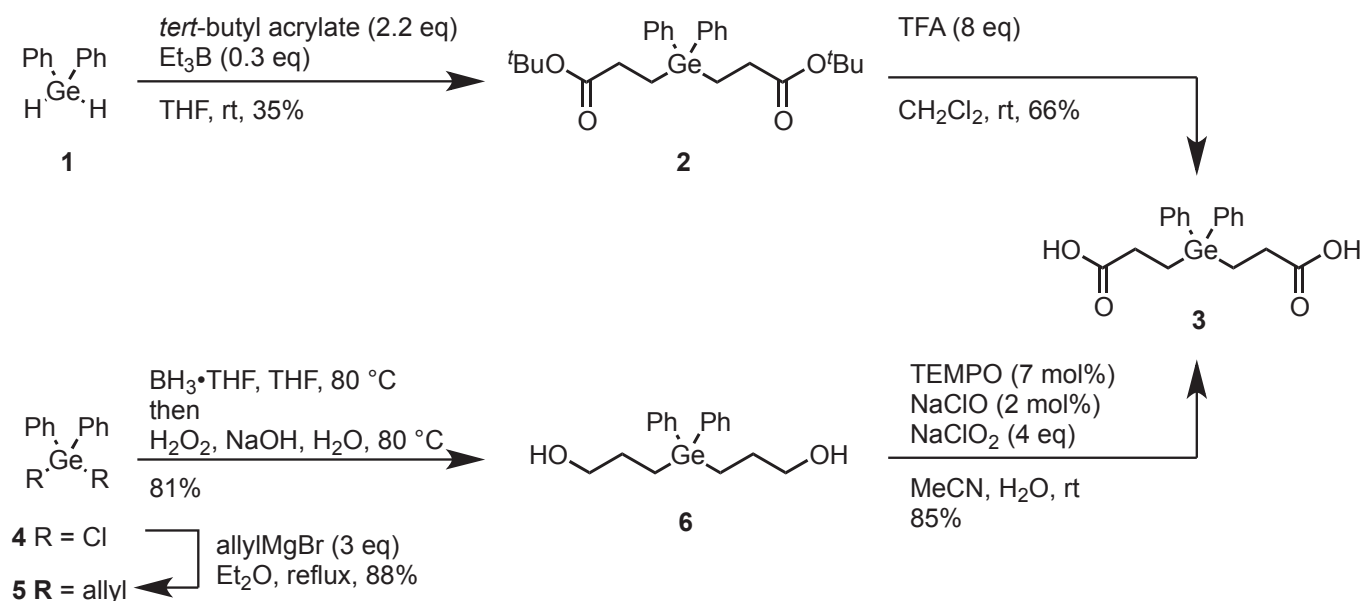
Scheme 1. Synthesis of germanium dicarboxylic acid

With diphenyl dicarboxylic acid **3** in hand, we attempted further acid treatment to remove the phenyl group by protodegermylation (Scheme 2). Trifluoromethanesulfonic acid did not give isolable materials, probably leading to polymerization to germoxanes. After optimization of the reaction conditions, the use of trifluoroacetic acid and dichloromethane as solvents helped suppress the overreactions, and successfully afforded pentacoordinate germane **7**.
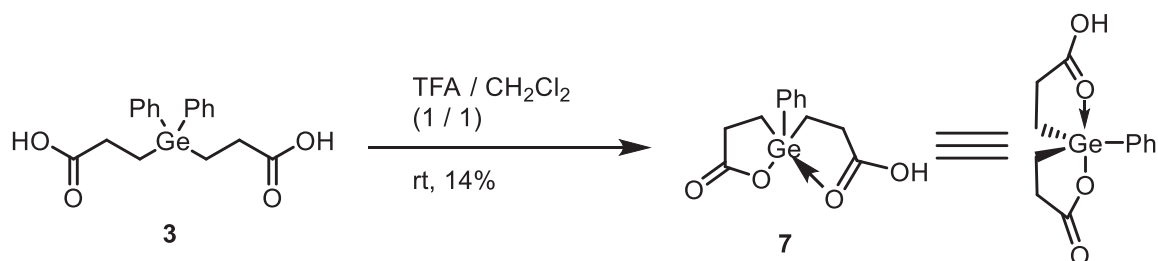


Scheme 2. Synthesis of pentacoordinate germanium dilactone

The obtained crystalline materials **3** and **7** were subjected to single-crystal X-ray analysis.[18] Dicarboxylic acid **3** was obtained as a cocrystal with recrystallization solvent chloroform (Figure 2). Intermolecular hydrogen bonding between two carboxylic acid moieties is observed.
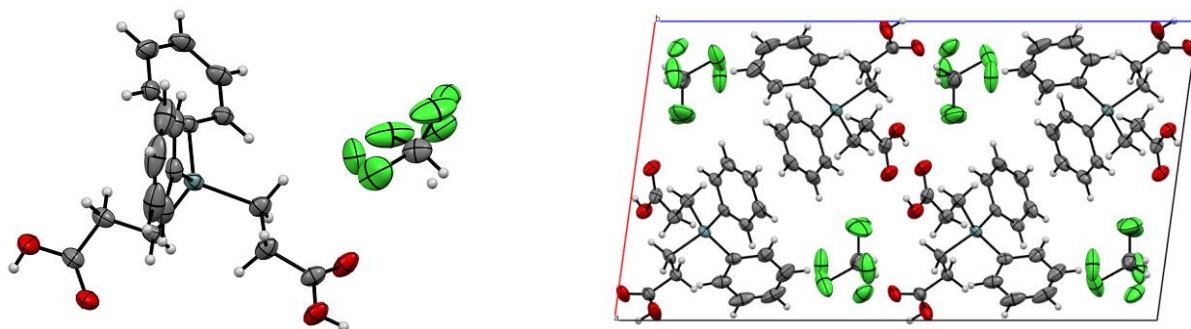
Figure 2. ORTEP figures of dicarboxylic acid **3** with disordered chloroform and their packing view from the b axis

On the other hand, compound **7** is found in a spirocycle-like pentacoordinate germanium conformation (Figure 3). The counter cation of a proton is not observed in the X-ray analysis. A possible tetracoordinate germanium monolactone with an acyclic carboxylic acid chain is not found, yet **7'** and **7''** are observed, both in a trigonal bipyramidal form with two apical germanium-oxygen bonds.
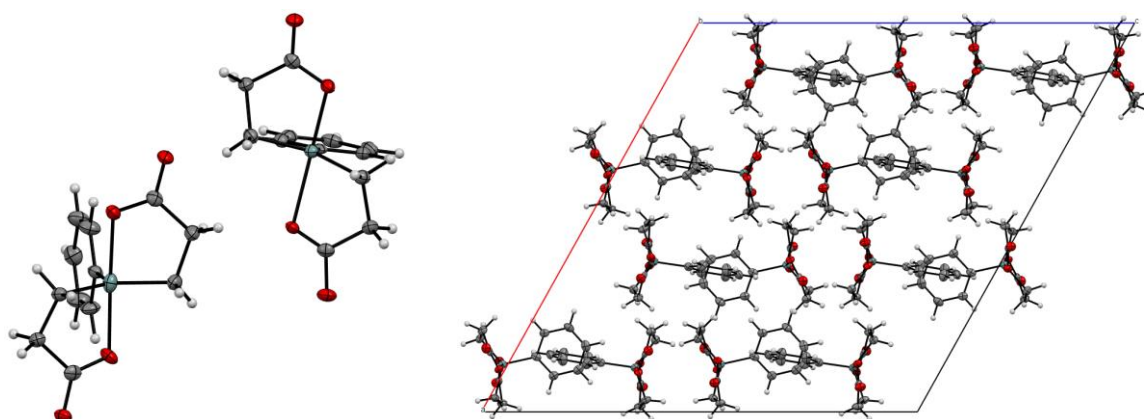


Figure 3. ORTEP figures of pentacoordinate germane **7** (**7'** and **7''** for each independent molecule) and the packing view from the b axis. Carboxylic acid protons or free protons as counterions are not observed.

The detailed parameters for the X-ray crystallographic analyses are listed in Table 1. The germanium-carbon bond length in germanes **7'** and **7''** are slightly shorter than that in dicarboxylic acid **3**. On the other hand, the germanium-carboxylate oxygen bonds at the apical positions in **7'** and **7''** are sufficiently long (~2.1 Å), compared to those of pentacoordinate germane of trigonal bipyramid but distorted toward square pyramid (~1.9 Å), reported by Tacke and co-workers,[19] and the germanium-ether oxygen bond lengths of trigonal bipyramidal germane with Martin ligand (~2.0 Å), reported by Denmark and co-workers.[20] The oxygen-germanium-oxygen angles in **7'** and **7''** are around 169°; these angles are slightly narrower than that of Martin ligand germane (174°), owing to the structural differences between the two compounds which results from the alkyl chain of **7** as opposed to the aromatic ring chain in

Denmark's germanate).[20] A large carbon-germanium-carbon angles compared to **3** represents the hypercoordinate form of **7**.

Table 1. Selected crystallographic parameters

| Parameters | Dicarboxylic acid **3** | Pentacoordinate germanes **7' (7")** |
|---|---|---|
| R1 ($I > 2\sigma$ ($I$)]) | 0.0427 | 0.0635 |
| wR2 (all data) | 0.1117 | 0.1497 |
| Space Group | P2$_1$/c (#14) | C2/c (#15) |
| Ge–Ph (Å) | 1.954(3), 1.946(3) | 1.933(7) (1.915(8)) |
| Ge–C$_{sp3}$ (Å) | 1.950(3), 1.948(3) | 1.931(5), 1.936(7) (1.948(5), 1.934(6)) |
| Ge–O (Å) | — | 2.129(4), 2.134(4) (1.994(4), 2.293(4)) |
| ∠O–Ge–O (°) | — | 168.69(19) (170.04(19)) |
| ∠C$_{sp3}$–Ge–C$_{sp3}$ (°) | 105.47(13) | 126.5(3) (127.1(3)) |

To the best of our knowledge, this type of hypercoordinate germanium or silicon compounds consisting of spirocyclic dilactone-like structure (one lactone and dative-bonding carboxylic acid) has not been reported. For this reason, we also compared our compound to pentacoordinate bis(thioglycolato)-germanium materials possessing similar γ-lactone-like ring structures.[21,22] The germanium-oxygen bonds in **7'** and **7"** are still slightly longer than those in pentacoordinate bis(thioglycolato)germanium (~2.04 Å),[21] and significantly longer than covalent-bonding lactones in hypercoordination (~1.9 Å).[23] The equal lengths of the two Ge-O bonds in **7'** are also reported in the pentacoordinate bis(thioglycolato) compound.[21a] Although hydrogen atoms of carboxylic acids are not observed, this would be due to the intermolecular hydrogen bonding as similar to the report by Takeuchi's group.[21a] Incontrast, those in **7"** differ by 0.3 Å, which is indicative of weaker dative-bonding than that in **7'**, and is a characteristic feature of one carboxylic acid moiety, as reported in the ether material.[21c] This may be attributed to intramolecular coordination of the carboxylic acid hydrogen, which reduces dative bonding, thereby increasing the dative bond length (Figure 4). Similar to the pentacoordinate bis(thioglycolato)germane,[21] the $^1$H and $^{13}$C NMR spectra of **7** in solution exhibit only two broad signals for both CH$_2$ protons and one

for the carbonyl carbon nuclei. This can be interpreted as a rapid equilibrium between the pentacoordinate species in solution at room temperature, which could prove to be useful in the molecular design of bioactive hypercoordinate pharmaceuticals.
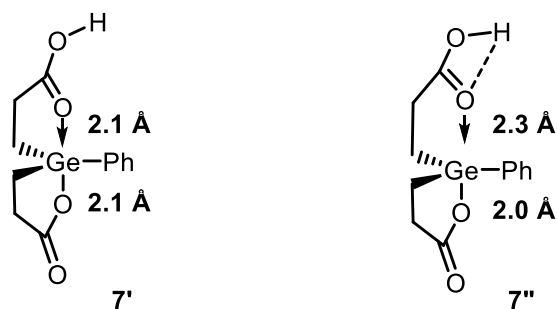


Figure 4. Possible conformations of the observed pentacoordinate germane **7** in a crystal

In summary, a pentacoordinate organogermanium compound possessing a spirocyclic dilactone-like structure was synthesized. Diphenylgermane with two propionic acid moieties, prepared by either radical or oxidation routes, was converted to the germane by mono-protodearylation. The obtained germane adopts a trigonal bipyramidal geometry with the carboxylate oxygen atoms at the apical positions, and it has long germanium-oxygen bonds. Further research on the development of germane and silane molecules for use as organic reaction catalysts and pharmaceutical candidates, and in complexation chemistry is in progress.

**EXPERIMENTAL**

**General Information:** $^1$H and $^{13}$C NMR spectra were recorded on a JEOL JNM-ECP500 spectrometer (500 MHz for $^1$H NMR and 126 MHz for $^{13}$C NMR). Chemical shifts are reported as δ values in ppm and calibrated with respect to the residual solvent peak (CDCl$_3$: δ 7.26 for $^1$H NMR and δ 77.00 for $^{13}$C NMR; CD$_3$OD: δ 3.31 for $^1$H NMR, and 49.00 for $^{13}$C NMR). The abbreviations used are as follows: s (singlet), d (doublet), t (triplet), q (quartet), br (broad), m (complex multiplet). Melting points were measured using a Yanaco Micro melting point apparatus. Infrared spectra were recorded on a JASCO FT-IR-4200 spectrometer. Mass spectra were recorded using a JEOL JMS-700 MStation (EI, 70 eV; CI, FAB, and ESI). All measurements for single-crystal X-ray diffraction analysis were performed on a Rigaku R-AXIS RAPID diffractometer using multi-layer mirror monochromated Mo-Kα radiation. The data were usually collected at a temperature of -150 °C. Elemental analysis was performed using a PerkinElmer 2400IICHNS/O. Flash column chromatography was performed using Merck Silica gel 60. The progress of the reactions was monitored by silica gel thin-layer chromatography (TLC) (Merck TLC Silica gel 60 F254). The impure materials even after silica gel chromatogprahy were further purified by recycling gel

permeation chromatography (GPC) using a LC-908 equipped with a JAIGEL 2H-40 column (CHCl$_3$ elution) manufactured by Japan Analytical Industry Co., Ltd. All reagents were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Ltd., TCI (Tokyo Chemical Industry, Co., Ltd), Kanto Chemical, Co., Inc., and Nakalai Tesque, Inc. Anhydrous tetrahydrofuran (THF) and diethyl ether (Et$_2$O) were purchased from Kanto Chemical. Co., Inc. and Wako Pure Chemical Industries, Ltd. Ion-exchanged distilled water was used for purification and recrystallization.

**3,3'-(Diphenylgermanediyl)di(*tert*-butyl)propionate (2):** To a stirred solution of diphenylgermane **1** (1.3 g, 5.8 mmol)[14] and *tert*-butyl acrylate (1.9 mL, 13 mmol) in THF (29 mL) was added triethylborane (1.0 M *n*-hexane solution, 1.7 mL, 1.7 mmol) at room temperature under rough nitrogen atmosphere. After 5 h, the reaction was quenched with water. The mixture was extracted with Et$_2$O and was washed with brine. The collected organic layer was dried over magnesium sulfate. Concentration *in vacuo* followed by silica gel column chromatography (hexane / CH$_2$Cl$_2$= 2 / 1 to 1 / 1) gave **2** (0.992 g, 35%) as a colorless oil.

Colorless oil; R$_f$ value 0.41 (hexane / CH$_2$Cl$_2$ = 1 / 1); IR (NaCl, neat) v$_{max}$ 3069, 2980, 2928, 1726, 1363, 1228, 1165, 999 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.45–7.43 (m, 4H), 7.37–7.35 (m, 6H), 2.31–2.27 (m, 4H), 1.53–1.50 (m, 4H), 1.40 (s, 18H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.8, 136.5, 134.4, 128.9, 128.2, 80.2, 30.7, 28.0, 8.0; LRMS (ESI, [M+Na]$^+$ = C$_{26}$H$_{36}$GeNaO$_4$) *m/z* 509, 507, 505; Anal. Calcd: C. 64.36%; H. 7.48%, found: C. 64.59%; H. 7.47%.

**3,3'-(Diphenylgermanediyl)dipropionic acid (3, CCDC 1993114) from 2:** To a stirred solution of di-*tert*-butyl ester **2** (100 mg, 0.21 mmol) in CH$_2$Cl$_2$ (1.0 mL) was added trifluoroacetic acid (0.13 mL, 1.65 mmol) at room temperature. After 2 days, the mixture was concentrated *in vacuo*, and the obtained residue was purified by silica gel column chromatography (hexane / EtOAc = 2 / 1 to 1 / 2) to give **3** (50.6 mg, 66%) as a white solid. Single crystal for X-ray crystallographic analysis was obtained by recrystallization from CHCl$_3$.

White solid; R$_f$ value 0.55 (hexane / EtOAc = 1 / 3); mp 136–137 °C; IR (KBr, disc) v$_{max}$ 3065, 1712, 1486, 1429, 1340, 1294, 1254, 1186, 1129, 1092, 903, 739 cm$^{-1}$; $^1$H NMR (500 MHz, CD$_3$OD) δ 7.47–7.45 (m, 4H), 7.38–7.37 (m, 6H), 2.36 (t, 4H, *J* = 8.5 Hz), 1.56 (t, 4H, *J* = 8.5 Hz); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 178.3, 137.7, 135.5, 130.1, 129.4, 30.4, 8.2; MS: not found. Anal. Calcd [as 2×(C$_{18}$H$_{20}$GeO$_4$) + H$_2$O]: C. 56.60%; H. 5.54%; found: C. 56.77%, H. 5.46%.

**Diallyldiphenylgermane (5):** Compound **5** was prepared following Wnuk's report.[16] To a stirred solution of dichlorodiphenylgermane **4** (1.0 g, 3.4 mmol) in Et$_2$O (7 mL) was added allylmagnesium bromide (1.0 M, 10.7 mL, 10.7 mmol) at 0 °C. After 1 h, the mixture was heated under reflux condition, and was stirred overnight. Then, the reaction was quenched with saturated ammonium chloride aqueous solution and water at 0 °C. The mixture was extracted with Et$_2$O and was washed with water and brine. The

collected organic layer was dried over magnesium sulfate. Concentration in vacuo followed by silica gel column chromatography (hexane elution) gave **5** (0.915 g, 88%) as a colorless oil.

Colorless oil; R$_f$ value 0.43 (hexane only); IR (NaCl, neat) $\nu_{max}$ 3069, 3051, 2997, 2972, 1630, 1458, 1192, 1143, 1092, 1027, 990 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.61–7.59 (m, 4H), 7.48–7.46 (m, 6H), 6.00 (ddd, $J$ = 16.0, 10.5, 8.0 Hz), 5.08 (dd, 2H, $J$ = 16.0, 1.0 Hz), 5.00 (dd, 2H, $J$ = 10.5, 1.0 Hz), 2.37 (d, 4H, $J$ = 8.0 Hz); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 137.0, 134.5, 134.4, 128.9, 128.0, 114.1, 20.0; MS: not found. Anal. Calcd: C. 69.97%; H. 6.52%; found: C. 70.03%, H. 6.61%.

**3,3'-(Diphenylgermanediyl)bis(propan-1-ol) (6):** To a stirred solution of diallylgermane **5** (771 mg, 2.45 mmol) in THF (4.6 mL) was added borane THF complex (1.0 M in THF, 1.9 mL, 1.9 mmol) at 0 °C under nitrogen atmosphere. After 40 min, the mixture was heated under reflux condition. After 1 h, the reaction was quenched with water at 0 °C, and then, sodium hydroxide (3.0 M in water, 0.61 mL, 1.83 mmol) and hydrogen peroxide (35 wt%, 0.63 mL, 5.5 mmol) was added, and the mixture was heated at 80 °C. After 3h, the mixture was extracted with Et$_2$O, and was washed with water and brine. The collected organic layer was dried over magnesium sulfate. Concentrated *in vacuo* followed by silica gel column chromatography (hexane / EtOAc = 1 / 1) to give **6** (695 mg, 81%) as a white solid.

White solid; R$_f$ value 0.27 (hexane / EtOAc = 1 / 1); mp 80–81 °C; IR (KBr, disc) $\nu_{max}$ 3306, 3063, 2939, 2904, 1483, 1429, 1367, 1089, 1051, 1011, 886, 737, 700 cm$^{-1}$; $^1$H NMR (500 MHz, CD$_3$OD) δ 7.47–7.45 (m, 4H), 7.36–7.33 (m, 4H), 3.52 (t, 4H, $J$ = 7.0 Hz), 1.64 (m, 4H), 1.28 (m, 4H); $^{13}$C NMR (126 MHz, CD$_3$OD) δ 139.3, 135.6, 129.9, 129.4, 65.7, 29.3, 10.0; MS: not found. Anal. Calcd: C. 62.66%; H. 7.01%, found: C. 62.92%, H. 7.14%.

**3,3'-(Diphenylgermanediyl)dipropionic acid (3) from 6:** To a stirred solution of di-(3-hydroxypropyl)diphenylgermane **6** (173 mg, 0.5 mmol) and 2,2,6,6-tetramethylpiperidine 1-oxyl (5.5 mg, 0.035 mmol) in MeCN (2.5 mL) were added sodium chlorite 2 M aqueous solution (1.0 mL, 2.0 mmol) and sodium hypochlorite 0.25 wt% aqueous solution (0.25 mL, 0.01 mmol) dropwise independently by two addition funnel, and the mixture was stirred at room temperature for four days. The mixture was quenched with water, 1 M sodium hydroxide aqueous solution, and 10 wt% sodium sulfite aqueous solution at 0 °C successively. After 1 h, the mixture was treated with Et$_2$O and 1 M sodium hydroxide aqueous solution, and the organic layer was discarded. Then, the aqueous layer was acidified by 1 M hydrogen chloride aqueous solution, and the desired organic component was extracted with Et$_2$O. The corrected organic layer was dried over magnesium sulfate. Concentration *in vacuo* followed by silica gel column chromatography (hexane / EtOAc = 1 / 1 to 1 / 2) to give **3** (158 mg, 85%) as a white solid.

**Pentacoordinated germane (7, CCDC 1993115):** To a stirred solution of dicarboxylic acid **3** (373 mg, 1.0 mmol) in CH$_2$Cl$_2$ (2.5 mL) was added trifluoroacetic acid (2.5 mL) at room temperature. After 3 days, the mixture was treated poured in to CH$_2$Cl$_2$ and water, and then, organic layer was discarded. Collected

water layer was concentrated in vacuo to obtain crude solid residue which was recrystallized to give pure **7** (42 mg, 14%) as a white crystal. Single crystal for X-ray crystallographic analysis was obtained by recrystallization from water.

White crystal; $R_f$ value 0.54 (MeOH / water = 50 / 1); mp 196–197 °C; IR (KBr, disc) $\nu_{max}$ 2432, 1951, 1654, 1578, 1433, 1341, 1241, 1138, 1092, 1052, 882, 749 cm$^{-1}$; $^1$H NMR (500 MHz, CD$_3$OD) δ 7.62–7.61 (m, 2H), 7.43–7.37 (m, 3H), 2.71 (t, 4H, $J$ = 7.2 Hz), 1.71 (br, 4H); $^{13}$C NMR (126 MHz, CD$_3$OD) δ 183.6, 138.4, 134.1, 130.7, 129.3, 30.0, 12.0; LRMS (ESI, [M-H]$^-$ = C$_{12}$H$_{13}$GeO$_4$) $m/z$ 295, 293, 291; Anal. Calcd: C. 48.88%; H. 4.79%, found: C. 48.92%, H. 4.65%.

## ACKNOWLEDGEMENTS

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