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Study on the electronic effect on coordinating donors in heptacoordinate trichlorogermanes

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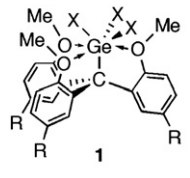
Abstract—Trichloro[tris(2,5-dimethoxyphenyl)methyl]germane (**1a**), trichloro[tris(3-fluoro-6-methoxyphenyl)methyl]germane (**1b**), and trichloro[tris(2-methoxy-5-trifluoromethylphenyl)methyl]germane (**1c**) were synthesized. X-ray crystallographic analyses of **1a–c** revealed their heptacoordinate geometries around the germanium atoms. The interatomic distances between the oxygen atoms and the central germanium atoms in the crystalline state were not significantly affected by change of functional groups on the benzene rings, while the optimized structures by theoretical calculations and Atoms in Molecules (AIM) analysis indicated linear relationship between the donating ability of functional groups and the O···Ge interatomic interactions.

1. Introduction

Hypercoordinate main group element compounds are well studied because of their interesting structures and reactivities and also as models of the transition state or the intermediate of S_N2 type reaction.[1] Among group 14 element compounds, penta- and hexacoordinate silicon compounds have been intensively and widely studied from a viewpoint of usefulness of their synthetic applications,[2] while germanium and tin derivatives are rather less studied.[3] In contrast to penta- and hexacoordinate compounds, heptacoordinate compounds are much rare. Although there have been several reports of the synthesis of neutral heptacoordinate compounds with four covalent bonds and three dative bonds, the systematic comparisons of these structural properties have been scant so far.[4]

Recently, we have developed heptacoordinate trihalogermanes **1d–g** (Fig. 1) by taking advantage of a triarylmethyl-type tetradentate ligand bearing three methoxy groups as coordinating sites.[5] X-ray structural analyses and NMR spectroscopy showed the presence of heptacoordinate structures both in the solid state and in solution, with three interatomic interactions between the oxygen atoms and the central germanium atom. Systematic comparisons of these interatomic interactions were performed and it was found that the Lewis acidity of the germanium atom controls the strength of the interatomic interactions.



	R	X
1a	OMe	Cl
1b	F	Cl
1c	CF_3	Cl
1d	*t*-Bu	Cl
1e	*t*-Bu	F
1f	*t*-Bu	Br
1g	*t*-Bu	I

Figure 1. Heptacoordinate trihalogermanes.

In this type of heptacoordinate compounds, the interaction between the central atom and the donor sites can be controlled not only by altering the central atoms or the halogen atoms attached to the central atom, but also by tuning the electron-donating ability of oxygen atoms. From this point of view, we report here the synthesis of trichlorogermanes **1a–c**, which have a different functional group at *para*-positions against coordinating methoxy groups on benzene rings, and the comparison of the X-ray structures of the compounds.

2. Results and discussion

2.1. Syntheses

o-Bromoanisoles **4a–c** were synthesized by the reported methods. Triarylmethanes **6a–c** were synthesized in similar ways to that previously reported for triarylmethane **6d**,[5] but some of the reaction conditions and reagents must be modified (Scheme 1). Triarylmethanols **5a** and **5d** were reduced easily with ethanol in hydrochloric acid. However, triarylmethanols **5b** and **5c** with fluorine atoms and trifluoromethyl groups, respectively, were not reduced to the corresponding

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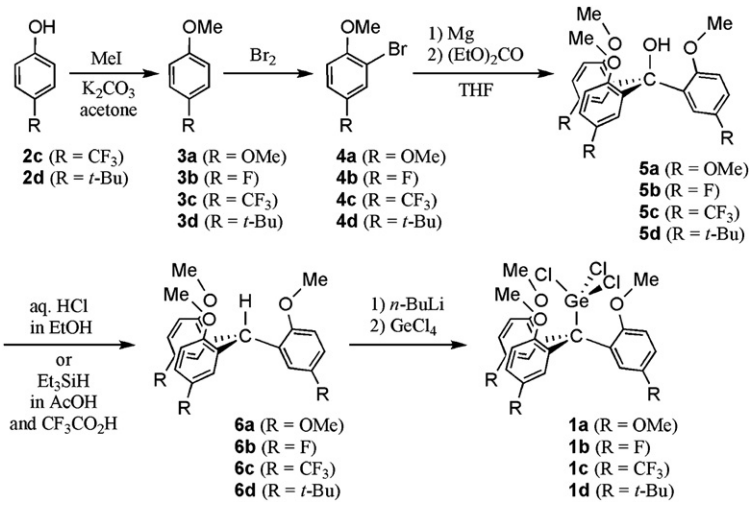


Scheme 1. Synthetic route of heptacoordinate trichlorogermanes **1a**–**d**.

triarylmethanes **6b** and **6c** under the same conditions, due to destabilization of intermediary carbocation by the electron withdrawing effect of fluorine atom or trifluoromethyl group. Even the reaction with triethylsilane in acetic acid gave the corresponding triarylmethanes **6b** and **6c** only in the low conversion yields. However, addition of 1.1 equiv of trifluoroacetic acid accelerated the reaction to give **6b** or **6c** in a good yield. The deprotonations of triarylmethanes **6a**–**c** were achieved by treatment with *n*-butyllithium in a similar way to that for **6d**. But, the reaction time in the cases of **6b** and **6c**, was remarkably reduced (6–7 h) compared with 12 h in the case of **6d**, due to the stabilization of formed carbanion by electron withdrawing substituents at the *meta*-positions. The side-product, in which *n*-butyl groups were introduced on the benzene rings, was formed in the case of the reaction of **6b**, presumably via the benzyne intermediate. Target compounds **1a**–**c** were obtained by subsequent treatment of in situ generated carbanions with tetrachlorogermane in low to moderate yields.

2.2. Structures

Single crystals of **1a**–**c** suitable for X-ray analyses were obtained in each case by slow evaporation from acetonitrile/hexane solution for **1a**, benzene/$CHCl_3$ solution for **1b** and $CHCl_3$ solution for **1c**, respectively. The crystal structures of **1a**–**c** were determined by X-ray crystallographic analyses, and the ORTEP drawings are shown in Figure 2. All the compounds have approximate C_3 symmetrical propeller-like structures, as had been found in the previously reported trichlorogermane **1d**.[5] The oxygen atoms adopt backside positions to the halogen atoms (O···Ge–Cl angles are 170–178°), and the three aryl rings have the same twist angles out of their common coordination plane with the germanium atom.

The each O···Ge interatomic distance of trichlorogermanes **1a**–**c** showed no significant difference among **1a**–**c** (Table 1). This result shows sharp contrast to the systematic difference of the O···Ge distances of **1d**–**g**, when changing halogen atoms on the central germanium atom. Torsion angles Ge–C^1–C^2–C^3 were also converged within the standard deviations.

2.3. Theoretical calculations

For the detailed investigation, Atoms in Molecules (AIM) analyses of **1a**–**c** and a model compound **1h** (R=H) were performed at the B3PW91/6-31+G(d)[Cl,Ge,O]:6-31G(d)[C,F,H] level (Table 2)[6,7]. The X-ray structures are well reproduced by theoretical calculations, and bond critical points were found on the bond paths between the oxygen atoms and the germanium atom in their optimized structures, indicating the existence of bonding interaction between oxygen and germanium atoms. These interactions showed a systematic tendency between functional group (R) and O···Ge distances, as well as electron densities on the bond

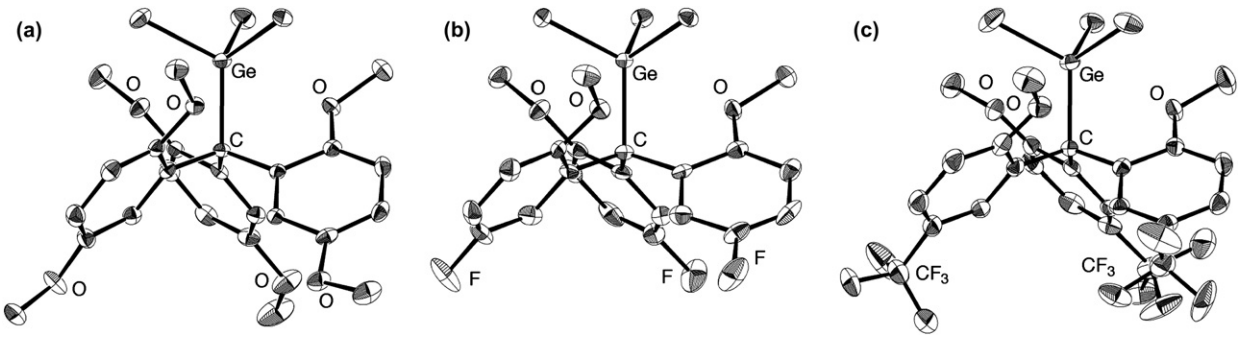
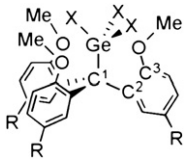


Figure 2. ORTEP drawings of trihalogermanes (a) **1a**, (b) **1b**, and (c) **1c** (50% probability level).

Table 1. Selected interatomic distances and torsion angles in **1a–g**[a]



	R	X	Ge···O/Å	Ge–C^1–C^2–C^3/°
1a	OMe	Cl	2.769(2)	50.9(2)
1b	F	Cl	2.793(4)	53.2(5)
1b[b]	F	Cl	2.760(4)	54.3(5)
1c	CF_3	Cl	2.781(2)	52.5(3)
1d	*t*-Bu	Cl	2.768(5)	51.5(7)
1e	*t*-Bu	F	2.621(4)	47.8(2)
1f	*t*-Bu	Br	2.821(3)	55.3(4)
1g	*t*-Bu	I	2.853(5)	54.7(6)

[a] Values are the average of the symmetric parts of the compounds.
[b] There were two independent structures in the unit cell.

Table 2. AIM analyses of **1a–c** and **1h**

	R	Ge···O/Å	Ge–C–C–C/°	ρ^a/e a_0^{-3}	$\nabla^2\rho^b$/e a_0^{-5}
1a	OMe	2.778	51.28	0.01921	0.0490
1h	H	2.785	51.27	0.01897	0.0486
1b	F	2.790	51.55	0.01883	0.0482
1c	CF_3	2.812	52.26	0.01801	0.0470

[a] Electron density at the bond critical points.
[b] Laplacian value of electron density.

critical points, that is, electron withdrawing groups (F, CF_3) weaken the electronic interactions at the bond critical points presumably due to decrease in the electron density of methoxy groups, while electron-donating methoxy groups enhance the electronic interaction. These results indicate that altering functional groups on benzene rings affects the interatomic interactions. However, these effects are too small to be observed in crystalline state because of other factors like packing effect will also affect the molecular structures.

3. Conclusion

In conclusion, we reported the synthesis, structures, and theoretical calculations of trichlorogermanes with various functional groups on their benzene rings. While all the trichlorogermanes had heptacoordinate geometries, the significant differences of the interatomic distances between oxygen atoms and germanium atoms were not observed in the crystalline state. However, the theoretical calculations suggest the existence of the bonding interactions and the relationship between functional groups and the strength of the interactions. These results indicate that the electronic effect on the donating oxygen atom caused by electron-donating ability of the functional groups at its *para*-position may be too small to detect those differences in the crystalline state.

4. Experimental

4.1. General

General chemicals were used as received. All manipulations were carried out using modified Schlenk technique under an argon atmosphere unless otherwise noted. Solvents were purified by MBRAUN MB-SPS system. Wet column chromatography (WCC) was performed using Kanto Silica Gel 60 N. Gel permeation liquid chromatography (GPLC) was performed using LC-918 or LC-908 with JAIGEL 1H+2H columns (Japan Analytical Industry) using chloroform or toluene as solvents, respectively. NMR spectra were recorded by a JEOL AL-400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz; ^{19}F, 396 MHz) and a Bruker DRX-500 spectrometer (^{1}H, 500 MHz; ^{13}C, 126 MHz). Chemical shifts are reported in δ. ^{1}H NMR spectra are referenced to residual protons in deuterated solvent; ^{13}C NMR spectra are referenced to carbon-13 in the deuterated solvent; ^{19}F NMR spectra are referenced to an external standard of $CFCl_3$. High resolution mass spectra were recorded by a JEOL JMS-700P using PEG400, PEG600, or Ultramark® as internal standards. All melting points were measured with Yanaco MP-S3 and uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo.

4.1.1. 2-Bromo-1,4-dimethoxybenzene 4a.[8] In the open atmosphere, to a solution of 1,4-dimethoxybenzene **3a** (16.8 g, 121 mmol) in AcOH (170 mL) was added a solution of bromine (6.7 mL, 130 mmol) in AcOH (90 mL) by dropwise at room temperature. After stirring for 1 h, H_2O (100 mL) was added to the reaction mixture. After stirring for another 1 h, the organic layer was extracted with $CHCl_3$. The extracts were combined and dried over anhydrous $MgSO_4$, and then the solvent was removed under reduced pressure. The residue was distilled in vacuo (105 °C at 1 mmHg) to afford **4a** (19.3 g, 73%). Compound **4a**: brown liquid. ^{1}H NMR (400 MHz, 27 °C) δ 3.78 (s, 3H), 3.84 (s, 3H), 6.81–6.83 (m, 2H), 7.12 (d, 1H, J=2.4 Hz).

4.1.2. Tris(2,5-dimethoxyphenyl)methane 6a. To Mg turnings (3.25 g, 134 mmol) was added a solution of **4a** (19.3 g, 89.0 mmol) in THF (50 mL) and the reaction mixture was refluxed for 4 h. To the reaction mixture was added a solution of diethyl carbonate (3.6 mL, 30 mmol) in THF (10 mL) and the reaction mixture was refluxed overnight. The reaction mixture was treated with EtOH (30 mL) and solvent was removed in vacuo. To the residue, EtOH (200 mL) and aq HCl (30 mL) were added and heated at 60 °C for 3.5 h. The reaction mixture was concentrated to 100 mL in vacuo, and neutralized with aq NaOH, and extracted with $CHCl_3$. The extracts were combined and dried over anhydrous $MgSO_4$, and then the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel. Elution with $CHCl_3$ gave **6a**, which was further purified by washing with EtOH to afford pure product (4.67 g, 37%). Compound **6a**: white crystal, mp 157.3–157.7 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 3.63 (s, 9H), 3.64 (s, 9H), 6.33 (s, 1H), 6.38 (d, 3H, J=3.1 Hz), 6.67 (dd, 3H, J=3.1, 8.8 Hz), 6.76 (d, 3H, J=8.8 Hz); ^{13}C NMR (126 MHz, $CDCl_3$, 27 °C) δ 37.4 (d), 55.4 (q), 56.6 (q), 110.3 (d), 111.9 (d), 116.9 (d), 133.7 (s), 151.7 (s), 153.2 (s). Anal. Calcd for $C_{25}H_{28}O_6$: C, 70.74; H, 6.65. Found: C, 70.58; H, 6.78.

4.1.3. Trichloro[tris(2,5-dimethoxyphenyl)methyl]germane 1a. To a solution of **6a** (1.50 g, 3.53 mmol) in benzene

(50 mL) was added *n*-BuLi (1.67 M hexane solution, 17.7 mmol) at 50 °C. The reaction mixture was stirred at 50 °C for 8 h. After removal of the solvent under reduced pressure, DME (25 mL) and HMPA (2.50 mL, 14.4 mmol) were added to the residue. To the mixture was added tetrachlorogermane (4.05 mL, 35.3 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and at room temperature overnight. After removal of the solvent, the residue was treated with 30 mL of EtOH and then 20 mL of H_2O. The organic layer was extracted with $CHCl_3$. After removal of the solvent under reduced pressure, the residue was dissolved in ether, and insoluble solids were filtered off. The filtrate was washed with 2% aq NaOH, and the organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was subjected to GPLC to afford **1a** (265 mg, 37%). Compound **1a**: colorless crystal, mp 230.8–231.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 3.60 (s, 9H), 3.65 (s, 9H), 6.03 (d, 3H, J=2.9 Hz), 6.82 (d, 3H, J=8.8 Hz), 6.87 (dd, 3H, J=2.9, 8.8 Hz); ^{13}C NMR (126 MHz, $CDCl_3$, 27 °C) δ 54.2 (q), 55.5 (q), 67.9 (s), 110.2 (d), 112.9 (d), 117.3 (d), 127.8 (s), 150.8 (s), 153.5 (s). Anal. Calcd for $C_{25}H_{27}Cl_3GeO_6$: C, 49.84; H, 4.52. Found: C, 49.69; H, 4.55.

4.1.4. 2-Bromo-4-fluoroanisole 4b.[9] In the open atmosphere, to a solution of 4-fluoroanisole **3b** (16.8 g, 121 mmol) in CH_2Cl_2 (100 mL) was added a solution of bromine (12 mL, 230 mmol) in AcOH (100 mL) dropwise at room temperature. After the solution was stirred overnight, aq Na_2SO_3 (100 mL) was added. The organic layer was extracted with $CHCl_3$. The extracts were combined and dried over anhydrous $MgSO_4$, and then the solvent was removed under reduced pressure. The residue was distilled in vacuo (70 °C at 1 mmHg) to afford **4b** (36.0 g, 88%). Compound **4b**: colorless liquid. ^{1}H NMR (400 MHz, 27 °C) δ 3.86 (s, 3H), 6.83 (dd, 1H, $^3J_{HH}$=9.2 Hz, $^4J_{HF}$=4.8 Hz), 6.99 (ddd, 1H, $^3J_{HH}$=9.2 Hz, $^4J_{HH}$=2.8 Hz, $^3J_{HF}$=8.0 Hz), 7.29 (dd, $^4J_{HH}$=2.8 Hz, $^3J_{HF}$=8.0 Hz); ^{19}F NMR (376 MHz, 27 °C) δ 8.72.

4.1.5. Tris(3-fluoro-6-methoxyphenyl)methanol 5b. To Mg turnings (3.25 g, 134 mmol) was added a solution of **4b** (18.0 g, 87.8 mmol) in THF (50 mL) and the reaction mixture was refluxed for 4 h. To the reaction mixture was added a solution of diethyl carbonate (2.6 mL, 22 mmol) in THF (10 mL) and the reaction mixture was refluxed overnight. The reaction mixture was treated with EtOH (30 mL) and then H_2O (20 mL). The organic layer was extracted with $CHCl_3$. The extracts were combined and dried over anhydrous $MgSO_4$, and then the solvent was removed under reduced pressure. The residue was purified by reprecipitation from hexane/$CHCl_3$ to afford **5b** (2.23 g, 24%). Compound **5b**: white crystal, mp 160.5–161.0 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 3.48 (s, 9H), 5.47 (s, 1H), 6.81 (dd, 3H, $^3J_{HH}$=8.8 Hz, $^4J_{HF}$=4.6 Hz), 6.91 (dd, 3H, $^4J_{HH}$=3.0 Hz, $^3J_{HF}$=10.3 Hz), 6.95 (ddd, 3H, $^3J_{HH}$=8.8 Hz, $^4J_{HH}$=3.0 Hz, $^3J_{HF}$=10.3 Hz); ^{13}C NMR (126 MHz, $CDCl_3$, 27 °C) δ 56.1 (q), 79.3 (s), 113.2 (dd, $^3J_{CF}$=8 Hz), 114.5 (dd, $^2J_{CF}$=23 Hz), 116.6 (dd, $^2J_{CF}$=25 Hz), 134.2 (d, $^3J_{CF}$=6 Hz), 153.2 (s), 156.8 (d, $^1J_{CF}$=238 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 27 °C) δ 7.01–7.04 (m). Anal. Calcd for $C_{22}H_{19}F_3O_4$: C, 65.34; H, 4.74. Found: C, 65.13; H, 4.88.

4.1.6. Tris(3-fluoro-6-methoxyphenyl)methane 6b. To the solution of **5b** (1.26 g, 3.12 mmol) in AcOH (15 mL) with CF_3COOH (0.27 mL, 3.52 mmol) was added Et_3SiH (6.5 mL, 40.7 mmol) and the solution was stirred at 90 °C for 14 h, and then 100 °C overnight. H_2O (30 mL) was added to the reaction mixture and white precipitate was collected by filtration. The precipitate was subjected to column chromatography on silica gel. Elution with hexane/$CHCl_3$=1:4 to afford **6b** (772 mg, 64%). Compound **6b**: white crystal, mp 183.1–183.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 3.66 (s, 9H), 6.26 (s, 1H), 6.44 (dd, 3H, $^4J_{HH}$=3.1 Hz, $^3J_{HF}$=9.5 Hz), 6.78 (dd, 3H, $^3J_{HH}$=8.9 Hz, $^4J_{HF}$=4.6 Hz), 6.88 (ddd, 3H, $^3J_{HH}$=8.9 Hz, $^4J_{HH}$=3.1 Hz, $^3J_{HF}$=8.9 Hz); ^{13}C NMR (126 MHz, $CDCl_3$, 27 °C) δ 37.6 (d), 56.3 (q), 111.7 (dd, $^3J_{CF}$=8 Hz), 113.3 (dd, $^2J_{CF}$=23 Hz), 116.3 (dd, $^2J_{CF}$=24 Hz), 133.1 (d, $^3J_{CF}$=7 Hz), 153.3 (s), 156.9 (d, $^1J_{CF}$=238 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 27 °C) δ 7.11–7.16 (m). Anal. Calcd for $C_{22}H_{19}F_3O_3$: C, 68.04; H, 4.93. Found: C, 67.80; H, 5.12.

4.1.7. Trichloro[tris(3-fluoro-6-methoxyphenyl)methyl]-germane 1b. To a solution of **6b** (1.00 g, 2.57 mmol) in benzene (30 mL) was added *n*-BuLi (1.67 M hexane solution, 13 mmol) at 50 °C. The reaction mixture was stirred at 50 °C for 7 h. After removal of the solvent under reduced pressure, DME (15 mL) and HMPA (1.80 mL, 10.0 mmol) were added to the residue. To the reaction mixture was added tetrachlorogermane (3.0 mL, 26 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and at room temperature overnight. After removal of the solvent, the residue was treated with 20 mL of EtOH and then 10 mL of H_2O. The organic layer was extracted with $CHCl_3$. After removal of the solvent under reduced pressure, the residue was dissolved in ether, and insoluble solids were filtered off. The filtrate was washed with 2% aq NaOH, and the organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was subjected to GPLC to afford **1b** (293 mg, 60%). Compound **1b**: colorless crystal, mp 241.4–241.9 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 3.68 (s, 9H), 6.16 (dd, 3H, $^4J_{HH}$=3.0 Hz, $^3J_{HF}$=9.9 Hz), 6.88 (dd, 3H, $^3J_{HH}$=8.9 Hz, $^4J_{HF}$=4.4 Hz), 7.08 (ddd, 3H, $^3J_{HH}$=8.9 Hz, $^4J_{HH}$=3.0 Hz, $^3J_{HF}$=9.9 Hz); ^{13}C NMR (126 MHz, $CDCl_3$, 27 °C) δ 54.4 (q), 66.7 (s), 111.0 (dd, $^3J_{CF}$=8 Hz), 115.9 (dd, $^2J_{CF}$=24 Hz), 116.9 (dd, $^2J_{CF}$=24 Hz), 127.5 (d, $^3J_{CF}$=8 Hz), 157.2 (d, $^1J_{CF}$=239 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 27 °C) δ 8.01–8.08 (m). Anal. Calcd for $C_{22}H_{18}Cl_3F_3GeO_3$: C, 46.65; H, 3.20. Found: C, 46.47; H, 3.39.

4.1.8. 4-Trifluoromethylanisole 3c.[10] In the open atmosphere, to a solution of 4-fluorophenol **2c** (5 g, 30 mmol) and potassium carbonate (4.30 g, 30.1 mmol) in acetone (50 mL) was added iodomethane (4.29 mL, 46.3 mmol) and the mixture was refluxed for 1 day. After the solvent was removed under reduced pressure, H_2O (50 mL) was added and the mixture was extracted from AcOEt. The extracts were combined and dried over anhydrous $MgSO_4$, and then the solvent was removed under reduced pressure to afford **3c** (4.79 g, 88%). The product was used without further purification. Compound **3c**: white solid. ^{1}H NMR (400 MHz, 27 °C) δ 3.85 (s, 3H), 4.94–4.96 (m, 2H), 7.53–7.50 (m, 2H).

4.1.9. 2-Bromo-4-trifluoromethylanisole 4c.[10] In the open atmosphere, to a solution of 4-trifluoromethylanisole **3c** (4.79 g, 27.2 mmol) and sodium acetate (2.50 g, 30.5 mmol) in AcOH (100 mL) was added a solution of bromine (1.6 mL, 31 mmol) in AcOH (10 mL) by dropwise at room temperature. After the reaction mixture was stirred for 1 day, bromine (0.5 mL, 9.8 mmol) was added. After stirring for 1 day, the mixture was treated with aq Na_2SO_3 (100 mL) and extracted with $CHCl_3$. The extracts were combined and dried over anhydrous $MgSO_4$, and then the solvent was removed under reduced pressure. The residue was distilled in vacuo (41 °C at 1 mmHg) to afford **4c** (2.77 g, 40%). Compound **4c**: colorless liquid. ^{1}H NMR (400 MHz, 27 °C) δ 3.95 (s, 3H), 7.67 (d, 1H, J=8.8 Hz), 7.54 (dd, 1H, J=1.5, 8.8 Hz), 7.80 (d, 1H, J=1.5 Hz).

4.1.10. Tris(2-methoxy-5-trifluoromethylphenyl)methanol 5c. To Mg turnings (1.33 g, 54.6 mmol) was added a solution of **4c** (9.29 g, 36.4 mmol) in THF (20 mL) and the reaction mixture was refluxed for 3 h. To the reaction mixture was added a solution of diethyl carbonate (1.10 mL, 9.10 mmol) in THF (10 mL) and the reaction mixture was refluxed overnight. The reaction mixture was treated with EtOH (20 mL) and then H_2O (10 mL). The organic layer was extracted with $CHCl_3$. The extracts were combined and dried over anhydrous $MgSO_4$, and then the solvent was removed under reduced pressure. The residue was subjected to GPLC to afford **5c** (239 mg, 1.2%) and a mixture including **5c** (2.45 g). The mixture was used in the next step of reactions without further purification. Compound **5c**: white crystal, mp 188.4–188.7 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 3.56 (s, 9H), 5.30 (s, 1H), 6.94 (d, 3H, J=8.6 Hz), 7.44 (d, 3H, J=1.9 Hz), 7.56 (dd, 3H, J=1.9, 8.6 Hz); ^{13}C NMR (126 MHz, $CDCl_3$, 27 °C) δ 55.4 (q), 79.6 (s), 111.7 (d), 122.2 (q, $^2J_{CF}$=33 Hz), 124.5 (q, $^1J_{CF}$=272 Hz), 126.3 (dq, $^3J_{CF}$=3.8 Hz), 127.0 (dq, $^3J_{CF}$=3.7 Hz), 131.6 (s), 159.2 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 27 °C) δ −63.5. HRMS-FAB (m/z): $[M]^+$ calcd for $C_{25}H_{19}F_9O_4$: 554.1140, found: 554.1134. Anal. Calcd for $C_{25}H_{19}F_9O_4$: C, 54.16; H, 3.45. Found: C, 54.19; H, 3.59.

4.1.11. Tris(2-methoxy-5-trifluoromethylphenyl)methane 6c. To a solution of the mixture including **5c** (2.45 g) and CF_3COOH (0.40 mL, 5.2 mmol) in AcOH (15 mL) was added Et_3SiH (10.0 mL, 62.6 mmol) and the reaction mixture was stirred at 100 °C for 1 day. The mixture was monitored by ^{1}H NMR, and CF_3COOH (0.10 mL, 1.3 mmol) was added twice after 24 h and 48 h. After the completion of the reaction, the reaction mixture was treated with aq NaOH and extracted with $CHCl_3$. The extracts were combined and dried over anhydrous $MgSO_4$, and then the solvent was removed under reduced pressure. The residue was purified by recrystallization from EtOH to afford **6c** (740 mg, 14% from **4c**). Compound **6c**: white crystal, mp 140.5–140.6 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 3.71 (s, 9H), 6.24 (s, 1H), 6.92 (d, 3H, J=8.7 Hz), 6.93 (d, 3H, J=1.9 Hz), 7.51 (dd, 3H, J=1.9, 8.7 Hz); ^{13}C NMR (126 MHz, $CDCl_3$, 27 °C) δ 38.6 (d), 55.7 (q), 110.4 (d), 122.3 (q, $^2J_{CF}$=33 Hz), 124.4 (q, $^1J_{CF}$=272 Hz), 125.5 (dq, $^3J_{CF}$=3.5 Hz), 126.2 (dq, $^3J_{CF}$=3.5 Hz), 130.9 (s), 159.5 (s); ^{19}F NMR (376 MHz, $CDCl_3$, 27 °C) δ −63.4. Anal. Calcd for $C_{25}H_{19}F_9O_3$: C, 55.77; H, 3.56. Found: C, 55.81; H, 3.80; HRMS-FAB (m/z): $[M]^+$ calcd for $C_{25}H_{19}F_9O_3$: 538.1190, found: 538.1177.

4.1.12. Trichloro[tris(2-methoxy-5-trifluoromethylphenyl)methyl]germane 1c. To a solution of **6c** (600 mg, 1.11 mmol) in benzene (15 mL) was added *n*-BuLi (1.67 M hexane solution, 5.6 mmol) at 50 °C. The mixture was stirred at 50 °C for 6 h. After removal of the solvent under reduced pressure, DME (15 mL) and HMPA (0.78 mL, 4.5 mmol) were added to the residue. To the mixture was added tetrachlorogermane (1.2 mL, 11 mmol) at 0 °C. The mixture was stirred at 0 °C for 2 h and at room temperature overnight. After removal of the solvent, the residue was treated with 20 mL of EtOH and then 10 mL of H_2O. The mixture was extracted with $CHCl_3$. The residue was dissolved in ether and washed with 2% aq NaOH. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was subjected to GPLC to afford **1c** (166 mg, 21%). Compound **1c**: colorless crystal, mp 280.1–281.4 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 3.72 (s, 9H), 6.68 (d, J=1.9 Hz), 7.05 (d, J=8.6 Hz), 7.71 (dd, J=1.9, 8.6 Hz); ^{13}C NMR (126 MHz, $CDCl_3$, 27 °C) δ 54.5 (q), 66.9 (s), 110.6 (d), 123.5 (q, $^2J_{CF}$=33 Hz), 124.0 (q, $^1J_{CF}$=272 Hz), 125.6 (s), 127.1 (dq $^3J_{CF}$=3.5 Hz), 127.7 (dq $^3J_{CF}$=3.6 Hz), 158.8 (d); ^{19}F NMR (376 MHz, $CDCl_3$, 27 °C) δ −63.6. Anal. Calcd for $C_{25}H_{18}Cl_3F_9GeO_3$: C, 41.91; H, 2.53. Found: C, 41.92; H, 2.70; HRMS-FAB (m/z): $[M–F]^+$ calcd for $C_{25}H_{18}{}^{35}Cl_3F_8{}^{74}GeO_3$: 696.9406, found: 696.9405; calcd for $C_{25}H_{18}{}^{35}Cl_2{}^{37}ClF_8{}^{74}GeO_3$: 698.9376, found, 698.9377; calcd for $C_{25}H_{18}{}^{35}Cl_3F_8{}^{72}GeO_3$: 694.9415, found: 694.9521.

4.2. X-ray structural analysis

Single crystals of **1a–c** were grown from appropriate solution (acetonitrile/hexane solution for **1a**, benzene/$CHCl_3$ solution for **1b** and $CHCl_3$ solution for **1c**). The intensity data were collected on a Rigaku/MSC Mercury CCD with Mo Kα radiation (λ=0.71069 Å). The structures were solved by the direct method and refined by full-matrix least squares on F^2 using SHELXS-97.[11] Crystallographic data are listed in Table 3. The structures were refined anisotropically except

Table 3. Crystallographic parameters of **1a–c**

	1a	1b	1c
R	OMe	F	CF_3
Formula	$C_{25}H_{27}Cl_3GeO_6$	$C_{22}H_{18}Cl_3GeO_3F_3$	$C_{25}H_{18}Cl_3F_9GeO_3$
Temperature/K	120(2)	120(2)	120(2)
Crystal system	Monoclinic	Trigonal	Monoclinic
Space group	$P2_1/c$	$R\bar{3}$	$P2_1/c$
a/Å	17.083(6)	14.18(1)	16.911(5)
b/Å	10.045(3)	14.18(1)	9.701(5)
c/Å	17.980(6)	21.65(2)	18.464(5)
β/°	110.381(2)	—	113.715(5)
V/Å^3	2892(2)	3769(5)	2773(2)
Z	4	6	4
D_{calcd}/g cm^{-3}	1.478	1.497	1.716
Reflections collected	15,370	7769	16,902
Unique reflections	4378	2751	4833
Goodness of fit	1.104	1.049	1.065
$R1$ ($I>2\sigma(I)$)	0.0259	0.0429	0.0356
w$R2$ (all data)	0.0628	0.1203	0.0900

hydrogen atoms. Hydrogen atoms were idealized by using the riding models. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 649686, CCDC 649687, CCDC 649688. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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