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# Synthesis of Ferrocenyl-Substituted Organochalcogenyldichlorogermanes

**Takahiro Sasamori [1,*], Yuko Suzuki [2], Koh Sugamata [3], Tomohiro Sugahara [2] and Norihiro Tokitoh [2]**

[1] Graduate School of Natural Sciences, Nagoya City University, Yamanohata 1, Mizuho-cho, Mizuho-ku, Nagoya, Aichi 467-8501, Japan
[2] Institute for Chemical Research, Gokasho, Uji, Kyoto 611-0011, Japan; y_suzuki@boc.kuicr.kyoto-u.ac.jp (Y.S.); sugahara@boc.kuicr.kyoto-u.ac.jp (T.S.); tokitoh@boc.kuicr.kyoto-u.ac.jp (N.T.)
[3] Department of Chemistry, College of Science, Rikkyo University, 3-34-1 Nishi-Ikebukuro, Toshima-ku, Tokyo 171-8501, Japan; sugamata@rikkyo.ac.jp
* Correspondence: sasamori@nsc.nagoya-cu.ac.jp; Tel.: +81-52-872-5820

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**Abstract:** Reaction of the isolable ferrocenyldichlorogermyl anion, $Fc^{*}GeCl_2^{-}$ ($Fc^{*}$ = 2,5-bis(3,5-di-*t*-butylphenyl)-1-ferrocenyl), with the isolable chalcogenenyl halides resulted in the formation of the corresponding organochalcogenyldichlorogermanes that were structurally characterized. Thus, it was demonstrated the use of sterically demanding ferrocenyl groups allowed isolating stable crystalline organochalcogenyldichlorogermanes.

**Keywords:** ferrocene; steric protection; germanium; selenide; telluride; selenenylchloride; tellurenylchloride

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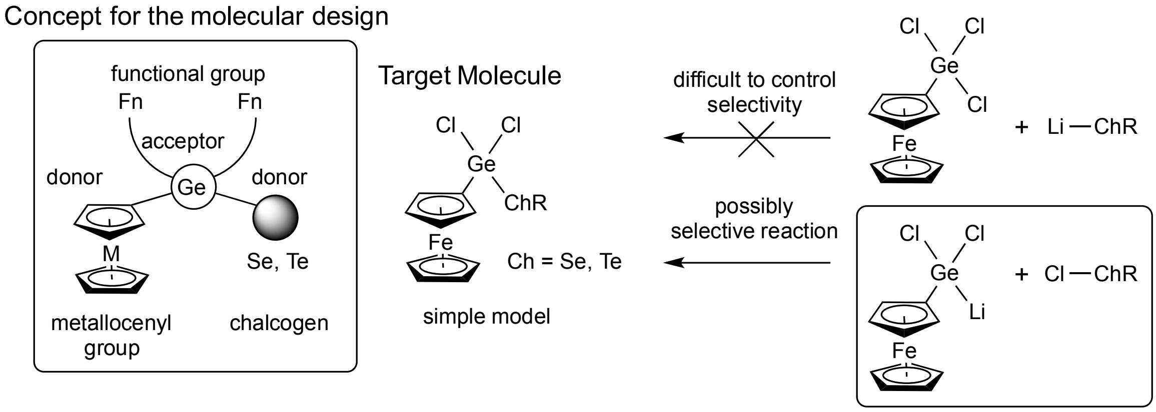
## 1. Introduction

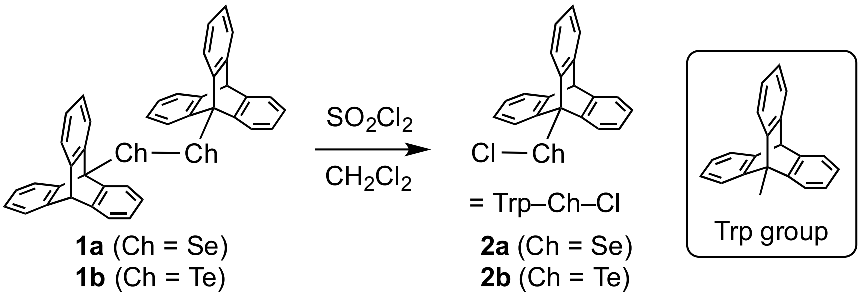
Germanium chalcogenides are interesting chemical species for optoelectronic modules due to the appropriate combination between the electron-accepting element Ge and an electron-donating element, such as Se or Te, because the size and energy levels of frontier orbitals should be close to each other (4p and 4p/5p) [1,2]. Therefore, organogermanium species that bear a chalcogen (Ch) moiety should be able to serve as building blocks for organic–inorganic hybrid materials that contain a Ge–Ch bond. Given that the Ge–Ch bond is redox-active, metallocenyl-substituted germanium chalcogenides could be promising prospective building blocks for such Ge–Ch hybrid materials. Although the appropriate molecular design for such building blocks should be Mc–GeX$_2$–ChR (Mc = metallocenyl; R = organic substituent; X = leaving group), it is generally difficult to isolate such species on account of the lability due to facile hydrolysis of the Ge–Ch and Ge–X bonds. In addition, a conceivable synthetic strategy such as the nucleophilic substitution of the RCh moiety toward Mc-GeCl$_3$, would most likely not be selective, i.e., two- and three-fold substitution could easily occur (Scheme 1). In this paper, we report a solution to this problem by using a method that is based on kinetic control using a bulky ferrocenyl group. We have already prepared sterically demanding ferrocenyl groups [3–6] that are able to stabilize anionic species that bear a halogen group due to multi-hydrogen bonding [7]. The use of the sterically demanding ferrocenyl group Fc* (2,5-bis(3,5-di-*t*-butylphenyl)-1-ferrocenyl) enabled us to isolate the dichlorogermyl anion $[Fc^{*}GeCl_2]^{-}$, which was identified as a chlorogermylenoid [7]. Subsequently, we speculated that the germylenoid could not only work as an electrophile but also as a nucleophile towards chalcogens, even in the presence of two halogen atoms. Herein, we demonstrate the reactions of a stable germylenoid with selenenyl and tellurenyl chlorides, which affords stable dichlorochalcogenagermanes that bear a bulky ferrocenyl group. These dichlorochalcogenagermanes represent promising prospective building blocks for organogermanium chalcogenides.



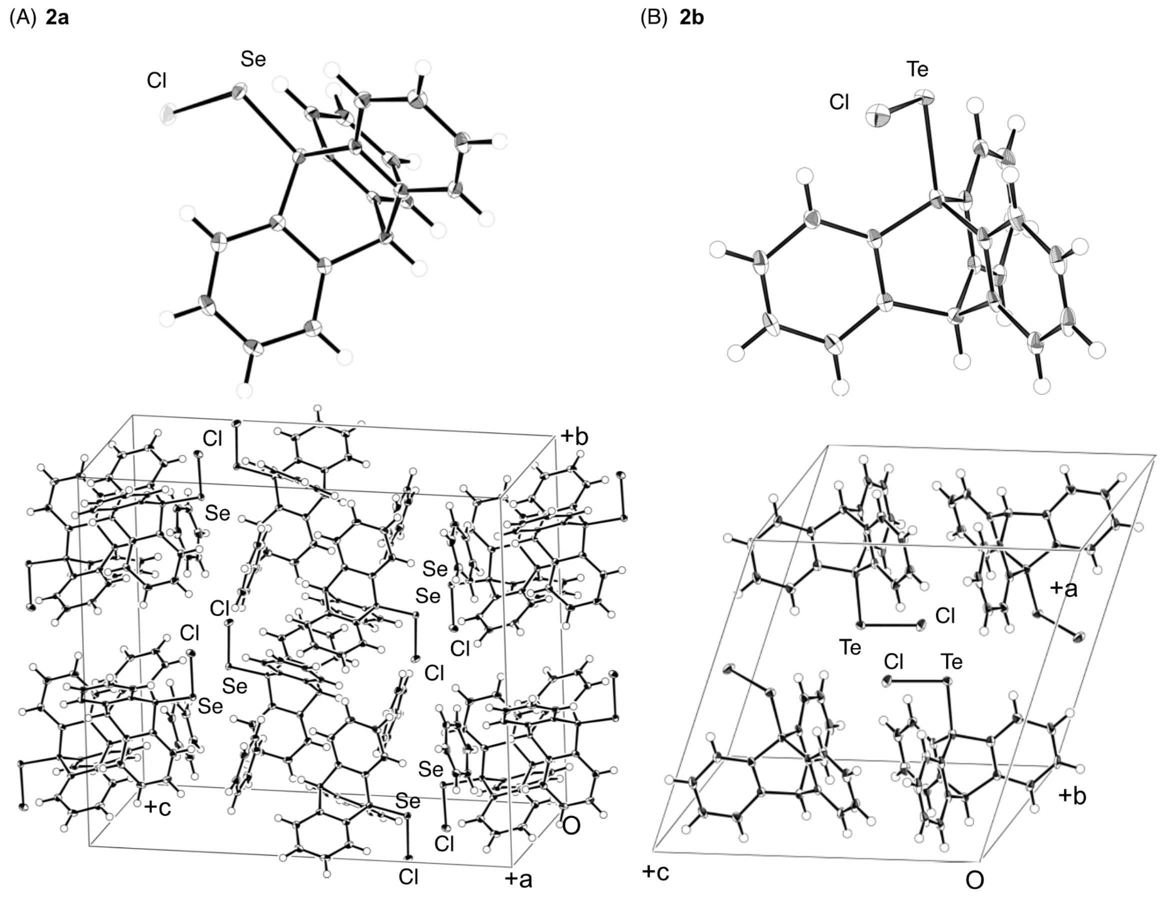
**Scheme 1.** Schematic illustration of the synthetic strategy applied in this study for the generation of ferrocenyl-substituted chalcogenyldichlorogermanes.

## 2. Results and Discussions

To isolate stable chalcogenenyl halides, it is necessary to introduce sterically demanding substituents on the Ch atom [8–10]. We have decided to use the 9-triptycyl (Trp) group as a steric protection group, as the simple synthesis of the corresponding dichalcogenides (**1a**,**b**) has already been reported [11–13]. The treatment of an ether solution of TrpSeSeTrp (**1a**) [11] with $SO_2Cl_2$ at room temperature afforded the corresponding selenenyl chloride, TrpSeCl (**2a**), as a stable crystalline compound (Scheme 2). In a similar fashion, TrpTeCl (**2b**) was obtained from the reaction of TrpTeTeTrp (**1b**) [12,13] with $SO_2Cl_2$. The molecular structures of TrpSeCl (**2a**) and TrpTeCl (**2b**) were unambiguously determined by X-ray diffraction (XRD) analyses, which delivered C–Ch–Cl angles of 99.93(6)° (Ch = Se) and 96.38(9)° (Ch = Te), as well as Ch–Cl bond lengths of 2.1860(7) Å (Ch = Se) and 2.348(1) Å (Ch = Te). These structural parameters are similar to those of previously reported stable selenenyl- and tellurenyl-chlorides [8–10], indicating negligible electronic perturbations from the Trp group toward the Ch–Cl moieties. The packing structures of **2a** and **2b** suggest that these compounds are monomeric in the crystalline state (Figure 1). As only **2a** contains one molecule of benzene per unit cell, the packing structures and space groups of **2a** and **2b** are different. While **2b** exhibits head-to-tail-type interactions, **2a** shows head-to-head-type interactions, albeit that the intramolecular interactions should be negligible due to the long intramolecular Ch···Ch, Ch···Cl, and Cl···Cl distances. In addition, the $^{77}$Se (907 ppm) and $^{125}$Te NMR chemical shifts (1756 ppm) are consistent with those of previously reported monomeric chalcogenenylhalides [8–10].



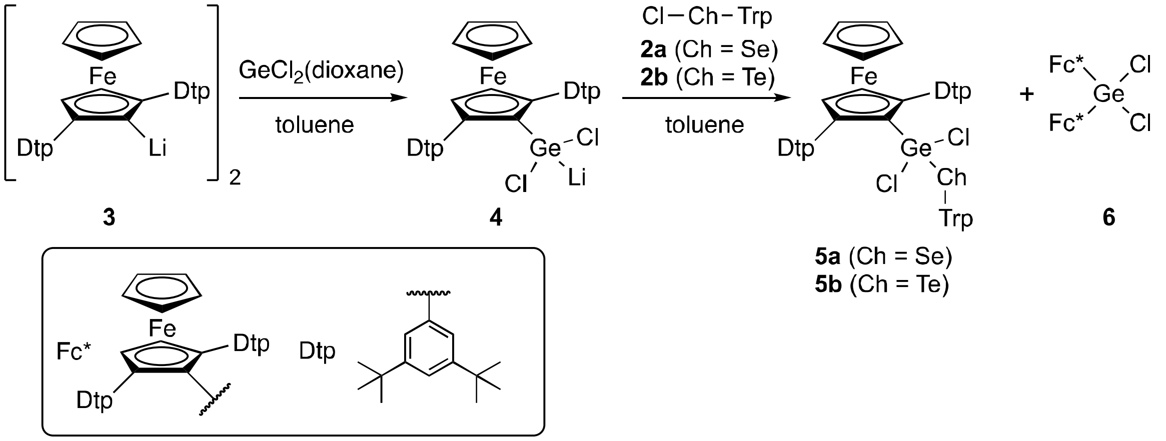
**Scheme 2.** Synthesis of stable chalcogenylchlorides **2**.


(A) **2a**

(B) **2b**

**Figure 1.** Molecular structures (ORTEP drawing at 50% probability) and crystal packing of (**A**) [**2a·benzene**] and (**B**) **2b** with atomic displacement parameters set at 50% probability. Selected bond lengths (Å) and angles (°): (**A**) Se–Cl, 2.1860(7); Se–C, 1.965(2); C–Se–Cl, 99.93(6), (**B**) Te–Cl, 2.348(1); Te–C, 2.166(3); C–Te–Cl, 96.38(9). Intermolecular atom-atom distances (Å): (**A**) Se···Se, 5.1687(3); Se···Cl, 5.5440(6); Cl···Cl, 5.6875(6), (**B**) Te···Te, 5.3089(7); Te···Cl, 4.395(1); Cl···Cl, 4.634(1).

The sterically hindered germylenoid Fc*$GeCl_2Li$ (**4**) was prepared according to literature procedures [5] from the reaction of the isolable lithioferrocene dimer **3** with $GeCl_2$·(dioxane). Subsequently, **4** was treated with the isolated chalcogenenylchlorides **2a** or **2b** in toluene at room temperature. The NMR spectra of the crude reaction mixtures suggested the predominant formation of the expected products (**5a**,**b**) together with small amounts of the by-product $Fc^*{}_2GeCl_2$ (**6**) [14] in both cases (**5**:**6** = 8:1 for Ch = Se; **5**:**6** = 21:1 for Ch = Te). The purification processes, including GPC separation and recrystallization from hexane, afforded the stable chalcogenyldichlorogermanes **5a** and **5b** in 41% and 58% isolated yields, respectively, together with the corresponding bis(ferrocenyl)dichlorogermane in both cases (31% for Ch = Se; 17% for Ch = Te) (Scheme 3). Although the formation mechanism for **6** cannot be explained unequivocally at present, the oxidation of germylenoid **4** by chalcogenenylchloride **2** could initiate the unexpected formation of **6**.



**Scheme 3.** Synthesis of chalcogenyldichlorogermanes **5a**,**b**.

The molecular structures of chalcogenyldichlorogermanes **5a** and **5b** were determined by single-crystal XRD analyses (Figure 2). Unexpectedly, their geometries are different, i.e., the Ch moiety in **5a** (Ch = Se) is spatially removed from the Fe atom or located "outside of the ferrocenyl unit" (Form A), while that of **5b** (Ch = Te) is close to the Fe atom or oriented "toward the ferrocenyl unit" (Form B). In both cases, the two energy minima, i.e., Form A and B, were identified by theoretical calculations at the M062x/6-311G(3d) (Ge, Cl, Fe)/ 6-31G(d) (C, H)/ SDD (Se, Te) level of theory [15]. The optimized structures of **5a-Form A** and **5b-Form B** were in good agreement with those experimentally obtained from the XRD analyses (Table 1). Although the thermodynamic energies of Form A and Form B are similar in both cases, **5a-Form A** and **5b-Form B** are more stable than their imaginary forms, i.e., **5a-Form B** (+0.33 kcal/mol) and **5b-Form A** (+1.38 kcal/mol), which supports the experimental results. At present, however, we do not have a reasonable explanation regarding the energy differences between Form A and Form B.

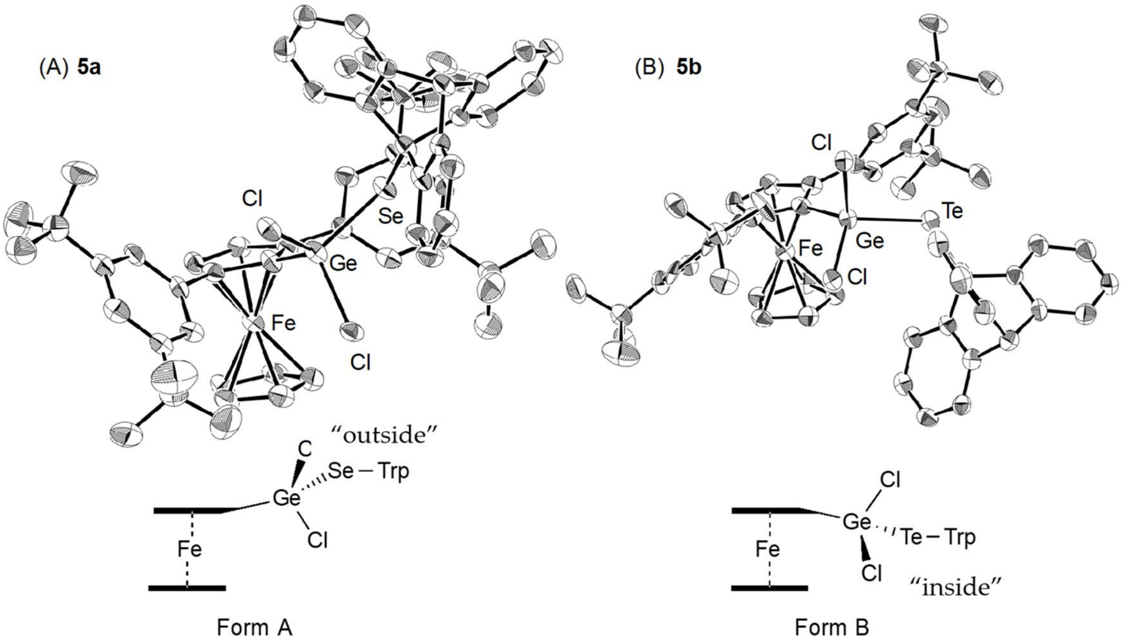
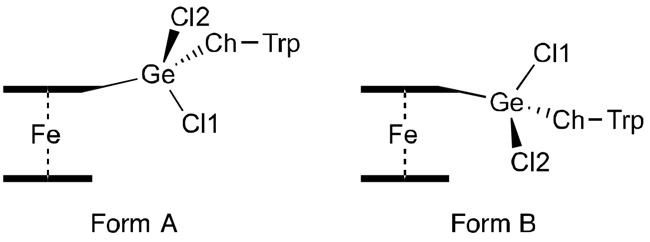


**Figure 2.** Molecular structures of (**A**) **5a** and (**B**) **5b** with atomic displacement parameters set at 50% probability. All hydrogen atoms and solvent molecules were omitted for clarity and only selected atoms are labeled.

**Table 1.** Selected structural parameters for **5a-Form A** and **5b-Form B** (observed: XRD analysis) together with the corresponding theoretical (calculated) values for **5a-Form A**, **5a-Form B**, **5b-Form A**, and **5b-Form B** that were optimized at the M062x/6-311G(3d) (Ge, Cl, Fe)/ 6-31G(d) (C, H)/ SDD (Se, Te) level of theory.



| Distance/Å | 5a (Ch = Se) Form A Observed | 5a (Ch = Se) Form A Calculated | 5a (Ch = Se) Form B Calculated | 5b (Ch = Te) Form A Calculated | 5b (Ch = Te) Form B Calculated | 5b (Ch = Te) Form B Observed |
|---|---|---|---|---|---|---|
| C(Cp)–Ge | 1.926(6) | 1.9289 | 1.9290 | 1.9308 | 1.9309 | 1.927(8) |
| Ge–Ch | 2.3474(9) | 2.3870 | 2.3904 | 2.5878 | 2.5869 | 2.5489(8) |
| Ge–Cl1 | 2.209(2) | 2.1873 | 2.2018 | 2.1979 | 2.2081 | 2.212(2) |
| Ge–Cl2 | 2.164(2) | 2.1577 | 2.1561 | 2.1609 | 2.1624 | 2.164(2) |
| Fe···Ge | 3.696(1) | 3.6587 | 3.5460 | 3.7326 | 3.5252 | 3.505(2) |
| Fe···Cl1 | 4.194(2) | 4.0287 | 5.3396 | 4.2108 | 5.3303 | 5.305(3) |
| Fe···Cl2 | 5.176(2) | 5.1614 | 4.3337 | 5.1220 | 4.2763 | 4.317(2) |
| Fe···Ch | 5.229(1) | 5.3217 | 4.6049 | 5.6007 | 4.7724 | 4.761(1) |
| Angles/° | | | | | | |
| Cl1–Ge–Cl2 | 104.06(7) | 105.85 | 105.68 | 102.93 | 105.82 | 104.51(8) |
| Cl1–Ge–Ch | 110.59(5) | 103.47 | 108.33 | 108.95 | 108.17 | 106.62(6) |
| Cl2–Ge–Ch | 110.92(5) | 110.60 | 110.15 | 110.48 | 109.03 | 110.32(6) |

The experimentally observed and theoretically optimized structural parameters are summarized in Table 1. In both cases, i.e., Form A and Form B, one of the two chlorine atoms (Cl1) is vertically oriented toward the Cp plane of the ferrocenyl unit. In both cases, the Ge–Cl1 bonds are slightly longer than the Ge–Cl2 bonds, indicating an orbital interaction between the σ*(Ge–Cl1) orbital and lone pairs on the Cl2 and Ch (Se or Te) atoms. Indeed, the NBO (Natural Bond Orbitals) calculations [16] suggested effective π(Cp) → σ*(Ge–Cl1), LP(Cl2) → σ*(Ge–Cl1), and LP(Ch) → σ*(Ge–Cl1) interactions, all of which would result in an elongation of the Ge–Cl1 bond. These results indicate that the Ge–Ch and Ge–Cl2 bonds would be maintained, even after the functionalization of the Ge–Cl1 moiety, given that the Ge–Ch and Ge–Cl2 bonds should strengthen rather than weaken the Ge–Cl1 bond. Thus, **5a** and **5b** should be suitable as potential building blocks for ferrocenyl-substituted germanium chalcogenides.

## 3. Materials and Methods

### 3.1. General Information

All manipulations were carried out under an argon atmosphere using either Schlenk-line or glovebox techniques. Solvents were purified using the Ultimate Solvent System (Glass Contour Company, CA, USA) [17]. $^{1}$H, $^{13}$C, $^{77}$Se, and $^{125}$Te NMR spectra were measured on JEOL 300 or 400 MHz spectrometers (JEOL, Tokyo, Japan). Signals arising from residual $C_6D_5H$ (7.15 ppm) in $C_6D_6$ and $CHCl_3$ (7.25 ppm) in $CDCl_3$ were used as an internal standard for the $^{1}$H NMR spectra, while signals of $C_6D_6$ (128.0 ppm) and $CDCl_3$ (77.0 ppm) where used to reference the $^{13}$C NMR spectra. PhSeSePh (460 ppm) and PhTeTePh (450 ppm) were used as external standards for the $^{77}$Se and $^{125}$Te NMR spectra. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF focus-Kci mass spectrometer (DART) (Bruker Japan K.K. Daltonics Division, Kanagawa, Japan) or a JEOL JMS-700 spectrometer (FAB) (JEOL, Tokyo, Japan). All melting points were determined on a Büchi Melting Point Apparatus M-565 (Büchi Japan, Tokyo, Japan) and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory, Institute for Chemical Research, Kyoto University. Dichalcogenides **1a** and **1b** [11–13] as well as chlorogermylenoid **4** [7] were prepared according to literature procedures.

### *3.2. Experimental Details*

#### 3.2.1. Synthesis of Selenenylchloride **2a**

A suspension of TrpSeSeTrp (**1a**, 665 mg, 1.00 mmol) in $CH_2Cl_2$ (10 mL) was treated with $SO_2Cl_2$ (135 mg, 1.00 mmol) at room temperature for 1 h. After the removal of all volatiles, the residue was recrystallized from $CH_2Cl_2$ at room temperature to give **2a** as orange crystals in 51% yield (376 mg, 1.02 mmol). Data for **2a**: orange crystals, m.p. = 212.2 °C (dec.); $^1$H NMR (400 MHz, $CDCl_3$, 298 K): $\delta$ (ppm) 5.41 (s, 1H), 7.00–7.10 (m, 6H), 7.40–7.42 (m, 3H), 7.50–7.52 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): $\delta$ (ppm) 54.1 (d), 64.3 (s), 123.5 (d), 123.7 (d), 125.3 (d), 126.1 (d), 143.7 (s), 145.4 (d); $^{77}$Se NMR (76 MHz, $CDCl_3$, 298 K): $\delta$ (ppm) 907; Anal. Calcd. for $C_{20}H_{13}ClSe$: C, 65.32; H, 3.56. Found: C, 65.01; H, 3.73. MS (DART-TOF, positive mode): $m/z$ Calcd. for $C_{20}H_{13}{}^{35}Cl^{80}Se$ 367.9871 ($[M]^+$), found 367.9886 ($[M]^+$).

#### 3.2.2. Synthesis of Tellurenylchloride **2b**

A suspension of TrpTeTeTrp **1b** (762 mg, 1.00 mmol) in $CH_2Cl_2$ (10 mL) was treated with $SO_2Cl_2$ (135 mg, 1.00 mmol) at room temperature for 1 h. After the removal of all volatiles, the residue was recrystallized from $CH_2Cl_2$/benzene at room temperature to give **2b** as blue crystals in 57% yield (416 mg, 1.13 mmol). Data for **2b**: blue crystals, m.p. = 228.1 °C (dec.); $^1$H NMR (400 MHz, $CDCl_3$, 298 K): $\delta$ (ppm) 5.44 (s, 1H), 7.00–7.10 (m, 6H), 7.32–7.35 (m, 3H), 7.40–7.43 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): $\delta$ (ppm) 54.5 (d), 57.3 (s), 123.8 (d), 125.6 (d), 126.0 (d), 126.3 (d), 145.4 (s), 145.8 (d); $^{125}$Te NMR (125 MHz, $CDCl_3$, 298 K): $\delta$ (ppm) 1756; Anal. Calcd. for $C_{20}H_{13}ClTe$: C, 57.69; H, 3.15. Found: C, 57.46; H, 3.14. MS (DART-TOF, positive mode): $m/z$ Calcd. for $C_{20}H_{13}{}^{35}Cl^{130}Te$ 417.9768 ($[M]^+$), found 417.9733 ($[M]^+$).

#### 3.2.3. Reaction of Chlorogermylenoid **4** with Selenenylchloride **2a**

A toluene solution (3 mL) of chlorogermylenoid **4** (123.5 mg, 0.173 mmol) was treated with TrpSeCl (**2a**, 64.8 mg, 0.176 mmol) at room temperature. After stirring the reaction mixture for 3 h, the solvent was removed under reduced pressure. The residue was extracted into toluene and filtered before the solvent was removed from the filtrate under reduced pressure. The residue was purified by high performance liquid chromatography (HPLC) (eluent: toluene) and recrystallization from hexane to give **5a** as the main product in 41% yield (73.7 mg, 0.0710 mmol), and **6** (34.0 mg, 0.0268 mmol, 31%). Data for **5a**: orange crystals, m.p. 231 °C (dec.); $^1$H NMR (300 MHz, $C_6D_6$, r.t.): $\delta$ (ppm) 1.40 (s, 36H), 4.47 (s, 5H), 4.72 (s, 2H), 4.96 (s, 1H), 6.67–6.72 (m, 3H), 6.76–6.79 (m, 3H), 6.99 (d, 3H, $J$ = 7.1 Hz), 7.55 (t, 2H, $J$ = 1.7 Hz), 7.76 (d, 3H, $J$ = 7.4 Hz), 7.91 (d, 4H, $J$ = 1.7 Hz); $^{13}$C NMR (75 MHz, $C_6D_6$, 298 K): $\delta$ (ppm) 31.77 (q), 35.22 (s), 54.52 (d), 66.94 (s), 71.86 (d), 73.06 (d), 83.69 (s), 96.62 (s), 122.30 (d), 123.20 (d), 124.91 (d), 125.28 (d), 125.89 (d), 126.13 (d), 136.92 (s), 145.07 (s), 146.01 (s), 151.02 (s); $^{77}$Se NMR (57 MHz, $C_6D_6$, 298 K): $\delta$ (ppm) 168; MS (DART-TOF, positive mode): $m/z$ Calcd. for $C_{58}H_{63}{}^{37}Cl_2{}^{57}Fe^{72}Ge^{76}Se$ 1038.2068 ($[M + H]^+$), found 1038.2084 ($[M + H]^+$); Anal. Calcd. for $C_{58}H_{62}Cl_2FeGeSe$: C, 67.15; H, 6.02. Found: C, 66.90; H, 6.16.

#### 3.2.4. Reaction of Chlorogermylenoid **4** with Tellurenylchloride **2b**

A toluene solution (3 mL) of chlorogermylenoid **4** (109.9 mg, 0.154 mmol) was treated with TrpTeCl (**2b**, 65.0 mg, 0.156 mmol) at room temperature. After stirring the reaction mixture for 3 h, the solvent was removed under reduced pressure. The residue was extracted into toluene and filtered before the solvent was removed from the filtrate under reduced pressure. The residue was purified by HPLC (eluent: toluene) and recrystallized from hexane to give **5b** as the main product (58% yield, 95.1 mg, 0.0874 mmol) together with **6** (17%, 16.0 mg, 0.0126 mmol). Data for **5b**: orange crystals, m.p. 151 °C (dec.); $^{1}$H NMR (300 MHz, $C_6D_6$, r.t.): $\delta$ (ppm) 1.42 (s, 36H), 4.62 (s, 5H), 4.63 (s, 2H), 5.03 (s, 1H), 6.67–6.72 (m, 3H), 6.79–6.83 (m, 3H), 7.01 (d, 3H, $J$ = 7.1 Hz), 7.56 (t, 2H, $J$ = 1.7 Hz), 7.90 (d, 3H, $J$ = 7.3 Hz), 7.97 (d, 4H, $J$ = 1.7 Hz); $^{13}$C NMR (75 MHz, $C_6D_6$, 298 K): $\delta$ (ppm) 31.71 (q), 35.21 (s), 54.94 (d), 60.81 (s), 72.83 (d), 72.97 (d), 78.16 (s), 96.94 (s), 122.44 (d), 123.24 (d), 125.03 (d), 126.11 (d), 128.51 (d), 129.28 (d), 136.21 (s), 145.04 (s), 147.01 (s), 151.09 (s); $^{125}$Te NMR (94 MHz, $C_6D_6$, 298 K): $\delta$ (ppm) 244; MS (FAB): *m/z* calcd. for $C_{58}H_{62}{}^{37}Cl_2{}^{58}Fe^{74}Ge^{122}Te$ 1086.1849 ([M]$^+$), found 1086.1853 ([M]$^+$); Anal. Calcd. for [$C_{58}H_{62}Cl_2FeGeTe + C_6H_{14}$]: C, 65.57; H, 6.53. Found: C, 65.32; H, 6.66.

### 3.3. Computational Methods

The level of theory and the basis sets used for the structural optimization are given in the main text. Frequency calculations confirmed minimum energies for all optimized structures. All calculations were carried out using the *Gaussian 09* program package [15].

### 3.4. X-ray Crystallographic Analyses

Single crystals of [**2a·benzene**], **2b**, **5a**, and **5b** were obtained upon recrystallizations from benzene ([**2a·benzene**]) or hexane (**2b**, **5a**, and **5b**). Intensity data for [**2a·benzene**], **5a**, and **5b** were collected on a RIGAKU Saturn70 CCD system (RIGAKU, Tokyo, Japan) with VariMax Mo Optics using Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å), while those for **2b** were collected at the BL40XU beam line at Spring-8 (JASRI, projects 2017A1647, 2017B1179, 2018A1167, and 2018A1405) on a Rigaku Saturn 724 CCD system (RIGAKU, Tokyo, Japan) using synchrotron radiation (λ = 0.7823 Å). Crystal data are shown in the references. The structures were solved by direct methods (*SHELXT*-2014 [18]) and refined by a full-matrix least square method on $F^2$ for all reflections (*SHELXL*-2014 [19]). All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically. Supplementary crystallographic data were deposited at the Cambridge Crystallographic Data Centre (CCDC; under reference numbers 1846194–1846197 for [**2a·benzene**], **2b**, **5a**, and **5b**, respectively) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request.cif. Crystal data; [**2a·benzene**] ($C_{26}H_{19}ClSe$): $M$ = 445.82, $\lambda$ = 0.71073 Å, $T$ = –170 °C, orthorhombic, *Pbca* (no. 61), $a$ = 10.3039(3) Å, $b$ = 18.5923(5) Å, $c$ = 21.1023(6) Å, $V$ = 4042.6(2) Å$^3$, $Z$ = 8, $D_{\mathrm{calc}}$ = 1.465 g cm$^{-3}$, $\mu$ = 1.998 mm$^{-1}$, $2\theta_{\mathrm{max}}$ = 51.0°, measd./unique refls. = 33309/3943 ($R_{\mathrm{int}}$ = 0.0495), param = 253, GOF = 1.035, $R_1$ = 0.0279/0.0411 [$I > 2\ \sigma(I)$/all data], $wR_2$ = 0.0570/0.0615 [$I > 2\sigma(I)$/all data], largest diff. peak and hole 0.341 and $-$0.279 e·Å$^{-3}$ (CCDC-1846194); **2b** ($C_{20}H_{13}ClTe$): $M$ = 416.35, $\lambda$ = 0.7823 Å, $T$ = $-$180 °C, monoclinic, $P2_1/c$ (no. 14), $a$ = 15.3100(3) Å, $b$ = 8.0496(1) Å, $c$ = 13.8261(3) Å, $\beta$ = 115.690(3)°, $V$ = 1535.49(6) Å$^3$, $Z$ = 4, $D_{\mathrm{calc}}$ = 1.801 g·cm$^{-3}$, $\mu$ = 2.690 mm$^{-1}$, $2\theta_{\mathrm{max}}$ = 56.0°, measd./unique refls. = 20016/4065 ($R_{\mathrm{int}}$ = 0.0676), param = 218, GOF = 1.084, $R_1$ = 0.0483/0.0517 [$I > 2\sigma(I)$/all data], $wR_2$ = 0.1270/0.1284 [$I > 2\ \sigma(I)$/all data], largest diff. peak and hole 2.241 and $-$0.948 e·Å$^{-3}$ (CCDC-1846195); **5a** ($C_{58}H_{62}Cl_2FeGeSe$): $M$ = 1037.37, $\lambda$ = 0.71073 Å, $T$ = $-$170 °C, triclinic, $P-1$ (no. 2), $a$ = 9.3412(3) Å, $b$ = 13.2993(7) Å, $c$ = 21.3355(14) Å, $\alpha$ = 93.977(4)°, $\beta$ = 101.963(4)°, $\gamma$ = 103.821(2)°, $V$ = 2498.1(2) Å$^3$, $Z$ = 2, $D_{\mathrm{calc}}$ = 1.379 g cm$^{-3}$, $\mu$ = 1.765 mm$^{-1}$, $2\theta_{\mathrm{max}}$ = 53.0°, measd./unique refls. = 48637/10245 ($R_{\mathrm{int}}$ = 0.1265), param = 596, GOF = 1.136, $R_1$ = 0.0736/0.1313 [$I > 2\sigma(I)$/all data], $wR_2$ = 0.1431/0.1712 [$I > 2\sigma(I)$/all data], largest diff. peak and hole 0.831 and –0.594 e·Å$^{-3}$ (CCDC-1846196); **5b** ($C_{58}H_{62}Cl_2FeGeTe$): $M$ = 1086.01, $\lambda$ = 0.71073 Å, $T$ = $-$170 °C, triclinic, $P$–1 (no. 2), $a$ = 12.6102(6) Å, $b$ = 15.3206(4) Å, $c$ = 15.9034(7) Å, $\alpha$ = 66.692(2)°, $\beta$ = 68.112(2)°, $\gamma$ = 71.139(3)°, $V$ = 2562.03(19) Å$^3$, $Z$ = 2, $D_{\mathrm{calc}}$ = 1.408 g cm$^{-3}$, $\mu$ = 1.568 mm$^{-1}$, $2\theta_{\mathrm{max}}$ = 53.0°, measd./unique refls. = 29752/10195 ($R_{\mathrm{int}}$ = 0.0891), param = 632, GOF = 1.167, $R_1$ = 0.0680/0.1112 [$I > 2\sigma(I)$/all data], $wR_2$ = 0.1261/0.1487 [$I > 2\sigma(I)$/all data], largest diff. peak and hole 0.900 and –0.851 e·Å$^{-3}$ (CCDC-1846197).

## 4. Conclusions

Chalcogenyldichlorogermanes **5a** and **5b** were successfully synthesized from the reaction between an isolable ferrocenyl-substituted chlorogermylenoid and a sterically demanding ferrocenyl group (Fc*). Ferrocenylchlorogermylenoid **4** is an appropriate precursor for the targeted ferrocenyl-substituted chalcogenyldichlorogermanes via nucleophilic reactions towards the sterically hindered chalcogenenyl chlorides. Thus, reactions of a halogermylenoid with a chalcogenenyl chloride represent an effective synthetic route to chalcogenyldichlorogermanes. Theoretical calculations showed that the Ge–Ch bonds in these chalcogenyldichlorogermanes are strengthened due to LP(Ch) → σ*(Ge–Cl) interactions, suggesting promising potential for such chalcogenyldichlorogermanes as building blocks for organochalcogenylgermanes that bear a redox-active ferrocenyl moiety.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2304-6740/6/3/68/s1, CIF and checkCIF files of complexes [**2a·benzene**], **2b**, **5a**, and **5b**.

**Author Contributions:** T.S. (Takahiro Sasamori) conceived and designed the experiments; Y.S. and K.S. performed the experiments and measurements; N.T. provided laboratory space, access to machines, and financial support; T.S. (Takahiro Sasamori), Y.S., K.S., and T.S. (Tomohiro Sugahara) collected the chemical data and performed the XRD analyses; T.S. (Takahiro Sasamori) performed the theoretical calculations and wrote the manuscript.

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