# Synthesis and Reactions of Titanacycles Containing Group 14 Elements and Their Zirconium Analogues

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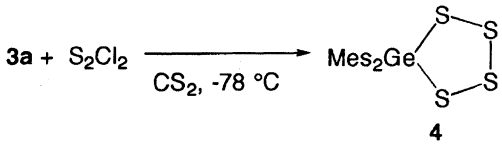
Lithium dimesitylgermanedithiolate reacted with titanocene or zirconocene dichloride to give 2,2-dimesityl-1,3-dithia-2-germa-4-titanacycle (**3a**) and its zirconocene analogue (**3b**), which afforded a stable 2,3,4,5-tetrathiagermolane (**4**) in treatment with $S_2Cl_2$. The reaction of **3b** with $Ph_2GeCl_2$ gave unsymmetric 1,3,2,4-dithiadigermetane (**5**). The bis($\eta^5$-cyclopentadienyl) derivative of *cis*-2,3-di-*t*-butyl-2,3-diphenyl-1,4-dithia-2,3-disila-5-titanacyclopentane (**7a**) obtained from lithium 1,2-di-*t*-butyl-1,2-diphenyldisilane-1,2-dithiolate reacted with electrophilic reagents ($SCl_2$, $S_2Cl_2$, $Se_2Cl_2$, $R_2GeCl_2$) to give the corresponding heterocycles.

Heterocycles containing group 14 elements[1] have received much attention not only as their carbon-based analogues[2] but also in the field of material science. On the other hand, the chemistry of metallacycles with incorporated titanocene or zirconocene units[3] has attracted much interest, and these compounds have found widespread applications in organic synthesis.[4] Nevertheless, the utility of these promising building blocks as precursors of heterocyclic compounds containing silicon and germanium has not been fully realized. The titanacycles containing four-membered $TiS_2E$ rings (E=Si, Ge, Sn) were synthesized by Rauchfuss[4c] and Steudel,[3d] and showed synthetic limitation for the bulky group substituted titanacycles. We have succeeded in the synthesis of bulky group substituted titanacycle, namely 2, 2-bis(2,4,6-trimethylphenyl)-1,3-dithia-2-germa-4-titanacycle (**3a**) (hereafter 2,4,6-trimethylphenyl = mesityl, abbreviated to Mes), and its zirconium analogue (**3b**) by using dimesitylgermanedithiol (**2**) as a starting material. By using disilane-1,2-dithiol in a similar manner, we could achieve the preparation of dithiadisilatitanacycle and zirconacycle. Our preliminary paper reported the synthesis and reaction of bis($\eta^5$-cyclopentadienyl) derivative of *cis*-2,3-di-*t*-butyl-2, 3-diphenyl-1,4-dithia-2,3-disila-5-titanacyclopentane (**7a**).[5] In the present paper we report the full details of synthesis as well as structural features of disilatitanacycle **7a** and its zirconocene analogue **7b**; furthermore, we demonstrate their suitability as precursor for a variety of heterocycles containing a 1,4-dithia-2,3-disila fragment.

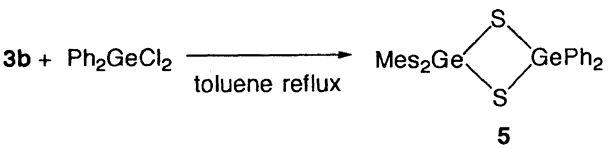
## Results and Discussion

**Synthesis of Germatitanacycle and Its Zirconium Analogue.** Diphenyldichlorogermane and -silane were easily reacted with 2 equiv of $Li_2S$ to provide germane- and silane-dithiolate. But dimesityldichlorogermane reacted with 2 equiv of $Li_2S$ and did not yield lithium germanedithiolate but rather dithiadigermetane (**1**) (Scheme 1).[3d] Dilithium dimesitylgermanedithiolate was readily obtained by the treatment of a THF solution of $Mes_2Ge(SH)_2$ (**2**) with a THF solution of $LiBEt_3H$ (2.2 equiv) at room temperature. Successive addition of a THF solution of dichlorobis($\eta^5$-cyclopentadienyl)titanium to $Mes_2Ge(SLi)_2$ gave a germatitanacycle **3a** as a green crystalline solid in 70% yield as shown in Scheme 2. Germazirconacycle **3b** was also obtained as a yellow solid in 90% yield in a similar manner. Depending on the synthetic target, the titanium or zirconium metallacycle need not be isolated, but "one-pot" synthesis can be carried out.

**Reaction of Titanacycle 3a and Zirconacycle 3b with Some Electrophiles.** Germatitanacycle **3a** underwent ready substitution reaction at the titanocene moiety with $S_2Cl_2$ in $CS_2$ to give tetrathiagermolane **4** as a yellow oil in 53% yield (Eq. 1). When a toluene solution of **3b** and $Ph_2GeCl_2$ was refluxed for 20 h, unsymmetric 1,3,2,4-di thiadigermetane **5** was isolated after preparative gel permeation liquid chromatography (GPC) in 52% yield (Eq. 2).

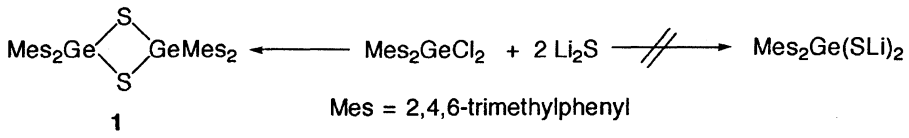



**4** (1)

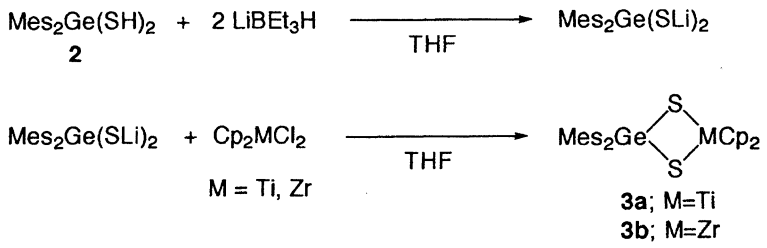



**5** (2)

**Synthesis of 1,4-Dithia-2,3-disilametallacyclopentanes (7a and 7b).** 1,2-Di-*t*-butyl-1,2-diphenyldisilane-1,2-bis(trifluoromethanesulfonate) was treated with 2 equiv of $Li_2S$ and with some added $Cp_2TiCl_2$ at room temperature, the disilati-



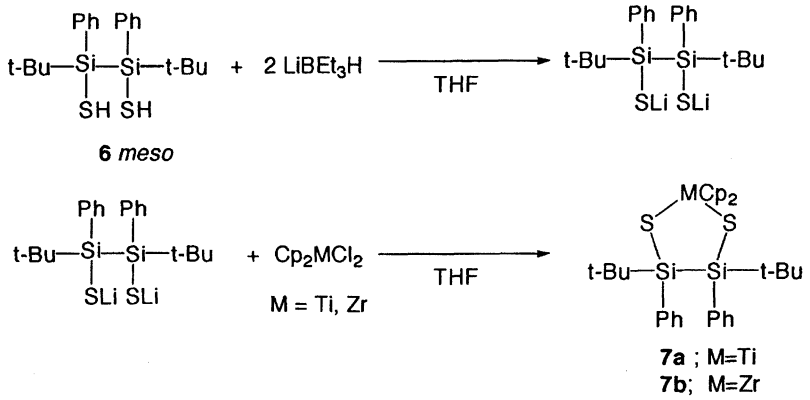

Scheme 1.



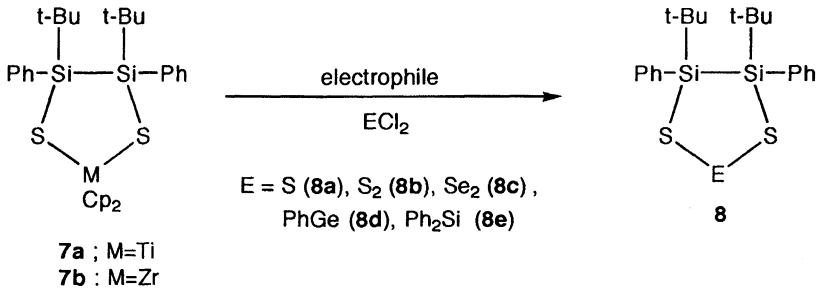

Scheme 2.

tanacycle **7a** was obtained in very low yield. Disilametallacyclopentanes, **7a** and **7b** could be prepared from *meso*-1,2-di-*t*-butyl-1,2-diphenyldisilane-1,2-dithiol **6** in high yield, as shown in Scheme 3. Disilatitanacycle **7a** was isolated as green crystals after GPC (eluent; toluene) purification in 80% yield, and zirconacycle **7b** as a yellow crystalline solid in 90% yield. Disilatitanacycle **7a** is relatively stable toward moisture and air, but zirconacycle **7b** is unstable toward moisture and is air sensitive. The structure of **7a** was unequivocally determined by single crystal X-ray diffraction analysis.

**Reaction of Disilatitanacycle 7a with Various Electrophiles.** By using the disilametallacycles **7a** and **7b**, the various disilaheterocycles are readily prepared, as shown in Scheme 4 and Table 1. When a disilatitanacycle **7a** was treated with 1.0 equiv of sulfur dichloride or sulfur monochloride in $CS_2$ at −78 °C, the green solution turned to red during a 30 min period. The solvent was removed in vacuo and pentane was added. After the resulting $Cp_2TiCl_2$ was filtered off, and the solvent was evaporated, the residue recrystallized from pentane to afford 1,2,3-trithia-4,5-disilacyclopentane (**8a**) or 1,2,3,4-tetrathia-5,6-disilacyclohexane (**8b**). The products **8a** and **8b** could be readily isolated by GPC in 90% and 92% yields, respectively. The unequivocal molecular structure of **8a** was determined by single-crystal X-ray diffraction analyses. Compounds, **8a** and **8b** are rare, and no general synthetic route to these compounds had been reported prior to our studies.[5] Although silyl-sub-




Scheme 3.



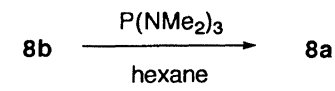

Scheme 4.

Table 1. Reactions of **7a** or **7b** with Various Electrophiles

| Entry | Electrophile | Product | Solvent | Time | Temp | Yield/% | |
|---|---|---|---|---|---|---|---|
| | | | | h | °C | **7a** | **7b** |
| 1 | $SCl_2$ | **8a** | $CS_2$ | 0.5 | −78 | 90 | 93 |
| 2 | $S_2Cl_2$ | **8b** | $CS_2$ | 0.5 | −78 | 92 | 66 |
| 3 | $Se_2Cl_2$ | **8c** | $CS_2$ | 0.5 | −78 | 90 | Quant. |
| 4 | $Ph_2GeCl_2$ | **8d** | Toluene | 24 | 110 | 55 | 40 |
| 5 | $Ph_2SiCl_2$ | **8e** | Xylene | 72 | 140 | — | — |

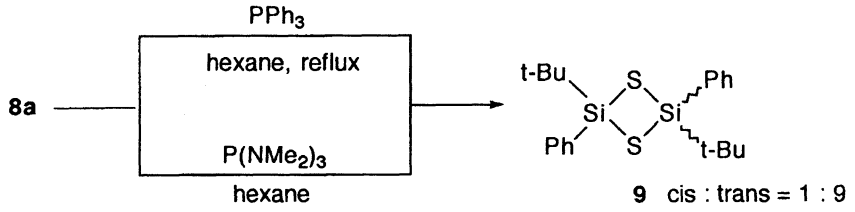
stituted sulfides are well-known as sulfur-transfer reagents[6] by Si–S bond cleavage, the reaction of **7a** or **7b** with $SCl_2$ or $S_2Cl_2$ was performed on the site of Ti or Zr. The relative reactivity of the Ti–S and Si–S bonds in four-membered $TiS_2Si$ ring was explained as an example of frontier orbital control by Rauchfuss et al.[7] Treatment of disilametallacycles, **7a** and **7b** with selenium monochloride at −78 °C afforded the dithiadiselenadisilacyclohexane **8c** in 90—100% yield. Compound **8c** was stable at room temperature, but decomposed under irradiation, liberating selenium as a red precipitate to yield dithiaselenadisilacyclopentane. In the transformations of **7a** with $Ph_2GeCl_2$ more drastic conditions, i.e. high temperature and long reaction time, were necessary to achieve full conversion. The reaction of **7a** with dichlorodiphenylgermane afforded a corresponding dithiadisilagermacyclopentane derivative **8d** in 55% yield. On the other hand, the reaction of **7a** with halosilane produced dithiatrisilacyclopentane **8e** only with difficulty. Indeed, **7a** did not react with dichlorodiphenylsilane even at xylene reflux for 72 h.

**Dechalcogenation of 8a and 8b.** Furthermore, we have investigated the desulfurization of compounds **8a** and **8b** by phosphines. To a benzene-$d_6$ solution of the compound **8b** (0.06 mmol) hexamethylphosphorous triamide (HMPT, 1.1 equiv) was added at room temperature in an NMR tube (Eq. 3). We observed the formations of **8a** and

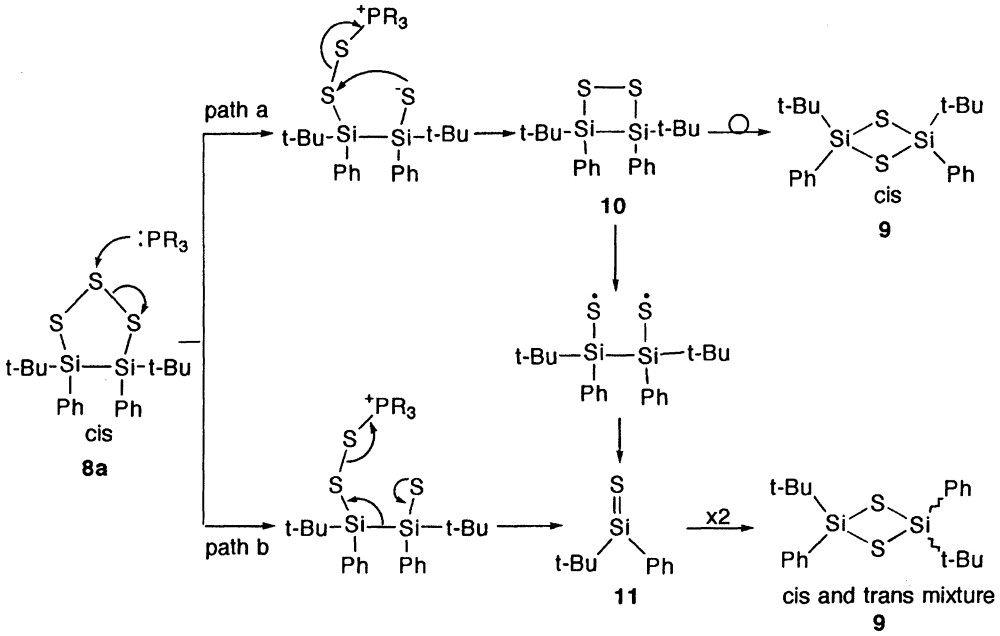



(3)

$(Me_2N)_3P{=}S$ in a few minutes. Desulfurization of **8a** was carried out by $PPh_3$ (1.1 equiv) at hexane reflux for 1 h. After the usual work up, recrystallization from hexane gave 2,4-di-*t*-butyl-2,4-diphenyl-1,3-dithia-2,4-disilacyclobutane **9** containing *cis* and *trans* isomers (ratio: *cis*/*trans*=1/9) without 1,2-dithia-3,4-disilacyclobutane **10** as shown in Scheme 5. The desulfurization of **8a** by HMPT at room temperature also gave similar results. The mixture of *cis*- and *trans*-isomers **9** was also obtained from desulfurization of **8b** (*cis*). The formation of **9** admits of two plausible routes, as shown in Scheme 6. One possible route is an intramolecular rearrangement via an intermediate **10**. The stereospecific rearrangement of 1,2-dioxa-3,4-disilacyclobutanes to 1,3-dioxa-




Scheme 5.




Scheme 6.

2,4-disilacyclobutanes are reported by West et al.[8] Since this reaction is not stereospecific, the first route (a) is not likely. Another route (b) is likely, which is the dimerization of thioxosilane derivative **11**.

**Structures of Dithiadisilatitanacycle 7a, Trithiadisilacyclopentane 8a, and Cyclodisilathiane 9.** Crystal data of **7a**, **8a**, and **9** are summarized in Table 2. An ORTEP drawings of **7a** (molecule 1), **8a** and **9** are shown in Figs. 1, 2, and 3, respectively. Their selected bond distances (Å) and angles (degree) for the core rings are listed in Tables 3, 4, 5, and 6. Compound **7a** crystallized with two independent molecules in a crystal unit. Both independent molecules of **7a** are essentially identical structurally. The titanacycle of **7a** exhibits a half-chair conformation as depicted in Fig. 1. The Ti–S bond lengths (2.39 Å resp. 2.47 Å) are within the normal range (2.42—2.45 Å),[3c] the Si–S bonds (2.13 Å) are slightly shortened (usually 2.16—2.17 Å)[3c]. Interestingly, the Ti–S–Si bond angles (109.7° resp. 113.2°) are larger than those of other five-membered dithiatitanacycles (e.g. *o*-(–$SC_6H_4S$–)$TiCp_2$: 95.7—97.0°;[9a] (–SCH=CHS–)$TiCp_2$: 94.2—95.0°)[9b] and resemble those of acyclic derivatives (e.g. $Cp_2Ti(SPh)_2$: 113.6—115.5°).[9c] On the other hand, the S–Ti–S bond angle (93.9°) takes an intermediate value

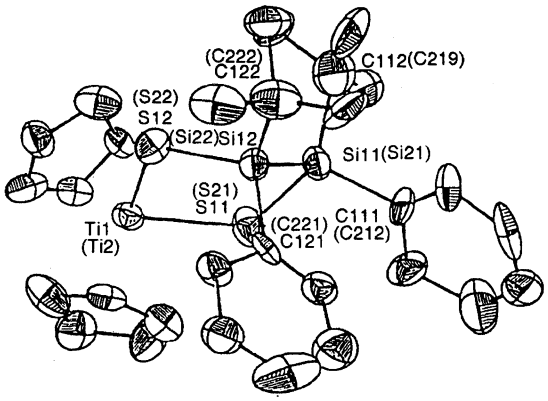



Fig. 1. Molecular structure of **7a** (molecule 1).

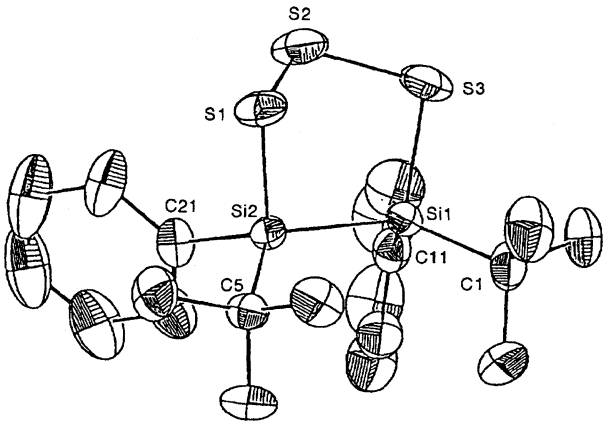



Fig. 2. Molecular structure of **8a**.

Table 2. Crystallographic Data for **7a**, **8a**, and **9**

| | **7a** | **8a** | **9**(*trans*) |
|---|---|---|---|
| Formula | $C_{30}H_{38}Si_2S_2Ti$ | $C_{20}H_{28}Si_2S_3$ | $C_{20}H_{28}Si_2S_2$ |
| $M_w$ | 566.84 | 420.81 | 388.75 |
| Color, habit | Green, rod | Yellow, rod | White, rod |
| Cryst dim./mm | 0.50×0.50×0.40 | 0.50×0.50×0.20 | 0.50×0.50×0.80 |
| Cryst. system | Tetragonal | Triclinic | Orthorhombic |
| Space group | $I\bar{4}$ | $P\bar{1}$ | $P2_12_12_1$ |
| $a$/Å | 16.954(1) | 8.013(1) | 9.781(1) |
| $b$/Å | | 9.860(1) | 14.337(1) |
| $c$/Å | 41.679(3) | 16.423(2) | 15.428(1) |
| $\alpha$/deg | | 86.60(1) | |
| $\beta$/deg | | 82.50(1) | |
| $\gamma$/deg | | 64.56(26) | |
| Cell volume/Å$^3$ | 11980.3(11) | 1161.8(8) | 2163.4(3) |
| $Z$ | 16 | 2 | 4 |
| $d$/g cm$^{-3}$ | 1.26 | 1.20 | 1.19 |
| $F_{000}$ | 4800 | 448 | 832 |
| Temp/°C | 23±1 | 23±1 | 23±1 |
| Scan range/deg | 0.8+0.530 tan $\theta$ | 0.4+0.450 tan $\theta$ | 0.6+0.520 tan $\theta$ |
| Radiation ($\lambda$ =0.71073 Å) | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ |
| 2$\theta$ max/deg | 50.0 | 50.0 | 50.0 |
| $\mu$/cm$^{-1}$ | 5.1 | 4.1 | 3.4 |
| No. of obsd refltns ($I>3\sigma(I)$) | 3212 | 3367 | 1537 |
| No. of refined params | 631 | 226 | 217 |
| $R$ | 0.055 | 0.061 | 0.032 |
| $R_w$ | 0.063 | 0.087 | 0.031 |
| (shift/error)$_{max}$ | 4.93$\sigma$ | 0.22$\sigma$ | 0.41$\sigma$ |
| Largest/lowest peak in final diff map/e Å$^{-3}$ | 0.21(4)/−0.06(0) | 0.53(10)/−0.33(0) | 0.25(3)/−0.11(0) |

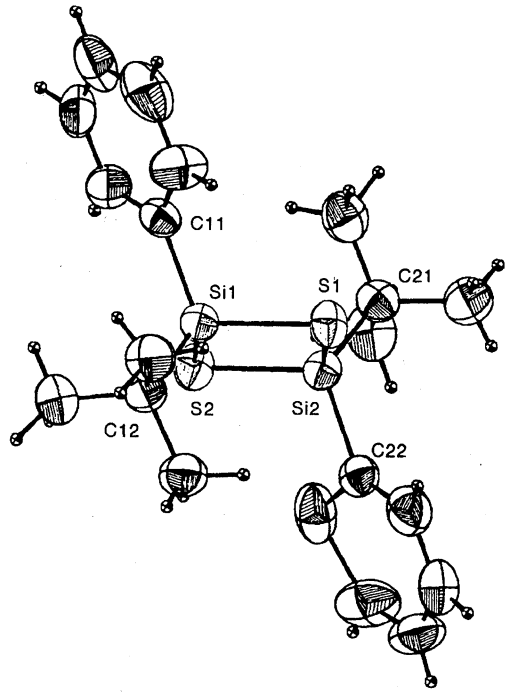



Fig. 3. Molecular structure of **9**.

Table 3. Selected Bond Lengths (Å) of **7a**

| Molecule 1 | | Molecule 2 | |
|---|---|---|---|
| Ti1–S11 | 2.467(4) | Ti2–S21 | 2.437(4) |
| Ti1–S12 | 2.388(4) | Ti2–S22 | 2.430(4) |
| S11–Si11 | 2.134(5) | S21–Si21 | 2.124(5) |
| S12–Si12 | 2.130(5) | S22–Si22 | 2.104(6) |
| Si11–Si12 | 2.408(5) | Si21–Si22 | 2.372(5) |
| Si11–C111 | 1.90(1) | Si21–C212 | 1.88(1) |
| Si11–C112 | 2.03(2) | Si21–C219 | 1.92(1) |
| Si12–C121 | 1.88(1) | Si22–C221 | 1.91(1) |
| Si12–C122 | 1.99(2) | Si22–C222 | 1.88(1) |

Table 4. Selected Bond Angles (degree) of **7a**

| Molecule 1 | | Molecule 2 | |
|---|---|---|---|
| S11–Ti1–S12 | 93.9(2) | S21–Ti2–S22 | 93.9(1) |
| Ti1–S11–Si11 | 113.2(2) | Ti2–S21–Si21 | 108.4(2) |
| Ti1–S12–Si12 | 109.7(2) | Ti2–S22–Si22 | 113.0(2) |
| S11–Si11–Si12 | 99.0(2) | S21–Si21–Si22 | 100.3(2) |
| S12–Si12–Si11 | 100.9(2) | S22–Si22–Si21 | 102.5(2) |
| S11–Si11–C111 | 108.2(5) | S21–Si21–C212 | 105.0(4) |
| S11–Si11–C112 | 110.7(6) | S21–Si21–C219 | 110.4(5) |
| Si12–Si11–C111 | 113.2(5) | Si22–Si21–C212 | 120.0(4) |
| Si12–Si11–C112 | 119.2(6) | Si22–Si21–C219 | 113.7(5) |
| C111–Si11–C112 | 106.1(7) | C212–Si21–C219 | 106.8(6) |
| S12–Si12–C121 | 114.9(4) | S22–Si22–C221 | 106.5(5) |
| S12–Si12–C122 | 108.7(6) | S22–Si22–C222 | 109.4(4) |
| Si11–Si12–C121 | 109.9(4) | Si21–Si22–C221 | 109.9(5) |
| Si11–Si12–C122 | 122.0(6) | Si21–Si22–C222 | 121.7(4) |
| C121–Si12–C122 | 101.1(6) | C221–Si22–C222 | 106.1(6) |

between five-membered titanacycles (e.g. *o*-(–$SC_6H_4S$–)-$TiCp_2$: 82.2°;[9a] (–SCH=CHS–)$TiCp_2$: 83.2°)[9b] and acyclic ones (e.g. $Cp_2Ti(SPh)_2$: 99.3°).[9c] The trithiadisilacyclopentane skeleton in compound **8a** has a half-chair conformation. The central four-membered ring of **9** was found to be completely planar (dihedral angle; S1–Si1–Si2–S2=0.7°). The Si–S bond lengths (2.148(2)—2.149(2) Å) are within the normal range.[3c] The Si–S–Si angles (80.64(6)° resp. 80.66(6)°) and smaller than those of other cyclodisilathianes (e.g. tetramethylcyclodisilathiane 82.46(6)°;[10a] tetra-*t*-butoxycyclodisilathiane 82.2(1)°)[10b] and the S–Si–S angles (99.40(7) resp. 99.30(7)°) are larger than those of other cyclodisilathiane derivatives (97.54(7)[10a] and 97.8(1)°[10b]). Non-bonding Si···Si and S···S distances are 2.78 and 3.28 Å, respectively, which are within the normal range of those of cyclodisilathianes ($R_2Si)_2S_2$(Si···Si; R=Me; 2.837(2),[10a] R=Cl; 2.725(1),[10c] R=Br; 2.741(6) Å).[10c]

Table 5. Selected Bond Lengths (Å) and Angles (degree) of **8a**

| Bond lengths (Å) | | Bond angles (degree) | |
|---|---|---|---|
| S1–S2 | 2.060(2) | S1–S2–S3 | 103.3(1) |
| S2–S3 | 2.064(3) | Si2–S1–S2 | 92.7(1) |
| S1–Si2 | 2.171(2) | Si1–S3–S2 | 97.9(1) |
| S3–Si1 | 2.178(2) | S1–Si2–Si1 | 100.2(1) |
| Si1–Si2 | 2.408(2) | S3–Si1–Si2 | 100.6(1) |
| Si1–C11 | 1.876(7) | S3–Si1–C1 | 103.2(2) |
| Si1–C1 | 1.912(7) | S3–Si1–C11 | 109.4(2) |
| Si1–C5 | 1.909(5) | Si2–Si1–C1 | 122.2(2) |
| Si2–C21 | 1.881(6) | Si2–Si1–C11 | 110.4(2) |
| | | C1–Si1–C11 | 109.9(3) |
| | | S1–Si2–C5 | 104.8(2) |
| | | S1–Si2–C21 | 108.3(2) |
| | | Si1–Si2–C5 | 123.3(2) |
| | | Si1–Si2–C21 | 110.7(2) |
| | | C5–Si2–C21 | 108.2(2) |

Table 6. Selected Bond Lengths (Å) and Angles (degree) of **9**

| Bond lengths (Å) | | Bond angles (degree) | |
|---|---|---|---|
| S1–Si1 | 2.148(2) | Si1–S1–Si2 | 80.7(1) |
| S1–Si2 | 2.149(2) | Si1–S2–Si2 | 80.6(1) |
| S2–Si1 | 2.149(2) | S1–Si1–S2 | 99.4(1) |
| S2–Si2 | 2.149(2) | S1–Si2–S2 | 99.3(1) |
| Si1–C11 | 1.889(4) | S1–Si1–C11 | 110.2(1) |
| Si1–C12 | 1.854(5) | S1–Si1–C12 | 111.3(1) |
| Si2–C21 | 1.885(4) | S2–Si1–C11 | 111.9(2) |
| Si2–C22 | 1.865(4) | S2–Si1–C12 | 110.6(1) |
| | | C11–Si1–C12 | 112.8(2) |
| | | S1–Si2–C21 | 111.2(2) |
| | | S1–Si2–C22 | 110.9(1) |
| | | S2–Si2–C21 | 111.2(1) |
| | | S2–Si2–C22 | 110.6(1) |
| | | C21–Si2–C22 | 112.8(2) |

## Experimental

All manipulations were conducted under an argon atmosphere using standard Schlenk techniques. THF, diethyl ether, toluene, benzene, hexane, and pentane were dried over sodium benzophenone ketyl, distilled, and degassed prior to use. Triethylamine and carbon disulfide were dried over $CaH_2$, and distilled. The super hydride (THF solution of $LiBEt_3H$) was purchased from Aldrich. The reagents used in this study were purchased from commercial

sources and purified, dried, and degassed as necessary. Preparative gel permeation liquid chromatography (GPC) was carried out on LC-908 on JAIGEL 1H and 2H columns (Japan Analytical Industry, styrene-divinylbenzene copolymer, pore size 25 Å) with toluene as solvent. NMR spectra were run on either a Bruker AC400 or AC300 spectrometer at 400 or 300 MHz, respectively. $^{1}H$ and $^{13}C$ NMR spectra were referenced to residual solvent resonances which were calibrated against tetramethylsilane. $^{29}Si$ NMR spectra were referenced to external tetramethylsilane. Mass spectra and high-resolution mass spectra were obtained on a JEOL JMS SX102A mass spectrometer. All melting points are uncorrected.

**Preparation of $(Mes)_2Ge(SH)_2$ (2).** A three-necked 500 mL round-bottom flask prepared with a gas inlet tube was charged with $Et_3N$ (0.27 mL, 1.9 mmol) and diethyl ether (100 mL). The flask was cooled to −70 °C (dry ice/MeOH bath), and then $H_2S$ was introduced at 1 atm for 1 h. A diethyl ether solution of $Mes_2GeCl_2$ (381 mg, 1.0 mmol; $Et_2O$, 150 mL) was added dropwise to the flask with bubbling of $H_2S$. After the addition was completed, the introduction of $H_2S$ was stopped and the reaction mixture was gradually warmed to −40 °C with stirring for 12 h. The flask was then allowed to warm to room temperature by removing the cooling bath. Volatile components were removed from the flask in vacuo. The residue was extracted with small portions of hexane (a total of 20 mL), and each portion was filtered and combined. Hexane was removed from this in vacuo. The residue was purified by preparative GPC to yield **2** (325 mg, 86% yield) as a while solid. $^{1}H$ NMR (300 MHz, $C_6D_6$) $\delta$=0.90 (2H, s), 2.03 (6H, s), 2.46 (12H, s), 6.61 (4H, s); $^{13}C$ NMR (75 MHz, $C_6D_6$) $\delta$=20.8 (q), 24.0 (q), 130.1 (d), 138.2 (s), 139.6 (s), 141.6 (s); MS *m/z* 378 ($M^+$). Found: C, 57.42; H, 6.38%. Calcd for $C_{18}H_{24}GeS_2$: C, 57.34; H, 6.41%.

**Preparation of $(Mes)_2GeS_2TiCp_2$ (3a).** A three-necked 30 mL round-bottom flask prepared with a solid inlet tube was charged with **2** (100 mg, 0.267 mmol) and THF (2.0 mL). $LiEt_3BH$ (0.55 mL of a 1.0 M solution (M=mol dm$^{-3}$) in THF) was added dropwise to the flask. After the addition was completed, the reaction mixture was stirred for 30 min. When $Cp_2TiCl_2$ (78.0 mg, 0.27 mmol) was added via a solid inlet tube, it was green in color. After stirring for 24 h, the green solution was concentrated in vacuo. The residue was extracted with small portions of benzene (a total of 10 mL), and each portion was filtered and combined. After removal of solvent, the residue was charged on preparative GPC to give **3a** (103 mg, 70%) as a green crystalline solid. $^{1}H$ NMR (300 MHz, $C_6D_6$) $\delta$=2.02 (6H, s), 3.03 (12H, s), 6.01 (10H, s), 6.73 (4H, s); $^{13}C$ NMR (75 MHz, $C_6D_6$) $\delta$=20.9 (q), 24.0 (q), 119.0 (d), 128.5 (d), 139.3 (s), 130.3 (s), 143.2 (s); MS *m/z* 554 ($M^+$). Found: *m/z* 554.0623. Calcd for $C_{28}H_{32}S_2^{74}GeTi$: M, 554.0637.

**Preparation of $(Mes)_2GeS_2ZrCp_2$ (3b).** A three-necked 30 mL round-bottom flask prepared with a dropping funnel was charged with **2** (210.5 mg, 0.588 mmol) and THF (5.0 mL). After 1.0 M $LiEt_3BH$ (1.13 mL, 1.13 mmol) was added, it was stirred for 30 min. When a THF solution of $Cp_2ZrCl_2$ (164 mg, 0.560 mmol) was added via a dropping funnel, this solution was yellow. After stirring for 20 h, the resulting yellow solution was concentrated in vacuo. The residue was extracted with small portions of benzene (a total of 15 mL), and each portion was filtered and combined. After removal of solvent, recrystallization of the residue from pentane gave **3b** (300 mg, 90% yield) as a yellow solid. $^{1}H$ NMR (300 MHz, $C_6D_6$) $\delta$=2.08 (6H, s), 2.99 (12H, s), 5.95 (10H, s), 6.73 (4H, s); $^{13}C$ NMR (75 MHz, $C_6D_6$) $\delta$=20.9 (q), 24.0 (q), 115.1 (d), 130.4 (d), 138.2 (s), 138.4 (s), 141.0 (s); MS *m/z* 596 ($M^+$). Found: *m/z* 596.0198. Calcd for $C_{28}H_{32}S_2^{74}GeZr$: M, 596.0205.

**Reaction of $(Mes)_2GeS_2TiCp_2$ (3a) with $S_2Cl_2$.** A three-necked 30 mL round-bottom flask was charged with **3a** (42.6 mg, 0.0769 mmol) and $CS_2$ (4.0 mL). The flask was cooled to −78 °C (dry ice/MeOH bath), and then a $CS_2$ (4.0 mL) solution of $S_2Cl_2$ (9.6 mg, 0.0711 mmol) was added dropwise to the flask. After 30 min, the solvent was removed in vacuo, and the residue was extracted with ca. 5 mL of hexane and then was filtered. After removal of solvent, the residue was purified by preparative GPC to yield **4** (18.1 mg, 53%) as a yellow oil. $^{1}H$ NMR (300 MHz, $C_6D_6$) $\delta$=1.99 (6H, s), 2.38 (12H, s), 6.57 (4H, s); $^{13}C$ NMR (75 MHz, $C_6D_6$) $\delta$=20.9 (q), 23.8 (q), 129.9 (d), 136.2 (s), 142.2 (s), 142.7 (s); MS *m/z* 440 ($M^+$). Found: C, 49.42; H, 5.12%. Calcd for $C_{18}H_{22}GeS_4$: C, 49.23; H, 5.04%.

**Reaction of $(Mes)_2GeS_2ZrCp_2$ (3b) with $Ph_2GeCl_2$.** A three-necked 10 mL round-bottom flask was charged with **3b** (100 mg, 0.168 mmol) and toluene (5.0 mL). $Ph_2GeCl_2$ (69.5 mg, 0.233 mmol) was added to the flask, and the mixture was refluxed for 20 h. After removal of the solvent, the residue was extracted with ca. 10 mL of benzene. After being filtered and purified with preparative GPC, the product **5** (46.4 mg, 52% yield) was yielded as a while solid. $^{1}H$ NMR (300 MHz, $C_6D_6$) $\delta$=2.05 (6H, s), 2.71 (12H, s), 6.64 (4H, s), 7.06—7.15 (6H, m), 7.78—7.88 (4H, m); $^{13}C$ NMR (75 MHz, $C_6D_6$) $\delta$=20.9 (q), 23.6 (q), 128.8 (d), 130.3 (d), 130.4 (d), 133.6 (d), 138.5 (s), 139.50 (s), 139.52 (s), 142.2 (s); MS *m/z* 602 ($M^+$). Found: C, 59.91; H, 5.28%. Calcd for $C_{30}H_{32}Ge_2S_2$: C, 59.87; H, 5.35%.

**Preparation of [*t*-BuPh(HS)Si]$_2$ (6).** A three-necked 500 mL round-bottom flask was charged with 1,2-di-*t*-butyl-1,1,2,2-tetraphenyldisilane (10.0 g, 21.0 mmol) and toluene (370 mL). The flask was cooled to −15 °C with a cryogenic storage apparatus (EYELA COOL ESC-50). Trifluoromethanesulfonic acid (6.0 mL, 69.0 mmol) was slowly added to the mixture at −15 °C and the mixture was warmed to room temperature. It was stirred for 19 h. Solvent and remaining acid were removed under reduced pressure. The residue was dissolved in diethyl ether (370 mL), and $Et_3N$ (6.0 mL, 43.0 mmol) was added. $H_2S$ was introduced at 1 atm into the flask via a gas inlet tube for 5 h. It was stirred for 12 h. After removal of solvent, hexane (100 mL) was added and the salts were filtered. The solvent was removed in vacuo, and the white solid was twice recrystallized from hexane to yield pure **6** (*meso* form, 5.53 g, 67.4%) as while crystals. Mp 138—139 °C; $^{1}H$ NMR (400 MHz, $C_6D_6$) $\delta$=0.23 (2H, s), 0.95 (18H, s), 7.16—7.18 (6H, m), 7.99—8.01 (4H, m); $^{13}C$ NMR (100 MHz, $C_6D_6$) $\delta$=22.3 (s), 28.0 (q), 128.7 (d), 129.9 (d), 135.1 (s), 135.9 (d); $^{29}Si$ NMR (80 MHz, $C_6D_6$) $\delta$=1.10; MS *m/z* 389 ($M^+-1$), 333 ($M^+-57$). Found: C, 61.31; H, 7.61; S, 16.42. Calcd for $C_{20}H_{30}S_2Si_2$: C, 61.48; H, 7.74; S, 16.41.

**Preparation of 7a.** A 50 mL round-bottom flask was charged with **6** (0.819 g, 2.1 mmol) and THF (20.0 mL). 1 M $LiEt_3BH$ (4.6 mL, 4.6 mmol, THF solution) was added to the flask. It was stirred for 2.5 h. A THF (10.0 mL) solution of $Cp_2TiCl_2$ (0.522 g, 2.1 mmol) was added via a dropping funnel. The mixture was stirred for 24 h. After removal of solvent the green residue was extracted with benzene (a total of 30 mL). Salts were filtered and the solvent was removed in vacuo. The residue was purified by GPC (eluent; toluene) to afford **7a** (950 mg, 80%) as green crystals. Mp 113 °C; $^{1}H$ NMR (400 MHz, $C_6D_6$) $\delta$=1.39 (18H, s), 5.77 (5H, s), 6.21 (5H, s), 7.18—7.25 (6H, m), 8.03—8.05 (4H, m); $^{13}C$ NMR (100 MHz, $C_6D_6$) $\delta$=24.8 (s), 28.6 (q), 118.27 (d), 118.45 (d), 127.6 (d), 129.0 (d), 136.4 (d), 141.4 (s); $^{29}Si$ NMR (80 MHz, $C_6D_6$) $\delta$=40.99; MS *m/z* 566 ($M^+$), 509 ($M^+-57$). Found: *m/z* 566.1422. Calcd for $C_{30}H_{38}Si_2S_2Ti$: M, 566.1433.

**Preparation of 7b.** A 50 mL round-bottom flask prepared

with a dropping funnel was charged with **6** (952 mg, 2.44 mmol) and THF (25.0 mL). 1 M $LiEt_3BH$ (5.20 mL, 5.20 mmol, THF solution) was added to the solution. It was stirred for 30 min. When a THF (10 mL) solution of $Cp_2ZrCl_2$ (707 mg, 2.44 mmol) was added via a dropping funnel, it was yellow in color. After stirring for 22 h, the solvent was removed in vacuo. The residue was extracted with small portions of benzene (a total of 50 mL), and each portion was filtered and combined. After removal of solvent, the recrystallization of the residue from pentane gave **7b** (1.33 g, 90%) as yellow crystals. $^1$H NMR (400 MHz, $C_6D_6$) $\delta$=1.41 (18H, s), 5.66 (5H, s), 6.12 (5H, s), 7.10—7.25 (6H, m), 7.98—8.05 (4H, m); $^{13}$C NMR (100 MHz, $C_6D_6$) $\delta$=24.4 (s), 28.5 (q), 115.1 (d), 115.3 (d), 127.6 (d), 129.1 (d), 136.3 (d), 140.3 (s); $^{29}$Si NMR (80 MHz, $C_6D_6$) $\delta$=31.73; MS *m/z* 608 ($M^+$), 551 ($M^+-57$). Found: *m/z* 608.1077. Calcd for $C_{30}H_{38}S_2Si_2Zr$: M, 608.1001.

**Reaction of 7a with $SCl_2$.** A 50 mL round-bottom flask was charged with **7a** (247 mg, 0.436 mmol) and $CS_2$ (10.0 mL). The flask was cooled to −78 °C (dry ice/MeOH bath), and then a $CS_2$ (10.0 mL) solution of $SCl_2$ (45.0 mg, 0.436 mmol) was added dropwise to the solution. The solution color changed from green to red. After 30 min, it was warmed to room temperature. Solvent was removed in vacuo, and the residue was extracted with ca. 20 mL of pentane and filtered. After removal of solvent, the residue was recrystallized from pentane to yield **8a** (120 mg, 90%) as yellow crystals. Mp 119 °C; $^1$H NMR (400 MHz, $C_6D_6$) $\delta$=0.95 (18H, s), 6.63—6.73 (6H, m), 6.90—6.91 (4H, m); $^{13}$C NMR (100 MHz, $C_6D_6$) $\delta$=22.5 (s), 29.5 (q), 127.8 (d), 127.9 (d), 129.4 (d), 135.6 (s); $^{29}$Si NMR (80 MHz, $C_6D_6$) $\delta$=28.42; MS *m/z* 420 ($M^+$), 363 ($M^+-57$). Found: C, 57.31; H, 6.61%. Calcd for $C_{20}H_{28}S_3Si_2$: C, 57.09; H, 6.66%.

**Reaction of 7b with $SCl_2$.** A 20 mL round-bottom flask was charged with **7b** (149 mg, 0.220 mmol) and $CS_2$ (5.0 mL). The flask was cooled to −78 °C (dry ice/MeOH bath), and then a $CS_2$ (3.0 mL) solution of $SCl_2$ (24.8 mg, 0.240 mmol) was added dropwise to the mixture. After 30 min, it was warmed to room temperature. Solvent was removed in vacuo, and the residue was extracted with ca. 20 mL of hexane and filtered. After removal of solvent, the residue was separated by GPC (eluent; toluene) to yield **8a** (85.8 mg, 93%) as yellow crystals.

**Reaction of 7a with $S_2Cl_2$.** A three-necked 30 mL round-bottom flask was charged with **7a** (134 mg, 0.237 mmol) and $CS_2$ (10.0 mL). The flask was cooled to −78 °C (dry ice/MeOH bath), and then a $CS_2$ (10.0 mL) solution of $S_2Cl_2$ (32.0 mg, 0.237 mmol) was added dropwise to the flask. The solution color changed from green to red. After 30 min, it was warmed to room temperature. Solvent was removed in vacuo, and the the residue was extracted with ca. 20 mL of pentane and it was filtered. After removal of solvent, the residue was recrystallized from pentane to yield **8b** (98.5 mg, 92%) as yellow crystals. $^1$H NMR (90 MHz, $C_6D_6$) $\delta$= 1.25 (18H, s), 7.03—7.16 (6H, m), 7.50—7.61 (4H, m); $^{29}$Si NMR (80 MHz, $C_6D_6$) $\delta$=−7.79; MS *m/z* 452 ($M^+$), 420 ($M^+-32$), 395 ($M^+-57$). Found: C, 53.36; H, 5.92%. Calcd for $C_{20}H_{28}S_4Si_2$: C, 53.04; H, 6.19%.

**Reaction of 7b with $S_2Cl_2$.** A 30 mL round-bottom flask was charged with **7b** (259 mg, 0.425 mmol) and $CS_2$ (10.0 mL). The flask was cooled to −78 °C (dry ice/MeOH bath), and then a $CS_2$ (10.0 mL) solution of $S_2Cl_2$ (62.5 mg, 0.46 mmol) was added dropwise to the mixture. After 30 min, it was warmed to room temperature. Solvent was removed in vacuo, and the residue was extracted with ca. 20 mL of hexane and filtered. After removal of solvent, the residue was separated by GPC (eluent; toluene) to yield **8b** (127 mg, 66%) as yellow crystals.

**Reaction of 7a with $Se_2Cl_2$.** A three-necked 30 mL round-bottom flask was charged with **7a** (129 mg, 0.288 mmol) and $CS_2$ (8.0 mL). The flask was cooled to −78 °C (dry ice/MeOH bath), and then a $CS_2$ (8.0 mL) solution of $Se_2Cl_2$ (53.7 mg, 0.251 mmol) was added dropwise to the flask. The solution color changed from green to red. After 30 min, it was warmed to room temperature. Solvent was removed under reduced pressure, and the residue was extracted with ca. 10 mL of pentane and filtered. After removal of solvent, almost pure **8c** (112 mg, 90%) was yielded as a yellow solid. $^1$H NMR (300 MHz, $C_6D_6$) $\delta$=1.21 (18H, s), 6.92—7.03 (6H, m), 7.48—7.51 (4H, m); $^{13}$C NMR (100 MHz, $C_6D_6$) $\delta$=23.4 (s), 29.3 (q), 127.8 (d), 129.3 (d), 133.6 (d), 135.6 (s); $^{29}$Si NMR (80 MHz,$C_6D_6$) $\delta$=30.0; MS *m/z* 546 ($M^+$). Found: C, 44.23; H, 5.02%. Calcd for $C_{20}H_{28}S_2Se_2Si_2$: C, 43.94; H, 5.13%.

**Reaction of 7b with $Se_2Cl_2$.** A three-necked 30 mL round-bottom flask was charged with **7b** (139 mg, 0.228 mmol) and $CS_2$ (8.0 mL). The flask was cooled to −78 °C (dry ice/MeOH bath), and then a $CS_2$ (8.0 mL) solution of $Se_2Cl_2$ (53.7 mg, 0.251 mmol) was added dropwise to the flask. After 30 min, it was warmed to room temperature. Solvent was removed in vacuo, and the residue was extracted with ca. 10 mL of pentane and filtered. After removal of solvent, almost pure **8c** (123 mg, quant.) was yielded as a yellow solid.

**Reaction of 7a with $Ph_2GeCl_2$.** A 20 mL round-bottom flask prepared with a reflux condenser was charged with **7a** (143 mg, 0.252 mmol) and toluene (10.0 mL). $Ph_2GeCl_2$ (75.0 mg, 0.252 mmol) was added to the flask, and the mixture was refluxed for 24 h. The solution color changed from green to red. After removal of solvent, the residue was extracted with ca. 20 mL of pentane. After being filtered and purified with GPC (eluent; toluene), the product **8d** (85.3 mg, 55%) was given as a white solid. $^1$H NMR (90 MHz, $C_6D_6$) $\delta$=1.26 (18H, s), 6.92—8.22 (20H, m); $^{13}$C NMR (75 MHz, $C_6D_6$) $\delta$=22.5 (s), 28.5 (q), 127.7 (d), 128.2 (d), 128.72 (d), 128.76 (d), 129.77 (d), 130.2 (d), 133.81 (d), 133.85 (d), 134.3 (s), 136.2 (d), 139.5 (s), 139.8 (s); $^{29}$Si NMR (80 MHz,$C_6D_6$) $\delta$=17.43; MS *m/z* 616 ($M^+$), 559 ($M^+-57$). Found: C, 62.66; H, 6.22%. Calcd for $C_{32}H_{38}S_2GeSi_2$: C, 62.44; H, 6.21%.

**Reaction of 7b with $Ph_2GeCl_2$.** A 20 mL round-bottom flask prepared with a reflux condenser was charged with **7b** (131 mg, 0.215 mmol) and toluene (5.0 mL). A toluene (5.0 mL) solution of $Ph_2GeCl_2$ (111 mg, 0.373 mmol) was added to a toluene solution of **7b**, and the mixture was refluxed for 24 h. After removal of solvent, the residue was extracted with ca. 20 mL of benzene. After filtration and purification with GPC (eluent; toluene), the product **8d** (52.7 mg, 40%) was given as a while solid.

**Desulfurization of 8b with $P(NMe_2)_3$.** A 5$\phi$ NMR tube was charged with **8b** (25 mg, 0.06 mmol) and benzene-$d_6$ (300 μL). Hexamethylphosphorous triamide (11 μL, 0.066 mmol) was added to a benzene solution of **8b**. The reaction was monitored by $^1$H NMR spectrum. After 15 min, **8b** was completely consumed and the $^1$H, $^{13}$C, and $^{29}$Si NMR spectra of the solution showed a single product, which agreed with those of **8a**.

**Desulfurization of 8a with $PPh_3$.** A mixture of **8a** (100 mg, 0.238 mmol), triphenylphosphine (68.6 mg, 0.262 mmol) and 5 mL of hexane was heated at 65 °C for 1 h. White precipitates were filtered off through celite under argon atmosphere. After removal of solvent, the residue was recrystallized from pentane to give **9** (92.0 mg, *cis* : *trans*=1 : 9), quantitatively. For **9** (*trans* form) : Mp 193—196 °C; $^1$H NMR (400 MHz, $C_6D_6$) $\delta$=0.94 (18H, s), 7.14—7.19 (6H, m), 7.28—7.84 (4H, m); $^{13}$C NMR (125 MHz, $C_6D_6$) $\delta$=23.0 (s), 24.6 (q), 127.9 (d), 128.3 (d), 130.2 (d), 134.1 (s); $^{29}$Si NMR (80 MHz,$C_6D_6$) $\delta$=14.02; MS *m/z* 388 ($M^+$), 331 ($M^+-57$). For

**9** (*cis* form): $^1$H NMR (400 MHz, $C_6D_6$) $\delta$=1.12 (18H, s), 6.94—6.99 (6H, m), 7.70—7.72 (4H, m); $^{29}$Si NMR (80 MHz, $C_6D_6$) $\delta$=13.93; MS *m/z* 388 ($M^+$), 331 ($M^+-57$). Found: C, 62.15; H, 6.85%. Calcd for $C_{20}H_{28}S_2Si_2$: C, 61.80; H, 7.21%.

**Desulfurization of 8a with P(NMe$_2$)$_3$.** A 5$\phi$ NMR tube was charged with **8a** (25 mg, 0.06 mmol) and benzene-$d_6$ (300 μL). Hexamethylphosphorous triamide (11 μL, 0.066 mmol) was added to a benzene solution of **8a**. The reaction was monitored by $^1$H NMR spectrum. After 15 min, **8a** was completely consumed and the $^1$H and $^{29}$Si NMR spectra of the mixture agreed with those of **9** (*cis* : *trans*=1 : 9).

**Crystallographic Analyses.** A green crystal of dimensions 0.50×0.50×0.40 mm$^3$ for **7a**, a yellow crystal of dimensions 0.50×0.50×0.20 mm$^3$ for **8a**, and a white crystal of dimensions 0.50×0.50×0.80 mm$^3$ for **9** obtained by recrystallization from a hexane or pentane were used for X-ray analyses. Diffraction measurements were made on an Enraf–Nonius CAD4 computer-controlled Kappa axis diffractometer by using graphite monochromatized Mo $K\alpha$ radiation. The unit cell was determined and refined from 25 randomly selected reflections obtained by using the CAD4 automatic search, center, index, and least-squares routines. Crystal data, data-collection parameters, and results of the analyses are listed in Table 2. All data processing was performed on a Micro VAX 3100 computer by using the MolEN structure-solving program obtained from Enraf–Nonius Corp., Delft, Netherlands. The $\omega$–2$\theta$ scan technique was adopted by varying the $\omega$ scan width as a function of $\theta$. All intensities were corrected for Lorents and polarization factors as well as decay correction. An empirical absorption correction based on a series of $\psi$-scan was also applied to the data. Neutral-atom scattering factors were calculated by the standard procedures.[11a] An anomalous dispersion correction was applied to all non-hydrogen atoms.[11b] Full-matrix least-squares refinements minimized the function $\Sigma w(|F_o|-|F_c|)^2$, $w$=1. The molecular structures with atomic labeling schemes and the bond lengths and angles of **7a**, **8a**, and **9** are given in Figs. 1, 2, and 3 and Tables 3, 4, 5, and 6, respectively.[12]

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