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Synthesis and Spectroscopic Properties of Novel Silacyclic Compounds Containing a Titanium and Some Chalcogen Atoms

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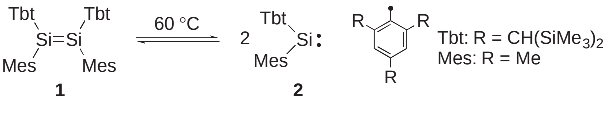
Novel silacyclic compounds containing a titanium and some chalcogen atoms, [Tbt(Mes)Si(μ-Ch)$_2$TiCp$_2$] and [Tbt(Mes)Si(μ-Ch)(μ-Ch$_2$)TiCp$_2$] (Ch = S and Se; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Mes = mesityl; Cp = cyclopentadienyl), were synthesized by the reactions of the disilene Tbt(Mes)Si=Si(Mes)Tbt with the corresponding [Cp$_2$TiCh$_5$] (Ch = S and Se). The spectroscopic properties of these compounds are presented together with the results of theoretical calculations.

The chemistry of metal polychalcogenido complexes has been extensively studied from the viewpoint of not only fundamental chemistry but also their potential for applications.[1–4] In recent years, silanechalcogenolato complexes of transition metals have attracted much attention as potential precursors for the controlled synthesis of mixed-metal chalcogenido clusters, and a number of such complexes have been synthesized.[5–8] By contrast, there are few reports on the chemistry of cyclic compounds having an Si–(Ch)$_n$–M (Ch = chalcogen, M = transition metal) linkage such as chelating silanedichalcogenolato complexes of transition metals.[9–14] Silacyclic compounds containing titanium and chalcogen atoms are very rare, and only three examples have been published to date; [Me$_2$Si(μ-S)$_2$Ti{C$_5$(Me)H$_4$}$_2$],[12] [Ph$_2$Si(μ-S)$_2$Ti(C$_5$H$_5$)$_2$],[11] and [{*t*-Bu(Ph)Si}$_2$(μ-S)$_2$Ti(C$_5$H$_5$)$_2$].[15] In addition, to the best of our knowledge, there is no report on the synthesis of cyclic compounds having silicon and transition-metal atoms bridged by selenium atoms. Even for the carbon analogues, only a few examples, such as [Cp$_2$Ti(μ-S)$_2$C=CR$_2$],[16] [Cp$_2$Ti(μ-S$_2$)$_2$CR$_2$], and [Cp$_2$Ti(μ-S)(μ-S$_3$)CR$_2$],[17] have been reported.

On the other hand, we have reported the synthesis of a variety of novel compounds of heavier main group elements, such as cyclic polychalcogenides containing a group 14 or 15 element,[18–25] multiply bonded compounds containing heavier group 14 or 15 elements,[19,26] and aromatic compounds containing a heavier group 14 element,[27] by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). In addition, we have synthesized an overcrowded disilene **1** having Tbt and mesityl (Mes) groups and found that it dissociates to the corresponding silylene **2** under mild conditions such as heating at 60 °C (Scheme 1).[28–30] It was shown that **2** reacts with S$_8$ to give the corresponding tetrathiosilolane Tbt(Mes)SiS$_4$ in a good yield via the insertion of the silylene into the S–S bond accompanied by the desulfurization.[29,30]



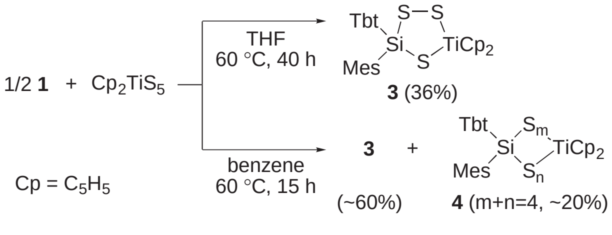
Scheme 1. Generation of silylene **2** from disilene **1**.

In this paper, we present the reactions of silylene **2** with titanocene pentachalcogenides giving novel silacyclic compounds containing a titanium and some chalcogen atoms together with the spectroscopic properties of the resulting heterocyclic compounds.

Results and Discussion

Synthesis of Silacyclic Compounds Containing Ti and S Atoms. After silylene **2**, generated from disilene **1**, was allowed to react with an equimolar amount of titanocene pentasulfide in THF at 60 °C for 40 h, the ^{1}H NMR spectrum of the crude mixture showed the formation of the five-membered ring compound **3**, Tbt(Mes)SiS$_4$ (≈15%),[24] Tbt(Mes)Si(μ-S)$_2$Si(Mes)Tbt (≈8%)[31] and unreacted titanocene pentasulfide. Compound **3**, having a novel ring structure consisting of Si, Ti, and S atoms, was isolated as air-stable dark green crystals in 36% yield (Scheme 2); however, all the compounds except for **3** could not be separated from the mixture. The structure of **3** was determined by the ^{1}H, ^{13}C, and ^{29}Si NMR spectra, mass spectrum, and elemental analysis. Although titanocene pentasulfide is known to react with alkynes to give the corresponding ethylene-1,2-dithiolato complexes,[1,32,33] no adduct between titanocene pentasulfide and disilene **1** was obtained in this reaction.

On the other hand, when benzene was used as the reaction solvent instead of THF, the reaction of **1** with titanocene pentasulfide gave a mixture of **3** (≈60%) and a six-membered ring compound **4** (≈20%) (Scheme 2) together with a small amount of Tbt(Mes)SiS$_4$ and Tbt(Mes)Si(μ-S)$_2$Si(Mes)Tbt. Attempts to separate the mixture of **3** and **4** by gel permeation



Scheme 2. Reaction of disilene **1** with [Cp$_2$TiS$_5$].

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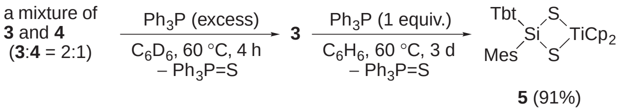
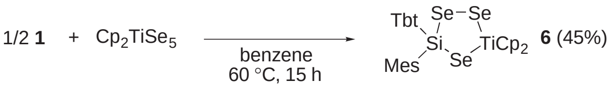
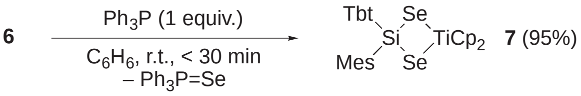


Scheme 3. Desulfurization of **3** and **4**.



Scheme 4. Reaction of disilene **1** with $[Cp_2TiSe_5]$.



Scheme 5. Deselenation of **6**.

liquid chromatography (GPLC), wet column chromatography (WCC), and recrystallization were unsuccessful. The mass spectrum of the mixture of **3** and **4** showed a peak envelope corresponding to that of the six-membered ring compound, $C_{46}H_{81}S_4Si_7Ti$ ($[M + H]^+$), without the peaks in the region of the larger mass numbers. Since the thermolysis of the mixture of **3** and **4** (**3**:**4** = 5:3) in THF-d_8 at 60 °C for 12 h and the reaction of **3** with elemental sulfur (5 molar amounts as S) in C_6D_6 at 60 °C for 12 h resulted in no reaction, the interconversion between **3** and **4** does not occur in the reaction of **1** with titanocene pentasulfide.

The reaction of a mixture of **3** and **4** (**3**:**4** = 2:1) with an excess amount of Ph_3P in C_6D_6 at 60 °C for 4 h resulted in the quantitative conversion to **3** along with the formation of a 0.33 molar amount of $Ph_3P{=}S$ (Scheme 3), which supports the six-membered ring structure of **4**. The desulfurization of **3** with an equimolar amount of Ph_3P in benzene at 60 °C for 3 days gave the corresponding silanedithiolato complex **5** as orange crystals in 91% yield together with $Ph_3P{=}S$ (quant). The characterization of **5** was also performed by using spectroscopic data. Attempts to desulfurize **3** with an excess amount of various phosphine reagents, R_3P (R = Ph, *n*-Bu, Me_2N, MeO, and Me), only resulted in the formation of **5** in a quantitative yield without further desulfurization of **5**.

Synthesis of Silacyclic Compounds Containing Ti and Se Atoms. The reaction of disilene **1** with titanocene pentaselenide in C_6D_6 at 60 °C for 15 h resulted in the formation of the corresponding five-membered ring compound **6** without yielding other cyclic compounds such as the selenium analog of **4** (Scheme 4). Since **6** is sensitive to air and moisture, the isolation of **6** required the purification of the reaction mixture with wet column chromatography using dried silica gel under argon atmosphere (isolated yield: 45%; green crystals). The structure of **6** was determined by ^1H, ^{13}C, ^{29}Si, ^{77}Se NMR spectroscopy and mass spectroscopy. X-ray structural analysis also supported its structure, although detailed structural features can not be discussed because of the poor quality of the crystals. The reactions of **1** with titanocene pentaselenide in various solutions such as benzene, THF, and ether also gave **6** in similar yields without the formation of other cyclic compounds. These results are in sharp contrast to the reactions with the sulfur analog which gave a mixture of **3** and **4** when benzene was used as the solvent.

Table 1. Observed and Calculated ^{29}Si NMR Chemical Shifts for the Silacyclic Compounds Containing a Titanium and Some Chalcogen Atoms

Compound	Observed δ_{Si}/ppm[a)]	Calculated δ_{Si}/ppm[b),c)]
3	46.5	66.6
5	−52.7	−56.8
6	32.0	81.3
7	−57.2	−53.2

a) 59 MHz, in C_6D_6. b) Both of Tbt and Mes groups are replaced by 2,6-dimethylphenyl groups. c) Calculated level: GIAO-B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d).

Table 2. Observed and Calculated ^{77}Se NMR Chemical Shifts for the Silacyclic Compounds Containing a Titanium and Some Selenium Atoms

Compound	Position	Observed δ_{Se} /ppm	Calculated δ_{Se} /ppm[a),b)]
6[c)]	α	681.0	691.6
	β	1282.6	1489.2
	γ	407.5	530.2
7[d)]		228.1	260.7, 261.6

a) Both of Tbt and Mes groups are replaced by 2,6-dimethylphenyl groups. b) Calculated level: GIAO-B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d). c) 95 MHz, in C_7D_8 at 330 K. d) 95 MHz, in C_6D_6 at 298 K.

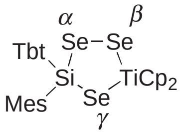


Chart 1.

The deselenation of **6** with an equimolar amount of Ph_3P proceeded smoothly at room temperature to give the corresponding silanediselenolato complex **7**, which is sensitive to air and moisture (Scheme 5). Compound **7** was isolated as yellow crystals in 95% yield upon the separation from $Ph_3P{=}Se$, which is only slightly soluble in hexane, by filtration of a hexane suspension of the reaction mixture. Compound **7** was characterized by the spectroscopic data.

Deselenation at room temperature appeared to occur more easily than the desulfurization of the mixture of **3** and **4**, which required heating at 60 °C. However, further deselenation of **7** with phosphine reagents, such as R_3P (R = Ph, Bu, Me_2N, and Me), did not proceed even on heating at 100 °C or by irradiating (λ = 300–500 nm).

NMR Spectra. Tables 1 and 2 show the ^{29}Si NMR data of **3**, **5**, **6**, and **7** and ^{77}Se NMR chemical shifts of **6** and **7**, respectively, along with the calculated chemical shifts of the model compounds, **3′**, **5′**, **6′**, and **7′**, in which both of the Tbt and Mes groups of the real molecules are replaced by 2,6-dimethylphenyl (Dmp) groups (Chart 1). The observed values are consistent with the calculated ones, and this result supports the proposed structure of these compounds. It is notable that the ^{29}Si NMR chemical shifts of four-membered ring com-

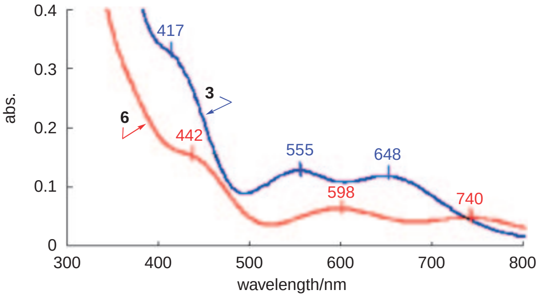


Fig. 1. UV–vis spectra of **3** (blue line) and **6** (red line) in hexane solutions (1×10^{-4} mol L^{-1}).

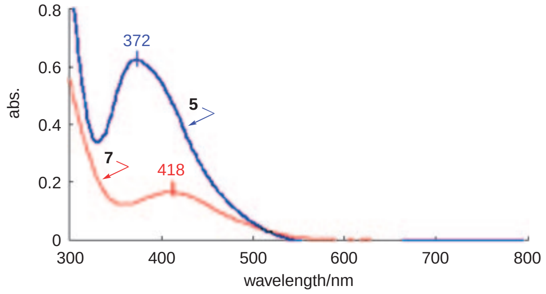


Fig. 2. UV–vis spectra of **5** (blue line) and **7** (red line) in hexane solutions (1×10^{-4} mol L^{-1}).

Table 3. Observed and Calculated Absorption Maxima of **3**, **5**, **6**, and **7**

Compound	Observed $\lambda_{\max}$ (ε) /nm	Calculated $\lambda_{\max}$ (f)[a),b)] /nm	Transitions	Atomic character[c)]
3	417 (3.2×10^3)	396 (0.0100)	HOMO−5 → LUMO	Dmp → Ti
	555 (1.3×10^3)	552 (0.0122)	HOMO−1 → LUMO	S_3 (p_z) → Ti
	648 (1.2×10^3)	600 (0.0067)	HOMO → LUMO	S_3 (p_z) → Ti
6	442 (1.5×10^3)	397 (0.0129)	HOMO−5 → LUMO	Dmp → Ti
	598 (6.3×10^2)	580 (0.0116)	HOMO−1 → LUMO	Se_3 (p_z) → Ti
	740 (4.7×10^2)	654 (0.0085)	HOMO → LUMO	Se_3 (p_z) → Ti
5	372 (6.0×10^3)	392 (0.0452)	HOMO−3 → LUMO	Dmp → Ti
		652 (0.0006)	HOMO−1 → LUMO	S_2 (p_z) → Ti
		684 (0.0024)	HOMO → LUMO	S_2 (p_z) → Ti
7	418 (2.0×10^3)	407 (0.0470)	HOMO−3 → LUMO	Dmp → Ti
		758 (0.0010)	HOMO−1 → LUMO	Se_2 (p_z) → Ti
		760 (0.0024)	HOMO → LUMO	Se_2 (p_z) → Ti

a) Both of Tbt and Mes groups are replaced by 2,6-dimethylphenyl groups. b) Calculated level: TD-B3LYP/6-31G(d)//B3LYP/6-31G(d). c) The major atomic character of the transition.

pounds **5** and **7** are observed in the high-field region. This is interesting because the NMR spectra of four-membered ring compounds generally show normal chemical shifts, although three-membered ring compounds show higher-field chemical shifts in the NMR spectra; for example, the ^{13}C NMR chemical shift of cyclopropane is −2.8 ppm while that of cyclobutane is 22.9 ppm.[34]

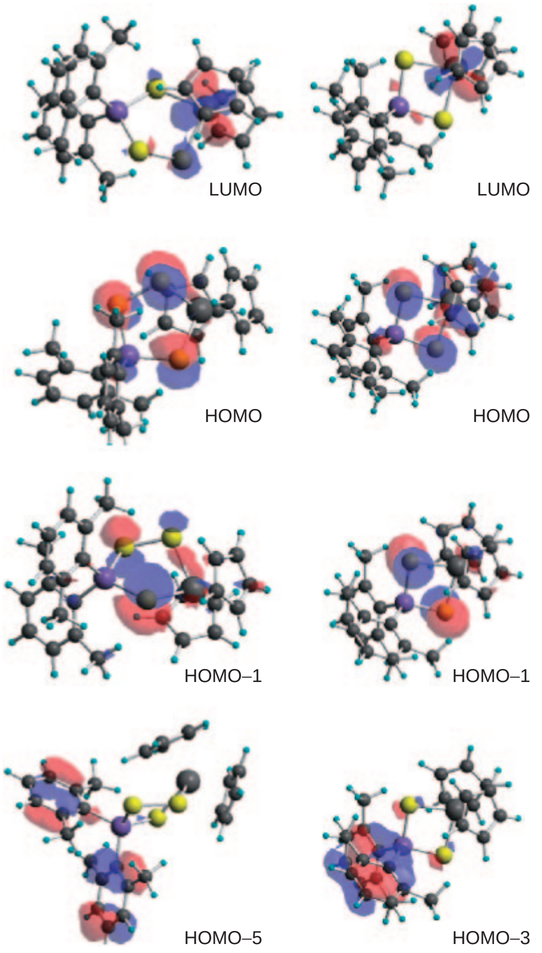
UV–Vis Spectra. Figure 1 shows the UV–vis spectra of the five-membered ring compounds **3** and **6**, both of which showed three absorption maxima in the visible region. The pattern of the UV–vis spectrum of the two compounds is similar, which indicates that **3** and **6** have similar electronic structures. In addition, the absorption maxima of the selenium congener **6** shifts to the longer wavelength region with smaller absorption coefficients compared with those of the sulfur congener **3**.

The UV–vis spectra of four-membered ring compounds **5** and **7** are shown in Fig. 2. The absorption maxima of **5** and **7** are observed around 400 nm, and also in this case, the absorption maximum in the UV–vis spectrum of **7** was observed at longer wavelength region with a smaller absorption coefficient than those of the sulfur analog **5**.

To assign the absorption maxima, time-dependent density-functional theory (TDDFT) calculations of model molecules were performed. The observed and calculated absorption maxima are listed in Table 3 and the calculated molecular orbitals of [$Dmp_2SiS_3TiCp_2$] (**3′**) and [$Dmp_2SiS_2TiCp_2$] (**5′**) are depicted in Fig. 3. The TD-B3LYP calculations of **3′** gave three absorption maxima in visible region similar to the observed UV–vis spectrum of **3**. The observed absorption maxima at 417, 555, and 648 nm can be assigned to HOMO−5 → LUMO (Dmp → Ti), HOMO−1 → LUMO (S_3 (p_z) → Ti), and HOMO → LUMO (S_3 (p_z) → Ti) transitions, respectively. The observed UV–vis spectrum of **5** showed one absorption maximum in visible region, while the TD-B3LYP calculations of **5′** indicated that there should be three absorption maxima in visible region. This difference is due to the small f values for the calculated absorptions at 652 ($f = 0.0006$) and 684 ($f = 0.0024$) nm.

The calculated molecular orbitals of the selenium analogues **6′** and **7′** are almost the same as those of the sulfur analogues **3′** and **5′**, respectively. The observed absorption maxima of **6** and **7** were assigned in a manner similar to the case of the sulfur analogues **3** and **5** (Table 3).

In conclusion, novel silacyclic compounds containing a titanium and some chalcogen atoms have been prepared by the reactions of a bulky silylene (**2**) with titanocene pentachalcogenide. The structures of the newly obtained silacyclic compounds were determined by the spectroscopy and elemental analysis, and the maxima in the UV–vis spectra were assigned based on TD-B3LYP calculations.



[$Dmp_2SiS_3TiCp_2$] (**3'**) [$Dmp_2SiS_2TiCp_2$] (**5'**)

Fig. 3. Molecular orbitals of **3′** and **5′**.

Experimental

General Procedure. All experiments were performed under anhydrous conditions and an argon atmosphere unless otherwise noted. All solvents used in the reactions were purified prior to use by the standard methods and/or by using an Ultimate Solvent System (Glass Contour Company).[35] C_6D_6, used as a reaction solvent, was dried over Na, and then a K mirror. ^{1}H NMR (300 MHz) spectra were measured in C_6D_6 on a JEOL AL-300 spectrometer using C_6D_5H (7.15 ppm) as an internal standard. ^{13}C NMR (75 MHz) spectra were recorded on a JEOL JNM AL-300 spectrometer. ^{13}C NMR chemical shifts are reported as ppm downfield from tetramethylsilane and were referenced to the signal of C_6D_6 (128.0 ppm). Multiplicity of signals in the ^{13}C NMR spectra was determined with the DEPT technique. ^{29}Si NMR (59 MHz) and ^{77}Se NMR (95 MHz) spectra were recorded on a JEOL JNM AL-300 spectrometer. IR and electronic spectra were recorded on a JASCO FT/IR-5300 spectrometer and a JASCO Ubest V-750 UV–vis spectrometer, respectively. Mass spectral data were obtained on a JEOL JMS-700 spectrometer. Elemental analyses were carried out at the Microanalytical Laboratory of Institute for Chemical Research, Kyoto University. All melting points were measured on a Yanaco micro melting points apparatus and are uncorrected. Wet column chromatography (WCC) and preparative thin-layer chromatography (PTLC) were performed using Wakogel C-200 and Merk Kieselgel 60 PF_{254}, respectively. Gel permeation liquid chromatography (GPLC) was performed on a LC-908, LC-918, or LC-908-C60 (Japan Analytical Industry Co., Ltd. Systems) equipped with JAIGEL 1H and 2H columns (eluent: chloroform or toluene).

Preparation of Materials. Disilene **1**,[29] titanocene pentasulfide, and titanocene pentaselenide[36] were prepared according to the reported methods.

Preparation of [Tbt(Mes)SiS$_3$TiCp$_2$] (3). In a 10 ϕ Pyrex glass tube was placed a THF solution (2.0 mL) of a mixture of disilene **1** (40.0 mg, 28.6 µmol) and titanocene pentasulfide (19.4 mg, 57.2 µmol). After three freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was heated at 60 °C for 40 h, during which time the original orange suspension turned into a deep black solution. The tube was opened, and the solvent was removed under reduced pressure. After the addition of C_6H_6 to the residue, the mixture was filtered through Celite®, and the solvent was evaporated. The residue was separated by GPLC (toluene) and then PTLC (hexane:Et$_2$O = 2:1) to afford pure [Tbt(Mes)SiS$_3$TiCp$_2$] (**3**) (20.0 mg, 21.0 µmol, 36%). **3**: dark green crystals, mp 78 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6) δ 0.1–0.5 (54H), 1.52 (s, 1H), 2.06 (s, 3H), 2.48 (s, 3H), 2.71 (s, 2H), 3.50 (s, 3H), 5.82 (s, 5H), 6.05 (s, 5H), 6.59 (s, 1H), 6.67 (s, 1H), 6.77 (s, 1H), 7.01 (s, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 1.22 (q), 2.17 (q), 2.48 (q), 20.94 (q × 2), 25.93 (d), 27.42 (d), 29.35 (d), 30.92 (q), 114.88 (d), 115.54 (d), 123.32 (d), 128.18 (d), 129.07 (d), 130.68 (d), 137.17 (s), 138.47 (s), 138.79 (s), 143.81 (s), 144.12 (s), 144.98 (s), 153.9 (s × 2); ^{29}Si NMR (59 MHz, C_6D_6) δ −0.6, 1.8, 46.5; MS (FAB$^+$): calcd for $C_{46}H_{80}S_3Si_7Ti$: 972, found: m/z 973 $[M + H]^+$, 907 $[M - Cp]^+$, 875 $[M - Cp - S]^+$; HRMS (FAB$^+$) calcd for $C_{46}H_{81}S_3Si_7Ti$ ($[M + H]^+$): 973.3365, found: m/z 973.3391 ($[M + H]^+$); UV–vis (hexane): λ_{max} 417 ($\varepsilon = 3.2 \times 10^3$ (M^{-1} cm^{-1})), 555 ($\varepsilon = 1.3 \times 10^3$), 648 ($\varepsilon = 1.2 \times 10^3$) nm. Anal. Calcd for $C_{46}H_{80}S_3Si_7Ti$: C, 56.74; H, 8.28%. Found: C, 56.68; H, 8.27%.

Preparation of a Mixture of [Tbt(Mes)SiS$_3$TiCp$_2$] (3) and [Tbt(Mes)SiS$_4$TiCp$_2$] (4). In a 10 ϕ Pyrex glass tube was placed a C_6H_6 solution (2.0 mL) of a mixture of disilene **1** (40.0 mg, 28.6 µmol) and titanocene pentasulfide (19.4 mg, 57.2 µmol). After three freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was heated at 60 °C for 15 h, during which time the original orange suspension turned into a deep black solution. The tube was opened, the solvent was removed under reduced pressure, and C_6H_6 was added to the residue. The mixture was filtered through Celite®, and the filtrate was evaporated. The residue was separated by GPLC (toluene) and PTLC (hexane: Et$_2$O = 2:1) to afford a mixture of [Tbt(Mes)SiS$_3$TiCp$_2$] (**3**) and [Tbt(Mes)SiS$_4$TiCp$_2$] (**4**). Although the mixture of **3** and **4** could not be separated, the yields of these products were estimated as 60 and 22%, respectively, based on the integrated intensity in the ^{1}H NMR spectrum. **4** (not isolated): ^{1}H NMR (300 MHz, C_6D_6) δ 0.21 (s, 36H), 0.44 (s, 18H), 1.53 (s, 1H), 2.11 (s, 3H), 2.81 (s, 2H), 2.96 (s, 6H), 5.64 (s, 5H), 5.96 (s, 5H), 6.60 (s, 1H), 6.68 (s, 1H), 6.76 (s, 2H); ^{13}C NMR (75 MHz, C_6D_6) δ 1.17 (q), 2.16 (q), 2.48 (q), 20.92 (q), 27.18 (q), 27.40 (d), 29.31 (d), 31.90 (d), 113.98 (d), 114.46 (d), 123.93 (d), 129.53 (d), 130.34 (d), 133.91 (s), 139.05 (s), 140.50 (s), 143.88 (s), 144.62 (s), 144.99 (s), 145.56 (s); MS (FAB$^+$) calcd for $C_{46}H_{80}S_4Si_7Ti$: 1004, found: m/z 1005 $[M + H]^+$, 1004 $[M]^+$, 939 $[M - Cp]^+$; HRMS (FAB$^+$) calcd for $C_{46}H_{81}S_4Si_7Ti$ ($[M + H]^+$): 1005.3085, found: m/z 1005.3129 ($[M + H]^+$).

Reaction of [Tbt(Mes)SiS$_3$TiCp$_2$] (3) with an Equimolar

Amount of Triphenylphosphine (Preparation of [Tbt(Mes)SiS$_2$TiCp$_2$] (5)). In a 5 ϕ Pyrex glass tube was placed a C_6D_6 solution (0.5 mL) of a mixture of [Tbt(Mes)SiS$_3$TiCp$_2$] (**3**) (65.6 mg, 67.4 µmol) and triphenylphosphine (17.7 mg, 67.4 µmol). After three freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was heated at 60 °C for 3 days, during which time the original dark green color turned into orange color. The tube was opened, and the solvent was removed under reduced pressure in a glovebox filled with argon. Hexane was added to the mixture containing [Tbt(Mes)SiS$_2$TiCp$_2$] (**5**) and triphenylphosphine sulfide. The mixture was filtered through Celite® to remove triphenylphosphine sulfide, which is only slightly soluble in hexane. Evaporation of the solvent from filtrate gave pure **5** (57.6 mg, 61.3 µmol, 91%). **5**: orange solid; ^{1}H NMR (300 MHz, C_6D_6) δ 0.23 (s, 18H), 0.34 (s, 18H), 0.42 (s, 18H), 1.53 (s, 1H), 2.11 (s, 3H), 3.06 (s, 6H), 3.23 (s, 1H), 3.69 (s, 1H), 5.85 (s, 5H), 6.30 (s, 5H), 6.63 (s, 1H), 6.71 (s, 1H), 6.83 (s, 2H); ^{13}C NMR (75 MHz, C_6D_6) δ 1.38 (q), 2.48 (q), 2.56 (q), 20.94 (q), 26.56 (q), 27.97 (d), 28.16 (d), 30.73 (d), 119.42 (d), 120.01 (d), 124.80 (d), 128.56 (d), 130.46 (d), 130.53 (s), 138.03 (s), 140.33 (s), 143.50 (s), 144.80 (s), 153.28 (s), 153.89 (s); ^{29}Si NMR (59 MHz, C_6D_6) δ −52.7, 2.0, 2.6; MS (FAB$^+$) calcd for $C_{46}H_{81}S_2Si_7Ti$: 940, found: m/z 941 $[M+H]^+$, 875 $[(M-Cp)]^+$; HRMS (FAB$^+$) calcd for $C_{46}H_{81}S_2Si_7Ti$ ($[M+H]^+$): 941.3644, found: m/z 941.3681 ($[M+H]^+$); UV–vis (hexane): λ_{max} 372 ($\varepsilon = 6 \times 10^3$) nm.

Reaction of a Mixture of [Tbt(Mes)SiS$_3$TiCp$_2$] (3) and [Tbt(Mes)SiS$_4$TiCp$_2$] (4) with an Excess Amount of Triphenylphosphine. In a 5 ϕ Pyrex glass tube was placed a C_6D_6 solution (0.5 mL) of a mixture of [Tbt(Mes)SiS$_3$TiCp$_2$] (**3**) and [Tbt(Mes)SiS$_4$TiCp$_2$] (**4**) (total 50 mg, with a ratio of **3**:**4** = 2:1) and triphenylphosphine (60 mg, 228.5 µmol). After three freeze–pump–thaw cycles, the tube was evacuated and sealed. When the solution was heated at 60 °C for 4 h, the original mixture of **3** and **4** converged to **3**, and the formation of a 0.33 molar amount of $Ph_3P{=}S$ was confirmed by ^{1}H NMR spectroscopy. Further heating at 60 °C for 4 days gave [Tbt(Mes)SiS$_2$TiCp$_2$] (**5**) quantitatively.

Reaction of [Tbt(Mes)SiS$_3$TiCp$_2$] (3) with an Excess Amount of R_3P (R = Ph, *n*-Bu, Me$_2$N, Me, and MeO). Except for triphenylphosphine (solid) and trimethylphosphine, other trivalent phosphorus reagents were distilled from CaH_2 or Na under an argon atmosphere or reduced pressure. In a 5 ϕ Pyrex glass tube was placed a C_6D_6 solution (0.5 mL) of a mixture of [Tbt(Mes)SiS$_3$TiCp$_2$] (**3**) and an excess amount of a trivalent phosphorus reagent. After three freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was left at room temperature or heated. All of the reactions gave [Tbt(Mes)SiS$_2$TiCp$_2$] (**5**) quantitatively together with an equimolar amount of the corresponding phosphine sulfide.

Preparation of [Tbt(Mes)SiSe$_3$TiCp$_2$] (6). In a 10 ϕ Pyrex glass tube was placed a THF solution (2.0 mL) of a mixture of disilene **1** (50.0 mg, 35.7 µmol) and titanocene pentaselenide (41.0 mg, 71.6 µmol). After three freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was heated at 60 °C for 15 h, during which time the original orange suspension turned into a green solution. The tube was opened, and the solvent was removed under reduced pressure in a glovebox filled with argon. After the addition of C_6H_6 to the residue, the mixture was filtered through Celite®, and the solvent was evaporated from the filtrate. The residue was separated by PTLC (hexane, then benzene) to afford pure [Tbt(Mes)SiSe$_3$TiCp$_2$] (**6**) (35.9 mg, 32.2 µmol, 45%) as a green solid. **6**: dark green crystals, mp 157 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6) δ −0.2–0.8 (54H), 1.51 (s, 1H), 2.10 (s, 3H), 2.51 (s, 3H), 2.60 (s, 1H), 2.62 (s, 1H), 3.61 (s, 3H), 5.83 (s, 5H), 6.02 (s, 5H), 6.5–6.8 (2H), 6.79 (s, 1H), 7.02 (s, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 1.34 (q), 1.37 (q), 2.61 (q), 2.72 (q), 20.94 (q), 26.95 (q), 28.36 (d), 28.63 (d), 30.74 (d), 119.21 (d), 119.81 (d), 124.84 (d), 130.25 (s), 132.94 (s), 133.08 (s), 137.94 (s), 139.14 (s), 143.59 (d), 144.59 (d), 153.45 (s), 154.27 (s); ^{29}Si NMR (59 MHz, C_6D_6) δ 2.2, 32.0; ^{77}Se NMR (95 MHz, C_7D_8, 60 °C) δ 407.5, 681.0, 1282.6; MS (FAB$^+$) calcd for $C_{46}H_{80}{}^{78}Se^{80}Se_2Si_7Ti$: 1114, found: m/z 1114 $[M]^+$, 1049 $[M-Cp]^+$; HRMS (FAB$^+$) calcd for $C_{46}H_{80}{}^{78}Se^{80}Se_2Si_7Ti$ ($[M]^+$): 1114.1628, found: m/z 1114.1649 $[M]^+$; UV–vis (hexane): λ_{max} 442 ($\varepsilon = 1.5 \times 10^3$), 598 ($\varepsilon = 6.3 \times 10^2$), 740 ($\varepsilon = 4.7 \times 10^2$) nm.

Reaction of [Tbt(Mes)SiSe$_3$TiCp$_2$] (6) with an Equimolar Amount of Triphenylphosphine (Preparation of [Tbt(Mes)SiSe$_2$TiCp$_2$] (7)). In a 5 ϕ Pyrex glass tube was placed a C_6D_6 solution (0.5 mL) of a mixture of [Tbt(Mes)SiSe$_3$TiCp$_2$] (**6**) (63.6 mg, 57.3 µmol) and triphenylphosphine (15.0 mg, 57.3 µmol). After three freeze–pump–thaw cycles, the tube was evacuated and sealed. The mixture was stirred for 30 min, during which time the original green color turned into dark yellow color. The ^{1}H NMR spectrum of the reaction mixture showed the quantitative formation of [Tbt(Mes)SiSe$_2$TiCp$_2$] (**7**) and triphenylphosphine selenide. The tube was opened in a glovebox filled with argon, and the solvent was removed under reduced pressure. After the addition of hexane to the residue, the mixture was filtered through Celite® to remove triphenylphosphine selenide. The filtrate was evaporated to give pure compound **7** (56.4 mg, 54.4 µmol, 95%). **7**: yellow solid; ^{1}H NMR (300 MHz, C_6D_6) δ 0.22 (s, 18H), 0.36 (s, 18H), 0.44 (s, 18H), 1.51 (s, 1H), 2.13 (s, 3H), 3.14 (s, 6H), 3.23 (s, 1H), 3.64 (s, 1H), 5.97 (s, 5H), 6.31 (s, 5H), 6.63 (s, 1H), 6.73 (s, 1H), 6.85 (s, 2H); ^{13}C NMR (75 MHz, C_6D_6) δ 1.34 (q), 1.37 (q), 2.61 (q), 2.72 (q), 20.94 (q), 26.95 (q), 28.36 (d), 28.63 (d), 30.74 (d), 119.21 (d), 119.81 (d), 124.84 (d), 130.25 (s), 132.94 (s), 133.08 (s), 137.94 (s), 139.14 (s), 143.59 (d), 144.59 (d), 153.45 (s), 154.27 (s); ^{29}Si NMR (59 MHz, C_6D_6) δ −57.2, 2.1, 2.6; MS (FAB$^+$) calcd for $C_{46}H_{80}{}^{80}Se_2Si_7Ti$: 1036, found: m/z 1036 $[M]^+$, 971 $[(M-Cp)]^+$; HRMS (FAB$^+$) calcd for $C_{46}H_{80}{}^{80}Se_2Si_7Ti$ ($[M]^+$): 1036.2455, found: m/z 1036.2466 ($[M]^+$); UV–vis (hexane) λ_{max} 418 ($\varepsilon = 2.0 \times 10^3$).

Reaction of [Tbt(Mes)SiSe$_3$TiCp$_2$] (6) with an Excess Amount of R_3P (R = Ph, Bu, Me$_2$N, and Me). Except for triphenylphosphine (solid) and trimethylphosphine, other trivalent phosphorus reagents were all distilled from CaH_2 or Na under an argon atmosphere or reduced pressure. In a 5 ϕ Pyrex glass tube was placed a C_6D_6 solution (0.5 mL) of a mixture of [Tbt(Mes)SiSe$_3$TiCp$_2$] (**6**) and an excess amount of a trivalent phosphorus reagent. After three freeze–pump–thaw cycles, the tube was evacuated and sealed. In all cases, the reaction immediately proceeded at room temperature to give quantitatively [Tbt(Mes)SiSe$_2$TiCp$_2$] (**7**) together with an equimolar amount of the corresponding phosphine selenide.

Photoreaction of a Mixture of [Tbt(Mes)SiSe$_2$TiCp$_2$] (7) and Hexamethylphosphorous Triamide (HMPT). In a 5 ϕ Pyrex glass tube was placed a C_6D_6 solution (0.5 mL) of [Tbt(Mes)SiSe$_2$TiCp$_2$] (**7**) (36.4 mg, 32.7 µmol). HMPT (53.4 µL, 294.3 µmol), distilled from CaH_2, was added to the solution. After three freeze–pump–thaw cycles, the tube was evacuated and sealed. Heating of the solution at 100 °C for 3 h resulted in no reaction. The solution was irradiated (λ = 300–500 nm) using a Xe lamp through a UV cut filter (HOYA colored optical glass B390,

$300 < \lambda < 500$ nm transfer). No reaction occurred, even after irradiation for 15 h. Further irradiation resulted in the formation of a complicated mixture.

X-ray Crystallography of [Tbt(Mes)SiSe$_3$TiCp$_2$] (6). Crystals used in X-ray structural analysis of **6** were grown from hexane at room temperature. Intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromator Mo Kα radiation ($\lambda = 0.71070$ Å). The structure was solved by using direct methods (SIR-97)[37] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[38] All of the non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in calculated positions. **6**: green crystals; formula $C_{46}H_{80}Se_3Si_7Ti \cdot 0.5(C_6H_{14})$, MW 1157.57; monoclinic; space group $P2_1/a$ (#14); $a = 24.815(4)$ Å, $b = 9.4770(13)$ Å, $c = 25.627(5)$ Å; $\alpha = 90°$, $\beta = 94.030(8)°$, $\gamma = 90°$; $V = 6011.8(16)$ Å^3; $Z = 4$; $\mu = 3.404$ mm^{-1}; $D_{\text{calcd}} = 1.468$ Mg m^{-3}; $2\theta_{\max} = 50.0°$; $T = 103(2)$ K; R_1 ($I > 2\sigma(I)$) = 0.1284; wR_2 (all data) = 0.4325; GOF = 1.005 for 8254 reflections and 535 parameters.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-607936 for compound **6**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Computational Methods. The geometries of [Dmp$_2$SiS$_3$TiCp$_2$] (**3′**), [Dmp$_2$SiS$_2$TiCp$_2$] (**5′**), [Dmp$_2$SiSe$_3$TiCp$_2$] (**6′**), and [Dmp$_2$SiSe$_2$TiCp$_2$] (**7′**) were optimized by using the Gaussian 98 program[39] using the B3LYP/6-31G(d) basis set. The GIAO-B3LYP calculations were carried out with 6-311G(2d,p) for Si and 6-311G(d) for C and H as basis sets, and the TD-B3LYP calculations were carried out with 6-31G(d) basis sets.

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Supporting Information

Atomic coordinates for the calculated molecules **3′**, **5′**, **6′**, and **7′** and the ^{1}H and ^{13}C NMR spectra of **3**, **5**, **6**, and **7**. These materials are available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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