



# Syntheses and structures of overcrowded silanedichalcogenols and their applications to the syntheses of silanedichalcogenolato complexes

Taro Tanabe, Yoshiyuki Mizuhata, Nobuhiro Takeda<sup>1</sup>, Norihiro Tokitoh<sup>\*</sup>

*Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*

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## ABSTRACT

Overcrowded silanedichalcogenols  $\text{Tbt}(\text{Mes})\text{Si}(\text{EH})(\text{E}'\text{H})$ , such as silanedithiol ( $\text{E} = \text{E}' = \text{S}$ ), hydroxysilanethiol ( $\text{E} = \text{O}$ ,  $\text{E}' = \text{S}$ ) and hydroxysilaneselenol ( $\text{E} = \text{O}$ ,  $\text{E}' = \text{Se}$ ), bearing an efficient combination of steric protection groups, Tbt and Mes (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Mes = 2,4,6-trimethylphenyl), were synthesized and isolated as air- and moisture-stable crystals, and their structures were fully characterized by spectroscopic and elemental analyses together with X-ray crystallographic analyses. The results of IR spectroscopy and the X-ray structural analyses suggested that these compounds exist as monomers without any intra- and intermolecular interactions such as hydrogen bonds even in the solid state and in solution. Novel four-membered-ring compounds, such as  $\text{Tbt}(\text{Mes})\text{Si}(\mu\text{-S})_2\text{PnBbt}$  and  $[\text{Tbt}(\text{Mes})\text{Si}(\mu\text{-E})(\mu\text{-E}')\text{ML}_n]$  [ $\text{E}$ ,  $\text{E}' = \text{O}$ ,  $\text{S}$ ,  $\text{Se}$ ;  $\text{Pn} = \text{Sb}$ ,  $\text{Bi}$ ;  $\text{Bbt} = 2,6\text{-bis}[\text{bis}(\text{trimethylsilyl})\text{methyl}]\text{-4-[tris}(\text{trimethylsilyl})\text{methyl}]\text{phenyl}$ ;  $\text{ML}_n = \text{Pd}(\text{PPh}_3)_2$ ,  $\text{Pt}(\text{PPh}_3)_2$ ,  $\text{Ru}(\eta^6\text{-benzene})$ ] were synthesized by utilizing the silanedichalcogenols as key building blocks. The molecular structures of these newly isolated compounds were determined by NMR spectroscopic data together with X-ray crystallographic analyses.

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## 1. Introduction

The chemistry of organosilanethiols has been extensively studied and their wide utilities in organic synthesis have been reported so far as  $\text{H}_2\text{S}$  equivalents, homolytic reducing reagent for alkyl halides, polarity reversal catalysts (PRC), and so on [1,2]. Silanedithiols are also interesting in their structures, properties, and utilities as the building block for the synthesis of novel class of cyclic organosilicon compounds. Silanedithiolato complexes, which are expected as potential precursors for the controlled synthesis of cyclic mixed-metal sulfido clusters [3], would be synthesized by utilizing silanedithiols. However, silanedithiols are very rare and their X-ray structural analyses have not been reported so far probably due to their high sensitivity toward  $\text{H}_2\text{O}$  and extreme liability to self-oligomerizations [4,5]. As for the main group element compounds having two terminal SH groups on the central atom, there are some examples of structurally characterized compounds, such as  $\text{TbtB}(\text{SH})_2$  (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) [6],  $\text{LAl}(\text{SH})_2$  ( $\text{L} = \{\text{N}(\text{Dip})\text{C}(\text{Me})_2\text{CH}$ , Dip = 2,6-diisopropylphenyl) [7],  $\text{Dep}(\text{Dip})\text{Ge}(\text{SH})_2$  (Dep = 2,6-diethylphenyl) [8]. It should be noted that the introduction of (a) bulky substituent(s) on the central

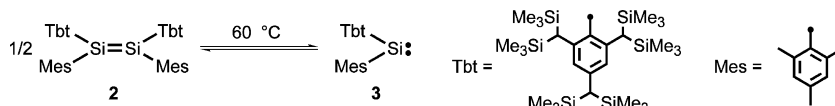
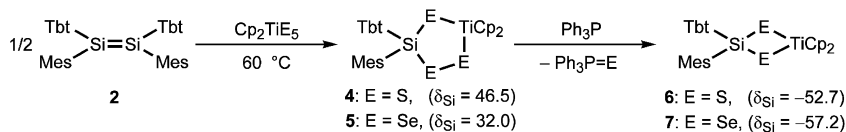
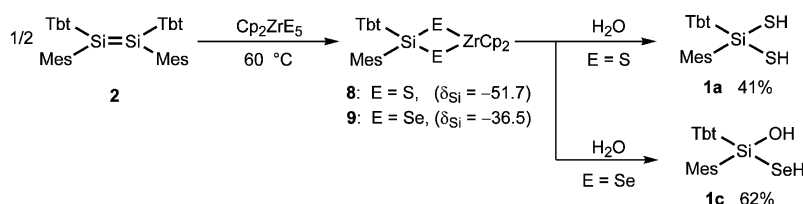
atom made it possible to isolate these highly reactive species. These compounds are considered to be good precursors for the syntheses of the corresponding dithiolates, which could be easily converted to heterobimetallic sulfido clusters [6–8].

On the other hand, we have reported the synthesis and isolation of a variety of highly reactive organosilicon compounds, such as silicon–chalcogen double-bond compounds [9], sila-aromatic compounds [10], and silacyclopentabenzene [11], by taking advantage of an effective steric protection group, Tbt [12]. An overcrowded *cis*-disilene **2**,  $\text{Tbt}(\text{Mes})\text{Si}=\text{Si}(\text{Mes})\text{Tbt}$ , has been synthesized and found to dissociate to the corresponding silylene **3**,  $\text{Tbt}(\text{Mes})\text{Si}$ , under mild conditions such as heating at 60 °C (Scheme 1) [13]. Very recently, we have reported the synthesis and properties of silanedichalcogenolato titanium complexes, **6** and **7**, by the dehalogenation of the five-membered ring compounds, **4** and **5**, which were synthesized by the reactions of **3** with titanocenepentasulfide and titanocenepentaselelide, respectively (Scheme 2) [14]. For the development of our studies on the chemistry of silacyclic compounds containing group 4 metal and chalcogen atoms, their zirconium analogues, **8** or **9**, have also been synthesized. They are unprecedented and expected to be good precursors for the corresponding silanedichalcogenols due to the high reactivity of zirconium–chalcogen bonds. During the course of our studies, we found the formation of stable silanedichalcogenols  $\text{Tbt}(\text{Mes})\text{Si}(\text{EH})(\text{E}'\text{H})$  **1a–c**, silanedithiol (**1a**:  $\text{E} = \text{E}' = \text{S}$ ), hydroxysilanethiol (**1b**:  $\text{E} = \text{O}$ ,  $\text{E}' = \text{S}$ ), and hydroxysilaneselenol (**1c**:  $\text{E} = \text{O}$ ,  $\text{E}' = \text{Se}$ ) [15]. In addition, we have achieved the synthesis of silanedichalcogenolato

<sup>\*</sup> Corresponding author. Tel.: +81774 38 3200; fax: +81 774 38 3209.

E-mail address: [tokitoh@boc.kuicr.kyoto-u.ac.jp](mailto:tokitoh@boc.kuicr.kyoto-u.ac.jp) (N. Tokitoh).

<sup>1</sup> Present address: Department of Chemistry and Chemical Biology, Graduate School of Engineering, Gunma University, 1-5-1, Tenjin-cho, Kiryu, Gunma 376-8515, Japan.

Scheme 1. Reactions of **2** with  $\text{Cp}_2\text{TiE}_5$  ( $\text{E}=\text{S},\text{Se}$ ).Scheme 2. Generation of silylene **3** from disilene **2**.Scheme 3. Syntheses of **8** and **9** and their hydration reactions.

complexes of group 10 transition metals by taking advantage of the isolated silanedichalcogenols. Portions of this work were communicated as preliminary reports [16,17]. In this paper, we will report the detailed synthesis, structures, and properties of the newly isolated silanedichalcogenols and their applications to the synthesis of novel four-membered-ring compounds consisting of one silicon and two chalcogen atoms together with a heavier group 15 atom [Sb, Bi] or a transition metal [Pd, Pt, Ru].

## 2. Results and discussions

### 2.1. Synthesis of silanedichalcogenolato zirconium complexes and their hydration reactions affording silanedichalcogenols **1a–c**

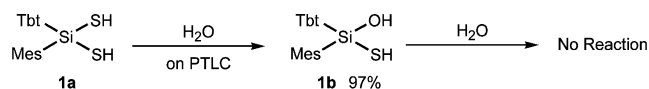
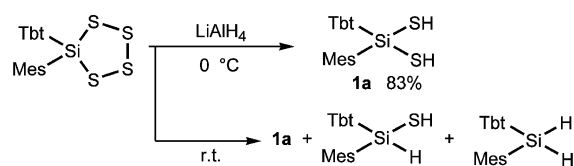
The reaction of **2** with 2 molar equiv. of zirconocene pentasulfide at 60 °C afforded silanedithiolato zirconium complex  $[\text{Tbt}(\text{Mes})\text{Si}(\mu\text{-S})_2\text{ZrCp}_2]$  (**8**) in a moderate yield. Similarly, the reaction of **2** with 2 molar equiv. of zirconocene pentaselenide afforded the selenium analogue,  $[\text{Tbt}(\text{Mes})\text{Si}(\mu\text{-Se})_2\text{ZrCp}_2]$  (**9**). These are the first examples of silanedichalcogenolato zirconium complexes. Although complexes **8** and **9** could not be isolated due to their high sensitivity to the hydrolysis as compared with their titanium analogues, their structures were suggested by the  $^{29}\text{Si}$  NMR chemical shifts [ $\delta_{\text{Si}} = -51.7$  (**8**),  $\delta_{\text{Si}} = -36.5$  (**9**)], which are similar to those of the four-membered-ring titanium analogues [ $\delta_{\text{Si}} = -57.2$  (**6**),  $\delta_{\text{Si}} = -52.7$  (**7**)] and different from those of the five-membered-ring ones [ $\delta_{\text{Si}} = +46.5$  (**4**),  $\delta_{\text{Si}} = +32.0$  (**5**)]. It is interesting that the four-membered-ring compounds were obtained directly in contrast to the titanium cases [14].

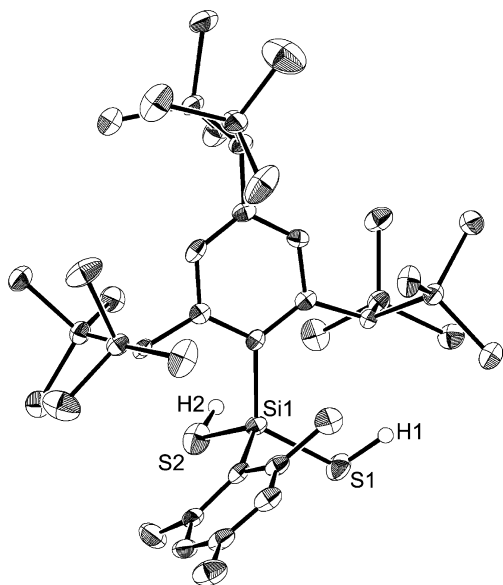
The reaction of **8** with excess of  $\text{H}_2\text{O}$  gave silanedithiol **1a** as colorless crystals, where the hydrolysis of the Zr–S bonds should occur selectively. On the other hand, the reaction of **9** with excess of  $\text{H}_2\text{O}$  afforded hydroxysilaneselenol **1c**. Although silanediselenol,  $\text{Tbt}(\text{Mes})\text{Si}(\text{SeH})_2$ , was considered to be an intermediate in this reaction, the intermediary silanediselenol could not be isolated and observed due to its high sensitivity toward  $\text{H}_2\text{O}$ . Isolated **1a** was found to be quite stable toward air and moisture and did not decompose even in  $\text{C}_6\text{D}_6$  solution in the presence of  $\text{H}_2\text{O}$  for 1 day. When **1a** was subjected to preparative thin-layer chromatography (PTLC) on  $\text{SiO}_2$ , it was converted quantitatively to the cor-

responding hydroxysilanethiol **1b** (colorless crystals, 97%) (Scheme 4). Compounds **1b** or **1c** did not undergo any decomposition even in the presence of  $\text{O}_2$  and  $\text{H}_2\text{O}$  or during the separation process with PTLC. Alternatively, silanedithiol **1a** could be synthesized by the reaction of tetrathiasilolane  $\text{Tbt}(\text{Mes})\text{SiS}_4$  with 1.5 molar equiv. of  $\text{LiAlH}_4$  at 0 °C in 83% isolated yield (Scheme 5). When this reaction was carried out at room temperature, a mixture of **1a**,  $\text{Tbt}(\text{Mes})\text{Si}(\text{H})\text{SH}$ , and  $\text{Tbt}(\text{Mes})\text{SiH}_2$  was obtained, suggesting the over-reduction resulting from the reaction of hydrides with the Si–S bond(s) together with the S–S bonds (see Scheme 3).

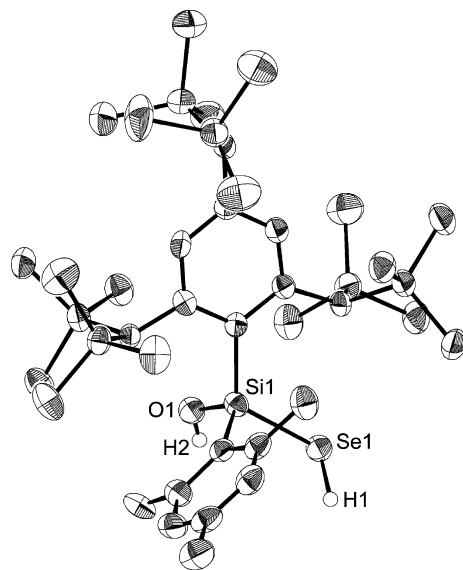
### 2.2. Structures of silanedithiol **1a**, hydroxysilanethiol **1b**, and hydroxysilaneselenol **1c**

The structures of silanedithiol **1a**, hydroxysilanethiol **1b**, and hydroxysilaneselenol **1c** were confirmed by the spectroscopic data and elemental analyses, and finally determined by X-ray crystallographic analysis. The thermal ellipsoids of **1a–c** are shown in Figs. 1–3 and the crystal data are summarized in Table 1. To the best of our knowledge, these are the first examples of the X-ray structural analyses of silanedithiol, hydroxysilanethiol, and hydroxysilaneselenol. The bond lengths of Si–S, Si–Se, and Si–O in **1a–c** are typical and the shortest intermolecular E...E distances (**1a**: S...S 3.8594 Å,

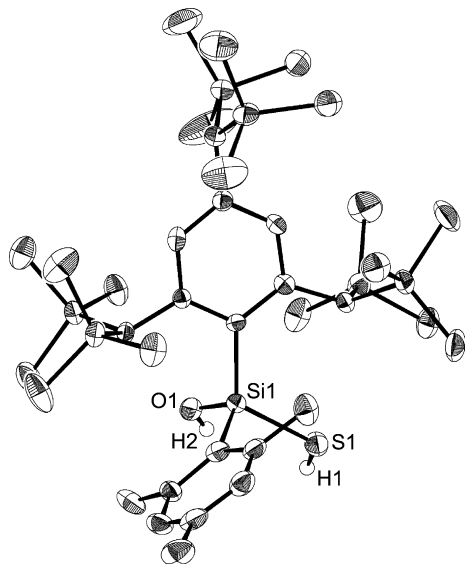
Scheme 4. Hydrolysis of **1a**.Scheme 5. Reactions of tetrathiasilorane with  $\text{LiAlH}_4$ .



**Fig. 1.** The thermal ellipsoid of **1a** drawn at the 50% probability level. Hydrogen atoms except for SH are omitted for clarity. Selected bond lengths (Å) and angles (°). Si(1)–S(1) 2.1576(16), Si(1)–S(2) 2.1436(15), S(1)–Si(1)–S(2) 101.73(6).



**Fig. 3.** The thermal ellipsoid of **1c** drawn at the 50% probability level. Hydrogen atoms except for OH and SeH are omitted for clarity. Selected bond lengths (Å) and angles (°). Si(1)–Se(1) 2.350(2), Si(1)–O(1) 1.635(6), Se(1)–Si(1)–O(1) 103.1(2).



**Fig. 2.** The thermal ellipsoid of **1b** drawn at the 50% probability level. Hydrogen atoms except for OH and SH are omitted for clarity. Selected bond lengths (Å) and angles (°). Si(1)–S(1) 2.192(2), Si(1)–O(1) 1.659(4), S(1)–Si(1)–O(1) 103.84(15).

**1b:** S···O 3.319 Å, **1c:** Se···O 3.500 Å) suggest the absence of the intermolecular interactions such as hydrogen bonds between the E···H (E = O, S, Se) parts in the solid state (Fig. 4). The intramolecular E···E distances (**1a:** S···S 3.3363 Å, **1b:** S···O 3.049 Å, **1c:** Se···O 3.152 Å) are slightly shorter than the sums of their van der Waals radii (S···S 3.60 Å, S···O 3.32 Å, Se···O 3.42 Å) [18].

In IR spectra, it is well-known that the absorptions assignable to the E–H (E = O, S, Se) vibrations with E–H···E hydrogen bonding should be broadened and shifted to the lower wavenumber region [19]. The IR spectra of **1a**, **1b**, and **1c** in the solid state (KBr or NaCl) showed sharp peaks [**1a:** 2572 cm<sup>-1</sup> (S–H stretch), **1b:** 2661 cm<sup>-1</sup> (S–H stretch), 3646 cm<sup>-1</sup> (O–H stretch), **1c:** 2479 cm<sup>-1</sup> (Se–H stretch), 3656 cm<sup>-1</sup> (O–H stretch)], suggesting the absence of the

**Table 1**  
Crystal data and structure refinements for **1a–c**.

	<b>1a</b>	<b>1b</b>	<b>1c</b>
Empirical formula	C <sub>36</sub> H <sub>72</sub> S <sub>2</sub> Si <sub>7</sub>	C <sub>36</sub> H <sub>72</sub> OSSi <sub>7</sub>	C <sub>36</sub> H <sub>72</sub> OSSi <sub>7</sub>
Formula weight	765.69	749.63	796.53
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$ (#2)	<i>P</i> $\bar{1}$ (#2)	<i>P</i> $\bar{1}$ (#2)
<i>a</i> (Å)	9.2535(4)	9.3654(3)	9.2373(6)
<i>b</i> (Å)	15.9925(5)	13.0538(4)	13.1271(4)
<i>c</i> (Å)	15.8055(7)	21.1294(9)	20.9732(14)
$\alpha$ (°)	82.9726(15)	72.5813(16)	75.135(2)
$\beta$ (°)	81.9726(15)	77.9579(16)	80.846(2)
$\gamma$ (°)	81.365(4)	71.303(3)	70.744(3)
<i>V</i> (Å <sup>3</sup> )	2276.62(16)	2316.41(14)	2312.8(2)
<i>Z</i>	2	2	2
<i>D</i> <sub>calcd.</sub> (g cm <sup>-3</sup> )	1.117	1.075	1.144
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.324	0.276	1.018
Crystal size (mm)	0.30 × 0.10 × 0.10	0.10 × 0.10 × 0.02	0.20 × 0.20 × 0.05
Reflections	23256	19769	18622
collected			
Independent reflections	8315 (0.0772)	8097 (0.0885)	7955 (0.1003)
[ <i>R</i> <sub>(int)</sub> ]			
Parameters	427	459	429
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0563	0.0855	0.0962
<i>wR</i> <sub>2</sub> (all data)	0.1350	0.1923	0.2346
Goodness-of-fit (GOF)	1.049	1.112	1.136
Largest peak, hole (e <sup>-</sup> Å <sup>-3</sup> )	0.580, -0.471	0.806, -0.412	0.984, -0.682

intra- and intermolecular interactions such as hydrogen bonding(s) between the E–H (E = O, S, Se) parts in the solid state. On the other hand, their IR spectra in a CCl<sub>4</sub> solution showed some signals in the region of the normal E–H stretch vibrations. When the concentration of the CCl<sub>4</sub> solution was changed, disappearance of these signals and appearance of new signals were not observed. In addition, the sharp signals in the <sup>1</sup>H NMR spectra assigned to the E–H protons (E = O, S, Se) of **1a–c** [**1a:**  $\delta_{\text{H}} = 1.18$  (SH), **1b:**  $\delta_{\text{H}} = 0.87$  (SH), 2.50 (OH), **1c:**  $\delta_{\text{H}} = -0.90$  (SeH), 2.12 (OH)] were neither shifted nor broadened on changing the concentrations. These results suggested that the compounds **1a–c** exist as a monomer without any intermolecular interactions even in solution.

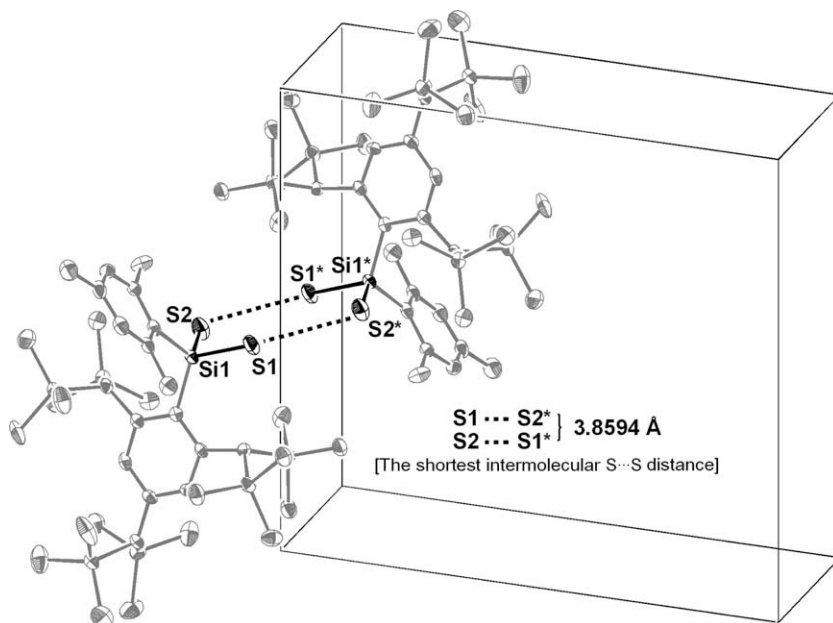


Fig. 4. The crystal packing of silanedithiol **1a**.

### 2.3. Synthesis of novel four-membered-ring compounds containing heavier group 15 element: 1,3,2,4-dithiastibasiletane and 1,3,2,4-dithiabismasiletane

Treatment of silanedithiol **1a** with 2 molar equiv. of *n*-BuLi in THF at 0 °C and the addition of excess methyl iodide resulted in the quantitative formation of bis(methylthio)silane, Tbt(Mes)-Si(SMe)<sub>2</sub> (**11**) (Scheme 6 and Fig. 5). The exclusive formation of **11** can be explained in terms of the quantitative generation of the corresponding dilithium silanedithiolate, Tbt(Mes)Si(SLi)<sub>2</sub> (**10a**). The reaction of the **10a** with 1 molar equiv. of Bbt-substituted dibromostibine or dibromobismuthine afforded the corresponding 1,3-dithietane derivatives containing a silicon atom and a heavier group 15 atom, 1,3,2,4-dithiastibasiletane (**12**) and 1,3,2,4-dithiabismasiletane (**13**), as pale yellow crystals in moderate yields, respectively (Scheme 6).

The structures of **12** and **13** were revealed by X-ray structural analysis. The structural parameters of **13** could not be discussed in detail because of its inevitable disorder. Their four-membered-ring cores were found to be almost planar. The extremely bulky Tbt (on the silicon) and Bbt (on the antimony) groups of **12** were attached to the four-membered-ring core in the *trans* position to each other. The Si–S bond lengths of **12** were found to be slightly shorter than those of Tbt(Mes)Si(μ-S)<sub>2</sub>Si(Mes)Tbt (**14**), and the Sb–S bond lengths of **12** and BbtSb(μ-S)<sub>2</sub>SbBbt (**15**) were almost

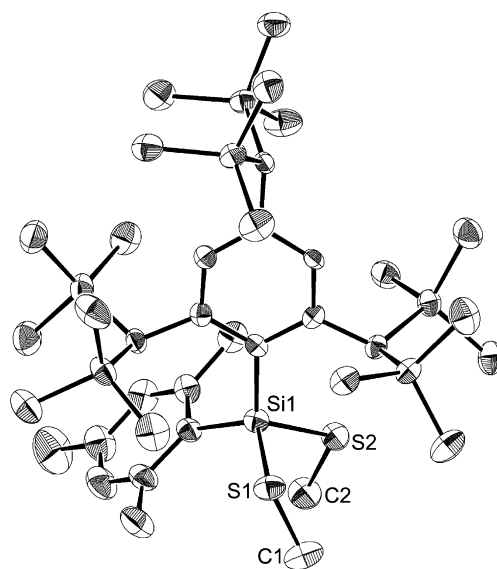
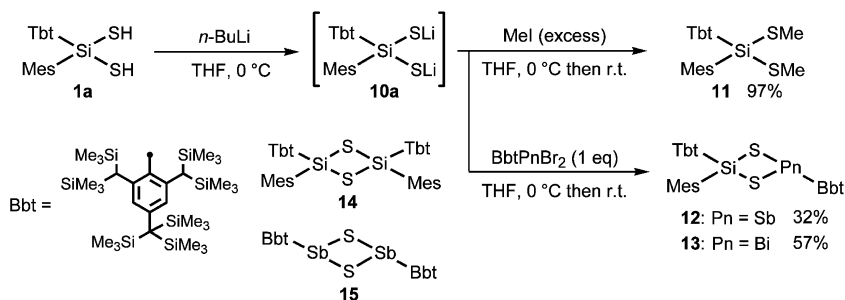
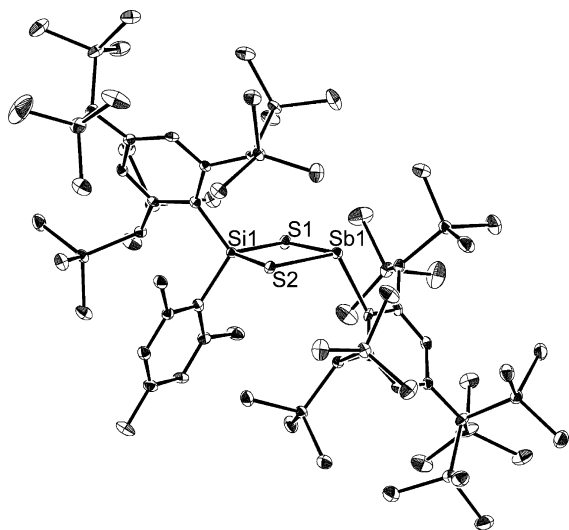


Fig. 5. The thermal ellipsoid of **11** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°). Si(1)–S(1) 2.1546(18), Si(1)–S(2) 2.174(2), S(1)–C(1) 1.811(6), S(2)–C(2) 1.831(5), S(1)–Si(1)–S(2) 103.00(8).



Scheme 6. Generation of silanedithiolate **10a** and its reactions with electrophiles.



**Fig. 6.** The thermal ellipsoid of **12** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°). Si(1)–S(1) 2.1510(12), Si(1)–S(2) 2.1744(12), Sb(1)–S(1) 2.4515(9), Sb(1)–S(2) 2.4577(8), S(1)–Si(1)–S(2) 98.97(5), S(1)–Sb(1)–S(2) 84.11(3), Si(1)–S(1)–Sb(1) 88.74(4), Si(1)–S(2)–Sb(1) 88.05(3).

similar to those for the related compounds [15,20] (see Fig. 6 and Table 2).

#### 2.4. Synthesis of silanedithiolato complexes containing a group 10 transition metal

Silanethiolato or silanedithiolato complexes of late transition metals have been known to be good precursors for mixed-metal sulfido clusters *via* the ligand exchange reactions accompanying

the Si–S bond cleavage [3]. However, chelating silanedithiolato complexes,  $[R_2Si(\mu-S)_2ML_n]$ , are less common due to the limitation of an appropriate synthetic methodology. Typically, excess amount of 1,3,5,2,4,6-trithiatrisilane ( $SSiMe_2$ )<sub>3</sub> should be required as a sulfur transfer reagent for the synthesis of silanedithiolato complexes [3a]. The silanedithiol **1a** was considered to be applicable toward the development of a new synthetic strategy for silanedithiolato transition metal complexes. The addition of *cis*- $[MCl_2(PPh_3)_2]$  (M = Pd, Pt) to the THF solution of silanedithiolato **10a** resulted in the almost quantitative formation of the corresponding silanedithiolato complexes of palladium and platinum,  $[Tbt(Mes)Si(\mu-S)_2M(PPh_3)_2]$  (**16**: M = Pd, **17a**: M = Pt), respectively, as air- and moisture-stable yellow crystals (Scheme 7) [16]. Both of the central four-membered rings in **16** and **17a** consisting of Si, two S, and Pd or Pt atoms have puckered structures (Figs. 7 and 8), although the corresponding PdS<sub>2</sub>Si ring of the silanedithiolato palladium complex  $[Me_2Si(\mu-S)_2Pd(PEt_3)_2]$  reported by Tatsumi et al. [3a] has an almost planar structure. This is probably due to the steric repulsion between the extremely bulky Tbt group and thiphenylphosphine moiety. In the <sup>29</sup>Si NMR, the signals of the central silicon atoms in the silanedithiolato complexes **16** ( $\delta_{Si} = 15.3$ ) and **17a** ( $\delta_{Si} = 14.2$ ) were observed in the region characteristic of silanedithiolato late transition metal complexes [3] and lay in lower field than that of free ligand **1a** ( $\delta_{Si} = -1.8$ ).

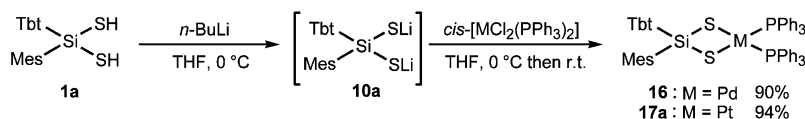
#### 2.5. Synthesis of silaneoxylatochalcogenolato platinum complexes

The stable silanedithiol **1a** was found to be a key species as a building block for several types of silanedithiolato complexes. This finding prompted us to investigate the synthetic utility of **1b** and **1c** for the synthesis of metal siloxides bridged by a sulfur or selenium atom from the standpoints of structural elucidation for silanechalcogenolato complexes systematically. The reactions of **1b** or **1c** with 2 molar equiv. of sodium hydride and the addition of

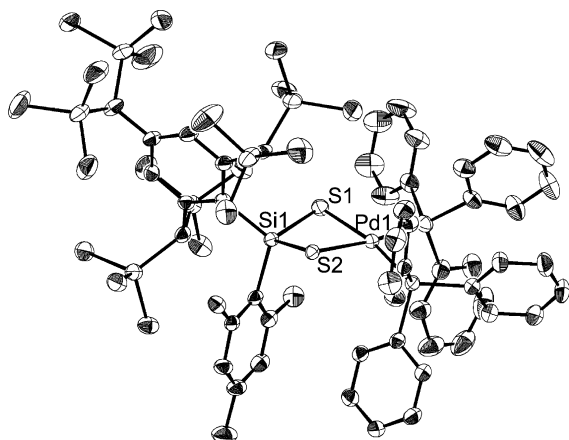
**Table 2**

Crystal data and structure refinements for **11**, **12**, and **16**.

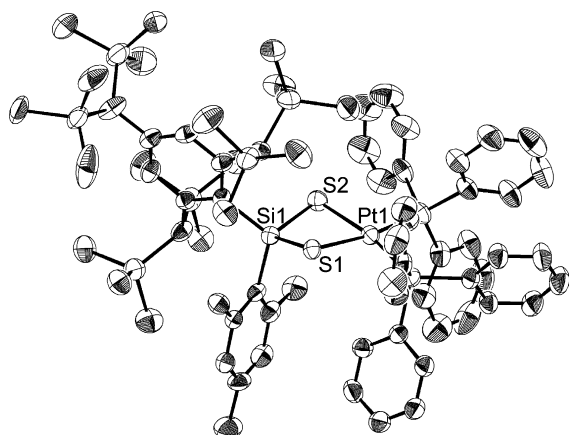
	<b>11</b> · 0.5hexane	<b>12</b> · 0.5benzene	<b>16</b> · hexane · benzene
Empirical formula	C <sub>38</sub> H <sub>76</sub> S <sub>2</sub> Si <sub>7</sub> · 0.5(C <sub>6</sub> H <sub>14</sub> )	C <sub>66</sub> H <sub>137</sub> S <sub>2</sub> SbSi <sub>14</sub> · 0.5(C <sub>6</sub> H <sub>6</sub> )	C <sub>72</sub> H <sub>100</sub> P <sub>2</sub> PdS <sub>2</sub> Si <sub>7</sub> · C <sub>6</sub> H <sub>14</sub> · C <sub>6</sub> H <sub>6</sub>
Formula weight	836.82	1548.94	1558.89
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> 1̄ (#2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (#14)	<i>P</i> 1̄ (#2)
<i>a</i> (Å)	9.3953(6)	12.43510(10)	13.7523(2)
<i>b</i> (Å)	12.5768(7)	19.5286(2)	16.9131(3)
<i>c</i> (Å)	24.2983(19)	36.7653(4)	21.1525(4)
$\alpha$ (°)	93.186(3)	90	113.2919(12)
$\beta$ (°)	97.807(4)	91.1935(5)	102.4982(7)
$\gamma$ (°)	113.381(7)	90	92.0075(7)
<i>V</i> (Å <sup>3</sup> )	2592.0(3)	8926.15(15)	4371.81(13)
<i>Z</i>	2	4	2
<i>D</i> <sub>calcd.</sub> (g cm <sup>-3</sup> )	1.072	1.153	1.184
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.290	0.578	0.433
Crystal size (mm)	0.30 × 0.20 × 0.10	0.20 × 0.10 × 0.05	0.30 × 0.20 × 0.20
Reflections collected	21 491	89 299	37 331
Independent reflections [ <i>R</i> <sub>int</sub> ]	8951 (0.1288)	15 726 (0.0570)	15 293 (0.0322)
Parameters	474	867	984
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0688	0.0419	0.0416
<i>wR</i> <sub>2</sub> (all data)	0.1392	0.1022	0.1171
Goodness-of-fit (GOF)	1.032	1.061	1.048
Largest peak, hole (e Å <sup>-3</sup> )	0.497, -0.344	3.690, -0.837	1.245, -0.976



**Scheme 7.** Synthesis of silanedithiolato complexes containing a group 10 transition metal **16** and **17a**.

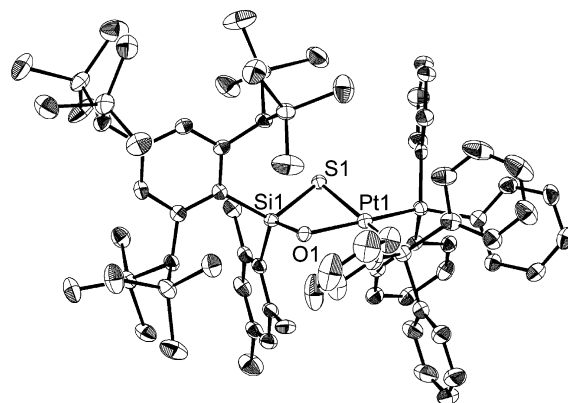


**Fig. 7.** The thermal ellipsoid of **16** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°). Si(1)–S(1) 2.1142(11), Si(1)–S(2) 2.1548(11), Pd(1)–S(1) 2.3242(8), Pd(1)–S(2) 2.3577(7), S(1)–Si(1)–S(2) 95.48(4), S(1)–Pd(1)–S(2) 84.88(3).

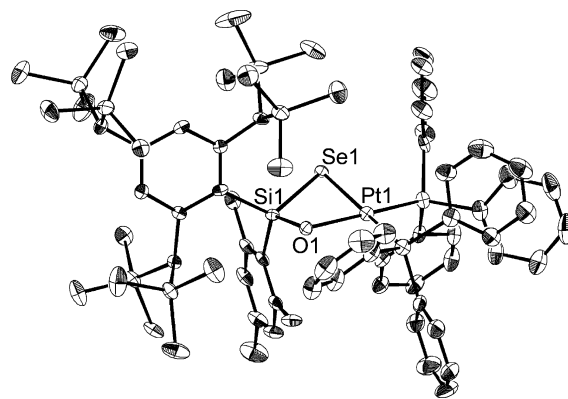


**Fig. 8.** The thermal ellipsoid of **17a** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°). Si(1)–S(1) 2.157(2), Si(1)–S(2) 2.115(2), Pt–S(1) 2.3667(15), Pt–S(2) 2.3333(17), S(1)–Si(1)–S(2) 94.92(9), S(1)–Pt–S(2) 84.09(6).

*cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] in THF afforded [Tbt(Mes)Si(μ-O)(μ-E)Pt(PPh<sub>3</sub>)<sub>2</sub>], **17b** [E = S (89%)] and **17c** [E = Se (95%)], respectively, as air- and moisture-stable pale yellow crystals in high yields (Scheme 8) [17]. When the reactions were performed by utilizing *n*-BuLi as a base instead of sodium hydride, the same products were obtained in similar yields. Their four-membered-ring cores have an almost puckered geometry. Although the sum of the bond angles around the platinum atoms of **17b** and **17c** are 360.82° and 361.01°, respectively, the values of which are normal for the neutral *cis*-platinum complexes two-valent and four-coordinated [21], their central platinum atoms deviate from the planar geometry (Figs. 9 and 10 and Table 3). In the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **17b**, two distinguishable doublet signals of triphenylphosphine ligands were observed at 25.1 (<sup>1</sup>J<sub>Pt</sub> = 3209 Hz) and 6.9 (<sup>1</sup>J<sub>Pt</sub> = 3532 Hz) ppm. They are slightly upfield shifted compared with those of **17c**

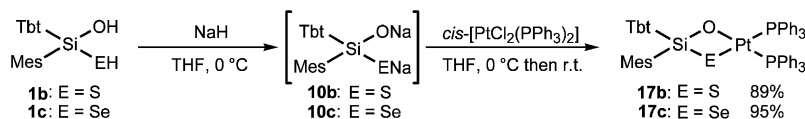


**Fig. 9.** The thermal ellipsoid of **17b** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°). Si(1)–S(1) 2.1708(13), Si(1)–O(1) 1.636(3), Pt(1)–S(1) 2.3495(9), Pt(1)–O(1) 2.076(2), Pt(1)–P(1) 2.2397(9), Pt(1)–P(2) 2.2758(10), S(1)–Si(1)–O(1) 97.07(10), Si(1)–O(1)–Pt(1) 100.02(12), Si(1)–S(1)–Pt(1) 78.34(4), S(1)–Pt(1)–O(1) 80.77(7), S(1)–Pt(1)–P(1) 87.48(3), P(1)–Pt(1)–P(2) 99.30(4), P(2)–Pt(1)–O(1) 93.27(7).



**Fig. 10.** The thermal ellipsoid of **17c** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°). Si(1)–Se(1) 2.3152(12), Si(1)–O(1) 1.635(3), Pt(1)–Se(1) 2.4565(5), Pt(1)–O(1) 2.067(3), Pt(1)–P(1) 2.2324(12), Pt(1)–P(2) 2.2835(12), Se(1)–Si(1)–O(1) 95.82(11), Si(1)–O(1)–Pt(1) 103.37(14), Si(1)–Se(1)–Pt(1) 75.32(3), Se(1)–Pt(1)–O(1) 81.47(8), Se(1)–Pt(1)–P(1) 87.00(3), P(1)–Pt(1)–P(2) 99.71(4), P(2)–Pt(1)–O(1) 92.83(8).

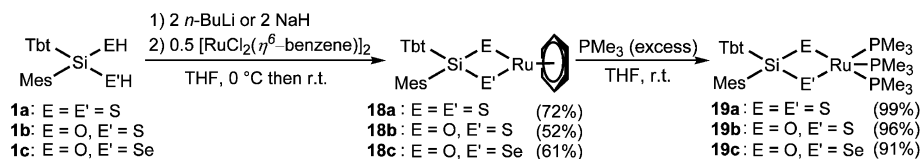
[24.7 (<sup>1</sup>J<sub>Pt</sub> = 3206 Hz) and 6.2 (<sup>1</sup>J<sub>Pt</sub> = 3537 Hz) ppm]. It should be noted in both cases that the doublet signals at upper fields have larger <sup>1</sup>J<sub>Pt</sub> coupling constants than those at lower fields have. The doublet signals at 6.9 (**17b**) and 6.2 (**17c**) ppm are assigned to the phosphorus atoms situated in the *trans* position to the oxygen atom and the doublet signals at 25.1 (**17b**) and 24.7 (**17c**) ppm are assigned to those in the *trans* position to the sulfur or selenium atom. X-ray structural analyses revealed that Pt–P bond lengths situated in the *trans* position to the oxygen atom [**17b**: 2.2327(9) Å; **17c**: 2.2324(12) Å] are slightly shorter than those situated in the *trans* position to the sulfur [for **17b**: 2.2758(10) Å] or selenium atom [for **17c**: 2.2835(12) Å], resulting from the *trans* influence of the chalcogen atoms on the silicon atom. Taking the results of their <sup>31</sup>P NMR into consideration, the *trans* influence of the sulfur or the selenium atoms on the silicon atom is much larger



**Scheme 8.** Synthesis of silaneoxylatochalcogenolato platinum complexes **17b** and **17c**.

**Table 3**Crystal data and structure refinements for **17a**, **17b**, **17c**, **18b**, and **18c**.

	<b>17a</b> · hexane	<b>17b</b> · hexane	<b>17c</b> · 2benzene	<b>18b</b>	<b>18c</b> · benzene
Empirical formula	C <sub>72</sub> H <sub>100</sub> P <sub>2</sub> PtS <sub>2</sub> Si <sub>7</sub> · C <sub>6</sub> H <sub>14</sub>	C <sub>72</sub> H <sub>100</sub> OP <sub>2</sub> PtSSi <sub>7</sub> · C <sub>6</sub> H <sub>14</sub>	C <sub>72</sub> H <sub>100</sub> OP <sub>2</sub> PtSeSi <sub>7</sub> · 2(C <sub>6</sub> H <sub>6</sub> )	C <sub>42</sub> H <sub>76</sub> PORuSi <sub>7</sub>	C <sub>42</sub> H <sub>76</sub> ORuSeSi <sub>7</sub> · C <sub>6</sub> H <sub>6</sub>
Formula weight	1569.47	1553.41	1670.36	926.79	1051.80
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P $\bar{1}$ (#2)	P $\bar{1}$ (#2)	P $\bar{1}$ (#2)	C2/c (#15)	C2/c (#15)
<i>a</i> (Å)	13.7853(8)	13.5758(2)	13.5365(9)	43.7641(6)	39.8562(16)
<i>b</i> (Å)	16.8910(9)	16.6860(4)	16.6705(12)	13.4000(3)	13.1996(7)
<i>c</i> (Å)	21.0444(17)	21.1691(4)	21.2730(19)	21.7659(9)	21.8447(13)
$\alpha$ (°)	113.276(7)	112.5927(8)	113.098(2)	90	90
$\beta$ (°)	102.504(4)	102.7127(9)	104.790(2)	116.3546(17)	94.052(3)
$\gamma$ (°)	92.842(3)	91.7477(9)	90.279(2)	90	90
<i>V</i> (Å <sup>3</sup> )	4344.4(5)	4283.43(15)	4239.5(6)	11437.7(6)	11463.5(10)
<i>Z</i>	2	2	2	8	8
<i>D</i> <sub>calcd.</sub> (g cm <sup>-3</sup> )	1.200	1.204	1.309	1.076	1.219
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	1.833	1.836	2.263	0.483	1.086
Crystal size (mm)	0.20 × 0.10 × 0.10	0.20 × 0.10 × 0.10	0.30 × 0.20 × 0.20	0.20 × 0.10 × 0.10	0.15 × 0.10 × 0.10
Reflections collected	36 803	36 449	35 867	51 664	46 146
Independent reflections [ <i>R</i> <sub>int</sub> ]	15 211 (0.0689)	14 966 (0.0311)	14 860 (0.0422)	10 066 (0.0728)	10 024 (0.0773)
Parameters	870	998	963	598	545
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0511	0.0345	0.0445	0.0748	0.0666
<i>wR</i> <sub>2</sub> (all data)	0.1272	0.0834	0.0803	0.1902	0.2018
Goodness-of-fit (GOF)	1.078	1.065	1.125	1.164	1.052
Largest peak, hole (e Å <sup>-3</sup> )	0.974, -0.918	1.462, -1.165	0.979, -0.521	3.763, -1.270	3.740, -1.082

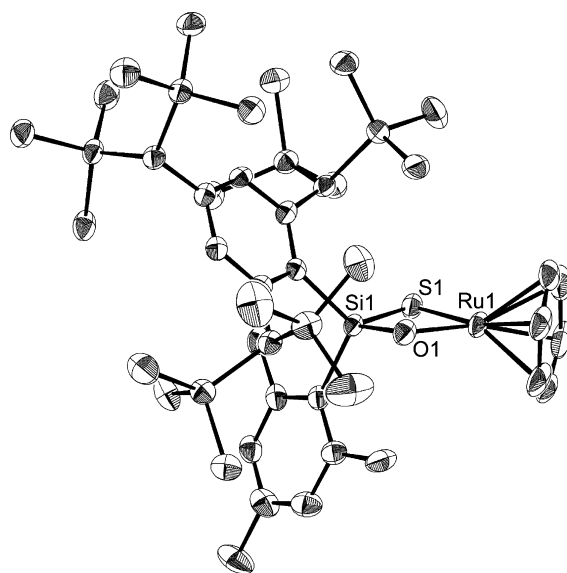
**Scheme 9.** Synthesis of silanedichalcogenolato ruthenium complexes **18** and **19**.

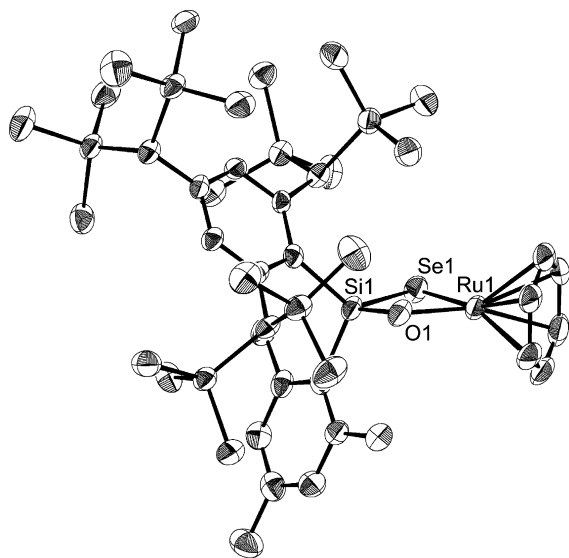
than that of the oxygen atom. On the other hand, the degree of *trans influence* between sulfur and selenium are almost similar to each other [22]. The <sup>29</sup>Si NMR resonances in the central silicon atoms of **17b** ( $\delta_{\text{Si}} = 5.3$ ) and **17c** ( $\delta_{\text{Si}} = -3.3$ ) lay in a lower field than those of **1b** ( $\delta_{\text{Si}} = -5.3$ ) and **1c** ( $\delta_{\text{Si}} = -9.5$ ) and in a higher field than that of silanedithiolato platinum complex **17a** ( $\delta_{\text{Si}} = 14.2$ ).

## 2.6. Synthesis of silanedichalcogenolato ruthenium complexes

Chalcogenolate ligands are known to possess a  $\sigma$ -donor orbital along with lone pair orbitals that have the correct symmetry for  $\pi$ -interaction with a metal d orbital. Actually it has been demonstrated that some of bulky thiolate ligands effectively stabilized coordinatively unsaturated mononuclear complexes of late or middle transition metals [23]. The stable silanedichalcogenols **1a–c** were expected to be building blocks for coordinatively unsaturated ruthenacycles. The addition of 0.5 molar equiv. of [RuCl<sub>2</sub>( $\eta^6$ -benzene)<sub>2</sub>] to the THF solution of dilithium or disodium silanedichalcogenolates **10a–c**, gave the corresponding silanedichalcogenolato ruthenium complexes **18a–c** as deep green, deep violet, and deep blue crystals, respectively, in moderate yields (Scheme 9). The X-ray crystallographic analysis revealed their monomeric structures and the molecular structures of **18b** and **18c** are shown in Fig. 11. Their four-membered-ring cores have an almost planar geometry and the dihedral angles between the four-membered-ring cores and  $\eta^6$ -coordinated benzene rings are almost 90°. The planar geometry would enhance the  $\pi$  overlap between the  $p\pi$  orbitals of O, S, or Se atoms and the vacant d orbital of Ru atom to ease the electron deficiency at Ru atom, as discussed for the related complexes in the previous reports [8a,23]. The Ru–E bonds of **18b** [Ru–O = 1.991(4) Å, Ru–S = 2.3007(14) Å] and **18c** [Ru–O = 2.008(3) Å, Ru–Se = 2.3122(14) Å] are similar to the Ru–E bond lengths of the electron-deficient ruthenium thiolates reported pre-

viously [8a,23]. The UV–Vis spectra of **18a–c** in hexane showed characteristic absorptions of coordinatively unsaturated ruthenium complexes [**18a**: 676 nm, **18b**: 578 nm, **18c**: 610 nm] assignable to the HOMO–LUMO transition from the  $p\pi$  orbitals of the bridging chalcogens to the vacant d orbitals of the Ru atom [23]. These experimental results were supported by the TD-DFT calcula-

**Fig. 11.** The thermal ellipsoid of **18b** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°). Si(1)–O(1) 1.628(4), Si(1)–S(1) 2.149(2), Ru(1)–S(1) 2.3007(14), Ru(1)–O(1) 1.991(4), S(1)–Si(1)–O(1) 95.79(16), Si(1)–O(1)–Ru(1) 102.8(2), Si(1)–S(1)–Ru(1) 79.18(6), S(1)–Ru(1)–O(1) 81.95(11).



**Fig. 12.** The thermal ellipsoid of **18c** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°). Si(1)–O(1) 1.629(5), Si(1)–Se(1) 2.312(2), Ru(1)–Se(1) 2.4206(9), Ru(1)–O(1) 2.016(4), Se(1)–Si(1)–O(1) 95.23(18), Si(1)–O(1)–Ru(1) 105.6(2), Si(1)–Se(1)–Ru(1) 75.96(5), Se(1)–Ru(1)–O(1) 82.71(13).

tions [TD-B3LYP/6-31G(d) (LANL2DZ on Ru)//B3LYP/6-31G(d) (LANL2DZ on Ru); Tbt and Mes were replaced by 2,6-dimethylphenyl]. Despite the coordinative unsaturation of the Ru atom, these complexes are quite stable in the air and even in solution due to the effective combination of steric protection by Tbt and Mes groups. The reactions of **18a–c** with excess of  $\text{PMe}_3$  in THF resulted in the replacement of the  $\eta^6$ -benzene ligand with three  $\text{PMe}_3$  ligands leading to the quantitative formation of  $[\text{Tbt}(\text{Mes})\text{Si}(\mu\text{-E})(\mu\text{-E}')\text{Ru}(\text{PMe}_3)_3]$  (**19a–c**). The reactions of **18a–c** with 1 molar equiv. of  $\text{PMe}_3$  afforded the mixture of **18** (ca. 70%) and **19** (ca. 30%), in all cases. The bulky substituents on the silicon atoms may prevent the formation of the coordinatively saturated addition products, such as  $[\text{Tbt}(\text{Mes})\text{Si}(\mu\text{-E})(\mu\text{-E}')\text{Ru}(\eta^6\text{-benzene})(\text{PMe}_3)]$  or  $[\text{Tbt}(\text{Mes})\text{Si}(\mu\text{-E})(\mu\text{-E}')\text{Ru}(\text{PMe}_3)_4]$  (see Fig. 12).

### 3. Conclusion

In summary, overcrowded silanedichalcogenols  $\text{Tbt}(\text{Mes})\text{Si}(\text{EH})(\text{E}'\text{H})$  (**1a**: E = E' = S, **1b**: E = O, E' = S, **1c**: E = O, E' = Se), bearing an efficient combination of steric protection groups, Tbt and Mes, were synthesized and isolated as air- and moisture-stable crystals. These new compounds were fully characterized by the spectroscopic data, elemental analyses, and X-ray structural analyses. Silanedichalcogenols **1** were found to exist as a monomer without any intermolecular contact such as hydrogen bonds both in the solid state. Novel four-membered silacyclic compounds,  $[\text{Tbt}(\text{Mes})\text{Si}(\mu\text{-S})_2\text{PnBbt}]$  (**12**: Pn = Sb, **13**: Pn = Bi) or  $[\text{Tbt}(\text{Mes})\text{Si}(\mu\text{-E})(\mu\text{-E}')\text{ML}_n]$  [**16**:  $\text{ML}_n = \text{Pd}(\text{PPh}_3)_2$ , **17**:  $\text{ML}_n = \text{Pt}(\text{PPh}_3)_2$ , **18**:  $\text{ML}_n = \text{Ru}(\eta^6\text{-benzene})$ , **19**:  $\text{ML}_n = \text{Ru}(\text{PMe}_3)_3$ ], were synthesized by utilizing **1a–c** as key building blocks. Further investigations on their reactivities are currently under way.

### 4. Experimental

#### 4.1. General experimental details

All experiments were performed under anhydrous conditions under an argon atmosphere unless otherwise noted. All solvents used in the reactions were purified prior to use by the standard methods and/or by the Ultimate Solvent System (Glass Contour

Company) [24].  $\text{C}_6\text{D}_6$  used as a solvent was dried over Na, then K mirror. The  $^1\text{H}$  NMR (300 or 400 MHz) spectra were measured in  $\text{CDCl}_3$  or  $\text{C}_6\text{D}_6$  with a JEOL AL-400 or AL-300 spectrometer using residual  $\text{CHCl}_3$  (7.25 ppm) or  $\text{C}_6\text{D}_5\text{H}$  (7.15 ppm) as an internal standard.  $^{13}\text{C}$  NMR (75 MHz) spectra were recorded on a JEOL JNM AL-300 spectrometer.  $^{13}\text{C}$  NMR chemical shifts were reported in ppm downfield from tetramethylsilane and referenced to the carbon signal of  $\text{CDCl}_3$  (77.0 ppm) or  $\text{C}_6\text{D}_6$  (128.0 ppm). Multiplicity of signals in  $^{13}\text{C}$  NMR spectra was determined by DEPT technique. The  $^{29}\text{Si}$  NMR (59 MHz),  $^{31}\text{P}$  NMR (120 MHz),  $^{77}\text{Se}$  NMR (95 MHz), and  $^{195}\text{Pt}$  NMR (64 MHz) spectra were recorded on a JEOL JNM AL-300 spectrometer. IR spectra were recorded on a JASCO FT/IR-5300 spectrometer. High- and low-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. All melting points were measured on a Yanaco micro melting points apparatus and uncorrected. Wet column chromatography (WCC) and preparative thin-layer chromatography (PTLC) were performed using Wakogel C-200 and Merk Kieselgel 60 PF254, respectively. GLPC (gel permeation liquid chromatography) was performed on LC-908, LC-918 (Japan Analytical Industry Co., Ltd. Systems) equipped with JAIGEL 1H and 2H columns (eluent: toluene).  $\text{Tbt}(\text{Mes})\text{Si}_4$  [25],  $\text{Tbt}(\text{Mes})\text{Si}=\text{Si}(\text{Mes})\text{Tbt}$  [25],  $[\text{Cp}_2\text{ZrE}_5]$  (E = S, Se) [26],  $\text{BbtPnBr}_2$  (Pn = Sb, Bi) [27], and  $[\text{RuCl}_2(\eta^6\text{-benzene})]_2$  [28] were prepared according to the reported methods.

#### 4.2. Synthesis of $\text{Tbt}(\text{Mes})\text{Si}(\text{SH})_2$ (**1a**); hydrolysis of the $[\text{Tbt}(\text{Mes})\text{Si}(\mu\text{-S})_2\text{ZrCp}_2]$

In a 5φ Pyrex glass tube was placed a THF solution (0.5 mL) of a mixture of disilene  $\text{Tbt}(\text{Mes})\text{Si}=\text{Si}(\text{Mes})\text{Tbt}$  (59.8 mg, 0.0424 mmol) and  $[\text{Cp}_2\text{ZrS}_5]$  (36.2 mg, 0.0961 mmol). After three freeze-pump-thaw cycles, the tube was evacuated and sealed. The solution was heated at 60 °C for 20 h, during which time the original orange suspension turned into a pale orange solution. The tube was opened and the solvent was removed under reduced pressure in a glovebox filled with argon. Benzene (5 ml) was added to the residue, and the mixture was filtered through Celite®. After the removal of the solvent,  $\text{C}_6\text{D}_6$  (0.5 ml) was added to the mixture. The measurement of  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectra indicated the formation of  $[\text{Tbt}(\text{Mes})\text{Si}(\mu\text{-S})_2\text{ZrCp}_2]$  ( $\delta_{\text{Si}} = -51.7$ , ~40%) and 1,2,3,4,5-tetra-thiasilolane,  $\text{Tbt}(\text{Mes})\text{Si}_4$ , ( $\delta_{\text{Si}} = 32.0$ , ~30%), respectively, the yields of which were judged by the ratio of the integrated intensity of the  $^1\text{H}$  NMR. The THF solution of the reaction mixture containing  $[\text{Tbt}(\text{Mes})\text{Si}(\mu\text{-S})_2\text{ZrCp}_2]$  and  $\text{Tbt}(\text{Mes})\text{Si}_4$  was opened in the air and the solvent was removed. Benzene (5 ml) was added to the residue, and the mixture was filtrated through Celite®. After concentration under reduced pressure, the residue was separated by GLPC (toluene) and silica gel chromatography (hexane) to afford pure silanedithiol **1a** (30.2 mg, 0.0394 mmol, 41%) as a colorless solid together with 1,2,3,4,5-tetra-thiasilolane,  $\text{Tbt}(\text{Mes})\text{Si}_4$  (25.6 mg, 0.0250 mmol, 26%), as a colorless solid. Colorless crystals of **1a** suitable for X-ray structural analysis were grown from hexane. **1a**: colorless crystals, m.p. 177–178 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  -0.02 (s, 18H), 0.00 (s, 18H), 0.04 (s, 18H), 1.18 (s, 2H, SH), 1.31 (s, 1H), 2.22 (s, 3H), 2.49 (s, 1H), 2.57 (s, 6H), 2.63 (s, 1H), 6.24 (s, 1H), 6.38 (s, 1H), 6.76 (s, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  0.9 (CH<sub>3</sub>), 1.6 (CH<sub>3</sub>), 1.9 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>), 26.4 (CH<sub>3</sub>), 28.0 (CH), 28.3 (CH), 30.6 (CH), 123.3 (CH), 126.3 (C), 128.5 (CH), 130.5 (CH), 134.9 (C), 139.7 (C), 142.8 (C), 145.5 (C), 151.9 (C), 152.2 (C);  $^{29}\text{Si}$  NMR (59 MHz,  $\text{CDCl}_3$ )  $\delta$  -1.8, 1.9, 2.9, 3.0; IR (KBr) 2572 [ $\nu(\text{S-H})$ ]; LRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for  $\text{C}_{36}\text{H}_{72}\text{S}_2\text{Si}_7$  ( $[\text{M}]^+$ ) 764, found 764; HRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for  $\text{C}_{36}\text{H}_{72}\text{S}_2\text{Si}_7$  ( $[\text{M}]^+$ ) 764.3460, found 764.3472. Anal. Calc. for  $\text{C}_{36}\text{H}_{72}\text{S}_2\text{Si}_7$ : C, 56.47; H, 9.48; S, 8.38. Found: C, 56.51; H, 9.57; S, 8.81%.



#### 4.3. Synthesis of *Tbt(Mes)Si(SH)<sub>2</sub>* (**1a**); reaction of *Tbt(Mes)SiS<sub>4</sub>* with *LiAlH<sub>4</sub>*

To a solution of *Tbt(Mes)SiS<sub>4</sub>* (165 mg, 0.238 mmol) in THF (15 mL) was added *LiAlH<sub>4</sub>* (13.5 mg, 0.356 mmol) at 0 °C. After the mixture was stirred at 0 °C for 1 h, ethyl acetate (5 mL) was added. After the removal of the solvent, hexane (3 mL) was added to the residue. The suspension was filtrated through Celite<sup>®</sup>, and the solvent was removed under reduced pressure. The residue was separated with silica gel chromatography (hexane) to afford *Tbt(Mes)Si(SH)<sub>2</sub>* **1a** (150 mg, 0.196 mmol, 83%).

#### 4.4. Synthesis of *Tbt(Mes)Si(OH)SH* (**1b**)

Treatment of *Tbt(Mes)Si(SH)<sub>2</sub>* **1a** (51.2 mg, 0.0668 mmol) on PTLC (SiO<sub>2</sub>/hexane) afforded *Tbt(Mes)Si(OH)SH* **1b** (46.6 mg, 0.0622 mmol, 93%). Colorless crystals suitable for X-ray structural analysis of **1b** were grown from hexane at –20 °C. **1b**: colorless crystals, m.p. 169–171 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ –0.14 (s, 9H), 0.09 (s, 9H), 0.04 (s, 18H), 0.06 (s, 18H), 0.87 (s, 1H, SH), 1.31 (s, 1H), 2.22 (s, 3H), 2.48 (s, 6H), 2.50 (s, 1H, OH), 2.53 (s, 1H), 2.68 (s, 1H), 6.24 (s, 1H), 6.38 (s, 2H), 6.75 (s, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 0.9 (CH<sub>3</sub>), 1.1 (CH<sub>3</sub>), 1.2 (CH<sub>3</sub>), 1.7 (CH<sub>3</sub>), 21.2 (CH<sub>3</sub>), 25.2 (CH<sub>3</sub>), 27.8 (CH), 28.0 (CH), 30.8 (CH) 123.3 (CH), 127.5 (C), 128.4 (CH), 130.1 (CH), 135.4 (C), 139.9 (C), 143.1 (C), 145.3 (C), 151.4 (C), 151.6 (C); <sup>29</sup>Si NMR (59 MHz, CDCl<sub>3</sub>) δ –5.3, 2.1, 2.2, 2.7, 2.9, 3.2; IR (KBr) 2561 [ν(S–H)], 3648 [ν(O–H)]; LRMS (FAB<sup>+</sup>) *m/z*: calcd. for C<sub>36</sub>H<sub>72</sub>OSSi<sub>7</sub> ([M]<sup>+</sup>) 748, found 748; HRMS (FAB<sup>+</sup>) *m/z*: calcd. for C<sub>36</sub>H<sub>72</sub>OSSi<sub>7</sub> ([M]<sup>+</sup>) 748.3689, found 748.3690. Anal. Calc. for C<sub>36</sub>H<sub>72</sub>OSSi<sub>7</sub>: C, 57.68; H, 9.68; S, 4.28. Found: C, 57.84; H, 9.74; S, 4.09%.

#### 4.5. Synthesis of *Tbt(Mes)Si(OH)SeH* (**1c**); hydrolysis of the [*Tbt(Mes)Si(μ-Se)<sub>2</sub>ZrCp<sub>2</sub>*]

In a 5φ Pyrex glass tube was placed a THF solution (0.5 mL) of a mixture of *Tbt(Mes)Si=Si(Mes)Tbt* (30.6 mg, 0.0215 mmol) and [*Cp<sub>2</sub>ZrSe<sub>5</sub>*] (28.4 mg, 0.0461 mmol). After three freeze-pump-thaw cycles, the tube was evacuated and sealed. The solution was heated at 60 °C for 20 h, during which time the original orange suspension turned into a deep red solution. The tube was opened and the solvent was removed under reduced pressure in a glovebox filled with argon. Benzene (5 ml) was added to the residue, and the mixture was filtered through Celite<sup>®</sup>. After concentration under reduced pressure, C<sub>6</sub>D<sub>6</sub> (0.5 ml) was added to the mixture and the measurement of <sup>1</sup>H and <sup>29</sup>Si NMR spectra indicated the formation of [*Tbt(Mes)Si(μ-Se)<sub>2</sub>ZrCp<sub>2</sub>*] (δ<sub>Si</sub> = –36.5, ~60%), the yield of which was judged by the ratio of the integrated intensity of the <sup>1</sup>H NMR. The THF solution of the reaction mixture containing [*Tbt(Mes)Si(μ-Se)<sub>2</sub>ZrCp<sub>2</sub>*] was opened in the air and the solvent was removed. After the residue was dissolved in benzene and filtrated through Celite<sup>®</sup>, the solvent was removed again under reduced pressure. The residue was separated by GPLC (toluene) to afford pure hydroxysilaneselenol **1c** (21.2 mg, 0.0285 mmol, 62%) as an orange solid. Pale orange crystals suitable for X-ray structural analysis of **1c** were grown from hexane at –20 °C. **1c**: pale orange crystals, m.p. 76 °C (dec.); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 0.90 (s, 1H, <sup>1</sup>J<sub>SeH</sub> = 48.4 Hz, SeH), 0.09 (s, 9H), 0.12 (s, 9H), 0.17 (s, 18H), 0.27 (s, 9H), 0.28 (s, 9H), 1.47 (s, 1H), 2.07 (s, 3H), 2.12 (s, 1H, OH), 2.51 (s, 6H), 2.77 (s, 1H), 2.86 (s, 1H), 6.49 (s, 1H), 6.62 (s, 1H), 6.68 (s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.00 (CH<sub>3</sub>), 1.13 (CH<sub>3</sub>), 1.40 (CH<sub>3</sub>), 1.86 (CH<sub>3</sub>), 2.16 (CH<sub>3</sub>), 20.92 (CH<sub>3</sub>), 25.23 (CH<sub>3</sub>), 28.10 (CH), 28.39 (CH), 30.94 (CH), 123.46 (CH), 128.11 (C), 128.53 (CH), 130.23 (CH), 136.71 (C), 139.74 (C), 142.72 (C), 145.21 (C), 151.38 (C), 151.65 (C); <sup>29</sup>Si NMR (59 MHz, C<sub>6</sub>D<sub>6</sub>) δ –9.53, 2.02, 2.08, 2.76, 3.16, 3.28; <sup>77</sup>Se NMR (95 MHz, C<sub>6</sub>D<sub>6</sub>) δ

–96.4; IR (KBr) 3511 [ν(O–H)], 2479 [ν(Se–H)]; LRMS (FAB<sup>+</sup>) *m/z*: calcd. for C<sub>36</sub>H<sub>72</sub>O<sup>80</sup>SeSi<sub>7</sub> ([M]<sup>+</sup>) 796, found 796; HRMS (FAB<sup>+</sup>) *m/z*: calcd. for C<sub>36</sub>H<sub>72</sub>O<sup>80</sup>SeSi<sub>7</sub> ([M]<sup>+</sup>) 796.3133, found 796.3101. Anal. Calc. for C<sub>36</sub>H<sub>72</sub>OSeSi<sub>7</sub>: C, 54.28; H, 9.11. Found: C, 54.52; H, 9.05%.

#### 4.6. Synthesis of *Tbt(Mes)Si(SMe)<sub>2</sub>* (**11**)

To a solution of **1a** (40.0 mg, 0.0522 mmol) in THF (3 mL) was added *n*-BuLi (1.64 N hexane solution, 0.0800 mL, 0.131 mmol) at 0 °C. After the mixture was stirred at 0 °C for 30 min, iodomethane (0.976 mL, 15.7 mmol) was added. After the removal of the solvent, hexane (10 mL) was added to the residue. The mixture was filtrated through Celite<sup>®</sup>, and the solvent was removed under reduced pressure. The residue was separated with PTLC (hexane) to afford **11** (40.2 mg, 0.0506 mmol, 97%) as a colorless solid. Colorless crystals suitable for X-ray structural analysis were grown from hexane at –20 °C. **11**: colorless crystals, m.p. 138–140 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.04 (s, 36H), 0.06 (s, 18H), 1.29 (s, 1H), 1.87 (s, 6H, SMe), 2.21 (s, 3H), 2.49 (s, 1H), 2.59 (s, 6H), 2.63 (s, 1H), 6.23 (s, 1H), 6.38 (s, 1H), 6.75 (s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 0.86 (CH<sub>3</sub>), 1.01 (CH<sub>3</sub>), 1.68 (CH<sub>3</sub>), 1.96 (CH<sub>3</sub>), 13.02 (CH<sub>3</sub>, SMe), 20.85 (CH<sub>3</sub>), 24.63 (CH<sub>3</sub>), 28.54 (CH), 28.97 (CH), 29.70 (CH), 122.87 (C), 122.96 (C), 126.98 (C), 128.10 (C), 130.17 (CH), 130.60 (C), 139.22 (CH), 144.31 (CH), 144.77 (C), 150.62 (C); <sup>29</sup>Si NMR (59 MHz, CDCl<sub>3</sub>) δ 1.84, 3.03, 8.21; LRMS (FAB<sup>+</sup>) *m/z*: calcd. for C<sub>38</sub>H<sub>76</sub>Si<sub>7</sub>S<sub>2</sub> ([M]<sup>+</sup>) 792, found 792; HRMS (FAB<sup>+</sup>) *m/z*: calcd. for C<sub>38</sub>H<sub>76</sub>Si<sub>7</sub>S<sub>2</sub> ([M]<sup>+</sup>) 792.3773, found: 792.3790. Anal. Calc. for C<sub>38</sub>H<sub>76</sub>S<sub>2</sub>Si<sub>7</sub>: C, 57.50; H, 9.65; S, 8.08. Found: C, 57.75; H, 9.62; S, 8.12%.

#### 4.7. Synthesis of *Tbt(Mes)Si(μ-S)<sub>2</sub>SbBbt* (**12**)

To a solution of **1a** (83.5 mg, 0.109 mmol) in THF (5 mL) was added *n*-BuLi (1.64 N hexane solution, 0.166 mL, 0.273 mmol) at 0 °C. After the mixture was stirred at 0 °C for 30 min, a THF (10 mL) solution of *BbtSbBr<sub>2</sub>* (148 mg, 0.164 mmol) was added. After the removal of the solvent, hexane (10 mL) was added to the residue. The mixture was filtrated through Celite<sup>®</sup>, and the solvent was removed under reduced pressure. The residue was separated with GPLC (toluene) and WCC (hexane) to afford **12** (52.3 mg, 0.0346 mmol, 32%) as a pale yellow solid. Pale yellow crystals suitable for X-ray structural analysis were grown from hexane at –20 °C. **12**: pale yellow crystals, m.p. 147 °C (dec.); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 0.20 (s, 18H), 0.24 (s, 36H), 0.31 (s, 27H), 0.33 (s, 36H), 1.53 (s, 1H), 2.08 (s, 3H), 2.41 (s, 2H), 2.78 (s, 6H), 3.29 (s, 1H), 3.41 (s, 1H), 6.50 (s, 1H), 6.68 (s, 2H), 6.70 (s, 1H), 6.96 (s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.21 (CH<sub>3</sub>), 1.59 (CH<sub>3</sub>), 2.12 (CH<sub>3</sub>), 5.64 (CH<sub>3</sub>), 20.79 (CH<sub>3</sub>), 22.76 (CH<sub>3</sub>), 25.90 (CH<sub>3</sub>), 29.10 (CH), 31.88 (CH), 32.57 (CH), 122.06 (CH), 128.26 (CH), 128.29 (CH), 129.13 (C), 130.73 (CH), 131.32 (C), 139.31 (C), 140.95 (C), 141.87 (C), 143.69 (C), 145.42 (C), 147.35 (C), 150.49 (C), 152.59 (C); <sup>29</sup>Si NMR (59 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.16, 2.08, 2.37, 2.97, 3.18, 31.3; LRMS (FAB<sup>+</sup>) *m/z*: calcd. for C<sub>66</sub>H<sub>137</sub>S<sub>2</sub><sup>123</sup>SbSi<sub>14</sub> 1510, found 1510; HRMS (FAB<sup>+</sup>) *m/z*: calcd. for C<sub>66</sub>H<sub>137</sub>S<sub>2</sub><sup>123</sup>SbSi<sub>14</sub> ([M]<sup>+</sup>) 1508.5973, found: 1508.5959. Anal. Calc. for C<sub>66</sub>H<sub>137</sub>S<sub>2</sub>SbSi<sub>14</sub>: C, 52.50; H, 9.15; S, 4.25. Found: C, 52.86; H, 9.28; S, 4.09%.

#### 4.8. Synthesis of *Tbt(Mes)Si(μ-S)<sub>2</sub>BiBbt* (**13**)

To a solution of **1a** (98.7 mg, 0.129 mmol) in THF (5 mL) was added *n*-BuLi (1.64 N hexane solution, 0.157 mL, 0.257 mmol) at 0 °C. After the mixture was stirred at 0 °C for 30 min, a THF (10 mL) solution of *BbtBiBr<sub>2</sub>* (128 mg, 0.129 mmol) was added. After the removal of the solvent, hexane (10 mL) was added to the residue. The mixture was filtrated through Celite<sup>®</sup>, and the sol-

vent was removed under reduced pressure. The residue was separated with GLPC (toluene) and WCC (hexane) to afford **13** (117 mg, 0.0735 mmol, 52%) as an orange solid. Orange crystals of **13** suitable for X-ray structural analysis were grown from hexane at  $-20^{\circ}\text{C}$ . **13**: orange crystals, m.p.  $122^{\circ}\text{C}$  (dec.);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.21 (s, 18H), 0.22 (s, 36H), 0.32 (s, 27H), 0.33 (s, 36H), 1.53 (s, 1H), 2.09 (s, 3H), 2.23 (s, 2H), 2.93 (s, 6H), 3.46 (s, 2H), 6.59 (s, 1H), 6.68 (s, 2H), 6.70 (s, 1H), 7.40 (s, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ , 323 K)  $\delta$  1.22 ( $\text{CH}_3$ ), 1.44 ( $\text{CH}_3$ ), 2.30 ( $\text{CH}_3$ ), 5.63 ( $\text{CH}_3$ ), 20.81 ( $\text{CH}_3$ ), 22.95 (CH), 26.35 ( $\text{CH}_3$ ), 28.94 (CH), 31.17 (CH), 34.71 ( $\text{CH}\times 2$ ), 127.79 (C), 128.10 (CH), 128.53 (CH), 130.96 (CH), 130.98 (CH), 133.14 (C), 138.98 (C), 141.96 (C), 143.79 (C), 144.91 (C), 146.36 (C), 151.99 (C), 152.17 (C), 152.23 (C);  $^{29}\text{Si}$  NMR (59 MHz,  $\text{C}_6\text{D}_6$ , 323 K)  $\delta$  1.14, 1.75, 1.98, 2.93, 3.20, 7.06; LRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for  $\text{C}_{66}\text{H}_{137}\text{BiS}_2\text{Si}_{14}$  1595, found 1595; HRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for  $\text{C}_{66}\text{H}_{137}\text{BiS}_2\text{Si}_{14}$  ([M]<sup>+</sup>) 1595.6814, found 1595.6798. Anal. Calc. for  $\text{C}_{66}\text{H}_{137}\text{BiS}_2\text{Si}_{14}$ : C, 49.63; H, 8.65; S, 4.02. Found: C, 49.89; H, 8.57; S, 3.74%.

#### 4.9. Synthesis of [Tbt(Mes)Si( $\mu$ -S)<sub>2</sub>Pd(PPh<sub>3</sub>)<sub>2</sub>] (**16**)

To a solution of **1a** (69.9 mg, 0.0913 mmol) in THF (5 mL) was added *n*-BuLi (1.64 N hexane solution, 0.156 mL, 0.256 mmol) at  $0^{\circ}\text{C}$ , during which time the original colorless solution turned pale yellow. After the mixture was stirred at  $0^{\circ}\text{C}$  for 30 min, a THF solution (15 mL) of *cis*-[PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (96.1 mg, 0.137 mmol) was added. The pale yellow solution turned deep brown. After the removal of the solvent, benzene (3 mL) was added to the residue. The mixture was filtrated through Celite<sup>®</sup>, and the solvent was removed under reduced pressure. The residue was separated with GLPC (toluene) to afford **16** (114 mg, 0.0819 mmol, 90%) as an orange solid. Orange crystals suitable for X-ray structural analysis were grown from hexane and benzene. **16**: orange crystals, m.p.  $214^{\circ}\text{C}$  (dec.);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.22 (s, 18H), 0.29 (s, 18H), 0.34 (s, 18H), 1.50 (s, 1H), 2.29 (s, 3H), 2.72 (s, 1H), 2.91 (s, 1H), 2.94 (s, 6H), 6.50 (s, 1H), 6.62 (s, 1H), 6.83 (s, 2H), 6.83–6.93 (m, 18H, PPh<sub>3</sub>), 7.45–7.56 (m, 12H, PPh<sub>3</sub>);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.2 ( $\text{CH}_3$ ), 2.2 ( $\text{CH}_3$ ), 2.5 ( $\text{CH}_3$ ), 21.1 ( $\text{CH}_3$ ), 25.5 (CH), 27.0 ( $\text{CH}_3$ ), 30.4 (CH), 123.5 (CH), 128.0 [AA'X pattern,  $1/2(^2J_{\text{CP}} + ^5J_{\text{CP}}) = 4.9$  Hz, CH], 128.6 (CH), 123.0 (CH), 130.1 (CH), 132.0 [AA'X pattern,  $1/2(^1J_{\text{CP}} + ^3J_{\text{CP}}) = 21.6$  Hz, C], 135.2 [AA'X pattern,  $1/2(^2J_{\text{CP}} + ^4J_{\text{CP}}) = 5.9$  Hz, CH], 136.2 (C), 136.6 (C), 141.9 (C), 143.0 (C), 143.4 (C), 150.8 (C), 151.5 (C);  $^{29}\text{Si}$  NMR (59 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.8, 2.6, 15.2;  $^{31}\text{P}$  NMR (120 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  30.6; LRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for  $\text{C}_{72}\text{H}_{100}\text{P}_2^{108}\text{PdS}_2\text{Si}_7$  ([M]<sup>+</sup>) 1394, found 1394; HRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for  $\text{C}_{72}\text{H}_{101}\text{P}_2^{108}\text{PdS}_2\text{Si}_7$  ([M+H]<sup>+</sup>) 1395.4244, found 1395.4236. Anal. Calc. for  $\text{C}_{72}\text{H}_{100}\text{P}_2\text{PdS}_2\text{Si}_7$ : C, 62.01; H, 7.23; S, 4.60. Found: C, 62.29; H, 7.48; S, 4.49%.

#### 4.10. Synthesis of [Tbt(Mes)Si( $\mu$ -S)<sub>2</sub>Pt(PPh<sub>3</sub>)<sub>2</sub>] (**17a**)

To a solution of **1a** (27.8 mg, 0.0363 mmol) in THF (3 mL) was added *n*-BuLi (1.64 N hexane solution, 0.0510 mL, 0.0821 mmol) at  $0^{\circ}\text{C}$ . After the mixture was stirred at  $0^{\circ}\text{C}$  for 30 min, a THF solution (15 mL) of *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (43.1 mg, 0.0544 mmol) was added. The pale yellow solution turned deep yellow. After the removal of the solvent, benzene (3 mL) was added to the residue. The mixture was filtrated through Celite<sup>®</sup>, and the solvent was removed under reduced pressure. The residue was separated with GLPC (toluene) to afford **17a** (50.5 mg, 0.0341 mmol, 94%) as a pale yellow solid. Pale yellow crystals suitable for X-ray structural analysis were grown from hexane at  $-20^{\circ}\text{C}$ . **17a**: pale yellow crystals, m.p.  $250^{\circ}\text{C}$  (dec.);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.21 (s, 18H), 0.29 (s, 18H), 0.34 (s, 18H), 1.49 (s, 1H), 2.11 (s, 1H), 2.31 (s, 3H), 2.53 (s, 1H), 2.93 (s, 6H), 6.50 (s, 1H), 6.62 (s, 1H), 6.83 (s, 2H), 6.85–6.94 (m, 18H, PPh<sub>3</sub>), 7.49–7.55 (m, 12H, PPh<sub>3</sub>);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,

$\text{C}_6\text{D}_6$ )  $\delta$  1.2 ( $\text{CH}_3$ ), 2.1 ( $\text{CH}_3$ ), 2.5 ( $\text{CH}_3$ ), 21.1 ( $\text{CH}_3$ ), 25.3 (CH), 25.6 (CH), 26.9 ( $\text{CH}_3$ ), 30.5 (CH), 127.8 (CH), 128.3 (CH), 128.5 (CH), 128.6 (d,  $^4J_{\text{CP}} = 1.2$  Hz, CH), 131.41 (d,  $^3J_{\text{CP}} = 1.9$  Hz, CH), 131.42 (dd,  $^1J_{\text{CP}} = 54.9$  Hz,  $^3J_{\text{CP}} = 6.8$  Hz, C), 135.3 [AA'X pattern,  $1/2(^2J_{\text{CP}} + ^4J_{\text{CP}}) = 5.5$  Hz, CH], 136.6 (C), 137.9 (C), 141.9 (C), 143.1 (C), 143.3 (C), 151.3 (C), 151.6 (C);  $^{29}\text{Si}$  NMR (59 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.6, 2.5, 14.1;  $^{31}\text{P}$  NMR (120 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  21.2 (s, with platinum satellites,  $^1J_{\text{PPT}} = 3047$  Hz);  $^{195}\text{Pt}$  NMR (64 MHz,  $\text{C}_6\text{D}_6$ ,  $\text{Na}_2\text{PtCl}_4$ )  $\delta$   $-4527.7$  (t,  $^1J_{\text{PPT}} = 3047$  Hz); LRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for  $\text{C}_{72}\text{H}_{100}\text{P}_2^{195}\text{PtS}_2\text{Si}_7$  ([M]<sup>+</sup>) 1481, found 1481; HRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for  $\text{C}_{72}\text{H}_{100}\text{P}_2^{195}\text{PtS}_2\text{Si}_7$  ([M]<sup>+</sup>) 1481.4774, found 1481.4771. Anal. Calc. for  $\text{C}_{72}\text{H}_{100}\text{P}_2\text{PtS}_2\text{Si}_7$ : C, 58.30; H, 6.80; S, 4.32. Found: C, 58.39; H, 6.89; S, 4.31%.

#### 4.11. Synthesis of [Tbt(Mes)Si( $\mu$ -O)( $\mu$ -S)Pt(PPh<sub>3</sub>)<sub>2</sub>] (**17b**)

To a solution of **1b** (60.1 mg, 0.0802 mmol) in THF (3 mL) was added NaH (4.23 mg, 0.176 mmol) at  $0^{\circ}\text{C}$ . After the mixture was stirred at  $0^{\circ}\text{C}$  for 30 min, a THF solution (15 mL) of *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (63.4 mg, 0.0802 mmol) was added, and the mixture was stirred for 30 min at  $0^{\circ}\text{C}$  and then for 1.5 h while being warmed up to room temperature. After the removal of the solvent, hexane (5 mL) was added to the residue. The mixture was filtrated through Celite<sup>®</sup>, and the solvent was removed under reduced pressure. The residue was recrystallized from hexane at  $-20^{\circ}\text{C}$  to give pure **17b** (105 mg, 0.0714 mmol, 89%) as pale yellow crystals. **17b**: pale yellow crystals, m.p.  $185^{\circ}\text{C}$  (dec.);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.21 (s, 18H), 0.23 (s, 36H), 1.50 (s, 1H), 2.40 (s, 3H), 2.61 (s, br, 3H), 2.84 (s, br, 3H), 6.52 (s, 1H), 6.65 (s, 1H), 6.76 (s $\times$ 2, br, 2H), 6.81–6.87 (m, 6H), 6.90–6.97 (m, 12H), 7.40–7.46 (m, 6H), 7.59–7.63 (m, 6H), *o*-benzyl protons of the Tbt group could not be observed because of the overlap with those of the Mes group;  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.21 ( $\text{CH}_3$ ), 1.36 ( $\text{CH}_3$ ), 1.90 ( $\text{CH}_3$ ), 21.33 ( $\text{CH}_3\times 2$ ), 26.12 (CH), 26.63 (CH), 30.17 (CH), 30.66 ( $\text{CH}_3$ ), 127.56 (CH), 128.17 (CH), 128.54 (CH), 129.32 (CH), 130.12 (C, dd,  $^1J_{\text{CP}} = 22.2$  Hz,  $^3J_{\text{CP}} = 2.5$  Hz), 130.69 (C, dd,  $^1J_{\text{CP}} = 22.2$  Hz,  $^3J_{\text{CP}} = 2.5$  Hz), 130.97 (C), 131.22 (CH, d,  $^3J_{\text{CP}} = 3.7$  Hz), 131.37 (CH, d,  $^3J_{\text{CP}} = 3.7$  Hz), 131.44 (CH, d,  $^4J_{\text{CP}} = 1.2$  Hz), 131.68 (C), 132.25 (CH, d,  $^4J_{\text{CP}} = 1.2$  Hz), 132.55 (C), 135.23 [CH, d, AA'X pattern,  $1/2(^2J_{\text{CP}} + ^4J_{\text{CP}}) = 6.4$  Hz], 135.69 [CH, d, AA'X pattern,  $1/2(^2J_{\text{CP}} + ^4J_{\text{CP}}) = 6.4$  Hz], 136.36 (C), 143.19 (C), 145.07 (C), 149.98 (C), 150.39 (C);  $^{29}\text{Si}$  NMR (59 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.7, 2.0, 5.3;  $^{31}\text{P}$  NMR (120 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  6.68 (d, with platinum satellites,  $^1J_{\text{PPT}} = 3532$  Hz,  $^2J_{\text{PP}} = 21$  Hz), 25.10 (d, with platinum satellites,  $^1J_{\text{PPT}} = 3209$  Hz,  $^2J_{\text{PP}} = 21$  Hz); HRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for  $\text{C}_{72}\text{H}_{100}\text{OP}_2^{196}\text{PtSSi}_7$  1466.5004, found 1466.5013. Anal. Calc. for  $\text{C}_{72}\text{H}_{100}\text{OP}_2\text{PtSSi}_7$ : C, 58.94; H, 6.87; S, 2.19. Found: C, 58.90; H, 6.83; S, 2.12%.

#### 4.12. Synthesis of [Tbt(Mes)Si( $\mu$ -O)( $\mu$ -Se)Pt(PPh<sub>3</sub>)<sub>2</sub>] (**17c**)

To a solution of hydroxysilaneselelenol **1c** (47.3 mg, 0.0594 mmol) in THF (3 mL) was added NaH (3.60 mg, 0.150 mmol) at  $0^{\circ}\text{C}$ . After the mixture was stirred at  $0^{\circ}\text{C}$  for 30 min, a THF solution (15 mL) of *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (46.9 mg, 0.0593 mmol) was added, and the mixture was stirred for 30 min at  $0^{\circ}\text{C}$  and then for 1.5 h while being warmed up to room temperature. After the removal of the solvent, hexane (5 mL) was added to the residue. The mixture was filtrated through Celite<sup>®</sup>, and the solvent was removed under reduced pressure. The residue was recrystallized from benzene at room temperature to give pure **17c** (80.7 mg, 0.0533 mmol, 90%) as pale yellow crystals. **17c**: pale yellow crystals, m.p.  $172^{\circ}\text{C}$  (dec.);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.15 (s, 18H), 0.22 (s, 36H), 1.49 (s, 1H), 2.41 (s, 3H), 2.58 (br, s, 3H), 2.73 (br, s, 3H), 6.48 (s, 1H), 6.60 (s, 1H), 6.76 (s $\times$ 2, 2H), 6.78–6.85 (m, 6H), 6.88–6.93 (m, 12H), 7.42–7.48 (m, 6H), 7.59–7.66 (m, 6H), *o*-benzyl protons of the Tbt group could not be observed because of

the overlap with those of the Mes group;  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.27 (CH<sub>3</sub>), 1.32 (CH<sub>3</sub>), 2.20 (CH<sub>3</sub>), 21.26 (CH<sub>3</sub>×2), 26.15 (CH), 27.31 (CH), 30.95 (CH), 31.87 (CH<sub>3</sub>), 127.53 (CH), 128.12 (CH), 128.53 (CH), 129.33 (CH), 129.9 (C, dd,  $^1J_{\text{CP}} = 22.8$  Hz,  $^3J_{\text{CP}} = 2.5$  Hz), 130.21 (C, dd,  $^1J_{\text{CP}} = 22.8$  Hz,  $^3J_{\text{CP}} = 2.5$  Hz), 131.45 (C), 132.13 (C), 132.24 (CH, d,  $^3J_{\text{CP}} = 2.9$  Hz), 132.45 (C), 133.06 (CH, d,  $^3J_{\text{CP}} = 2.9$  Hz), 133.85 (CH, d,  $^4J_{\text{CP}} = 1.2$  Hz), 134.42 (CH, d,  $^4J_{\text{CP}} = 1.2$  Hz), 135.29 [CH, d, AA'X pattern,  $1/2 (^2J_{\text{CP}} + ^4J_{\text{CP}}) = 6.8$  Hz], 135.69 [CH, d, AA'X pattern,  $1/2 (^2J_{\text{CP}} + ^4J_{\text{CP}}) = 6.8$  Hz], 136.51 (C), 143.48 (C), 145.60 (C), 152.09 (C), 152.44 (C);  $^{29}\text{Si}$  NMR (59 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -3.3, 1.7, 2.2;  $^{77}\text{Se}$  NMR (95 MHz,  $\text{C}_6\text{D}_6$ , 330 K)  $\delta$  14.4 ( $^1J_{\text{SePt}} = 256$  Hz,  $^2J_{\text{SePt}} = 27$  Hz);  $^{31}\text{P}$  NMR (120 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  6.21 (d, with platinum satellites,  $^1J_{\text{PPt}} = 3537$  Hz,  $^2J_{\text{PPt}} = 19$  Hz), 24.67 (d, with platinum satellites,  $^1J_{\text{PPt}} = 3206$  Hz,  $^2J_{\text{PPt}} = 19$  Hz); HRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for  $\text{C}_{72}\text{H}_{100}\text{OP}_2^{195}\text{Pt}^{80}\text{SeSi}_7$  1513.4448, found 1513.4446. Anal. Calc. for  $\text{C}_{72}\text{H}_{100}\text{OP}_2\text{PtSeSi}_7$ : C, 57.11; H, 6.66. Found: C, 57.31; H, 6.66%.

#### 4.13. Synthesis of [Tbt(Mes)Si( $\mu$ -S)<sub>2</sub>Ru( $\eta^6$ -benzene)] (18a)

To a solution of **1a** (76.6 mg, 0.100 mmol) in THF (2 mL) was added *n*-BuLi (1.64 N hexane solution, 0.124 mL, 0.200 mmol) at 0 °C. After the mixture was stirred at 0 °C for 30 min, a THF solution (25 mL) of [RuCl<sub>2</sub>(benzene)]<sub>2</sub> (25.0 mg, 0.0502 mmol) was added. The pale yellow solution turned deep brown. After the removal of the solvent, hexane (10 mL) was added to the residue. The mixture was filtrated through Celite<sup>®</sup>, and the solvent was removed under reduced pressure. The residue was separated with WCC (hexane:Et<sub>2</sub>O = 2:1) to afford **18a** (69.0 mg, 0.0725 mmol, 72%) as a deep green solid. Deep green crystals suitable for X-ray structural analysis were grown from benzene. **18a**: deep green crystals, m.p. 190 °C (dec.);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.21 (s, 18H), 0.30 (s, 18H), 0.32 (s, 18H), 1.50 (s, 1H), 2.02 (s, 3H), 2.85 (s, 6H), 3.03 (s, 1H), 3.12 (s, 1H), 4.71 (s, 6H), 6.52 (s, 1H), 6.64 (s, 1H), 6.69 (s, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.14 (CH<sub>3</sub>), 1.99 (CH<sub>3</sub>), 2.32 (CH<sub>3</sub>), 20.83 (CH<sub>3</sub>), 27.93 (CH<sub>3</sub>), 27.61 (CH), 30.35 (CH), 30.72 (CH), 78.56 (CH), 128.62 (CH), 128.91 (CH), 129.97 (CH), 133.16 (C), 136.98 (C), 137.91 (C), 143.41 (C), 144.16 (C), 151.59 (C), 152.98 (C);  $^{29}\text{Si}$  NMR (59 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.9, 2.7, 44.1; LRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for  $\text{C}_{42}\text{H}_{76}^{102}\text{RuS}_2\text{Si}_7$  ([M]<sup>+</sup>) 942, found 942; HRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for  $\text{C}_{42}\text{H}_{76}^{102}\text{RuS}_2\text{Si}_7$  ([M]<sup>+</sup>) 942.2817, found 942.2811. Anal. Calc. for  $\text{C}_{42}\text{H}_{76}\text{RuS}_2\text{Si}_7$ : C, 53.50; H, 8.12. Found: C, 53.69; H, 8.34%.

#### 4.14. Synthesis of [Tbt(Mes)Si( $\mu$ -O)( $\mu$ -S)Ru( $\eta^6$ -benzene)] (18b)

To a solution of **1b** (80.0 mg, 0.108 mmol) in THF (2 mL) was added NaH (5.20 mg, 0.217 mmol) at 0 °C. After the mixture was stirred at 0 °C for 30 min, a THF solution (25 mL) of [RuCl<sub>2</sub>(benzene)]<sub>2</sub> (29.6 mg, 0.0593 mmol) was added, and the pale yellow solution turned deep brown. After the removal of the solvent, hexane (10 mL) was added to the residue. The mixture was filtrated through Celite<sup>®</sup>, and the solvent was removed under reduced pressure. The residue was separated with WCC (hexane:Et<sub>2</sub>O = 2:1) to afford **18b** (51.9 mg, 0.0561 mmol, 52%) as a deep violet solid. Deep violet crystals suitable for X-ray structural analysis were grown from benzene. **18b**: deep violet crystals, m.p. 195 °C (dec.);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.17 (s, 18H), 0.20 (s, 36H), 1.49 (s, 1H), 2.12 (s, 3H), 2.71 (s, 6H), 3.24 (s, 1H), 3.29 (s, 1H), 4.80 (s, 6H), 6.48 (s, 1H), 6.61 (s, 1H), 6.74 (s, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.02 (CH<sub>3</sub>), 1.17 (CH<sub>3</sub>), 23.00 (CH<sub>3</sub>), 25.26 (CH<sub>3</sub>), 27.19 (CH), 27.81 (CH), 30.63 (CH), 76.73 (CH), 128.54 (CH), 128.63 (CH), 129.35 (CH), 133.06 (C), 136.89 (C), 138.11 (C), 142.95 (C), 143.90 (C), 151.00 (C), 151.28 (C);  $^{29}\text{Si}$  NMR (59 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.9, 2.7, 25.2; LRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for  $\text{C}_{42}\text{H}_{77}\text{O}^{102}\text{RuSSi}_7$  ([M+H]<sup>+</sup>) 927, found 927; HRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for

$\text{C}_{42}\text{H}_{77}\text{O}^{102}\text{RuSSi}_7$  ([M+H]<sup>+</sup>) 927.3123, found 927.3120. Anal. Calc. for  $\text{C}_{42}\text{H}_{76}\text{ORuSSi}_7$ : C, 54.43; H, 8.27. Found: C, 54.14; H, 7.98%.

#### 4.15. Synthesis of [Tbt(Mes)Si( $\mu$ -O)( $\mu$ -Se)Ru( $\eta^6$ -benzene)] (18c)

To a solution of **1c** (66.7 mg, 0.0845 mmol) in THF (2 mL) was added NaH (4.40 mg, 0.184 mmol) at 0 °C. After the mixture was stirred at 0 °C for 30 min, a THF solution (25 mL) of [RuCl<sub>2</sub>(benzene)]<sub>2</sub> (25.3 mg, 0.0507 mmol) was added, and the pale yellow solution turned deep brown. After the removal of the solvent, hexane (10 mL) was added to the residue. The mixture was filtrated through Celite<sup>®</sup>, and the solvent was removed under reduced pressure. The residue was separated with WCC (hexane:Et<sub>2</sub>O = 2:1) to afford **18c** (50.3 mg, 0.0516 mmol, 61%) as a deep blue solid. Deep blue crystals suitable for X-ray structural analysis were grown from benzene. **18c**: deep blue crystals, m.p. 168 °C (dec.);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.15 (s, 18H), 0.17 (s, 18H), 0.46 (s, 18H), 1.49 (s, 1H), 2.13 (s, 3H), 2.70 (s, 6H), 3.29 (s, 1H), 3.31 (s, 1H), 4.79 (s, 6H), 6.50 (s, 1H), 6.62 (s, 1H), 6.73 (s, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.03 (CH<sub>3</sub>), 1.19 (CH<sub>3</sub>), 1.37 (CH<sub>3</sub>), 21.06 (CH<sub>3</sub>), 25.19 (CH<sub>3</sub>), 27.69 (CH), 27.97 (CH), 30.65 (CH), 76.25 (CH), 128.33 (CH), 128.54 (CH), 129.41 (CH), 132.56 (C), 137.12 (C), 138.20 (C), 142.64 (C), 143.94 (C), 150.82 (C), 151.15 (C);  $^{77}\text{Se}$  NMR (95 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  543.1;  $^{29}\text{Si}$  NMR (59 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.9, 2.0, 2.8, 19.9; LRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for  $\text{C}_{42}\text{H}_{77}\text{O}^{102}\text{Ru}^{80}\text{SeSi}_7$  ([M+H]<sup>+</sup>) 975, found 975; HRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for  $\text{C}_{42}\text{H}_{77}\text{O}^{102}\text{Ru}^{80}\text{SeSi}_7$  ([M+H]<sup>+</sup>) 975.2568, found 975.2573. Anal. Calc. for  $\text{C}_{42}\text{H}_{76}\text{ORuSeSi}_7$ : C, 51.81; H, 7.87. Found: C, 51.56; H, 8.05%.

#### 4.16. Synthesis of [Tbt(Mes)Si( $\mu$ -S)<sub>2</sub>Ru(PMe<sub>3</sub>)<sub>3</sub>] (19a)

To a solution of **18a** (80.5 mg, 0.0854 mmol) in THF (3 mL) was added PMe<sub>3</sub> (1.0 [M] THF solution, 0.850 mL, 0.850 mmol) at room temperature. After the mixture was stirred at the temperature for 10 min, the deep green solution turned deep red. After the removal of the solvent under reduced pressure, the residue was recrystallized from hexane to afford **19a** (92.4 mg, 0.0845 mmol, 99%). **19a**: red crystals, m.p. 202 °C (dec.);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.24 (s, 18H), 0.39 (s, 18H), 0.40 (s, 18H), 1.05 (m, 27H), 1.53 (s, 1H), 2.18 (s, 3H), 3.13 (s, 6H), 3.98 (s, 1H), 4.05 (s, 1H), 6.57 (s, 1H), 6.67 (s, 1H), 6.82 (s, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.33 (CH<sub>3</sub>), 2.44 (CH<sub>3</sub>), 2.72 (CH<sub>3</sub>), 20.94 (CH<sub>3</sub>), 21.28 (PMe<sub>3</sub>, m), 25.83 (CH), 26.02 (CH), 27.11 (CH<sub>3</sub>), 30.41 (CH), 123.81 (CH), 128.54 (C), 129.39 (CH), 129.99 (CH), 136.60 (C), 141.43 (C), 142.35 (C), 143.95 (C), 151.02 (C), 151.24 (C);  $^{31}\text{P}$  NMR (120 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  21.99;  $^{29}\text{Si}$  NMR (59 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.8, 2.6, 31.1; LRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for  $\text{C}_{45}\text{H}_{97}\text{P}_3^{102}\text{RuS}_2\text{Si}_7$  ([M]<sup>+</sup>) 1092, found 1092; HRMS (FAB<sup>+</sup>)  $m/z$ : calcd. for  $\text{C}_{45}\text{H}_{97}\text{P}_3^{102}\text{RuS}_2\text{Si}_7$  ([M]<sup>+</sup>) 1092.3673, found 1092.3684. Anal. Calc. for  $\text{C}_{45}\text{H}_{97}\text{P}_3\text{RuS}_2\text{Si}_7$ : C, 49.45; H, 8.95; S, 5.87. Found: C, 49.72; H, 9.01; S, 5.61%.

#### 4.17. Synthesis of [Tbt(Mes)Si( $\mu$ -O)( $\mu$ -S)Ru(PMe<sub>3</sub>)<sub>3</sub>] (19b)

To a solution of **18b** (57.7 mg, 0.0606 mmol) in THF (3 mL) was added PMe<sub>3</sub> (1.0 [M] THF solution, 0.600 mL, 0.600 mmol) at room temperature. After the mixture was stirred at the temperature for 10 min, the deep violet solution turned deep red. After the removal of the solvent under reduced pressure, the residue was recrystallized from hexane to afford **19b** (58.5 mg, 0.0543 mmol, 96%). Red crystals suitable for X-ray structural analysis were grown from benzene. **19b**: red crystals, m.p. 208 °C (dec.);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.23 (s, 18H), 0.25 (s, 18H), 0.48 (s, 18H), 1.08 (m, 27H), 1.52 (s, 1H), 2.22 (s, 3H), 2.95 (s, 6H), 4.14 (s, 1H), 4.15 (s, 1H), 6.56 (s, 1H), 6.66 (s, 1H), 6.81 (s, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.39 (CH<sub>3</sub>), 2.39 (CH<sub>3</sub>), 2.69 (CH<sub>3</sub>), 21.00 (CH<sub>3</sub>), 20.58 (PMe<sub>3</sub>, m), 25.93 (CH), 25.79 (CH), 27.23 (CH<sub>3</sub>), 30.51 (CH),

123.78 (CH), 128.66 (C), 129.40 (CH), 130.04 (CH), 136.72 (C), 141.49 (C), 142.57 (C), 143.93 (C), 151.05 (C), 151.44 (C);  $^{31}\text{P}$  NMR (120 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  26.52;  $^{29}\text{Si}$  NMR (59 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.9, 2.7, 25.2; LRMS(FAB $^+$ )  $m/z$ : calcd. for  $\text{C}_{45}\text{H}_{98}\text{OP}_3^{102}\text{RuSi}_7$  ([M+H] $^+$ ) 1077, found 1077; HRMS(FAB $^+$ )  $m/z$ : calcd. for  $\text{C}_{45}\text{H}_{98}\text{OP}_3^{102}\text{RuSi}_7$  ([M+H] $^+$ ) 1077.3980, found 1077.3961.

#### 4.18. Synthesis of [Tbt(Mes)Si( $\mu$ -O)( $\mu$ -Se)Ru(PMe $_3$ ) $_3$ ] (19c)

To a solution of **18c** (55.1 mg, 0.0566 mmol) in THF (3 mL) was added  $\text{PMe}_3$  (1.0 [M] THF solution, 0.550 mL, 0.550 mmol) at room temperature. After the mixture was stirred at the temperature for 10 min, the deep blue solution turned deep red. After the removal of the solvent under reduced pressure, the residue was recrystallized from hexane to afford **19c** (59.0 mg, 0.0524 mmol, 93%). **19c**: red crystals, m.p. 188 °C (dec.);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.13 (s, 18H), 0.25 (s, 18H), 0.47 (s, 18H), 1.08 (s, 27H), 1.52 (s, 1H), 2.22 (s, 3H), 2.93 (s, 6H), 4.08 (s, 1H), 4.25 (s, 1H), 6.57 (s, 1H), 6.66 (s, 1H), 6.80 (s, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.22 (CH $_3$ ), 2.17 (CH $_3$ ), 2.48 (CH $_3$ ), 20.94 (CH $_3$ ), 20.25 (PMe $_3$ , m), 25.93 (CH), 26.02 (CH), 27.35 (CH), 30.72 (CH $_3$ ), 123.96 (CH), 128.71 (C), 129.19 (CH), 130.02 (CH), 136.22 (C), 141.13 (C), 142.31 (C), 143.77 (C), 151.00 (C), 151.34 (C);  $^{31}\text{P}$  NMR (120 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  27.37;  $^{29}\text{Si}$  NMR (59 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.78, 1.80, 1.88, 3.57; LRMS(FAB $^+$ )  $m/z$ : calcd. for  $\text{C}_{45}\text{H}_{98}\text{OP}_3^{102}\text{Ru}^{80}\text{SeSi}_7$  ([M+H] $^+$ ) 1125, found 1125; HRMS(FAB $^+$ )  $m/z$ : calcd. for  $\text{C}_{45}\text{H}_{98}\text{OP}_3^{102}\text{Ru}^{80}\text{SeSi}_7$  ([M+H] $^+$ ) 1125.3424, found 1125.3448. Anal. Calc. for  $\text{C}_{45}\text{H}_{97}\text{OP}_3\text{RuSeSi}_7$ : C, 48.09; H, 8.70. Found: C, 48.37; H, 8.92%.

#### 4.19. X-ray crystallography

The preparation of all samples consisted of coating the crystal with silicon grease, mounting it on a glass fiber, and placing it under a cold stream of  $\text{N}_2$  on the diffractometer. The intensity data of **1a**, **1b**, **1c**, **11**, **12**, **16**, **17a**, **17b**, **17c**, **18b** and **18c** were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71071 \text{ \AA}$ ) to  $2\theta_{\text{max}} = 50^\circ$  at 103 K. The structures of **1a**, **1b**, **1c**, **11**, **12**, **16**, **17a**, **17b**, **17c**, **18b**, and **18c** were solved by direct method (SIR97) [29]. All crystallographic data were refined by full-matrix least-squares procedure on  $F^2$  for all reflections (SHELXL-97) [30]. All the non-hydrogen atoms of **1a**, **1b**, **1c**, **11**, **12**, **16**, **17a**, **17b**, **17c**, **18b** and **18c** were placed using AFIX instruction.

The crystal data of **1a**, **1b**, **1c**, **11**, **12**, **16**, **17a**, **17b**, **17c**, **18b** and **18c** were summarized in Tables 1–3. In the structural analysis of **12**, **17a**, **18b**, and **18c**, some different peaks larger than  $1.00 \text{ e \AA}^{-3}$  were observed near the heavy atom, antimony, platinum, or ruthenium, and could not be completely solved.

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#### Appendix A. Supplementary material

CCDC 627421, 627422, 627425, 703451, 703448, 627425, 627424, 673348, 673349, 703449 and 703450 contain the supplementary crystallographic data for **1a**, **1b**, **1c**, **11**, **12**, **16**, **17a**, **17b**,

**17c**, **18b** and **18c**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.11.001](https://doi.org/10.1016/j.jorganchem.2008.11.001).

#### References

- [1] (a) D.A. Armitage, S. Patai, Z. Rappoport (Eds.), *The Silicon–Heteroatom Bond*, John Wiley & Sons, Chichester, 1991, pp. 213–231; (b) D.A. Armitage, S. Patai, Z. Rappoport (Eds.), *The Silicon–Heteroatom Bond*, John Wiley & Sons, Chichester, 1991, pp. 233–243; (c) D.A. Armitage, S. Patai, Z. Rappoport (Eds.), *The Chemistry of Organic Silicon Compounds*, John Wiley & Sons, Chichester, 1989, pp. 1395–1413; (d) D.A. Armitage, Z. Rappoport, Y. Apeloig (Eds.), *The Chemistry of Organic Silicon Compounds*, vol. 2, Springer, Berlin, 1998, pp. 1869–1894.
- [2] (a) M. Ballestri, C. Chatgililoglu, G. Seconi, *J. Organomet. Chem.* 408 (1991) C1–C4; (b) B. Hache, Y. Gareau, *Tetrahedron Lett.* 35 (1994) 1837–1840; (c) E.I. Miranda, M.J. Diaz, I. Rosado, J.A. Soderquist, *Tetrahedron Lett.* 35 (1994) 3221–3224; (d) J. Daroszewski, J. Luszyk, M. Degueil, C. Navarro, B. Maillard, *J. Chem. Soc., Chem. Commun.* (1991) 586–587; (e) B.P. Roberts, *Chem. Soc. Rev.* 28 (1999) 25–35.
- [3] (a) T. Komuro, T. Matsuo, H. Kawaguchi, K. Tatsumi, *Inorg. Chem.* 42 (2003) 5340–5347; (b) T. Komuro, T. Matsuo, H. Kawaguchi, K. Tatsumi, *Chem. Commun.* (2002) 988–989; (c) J. Albertsen, R. Steudel, *J. Organomet. Chem.* 424 (1992) 153–158; (d) D.M. Giolando, T.B. Rauchfuss, G.M. Clark, *Inorg. Chem.* 26 (1987) 3080–3082; (e) D. Seyferth, R.S. Henderson, L.-C. Song, *Organometallics* 1 (1982) 125–133; (f) D. Seyferth, R.S. Henderson, L.-C. Song, *J. Organomet. Chem.* 192 (1980) C1–C5.
- [4] There are only few reports on dialkyl- or diarylsilanedithiols. Dimethylsilanedithiol has been characterized only by IR spectroscopy due to its extreme instability: (a) G. Gattow, H.P. Dewald, *Z. Anorg. Allg. Chem.* 604 (1991) 63–67; As for diphenylsilanedithiol, only the boiling point has been reported: (b) Y. Cai, B.P. Roberts, *Tetrahedron Lett.* 42 (2001) 763–766; Syntheses and some reactions of several dialkoxysilanedithiols have been reported: (c) W. Wojnowski, M. Wojnowska, *Z. Anorg. Allg. Chem.* 389 (1972) 302–306; (d) W. Wojnowski, M. Wojnowska, *Z. Anorg. Allg. Chem.* 398 (1973) 167–172; (e) W. Wojnowski, A. Herman, *Z. Anorg. Allg. Chem.* 425 (1976) 91–96; (f) W. Wojnowski, E.W. Felcyn, *Z. Anorg. Allg. Chem.* 546 (1987) 229–234.
- [5] Silanediols with the general formula  $\text{RR}'\text{Si}(\text{OH})_2$  (R, R' = alkyl, aryl, N-substituent, hydride) are stable compounds as compared with silanedithiols. There are several reports on silanediol studied by using X-ray diffraction techniques. See: (a) P.D. Lickiss, *Adv. Inorg. Chem.* 42 (1995) 147–262; (b) V. Chandrasekhar, S. Nagendran, R.J. Butcher, *Organometallics* 18 (1999) 4488–4492; (c) R.S. Simons, K.J. Galat, B.J. Rapp, C.A. Tessier, W.J. Youngs, *Organometallics* 19 (2000) 5799–5801; (d) E.A. Reyes-Garcia, F. Cervantes-Lee, K.H. Pannell, *Organometallics* 20 (2001) 4734–4740.
- [6] (a) N. Tokitoh, M. Ito, R. Okazaki, *Organometallics* 14 (1995) 4460–4462; (b) M. Ito, N. Tokitoh, R. Okazaki, *Organometallics* 16 (1997) 4314–4319.
- [7] (a) V. Jancik, Y. Peng, H.W. Roesky, J. Li, D. Neculai, A.M. Neculai, R. Herbst-Irmer, *J. Am. Chem. Soc.* 125 (2003) 1452–1453; (b) V. Jancik, H.W. Roesky, D. Neculai, A.M. Neculai, R. Herbst-Irmer, *Angew. Chem., Int. Ed.* 43 (2004) 6192–6196.
- [8] (a) T. Matsumoto, K. Tatsumi, *Chem. Lett.* (2001) 964–965; (b) T. Matsumoto, Y. Nakaya, K. Tatsumi, *Organometallics* 25 (2006) 4835–4845.
- [9] For reviews see: (a) R. Okazaki, N. Tokitoh, *Acc. Chem. Res.* 33 (2000) 625–630; (b) N. Tokitoh, R. Okazaki, *Adv. Organomet. Chem.* 47 (2001) 121–166.
- [10] For reviews see: (a) N. Tokitoh, *Acc. Chem. Res.* 37 (2004) 86–94; (b) N. Tokitoh, *Bull. Chem. Soc. Jpn.* 77 (2004) 429–441.
- [11] For reviews see: T. Sasamori, N. Tokitoh, *Organometallics* 25 (2006) 3522–3532.
- [12] (a) R. Okazaki, M. Unno, N. Inamoto, *Chem. Lett.* (1987) 2293–2294; (b) R. Okazaki, N. Tokitoh, T. Matsumoto, W.A. Herrmann (Eds.), *Synthetic Methods of Organometallic and Inorganic Chemistry*, vol. 2, Thieme, New York, 1996, pp. 260–269.
- [13] (a) N. Tokitoh, H. Suzuki, R. Okazaki, *J. Am. Chem. Soc.* 115 (1993) 10428–10429; (b) H. Suzuki, N. Tokitoh, R. Okazaki, *J. Am. Chem. Soc.* 116 (1994) 11572–11573; (c) H. Suzuki, N. Tokitoh, R. Okazaki, *Bull. Chem. Soc. Jpn.* 68 (1995) 2471–2481;

- (d) H. Suzuki, N. Tokitoh, R. Okazaki, *Organometallics* 14 (1995) 1016–1022;  
(e) N. Takeda, H. Suzuki, N. Tokitoh, R. Okazaki, S. Nagase, *J. Am. Chem. Soc.* 119 (1997) 1456–1457;  
(f) N. Takeda, N. Tokitoh, R. Okazaki, *Chem. Lett.* (2000) 622–623;  
(g) N. Takeda, T. Kajiwara, H. Suzuki, R. Okazaki, N. Tokitoh, *Chem. Eur. J.* 9 (2003) 3530–3543;  
(h) T. Kajiwara, N. Takeda, T. Sasamori, N. Tokitoh, *Organometallics* 23 (2004) 4723–4734;  
(i) T. Kajiwara, N. Takeda, T. Sasamori, N. Tokitoh, *Chem. Commun.* (2004) 2218–2219;  
(j) N. Takeda, N. Tokitoh, *Synlett* (2007) 2483–2491.
- [14] N. Takeda, T. Tanabe, N. Tokitoh, *Bull. Chem. Soc. Jpn.* 79 (2006) 1573–1579.
- [15] There are some reports on the synthesis of hydroxysilanethiols or hydroxysilaneselenols:  
(a) W. Wojnowski, E.W. Felcyn, *Z. Anorg. Allg. Chem.* 546 (1987) 229–234;  
(b) H. Suzuki, N. Tokitoh, R. Okazaki, S. Nagase, M. Goto, *J. Am. Chem. Soc.* 120 (1998) 11096–11105;  
(c) N. Choi, K. Asano, N. Sato, W. Ando, *J. Organomet. Chem.* 516 (1996) 155–165;  
(d) N. Tokitoh, T. Sadahiro, K. Hatano, T. Sasaki, N. Takeda, R. Okazaki, *Chem. Lett.* (2002) 34–35;  
(e) T. Iwamoto, K. Sato, S. Ishida, C. Kabuto, M. Kira, *J. Am. Chem. Soc.* 128 (2006) 16914–16920.
- [16] T. Tanabe, N. Takeda, N. Tokitoh, *Eur. J. Inorg. Chem.* (2007) 1225–1228.
- [17] T. Tanabe, Y. Mizuhata, N. Takeda, N. Tokitoh, *Organometallics* 27 (2008) 2156–2158.
- [18] A. Bondi, *J. Phys. Chem.* 68 (1964) 441–451.
- [19] For example,  $[\text{Ru}(\text{SH}_2)(\text{PPh}_3)_3\text{S}_4]$  shows one broad band for  $n(\text{S}-\text{H}\cdots\text{S})$  at  $2300\text{ cm}^{-1}$  (KBr): D. Sellmann, P. Lechner, F. Knoch, M. Moll, *J. Am. Chem. Soc.* 114 (1992) 922–930.
- [20] T. Sasamori, E. Mieda, N. Takeda, N. Tokitoh, *Chem. Lett.* 33 (2004) 104–105.
- [21] F.R. Hartley, in: P.L. Robinson (Ed.), *The Chemistry of Platinum and Palladium*, Applied Science Publishers Ltd., London, 1973, pp. 8–26.
- [22] This tendency is almost consistent with that reported for some related platinum chalcogenides, see:  
(a) C. Xu, J.W. Siria, G.K. Anderson, *Inorg. Chim. Acta* 206 (1993) 123–125;  
(b) K. Nagata, N. Takeda, N. Tokitoh, *Bull. Chem. Soc. Jpn.* 76 (2003) 1577–1587.
- [23] (a) K. Mashima, A. Mikami, A. Nakamura, *Chem. Lett.* (1992) 1473–1476;  
(b) K. Mashima, H. Kaneyoshi, S. Kaneko, A. Mikami, K. Tani, A. Nakamura, *Organometallics* 16 (1997) 1016–1025;  
(c) K. Mashima, S. Kaneko, K. Tani, H. Kaneyoshi, A. Nakamura, *J. Organomet. Chem.* 545–546 (1997) 345–356;  
(d) M. Herberhold, H. Yan, W. Milius, *J. Organomet. Chem.* 598 (2000) 142–149;  
(e) J.H. Won, H.G. Lim, B.Y. Kim, C. Lee, Y.J. Lee, S. Cho, J. Ko, S.O. Kang, *Organometallics* 21 (2002) 5703–5712.
- [24] A.B. Pangborn, M.A. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, *Organometallics* 15 (1996) 1518–1520.
- [25] N. Tokitoh, H. Suzuki, R. Okazaki, K. Ogawa, *J. Am. Chem. Soc.* 120 (1998) 10428–10429.
- [26] A. Shaver, J.M. McCall, *Organometallics* 3 (1984) 1823–1829.
- [27] T. Sasamori, Y. Arai, N. Takeda, R. Okazaki, Y. Furukawa, M. Kimura, S. Nagase, N. Tokitoh, *Bull. Chem. Soc. Jpn.* 75 (2002) 661–675.
- [28] M.A. Bennett, A.K. Smith, *J. Chem. Soc., Dalton Trans.* (1974) 233.
- [29] A. Altomare, M.C. Burla, M. Camalli, G.L. Casciarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* 32 (1999) 115.
- [30] G.M. Sheldrick, *SHELX-97 Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.