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Acyclic tetrachalcogenoether ligands tethered with bulky substituents: Their syntheses and coordination chemistry

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Abstract

New *o*-phenylene-bridged tetrachalcogenoether ligands tethered with an extremely bulky substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group, [TbtE(*o*-phenylene)Se]$_2$(*o*-phenylene) (**3**: E = S, **4**: E = Se), were synthesized. Complexation reactions of **3** and **4** with Na$_2$PdCl$_4$ gave the corresponding dichloropalladium(II) complexes **7** and **8**. X-ray structural analysis of **7** and **8** indicated that the central palladium metals are in a distorted octahedral environment, where the two inner selenium atoms and the two chlorine atoms form a square planar arrangement around the palladium metal and the two terminal chalcogen atoms weakly coordinate to the palladium center at the axial positions. The AIM calculations also supported the existence of the interaction between the palladium and the terminal chalcogen atoms in the crystalline state. On the other hand, the ^{77}Se NMR spectra suggested that there are no or very weak interactions between the palladium and the terminal chalcogen atoms in solution. The UV/Vis spectra of **7**, **8**, and related compounds imply the possibility of weak interaction between the terminal selenium atoms and the palladium center in solution.
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1. Introduction

Crown ethers are especially significant in the field of molecular recognition, since they have an effective size-selectivity for alkali and alkaline earth metals, and their complexes are soluble in organic solvent; alkali and alkaline earth metals are generally difficult to solvate in organic solvent [1].

In contrast to the development of crown ether chemistry, the chemistry of cyclic polychalcogenoethers, *i.e.*, crown ethers containing sulfur or selenium atoms instead of oxygen atoms, has not been extensively developed so far. The synthesis of some cyclic polythio- and polyseleno-ether ligands and their coordination modes were reported [2]. In contrast to the crown ethers, cyclic polychalcogenoethers prefer complexation with transition metals rather than that with alkali or alkaline earth metals. In
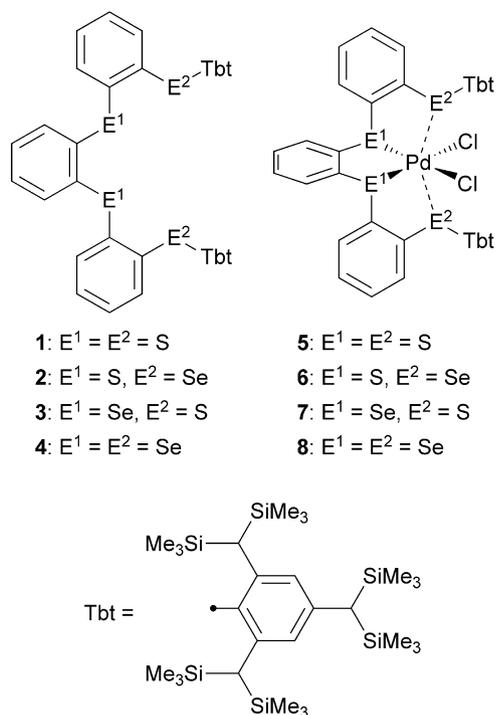
the case of palladium(II) complexes, they generally have planar four-coordinate structures [3], though some six-coordinate structures have been reported [4].

As for acyclic polychalcogenoethers, some examples have been reported so far [5], but their coordination and detachment of transition metal complexes are too flexible [6]. This leads to the difficulty of the synthesis and isolation of the transition metal complexes with acyclic polychalcogenoether ligands. Consequently, the studies of acyclic polychalcogenoether ligands are still elusive and their properties have not been disclosed yet so far.

Recently, we have succeeded in the syntheses of the acyclic tetrachalcogenoether ligands **1** and **2**, bearing an extremely bulky substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group, at both terminal chalcogen atoms, and their dichloropalladium(II) complexes **5** and **6**, respectively [7,8]. These complexes had a pseudo six-coordinate structure, in which the central two chalcogen atoms in tetrachalcogenoether ligand and two chlorine atoms were arranged in a square planar fashion around

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Chart 1.

Scheme 1.

compound **11** was difficult to isolate, it was used in the next reaction without further purification. The coupling reactions of **11** or **12** with 1,2-diiodobenzene gave the expected ligand **3** (3% from **9**) or **4** (32% from **12**) together with the mono-coupling products **13** (~50%) or **14** (56%). Ligand **4** was also obtained by the coupling reaction of **12** with **14** using Cu_2O in refluxing 2,4,6-trimethylpyridine.

Ligands **3** and **4** were characterized based on ^{1}H, ^{13}C, and ^{77}Se NMR and mass spectra together with the result of elemental analysis.

2.2. Syntheses and structures of palladium(II) complexes 7 and 8

The reactions of ligands **3** and **4** with Na_2PdCl_4 in ethanol at room temperature afforded the corresponding dichloropalladium complexes **7** and **8**, respectively, as orange crystals (Scheme 2). The structures of **7** and **8** were fully established by ^{1}H, ^{13}C, and ^{77}Se NMR and mass spectra, elemental analysis, and X-ray crystallographic analysis.

The X-ray structural analysis of complexes **7** and **8** showed *C2* symmetrical and distorted octahedral struc-
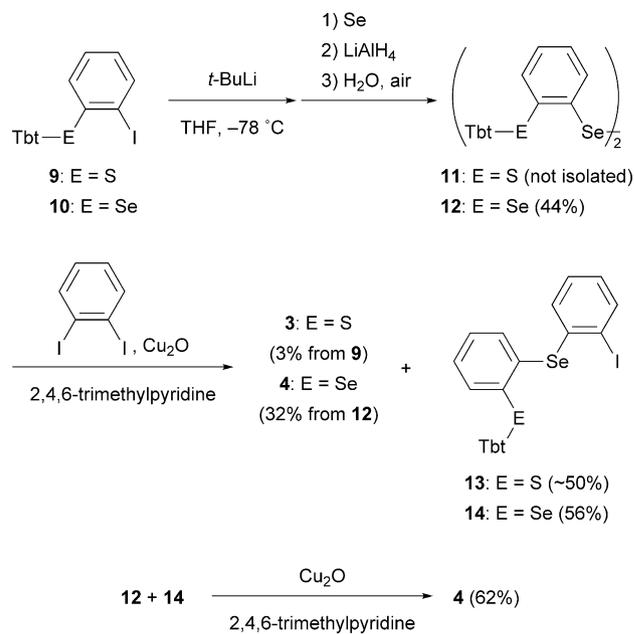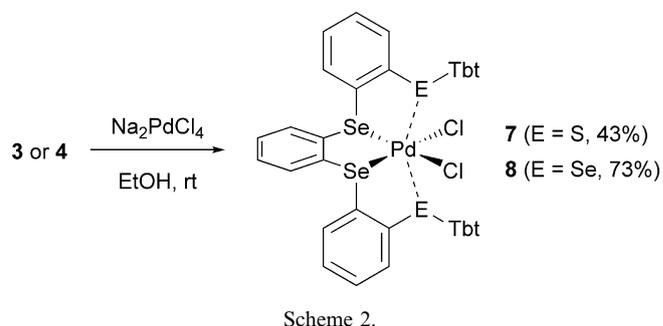
the palladium(II) atom and the terminal chalcogen atoms coordinated weakly to the palladium(II) atom. These are very few examples for six-coordinate structures of neutral palladium(II) complexes. In addition, selenoethers complex **6** had an advantage that the ^{77}Se NMR spectroscopic analyses of their complexes give useful information in solution about the characters of the coordination bonds between the selenium atoms and the transition metal center. Here, we reported the syntheses of new acyclic tetrachalcogenoether ligands **3** and **4** and their complexes **7** and **8**. Successful isolation of **7** and **8** in addition to the previously reported **5** and **6** enabled us to elucidate the coordination ability of polychalcogenoethers systematically (see Chart 1).

2. Results and discussion

2.1. Synthesis of 1,2-bis(2-chalcogenaphenylselanyl)benzene ligands 3 and 4

1,2-Bis(2-chalcogenaphenylselanyl)benzene ligands **3** and **4**, in which two or all sulfur atoms in ligand **1** were replaced with selenium atoms, were synthesized *via* diselenides **11** or **12** (Scheme 1). Although the synthesis of **1** and **2**, bearing sulfur atoms at inner positions, were achieved directly by the reactions of **9** or **10** with benzene-1,2-dithiol [7,8], we selected different methods for **3** and **4** due to the difficulty in the synthesis of benzene-1,2-diselenol [9]. Diselenides **11** and **12** were obtained in moderate yields by the reaction of **9** and **10** with *t*-BuLi and then with an excess amount of elemental selenium followed by the treatment with $LiAlH_4$, water and air [10]. Since the

Scheme 2.

tures, where the inner two selenium atoms of the ligands and the two chlorine atoms form a square planar arrangement around the palladium(II) atom and the two terminal chalcogen atoms of **3** and **4** were located at the axial positions of the palladium center (Fig. 1). Selected bond lengths, angles, and torsion angles of **7** and **8** are shown in Table 1. The distances between the terminal chalcogen and the palladium atoms [**7**: Pd···S(t) = 3.2309(9) Å, **8**: Pd···Se(t) = 3.1934(2) Å] are shorter than the sum of the van der Waals radii of palladium and sulfur atoms (3.43 Å) or that of palladium and selenium atoms (3.53 Å), respectively. This result suggests that complexes **7** and **8** have weak interactions between the palladium and the terminal chalcogen atoms leading to the pseudo

six-coordinate structure in the crystalline state as well as the complexes **5** and **6** [7,8] (see Table 2).

The complexes **5**–**8** were found to have structures quite similar to each other. The distances between the terminal chalcogen and the palladium atoms of **5**–**8** are shown in Fig. 2.

To estimate the effect of terminal chalcogen atoms, the comparison of **6** with **5**, both of which have inner sulfur atoms, was examined. The distances between Se(t) and Pd [3.14240(17) Å] in **6** were shorter than those between S(t) and Pd [3.1755(8) Å] in **5**, despite the van der Waals radius of selenium is larger than that of sulfur. This result indicated the interaction between Se(t) and Pd in **6** was stronger than that between S(t) and Pd in **5**. The bond lengths of Se(t)–C9 [1.9104(17) Å] of **6** are longer than those of S(t)–C9 [1.762(3) Å] of **5**, therefore, terminal selenium atoms of **6** should be able to approach more closely to the palladium metal center than the terminal sulfur atoms of **5**. Similar trend was observed in the comparison of **7** [S(t)···Pd = 3.2309(9) Å] with **8** [Se(t)···Pd = 3.1934(2) Å], both of which have inner selenium atoms.

The effect of inner chalcogen atoms could be estimated from the comparing between **7** with **5**, both of which have terminal sulfur atoms. We can accept easily the fact that bond-stretchings in **7** of E(i)–C4 and E(i)–Pd (E = S or Se) make the terminal sulfur atoms difficult to approach to the palladium metal center. Similar trend was confirmed in the relation between **6** and **8**, both of which have terminal selenium atoms.

These results suggested that the distances between the terminal chalcogen atoms and the palladium metal center got shorter in the case of the complex having inner sulfur or terminal selenium atoms. Therefore, those in complex **6**, which has inner sulfur and terminal selenium atoms, were the shortest among these complexes.

2.3. Atoms in molecule (AIM) analysis for the Se (or S)···Pd interactions

To estimate the interactions between the terminal chalcogen atoms and the palladium metal of complexes **5**–**8**, the topological analysis using Bader's theory of atoms in molecules (AIM) was examined [11]. In the AIM analysis, chemical bondings can be identified by the presence of a bond critical point (BCP), where the electron density becomes a minimum along the bond path. For the interaction between the terminal selenium (or sulfur) atoms and the palladium metal centers [E(t)···Pd (E = Se or S)] of complexes **5**–**8**, the BCPs could be located. The electron density (ρ) at a BCP correlates with the strength of atomic interaction. The ρ values of E(t)···Pd interaction of complexes **5**–**8** ($\rho_{E(t)···Pd}$) were 0.017, 0.020, 0.016, and 0.019 ea_0^{-3}, respectively (Table 3). The ρ values of **5**–**8** were smaller than those for normal covalent bonds, and larger than those for the practical boundary of molecules (ρ = 0. 001 ea_0^{-3}) [12], and these values are in good agreement with the interaction of E(t)···Pd in **5**–**8**. In addition,
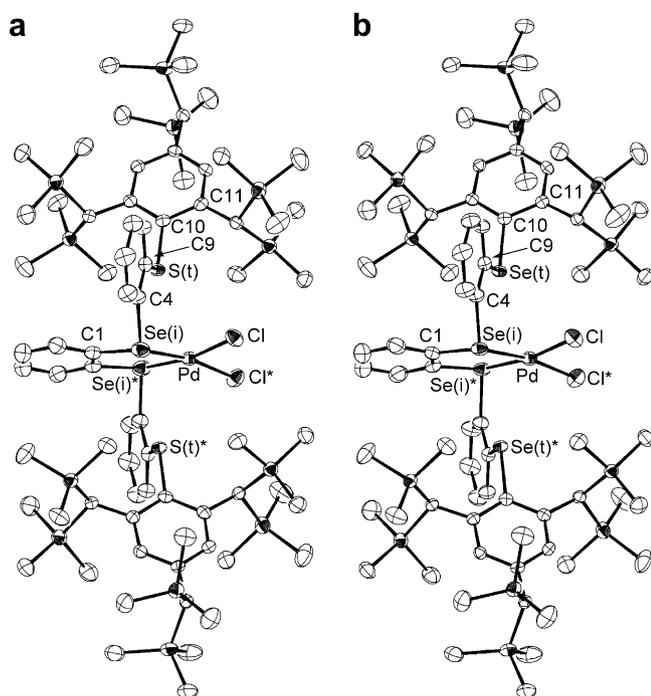

Fig. 1. ORTEP drawings of [**7** · C₂H₅OH · 0.5C₆H₁₄] (a) and [**8** · C₆H₁₄] (b) with thermal ellipsoid plots (50% probability). Hydrogen atoms and solvent molecules are omitted for clarity.

Table 1
Selected bond lengths (Å), angles (°), and torsion angles (°) of [**7** · C₂H₅OH · 0.5C₆H₁₄] and [**8** · C₆H₁₄] (E = S or Se)

	[**7** · C₂H₅OH · 0.5C₆H₁₄]	[**8** · C₆H₁₄]
E(i)–Pd	2.3499(5)	2.3725(3)
Pd–Cl	2.3220(11)	2.3222(6)
E(i)–C4	1.902(4)	1.930(2)
E(t)–C9	1.763(4)	1.912(2)
E(t)···Pd	3.2309(9)	3.1934(2)
Cl–Pd–Cl*	96.05(6)	95.41(4)
E(i)–Pd–Cl	87.17(3)	87.381(18)
E(i)–Pd–E(i)*	91.08(3)	91.066(15)
C4–C9–E(t)–C10	178.1(3)	177.40(19)
C9–E(t)–C10–C11	95.6(3)	97.82(16)

Table 2
Crystal data for [7 · C₂H₅OH · 0.5C₆H₁₄] and [8 · C₆H₁₄]

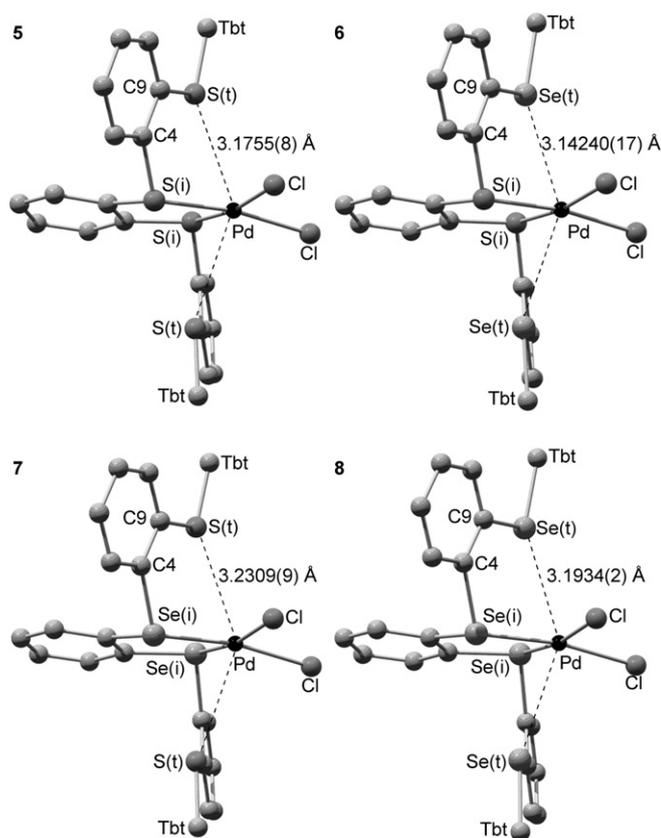|	[7 · C₂H₅OH · 0.5C₆H₁₄]	[8 · C₆H₁₄]
Formula	C₇₂H₁₃₀Cl₂PdS₂Se₂Si₁₂·C₂H₅OH · 0.5C₆H₁₄	C₇₂H₁₃₀Cl₂PdSe₄Si₁₂·C₆H₁₄
M_w	1821.33	1912.15
Crystal color, habit	Orange, plate	Orange, plate
Crystal system	Monoclinic	Monoclinic
Space group	C2/c (#15)	C2/c (#15)
a (Å)	41.6556(9)	42.2464(6)
b (Å)	12.8854(3)	12.8876(2)
c (Å)	19.2760(7)	19.2391(6)
β (°)	106.8433(14)	106.2999(19)
V (Å³)	9902.5(5)	10053.8(4)
Z	4	4
T (K)	103(2)	103(2)
ρ_{calcd} (g cm⁻¹)	1.222	1.263
μ (mm⁻¹)	1.201	1.864
Independent reflections	8696	9364
Number of parameters	475	483
Goodness-of-fit on F^2	1.071	1.062
R_1 [$I > 2\sigma(I)$]	0.0441	0.0272
wR_2 (all data)	0.1056	0.0613

Fig. 2. Distances between the terminal chalcogen atoms and the palladium atom in complexes 5–8.

the ρ values of E(t)···Pd of 5–8 corresponded to the distances of E(t)···Pd of 5–8 in the crystalline state. As the ρ values are larger, the distances of E(t)···Pd in these complexes are shorter. The Laplacian (∇^2) of ρ denotes the curvature of electron density in the 3D-topological space for two interacting atoms. In general, a negative value of

Table 3
The electron densities (ρ/ea_0^{-3}) and their Laplacians ($\nabla^2\rho/ea_0^{-5}$) of E···Pd in complexes 5–8.

	5	6	7	8
$\rho_{E(t)\cdots Pd}$	0.017	0.020	0.016	0.019
$\nabla^2\rho_{E(t)\cdots Pd}$	0.043	0.049	0.040	0.046
$\rho_{E(i)\cdots Pd}$	0.099	0.097	0.092	0.088
$\nabla^2\rho_{E(i)\cdots Pd}$	0.249	0.246	0.191	0.185

$\nabla^2\rho$ indicates that the electron density is locally concentrated, while a positive value of $\nabla^2\rho$ means that the electron density is locally depleted. The $\nabla^2\rho_{E(t)\cdots Pd}$ values of 5–8 were 0.043, 0.049, 0.040, and 0.046 ea₀⁻⁵, respectively (Table 3). These positive values of $\nabla^2\rho_{E(t)\cdots Pd}$ suggest that the E(t)···Pd interaction is dominantly electrostatic in nature.

2.4. ^{77}Se NMR spectra of dichloropalladium complexes

In order to estimate the interactions between the chalcogen atoms and the palladium metal in solution, the ^{77}Se NMR of complexes 7 and 8 were measured. The ^{77}Se NMR chemical shifts of dichloropalladium complexes coordinated with selenide have been reported to show distinct down-field shifts (about 130–250 ppm) compared with those of the corresponding selenide ligands [13].

Actually, the ^{77}Se NMR signal of selenium atoms in complex 7 in chloroform-d solution at 24 °C was observed at 523.2 ppm, which was down-field shifted by about 130 ppm compared with that of ligand 3 (390.0 ppm). This result indicated that complex 7 has coordinate bonds between the inner selenium atoms and the palladium metal in solution.

The ^{77}Se VT NMR spectra of complex 8 in chloroform-d or 1,1,2,2-tetrachloroethane-d_2 solution were measured at 100, 24, and −50 °C. In all cases, the inner selenium signals

of **8** (100 °C: 564.5 ppm, 24 °C: 561.7 ppm, −50 °C: 558.1 ppm) were down-field shifted by about 150–160 ppm compared with those of ligand **4** (100 °C: 410.8 ppm, 24 °C: 400.8 ppm, −50 °C: 393.6 ppm). By contrast, very little chemical shift change was observed for the terminal selenium atoms in each temperature (Fig. 3). In solution, complex **8** was considered to have coordination bonds between the inner selenium atoms and the palladium metal and very weak or no interactions between the terminal selenium atoms and the palladium metal. These results suggested that complex **8** in solution had a four-coordination structure, where the two inner selenium atoms of **8** and two chorine atoms coordinated to the palladium metal. These trends in the terminal selenium atoms were also observed for complex **6** (Scheme 3) [8].

2.5. UV/Vis spectrum of dichloropalladium complexes

The UV/Vis spectra of dichloropalladium complexes **5**–**8** were measured in CH_2Cl_2 (Fig. 4). The wavelengths at absorption maxima (λ_{max}) and the molar extinction coefficients (ε) are shown in Table 4. The λ_{max}s of **5**–**8** were observed at 391, 417, 396, and 421 nm, respectively. The λ_{max}s of selenoethers complexes (**6**–**8**) showed a red shift compared with that of thioether complexes **5**. Particularly, complexes **6** and **8**, bearing Tbt–Se moieties in ligands, showed a considerable red shift of λ_{max}. These results imply the possibility of weak interaction between the terminal selenium atoms and the palladium center in solution.
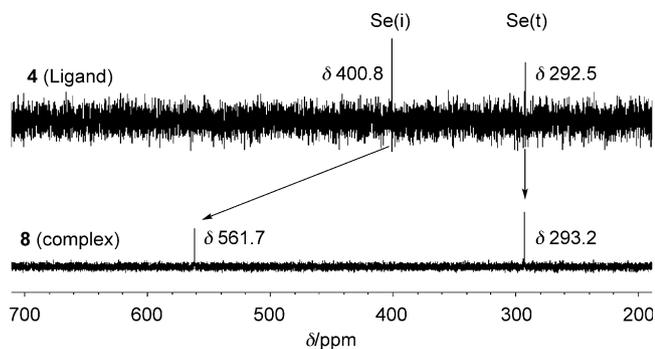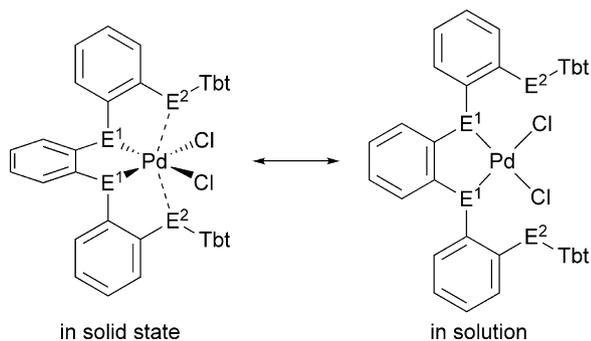

Fig. 4. UV/Vis spectra of dichloropalladium complexes **5**–**8**. [**5**] = [**6**] = [**7**] = [**8**] = 1.0×10^{-4} mol dm^{-3} in CH_2Cl_2.

Table 4
The wavelengths at absorption maxima (λ_{max}) and the molar extinction coefficients (ε) of UV/Vis spectrum of complexes **5**–**8**

	λ_{max} (nm)	ε (dm^3 mol^{-1} cm^{-1})
5	391	3.7×10^3
6	417	2.8×10^3
7	396	2.0×10^3
8	421	3.1×10^3

3. Conclusion

We have succeeded in the synthesis of new acyclic tetra-chalcogenoether ligands **3** and **4** tethered with two Tbt groups and their complexes **7** and **8**. The molecular structures of **7** and **8** were discussed systematically in comparison with those of related compounds **5** and **6** on the basis of their NMR and UV/Vis spectra, and X-ray crystallographic analysis.

The X-ray structural analyses of **5**–**8** showed their structures quite similar to each other. The distances between the terminal chalcogen atoms and the palladium metal center in **5**–**8** were shorter than the sum of the van der Waals radii of sulfur or selenium and palladium atoms. Therefore, complexes **5**–**8** were expected to have a weak interaction between the terminal chalcogen atoms and the palladium metal, and have a pseudo six-coordinate structure in the crystalline state. The AIM calculations also suggested the six-coordination characters of **5**–**8**.

On the other hand, the ^{77}Se NMR spectra of **6**–**8** indicated that the terminal selenium atoms in complexes **6** and **8** have no interactions to the palladium metal center, and they have a four-coordination structure in solution.

4. Experimental

4.1. General experimental details

All reactions were carried out under an argon atmosphere, unless otherwise noted. THF was purified prior to use by using an Ultimate Solvent System (Glass Contour Company) Laguna Beach, CA, USA [14], and

Fig. 3. The ^{77}Se NMR spectra of ligand **4** and complex **8** in chloroform-*d* at 24 °C.

Scheme 3.

other solvents were used without purification. Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-908 or LC-918 instruments with JAI gel 1H + 2H columns (Japan Analytical Industry) using chloroform as an eluent. Short column chromatography was performed with Nacalai Tesque Silica Gel 60. The ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured in CDCl$_3$ with a JEOL AL-300 spectrometer using CHCl$_3$ (7.25 ppm) as internal standards for ^{1}H NMR spectroscopy, and CDCl$_3$ (77.0 ppm) as those for ^{13}C NMR spectroscopy. The ^{77}Se NMR (95 MHz) spectra were measured in CDCl$_3$ or C$_2$D$_2$Cl$_4$ with a JEOL JNM AL-300 spectrometer using diphenyl diselenide (460 ppm) as an external standard. Mass spectral data were obtained on a JEOL JMS-700 spectrometer. All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. Tbt-substituted sulfide (9) [7] and selenide (10) [8] were prepared according to the reported procedure.

4.2. Synthesis of diselenide (11)

To a THF solution (150 mL) of Tbt-substituted sulfide (9) (6.28 g, 7.99 mmol) was gradually added *t*-BuLi (1.58 M pentane solution, 11.7 mL, 17.6 mmol) at −78 °C. After stirring for 1.5 h at this temperature, elemental selenium (4.3 g, 54 mmol) was added to the dark brown solution. The reaction mixture was stirred at −78 °C for 47 h and then at room temperature for 59 h. The resulting dark brown solution was added to a THF solution (20 mL) of LiAlH$_4$ (1.0 g, 26 mmol) at 0 °C. The reaction mixture was stirred for 24 h at room temperature. After EtOH solution of NaOH was added to the solution at 0 °C, the reaction mixture was stirred for 12 h. Then removal of the solvents under reduced pressure, water was added to the residue under air. The mixture was extracted with chloroform (500 mL). The solution was passed through a short column (SiO$_2$, CHCl$_3$) to remove water and inorganic salts. The eluate was evaporated, and the residue was subjected to GPLC (CHCl$_3$) to give diseleide (11) as a mixture of compounds (4.06 g).

4.3. Synthesis of diselenide (12)

To a THF solution (10 mL) of Tbt-substituted selenide 10 (300 mg, 0.360 mmol) was gradually added *t*-BuLi (1.58 M pentane solution, 0.53 mL, 0.79 mmol) at −78 °C. After stirring for 40 min at this temperature, elemental selenium (320 mg, 4.05 mmol) was added to the dark brown solution. The reaction mixture was stirred at −78 °C for 19 h and then at room temperature for 43 h. The resulting darkbrown solution was added to a THF solution (5 mL) of LiAlH$_4$ (200 mg, 5.26 mmol) at 0 °C. The reaction mixture was stirred for 8 h at room temperature. After removal of the solvents under reduced pressure,

ice water was added to the residue under air. The mixture was extracted with hexane (200 mL). MgSO$_4$ was added to the solution to remove the remaining water. After removal of the solvents under vacuum, the residue was subjected to GPLC (CHCl$_3$) to give diselenide 12 (126 mg, 0.0801 mmol, 44%) as yellow crystals. Compound 12: m.p. 89.7–90.1 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.00 (72H, br s), 0.07 (36H, br s), 1.36 (2H, br s), 2.87 (4H, br s), 6.41 (2H, br s), 6.55 (2H, br s), 6.91–7.06 (6H, m), 7.55 (2H, d, $^3J_{HH}$ = 6 Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 0.7 (q), 29.4 (d), 30.5 (d), 122.1 (d), 127.1 (d), 127.8 (d), 128.2 (s), 131.2 (d), 131.4 (s), 131.9 (d), 136.6 (s), 144.3 (s), 150.0 (s); ^{77}Se NMR (57 MHz, CDCl$_3$) δ 278.0, 438.6; LRMS (FAB) *m/z* 787 [$\frac{1}{2}$M]$^+$.

4.4. Synthesis of 1,2-bis(2-thiophenylselanyl)benzene (3)

The diselenide (11) (4.06 g), Cu$_2$O (5.00 g, 34.9 mmol), and 1,2-diiodobenzene (2.35 g, 7.12 mmol) in 2,4,6-trimethylpyridine (55 mL) was refluxed for 7.5 h. The mixture was washed with a 1.0 M aqueous solution of HCl four times (100 mL × 4). The organic layer was passed through a short column (SiO$_2$, CHCl$_3$) to remove water and inorganic salts, and then the eluate was evaporated. After the residue was subjected to GPLC (CHCl$_3$), the reprecipitation from CH$_2$Cl$_2$/CH$_3$CN gave 1,2-bis(2-thiophenylselanyl)benzene 3 (177.6 mg, 0.114 mmol, 3% from 9) as a colorless solid. Compound 3: m.p. 101.4–101.6 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ −0.03 (72H, s), 0.07 (36H, s), 1.38 (2H, s), 2.67 (4H, br s), 6.42 (2H, br s), 6.55 (2H, br s), 6.65 (4H, d, $^3J_{HH}$ = 7 Hz), 6.88–7.04 (4H, m), 7.08–7.18 (2H, m), 7.27–7.33 (2H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 0.8 (q), 26.4 (d), 30.6 (d), 122.7 (d), 125.6 (d), 127.4 (d), 127.6 (d), 127.83 (d), 127.84 (s), 128.3 (d), 128.6 (s), 133.1 (d), 133.8 (d), 136.0 (s), 142.4 (s), 143.4 (s), 150.2 (s); ^{77}Se NMR (57 MHz, CDCl$_3$) δ 390.0; HRMS (FAB) *m/z* calcd for C$_{72}$H$_{130}$S$_2$ ^{80}Se$_2$Si$_{12}$ [M]$^+$ 1554.5196. Found: 1554.5151. Anal. Calc. for C$_{72}$H$_{130}$S$_2$Se$_2$Si$_{12}$: C, 55.62; H, 8.43. Found: C, 55.68; H, 8.39%.

4.5. Synthesis of 1,2-bis(2-selanylphenylselanyl)benzene (4)

A mixture of Tbt-substituted diselenide (12) (248 mg, 0.158 mmol), Cu$_2$O (50 mg, 0.35 mmol), and 1,2-diiodobenzene (52.1 mg, 0.158 mmol) in 2,4,6-trimethylpyridine (19 mL) was refluxed for 6 h. The mixture was washed with a 1.0 M aqueous solution of HCl four times (100 mL × 4). The organic layer was passed through a short column (SiO$_2$, CHCl$_3$) to remove water and inorganic salts, and then the eluate was evaporated. The residue was subjected to GPLC (CHCl$_3$) to give 1,2-bis(2-selanylphenylselanyl)benzene (4) (84.6 mg, 0.0513 mmol, 32%) as a colorless solid, and mono-Tbt-substituted selenide (14) was also obtained (87.1 mg, 0.0880 mmol, 56%). Compound 4: m.p. 184.3–184.7 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ −0.03 (72 H, s), 0.07 (36H, s), 1.37 (2H, s), 2.77 (4H, br s), 6.42 (2H, br s), 6.56 (2H, br s), 6.82 (2H, dd,

$^3J_{HH} = 6$ Hz, $^4J_{HH} = 3$ Hz), 6.96–7.02 (4H, m), 7.13 (2H, dd, $^3J_{HH} = 6$ Hz, $^4J_{HH} = 4$ Hz), 7.24 (2H, dd, $^3J_{HH} = 6$ Hz, $^4J_{HH} = 3$ Hz), 7.32 (2H, dd, $^3J_{HH} = 6$ Hz, $^4J_{HH} = 4$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 0.8 (q), 29.2 (d), 30.5 (d), 122.0 (d), 126.4 (d), 126.9 (d), 127.3 (s), 128.3 (d), 130.4 (d), 130.5 (s), 132.8 (d), 134.4 (d), 136.0 (s), 139.9 (s), 144.3 (s), 150.8 (s); ^{77}Se NMR (57 MHz, CDCl$_3$) δ 292.5, 400.8; HRMS (APCI) m/z Calcd for C$_{72}$H$_{130}$^{78}Se^{80}Se$_3$Si$_{12}$ [M]$^+$: 1648.4098. Found: 1648.4042. Anal. Calc. for C$_{72}$H$_{130}$Se$_4$Si$_{12}$: C, 52.45; H, 7.95. Found: C, 52.62; H, 7.88%.

4.6. Synthesis of 1,2-bis(2-selanylphenylselanyl)benzene (4) [by the reaction of diselenide (12) with selenide (14)]

A mixture of Tbt-substituted diselenide (**12**) (248 mg, 0.158 mmol), selenide (**14**) (297 mg, 0.300 mmol), and Cu$_2$O (50 mg, 0.35 mmol) in 2,4,6-trimethylpyridine (55 mL) was refluxed for 8 h. The mixture was washed with a 1.0 M aqueous solution of HCl four times (100 mL × 4). The organic layer was passed through a short column (SiO$_2$, CHCl$_3$) to remove water and inorganic salts, and then the eluate was evaporated. The residue was subjected to GPLC (CHCl$_3$) to give 1,2-bis(2-selanylphenylselanyl)benzene (**4**) (282 mg, 0.0607 mmol, 62%) as colorless solid.

4.7. Synthesis of diseleno-dithio-dichloropalladium complex (7)

To EtOH (20 mL) and chloroform (1 mL) solution of diselenodithioether (**3**) (51.5 mg, 0.0331 mmol) was added a solution of Na$_2$PdCl$_4$ (14.1 mg, 0.0479 mmol) in 20 mL of EtOH. The mixture was stirred for 1.5 h at room temperature, and the resulting orange suspension was filtered. After the addition of CHCl$_3$ to the precipitates, the mixture was filtered. The orange filtrate was evaporated to give dichloropalladium complex **7** (24.8 mg, 0.0143 mmol, 43%) as orange crystals. Complex **7**: m.p. 226.7–227.3 °C (dec.); ^{1}H NMR (300 MHz, CDCl$_3$) δ −0.19 (18H, s), −0.11 (18H, s), −0.06 (18H, s), 0.07 (36H, s), 0.16 (18H, s), 1.40 (2H, s), 2.85 (4H, s), 6.36 (2H, br s), 6.50 (2H, d, $^3J_{HH} = 7$ Hz), 6.58 (2H, br s), 7.09 (2H, t, $^3J_{HH} = 7$ Hz), 7.19 (2H, t, $^3J_{HH} = 7$ Hz), 7.40–7.51 (2H, m), 7.55–7.65 (2H, m), 7.90 (2H, d, $^3J_{HH} = 7$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 0.8 (q), 1.2 (q), 1.5 (q), 26.5 (d), 30.9 (d), 121.1 (d), 125.0 (d), 125.4 (s), 127.7 (d), 131.3 (d), 131.6 (d), 133.1 (d), 134.1 (s), 136.1 (d), 142.3 (s), 144.0 (s), 145.8 (s), 150.1 (s); ^{77}Se NMR (57 MHz, CDCl$_3$) δ 523.2; LRMS (FAB) m/z 1696 [M−Cl]$^+$. Anal. Calc. for C$_{72}$H$_{130}$Cl$_2$PdS$_2$Se$_2$Si$_{12}$ C, 49.92; H, 7.56. Found: C, 49.66; H, 7.63%.

4.8. Synthesis of tetraseleno-dichloropalladium complex (8)

To an EtOH solution (20 mL) of tetraselenoether (**4**) (282 mg, 0.171 mmol) was added a solution of Na$_2$PdCl$_4$ (70.0 mg, 0.238 mmol) in 20 mL of EtOH. The mixture was stirred for 5.5 h at room temperature, and the resulting orange suspension was filtered. After the addition of CHCl$_3$ to the precipitates, the mixture was filtered. The orange filtrate was evaporated to give dichloropalladium complex **8** (226 mg, 0.123 mmol, 73%) as orange crystals. Complex **8**: m.p. 257.2–257.7 °C. (dec.); ^{1}H NMR (300 MHz, CDCl$_3$) δ −0.07 (72H, s), 0.07 (36H, s), 1.39 (2H, s), 2,57 (4H, br s), 6.43 (2H, br s), 6.56 (2H, br s), 6.71 (2H, dd, $^3J_{HH} = 6$ Hz, $^4J_{HH} = 3$ Hz), 7.12–7.16 (4H, m), 7.46 (2H, dd, $^3J_{HH} = 6$ Hz, $^4J_{HH} = 3$ Hz), 7.61 (2H, dd, $^3J_{HH} = 6$ Hz, $^4J_{HH} = 3$ Hz), 7.86 (2H, dd, $^3J_{HH} = 6$ Hz, $^4J_{HH} = 3$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 0.7 (q), 30.7 (d), 122.4 (d), 125.4 (s), 126.0 (d), 128.4 (s), 130.4 (d), 131.4 (d), 131.7 (d), 133.2 (d), 134.3 (s), 136.1 (d), 139.2 (s), 145.7 (s), 150.7 (s); ^{77}Se NMR (57 MHz, CDCl$_3$) δ 293.2, 561.7; LRMS (FAB) m/z 1792 [M−Cl]$^+$. Anal. Calc. for C$_{72}$H$_{130}$Cl$_2$PdSe$_4$Si$_{12}$ C, 47.36; H, 7.18. Found: C, 47.31; H, 7.17%.

4.9. X-ray crystallography

Single crystals of [**7** · C$_2$H$_5$OH · 0.5C$_6$H$_{14}$] and [**8** · C$_6$H$_{14}$] were grown by the slow evaporation of the saturated dichloromethane/hexane/ethanol solution. Their intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation ($l = 0.71071$ Å) to $2\theta_{max} = 50°$ at 103 K. Their structures were solved by direct method (SHELXS-97) and refined by full-matrix least-squares procedure on F^2 for all reflections (SHELXL-97) [15]. All the non-hydrogen atoms were refined anisotropically, and all hydrogens were placed using AFIX instruction.

4.10. Theoretical calculations

The calculations of the wave function of **5**–**8** were carried out using the GAUSSIAN 03 program [16] with density functional theory at the B3LYP level with TZV [17] (for Pd), 6-311+G(2d,p) (for S and Se), and 6-31G(d) (for C, Cl, H, and Si) basis sets. The atomic coordinates obtained by the X-ray crystallography of **5**–**8** were used as those for the calculations. Computation time was provided by the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University. The atoms in molecules (AIM) analysis was performed by using the AIM2000 package [18].

Appendix A. Supplementary material

CCDC 670083 and 670084 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via 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.2008.01.016.

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