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Synthesis of an Acyclic Diselenodithioether Ligand Tethered With Bulky Substituents and Its Application to the Synthesis of a Distorted Octahedral Palladium(II) Complex

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ABSTRACT: *A new o-phenylene-bridged diselenodithioether ligand tethered with an extremely bulky substituent, 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl (Tbt) group, at both terminal selenium atoms, [TbtSe(o-phenylene)S]$_2$(o-phenylene) (***3***), was synthesized by taking advantage of the reaction of TbtSeSeTbt (***4***) with 1,2-diiodobenzene using Cu$_2$O in 2,4,6-trimethylpyridine followed by the successive coupling reaction of the resulting bulky o-iodophenylselenide (***5***) with 1,2-benzenedithiol. Complexation of* **3** *with Na$_2$PdCl$_4$ gave the corresponding dichloropalladium(II) complex, [PdCl$_2$(***3***)] (***6***). The X-ray structural analysis of* **6** *indicated that the central palladium metal is in a distorted octahedral environment, where the two inner sulfur atoms of* **3** *and the two chlorine atoms form a square planar arrangement around the palladium metal and the two terminal selenium atoms of* **3** *weakly coordinate to the palladium center at the axial positions. The AIM calculations also indicated the existence of the interaction between palladium and selenium atoms in the crystalline state. On the other hand, the ^{77}Se NMR spectrum suggests that there are no or very weak interactions between the palladium and selenium atoms of* **3** *in solution.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:549–556, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20339

INTRODUCTION

It has been known that palladium(II) complexes generally have square planar geometry around the palladium atom, and there are very few examples for six-coordinate complexes of palladium(II). Cyclic polythioether (crown thioether) ligands such as 1,4,7-trithiacyclononane (9S3) [1,2], 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) [3], and 1,4,7-trithiacyclodecane (10S3) [4,5], reportedly complexed with a palladium(II) metal to give the corresponding five- or six-coordinate palladium(II) complexes, in which the four sulfur atoms are arranged in a square planar fashion around the palladium(II) atom and the other sulfur atoms weakly coordinate to the palladium(II) atom [Pd · · · S: 2.96–3.27 Å] at the axial positions.

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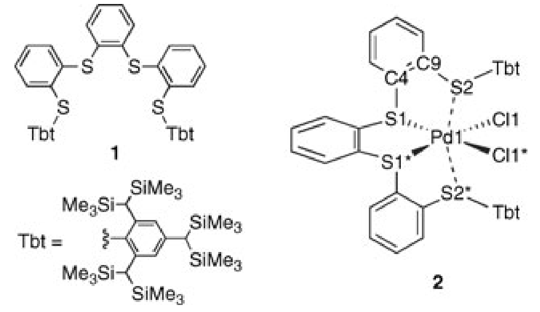


CHART 1

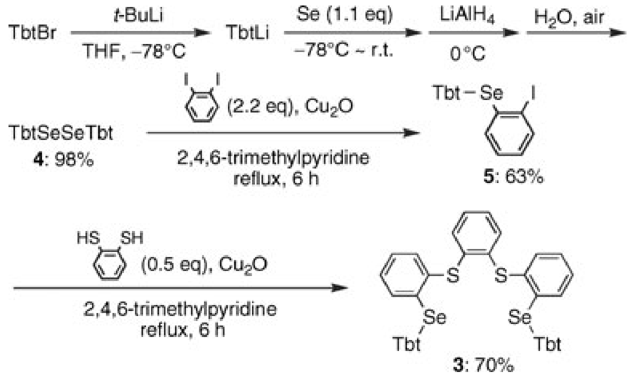
Recently, we have reported the synthesis of a new type of tetrathioether ligand **1** tethered with two 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) groups at both terminal sulfur atoms (Chart 1) [6]. Tbt group is an extremely bulky substituent and known to be effective to the stabilization of a variety of highly reactive species [7–9]. In addition, we have found that dichloropalladium complex **2** bearing the tetrathioether ligand **1** has a distorted octahedral structure, where the two inner sulfur atoms of **1** and the two chlorine atoms form a square planar arrangement around the palladium metal and the two terminal sulfur atoms of **1** weakly coordinate to the palladium center at the axial positions [6].

The coordination chemistry of selenoethers has also been studied extensively [10–12], and selenoethers have an advantage that the ^{77}Se NMR spectroscopic analysis of their transition metal complexes give much information about the coordinate bonds between the selenium atom and the metal center. This advantageous feature of selenoether ligands prompted us to synthesize a selenium analog of tetrathioether **1**.

In this article, we report the synthesis of a new bulky diselenodithioether ligand **3** having two inner sulfur atoms and two terminal selenium atoms and its application to the synthesis of the corresponding highly coordinated palladium(II) complex.

RESULTS AND DISCUSSION

Synthesis of a Diselenodithioether Ligand 3



SCHEME 1 Synthesis of diselenodithioether ligand **3**.

The synthetic strategy for the diselenodithioether ligand **3** consists of the successive coupling reactions of an iodobenzene derivative with a diselenide or thiol derivative in the presence of Cu_2O in 2,4,6-trimethylpyridine as well as that for the tetrathioether ligand **1**. Tbt-substituted diselenide **4** was synthesized by the reaction of TbtLi, prepared by the reaction of TbtBr and *tert*-butyllithium, with elemental selenium, followed by the treatment with $LiAlH_4$, H_2O, and air (Scheme 1). Coupling reaction of **4** with 1,2-diiodobenzene using Cu_2O in refluxing 2,4,6-trimethylpyridine [6,13] afforded sulfide **5** in 63% yield. Further coupling reaction of **5** with 0.5 equivalents of 1,2-benzenedithiol under the conditions similar to those for the transformation of **4** to **5** gave the expected diselenodithioether **3** in a good yield.

Structure of Diselenodithioether Ligand 3

Diselenodithioether ligand **3** was characterized on the basis of the ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopic data together with the results of MS measurement and elemental analysis. The molecular structure of **3** in the crystalline state was definitively determined by X-ray structural analysis. Figure 1 shows the ORTEP drawing of **3**, and the selected bond lengths, angles, and torsion angles are summarized in Table 1. All the C—S and C—Se bond lengths of **3** show usual values for the C—S and C—Se single bonds, respectively [14]. The bond angles around the selenium atoms are slightly smaller than those around the sulfur atoms. It is noteworthy that C1—Se1—C28 and C45—Se2—C46 planes in

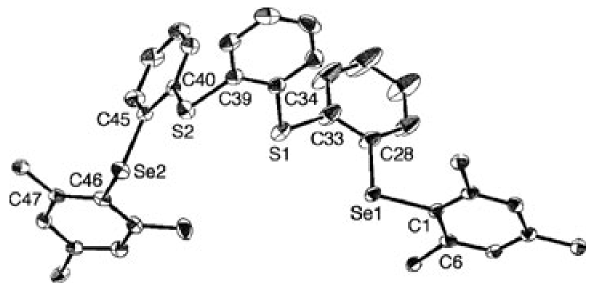


FIGURE 1 ORTEP drawing of **3** with thermal ellipsoids (50% probability). Hydrogen atoms, trimethylsilyl groups, and a solvent molecule (chloroform) were omitted for clarity.

TABLE 1 Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of **3**

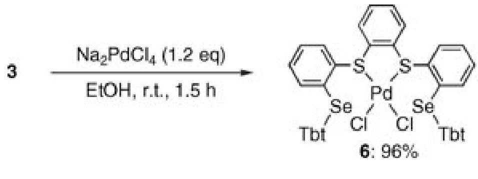
Se1—C1	1.938(3)	Se1—C28	1.927(3)
S1—C33	1.771(4)	S1—C34	1.776(3)
S2—C39	1.772(3)	S2—C40	1.778(3)
Se2—C45	1.921(3)	Se2—C46	1.933(3)
C28—Se1—C1	99.15(13)	C33—S1—C34	100.87(17)
C40—S2—C39	101.16(4)	C46—Se2—C45	99.94(12)
C28—Se1—C1—C6	−91.5(2)	C1—Se1—C28—C33	−175.8(3)
C34—S1—C33—C28	115.3(3)	C33—S1—C34—C39	156.4(2)
C40—S2—C39—C34	−74.0(3)	C39—S2—C40—C45	162.6(2)
C46—Se2—C45—C40	−163.2(2)	C45—Se2—C46–C47	−97.1(2)

3 are both nearly perpendicular to the benzene ring of its connecting Tbt group (C28—Se1—C1—C6 = −91.5(2)° and C45—Se2—C46—C47 = −97.1(2)°) and almost parallel to the neighboring *o*-phenylene moieties (C1—Se1—C28—C33 = −175.8(3)° and C46—Se2—C45—C40 = −163.2(2)°) as well as the case of tetrathioether ligand **1**. This conformation in **3** can be explained in terms of the steric hindrance caused by the bulky Tbt groups.

The ^{1}H and ^{13}C NMR spectra of **3** showed that the two terminal TbtSe(*o*-phenylene) units were equivalent to each other, suggesting flexible structure of **3** in solution. The ^{77}Se NMR spectrum of **3** showed a signal at 282 ppm, which is within a range of those reported for diaryl selenides [15].

Synthesis and Structure of Palladium(II) Complex **6** *of Diselenodithioether Ligand* **3**

When **3** was allowed to react with Na_2PdCl_4 in ethanol at room temperature for 1.5 h, the corresponding dichloropalladium complex **6** was obtained as orange crystals in a good yield (Eq. (1)). The structure of **6** was fully established by ^{1}H, ^{13}C, and ^{77}Se NMR spectrometry, MS, elemental analysis, and single crystal X-ray diffraction.



6: 96%

(1)

The X-ray structural analysis of **6** showed a structure similar to that of **2** [6], that is, the C_2 symmetrical, distorted octahedral structure, where the inner two sulfur atoms of ligand **3** and the two chlorine atoms form a square planar arrangement around the palladium(II) atom and the two terminal selenium atoms of **3** weakly coordinate to the palladium center at the axial positions (Fig. 2). There are only few reports on the X-ray structural analysis of neutral, 6-coordinate palladium(II) complexes [6,16,17], although some cationic, 6-coordinate complexes of palladium(II) have already been synthesized using crown thioether ligands [1–5], S- and N-donor macrocyclic ligands [18–20], and tris(2,4,6-trimethoxyphenyl)phosphine ligands [21].

The selected bond lengths, angles, and torsion angles of complex **6** are summarized in Table 2 together with those observed for complex **2**. The bond

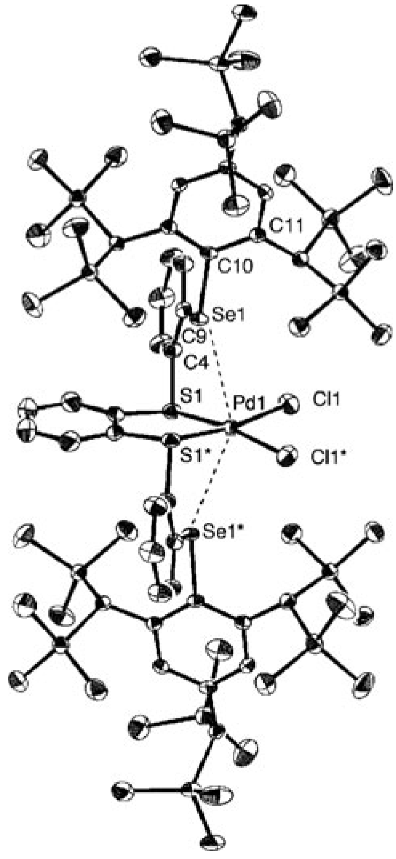


FIGURE 2 ORTEP drawing of **6** with thermal ellipsoids (50% probability). Hydrogen atoms and a solvent molecule (hexane) were omitted for clarity.

TABLE 2 Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of **6** and **2**

	6	**2**
Pd1—S1	2.2718(5)	2.2615(9)
Pd1—Cl1	2.3134(5)	2.3117(9)
Pd1···Se1(S2)	3.14240(17)	3.1755(8)
S1—Pd1—S1*	89.74(2)	89.45(5)
S1—Pd1—Cl1	88.379(17)	88.15(3)
Cl1—Pd1—Cl1*	94.51(3)	95.37(5)
S1—Pd1—Se1(S2)	74.292(11)	71.19(3)
S1*—Pd1—Se1(S2)	80.485(12)	82.08(3)
Cl1—Pd1—Se1(S2)	91.550(13)	89.37(3)
Cl1*—Pd1—Se1(S2)	112.990(12)	116.55(3)
C4—C9—Se1(S2)—C10	−178.09(14)	178.6(3)
C9—Se1(S2)—C10—C11	−96.98(14)	94.5(3)

distances of **6**[Pd1–Cl1 (2.3134(5) Å) and Pd1–S1 (2.2718(5) Å)] are close to those of tetrathioether complex **2**. The distances between the palladium and the two terminal selenium atoms [Pd1···Se1 = 3.14240(17) Å] are shorter than the sum of the van der Waals radii of palladium and selenium atoms (3.53 Å) [22]. This suggests weak interaction between the palladium atom (Pd1) and the terminal selenium atoms (Se1 and Se1*) in the crystalline state. In addition, the Pd1···Se1 distance is shorter than the Pd1···S2 distance of the sulfur analog **2**, although the van der Waals radii of selenium is larger than that of sulfur. This indicates the stronger interaction between Pd1 and Se1 in **6** than that between Pd1 and S in **2**. It is noteworthy that the torsion angles around the terminal selenium atoms in palladium complex **6** [C9—Se1—C10—C11 = −96.98(14)°, C4—C9—Se1—C10 = −178.09(14)°] are close to those of the free ligand **3**. This result suggests that the extremely bulky Tbt groups put the restrictions on the conformation of ligand **3** in the structure of complex **6** as well as in that of **3**, that is, ligand **3** preferably has the conformation in which the C—Se (terminal)—C planes are almost perpendicular to the benzene rings of the Tbt groups and nearly parallel to the neighboring *o*-phenylene rings.

In the ^{77}Se NMR spectrum of **6** measured in 1,1,2,2-tetrachloroethane-d_2 at 100°C, a signal appeared at slightly lower field (297 ppm) compared with that of ligand **3** (290 ppm in 1,1,2,2-tetrachloroethane-d_2 at 100°C). Since the ^{77}Se NMR chemical shifts of dichloropalladium complexes coordinated with selenides have been reported to show down-field shifts of 130–300 ppm compared with those of the corresponding selenide ligands [23], there may be no or very weak interaction between the palladium and selenium atoms of **6** in solution.

Atoms in Molecule Analysis for the Pd···Se Interactions

To estimate the Pd···Se interactions (Pd1···Se1 and Pd1···Se1*) of the palladium(II) complex **6**, we examined the topological analysis using Bader's theory of atoms in molecules (AIM) [24–28]. 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 Pd···Se interactions (Pd1···Se1 and Pd1···Se1*) of **6**, the BCPs could be located. The electron density (ρ) at a BCP correlates with the strength of an atomic interaction. The value of ρ obtained for the Pd···Se interactions ($\rho_{\mathrm{Pd\cdots Se}}$) is 0.021 ea_0^{-3}, which is smaller than those of normal covalent bonds (e.g., $\rho_{\mathrm{C—C}} = 0.24$ ea_0^{-3}) but larger than those for the practical boundary of molecules ($\rho = 0.001$ ea_0^{-3} [29]. In addition, the $\rho_{\mathrm{Pd\cdots Se}}$ value is within the range of those for neutral hydrogen bonds ($\rho = 0.002$–0.04 ea_0^{-3}). The Laplacian (∇^2) of ρ denotes the curvature of electron density in the 3D-topological space for two interacting atoms and, in general, a negative value of $\nabla^2\rho$ 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 positive value of ∇^2 $\rho_{\mathrm{Pd\cdots Se}}$ (0.054 ea_0^{-5}) suggests that the Pd1···Se1 and Pd1···Se1* interactions are dominantly electrostatic in nature.

CONCLUSION

A new diselenodithioether ligand **3** tethered with two Tbt groups was synthesized and applied to the complexation with Na_2PdCl_4, giving the corresponding dichloropalladium complex **6**. The X-ray structural analysis of **6** indicated its distorted octahedral structure with the weak intramolecular interactions between the two terminal selenium atoms and the central palladium metal. The AIM calculations also indicated the existence of the interaction between the palladium and selenium atoms of **6** in the crystalline state, though very weak or no interaction was suggested for **6** in solution as judged by the ^{77}Se NMR spectral data.

EXPERIMENTAL

General Procedures

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 [30], and other solvents were used without purification. Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-908 or LC-918 instrument 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 $C_2D_2Cl_4$ 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.

Synthesis of Diselenide **4**

To a THF solution (160 mL) of TbtBr (10.0 g, 15.8 mmol) was gradually added *t*-BuLi (2.2 M pentane solution, 15.8 mL, 34.8 mmol) at −78°C. After stirring for 1 h at this temperature, Se (1.35 g, 17.1 mmol) was added to the yellow solution. The reaction mixture was stirred at −78°C for 1 h and then at room temperature for 3 h. The resulting dark-brown solution was added to a THF solution (40 mL) of $LiAlH_4$ (1.0 g, 26.4 mmol) at 0°C. The reaction mixture was stirred for 14 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 (250 mL). After removal of the solvents under vacuum, the residue was passed through a short column (SiO_2, hexane) to remove the remaining water. The evaporation of the eluate gave diselenide **4** (9.75 g, 7.72 mmol, 98%) as purple crystals. **4**: mp 242.8–243.8°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (72H, s), 0.07 (36H, s), 1.32 (2H, s), 2.77 (2H, brs), 2.85 (2H, brs), 6.36 (2H, brs), 6.49 (2H, brs); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.76 (q), 0.81 (q), 1.07 (q), 30.45 (d), 31.36 (d), 31.48 (d), 121.73 (d), 126.67 (d), 128.72 (s), 143.87 (s), 149.73 (s), 149.96 (s); ^{77}Se NMR (57 MHz, $CDCl_3$) δ 367; HRMS (FAB) *m/z* calcd for $C_{54}H_{118}Se_2Si_{12}$ $[M]^+$: 1262.4795. Found: 1262.4810. Anal. Calcd for $C_{54}H_{118}Se_2Si_{12}$: C, 51.37; H, 9.42%. Found: C, 51.49; H, 9.42%.

Synthesis of Selenide **5**

A mixture of Tbt-substituted diselenide **4** (8.62 g, 6.83 mmol), Cu_2O (2.00 g, 14.0 mmol), and 1,2-diiodobenzene (5.0 mg, 15 mmol) in 2,4,6-trimethylpyridine (60 mL) was refluxed for 6 h. The reaction mixture was passed through a short column (SiO_2, $CHCl_3$) to remove inorganic salts. All fractions were collected and 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. After the eluate was evaporated, the reprecipitation from CH_2Cl_2/CH_3CN gave selenide **5** (7.2 g, 8.6 mmol, 63%) as colorless crystals. **5**: mp 180.8–182.0°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ-0.03 (36H, s), 0.06 (18H, s), 1.36 (1H, s), 2.71 (2H, brs), 6.42 (1H, brs), 6.55 (1H, brs), 6.79 (1H, ddd, $J = 7.8, 7.8, 1.5$ Hz), 6.80 (1H, dd, $J = 7.8, 1.5$ Hz), 7.01 (1H, ddd, $J = 7.8, 7.8, 1.5$ Hz), 7.71 (1H, dd, $J = 7.8, 1.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.79 (q), 29.51 (d), 30.56 (d), 98.56 (s), 122.14 (d), 126.88 (d), 128.24 (d), 129.39 (s), 131.09 (d), 139.10 (d), 141.27 (s), 144.67 (s), 150.22 (s); ^{77}Se NMR (57 MHz, $CDCl_3$) δ 354 (s); HRMS (FAB) *m/z* calcd for $C_{33}H_{63}ISeSi_6$ $[M]^+$: 834.1755. Found: 834.1758.

Synthesis of Diselenodithioether **3**

A mixture of Tbt-substituted selenide **5** (200 mg, 0.240 mmol), Cu_2O (34 mg, 0.24 mmol), and 1,2-benzenedithiol (17 mg, 0.12 mmol) in 2,4,6-trimethylpyridine (15 mL) was refluxed for 6 h. The reaction mixture was subjected to short column chromatography (SiO_2, $CHCl_3$) to remove inorganic salts. 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 diselenodithioether **3** (131 mg, 0.084 mmol, 70%) as colorless crystals. **3**: mp 107.8–108.5°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ–0.04 (72H, s), 0.07 (36H, s), 1.37 (2H, s), 2.76 (4H, brs), 6.43 (2H, brs), 6.57 (2H, brs), 6.80 (2H, m), 6.95–7.14 (8H, m), 7.24 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.49 (q), 0.84 (q), 29.23 (d × 2), 30.51 (d), 122.21 (d), 126.16 (d), 126.45 (s), 127.06 (d), 127.54 (d), 128.20 (d), 130.14 (d), 130.48 (d), 132.24 (s), 133.24 (d), 136.95 (s), 139.41 (s), 144.36 (s), 150.60 (s × 2); ^{77}Se NMR (57 MHz, $CDCl_3$) δ 282 (s); ^{77}Se NMR (57 MHz, $C_2D_2Cl_4$, 100°C) δ 290 (s); HRMS (FAB) *m/z* calcd for $C_{72}H_{130}S_2Se_2Si_{12}$ $[M]^+$: 1554.5176. Found:

1554.5196. Anal. calcd for $C_{72}H_{130}S_2Se_2Si_{12}$: C, 55.62; H, 8.43%. Found: C; 55.71; H, 8.35%.

Synthesis of Dichloropalladium Complex **6**

To an EtOH solution (40 mL) of diselenodithioether **3** (200 mg, 0.128 mmol) was added a solution of Na_2PdCl_4 (46.0 mg, 0.156 mmol) in 10 mL of EtOH. The mixture was stirred for 1.5 h at room temperature, and the resulting orange suspension was filtrated. After the addition of $CHCl_3$ to the precipitates, the mixture was filtered. The orange filtrate was evaporated to give dichloropalladium complex **6** (214 mg, 0.123 mmol, 96%) as orange crystals. **6**: mp 245.8–246.2°C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$, 50°C) δ $-$0.04 (72H, brs), 0.08 (36H, brs), 1.41 (2H, brs), 2.59 (4H, brs), 6.52 (4H, brs), 6.76 (2H, br), 7.18 (4H, br), 7.42 (4H, br), 7.82 (2H, br); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.73 (q), 1.27 (q), 1.27 (q), 30.71 (d), 30.71 (d × 2), 122.34 (d), 124.55 (s), 125.65 (d), 126.99 (s), 127.68 (s), 130.34 (d), 130.94 (d), 131.36 (d), 132.07 (d), 136.38 (d), 140.45 (s), 145.67 (s), 150.99 (s). ^{77}Se NMR (57 MHz, $C_2D_2Cl_4$, 100°C) δ 297 (s); LRMS (FAB) *m/z* 1695 [M−Cl]$^+$. Anal. calcd for $C_{72}H_{130}Cl_2PdS_2Se_2Si_{12}$: C, 49.92; H, 7.56%. found: C, 49.88; H, 7.73%.

X-Ray Structural Analysis of **3** · *0.5CHCl₃, and* **6** · *C₆H₁₄*

Single crystals of **3** · $0.5CHCl_3$ and **6** · C_6H_{14} suitable for X-ray structural analysis were obtained by slow recrystallization from $CHCl_3/CH_3CN$ and hexane/CH_2Cl_2/EtOH, respectively. The crystals were mounted on a glass fiber. The intensity data were collected on Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97) [31]. All the non-hydrogen atoms were refined anisotropically, and all hydrogens were placed using AFIX instructions. The structural data are shown in Table 3. CCDC No. 625473 for

TABLE 3 Crystal Data and Refinement Details for 3 · $0.5CHCl_3$, and 6 · C_6H_{14}

	3 · *0.5CHCl₃*	**6** · *C₆H₁₄*
Empirical formula	$C_{72}H_{130}S_2Se_2Si_{12} \cdot 0.5CHCl_3$	$C_{72}H_{130}Cl_2PdS_2Se_2Si_{12} \cdot C_6H_{14}$
Formula weight	1614.56	1818.35
Temperature	103(2) K	93(2) K
Crystal system	Triclinic	Monoclinic
Space group	*P*–1(#2)	*C*2/c(#15)
a (Å)	12.0661(2)	42.0219(3)
b (Å)	16.7641(3)	12.88340(10)
c (Å)	24.0984(9)	19.2052(2)
α (deg)	102.1972(13)	90
β (deg)	99.2470(15)	105.7534(5)
γ (deg)	100.6024(7)	90
V (Å^3)	4581.03(15)	10006.87(15)
Z	2	4
D_{calc} (mg m^{-3})	1.171	1.207
Absorption coefficient (mm^{-1})	1.089	1.187
Crystal size (mm)	0.30 × 0.05 × 0.05	0.15 × 0.10 × 0.10
θ range	2.48 to 25.00°	1.91 to 25.50°
No. of reflections measured	31080	58165
No. of independent reflections	15818	9277
R_{int}	0.0261	0.0291
Completeness	98.0%	99.50%
Data/restraints/parameters	15818/0/897	9277/35/483
Goodness of fit on F^2	1.015	1.069
Final *R* indices [$I > 2\sigma(I)$]^a	$R_1 = 0.0411$	$R_1 = 0.0242$
	$wR_2 = 0.1540$	$wR_2 = 0.0738$
	$wR_2 = 0.0977$	$wR_2 = 0.0628$
R indices (all data)^a	$R_1 = 0.0587$	$R_1 = 4\ 0.0270$
	$wR_2 = 0.1757$	$wR_2 = 0.0754$
	$wR_2 = 0.1073$	$wR_2 = 0.0654$
Largest diffraction peak and hole (e Å^{-3})	1.169 and −1.007	0.649 and −0.422

$^a R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, $wR_2 = [(\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

3 · 0.5$CHCl_3$ and CCDC No. 625474 for **6** · C_6H_{14} contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Theoretical Calculations

The calculations of the wave function of **6** were carried out using the Gaussian 98 program [32] with density functional theory at the B3LYP level [33–35]. The atomic coordinates obtained by the X-ray crystallography of **6** were used as those for the calculations. The LANL2DZ for Pd were used with effective core potential, and the 6-31G(d) basis sets were used for C, Cl, H, S, Se, and Si atoms. The LANL2DZ(ECP) basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database (http://www.emsl.pnl.gov/forms/basisform.html), Version 02/25/04, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact Karen Schuchardt for further information. 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 [36].

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