

Synthesis of mono- and trinuclear palladium(II) complexes via oxidative addition of a bulky hexathioether containing a disulfide bond to palladium(0)

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Abstract

The oxidative addition reactions of a bulky hexathioether containing a disulfide bond, $\text{TbtS}(o\text{-phen})\text{S}(o\text{-phen})\text{SS}(o\text{-phen})\text{S}(o\text{-phen})\text{STbt}$ (**1**) (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, *o*-phen = *o*-phenylene), to a palladium(0) complex were studied. In the reaction of **1** with 3 molar amounts of $[\text{Pd}(\text{PPh}_3)_4]$, a trinuclear palladium(II) complex, $[\text{Pd}_3\{\text{S}(o\text{-phen})\text{S}\}_2\{(o\text{-phen})\text{STbt}\}_2(\text{PPh}_3)_2]$ (**2**), was formed via three-step palladium insertion reaction including unusual C(aryl)–S bond cleavages. On the other hand, the reaction of **1** with an equimolar amount of $[\text{Pd}(\text{PPh}_3)_4]$ afforded mononuclear palladium(II) complex having a pseudo-octahedral structure, $[\text{Pd}\{\text{S}(o\text{-phen})\text{S}(o\text{-phen})\text{STbt}\}_2]$ (**3**). The hexa-coordinated geometry for the palladium center in **3** was confirmed by the atoms in molecule (AIM) analysis, which revealed the presence of the bond critical points between the central Pd atom and the S atoms at the axial positions. In contrast to the bulky system, the reaction of Ph-substituted hexathioether, $\text{PhS}(o\text{-phen})\text{S}(o\text{-phen})\text{SS}(o\text{-phen})\text{S}(o\text{-phen})\text{SPh}$ (**4**), with an equimolar amount of $[\text{Pd}(\text{PPh}_3)_4]$ gave a palladium(II) complex having square-planar structure, $[\text{Pd}\{\text{S}(o\text{-phen})\text{S}(o\text{-phen})\text{SPh}\}_2]$ (**5**). Theoretical calculations revealed that there is no remarkable difference among the energies of isomers of $[\text{Pd}\{\text{S}(o\text{-phen})\text{SPh}\}_2]$, **6a-syn**, **6a-anti**, **6b-syn**, and **6b-anti**. This result suggests that a reason for the preference of the *trans-anti*-conformation in **3** is the steric repulsion between the bulky Tbt groups, and that of the *cis-syn*-conformations in **5** and **6** is the intermolecular interactions.

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1. Introduction

Cleavage of E–E bonds (E = S, Se, and Te) mediated by transition metal complexes is one of the typical reactivities of diorganyl dichalcogenides, and various bis(chalcogenolato) mononuclear or chalcogenolato-bridged binuclear complexes of transition metals have been synthesized so far by the use of such oxidative additions of dichalcogenides [1]. Particularly, reactions of diorganyl disulfides with zero-valent palladium complexes, such as $[\text{Pd}(\text{PPh}_3)_4]$, are

one of the most explored systems due to two reasons. One is the great interest in the investigation of the mechanism for the S–S bond addition of diorganyl disulfides to alkynes catalyzed by $[\text{Pd}(\text{PPh}_3)_4]$, which is an efficient single-step method for the formation of two C–S bonds in a stereoselective manner [2]. Many mechanistic studies on this reaction have been performed using various types of disulfides and alkynes from the both aspects of experimental and theoretical studies [3,4]. The other reason is the possibility for the application to the synthesis of a variety of palladium complexes having thiolato ligands by taking advantage of the affinity of sulfur to palladium atoms [5]. For example, the reaction of disulfides $(\text{RS})_2$ with $[\text{Pd}(\text{PPh}_3)_4]$ initially yields a *cis*-bis(thiolato)palladium(II)

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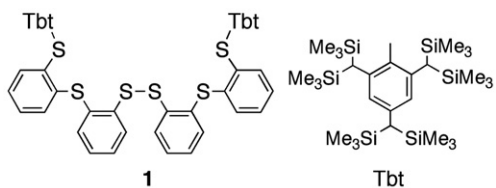


Chart 1.

complex cis -[Pd(SR)₂(PPh₃)₂] via oxidative addition and subsequently undergoes the dimerization along with the dissociation of a PPh₃ ligand to give cis and $trans$ isomers of sulfur-bridged binuclear complexes, cis - and $trans$ -[(RS)(Ph₃P)Pd(μ-SR)₂Pd(SR)(PPh₃)] [5b].

In addition, the transition-metal-mediated activation of a C–S bond has been extensively studied from the standpoints of synthetic chemistry, petrochemical hydrodesulfurization, and bioinorganic chemistry [6]. As far as C(sp²)–S activation is concerned, a number of examples on thiophene derivatives have been studied and well established [7]. On the contrary, there are relatively few reports on an aryl C(sp²)–S bond activation [8].

On the other hand, we have succeeded in the syntheses of a variety of highly reactive low-coordinate species containing main group metals by taking advantage of effective steric protection groups, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) groups [9]. We have recently reported that the reaction of a bulky, *o*-phenylene bridged hexathioether containing a disulfide bond, TbtS(*o*-phen)S(*o*-phen)SS(*o*-phen)S(*o*-phen)STbt (**1**) (*o*-phen = *o*-phenylene), with 3 molar amounts of [Pd(PPh₃)₄] affords tetrakis(μ-thiolato)tripalladium(II) complex **2** via the cleavage of the one S–S and the two C(aryl)–S bonds of **1** (see Chart 1) [10]. As a general rule, an aryl C(sp²)–S bond has been thought to be inactive against palladium(0) complexes, and this is the first example of the cleavage of aryl C(sp²)–S bond by a palladium(0) complex [11]. In this paper, we describe the details of the reaction of **1** with [Pd(PPh₃)₄], the studies to elucidate the mechanism for the formation of **2**, and the investigation on the pseudo-hexa-coordinated geometry of monopalladium(II) complex **3** obtained by the reaction of **1** with an equimolar amount of [Pd(PPh₃)₄].

2. Results and discussion

2.1. Synthesis of bulky hexathioether **1**

Coupling reaction of TbtSC₆H₄I [12] with an equimolar amount of 1,2-benedithiol in the presence of Cu₂O in refluxing 2,4,6-trimethylpyridine [13] generated the corresponding thiol intermediate. Oxidative coupling reaction of the thiol intermediate gave disulfide **1** in good yield (Scheme 1). Hexathioether **1** was characterized by NMR and mass spectrometry together with elemental analysis, and the molecular structure of **1** in the crystalline state was definitively determined by X-ray structural analysis.

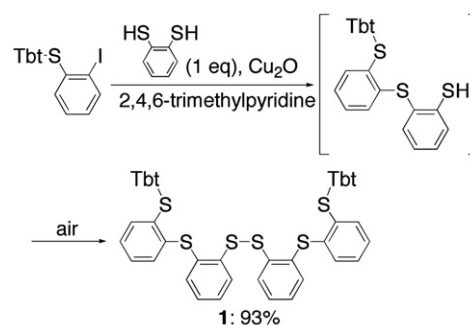
Scheme 1. Synthesis of bulky hexathioether **1**.

Fig. 1 shows the ORTEP drawing of **1** and the selected bond lengths, bond angles, and torsion angles are summarized in Table 1.

Hexathioether **1** is made up of the interlinked sulfide parts and the central disulfide moiety. In the crystal structure, hexathioether **1** has a conformation close to C₂ symmetry. All the C–S bond lengths of diarylsulfide moieties of **1** (1.772(4)–1.787(4) Å) are within the range of C–S distances reported for diarylsulfides [14]. The lengths of the C–S and S–S bonds of the diaryldisulfide moiety of **1** (1.794(4) Å for C(39)–S(3), 1.792(4) Å for C(40)–S(4), and 2.0364(15) Å for S(3)–S(4)) are also close to those observed in common diaryldisulfides (1.754–1.789 Å for aryl C–S bonds and 2.023–2.099 Å for S–S bonds) [15].

Interestingly, almost linear alignment of the four inner sulfur atoms (S2–S5) was observed. This alignment may be explained in terms of the n_p(S)–σ*(S–S)–n_p(S) four center-six electron bond, which has been proposed by Nakaniishi et al. based on the experimental and the theoretical studies to explain the linear alignments of chalcogen atoms in a bis[8-(aryltio)naphthyl]-1,1'-disulfide system [16]. The angles of S2–S3–S4 (163.5°) and S3–S4–S5 (162.2°) of **1** differ little from those observed in bis[8-(phenylthio)naphthyl]-1,1'-disulfide (168.6 and 166.0°). The distances of S2···S3 (3.056 Å) and S4···S5 (3.054 Å) of **1** are shorter than the sum of the van der Waals radii of sulfur atoms (3.70 Å) [17], though the distances are relatively longer than those observed in bis[8-(phenylthio)naphthyl]-1,1'-disulfide (2.988(2) Å), probably due to the difference between the 1,2-phenylene and 1,8-naphthylene systems. Consequently, the linear alignment of the four sulfur atoms observed in **1** might be interpreted in terms of the n_p(S)–σ*(S–S)–n_p(S) four center-six electron bond.

2.2. Reaction of **1** with [Pd(PPh₃)₄]

To a benzene solution of **1** was added 3 molar amounts of [Pd(PPh₃)₄], and the resulting yellow solution was stirred at room temperature for 12 h. The crude product was purified by GPC (gel permeation chromatography) to afford trinuclear palladium(II) complex **2** as yellow crystals in 71% yield (Scheme 2). Tripalladium(II) complex **2** was characterized by NMR and mass spectrometry and elemental analysis, and its molecular structure in

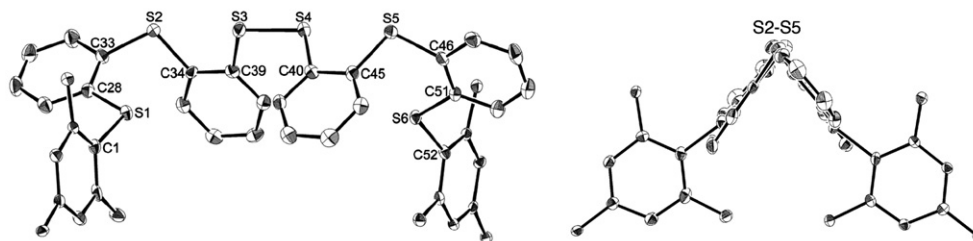


Fig. 1. ORTEP drawing of **1** (50% probability) (left: front view, right: side view). Hydrogen atoms, trimethylsilyl groups, and solvent molecules are omitted for clarity.

Table 1
Selected bond lengths (Å), angles (°), and torsion angles (°) of **1**

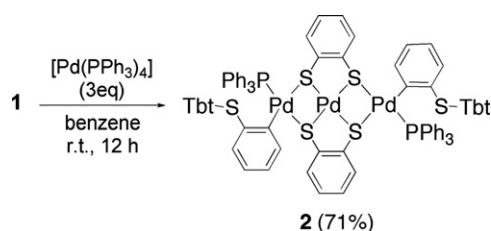
S1–C1	1.782(4)	S1–C28	1.772(4)
S2–C33	1.787(4)	S2–C34	1.781(4)
S3–C39	1.794(4)	S3–S4	2.0364(15)
S4–C40	1.792(4)	S5–C45	1.779(4)
S5–C46	1.773(4)	S6–C51	1.774(4)
S6–C52	1.784(4)		
C28–S1–C1	106.39(18)	C34–S2–C33	103.88(19)
C39–S3–S4	106.17(14)	C40–S4–S3	105.52(15)
C46–S5–C45	103.9(2)	C51–S6–C52	104.95(19)
C1–S1–C28–C33	167.8(3)	C28–C33–S2–C34	62.8(4)
C34–C39–S3–S4	–169.4(3)	C39–S3–S4–C40	–84.65(19)
S3–S4–C40–C45	–169.1(3)	C40–C45–S5–C46	–148.7(3)
C46–C51–S6–C52	169.2(3)		

the crystalline state was determined by X-ray structural analysis [10].

The formation of trinuclear palladium(II) complex **2** is most likely interpreted in terms of the three-step palladium insertion reaction into the one S–S and the two C–S bonds of hexathioether **1**. Since the insertion of transition metals toward S–S bonds is one of the typical reactions of disulfides, the S–S bond cleavage of hexathioether **1** is not so surprising. As mentioned above, the aryl C(sp²)–S bond cleavage mediated by a palladium(0) complex is unprecedented, albeit a number of studies on palladium complexes coordinated with sulfur ligand having aryl C(sp²)–S bonds have been reported so far. Therefore, the reaction mechanism of the aryl C(sp²)–S bond cleavage is very interesting.

2.3. Mechanism for the formation of **2**

To elucidate the mechanism for the formation of trinuclear palladium(II) complex **2**, we studied the reactions of hexathioether **1** with various amounts of [Pd(PPh₃)₄].

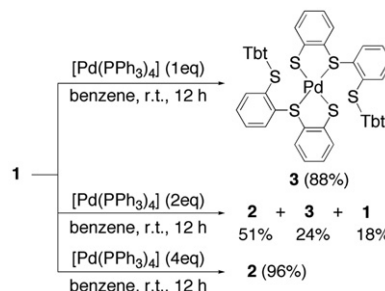


Scheme 2. Synthesis of trinuclear palladium(II) complex **2**.

First, we examined the reaction of **1** with an equimolar amount of [Pd(PPh₃)₄]. To a benzene solution of the bulky hexathioether **1** was added an equimolar amount of [Pd(PPh₃)₄] at room temperature. After stirring for 12 h at this temperature, the solvent was removed under reduced pressure. The residue was washed with acetonitrile and purified by recrystallization from chloroform/acetonitrile to give a mononuclear palladium(II) complex **3** in 88% yield as green crystals (Scheme 3). Monopalladium(II) complex **3** was characterized by NMR and mass spectrometry together with elemental analysis. The molecular structure of **3** in the crystalline state was definitively determined by X-ray structural analysis (vide infra).

In this reaction, the oxidative addition of the central disulfide bond of hexathioether **1** to the palladium(0) center occurred selectively. Taking this result into consideration, the formation of tripalladium(II) complex **2** by the reaction of **1** with 3 molar amounts of [Pd(PPh₃)₄] can be explained in terms of the initial oxidative addition of the central S–S bond to the palladium(0), followed by the oxidative addition of the aryl C(sp²)–S bonds toward monopalladium(0) species.

The reaction of **1** with 2 molar amounts of [Pd(PPh₃)₄] in benzene at room temperature for 12 h resulted in the formation of trinuclear palladium(II) complex **2** (51%) and monopalladium(II) complex **3** (24%) together with the recovery of **1** (18%) (Scheme 3). Interestingly, no bimetallic product was obtained in this reaction, suggesting that a bimetallic species generated by the oxidative addition of the aryl C–S bond of a monopalladium(II) intermediate to a palladium(0) complex is immediately converted to a tripalladium(II) species by the further palladium(0) insertion reaction.



Scheme 3. Reactions of hexathioether **1** with various amounts of [Pd(PPh₃)₄].

The reaction of **1** with 4 molar amounts of $[\text{Pd}(\text{PPh}_3)_4]$ in benzene at room temperature for 12 h gave trinuclear palladium(II) complex **2** in 96% yield (Scheme 3). In this reaction, no tetrapalladium species could not be obtained, although complex **2** still has unreacted thioether sites, Tbt–S–C₆H₄ moieties.

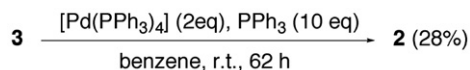
To understand the formation mechanism of tripalladium(II) complex **2** in more detail, we examined the stepwise synthesis of **2** from the monopalladium(II) complex **3**.

To a benzene suspension of **3** was added 2 molar amounts of $[\text{Pd}(\text{PPh}_3)_4]$, and the resulting mixture was stirred at room temperature for 62 h. After removal of the solvent, the residue was washed with acetonitrile to recover the starting material **3** quantitatively. This result indicates that a palladium(0) complex does not react directly with the aryl C–S bond of monopalladium(II) complex **3**, that is, tripalladium(II) complex **2** is not formed via monopalladium(II) complex **3**. Under the conditions for the formation of tripalladium(II) complex **2**, a certain amount of free PPh₃ molecules dissociated from $[\text{Pd}(\text{PPh}_3)_4]$ should exist in the reaction mixture. To increase the concentration of PPh₃ in the reaction mixture, the reaction of **2** with 2 molar amounts of $[\text{Pd}(\text{PPh}_3)_4]$ was examined in the presence of 10 molar amounts of PPh₃ (Scheme 4).

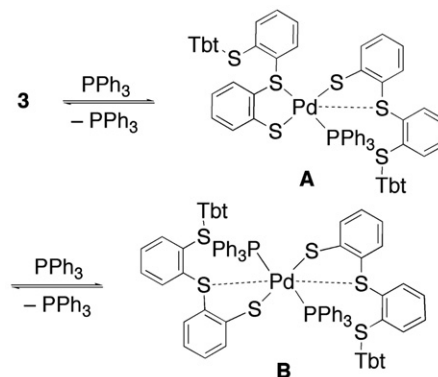
When 10 molar amounts of PPh₃ was added to a benzene suspension of **3** and 2 molar amounts of $[\text{Pd}(\text{PPh}_3)_4]$ was added at room temperature, the resulting yellow suspension gradually turned to a brown suspension. After stirring for 62 h at this temperature, the reaction mixture was filtered to recover **3** as green precipitates in 52% yield. The organic filtrate was evaporated and the residue was purified by GPC to afford trinuclear palladium(II) complex **2** in 28% yield. These results suggest that monopalladium(II) intermediates having PPh₃ ligand(s) are concerned in the unusual C(aryl)–S cleavage. Additionally, considering that the unusual C(aryl)–S cleavage by a palladium(0) complex should require a special electronic state around the C(aryl)–S bond significantly different from those of usual thioethers, 5- or 6-coordinated species, such as **A** or **B** shown in Scheme 5, might be reactive intermediates of the C(aryl)–S bond cleavage leading to the formation of **2**.

2.4. X-ray structural analysis of mononuclear Pd(II) complex **3**

Single crystals of **3** suitable for X-ray crystallographic analysis were obtained by recrystallization from benzene/acetonitrile. Fig. 2 shows the molecular structure of **3** in the crystalline state and the selected bond lengths, angles, and torsion angles are summarized in Table 2. The two thiolato-S atoms and the two sulfide-S atoms are situated



Scheme 4. Reaction of **3** with $[\text{Pd}(\text{PPh}_3)_4]$ in the presence of PPh₃.



Scheme 5. A plausible mechanism for the activation of **3**.

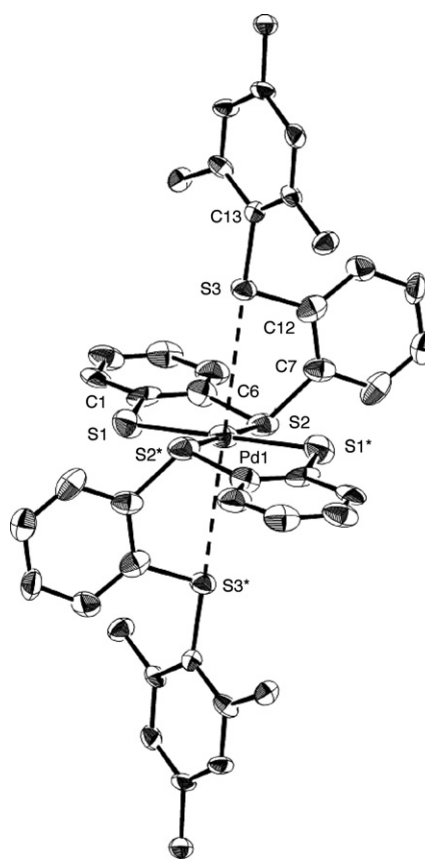


Fig. 2. ORTEP drawings of **3** (50% probability). Hydrogen atoms, trimethylsilyl groups, and a solvent molecule were omitted for clarity.

with a slightly distorted *trans*-square planar coordination geometry around the central palladium atom, and the two sulfur atoms next to the Tbt groups exist at the axial positions to construct a slightly distorted octahedral structure of **3**. The two thiolato–S–Pd bond distances (2.307(3) Å for S1–Pd1 and S1*–Pd1) are slightly longer than the two sulfide–S–Pd bond distances (2.270(3) Å for S2–Pd1 and S2*–Pd1). On the other hand, the distances between the palladium and the two sulfur atoms at the axial positions ($\text{Pd1}\cdots\text{S3}$ and $\text{Pd1}\cdots\text{S3}^* = 3.385(2)$ Å) are slightly shorter than the sum of the van der Waals radii

Table 2

Selected bond lengths (Å), atomic distances (Å), angles (°), and torsion angles (°) of monopalladium(II) complex **3**

Pd1–S1	2.307(3)	Pd1–S2	2.270(3)
S1–C1	1.759(10)	S2–C6	1.784(10)
S2–C7	1.743(10)	S3–C12	1.763(10)
S3–C13	1.782(8)	Pd1···S3	3.385(2)
S1···S2	3.196(3)		
S1–Pd1–S2	88.56(10)	S2–Pd1–S1*	91.44(10)
C1–S1–Pd1	102.2(4)	C6–S2–Pd1	104.2(4)
C6–S2–C7	104.6(5)	C12–S3–C13	103.8(4)
Pd1–S2–C7–C12	–54.8(8)	S1–Pd1–S2–C7	128.0(4)
C7–C12–S3–C13	177.0(7)	S3–Pd1–S1–C1	54.6(3)

of palladium and sulfur atoms (3.43 Å) [18], suggesting weak interactions between the palladium (Pd1) and the terminal sulfur atoms (S3 and S3*) in the crystalline state. Although some cationic species of 6-coordinate palladium(II) complex have been synthesized using crown thioether ligands [19], S- and N-donor macrocyclic ligands [20], and tris(2,4,6-trimethoxyphenyl)phosphine ligands [21], the neutral species are of great rarity [22].

2.5. Atoms in molecule (AIM) analysis for the Pd···S_{ax} interactions

To estimate the Pd···S_{ax} interactions (Pd1···S3 and Pd1···S3*) of the palladium(II) complex **3**, we examined the topological analysis using Bader's theory of atoms in molecules (AIM) [23,24]. 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···S_{ax} interactions (Pd1···S3 and Pd1···S3*) of **3**, the BCPs could be located. The BCP properties of the Pd···S_{ax} interactions are summarized in Table 3 together with those of Pd–S_{eq} bonds. The electron density (ρ) at a BCP correlates with the strength of an atomic interaction. The value of ρ obtained for the Pd···S_{ax} interactions ($\rho_{\text{Pd}\cdots\text{S}}$) is 0.013 ea_0^{-3} , which is smaller than those of normal covalent bonds (e.g., $\rho_{\text{C–C}} = 0.24 \text{ea}_0^{-3}$) but larger than those for the practical boundary of molecules ($\rho = 0.001 \text{ea}_0^{-3}$) [25]. In addition, the $\rho_{\text{Pd}\cdots\text{S}}$ value is approximately a seventh part of those for the Pd–S_{eq} bonds (0.091 ea_0^{-3} for the Pd1–S1 and Pd1–S1* and 0.097 ea_0^{-3} for the Pd1–S2 and Pd1–S2*), and within the range of those for neutral hydrogen bonds ($\rho = 0.002\text{--}0.04 \text{ea}_0^{-3}$). The Laplacian (∇^2) of ρ denotes the curvature of electron density in the 3D-topological space for two interacting atoms, and

Table 3
Estimated BCP properties of **3** by the AIM analysis

	ρ (ea_0^{-3})	$\nabla^2\rho$ (ea_0^{-5})
Pd1···S3, Pd1···S3*	0.013	0.033
Pd1–S1, Pd1–S1*	0.091	0.140
Pd1–S2, Pd1–S2*	0.097	0.193

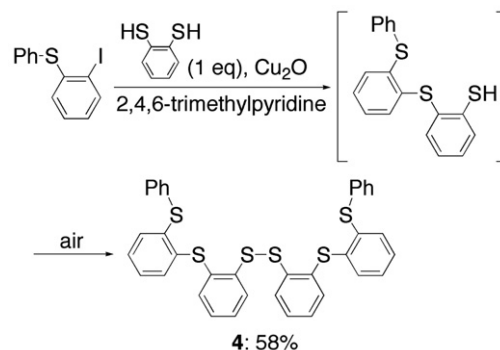
in general, a negative value of $\nabla^2\rho$ indicates that the electron density is locally concentrated, while a positive value of $\nabla^2\rho$ means that the electron density is locally depleted. The positive value of $\nabla^2\rho_{\text{Pd}\cdots\text{S}}$ (0.033 ea_0^{-5}) suggests that the Pd1···S3 and Pd1···S3* interactions are dominantly electrostatic in nature.

2.6. Synthesis of less bulky hexathioether **4**

In order to investigate the effect of the bulky substituents in the pseudo-6-coordination structure of **3**, we synthesized a phenyl analog of **1**, PhS(*o*-phen)S(*o*-phen)SS(*o*-phen)S(*o*-phen)SPh (**4**), and examined the reaction of **4** with an equimolar amount of [Pd(PPh₃)₄].

Ph-substituted hexathioether **4** was synthesized by the method similar to that for **1**, though in a relatively low yield (Scheme 6). Hexathioether **4** was characterized by NMR and mass spectrometry together with elemental analysis. The molecular structure of **4** in the crystalline states was definitively determined by X-ray structural analysis. Fig. 3 shows the ORTEP drawing of **4** and the selected bond lengths, angles, and torsion angles are summarized in Table 4.

The C–S bond lengths of the diarylsulfide moieties and the C–S and S–S bond lengths of the diaryldisulfide moiety of **4** are all close to those observed in common diarylsulfides [14] and diaryldisulfides [15], respectively. In contrast to the almost *C*₂ symmetrical conformation of bulky hexathioether **1**, Ph-substituted hexathioether **4** has no symmetrical conformation. This difference may be explained in terms of the intermolecular interactions. In the crystalline structure of **1**, no remarkable intermolecular interactions were observed probably due to the steric effect of the bulky Tbt groups. On the other hand, there were some intermolecular C–H··· π interactions in the crystalline structure of **4** (Fig. 4) [26]. Nevertheless, almost linear alignment of the four inner sulfur atoms (S2–S5) is also observed as in the case of **1**, probably due to the existence of an $n_{\text{p}}(\text{S})\text{--}\sigma^*(\text{S}\text{--}\text{S})\text{--}n_{\text{p}}(\text{S})$ four center-six electron bond (167.0° for S2–S3–S4, 165.9° for S3–S4–S5, 3.096 Å for S2···S3, and 3.043 Å for S4···S5).



Scheme 6. Synthesis of Ph-substituted hexathioether **4**.

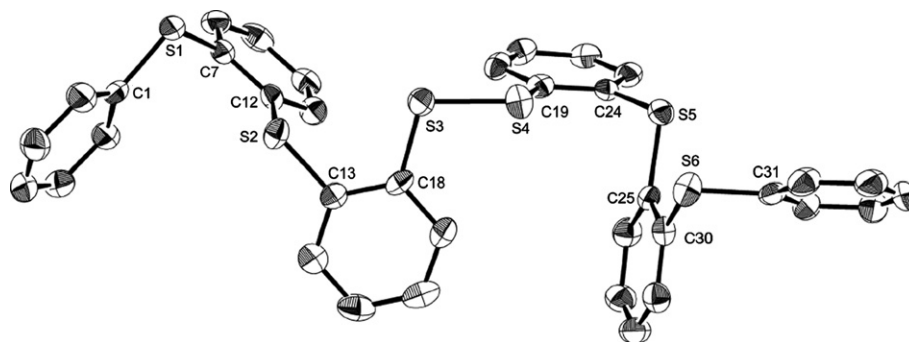
Fig. 3. ORTEP drawing of **4** (50% probability). Hydrogen atoms are omitted for clarity.

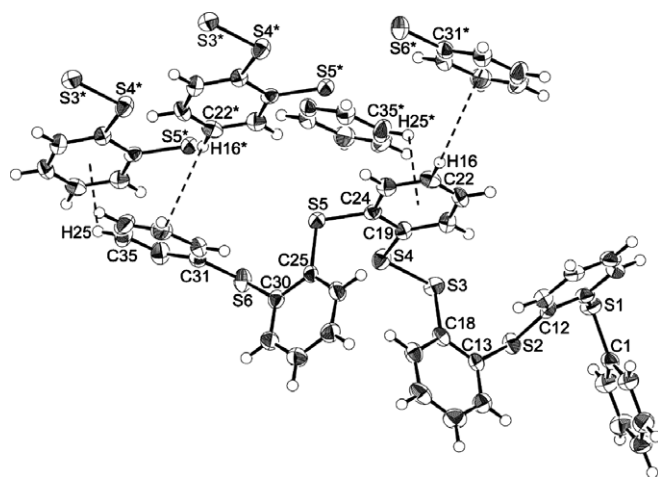
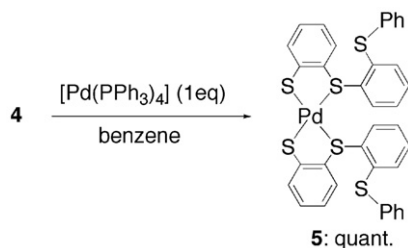
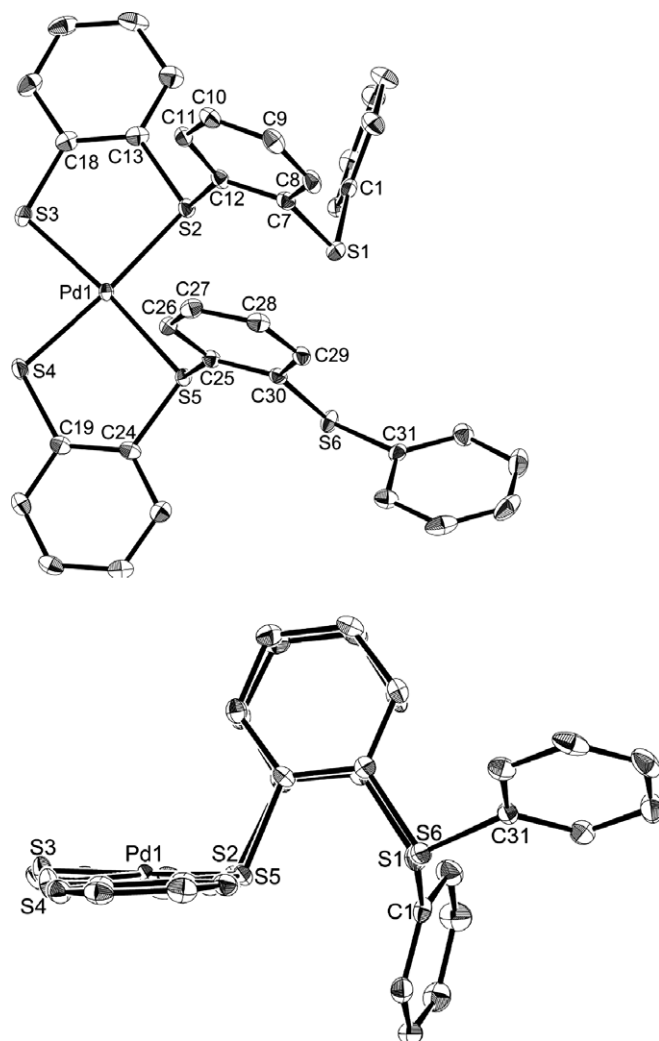
Table 4

Selected bond lengths (Å), angles (°), and torsion angles (°) of hexathioether **4**

S1–C1	1.782(5)	S1–C7	1.764(5)
S2–C12	1.767(5)	S2–C13	1.778(5)
S3–C18	1.777(5)	S3–S4	2.039(2)
S4–C19	1.775(5)	S5–C24	1.773(5)
S5–C25	1.787(5)	S6–C30	1.767(5)
S6–C31	1.777(5)		
C7–S1–C1	102.6(2)	C12–S2–C13	102.7(2)
C18–S3–S4	104.84(17)	C19–S4–S3	104.39(17)
C24–S5–C25	100.5(2)	C30–S6–C31	103.0(2)
C1–S1–C7–C12	–79.6(4)	C13–S2–C12–C7	170.6(4)
S4–S3–C18–C13	–178.6(3)	C18–S3–S4–C19	88.1(2)
S3–S4–C19–C24	–173.8(3)	C25–S5–C24–C19	78.5(4)
C31–S6–C30–C25	–96.3(4)		

2.7. Reactions of Ph-substituted hexathioether **4** with an equimolar amount of $[Pd(PPh_3)_4]$

The reaction of Ph-substituted hexathioether **4** with an equimolar amount of $[Pd(PPh_3)_4]$ was examined under conditions similar to those for the synthesis of monopalladium(II) (**3**). To a benzene solution of **4** was added an

Fig. 4. Intermolecular interactions in the crystalline structure of **4**.Scheme 7. Oxidative addition of hexathioether **4** to $[Pd(PPh_3)_4]$.Fig. 5. ORTEP drawings of **5** (top: the top view, bottom: the side view) (50% probability). Hydrogen atoms were omitted for clarity.

equimolar amount of $[\text{Pd}(\text{PPh}_3)_4]$ at room temperature. After stirring for 12 h at this temperature, the crude mixture was purified by the recrystallization from benzene/acetonitrile to give monopalladium(II) complex **5** as purple crystals (Scheme 7).

Palladium(II) complex **5** was characterized by NMR and mass spectrometry together with elemental analysis. The molecular structure of **5** in the crystalline state was definitively determined by X-ray structural analysis (Fig. 5). Table 5 shows the selected bond lengths, angles, and torsion angles of **5** together with those of $[\text{Pd}\{\text{S}(o\text{-phen})\text{SPh}\}_2]$ (**6**) (Chart 2), the synthesis and structure of which has been already reported by us [27].

The structure of **5** resembles that of **6** rather than that of **3**, i.e., the two thiolato-S atoms (S3 and S4) of **5** are in *cis* position and the two $\text{C}_6\text{H}_4\text{SPh}$ moieties are situated in *cis* position to each other. Furthermore, the two terminal sulfur atoms are on almost the same plane as the central PdS_4 part, indicating no interactions between the palladium and the terminal sulfur atoms. The central palladium atom of **5** has a slightly distorted square planar coordination geometry with the two thiolato-S atoms and the two sulfide-S atoms. The Pd1–S3 (2.2724(6) Å) and Pd1–S4 (2.2832(6) Å) bond distances are shorter than the thiolato-S–Pd bond distances (2.307(3) Å) observed in Tbt-analog **3**. By contrast, the Pd1–S2 (2.3192(6) Å) and Pd1–S5 (2.3330(6) Å) bond distances are longer than the sulfide-S–Pd bond distances (2.270(3) Å) observed in **3**. In complex **5**, the Pd1–S2 and Pd1–S5 bonds are slightly elongated due to the steric repulsion of the two $\text{C}_6\text{H}_4\text{SPh}$ moieties situated in *cis* position to each other, whereby the Pd1–S3 and Pd1–S4 bonds are shortened due to the *trans*-influence [28]. Indeed, the S2···S5 distance (3.481 Å) is comparatively

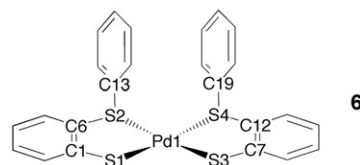


Chart 2.

longer than the S3···S4 distance (3.084 Å) as well as, in complex **6**, the S2···S4 distance is longer than the S1···S3 distance. Furthermore, as in the case of complex **6**, the two benzene rings constructed by C7–C12 and C25–C30 are parallel to each other and the distance between these planes is 3.77 Å average, suggesting the existence of a weak face-to-face π -stacking interaction [26,29].

2.8. Theoretical calculations

The palladium(II) complexes **3**, **5**, and **6** were synthesized by the reactions of the corresponding hexa- or tetra-thioethers **1**, **4**, and $[\text{PhS}(o\text{-phen})\text{S}]_2$, respectively, with an equimolar amount of $[\text{Pd}(\text{PPh}_3)_4]$. Although their formations result from the simple insertion reactions of the palladium(0) into the S–S bond, great differences were observed among their crystalline structures, i.e., the bulky palladium(II) complex **3** has the distorted octahedral structure containing the *trans*-planar 4-coordination environment, while the less bulky palladium(II) complexes **5** and **6** have the slightly distorted *cis*-planar 4-coordination geometries, respectively.

To clarify the reasons for the difference among the structures, the *trans*-conformation for **3** and the *cis*-conformation for **5** and **6**, theoretical calculations were performed

Table 5
Selected bond lengths (Å), angles (°), atomic distances (Å), and torsion angles (°) of monopalladium(II) complexes **5** and **6**

Complex 5		Complex 6 [27]	
Pd1–S2	2.3192(6)	Pd1–S3	2.2724(6)
Pd1–S4	2.2832(6)	Pd1–S5	2.3330(6)
S1–C1	1.786(2)	S1–C7	1.779(2)
S2–C12	1.793(2)	S2–C13	1.783(2)
S3–C18	1.757(2)	S4–C19	1.756(2)
S5–C24	1.799(2)	S5–C25	1.797(2)
S6–C30	1.782(2)	S6–C31	1.779(2)
Pd1···S1	4.5962(8)	Pd1···S6	5.2726(9)
S2···S5	3.4810(8)	S3···S4	3.0843(9)
S2–Pd1–S3	88.80(2)	S2–Pd1–S5	96.874(19)
S3–Pd1–S4	85.22(2)	S4–Pd1–S5	89.21(2)
Pd1–S2–C12	108.15(6)	Pd1–S2–C13	104.30(7)
Pd1–S5–C24	103.59(7)	Pd1–S5–C25	107.22(7)
Pd1–S3–C18	104.75(7)	Pd1–S4–C19	104.41(7)
C7–S1–C1	98.78(9)	C30–S6–C31	103.48(9)
C12–S2–Pd1–S3	106.16(7)	S4–Pd1–S5–C25	–108.03(7)
C12–S2–C13–C18	–112.24(17)	C19–C24–S5–C25	112.28(17)
C1–S1–C7–C8	–112.71(17)	C29–C30–S6–C31	16.64(18)
C18–S3–Pd1–S4	–172.88(7)	S3–Pd1–S4–C19	–178.18(7)
		S2–Pd1–S4	95.06(2)
		S1–Pd1–S3	87.47(2)
		S1–Pd1–S2	88.72(2)
		S3–Pd1–S4	88.61(2)
		Pd1–S2–C6	104.63(8)
		Pd1–S4–C12	104.53(8)
		S1–Pd1–S2–C13	111.01(8)
		S3–Pd1–S4–C19	–112.81(8)

for two conformational isomers of bis[2-(phenylsulfonyl)benzenethiolato]palladium(II) (*cis*-conformer: **6a** and *trans*-conformer: **6b**). As shown in Chart 3, both of **6a** and **6b** have two conformational possibilities, the *syn*-structure (two phenyl rings are on the same side of the $C_6H_4S_2PdS_2C_6H_4$ plane) and the *anti*-structure (two phenyl rings are on the opposite side of the $C_6H_4S_2PdS_2C_6H_4$ plane). Therefore, the energies of these four isomers, **6a-syn**, **6a-anti**, **6b-syn**, and **6b-anti**, were calculated with B3LYP/LANL2DZ(ECP) for Pd, 6-31G(2d) for S, and 6-31G(d) for C and H level [30]. Their optimized structures are shown in Fig. 6.

Contrary to the results of the X-ray structural analyses of **5** and **6**, the theoretical calculations revealed that the **6a-syn** type structure has the highest energy among the four isomers. However, there are little energy differences among them, and the preference of complexes **5** and **6** for the **6a-syn** type structure in the crystalline state may be caused by

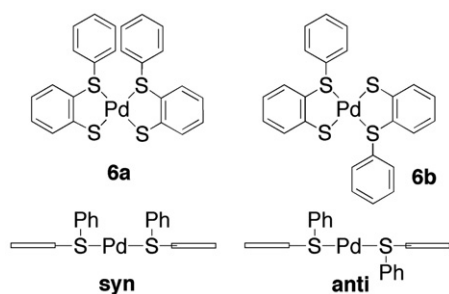


Chart 3.

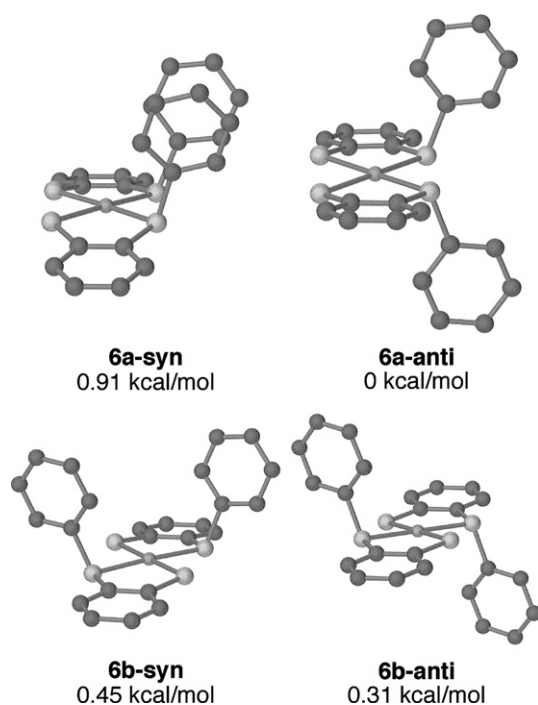


Fig. 6. Calculated structures for the four isomers, **6a-syn**, **6a-anti**, **6b-syn**, and **6b-anti**.

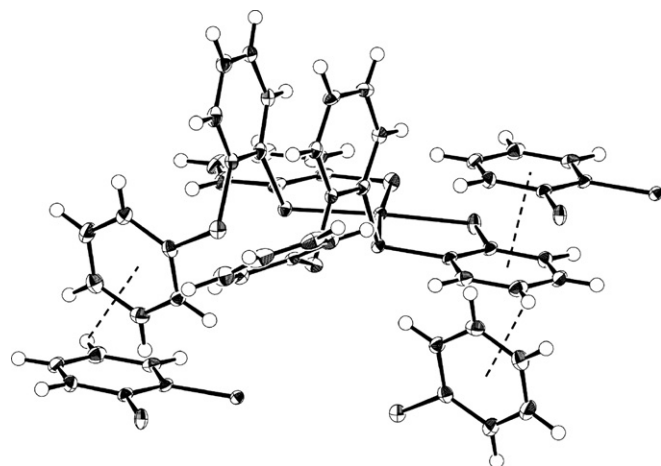


Fig. 7. Intermolecular interactions in the crystalline structure of **5**.

the intermolecular C–H··· π interactions, which are observed in the X-ray structural analyses (Fig. 7 and Ref. [27]). On the other hand, no significant intermolecular interactions were observed in the crystalline state of **3** probably due to the effect of the bulky Tbt groups, and the preference of complex **3** for the **6b-anti** type structure may be interpreted in terms of the effects of the steric repulsion of the two Tbt groups.

3. Conclusion

We reported the oxidative addition of the bulky hexathioether **1** to various amounts of $[Pd(PPh_3)_4]$. The reaction of **1** with 3 molar amounts of $[Pd(PPh_3)_4]$ afforded tripalladium(II) complex **2** via three-step palladium(0) insertion reactions including unusual aryl C–S bond cleavages. Furthermore, the reaction of **1** with an equimolar amount of $[Pd(PPh_3)_4]$ afforded monopalladium(II) complex **3**. The conversion of **3** into **2** was achieved by the reaction with $[Pd(PPh_3)_4]$ in the presence of an excess amount of PPh_3 , suggesting that the 5- or 6-coordinated monopalladium(II) species having PPh_3 ligand(s) are the key intermediates for the unusual aryl C–S bond cleavage by a palladium(0) complex. On the other hand, complex **3** has an interesting pseudo-octahedral structure in the crystalline state. AIM analysis supported the hexa-coordinated geometry for the palladium center in **3**. In contrast to the bulky system, the reaction of Ph-substituted hexathioether **4** with an equimolar amount of $[Pd(PPh_3)_4]$ generated monopalladium(II) complex **5** having square-planar environment around the Pd(II) atom. To clarify the factors contributing to the structural differences between **3** and **5**, theoretical calculations were performed for the *cis*- and *trans*-isomers of $[Pd\{S(o\text{-phen})SPh\}_2]$. These calculations indicate that there is little difference among the energies of **6a-syn**, **6a-anti**, **6b-syn**, and **6b-anti**. It is suggested that a reason for the preference of the *trans-anti*-conformation in **3** is steric repulsion between bulky Tbt groups, and those of *cis-syn*-conformations in **5** and **6** are the intermolecular interactions.

4. Experimental

4.1. General procedures

All experiments were performed under an argon atmosphere unless otherwise noted. All solvents were dried by standard methods and freshly distilled prior to use. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured in CDCl_3 with a JEOL JNM AL-300 spectrometer using CHCl_3 (7.25 ppm) and CDCl_3 (77.0 ppm) as internal standards for ^1H NMR and ^{13}C NMR, respectively. High-resolution mass spectral data (HRMS) were obtained on a JEOL JMS-700 spectrometer. Wet column chromatography (WCC) was performed on Wakogel C-200. Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-908, LC-918, or LC-908-C60 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: chloroform). All melting points were determined on a Yanaco micro-melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. 2-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenylthio} iodobenzenes (TbtSC₆H₄I) and 2-iodophenyl phenyl sulfide (PhSC₆H₄I) were prepared according to the reported procedure [12].

4.2. Synthesis of bis[2-(2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenylsulfanyl}phenylsulfanyl)phenyl]disulfide (**1**)

To a suspension of 1,2-benzenedithiol (437 mg, 3.07 mmol) and Cu_2O (293 mg, 2.05 mmol) in 2,4,6-trimethylpyridine (30 mL) was added dropwise a solution of TbtSC₆H₄I (1.61 g, 2.05 mmol) in 2,4,6-trimethylpyridine (20 mL) at 170 °C. The mixture was refluxed for 3 h under argon to generate the corresponding thiol intermediate. After stirring for further 12 h at room temperature in the open air, the reaction mixture was passed through a short column (SiO_2 , benzene) to remove inorganic salts. After addition of benzene (200 mL), the mixture was washed with a 0.2 M aqueous solution of HCl three times (100 mL \times 3). The organic layer was dried with MgSO_4 and the solvents were removed under reduced pressure to afford a light-yellow oil. The residue was subjected to GPLC (CHCl_3), and subsequently reprecipitated from $\text{CHCl}_3/\text{CH}_3\text{CN}$ to give hexathioether **1** (1.50 g, 0.93 mmol, 93%) as colorless crystals. **1**: m.p. 188.0–189.0 °C. ^1H NMR (300 MHz, CDCl_3): δ 0.03 (s, 72H, SiMe_3), 0.07 (s, 36H, SiMe_3), 1.38 (s, 2H, Tbt *p*-benzyl), 2.66 (s, 4H, Tbt *o*-benzyl), 6.42 (s, 2H), 6.57 (s, 2H), 6.63–6.68 (m, 2H), 6.92–7.01 (m, 6H), 7.08–7.24 (m, 4H), 7.29 (dd, $J = 1.4$, 7.4 Hz, 2H), 7.56 (dd, $J = 1.4$, 8.0 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 0.7 (q, SiMe_3), 0.9 (q, SiMe_3), 26.5 (d \times 2, Tbt *o*-benzyl), 30.6 (d, Tbt *p*-benzyl), 122.6 (d), 123.9 (s), 125.0 (d), 126.6 (d), 127.0 (d), 127.0 (d), 127.3 (d), 127.7 (d), 128.9 (d), 130.0 (d), 131.8 (s), 131.8 (s), 133.6 (d), 139.8 (s), 140.1

(s), 144.5 (s), 150.3 (s \times 2); HRMS (FAB): found m/z 1598.5974 ($[\text{M}]^+$), calcd. for $\text{C}_{78}\text{H}_{134}\text{S}_6\text{Si}_{12}$ 1598.6041. Anal. Calc. for $\text{C}_{78}\text{H}_{134}\text{S}_6\text{Si}_{12}$: C, 58.50; H, 8.43. Found: C, 58.44; H, 8.52%.

4.3. Reaction of **1** with 3 molar amounts of $[\text{Pd}(\text{PPh}_3)_4]$

To a benzene solution (5 mL) of hexathioether **1** (20 mg, 12.5 μmol) was added 3 molar amounts of tetrakis(triphenylphosphine)palladium (43.3 mg, 37.5 μmol) at room temperature. After the mixture was stirred for 12 h at the same temperature, the solvent was removed under reduced pressure. The residual brown solid was subjected to GPLC (CHCl_3) followed by WCC (benzene:hexane = 1:1) to give pure tripalladium complex **2** (21.4 mg, 8.8 μmol , 71%) as yellow crystals. **2**: m.p. 182.7–183.7 °C (decomp.). ^1H NMR (300 MHz, CDCl_3 , 50 °C): δ -0.22 (s, 18H, SiMe_3), -0.19 (s, 18H, SiMe_3), 0.08 (s, 18H, SiMe_3), 0.09 (s, 36H, SiMe_3), 0.16 (s, 18H, SiMe_3), 1.38 (s, 2H, Tbt *p*-benzyl), 2.53 (s, 2H, Tbt *o*-benzyl), 3.30 (s, 2H, Tbt *o*-benzyl), 5.11 (d, $^3J = 7.8$ Hz, 2H), 5.80–5.94 (m, 4H), 5.97 (ddd, $^3J = 7.8$, ~ 8.0 Hz, $^4J = 1.5$ Hz, 2H), 6.10–6.19 (m, 4H), 6.17–6.22 (m, 2H), 6.53 (ddd, $^3J = 7.2$, ~ 8.0 Hz, $^4J = 1.5$ Hz, 2H), 6.58 (s, 2H), 6.66 (s, 2H), 7.09–7.26 (m, 18H), 7.44–7.91 (m, 12H); ^{13}C NMR (75 MHz, CDCl_3 , 50 °C): δ 0.8 (q, SiMe_3), 0.9 (q, SiMe_3), 1.5 (q, SiMe_3), 2.0 (q, SiMe_3), 26.4 (d, Tbt *p*-benzyl), 27.1 (d, Tbt *o*-benzyl), 30.8 (d, Tbt *o*-benzyl), 122.0 (d), 122.5 (d), 122.6 (d), 123.8 (d), 124.6 (d), 125.5 (s), 128.1 (d), 128.3 (d), 130.3 (d), 131.7 (d), 134.4 (d \times 2), 134.7 (s), 136.2 (d), 136.3 (d), 142.1 (s), 143.4 (s), 143.8 (s), 146.0 (s), 150.4 (s), 151.9 (s), 152.5 (s); ^{31}P NMR (121 MHz, CDCl_3 , 50 °C): δ 28.1. Anal. Calc. for $\text{C}_{114}\text{H}_{164}\text{P}_2\text{Pd}_3\text{S}_6\text{Si}_{12}$: C, 56.00; H, 6.76. Found: C, 55.98; H, 6.83%.

4.4. Reaction of **1** with an equimolar amount of $[\text{Pd}(\text{PPh}_3)_4]$

To a benzene solution (5 mL) of hexathioether **1** (20 mg, 12.5 μmol) was added tetrakis(triphenylphosphine)palladium (14.4 mg, 12.5 μmol) at room temperature. After the mixture was stirred for 12 h at the same temperature, the solvent was removed under reduced pressure. The residue was subjected to GPLC (CHCl_3) to give mononuclear palladium complex **3** (18.7 mg, 11.0 μmol , 88%) as green crystals. **3**: m.p. 315.0–316.0 °C (decomp.). ^1H NMR (300 MHz, CDCl_3): δ -0.26 (s, 18H, SiMe_3), -0.24 (s, 18H, SiMe_3), -0.11 (s, 18H, SiMe_3), -0.01 (s, 18H, SiMe_3), 0.04 (s, 36H, SiMe_3), 1.35 (s, 2H, Tbt *p*-benzyl), 1.84 (s, 2H, Tbt *o*-benzyl), 2.71 (s, 2H, Tbt *o*-benzyl), 6.30 (s, 2H), 6.44 (s, 2H), 6.54 (d, $^3J = 8.0$ Hz, 2H), 6.70 (dd, $^3J = \sim 7.3$, $^4J = 1.2$ Hz, 2H), 6.73–6.80 (m, 4H), 6.84 (dd, $^3J = \sim 7.8$, $^4J = 1.2$ Hz, 2H), 7.03 (dd, $^3J = \sim 7.3$, $^4J = 1.4$ Hz, 2H), 7.17 (dd, $^3J = \sim 8.0$, $^4J = 1.4$ Hz, 2H), 7.42 (d, $^3J = 7.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3 , 50 °C): δ 0.1 (q, SiMe_3), 0.8 (q, SiMe_3), 0.9 (q, SiMe_3), 26.9 (d, Tbt

p-benzyl), 31.0 (d, Tbt *o*-benzyl), 122.1 (s), 122.5 (d), 122.6 (d), 126.3 (s), 127.7 (s), 128.0 (d), 128.4 (d), 128.9 (d), 129.0 (d), 129.6 (d), 131.0 (d), 135.7 (d), 144.3 (s), 145.0 (s), 150.8 (s), 152.8 (s); HRMS (FAB): found m/z 1706.5089 ($[M]^+$), calcd. for $C_{78}H_{134}^{108}PdS_6Si_{12}$ 1706.5080. Anal. Calc. for $C_{78}H_{134}PdS_6Si_{12}$: C, 54.86; H, 7.91. Found: C, 54.59; H, 7.93%.

4.5. Reaction of **1** with 2 molar amounts of $[Pd(PPh_3)_4]$

To a benzene solution (5 mL) of hexathioether **1** (20 mg, 12.5 μ mol) was added tetrakis(triphenylphosphine)palladium (28.9 mg, 25.0 μ mol) at room temperature. After the mixture was stirred for 12 h at the same temperature, the solvent was removed under reduced pressure. The residue was subjected to GLPC ($CHCl_3$) to give **2** (15.6 mg, 6.4 μ mol, 51%) and **3** (5.1 mg, 3.0 μ mol, 24%) together with the starting material **1** (3.6 mg, 2.2 μ mol, 18%).

4.6. Reaction of **1** with 4 molar amounts of $[Pd(PPh_3)_4]$

To a benzene solution (5 mL) of hexathioether **1** (20 mg, 12.5 μ mol) was added tetrakis(triphenylphosphine)palladium (57.8 mg, 50.0 μ mol) at room temperature. After the mixture was stirred for 12 h at the same temperature, the solvent was removed under reduced pressure. The residue was subjected to GLPC ($CHCl_3$) to give **2** (29.3 mg, 12.0 μ mol, 96%).

4.7. Reaction of **3** with 2 molar amounts of $[Pd(PPh_3)_4]$ in the presence of an excess amount of PPh_3

To a benzene suspension (20 mL) of **3** (50.0 mg, 29.0 μ mol) and 2 molar amounts of $[Pd(PPh_3)_4]$ (67.7 mg, 58.0 μ mol) was added 10 molar amounts of PPh_3 (76.8 mg, 290 μ mol) at room temperature. After stirring for 62 h at this temperature, the brown suspension was filtered through Celite. The filtrate was evaporated and the residue was subjected to GLPC ($CHCl_3$) to give **2** (18.1 mg, 8.0 μ mol, 28%) together with the starting material **3** (26.3 mg, 15.1 μ mol, 52%).

4.8. Synthesis of bis{2-[2-(phenylsulfanyl)phenylsulfanyl]-phenyl}disulfide (**4**)

To a suspension of 1,2-benzenedithiol (299.2 mg, 2.10 mmol) and Cu_2O (150.5 mg, 1.05 mmol) in 2,4,6-trimethylpyridine (30 mL) was added dropwise a solution of 2-iodophenyl phenyl sulfide ($PhSC_6H_4I$) (656.7 g, 2.10 mmol) in 2,4,6-trimethylpyridine (20 mL) at 170 °C. The mixture was refluxed for 3 h under argon to generate the corresponding thiol intermediate. After stirring for further 48 h at room temperature in the open air, the reaction mixture was passed through a short column (SiO_2 , benzene) to remove inorganic salts. After addition of benzene (100 mL), the mixture was washed with a 0.2 M aqueous solution of HCl three times (50 mL \times 3).

The organic layer was dried with $MgSO_4$ and the solvents were removed under reduced pressure to afford a light-yellow oil. The residue was subjected to GLPC ($CHCl_3$) to give Ph-substituted hexathioether **4** (396.5 mg, 0.61 mmol, 58%) as colorless crystals. **4**: m.p. 93.6–94.6 °C. 1H NMR (300 MHz, $CDCl_3$): δ 6.79–6.86 (m, 2H), 7.10–7.42 (m, 22H), 7.51–7.55 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 126.5 (d), 126.8 (d), 127.0 (d), 127.1 (d), 128.2 (d), 128.4 (d), 129.2 (d), 129.8 (d), 130.3 (s), 130.6 (d), 133.3 (d), 134.3 (s), 135.1 (s), 135.6 (d), 139.2 (s), 141.2 (s); HRMS (FAB): found m/z 650.0366 ($[M]^+$), calcd. for $C_{36}H_{26}S_6$ 650.0359. Anal. Calc. for $C_{36}H_{26}S_6$: C, 66.42; H, 4.03. Found: C, 66.47; H, 3.97%.

4.9. Synthesis of bis{2-[2-(phenylthio)phenylsulfanyl]-benzenethiolato}palladium (**5**)

To a benzene solution (15 mL) of Ph-substituted hexathioether **4** (60 mg, 92.0 μ mol) was added tetrakis(triphenylphosphine)palladium (106.5 mg, 92.0 μ mol) at room temperature. After the mixture was stirred for 12 h at the same temperature, the solvent was removed under reduced pressure. The residual red-violet solid was purified by recrystallization from chloroform/acetonitrile to give mononuclear palladium complex **5** (69.7 mg, 92.0 μ mol, 100%) as purple crystals. **5**: m.p. 192.7–193.7 °C (decomp.). 1H NMR (300 MHz, $CDCl_3$): δ 6.80 (ddd, $^3J = 7.5$, $^3J = 7.5$, $^4J = 1.2$ Hz, 2H), 6.94 (dd, $^3J = 7.5$, $^4J = 0.9$ Hz, 2H), 6.99 (ddd, $^3J = 8.1$, $^3J = 7.5$, $^4J = 0.9$ Hz, 2H), 7.05–7.12 (m, 4H), 7.33–7.39 (m, 12H), 7.52 (dd, $^3J = 8.1$, $^4J = 0.9$ Hz, 2H), 7.71 (dd, $^3J = \sim 8.3$, $^4J = 1.2$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 123.4 (d), 127.9 (d), 128.2 (d), 129.3 (d), 129.4 (d), 130.0 (d), 130.5 (d), 130.9 (d), 131.7 (s), 131.8 (d), 132.7 (d), 133.8 (s), 134.4 (s), 135.6 (d), 139.2 (s), 151.5 (s); HRMS (FAB): found m/z 756.9445 ($[M]^+$), calcd. for $C_{36}H_{26}^{106}PdS_6$ 756.9472. Anal. Calc. for $C_{36}H_{26}PdS_6$: C, 57.09; H, 3.46. Found: C, 57.08; H, 3.48%.

4.10. Synthesis of bis[2-(phenylsulfanyl)phenyl] disulfide

To a suspension of 1,2-benzenedithiol (697 mg, 4.90 mmol) and Cu_2O (350 mg, 2.45 mmol) in 2,4,6-trimethylpyridine (20 mL) was added dropwise a solution of iodobenzene (1.0 g, 4.90 mmol) in 2,4,6-trimethylpyridine (10 mL) at 170 °C. The mixture was refluxed for 3 h under argon to generate the corresponding thiol intermediate, and stirred for further 12 h at room temperature under the air. The reaction mixture was passed through a short column (SiO_2 , benzene) to remove inorganic salts. After addition of benzene (100 mL), the mixture was washed with a 0.2 M aqueous solution of HCl three times (50 mL \times 3). The organic layer was dried with $MgSO_4$ and the solvents were removed under reduced pressure to afford a light-yellow oil. The residue was subjected to WCC (SiO_2 , hexane) to give bis[2-(phenylsulfanyl)phenyl]

disulfide (591 mg, 1.37 mmol, 56%) as colorless crystals; mp. 119.5–120.5 °C. ^1H NMR (300 MHz, CDCl_3): δ 7.13–7.33 (m, 14H), 7.41 (dd, $J = 1.5$, ~ 7.4 Hz, 2H), 7.50 (dd, $J = 1.5$, ~ 7.8 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 93.1 (d), 93.2 (d), 93.6 (d), 95.8 (d), 95.9 (d), 96.0 (d), 98.2 (s), 101.6 (d), 102.4 (s), 107.0 (s); HRMS (EI): found m/z 434.0297 ($[\text{M}]^+$), calcd. for $\text{C}_{24}\text{H}_{18}\text{S}_4$ 434.0291.

4.11. Synthesis of bis[2-(phenylsulfanyl)benzenethiolato]-palladium (**6**)

To a benzene solution (5 mL) of bis[2-(phenylsulfanyl)phenyl] disulfide (50 mg, 120 μmol) was added tetrakis(triphenylphosphine)palladium (133 mg, 120 μmol) at room temperature. After the mixture was stirred for 12 h at the same temperature, the solvent was removed under reduced pressure. The residual red-violet solid was purified by recrystallization from chloroform/acetonitrile to give mononuclear palladium complex **6** (63.6 mg, 118 μmol , 98%) as red-purple crystals. **6**: m.p. 252.8–253.8 °C (decomp.). ^1H NMR (300 MHz, CDCl_3): δ 6.80 (dd, $^3J = 7.4$, $^3J = \sim 7.1$ Hz, 2H), 6.99 (d, $^3J = 7.4$ Hz, 2H), 7.06 (dd, $^3J = 8.2$, $^3J = \sim 8.0$ Hz, 2H), 7.10–7.23 (m, 6H), 7.23–7.31 (m, 2H), 7.36 (d, $^3J = 7.1$ Hz, 2H), 7.48 (d, $^3J = 7.4$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 123.5 (d), 129.7 (d), 129.9 (d), 130.0 (d), 130.6 (d), 131.0 (d), 132.4 (d), 133.9 (s), 134.3 (s), 152.3 (s); HRMS (FAB):

found m/z 541.9348 ($[\text{M}]^+$), calcd. for $\text{C}_{24}\text{H}_{18}^{108}\text{PdS}_4$ 541.9360. Anal. Calc. for $\text{C}_{24}\text{H}_{18}\text{PdS}_4$: C, 53.27; H, 3.35. Found: C, 53.00; H, 3.55%.

4.12. Theoretical calculations

The geometries of model compounds **6a-syn**, **6a-anti**, **6b-syn** and **6b-anti** were optimized by using the GAUSSIAN-98 program [31] with density functional theory at the B3LYP level. The LANL2DZ basis sets for Pd were used with effective core potential, and the 6-31G(2d) basis sets for S and 6-31G(d) basis sets for C and H atoms were used, respectively. The atoms in molecules (AIM) analysis was performed by using the AIM-2000 package [32].

4.13. X-ray structural determination

The crystallographic data for **1** · 0.5 CH_2Cl_2 · 0.5 C_6H_{14} , **3** · 2 CHCl_3 , **4**, and **5** are summarized in Table 6. Single crystals were grown at room temperature by the slow evaporation of the corresponding saturated solution in dichloromethane/hexane for **1** · 0.5 CH_2Cl_2 · 0.5 C_6H_{14} , and chloroform/acetonitrile for **3** · 2 CHCl_3 , **4**, and **5**, respectively. The intensity data were collected on a Rigaku/MS Mercury CCD diffractometer for **1** · 0.5 CH_2Cl_2 · 0.5 C_6H_{14} , **3** · 2 CHCl_3 , and **5** and a Rigaku Saturn70 CCD system with VariMax Mo Optic for **4** with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71070$ Å for

Table 6
Crystal data and refinement details for **1** · 0.5 CH_2Cl_2 · 0.5 C_6H_{14} , **3** · 2 CHCl_3 , **4**, and **5**

Complex	1 · 0.5 CH_2Cl_2 · 0.5 C_6H_{14}	3 · 2 CHCl_3	4	5
Empirical formula	$\text{C}_{81.5}\text{H}_{142}\text{ClS}_6\text{Si}_{12}$	$\text{C}_{80}\text{H}_{136}\text{Cl}_6\text{PdS}_6\text{Si}_{12}$	$\text{C}_{36}\text{H}_{26}\text{S}_6$	$\text{C}_{72}\text{H}_{52}\text{Pd}_2\text{S}_{12}$
Formula weight	1686.84	1946.43	650.93	1514.66
Temperature (K)	103(2)	103(2)	173(2)	103(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	10.920(2)	16.1441(5)	16.037(6)	10.161(2)
b (Å)	20.424(5)	12.4256(4)	7.395(2)	11.417(2)
c (Å)	23.068(5)	25.6096(10)	26.842(10)	14.967(3)
α (°)	71.290(7)	90	90	110.149(3)
β (°)	83.335(10)	96.3221(18)	99.107(7)	91.409(2)
γ (°)	83.675(11)	90	90	105.895(2)
V (Å ³)	4825.5(18)	5106.0(3)	3143.1(19)	1554.0(5)
Z	2	2	4	1
D_{calc} (Mg m^{-3})	1.161	1.266	1.376	1.618
Absorption coefficient (mm^{-1})	0.357	0.640	0.461	1.027
Crystal size (mm)	0.30 × 0.10 × 0.01	0.20 × 0.03 × 0.03	0.10 × 0.04 × 0.01	0.40 × 0.30 × 0.20
θ Range (°)	2.35–25.00	2.17–25.50	1.84–25.00	2.71–25.00
Number of reflections measured	31210	29394	20363	10083
Number of independent reflections	16506	9021	5519	5332
R_{int}	0.0454	0.1162	0.0821	0.0127
Completeness (%)	97.2	94.9	99.9	97.4
Number of parameters	941	494	379	388
Goodness of fit	1.081	1.061	1.127	1.053
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0647$, $wR_2 = 0.1482$	$R_1 = 0.0803$, $wR_2 = 0.1815$	$R_1 = 0.0748$, $wR_2 = 0.1416$	$R_1 = 0.0205$, $wR_2 = 0.0510$
R indices (all data)	$R_1 = 0.0914$, $wR_2 = 0.1661$	$R_1 = 0.1892$, $wR_2 = 0.2505$	$R_1 = 0.1115$, $wR_2 = 0.1583$	$R_1 = 0.0224$, $wR_2 = 0.0521$

$1 \cdot 0.5\text{CH}_2\text{Cl}_2 \cdot 0.5\text{C}_6\text{H}_{14}$, **4**, and **5** and 0.71069 \AA for $3 \cdot 2\text{CHCl}_3$). The structures were solved by direct method (SHELXS-97) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97) [33]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions.

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Appendix A. Supplementary material

CCDC 285412, 619301, 619302 and 619303 contain the supplementary crystallographic data for $1 \cdot 0.5\text{CH}_2\text{Cl}_2 \cdot 0.5\text{C}_6\text{H}_{14}$, **3** · 2CHCl_3 , **4** and **5**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorgchem.2006.10.056](https://doi.org/10.1016/j.jorgchem.2006.10.056).

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