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Synthesis and Structure of a Distorted Octahedral Palladium(II) Complex Coordinated with a Tetrathioether Ligand Tethered with Bulky Substituents

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A new type of an *o*-phenylene-bridged tetrathioether ligand tethered with extremely bulky substituents, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) groups, at its terminal sulfur atoms, TbtS[(*o*-phenylene)S]$_3$Tbt (**1**), was synthesized by taking advantage of the coupling reaction of thiols with iodobenzenes using Cu_2O in 2,4,6-trimethylpyridine. Complexation of **1** with Na_2PdCl_4 gave the corresponding dichloropalladium(II) complex, [PdCl$_2$(**1**)] (**7**). The X-ray structural analysis of **7** indicated that the central palladium metal is in a distorted octahedral environment, 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. In addition, a phenyl analogue of **1**, PhS[(*o*-phenylene)S]$_3$Ph (**2**), was synthesized by a method similar to that for **1**. Reaction of **2** with Na_2PdCl_4 gave the corresponding dichloropalladium(II) complex, [PdCl$_2$(**2**)] (**8**). X-ray crystallography of **8** showed a type of the structure different from the distorted octahedral structure in **7**, i.e., a square planar arrangement around the central palladium atom with the one terminal sulfur atom of **2**, its neighboring sulfur atom, and the two chlorine atoms. The results of the NMR studies on **8** in a $CDCl_3$ solution were not consistent with the results of the X-ray crystallography and suggested the coordination of the two inner sulfur atoms of **2** to the palladium metal, although a possibility of the existence of the rapid interconversion among isomers could not be excluded.

Introduction

Palladium(II) complexes generally have square planar geometry around the palladium atom, and six-coordinate complexes of palladium(II) are very rare. Cyclic polythioether (crown thioether) ligands such as 1,4,7-trithiacyclononane (9S3),[1] 1,4,7,10,13,16-hexathiacyclooctadecane (18S6),[2] and 1,4,7-trithiacyclodecane (10S3)[3] reportedly complexed with palladium(II) metals 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 remaining one or two sulfur atoms weakly coordinate to the palladium(II) atom [Pd···S: 2.96−3.27 Å] at the axial positions. In addition, the 9S3 ligand has been known to stabilize mononuclear palladium(III) species,[4] which are generally known to be unstable. These unique properties of cyclic polythioether ligands are considered to be caused by their moderate, geometric preference of facial coordination and their ability to adjust the coordination modes and conformations to the geometric preference of the oxidation states of the metals.[5] Acyclic polythioethers can more easily change their coor-

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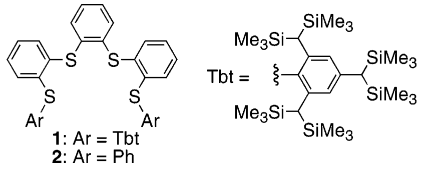
10.1021/ic050944v CCC: $30.25

Chart 1



1: Ar = Tbt
2: Ar = Ph

dination modes and conformations; however, the coordination chemistry of acyclic polythioether ligands has been less investigated probably due to their relatively low coordination ability to metals.[5b,c,6]

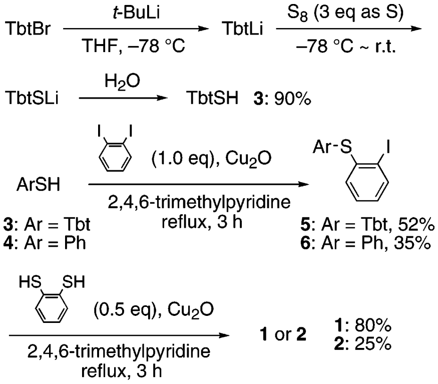
On the other hand, we have succeeded in the syntheses of a variety of highly reactive low-coordinate species containing main group metals by taking advantage of effective steric protection groups, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) groups.[7] In addition, we have recently succeeded in the application of the Tbt and Bbt groups to the stabilization of transition metal complexes, i.e., the synthesis of the first platinum−disulfido and −diselenido complexes by the use of extremely bulky aryldimethylphosphines bearing the Tbt or Bbt group.[8]

In this paper, we report the synthesis of a new bulky tetrathioether ligand **1** (Chart 1) tethered with two Tbt substituents and its application to the synthesis of a palladium(II) complex.[9] It is expected that the introduction of bulky substituents to an acyclic tetrathioether ligand leads to the moderate restriction of the conformation of the ligand and the kinetic stabilization of the metal center. To investigate the effect of the bulky substituents, synthesis of the phenyl analogue of **1** (**2**) and its complexation with a palladium metal are also described.

Results and Discussion

Synthesis of Tetrathioether Ligands 1 and 2. The synthesis of tetrathioether ligand **1** was examined by successive coupling reactions of thiols with iodobenzenes. Tbt-substituted thiol **3** was synthesized by the reaction of TbtLi, prepared from TbtBr and *tert*-butyllithium, with elemental sulfur, followed by the treatment of the resulting TbtSLi with H_2O (Scheme 1).

Scheme 1. Synthesis of Tetrathioether Ligands **1** and **2**



Coupling reaction of **3** with 1,2-diiodobenzene using Cu_2O in refluxing 2,4,6-trimethylpyridine[10] afforded sulfide **5** in 52% yield. Further coupling reaction of **5** with 0.5 equiv of 1,2-benzenedithiol under conditions similar to the above coupling reaction using Cu_2O gave the expected tetrathioether **1** in a good yield.

To study the effects of bulky substituents, we examined the synthesis of a ligand bearing phenyl groups instead of Tbt groups. The phenyl-substituted ligand **2** was synthesized by the method similar to that for **1**, though in a relatively low yield (Scheme 1).

Structure of Tetrathioether Ligands 1 and 2. Tetrathioether ligands **1** and **2** were characterized by the NMR spectra, MS, and elemental analysis, and their molecular structures in the crystalline states were definitively determined by X-ray structural analyses. Figures 1 and 2 show the ORTEP drawings of **1** and **2**, respectively, and the selected bond lengths, angles, and torsion angles are summarized in Table 1. While tetrathioether **2** has a conformation close to C_2 symmetry, in the case of **1** the conformations around the S2 and S3 atoms are very different from each other. All the C−S bond lengths of **1** and **2** [1.76−1.78 Å] are usual as those of common diaryl sulfides [1.762−1.774 Å].[11] It is noteworthy that each of the C1−S1−C28 and C45−S4−C46 planes in **1** is nearly perpendicular to the benzene ring of its connecting Tbt group (C28−S1−C1−C6 = 91.3(5)° and C45−S4−C46−C47 = 80.6(5)°) and is almost parallel to its neighboring *o*-phenylene ring (C1−S1−C28−C33 = 178.0(4)° and C46−S4−C45−C40 = 175.1(5)°). This conformation in **1** can be explained in terms of the steric hindrance caused by the Tbt groups.

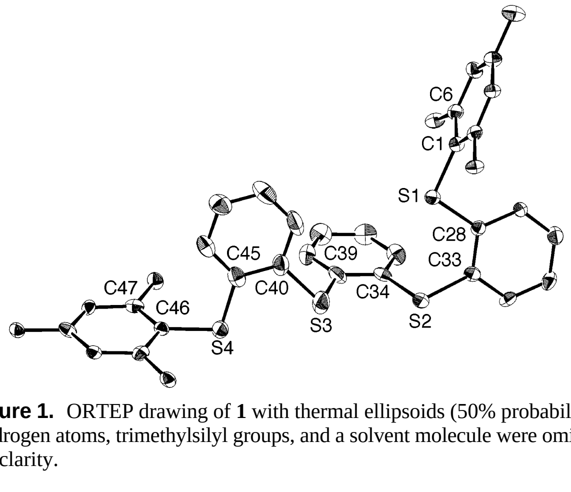


Figure 1. ORTEP drawing of **1** with thermal ellipsoids (50% probability). Hydrogen atoms, trimethylsilyl groups, and a solvent molecule were omitted for clarity.

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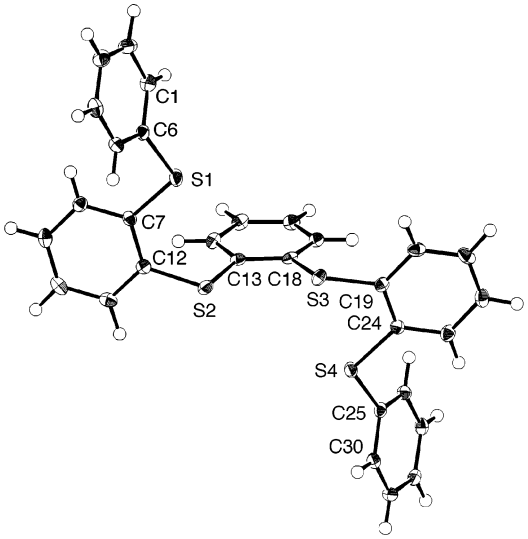
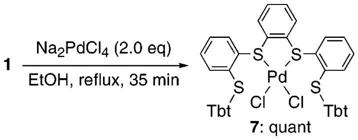


Figure 2. ORTEP drawing of **2** with thermal ellipsoids (50% probability).

The ^{1}H and ^{13}C NMR spectra of **1** and **2** showed that the two terminal TbtS(*o*-phenylene) (for **1**) and PhS(*o*-phenylene) (for **2**) units were equivalent, respectively, suggesting flexible structures of **1** and **2** in solution.

Synthesis and Structure of Palladium(II) Complex 7 of Tetrathioether Ligand 1. When **1** was allowed to react with Na_2PdCl_4 in ethanol at reflux for 5 min, the starting red solution turned yellow with the formation of orange precipitates. Further refluxing for 30 min resulted in the almost quantitative formation of the corresponding dichloropalladium complex **7** as orange crystals, which are slightly soluble in ethanol (eq 1). The structure of **7** was determined by NMR spectrometry, ESI MS, elemental analysis, and single-crystal X-ray diffraction.



(1)

The X-ray structural analysis of **7** showed the C_2 symmetrical distorted octahedral structure, where the inner two sulfur atoms of ligand **1** and the two chlorine atoms form a square planar arrangement around the palladium(II) atom and the two terminal sulfur atoms of **1** weakly coordinate to the palladium center at the axial positions (Figure 3). A few examples for cationic, 6-coordinate complexes of palladium(II) have been synthesized using crown thioether ligands (e.g., 9S3,[1] 18S6,[2] and 10S3[3]), S- and N-donor macrocyclic ligands [e.g., 1,4,10,13-tetrathia-7,16-diazacyclooctadecane ([18]aneN_2S_4)[12] and 1,4-dithia-7-azacyclononane ([9]aneNS_2)[13]], and tris(2,4,6-trimethoxyphenyl)phosphine ligands.[14] By contrast, to our knowledge, there has been no report on the X-ray structural analysis of a neutral, 6-coordinate palladium(II) complex except for 6-coordinate complexes having intermolecular or intramolecular Pd···H interactions.[15]

Table 1. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg)

1		2	
S1−C1	1.769(6)	S1−C6	1.7740(16)
S1−C28	1.765(6)	S1−C7	1.7621(16)
S2−C33	1.766(6)	S2−C12	1.7727(16)
S2−C34	1.776(6)	S2−C13	1.7822(16)
S3−C39	1.772(6)	S3−C18	1.7802(15)
S3−C40	1.771(7)	S3−C19	1.7757(16)
S4−C45	1.771(7)	S4−C24	1.7681(16)
S4−C46	1.767(6)	S4−C25	1.7775(15)
C28−S1−C1	101.8(3)	C7−S1−C6	103.53(7)
C33−S2−C34	103.9(3)	C12−S2−C13	102.48(7)
C40−S3−C39	101.1(3)	C19−S3−C18	102.64(7)
C46−S4−C45	103.2(3)	C24−S4−C25	104.63(7)
C28−S1−C1−C6	91.3(5)	C1−C6−S1−C7	−123.94(13)
C1−S1−C28−C33	178.0(4)	C6−S1−C7−C12	−157.99(13)
C34−S2−C33−C28	66.5(5)	C7−C12−S2−C13	−77.49(14)
C33−S2−C34−C39	−156.1(5)	C12−S2−C13−C18	164.94(12)
C40−S3−C39−C34	139.2(5)	C13−C18−S3−C19	165.82(12)
C39−S3−C40−C45	113.6(5)	C18−S3−C19−C24	−78.62(14)
C46−S4−C45−C40	−175.1(5)	C19−C24−S4−C25	167.38(12)
C45−S4−C46−C47	80.6(5)	C24−S4−C25−C30	132.39(12)

The Pd1−Cl1 (2.3117(9) Å) bond distance is within the range of those in the reported tetracoordinate palladium(II) complexes (2.298−2.354 Å).[16] The Pd1−S1 [2.2615(9) Å] bond distance is close to those of some 4- or 5-coordinate *cis*-dichloropalladium(II) complexes having macrocyclic thioether ligands (2.246−2.269 Å)[17] and is slightly shorter than those of cationic palladium(II)−crown thioether complexes (2.31−2.33 Å)[1,2] except for $[Pd(10S3)_2](PF_6)_2$ [2.2584(15) and 2.2789(14) Å].[3a] The distances between the palladium and the two terminal sulfur atoms [Pd1···S2 = 3.1755(8) Å] are shorter than the sum of the van der Waals radii of palladium and sulfur atoms (3.43 Å).[18] This suggests weak interactions between the palladium (Pd1) and the terminal sulfur atoms (S2 and S2*) in the crystalline state. It is noteworthy that the torsion angles around the terminal sulfur atoms in palladium complex **7** [C9−S2−C10−C11 = 94.5(3)°, C4−C9−S2−C10 = 178.6(3)°] are almost similar to those of the free ligand **1**. This result suggests that the extremely bulky Tbt groups put restrictions on the conformation of ligand **1** in the structure of complex **7** as

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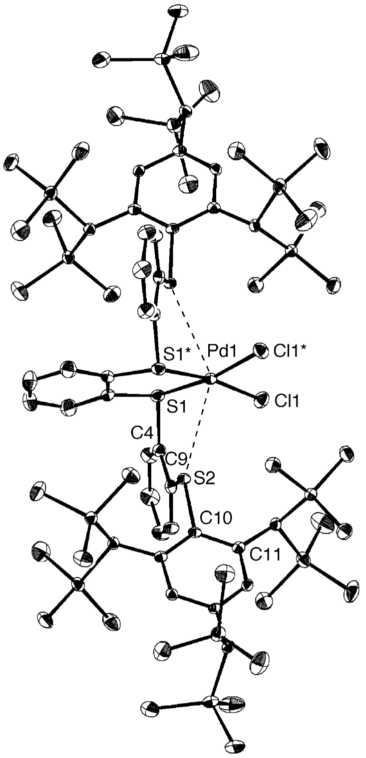

Figure 3. ORTEP drawing of **7** with thermal ellipsoids (50% probability). Hydrogen atoms and solvent molecules were omitted for clarity. Selected bond distances (Å), angles (deg), and torsion angles (deg): Pd1$-$S1 = 2.2615(9), Pd1$-$Cl1 = 2.3117(9), Pd1$\cdots$S2 = 3.1755(8); S1$-$Pd1$-$S1* = 89.45(5), S1$-$Pd1$-$Cl1 = 88.15(3), Cl1$-$Pd1$-$Cl1* = 95.37(5), S1$-$Pd1$-$S2 = 71.19(3), S1*$-$Pd1$-$S2 = 82.08(3), Cl1$-$Pd1$-$S2 = 89.37(3), Cl1*$-$Pd1$-$S2 = 116.55(3); C4$-$C9$-$S2$-$C10 = 178.6(3), C9$-$S2$-$C10$-$C11 = 94.5(3).

well as in that of **1**; that is, the ligand **1** preferably has the conformation in which the C$-$S(terminal)$-$C planes are almost perpendicular to the benzene rings of the Tbt groups and almost parallel to the neighboring *o*-phenylene rings.

As for the cationic 6-coordinate complexes of palladium(II) with crown thioether ligands or S- and N-donor macrocyclic ligands, it has been known that complexes with relatively strong interactions with the sulfur atom at the axial positions have a blue or green color, while complexes with relatively weak or no interactions have a yellow or brown color. For example, $[Pd(9S3)_2][PF_6]_2$ [ax Pd$-$S 2.952(4) Å],[1] $[Pd(10S3)_2][BPh_4]_2$ [ax Pd$-$S 3.11 Å],[3a] $[Pd(10S3)_2][PF_6]_2$ [ax Pd$-$S 3.034(1) Å],[3b] and $[Pd([18]aneN_2S_4)][BPh_4]_2$ [ax Pd$-$S 2.954(4) and 3.000(3) Å][12] have an absorption maximum in the visible region at 615 (blue), 602 (blue-green), 598 (green), and 514 nm (green) respectively, while $[Pd(18S6)](PF_6)_2$ [ax Pd$-$S 3.2730(17) Å] has yellow-brown color.[2] These absorptions around 500$-$600 nm have been assigned to d$-$d transitions by the small values of the extinction coefficient. Complex **7**, the X-ray crystallographic analysis of which suggests the weak interactions between the palladium (Pd1) and the terminal sulfur atoms (S2 and S2*) in the crystalline state, has an orange color with absorption maxima at 398 (ϵ 6.5 $\times$ 10^3), 305 (sh, 7.6 $\times$ 10^3), and 294 (sh, 5.3 $\times$ 10^3) nm in hexane. The diffuse UV/vis reflectance spectrum of **7** in the solid state showed the reflectance decrease in the region similar to the absorption region of **7** in hexane. This region is similar to the absorption region of square planar *cis*-dichloropalladium(II) complexes with dithioether ligands (λ_{max} = 380$-$450 nm).[19] If the trend of the UV/vis spectra for the cationic 6-coordinate complexes of palladium(II) with these macrocyclic ligands can be applied to the neutral dichloropalladium(II) complex **7**, this result may suggest relatively weak or no interaction between the palladium and the terminal sulfur atoms both in the solid state and in solution.

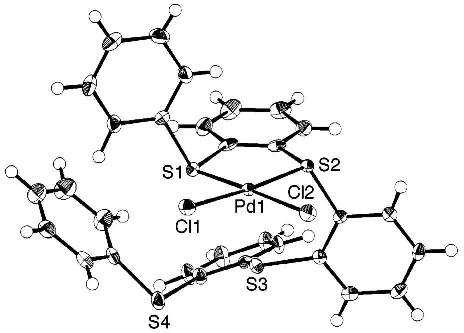

Figure 4. ORTEP drawing of **8** with thermal ellipsoids (50% probability). Selected bond distances (Å) and angles (deg): Pd1$-$S1 = 2.2448(7), Pd1$-$S2 = 2.2642(8), Pd1$-$Cl1 = 2.3115(8), Pd1$-$Cl2 = 2.3077(8), Pd1$\cdots$S3 = 3.4305(8); S1$-$Pd1$-$S2 = 90.22(3), S1$-$Pd1$-$Cl1 = 87.92(3), S2$-$Pd1$-$Cl2 = 88.76(3), Cl1$-$Pd1$-$Cl2 = 93.35(3).

Synthesis and Structure of Palladium(II) Complex 8 of Tetrathioether Ligand 2. To investigate the effects of bulky substituents, we examined the synthesis of a dichloropalladium complex coordinated with tetrathioether ligand **2**. When a mixture of **2** and Na_2PdCl_4 was refluxed in ethanol for 1 h, the corresponding dichloropalladium complex **8** was obtained as orange crystals (eq 2). The X-ray structural analysis of **8** showed that the palladium metal is coordinated by the one terminal and the one inner sulfur atoms of ligand **2** (Figure 4) in contrast to the distorted octahedral coordination structure of Tbt-analogue **7**. Complex **8** has a square planar structure with normal Pd$-$Cl bond lengths. The Pd1$-$S1 and Pd1$-$S2 bond lengths are similar to the Pd1$-$S1 bond lengths of **7**, and the Pd1$-$S3 distance [3.4305(8) Å] is close to the sum of the van der Waals radii of palladium and sulfur atoms (3.43 Å).[18] This result suggests that there is little interaction between Pd1 and S3 atoms in complex **8**.

$$\mathbf{2}\ \xrightarrow[\text{EtOH, reflux, 1 h}]{\text{Na}_2\text{PdCl}_4\text{ (1.0 eq)}}\ [\text{PdCl}_2(\mathbf{2})] \quad \underset{\mathbf{8}\text{: quant}}{} \qquad (2)$$

To clarify the reason for the preference of the **8b**-type structure over the **8a**-type structure in the crystalline state (Chart 2), the energies of these two linkage isomers, **8a**,**b**, were calculated with B3LYP/LANL2DZ(ECP) for the Pd and 6-31G(d) for C, S, Cl, and H (Figure 6).[20] Contrary to

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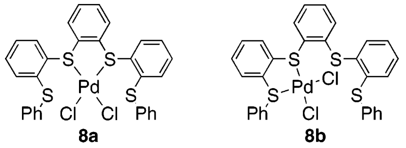
Chart 2



the result of the X-ray structural analysis, the theoretical calculations revealed that **8a** is more stable than **8b** by 4.3 kcal mol^{-1}. Furthermore, the conformation of the optimized structure for **8b** was different from that of the X-ray structure (Figures 4 and 6). Taking these results into consideration, the preference of the **8b**-type structure in the crystalline state may be interpreted in terms of the effects of the intermolecular interactions, which are observed in the X-ray structural analysis (Figure 5).

On the other hand, the calculated structure for **8a** showed the longer distances between the central palladium atom and the terminal sulfur atoms (Pd1···S1 = 3.575, Pd1···S4 = 3.589 Å) compared with those in complex **7** (Figures 3 and 6). This difference may be explained in terms of the effects of the bulky substituents; i.e., the steric hindrance of the Tbt groups in **7** leads to the conformation suitable for the coordination of the two terminal sulfur atoms to the central palladium atom.

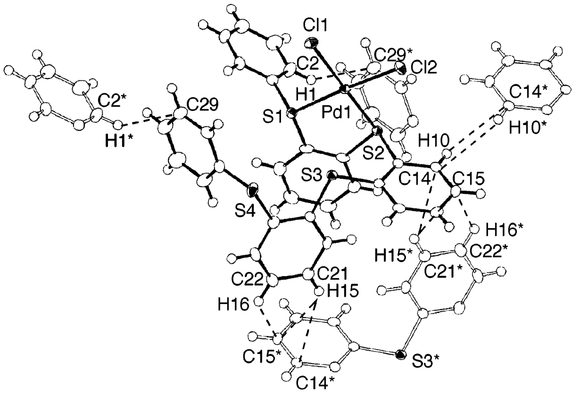
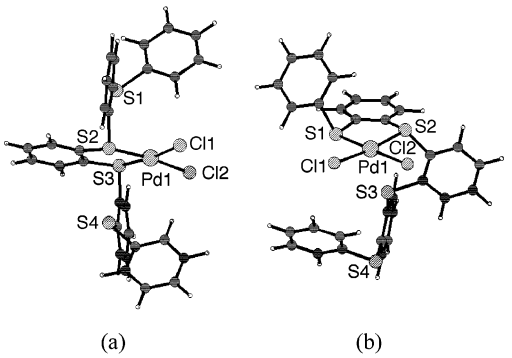


Figure 5. Intermolecular interaction in the crystalline state of **8**. Selected intermolecular C−C distances (Å): C14···C14* 3.461(3), C29···C2* 3.599(5), C14···C21* 3.582(4), C15···C21* 3.477(4), C15···C22* 3.460(4).



(a) (b)

Figure 6. (a) Theoretically optimized structure of **8a**. Selected bond distances (Å) and angles (deg): Pd1−S2 = 2.377, Pd1−S3 = 2.377, Pd1−Cl1 = 2.373, Pd1−Cl2 = 2.373, Pd1···S1 = 3.575, Pd1···S4 = 3.589; S2−Pd1−S3 = 88.323, S2−Pd1−Cl1 = 89.054, Cl1−Pd1−Cl2 = 94.085, S3−Pd1−Cl2 = 89.026, S1−Pd1−S2 = 65.8, S1−Pd1−S3 = 73.0, Cl1−Pd1−S1 = 101.0, Cl2−Pd1−S1 = 118.5, S4−Pd1−S2 = 72.2, S4−Pd1−S3 = 65.6, Cl1−Pd1−S4 = 118.5, Cl2−Pd1−S4 = 101.7. (b) Theoretically optimized structure of **8b**. Selected bond distances (Å) and angles (deg): Pd1−S1 = 2.383, Pd1−S2 = 2.369, Pd1−Cl1 = 2.375, Pd1−Cl2 = 2.366, Pd1···S3 = 3.537, S1−Pd1−S2 = 88.331; S1−Pd1−Cl1 = 88.313, S2−Pd1−Cl2 = 88.757, Cl1−Pd1−Cl2 = 94.742.

Table 2. Redox Potentials (V vs Fc/Fc$^+$) of **7**−**9**

compd	type	E_{pa}	E_{pc}	$E_{1/2}$
7	oxidn[a]	−0.24	−0.33	−0.29
	oxidn[b]	−0.04	−0.13	−0.09
	redn[b]		−1.84	
8	oxidn[a]	+0.97		
	redn[b]		−1.18	
9	oxidn[a]	−0.17	−0.26	−0.22
	oxidn[b]	−0.02	−0.10	−0.06
	redn[b]		−1.28	

[a] 0.1 M (n-Bu)$_4$NPF$_6$ in CH$_2$Cl$_2$. [b] 0.1 M (n-Bu)$_4$NPF$_6$ in THF.

Interestingly, the ^{13}C NMR spectrum of complex **8** in CDCl$_3$ at room temperature indicated that complex **8** has C_2 symmetry. This result suggests that **8** has the **8a**-type structure in solution, which is consistent with not the X-ray structure but the results of theoretical calculations. However, we cannot exclude a possibility of the existence of the rapid equilibrium among isomers such as **8a**,**b** in solution within the time scale of ^{13}C NMR spectrometry at room temperature.[21]

Electrochemistry of Palladium(II) Complexes 7 and 8. As described in the Introduction, the cyclic polythioether ligands have been known to stabilize mononuclear palladium(III) species,[4] which are generally known to be unstable. We investigated the electrochemical properties of complexes **7** and **8**, comparing with those of [PdCl$_2${PhS(o-phenylene)-SPh}] (**9**).[19] The redox potentials of **7**−**9** were summarized in Table 2. The cyclic voltammogram of **7** showed a chemically reversible one-electron oxidation [$E_{1/2}$ = −0.29 V (0.1 M (n-Bu)$_4$NPF$_6$ in CH$_2$Cl$_2$) or $E_{1/2}$ = −0.09 V (0.1 M (n-Bu)$_4$NPF$_6$ in THF) vs Fc/Fc$^+$ (ferrocene/ferrocenium)] and an irreversible reduction [E_{pc} = −1.84 V (0.1 M (n-Bu)$_4$NPF$_6$ in THF) vs Fc/Fc$^+$]. Since the $E_{1/2}$ values in the oxidation of **7** are close to those in the reversible one-electron oxidation of **9** [$E_{1/2}$ = −0.22 V (0.1 M (n-Bu)$_4$NPF$_6$ in CH$_2$Cl$_2$) or $E_{1/2}$ = −0.06 V (0.1 M (n-Bu)$_4$NPF$_6$ in THF) vs Fc/Fc$^+$], both these oxidations of **7** and **9** may be assigned to Pd(II)/Pd(III) couples as well as the case of the Pd complexes with crown thioethers.[1b,3] The differential pulse voltammograms of **7** and **9** suggested that the irreversible reduction waves of **7** and **9** are one- and two-electron processes, respectively, indicating that these reductions may be assigned to different processes. On the other hand, cyclic voltammograms of **8** showed irreversible oxidation and reduction at E_{pa} = +0.97 V (0.1 M (n-Bu)$_4$NPF$_6$ in CH$_2$Cl$_2$) and E_{pc} = −1.18 V (0.1 M (n-Bu)$_4$NPF$_6$ in THF) vs Fc/Fc$^+$, respectively. It is interesting that the redox process of **8** is considered to be completely different from those of **7**.

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(21) The ^{13}C DEPT 90 NMR spectra of **8** at low temperatures (0, −20, −40, and −60 °C) showed the upper or lower field shifts of some signals and the appearance of some new peaks. However, these measurements did not lead to the observation of splitting of the signals, which indicates the existence of the rapid equilibrium among isomers such as **8a**,**b**. These spectroscopic behaviors could not be analyzed in detail, though suggesting the existence of some equilibrium.

Conclusion

A new tetrathioether ligand **1** tethered with two bulky substituents, Tbt groups, was synthesized by taking advantage of the coupling reaction of thiols with iodobenzenes using Cu_2O in 2,4,6-trimethylpyridine. Complexation of **1** with Na_2PdCl_4 gave the corresponding dichloropalladium complex **7**, the X-ray structural analysis of which indicated its distorted octahedral structure with weak intramolecular interactions between the two terminal sulfur atoms and the central palladium metal.

On the other hand, a phenyl-substituted tetrathioether ligand **2** reacted with Na_2PdCl_4 to give the corresponding dichloropalladium complex **8**. X-ray crystallography revealed the structure of complex **8** in the crystalline state, where the dichloropalladium part is coordinated by the one terminal sulfur atom and the neighboring sulfur atom of **2**. By contrast, the ^{13}C NMR spectrum of **8** in $CDCl_3$ at room temperature suggested a type of structure in solution different from that in the crystalline state, i.e., the **8a**-type structure, where the two inner sulfur atoms of **2** coordinate to the central metal. However, a possibility of the existence of rapid equilibriums among isomers such as **8a**,**b** in solution within the time scale of ^{13}C NMR spectrometry could not be excluded.

We wish to propose a possible explanation for the distorted octahedral structure of **7** in the crystalline state as follows. Ligand **1** preferably has a conformation, in which the C−S (terminal)−C planes are almost perpendicular to the benzene rings of the Tbt groups and almost parallel to the neighboring *o*-phenylene rings, because of the steric effects of the bulky Tbt groups. It is considered that ligand **1** with this conformation can effectively stabilize the distorted octahedral structure.

Further studies on the properties and applications of the dichloropalladium complexes **7** and **8** are very interesting. In addition, the ligands **1** and **2** are expected to be useful for the synthesis of unusual complexes.

Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere, unless otherwise noted. THF was purified by distillation from sodium diphenylketyl before use. 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 or toluene as an eluent. Wet column chromatography (WCC) and short column chromatography were performed with Nacalai Tesque silica gel 60. The ^1H 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 ^1H NMR spectroscopy and $CDCl_3$ (77.0 ppm) as those for ^{13}C NMR spectroscopy. High-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer. The electronic spectra were recorded on a JASCO V-570 UV/vis spectrometer, and diffuse UV/vis reflectance spectra were recorded on a JASCO V-570 UV/vis spectrometer equipped with an integrating sphere accessory. All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. The electrochemical experiments were carried out with an ALS 602A potentiostat/galvanostat using a glassy carbon disk working electrode, a Pt wire counter electrode, and Ag/0.01 M $AgNO_3$ in 0.1 M n-Bu_4NPF_6/CH_3CN reference electrode. The measurements were carried out in CH_2Cl_2 and THF solution containing 0.1 M n-Bu_4NPF_6 as a supporting electrolyte with scan rates of 50−300 mV s^{-1} at ambient temperature.

Synthesis of 2,4,6-Tris[bis(trimethylsilyl)methyl]benzenethiol (3). To a THF solution (120 mL) of TbtBr[22] (7.54 g, 11.9 mmol) was gradually added *t*-BuLi (2.2 M pentane solution, 11.9 mL, 26.2 mmol) at −78 °C. After the yellow solution was stirred for 1 h at this temperature, S_8 (1.14 g, 4.46 mmol) was added. 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 poured into ice water. The mixture was extracted with hexane (200 mL), and the organic layer was dried with $MgSO_4$. After removal of the solvents under reduced pressure, reprecipitation from CH_2Cl_2/CH_3CN gave thiol **3** (6.27 g, 10.7 mmol, 90%) as colorless crystals. **3**: colorless solid; mp 167.8−169.8 °C; ^1H NMR (300 MHz, $CDCl_3$) δ −0.01 (s, 36H), 0.00 (s, 18H), 1.27 (s, 1H), 2.39 (s, 1H), 2.70 (s, 1H), 2.82 (s, 1H), 6.32 (s, 1H), 6.44 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.4 (q), 0.6 (q), 28.0 (d × 2), 30.0 (d), 120.8 (s), 121.8 (d), 126.6 (d), 141.6 (s), 146.8 (s × 2); HRMS (EI; *m/z*) found 584.3018 ($[M]^+$), calcd for $C_{27}H_{60}SSi_6$ 584.3031. Anal. Calcd for $C_{27}H_{60}SSi_6$: C, 55.40; H, 10.33. Found: C, 55.26; H, 10.27.

Synthesis of 2-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenylthio}-iodobenzene (5). To a mixture of thiol **3** (6.0 g, 10.3 mmol) and Cu_2O (1.54 g, 10.8 mmol) in 2,4,6-trimethylpyridine (35 mL) was added 1,2-diiodobenzene (1.34 mL, 10.3 mmol), and the mixture was refluxed for 3 h. The reaction mixture was passed through a short column (SiO_2, hexane) to remove inorganic salts. All fractions were collected and washed with a 0.2 M aqueous solution of HCl three times (100 mL × 3). The organic layer was dried with $MgSO_4$ and evaporated. The addition of EtOH to the resulting orange oil led to the formation of colorless precipitates, and the filtration of the mixture gave sulfide **5** (4.18 g, 5.31 mmol, 52%) as colorless crystals. **5**: colorless solid; mp 188.1−190.1 °C; ^1H NMR (300 MHz, $CDCl_3$) δ −0.03 (s, 36H), 0.06 (s, 18H), 1.37 (s, 1H), 2.60 (s, 2H), 6.41 (s, 1H), 6.54 (s, 1H), 6.65 (dd, $J = 1.5$, 7.8 Hz, 1H), 6.71−6.78 (m, 1H), 7.01−7.08 (m, 1H), 7.74 (dd, $J = 1.3$, 7.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.7 (q), 0.8 (q), 26.7 (d × 2), 30.7 (d), 96.4 (s), 122.5 (d), 126.1 (s), 126.2 (d), 127.3 (d), 128.1 (d), 128.4 (d), 139.1 (d), 143.7 (s), 144.8 (s), 150.1 (s × 2); HRMS (EI; *m/z*) found 786.2306 ($[M]^+$), calcd for $C_{33}H_{63}ISSi_6$ 786.2311. Anal. Calcd for $C_{33}H_{63}ISSi_6$: C, 50.34; H, 8.07. Found: C, 50.47; H, 8.10.

Synthesis of 1,2-Bis(2-{2,4,6-tris[bis(trimethylsilyl)methyl]-phenylthio}phenylthio)benzene (1). A red-purple suspension of sulfide **5** (1.0 g, 1.27 mmol), Cu_2O (186 g, 1.30 mmol), and 1,2-benzenedithiol (90 mg, 0.635 mmol) in 2,4,6-trimethylpyridine (13 mL) was refluxed for 3 h. The reaction mixture was subjected to short column chromatography (SiO_2, benzene) to remove inorganic salts. Hexane (100 mL) was added to the eluate, and then the mixture was washed with a 0.2 M aqueous solution of HCl three times (100 mL × 3). After drying with $MgSO_4$, the solvents were removed under reduced pressure to give an orange oil. The addition of EtOH to the residue resulted in the formation of colorless precipitates, and the filtration of the mixture gave pure tetrathioether **1** (743 mg, 0.51 mmol, 80%) as colorless crystals. **1**: colorless blocks; mp: 211.0−212.0 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 72H), 0.08 (s, 36H), 1.38 (s, 2H), 2.66 (s, 4H), 6.43 (s, 2H), 6.58 (s, 2H), 6.61−6.66 (m, 2H), 6.93−7.04 (m, 4H), 7.05−7.16

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(m, 4H), 7.20−7.25 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.8 (q), 0.9(q), 26.3 (d × 2), 30.6 (d), 122.7 (d), 123.9 (s), 125.2 (d), 127.3 (d), 127.5 (d), 127.6 (d), 127.7 (d), 130.3 (s), 130.6 (d), 132.8 (d), 137.0 (s), 142.1 (s), 144.4 (s), 150.4 (s × 2); HRMS (FAB; *m/z*) found *m/z* 1458.6298 ([M]$^+$), calcd for $C_{72}H_{130}S_4Si_{12}$ 1458.6287. Anal. Calcd for $C_{72}H_{130}S_4Si_{12}\cdot CHCl_3$: C, 55.48; H, 8.35. Found: C, 55.27; H, 8.34.

Synthesis of 2-Iodophenyl Phenyl Sulfide (6). A red-purple suspension of benzenethiol (**4**) (3.51 mL, 34.2 mmol), Cu_2O (4.80 g, 33.6 mmol), and 1,2-diiodobenzene (11.1 g, 33.6 mmol) in 2,4,6-trimethylpyridine (170 mL) was refluxed for 3 h. After addition of 150 mL of hexane, the mixture was washed with 0.2 M aqueous solution of HCl four times (100 mL × 4). The organic layer was dried with $MgSO_4$ and evaporated. The residue was separated with WCC (SiO_2, hexane) to give sulfide **6** (3.7 g, 11.8 mmol, 35%) as colorless crystals. **6**:[23] colorless solid; mp 52−53 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (dd, $J = 7.8$, ~8 Hz, 1H), 6.95 (d, $J = 7.8$ Hz, 1H), 7.19 (dd, $J = 7.8$, ~8 Hz, 1H), 7.34−7.47 (m, 5H), 7.83 (d, $J = 7.8$ Hz, 1H).

Synthesis of 1,2-Bis[2-(phenylthio)phenylthio]benzene (2). A red-purple suspension of sulfide **6** (3.69 g, 11.8 mmol), Cu_2O (1.69 g, 11.8 mmol), and 1,2-benzenedithiol (841 mg, 5.91 mmol) in 2,4,6-trimethylpyridine (20 mL) was refluxed for 3 h. The reaction mixture was subjected to short column chromatography (SiO_2, benzene) to remove inorganic salts. After addition of hexane (150 mL), the mixture was washed with a 0.2 M aqueous solution of HCl four times (100 mL × 4). The organic layer was dried with $MgSO_4$ and evaporated under reduced pressure. The residue was subjected to WCC (SiO_2, hexane) and reprecipitated from CH_2Cl_2/CH_3CN to give polythioether **2** (768 mg, 1.50 mmol, 25%) as colorless crystals. **2**: colorless solid; mp 107.7−108.7 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.12−7.22 (m, 6H), 7.26−7.47 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 127.3 (d), 127.5 (d), 127.8 (d), 128.0 (d), 129.2 (d), 131.0 (d), 131.4 (d), 132.0 (d), 132.2 (d), 134.2 (s), 135.1 (s), 136.6 (s), 138.8 (s); HRMS (EI; *m/z*) found 510.0594 ([M]$^+$), calcd for $C_{30}H_{22}S_4$ 510.0604. Anal. Calcd for $C_{30}H_{22}S_4$: C, 70.55; H, 4.34. Found: C, 70.63; H, 4.29.

Synthesis of [PdCl$_2$(1)] (7). Tetrathioether **1** (100 mg, 0.0684 mmol) was dissolved into EtOH (40 mL) by heating at reflux. To the solution was added Na_2PdCl_4 (40.3 mg, 0.137 mmol) using 3 mL of EtOH. The red solution was refluxed for 5 min, and the resulting orange suspension was further heated at reflux for 30 min. After evaporation of the solvents, $CHCl_3$ (20 mL) was added to the residue and the resulting orange suspension was filtered through Celite. The orange filtrate was evaporated to give pure palladium dichloride complex **7** (114.2 mg, quantitative). **7**: orange blocks; mp 254.2−259.2 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$, 50 °C) δ −0.10 (s, 36H), 0.09 (s, 72H), 1.41 (s, 2H), 2.06 (s, 2H), 2.78 (s, 2H), 6.52 (s, 4H), 6.55 (dd, $^3J = 7.8$, $^4J = 1.5$ Hz, 2H), 7.13 (ddd, $^3J = 7.6$, ~8 Hz, $^4J = 1.5$ Hz, 2H), 7.20−7.26 (ddd, $^3J = 7.8$, ~8 Hz, $^4J = 0.8$ Hz, 2H), 7.39−7.43 (m, 4H), 7.83 (dd, $^3J = 7.6$ Hz, $^4J = 0.8$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 50 °C) δ 0.5 (q), 0.8 (q), 1.4 (q), 26.5 (d), 27.2 (d), 30.9 (d), 120.4 (s), 123.2 (d), 124.3 (d), 127.8 (d), 128.1 (s), 128.3 (d), 130.6 (d), 131.3 (d), 132.1 (d), 135.9 (s), 136.3 (d), 142.8 (s), 145.8 (s), 149.9 (s), 151.8 (s); UV−vis ($CHCl_3$) λ_{max} 398 (ϵ 6.5 × 10^3), 305 (sh, 7.6 × 10^3), 294 (sh, 5.3 × 10^3); LRMS (ESI; *m/z*) found 1600 ([M − Cl]$^+$), calcd for $C_{72}H_{130}{}^{35}Cl^{106}PdS_4Si_{12}$ ([M − Cl]$^+$) 1600. Anal. Calcd for $C_{72}H_{130}ClPdS_4Si_{12}\cdot CHCl_3$: C, 49.88; H, 7.51. Found: C, 49.73; H, 7.42.

Synthesis of [PdCl$_2$(2)] (8). Tetrathioether **2** (25.0 mg, 0.0489 mmol) was dissolved into EtOH (10 mL) by heating at reflux. To the solution was added Na_2PdCl_4 (14.4 mg, 0.0489 mmol) using EtOH (3 mL). Heating of the orange solution at 60 °C for 5 min resulted in the formation of orange precipitates, and the resulting orange suspension was further refluxed for 30 min. After evaporation of the solvents, CH_2Cl_2 (100 mL) was added to the residue and the resulting orange suspension was filtered through Celite. The orange filtrate was evaporated to give pure palladium dichloride complex **8** (34.1 mg, quant) as orange crystals. **8**: orange plates; mp 295.2−305.2 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97−7.67 (m, 22H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 127.48 (d), 127.51 (d), 127.9 (d), 128.0 (d), 129.3 (d), 131.4 (d), 131.8 (d), 132.1 (d), 132.4 (d), 134.7 (s), 135.8 (s), 137.1 (s), 139.1 (s); UV−vis ($CHCl_3$) λ_{max} 417 (ϵ 3.6 × 10^3), 308 (sh, 1.4 × 10^3), 289 (sh, 9.8 × 10^2); HRMS (FAB; *m/z*) found 650.9342 ([M − Cl]$^+$), calcd for $C_{30}H_{22}{}^{35}Cl^{106}PdS_4$ ([M − Cl]$^+$) 650.9328.

X-ray Structural Analysis of 1·CHCl$_3$, 2, 7·2(CH$_2$Cl$_2$), and 8. Single crystals of **1**·$CHCl_3$, **2**, **7**·2(CH_2Cl_2), and **8** suitable for X-ray structural analysis were obtained by slow recrystallization from $CHCl_3$/CH_3CN, benzene, CH_2Cl_2/CH_3CN, and 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 (λ = 0.710 69 Å for **1**·$CHCl_3$ and λ = 0.710 70 Å for **2**, **7**·2(CH_2Cl_2), and **8**). The structures were solved by direct methods (SIR-97)[24] (for **1**·$CHCl_3$, **2**, and **8**) and Patterson methods (DIRDIF)[25] (for **7**·2CH_2Cl_2) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[26] All the non-hydrogen atoms were refined anisotropically. All hydrogens for **1**·$CHCl_3$ and **7**·2(CH_2Cl_2) were placed using AFIX instructions, and those for **2** and **8** were refined isotropically. The structural data are shown in Table 3. In the analysis of **7**·2CH_2Cl_2, there are the highest peak (1.559 e Å^{-3}) and the deepest hole (−1.634 e Å^{-3}) near the CH_2Cl_2 solvent molecule due to disorders that could not be completely solved.

Theoretical Calculations. All theoretical calculations were carried out using the Gaussian 98 program[27] with density functional theory at the B3LYP level.[20] The LANL2DZ basis sets for Pd were used with effective core potential, and the 6-31G(d) basis sets were used for C, H, S, and Cl 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

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Table 3. Crystal Data and Refinement Details for **1**·$CHCl_3$, **2**, **7**·$2CH_2Cl_2$, and **8**

param	**1**·$CHCl_3$	**2**	**7**·$2(CH_2Cl_2)$	**8**
empirical formula	$C_{72}H_{130}S_4Si_{12}\cdot CHCl_3$	$C_{30}H_{22}S_4$	$C_{72}H_{130}Cl_2PdS_4Si_{12}\cdot 2CH_2Cl_2$	$C_{30}H_{22}Cl_2PdS_4$
fw	1580.45	510.72	1808.23	688.02
temp (K)	103(2)	103(2)	103(2)	103(2)
cryst system	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a (Å)	14.0803(6)	7.5404(10)	41.273(3)	9.4221(18)
b (Å)	16.5775(7)	10.4513(16)	12.8906(6)	10.779(2)
c (Å)	19.9887(9)	16.759(3)	19.3198(11)	14.826(3)
α (deg)	90	88.513(6)	90	80.988(7)
β (deg)	90.613(3)	78.037(5)	105.752(2)	76.200(7)
γ (deg)	90	71.784(4)	90	73.758(5)
V (Å^3)	4665.4(3)	1226.2(3)	9892.9(10)	1397.5(5)
Z	2	2	4	2
D_{calc} (Mg m^{-3})	1.125	1.383	1.214	1.635
abs coeff (mm^{-1})	0.377	0.406	0.615	1.174
cryst size (mm)	0.40 × 0.25 × 0.03	0.40 × 0.20 × 0.10	0.35 × 0.20 × 0.10	0.20 × 0.10 × 0.05
θ range (deg)	1.78−25.50	2.36−26.00	1.91−25.00	2.63−25.00
no. of reflcns measd	27 097	8636	39 657	9167
no. of indep reflcns	14 849	4661	8658	4828
R_{int}	0.0834	0.0126	0.0219	0.0191
completeness (%)	98.90	96.70	99.20	97.80
data/restraints/params	14 849/1/865	4661/0/395	8658/0/456	4828/0/422
goodness−of−fit on F^2	1.005	1.051	1.079	1.092
final R indices [$I > 2\sigma(I)$]^a	$R_1 = 0.0636$ $wR_2 = 0.1540$	$R_1 = 0.0306$ $wR_2 = 0.0738$	$R_1 = 0.0549$ $wR_2 = 0.1393$	$R_1 = 0.0290$ $wR_2 = 0.0571$
R indices (all data)^a	$R_1 = 0.0930$ $wR_2 = 0.1757$	$R_1 = 0.0332$ $wR_2 = 0.0754$	$R_1 = 0.0576$ $wR_2 = 0.1414$	$R_1 = 0.0349$ $wR_2 = 0.0594$
absolute struct param	−0.10(9)			
largest diff peak and hole (e Å^{-3})	0.576 and −0.661	0.537 and −0.269	1.559 and −1.634	0.600 and −0.298

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

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Supporting Information Available: Crystallographic information files (CIF) for the compounds **1**·$CHCl_3$, **2**, **7**·$2(CH_2Cl_2)$, and **8**, atomic coordinates for the calculated molecules **8a**,**b**, VT-^{13}C DEPT 90 NMR spectra of **8** (at 50, 25, 0, −20, −40, and −60 °C), and cyclic voltammograms of **7**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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