Unusual carbon–sulfur bond cleavage in the reaction of a new type of bulky hexathioether with a zerovalent palladium complex†

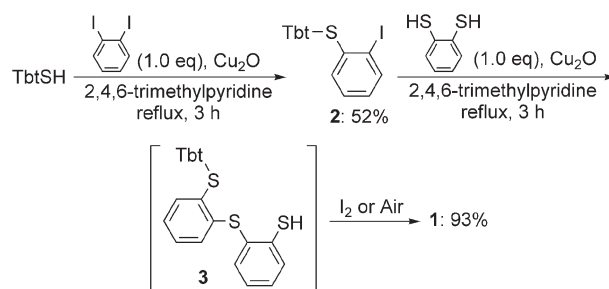**Daisuke Shimizu, Nobuhiro Takeda and Norihiro Tokitoh***

The reaction of a bulky hexathioether, TbtS(*o*-Phen)-S(*o*-Phen)SS(*o*-Phen)S(*o*-Phen)STbt (*o*-Phen = *o*-phenylene, Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) (**1**), with 3 molar amounts of Pd(PPh$_3$)$_4$ afforded trinuclear palladium complex **4** bridged by two benzenedithiolato ligands *via* a three-step palladium insertion reaction into one sulfur–sulfur and two carbon–sulfur bonds of **1**.

The transition-metal-mediated activation of a C–S bond has been paid great attention from the standpoints of synthetic chemistry, petrochemical hydrodesulfurization, and bioinorganic chemistry.[1] As far as C(sp^2)–S activation is concerned, a number of examples of thiophene derivatives have been studied and well established.[2] In contrast, there are relatively few reports on aryl C(sp^2)–S bond activation.[3] On the other hand, as an extension of our study on the sterically crowded organoelement compounds, we have recently synthesized a new bulky hexathioether ligand possessing a disulfide moiety, TbtS(*o*-Phen)S(*o*-Phen)SS(*o*-Phen)S(*o*-Phen)-STbt (*o*-Phen = *o*-phenylene, Tbt = 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl) (**1**).[4]
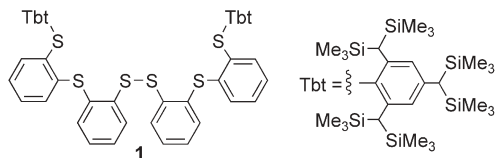
This hexathioether ligand **1** has two different reactive sites toward transition metals, namely, the thioether moieties and the disulfide moiety. While this ligand is considered to act simply as a Lewis base at its thioether sites, it may undergo cleavage of the S–S bond and the formation of metal–sulfur bonds when reacted *via* the disulfide site. Therefore, it will be a promising ligand for application to the synthesis of novel transition metal complexes. In this paper, we present the synthesis of **1** and its reactions with low-valent palladium(0) metal complexes.

Hexathioether **1** was synthesized by the reactions shown in Scheme 1. The coupling reaction of TbtSH with 1,2-diiodobenzene using Cu$_2$O in refluxing 2,4,6-trimethylpyridine afforded the corresponding Tbt-substituted sulfide **2** in 52% yield. Further coupling reaction of sulfide **2** with 1,2,-benzenedithiol under conditions similar to the above coupling reaction using Cu$_2$O gave

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Scheme 1

the thiol intermediate **3**. Oxidative coupling reaction of **3** using iodine was performed to give the expected hexathioether **1** as colorless crystals in 93% yield. The thiol intermediate **3** was similarly oxidized with air instead of iodine to give **1** in a comparable yield. Hexathioether **1** was characterized by the NMR spectra, MS, and elemental analysis, and its molecular structure in the crystalline state was determined by X-ray structural analysis.‡ The ORTEP drawing of **1** is shown in Fig. 1. Hexathioether **1** is made up of the interlinked sulfide parts and the central disulfide part. All the C–S bond lengths of the diarylsulfide moieties of **1** [1.782(4) Å for C(1)–S(1), 1.772(4) Å for C(28)–S(1), 1.787(4) Å for C(33)–S(2), 1.781(4) Å for C(34)–S(2), 1.779(4) Å for C(45)–S(5), 1.773(4) Å for C(46)–S(5), 1.774(4) Å for C(51)–S(6), 1.784(4) Å for C(52)–S(6)] are within the range of C–S distances reported for diarylsulfides.[5] 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
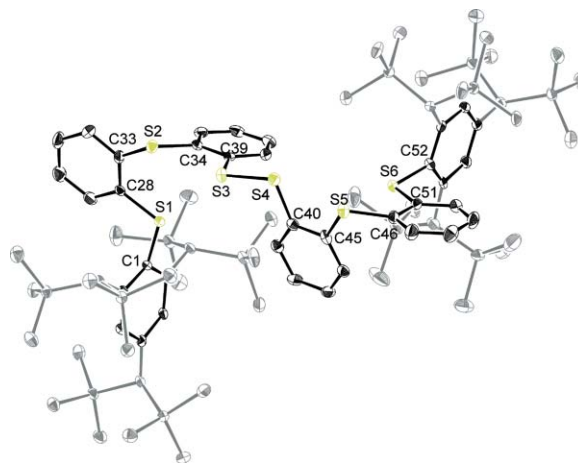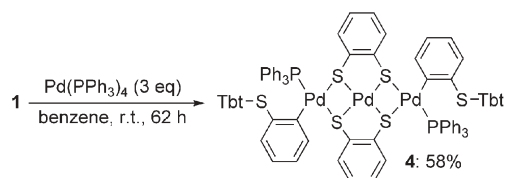

Fig. 1 ORTEP drawing of **1** (50% probability). The hydrogen atoms and solvent molecules are omitted for clarity.

Scheme 2

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].[6]

With the new hexathioether ligand **1** (bearing extremely bulky terminal substituents) in hand, we examined the complexation of **1** with [Pd(PPh$_3$)$_4$] (Scheme 2). To a benzene solution of **1** was added 3 molar amounts of [Pd(PPh$_3$)$_4$], and the resulting yellow solution was stirred at room temperature for 62 h. The crude product was purified by silica gel column chromatography to afford trinuclear Pd complex **4** as yellow crystals in 58% yield.

The formation of tripalladium complex **4** was 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 transition metal insertion reaction into the S–S bond is one of the typical reactions of disulfides,[7] the S–S bond cleavage of hexathioether **1** is not so surprising. However, as mentioned above, the transition-metal-mediated aryl C(sp^2)–S bond cleavage is very scarce and unprecedented by a palladium(0) metal complex, albeit a number of sulfur-coordinated palladium complexes have been synthesized so far.[8] This is, to the best of our knowledge, the first example of an oxidative addition of a palladium(0) metal complex toward an aryl C(sp^2)–S bond.

Single crystals of **4** were obtained by recrystallization from chloroform and benzene solution. The molecular structure of **4** was determined by X-ray crystallographic analysis,‡ and the ORTEP drawing of **4** is shown in Fig. 2. The three palladium atoms are linked by two bridging o-benzenedithiolato ligands to form the Pd$_3$S$_4$ core. Consequently, the palladium complex **4** is classified as a new type of tetrakis(μ-thiolato)tripalladium complex. The central palladium atom is coordinated by four sulfur atoms of the two o-benzenedithiolato ligands with a slightly distorted square-planar geometry. The two bite angles for S(1)–Pd(2)–S(2) and S(1)–Pd(2)–S(2)* are 89.95° and 89.62°, respectively. The Pd–S bond lengths [2.2873(10) Å for Pd(2)–S(1) and 2.2798(10) Å for Pd(2)–S(2)] are slightly shorter than the values of the previously reported tetrakis(μ-thiolato)tripalladium complexes (2.318– 2.387 Å).[9] On the other hand, the two lateral palladium atoms of the Pd$_3$S$_4$ core are coordinated by two sulfur atoms, one phosphorus atom, and one carbon atom in a more distorted square-planar geometry than that of the central Pd atom. This distortion is considered to be caused by the steric repulsion between the bulky Tbt and PPh$_3$ groups. Interestingly, as shown in Fig. 3, the nonbonded distances for Pd(1)···S(3) and Pd(1)*···S(3)* [3.090 Å] are shorter than the sum of the van der Waals radii of palladium and sulfur atoms (3.43 Å).[10] In addition, the nonbonded distances for Pd(1)···C(45) and Pd(1)*···C(45)* [3.339 Å] are approximately the same as the sum of the van der Waals radii of palladium and carbon atoms (3.33 Å), suggesting the existence of weak interactions in Pd(1)···H(72) and Pd(1)*···H(72)*.[11] So the two palladium atoms (Pd(1) and
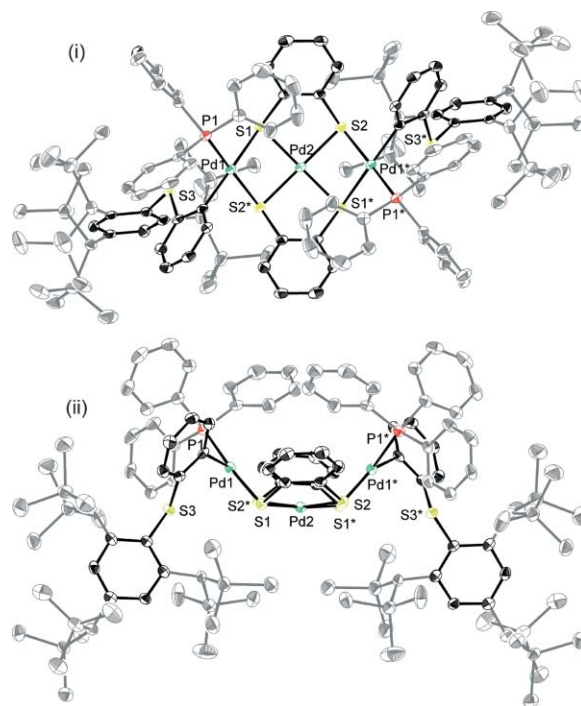

Fig. 2 ORTEP drawings of **4** (50% probability): (i) top view and (ii) view from the side of a central PdS$_4$ plane. The hydrogen atoms and solvent molecules are omitted for clarity.

Pd(1)*) in the Pd$_3$S$_4$ core could be treated as pseudo-distorted octahedral structures in the crystalline state.

The Pd(1)···Pd(2) distance [3.194 Å] is longer than the sum of the metallic radii (2.76 Å for Pd),[12] indicating no direct metal– metal interaction. It is noteworthy that the Pd(1)–Pd(2)–Pd(1)* angle [122.6°] differs substantially from those in most of the known tetrakis(μ-thiolato)tripalladium complexes (173.2–180°). They have been known to have linear tripalladium structures, in which the palladium atoms are bridged by four sulfur atoms at nonbonding Pd–Pd distances. The palladium complex **4** is the second example of the tetrakis(μ-thiolato)tripalladium complexes having a bent tripalladium structure. [Pd$_3$(μ-SCy)$_4$Cl$_2$(PMe$_3$)$_2$][13] is the only other example of a structurally characterized bent tripalladium complex (132.2°). The dihedral angles between the coordination plane of Pd(2) and those of Pd(1) and Pd(1)* [about 136°] are nearly equal to those of [Pd$_3$(μ-SCy)$_4$Cl$_2$(PMe$_3$)$_2$] (130 and 131°). This bent

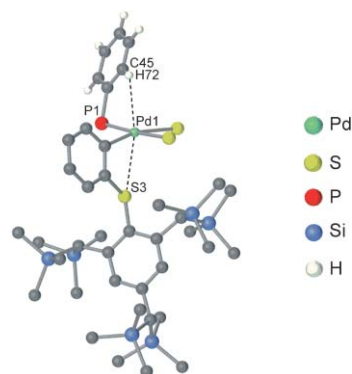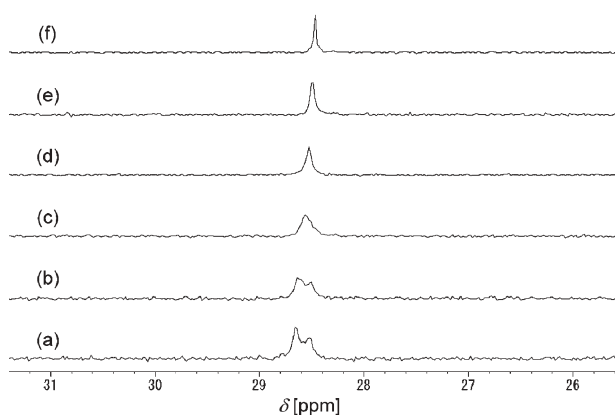**Fig. 3** The partial structure of **4**.

Fig. 4 Variable temperature-^{31}P{^{1}H}NMR spectra of **4** in benzene-d_6: (a) 25 °C, (b) 30 °C, (c) 40 °C, (d) 50 °C, (e) 60 °C, (f) 70 °C.

structure of **4** may result from steric interactions of bulky substituents, such as Tbt and PPh$_3$ groups, as well as in the case of [Pd$_3$(μ-SCy)$_4$Cl$_2$(PMe$_3$)$_2$].

The ^{1}H, ^{13}C, and ^{31}P NMR spectra of complex **4** measured at ambient temperature were not consistent with the structure determined by X-ray crystallographic analysis. For example, the ^{1}H NMR spectrum showed four nonequivalent methine protons assignable to the *ortho* benzyl protons of the two Tbt groups and considerably broad signals for PPh$_3$ groups. The ^{31}P{^{1}H} NMR spectrum of **4** in benzene-d_6 exhibited two signals ($\delta = 28.5$ and 28.7) for the PPh$_3$ groups at 25 °C (Fig. 4). The ^{31}P{^{1}H} NMR spectrum at 70 °C exhibited one sharp signal ($\delta = 28.5$) and the ^{1}H and ^{13}C NMR spectra of the same temperature could be reasonably attributed to the structure observed in the crystalline state. In addition, after heating the samples, there was no change in the NMR spectra at 25 °C. These results may stem from the existence of some isomers at 25 °C due to its overcrowded structure bearing bulky Tbt and PPh$_3$ groups, although we have no definitive interpretation for the behavior of the NMR spectra.

In summary, we have synthesized a new, bulky hexathioether **1** containing a disulfide moiety and found unusual C–S bond cleavage by the reaction of **1** with 3 molar amounts of Pd(PPh$_3$)$_4$ to give an interesting trinuclear palladium complex **4** with a novel structure. The studies on the formation mechanism and the intrinsic properties of **4** are currently in progress.

Notes and references

‡ *Crystal data* for **1**: C$_{81.50}$H$_{142}$ClS$_6$Si$_{12}$, $M = 1686.84$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.920(2)$, $b = 20.424(5)$, $c = 23.068(5)$ Å, $\alpha = 71.290(7)$, $\beta = 83.335(10)$, $\gamma = 83.675(11)°$, $V = 4825.5(18)$ Å^3, $Z = 2$, $D_{calc} = 1.161$ g cm^{-3}, $R_1(I > 2\sigma(I)) = 0.0647$, wR_2(all data) $= 0.1661$, $T = 103(2)$ K, GOF = 1.081; **4**: C$_{134}$H$_{184}$Cl$_{2.40}$P$_2$Pd$_3$S$_6$Si$_{12}$, $M = 2790.47$, monoclinic, space group $C2/c$ (no. 15), $a = 31.9316(5)$, $b = 24.7082(6)$, $c = 24.0157(5)$ Å, $\beta = 130.2043(8)°$,

$V = 14471.3(5)$ Å^3, $Z = 4$, $D_{calc} = 1.281$ g cm^{-3}, $R_1(I > 2\sigma(I)) = 0.0438$, wR_2(all data) $= 0.0936$, $T = 103(2)$ K, GOF = 1.058. The structures were solved by a direct method (SIR-97)[14] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[15] CCDC 285411 and 285412. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513339d

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