

Electronic Supplementary Information for:

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*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan.

E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp

Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere, unless otherwise noted. ^1H NMR (300 MHz), ^{13}C NMR (75 MHz), and ^{31}P NMR (121 ppm) spectra were measured in CDCl_3 with a JEOL AL-300 spectrometer. The ^1H NMR chemical shifts were reported in ppm downfield from tetramethylsilane (δ scale) and referenced to the internal residual CHCl_3 (7.25 ppm). The ^{13}C NMR chemical shifts were reported in ppm downfield from tetramethylsilane (δ scale) and referenced to the carbon-13 signals of CDCl_3 (77.0 ppm). Multiplicity of signals in ^{13}C NMR spectra was determined by DEPT techniques. The ^{31}P NMR chemical shifts were referenced to the external standards 85% H_3PO_4 in water (0 ppm). Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-908 or LC-918 instrument (Japan Analytical Industry Co., Ltd.) equipped with JAI gel 1H+2H columns using chloroform or toluene as an eluent. Column chromatography was performed with Nacalai Tesque Silica Gel 60. High-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer. All melting points were determined on Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University.

Synthesis of hexathioether (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 $\text{TbtSC}_6\text{H}_4\text{I}^1$ (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 intermediate **3**, 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 (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) followed by the reprecipitation from CHCl_3 and CH_3CN solution to give hexathioether **1** (1.50 g, 0.93 mmol, 93%) as colorless crystals. **1**: Mp: 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 × 2); HRMS (FAB): found m/z 1598.5974 ($[M]^+$), calcd for $C_{78}H_{134}S_6Si_{12}$ 1598.6041; Anal. Calcd for $C_{78}H_{134}S_6Si_{12}$: C, 58.50; H, 8.43. Found: C, 58.44; H, 8.52.

In the case of the oxidization with I₂ instead of air-oxidization.

After the generation of intermediate **3** by the above-mentioned method, to the reaction mixture was added a small excess of iodine, and the mixture was subsequently stirred for 3 h at room temperature under argon atmosphere. The reaction mixture was passed through a short column (SiO₂, benzene) to remove inorganic salts. After the addition of benzene, the mixture was washed with a 0.6 M aqueous solution of Na₂S₂O₃ before washing with a 0.2 M aqueous solution of HCl three times. The organic layer was dried with MgSO₄ and the solvents were removed under reduced pressure to afford a light yellow oil. The residue was subjected to GPLC (CHCl₃) followed by the reprecipitation from CHCl₃ and CH₃CN solution to give hexathioether **1** as colorless crystals.

Synthesis of trinuclear Pd complex (4). To a benzene solution (5 mL) of hexathioether **1** (30 mg, 18.7 μmol) was added 3 molar amounts of tetrakis(triphenylphosphine) palladium(0) (64.9 mg, 56.1 μmol) at room temperature. After stirring of the mixture for 62 h at the same temperature, the solvent was removed under reduced pressure. The residue was dissolved into CHCl₃ (15 mL) and the brown suspension was filtered through Celite[®]. The filtrate was evaporated and the residual brown solid was subjected to GPLC (CHCl₃) followed by silica gel column chromatography (benzene:hexane = 1:1) to give pure tripalladium complex **4** (26.5 mg, 10.8 μmol, 58%) as yellow crystals. **4**: Mp: 182.7–183.7 °C (decomp). ¹H NMR (300 MHz, CDCl₃, 50 °C): δ -0.22 (s, 18H, SiMe₃), -0.19 (s, 18H, SiMe₃), 0.08 (s, 18H, SiMe₃), 0.09 (s, 36H, SiMe₃), 0.16 (s, 18H, SiMe₃), 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); ¹³C NMR (75 MHz, CDCl₃, 50 °C): δ 0.8 (q, SiMe₃), 0.9 (q, SiMe₃), 1.5 (q, SiMe₃), 2.0 (q, SiMe₃), 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 × 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); ³¹P NMR (121 MHz, CDCl₃, 50 °C): δ 28.1; Anal. Calcd for C₁₁₄H₁₆₄P₂Pd₃S₆Si₁₂: C, 56.00; H, 6.76. Found: C, 55.98; H, 6.83.

X-Ray structural analysis of 1·0.5(CH₂Cl₂)·0.5(C₆H₁₄) and 4·3.2(C₆H₆)·0.8(CHCl₃). Single crystals of 1·0.5(CH₂Cl₂)·0.5(C₆H₁₄) and 4·3.2(C₆H₆)·0.8(CHCl₃) suitable for X-ray structural analysis were obtained by slow recrystallization from CH₂Cl₂/C₆H₁₄ and CHCl₃/C₆H₆, 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 = 0.71070 Å for 1·0.5(CH₂Cl₂)·0.5(C₆H₁₄) and λ = 0.71069 Å for 4·3.2(C₆H₆)·0.8(CHCl₃)). The structures were solved by direct methods (SIR-97)², and refined by

full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).³ The solvated dichloromethane was disordered and their occupancies were refined (0.50:0.50) in $1 \cdot 0.5(\text{CH}_2\text{Cl}_2) \cdot 0.5(\text{C}_6\text{H}_{14})$. In the crystal of $4 \cdot 3.2(\text{C}_6\text{H}_6) \cdot 0.8(\text{CHCl}_3)$, some molecules of **4** are solvated by two benzene molecules and others are solvated by one benzene and one chloroform molecules. The occupancies of one of the benzene molecules and the chloroform molecule were refined (0.60:0.40). All the non-hydrogen atoms, except for the carbon atom of solvated dichloromethane in $1 \cdot 0.5(\text{CH}_2\text{Cl}_2) \cdot 0.5(\text{C}_6\text{H}_{14})$, were refined anisotropically. All hydrogens were placed using AFIX instructions. The structural data are shown in Table 1. In the analysis of $1 \cdot 0.5(\text{CH}_2\text{Cl}_2) \cdot 0.5(\text{C}_6\text{H}_{14})$, there are the highest peak (1.554 e \AA^{-3}) and the deepest hole (-1.242 e \AA^{-3}) near to the CH_2Cl_2 solvent molecule due to disorders that could no be completely dissolved.

Table 1. Crystal Data and Refinement Details for $1 \cdot 0.5(\text{CH}_2\text{Cl}_2) \cdot 0.5(\text{C}_6\text{H}_{14})$ and $4 \cdot 3.2(\text{C}_6\text{H}_6) \cdot 0.8(\text{CHCl}_3)$

	$1 \cdot 0.5(\text{CH}_2\text{Cl}_2) \cdot 0.5(\text{C}_6\text{H}_{14})$	$4 \cdot 3.2(\text{C}_6\text{H}_6) \cdot 0.8(\text{CHCl}_3)$
empirical formula	$\text{C}_{81.50}\text{H}_{142}\text{ClS}_6\text{Si}_{12}$	$\text{C}_{134}\text{H}_{184}\text{Cl}_{2.40}\text{P}_2\text{Pd}_3\text{S}_6\text{Si}_{12}$
formula weight	1686.84	2790.47
temperature	103(2) K	103(2) K
crystal system	triclinic	monoclinic
space group	$P-1$ (# 2)	$C2/c$ (#15)
a (Å)	10.920(2)	31.9316(5)
b (Å)	20.424(5)	24.7082(6)
c (Å)	23.068(5)	24.0157(5)
α (deg)	71.290(7)	90
β (deg)	83.335(10)	130.2043(8)
γ (deg)	83.675(11)	90
V (Å ³)	4825.5(18)	14471.3(5)
Z	2	4
D_{calc} (Mg m ⁻³)	1.161	1.281
absorp coeff (mm ⁻¹)	0.357	0.666
crystal size (mm)	0.30 × 0.10 × 0.01	0.30 × 0.10 × 0.10
θ range	2.35 to 25.00°	2.95 to 25.00°
no. of reflns measd	31210	47590
no. of indep reflns	16506	12714
R_{int}	0.0454	0.0758
completeness	97.20%	99.70%
data/restraints/parameters	16506 / 0 / 941	12714 / 63 / 769
goodness-of-fit on F^2	1.081	1.058
final R indices [$I > 2\sigma(I)$] ^a	$R_1 = 0.0647$ $wR_2 = 0.1482$	$R_1 = 0.0438$ $wR_2 = 0.0841$
R indices (all data) ^a	$R_1 = 0.0914$ $wR_2 = 0.1661$	$R_1 = 0.0893$ $wR_2 = 0.0936$
largest diff. peak and hole (e \AA^{-3})	1.554 and -1.242	1.400 and -0.766

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

References

1. N. Takeda, D. Shimizu, and N. Tokitoh, *Inorg. Chem.*, in press.

2. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115-119.
3. G. M. Sheldrick, SHELX-97, program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.