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Synthesis of *syn*-2,4-Dimercapto-1,3,2,4-dithiadigermetane and Its Application to Ge_2PdS_4 Cluster Synthesis

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Dedicated to Professor Renji Okazaki on the occasion of his 70th birthday

Abstract: The sulfurization of $DmpGeH_3$ (Dmp = 2,6-dimesitylphenyl) afforded the trinuclear germanium sulfide $[DmpGe(\mu\text{-}S)]_2(\mu\text{-}S)_2Ge(SH)$-Dmp and a series of polythiadigermabicyclo[*x*.1.1]alkanes ($x = 3, 4, 5$). The reduction of the S–S bonds of these germabicycloalkanes by $NaBH_4$ at 0 °C afforded the dinuclear mercaptogermane *syn*-$[DmpGe(SH)(\mu\text{-}S)_2Ge(SH)Dmp]$ (**5**) in good yield. The reaction of $[Pd(dppe)Cl_2]$ (dppe = 1,2-bis(diphenylphosphanyl)ethane) and the dilithium salt of **5** prepared in situ by the addition of *n*BuLi (2 equiv) gave the Ge_2PdS_4 cluster $[DmpGe(\mu\text{-}S)]_2[(\mu\text{-}S)_2Pd(dppe)]$, in which the dithiadigermetanedithiolate is bound to the Pd atom at the two thiolato sulfur atoms. The same reaction with $[Pd(PPh_3)_2Cl_2]$ gave another Ge_2PdS_4 cluster, $[DmpGe(\mu\text{-}S)]_2[(\mu\text{-}S)_2Pd(PPh_3)]$, but with the dithiadigermetanedithiolate and the Pd center conjoined through a μ-S atom between the two germanium atoms in addition to the two thiolato sulfur atoms to form a highly distorted cluster core. The formation of two different types of Ge_2PdS_4 clusters represents the usefulness of **5** in the synthesis of various polynuclear complexes composed of germanium and transition metals.

Keywords: germanium · metal sulfides · palladium · polychalcogenides · polynuclear complexes

Introduction

Metal chalcogenides have been investigated owing to their diverse structures,[1] their versatile reactivities in relation to metalloenzymes,[2] and their properties, which are applicable to contemporary electronic devices.[3] Whereas transition-metal sulfides are ubiquitous, those of heavy Group 14 elements such as Si, Ge, and Sn are less common.[3–9] We have been interested in germanium polysulfides owing to their applicability as precursors of novel heteropolynuclear sulfide complexes composed of germanium and various transition metals. An important aspect of these complexes is the cooperation of Ge and Ru toward the reactions of sulfide bridges, as indicated in our recent study on a series of S/S- and S/O-bridged heterodinuclear Ge–Ru complexes.[10] The germanium sources for these dinuclear complexes were $Dmp(Dep)Ge(SH)_2$ and Dmp(Dep)Ge(SH)(OH), respectively; both were derived from the germapolysulfides Dmp(Dep)GeS_x ($x = 4, 6$; Dmp = 2,6-dimesitylphenyl, Dep = 2,6-diethylphenyl) in a few steps.[10,11] As an extension of our studies, we turned to polythiadigermabicyclo[*k.l.m*]alkanes as possible precursors of mercaptogermanes. Ando and coworkers reported that the sulfurization of Tsi-substituted trihydrogermanes and trihydrosilanes ($Tsi = C(SiMe_3)_3$) gave a series of polythiadigermabicycloalkanes and the silicon analogues, respectively.[7] Tin analogues bearing bulky *m*-terphenyl ligands were also reported by Saito et al.[9]

Herein we report the synthesis of 2,4-dimercapto-1,3,2,4-dithiadigermetane *syn*-$[DmpGe(SH)(\mu\text{-}S)_2Ge(SH)Dmp]$ as a new entry to mercaptogermanes, as well as its application to the synthesis of heteronuclear Ge_2PdS_4 clusters.[12] The precursors of the mercaptogermane are a series of polythiadigermabicyclo[*x*.1.1]alkanes ($x = 3–5$), which were obtained by sulfurization of the trihydrogermane $DmpGeH_3$. The Ge_2PdS_4 clusters obtained from the reactions of the mercaptogermane and $[Pd(dppe)Cl_2]$ or $[Pd(PPh_3)_2Cl_2]$ (dppe = 1,2-bis(diphenylphosphanyl)ethane) display various binding modes.

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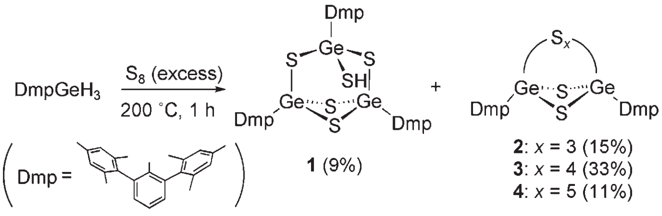
Results and Discussion

Sulfurization of $DmpGeH_3$: Synthesis of Polythiadigermabicyclo[*k.l.m*]alkanes

The Dmp-substituted trichlorogermane $DmpGeCl_3$ was prepared by the reaction of $GeCl_4$ and DmpLi.[10] Addition of HMPA (hexamethylphosphoramide) was required to obtain $DmpGeCl_3$ in sufficient yield. Subsequent reduction of $DmpGeCl_3$ by $LiAlH_4$ proceeded readily in THF to afford the trihydrogermane $DmpGeH_3$ in 89 % yield.

According to the reported sulfurization method of hydrogermanes, $DmpGeH_3$ was sulfurized in melted elemental sulfur at 200 °C (Scheme 1).[6–9] Complete consumption of the trihydrogermane within 1 h was confirmed by thin-layer chromatographic analysis. After removal of excess elemental sulfur, separation on gel-permeated chromatography (GPC) gave two fractions. One, which shows a shorter GPC retention time, was identified as $[DmpGe(\mu\text{-}S)]_2(\mu\text{-}S)_2Ge(SH)Dmp$ (**1**) by X-ray structural analysis (Figure 1). The GPC fraction with the longer retention time was further separated carefully on silica-gel column chromatography to isolate three digermapolysulfides, $Dmp_2Ge_2S_5$ (**2**), $Dmp_2Ge_2S_6$ (**3**), and $Dmp_2Ge_2S_7$ (**4**), in 11, 33, and 15 % yield, respectively.[13] These were formulated on the basis of elemental analysis and according to the GPC retention time. X-ray crystallographic analysis elucidated the molecular structures of **2** and **3** as 2,3,4,6,7-pentathia-1,5-digermabicyclo[3.1.1]heptane and 2,3,4,5,7,8-hexathia-1,6-digermabicyclo[4.1.1]octane, respectively (Figures 2 and 3). Unfortunately, single crystals of **4** were not obtained due to the gradual degradation of **4** into **2**, **3**, and elemental sulfur during crystallization. Although several structures for **4** are possible on the basis of the formula $Dmp_2Ge_2S_7$, the facile degradation of **4** into **2** and **3** suggests that **4**, like **2** and **3**, contains a $Ge(\mu\text{-}S)_2Ge$ portion, because in the case of Tsi-substituted polythiadigermabicyclo[*k.l.m*]alkanes, conversion from the $\mu\text{-}S_2$ compound into the μ-S requires UV irradiation in the presence of PPh_3.[7] Thus, the structure of **4** is tentatively attributed as 2,3,4,5,6,8,9-heptathia-1,7-digermabicyclo[5.1.1]nonane, $DmpGe(\mu\text{-}S)_2(\mu\text{-}S_5)GeDmp$.



Scheme 1. Sulfurization reaction of $DmpGeH_3$.

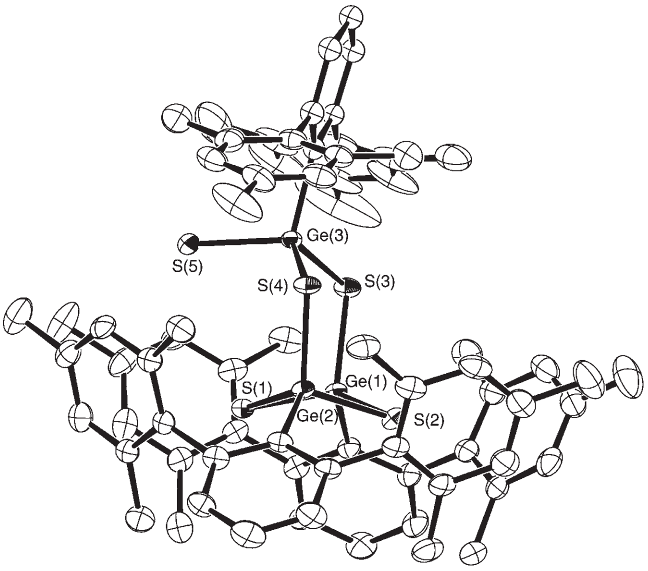


Figure 1. Molecular structure of **1** with thermal ellipsoids shown at the 40 % probability level. All hydrogen atoms are excluded for clarity.

Molecular Structures of 1, 2, and 3

Single crystals of **1**, **2**, and **3** suitable for X-ray structural analysis were grown from chloroform/ethanol (Table 1). The trinuclear germanium compound **1** crystallized in the monoclinic $P2_1/n$ space group. The cluster core is composed of three DmpGe portions and four μ-sulfides, each of which connects the two germanium atoms. The Ge(SH)(Dmp) portion is disordered over two positions in a 0.85:0.15 ratio. Only the main component is shown in Figure 1. The Ge(1)S(1)Ge(2)S(2) quadrangle is folded with a dihedral angle of 143.4° along the S–S axis. A notable feature of **1** is the terminal hydrosulfide bonded to Ge(3). The bulky Dmp groups surround the hydrosulfide to prevent further sulfide-bridge formation.

The molecular structure of 2,3,4,6,7-pentathia-1,5-digermabicyclo[3.1.1]heptane (**2**) is shown in Figure 2. It has one trisulfide and two monosulfide bridges between the two DmpGe portions. It crystallizes in the *C*2/*c* space group, and a crystallographic twofold axis passes through the midpoint

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Kazuyuki Tatsumi *obtained his BA (1971) and PhD (1976) at Osaka Univ. in Japan. After postdoctoral studies at Texas A&M Univ. (with Prof. M. Tsutsui) and Cornell Univ. (with Prof. Roald Hoffmann), he returned to Osaka Univ. as Assistant Professor in 1982. He was promoted to Professor at Nagoya Univ. in 1994, where he has been Director of the Research Center of Materials Science since 2003. His research interests cover various aspects of transition-metal chemistry, with a recent focus on bioinorganic and organometallic chemistry.*

"Chemistry is international by nature, but it may also evolve through the interplay of different cultural backgrounds. Chemistry—An Asian Journal *will surely play a key role as a pillar in the future of chemistry."*

Table 1. Crystallographic data and structure-refinement parameters for **1**, **2**, **3**, **5**, **6**, and **7**.

Compound	**1**·$CHCl_3$	**2**·$CHCl_3$	**3**	**5**	**6**	**7**
Formula	$C_{73}H_{76}Cl_3Ge_3S_5$	$C_{49}H_{52}Cl_3Ge_2S$	$C_{48}H_{50}Ge_2S_6$	$C_{48}H_{52}Ge_2S_4$	$C_{74}H_{74}Ge_2P_2PdS$	$C_{66}H_{65}Ge_2PPdS_4$
M_r	1437.83	1052.79	964.46	902.36	1405.17	1269.03
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (#14)	$C2/c$ (#15)	$Pna2_1$ (#33)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a [Å]	14.328(3)	19.088(4)	17.619(6)	13.1862(13)	14.2902(18)	12.9346(3)
b [Å]	20.651(4)	13.326(2)	14.447(7)	14.4540(14)	21.400(3)	33.9563(9)
c [Å]	24.153(5)	19.549(4)	18.593(6)	24.586(3)	22.008(3)	14.0377(5)
β [°]	106.963(2)	96.013(3)		102.0119(14)	95.351(3)	107.1848(14)
V [Å^3]	6935(2)	4945.2(16)	4733(2)	4583.3(8)	6701.1(15)	5890.3(3)
Z	4	4	4	4	4	4
D_{calcd} [g cm^{-3}]	1.377	1.414	1.354	1.308	1.393	1.431
μ [cm^{-1}]	15.980	16.208	15.658	15.241	13.705	15.247
F_{000}	2964	2164	1992	1872	2888	2600
$2\theta_{max}$ [°]	55.0	54.9	55.0	55.0	55.0	55.0
Collected reflections	52906	28441	51486	35528	75323	39906
Independent reflections (R_{int})	15482 (0.032)	5639 (0.021)	10672 (0.126)	10287 (0.021)	15343 (0.106)	12693 (0.022)
No. of parameters	803	333	556	537	822	732
$R1$[a]	0.0796	0.0421	0.0640	0.0342	0.0507	0.0923
$wR2$[b]	0.1801	0.0952	0.1764	0.0693	0.1447	0.2405
GOF on F^2[c]	0.951	1.056	0.906	1.018	0.848	1.147

[a] $R1=\Sigma||F_0|-|F_c||/\Sigma|F_0|$ $(I>2\sigma(I))$. [b] $wR2=[(\Sigma w(|F_0|-|F_c|)^2/\Sigma wF_0^2)]^{1/2}$ (all data). [c] $GOF=[\Sigma w(|F_0|-|F_c|)^2/(N_o-N_v)]^{1/2}$ (N_o = number of observations, N_v = number of variables).

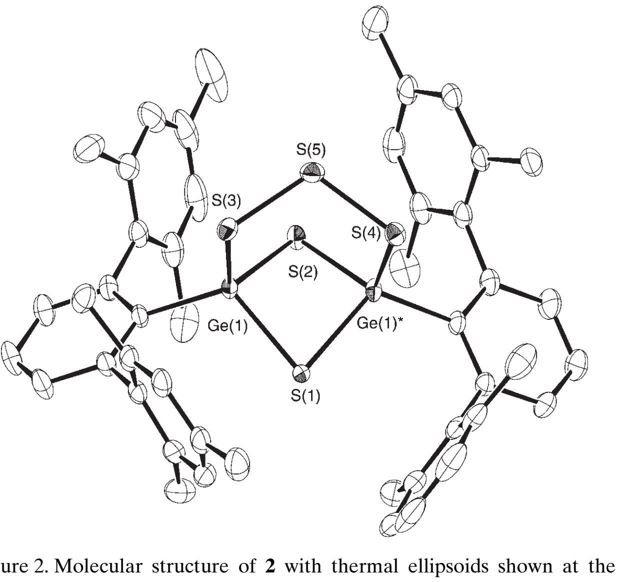


Figure 2. Molecular structure of **2** with thermal ellipsoids shown at the 30% probability level. All hydrogen atoms are excluded for clarity.

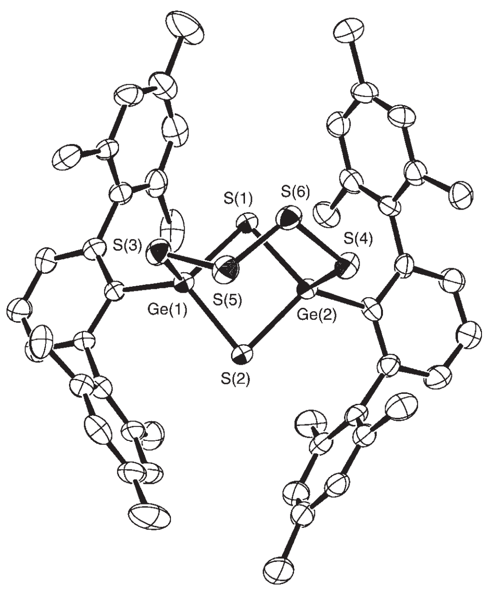


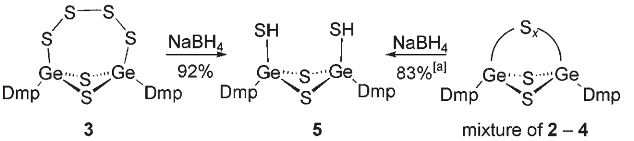
Figure 3. Molecular structure of **3** with thermal ellipsoids shown at the 40% probability level. All hydrogen atoms are excluded for clarity.

of Ge(1)–Ge(1)*. Whereas the Dmp groups and the germanium atoms bonded to them are tidily packed in the crystal, the three sulfide bridges are disordered over two positions in a 1:1 ratio, respectively, one of which is depicted in Figure 2. The structures of **2** and the tin analogue reported by Saito et al. are very much alike.[9] The six-membered rings defined by Ge(1)–S(1)–Ge(1)*–S(4)–S(5)–S(3) and Ge(1)–S(2)–Ge(1)*–S(4)–S(5)–S(3) assume chair and boat conformations, respectively. The central Ge_2S_2 quadrangle is significantly folded with a dihedral angle of 130.6° between the Ge(1)Ge(2)S(1) and Ge(1)Ge(2)S(2) planes.

Figure 3 shows the crystal structure of **3**. It crystallizes in the orthorhombic acentric space group $Pna2_1$. The digermabicyclo Ge_2S_6 core that contains one tetrasulfide and two monosulfide bridges connecting the two germanium bridgeheads assumes virtual C_2 symmetry, in which the C_2 axis passes through both the midpoints of the Ge_2S_2 quadrangle and the S(5)–S(6) bond. Due to the longer S_4 bridge, the Ge_2S_2 quadrangle assumes a large dihedral angle of 160.9° compared to that of **2**. Although a number of complexes containing S_4 ligands on metals have been reported, the bimetallic complexes $[M_2(\mu\text{-}S_2)_2(\mu\text{-}S_4)(S_2C_2Ph_2)_2]$ (M = Mo, W),[14] $[Cp_2Cr_2(\mu\text{-}OCMe_3)_2(\mu\text{-}S_4)]$ (Cp = cyclopentadienyl),[15] and cubane-like $Cs_6[Mo_4S_4(\mu\text{-}S_4)_4]$[16] are the only polynuclear complexes with S_4 bridges to have been reported.

Synthesis and Structures of *syn*-Dmp(SH)Ge(μ-S)$_2$Ge(SH)Dmp

The selective formation of polythiadigermabicyclo-[*x*.1.1]alkanes opens up a synthetic route to *syn*-Dmp(SH)Ge(μ-S)$_2$Ge(SH)Dmp (**5**). Following our previous work,[10] **3** was treated with NaBH$_4$ in THF/ethanol at 0 °C. Thus, selective S–S bond reduction proceeded to afford **5** in 92 % yield (Scheme 2). The formation of hydrosulfides is evident in the spectral data. The ^{1}H NMR spectrum exhibits a singlet signal for SH at $\delta = 1.49$ ppm, which instantly disappeared upon treatment with D$_2$O. The S–H stretching band was observed in the Raman spectra at 2563 cm^{-1}.



Scheme 2. Synthesis of **5**. [a] Yield calculated on the basis of DmpGeH$_3$.

Practically, **5** can be synthesized by the same procedure but by using a mixture of polythiadigermabicyclo-[*x*.1.1]alkanes, which affords **5** in 83 % yield based on DmpGeH$_3$. Compound **5** is resistant to air oxidation and hydrolysis even in solution, presumably owing to the bulky Dmp groups.

Single crystals of **5** suitable for X-ray structural analysis were obtained from CH$_2$Cl$_2$/ethanol (Table 1). The molecular structure of **5** is shown in Figure 4. As observed in **1**–**3**, the central Ge$_2$S$_2$ quadrangle of **5** is folded, even though one of the three sulfide bridges is dissociated. As significant intramolecular hydrogen-bonding interaction would not exist between the two hydrosulfides, which is evident in the considerably long S(3)–S(4) distance of 3.99 Å,[17] the folding of the quadrangle is due to the intramolecular steric congestion between the bulky Dmp groups. The dihedral angle of 153.9° around the S(1)–S(2) vector lies between those for **2** and **3** (Table 2).

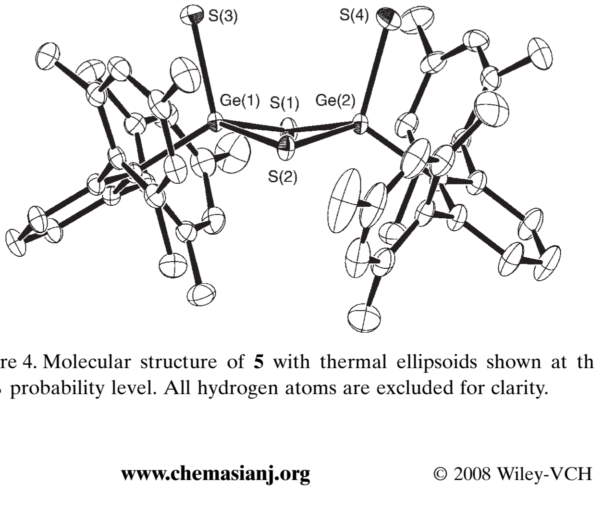


Figure 4. Molecular structure of **5** with thermal ellipsoids shown at the 40 % probability level. All hydrogen atoms are excluded for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for **1**, **2**, **3**, and **5**.

Compound	**1**	**2**[b]	**3**	**5**
Ge(1)–S(1)	2.2333(13)	2.294(4)	2.234(2)	2.2292(5)
Ge(1)–S(2)	2.2401(14)	2.162(4)	2.223(2)	2.2319(6)
Ge(2)–S(1)	2.2378(13)	2.330(4)	2.226(2)	2.2361(6)
Ge(2)–S(2)	2.2413(14)	2.123(8)	2.236(2)	2.2347(5)
Ge(1)–S(3)	2.2353(13)	2.3176(12)	2.256(2)	2.2361(5)
Ge(2)–S(4)	2.2249(13)	2.2634(12)	2.252(2)	2.2292(6)
Ge(1)–S(1)–Ge(2)	80.62(5)	77.21(13)	83.33(8)	82.31(2)
Ge(1)–S(2)–Ge(2)	80.40(4)	84.52(14)	83.35(8)	82.28(2)
S(1)–Ge(1)–S(2)	94.30(5)	96.05(15)	95.30(8)	95.16(2)
S(1)–Ge(2)–S(2)	94.14(5)	94.09(14)	95.15(8)	94.89(2)
S(1)–Ge(1)–S(3)	108.91(5)	118.74(7)	108.15(9)	106.84(2)
S(2)–Ge(1)–S(3)	108.91(5)	108.03(7)	110.58(9)	107.60(2)
S(1)–Ge(2)–S(4)	110.09(5)	100.95(7)	110.34(9)	108.14(2)
S(2)–Ge(2)–S(4)	108.58(5)	109.02(8)	109.28(9)	108.09(2)
dihedral[a]	143.4	130.6	160.9	153.9

[a] Dihedral angles between planes Ge(1)–S(1)–S(2) and Ge(2)–S(1)–S(2). [b] The Ge(2) for **2** means Ge(1)*.

Synthesis of Ge$_2$PdS$_4$ Clusters

As indicated in the structure of the trinuclear compound **1**, compound **5** is able to bind metals at the two terminal thiolates. This is realized by the reaction of [Pd(dppe)Cl$_2$] with [DmpGe(SLi)(μ-S)$_2$Ge(SLi)Dmp] prepared in situ from **5** and *n*BuLi (2 equiv) in THF, which gave [DmpGe(μ-S)]$_2$[(μ-S)$_2$Pd(dppe)] (**6**) in 94 % yield as orange crystals. As shown in Figure 5, the configuration of the [DmpGe(μ-S)]$_2$(μ-S)$_2$ moiety in **6** appears mostly identical to that of **1** (see also Table 3). Indeed, their structural similarity is manifested in their Ge$_2$S$_2$ dihedral angles, 142.9° for **6** (Table 3) and 143.4° for **1** (Table 2). Meanwhile, the geometry around Pd is a slightly distorted square plane composed of the dppe ligand and the two thiolato sulfur atoms. The structural parameters around Pd show similar values to those for reported [Pd-

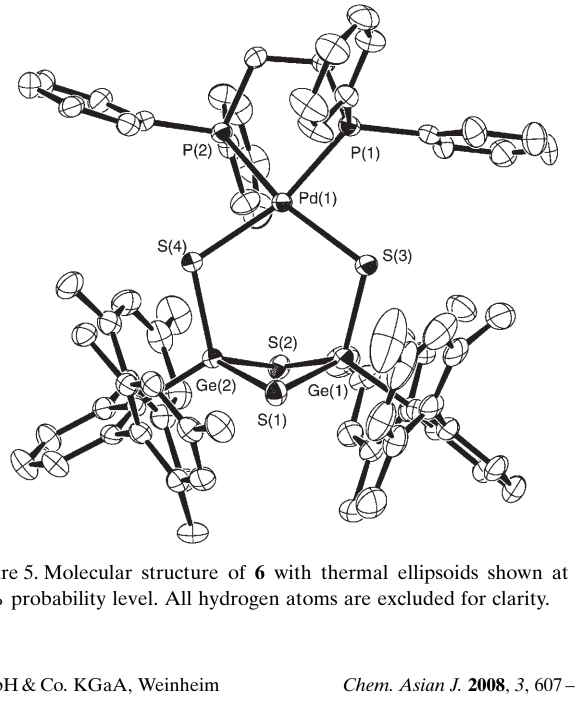


Figure 5. Molecular structure of **6** with thermal ellipsoids shown at the 40 % probability level. All hydrogen atoms are excluded for clarity.

Table 3. Selected bond lengths (Å) and angles (°) for **6** and **7**.

Compound	**6**	**7**
Ge(1)–S(1)	2.2372(13)	2.2968(19)
Ge(1)–S(2)	2.2371(14)	2.2524(18)
Ge(2)–S(1)	2.2511(14)	2.3018(19)
Ge(2)–S(2)	2.2363(15)	2.2483(19)
Ge(1)–S(3)	2.1837(11)	2.1777(17)
Ge(2)–S(4)	2.1751(13)	2.1788(18)
Pd(1)–S(1)	–	2.4870(17)
Pd(1)–S(3)	2.3852(12)	2.3528(16)
Pd(1)–S(4)	2.3642(14)	2.3470(17)
Pd(1)–P(1)	2.2535(14)	2.2588(19)
Pd(1)–P(2)	2.2659(12)	–
Ge(1)–S(1)–Ge(2)	80.21(4)	86.69(7)
Ge(1)–S(2)–Ge(2)	80.53(4)	89.07(7)
S(3)–Pd(1)–S(4)	108.88(4)	153.80(7)
S(1)–Pd(1)–P(1)	–	173.04(7)
dihedral[a]	142.9	165.6

[a] Dihedral angles between planes Ge(1)–S(1)–S(2) and Ge(2)–S(1)–S(2).

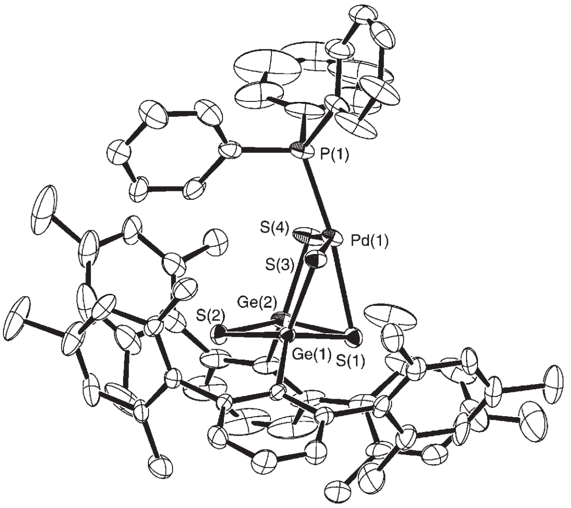


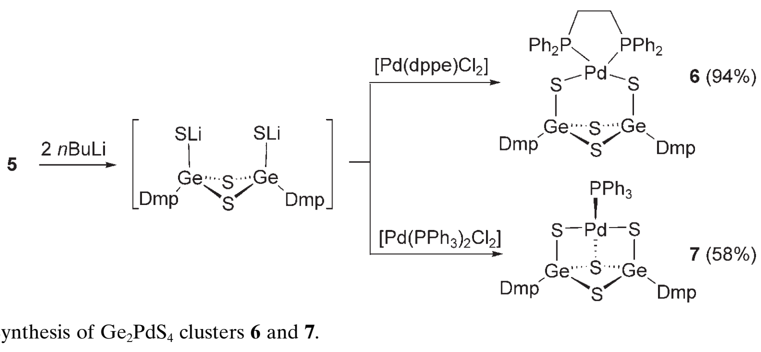
Figure 6. Molecular structure of **7** with thermal ellipsoids shown at the 40 % probability level. All hydrogen atoms are excluded for clarity.

(dppe)(SR)$_2$] complexes except for the rather larger S(3)–Pd(1)–S(4) angle (108.88(4)°) for **6**.[18] Of note are the considerably short bonds of Ge(1)–S(3) (2.170(2) Å) and Ge(2)–S(4) (2.185(2) Å) for **6**. These are about 0.5 Å shorter than those for both **1** and **5**, and are among the shortest Ge–S single bonds.[19] As a similar Ge–S bond shortening is observed for the potassium salt of the germanethiolate, Dmp(Dep)Ge(SK)$_2$, relative to Dmp(Dep)Ge(SH)$_2$, it might indicate a rather weak interaction of the palladium and the thiolato sulfur atoms due to the strong *trans* influence of dppe.[10c]

When the reaction of [DmpGe(SLi)(μ-S)$_2$Ge(SLi)Dmp] and [Pd(PPh$_3$)$_2$Cl$_2$] was examined in a similar way, a different type of Ge$_2$PdS$_4$ cluster, [DmpGe(μ-S)]$_2$[(μ-S)$_2$Pd(PPh$_3$)] (**7**) was obtained (Scheme 3). The structure of **7** is shown in Figure 6 (see also Table 3). Whereas dithiadigermetanedithiolate bonds to Pd at the two thiolato sulfur atoms in **6**, it coordinates to the Pd in **7** through three sulfur atoms, thus causing PPh$_3$ dissociation. The formation of the characteristic complex **7** in this particular case is probably due to steric repulsion occurring between the two triphenylphosphine ligands. The two thiolato sulfur atoms occupy *cis* positions to the PPh$_3$, and one of the μ-sulfides of the Ge$_2$S$_2$ quadrangle coordinates to the Pd *trans* to the phosphine. Thus, the square-planar Pd geometry is considerably distorted. The distortion is represented in the bowed S(3)–Pd(1)–S(4) bond, which deviates by 26.2° from the ideal, linear 180° (Table 3). Interestingly, the S(1)–Pd(1)–P(1) bond is also slightly bent toward the same side of the square plane around Pd, and thus the Pd atom is placed 0.32 Å above the least-square plane composed of S(1), S(3), S(4), and P(1). Although the bond lengths between Pd(1) and the thiolato sulfur atoms S(3) and S(4) are ordinary values for Pd^{II} thiolates, the Pd(1)–S(1) bond is considerably elongated; the Pd(1)–S(1) bond length is 2.4870(17) Å, whereas the Pd–S bonds in [Pd(SMe$_2$)$_4$]$^{2+}$ are 2.334–2.338 Å.[20] The elongation might be mostly due to the distortion of the core structure resulting from intramolecular steric congestion. The bonds between S(1) and the two germanium atoms also become longer by 0.5 Å than those for S(2), which indicates weakened Ge–S bonds upon Pd coordination to the μ-S atoms.[21]

Conclusions

We have synthesized *syn*-[DmpGe(SH)(μ-S)$_2$GeDmp-(SH)] (**5**) as a new entry to mercaptogermanes. It was obtained in good yield from polythiadigermabicyclo[*x*.1.1]alkanes (*x* = 3–5). The dilithium salt of **5** is bound to the palladium atoms in a bidentate or tridentate manner to form the correpsonding Ge$_2$PdS$_4$ clusters, [DmpGe(μ-S)]$_2$[(μ-S)$_2$Pd(dppe)] (**6**) and [DmpGe(μ-S)]$_2$[(μ-S)$_2$Pd(PPh$_3$)] (**7**), respectively. These results indicate that compound **5** is a useful precursor to various polynuclear clusters composed of germanium and transition metals.



Scheme 3. Synthesis of Ge$_2$PdS$_4$ clusters **6** and **7**.

Experimental Section

General

All reactions and manipulations of air-sensitive compounds were conducted under an inert atmosphere of dry nitrogen by employing standard Schlenk techniques. Toluene, THF, diethyl ether, and hexane were distilled from sodium/benzophenone ketyl under nitrogen. Dichloromethane was distilled from CaH_2. ^{1}H NMR (500 or 600 MHz) and ^{31}P NMR spectra (202 or 243 MHz) were recorded on a JEOL JNM-ECP500 or ECA600 spectrometer. ^{1}H NMR chemical shifts are quoted in ppm relative to those of the residual protons of the deuterated solvents. ^{31}P{^{1}H} NMR chemical shifts are referenced to external 85% H_3PO_4. Raman spectra were recorded on a Perkin–Elmer Spectrum 2000 spectrometer with an Nd:YAG laser. Elemental analysis was performed on LECO CHN-900 and CHNS-932 microanalyzers. GPC–HPLC was performed on an LC-908 chromatograph with JAI gel 1H and 2H columns (Japan Analytical Industry) with chloroform as solvent.

Syntheses

$DmpGeCl_3$: *n*BuLi (1.5 M in hexane, 27 mL, 43 mmol) was added to a solution of iodo-2,6-dimesitylbenzene (17.3 g, 39.3 mmol) in diethyl ether (600 mL) at −60 °C. After 1 h of stirring, hexamethylphosphoramide (17.5 mL, 100 mmol) and $GeCl_4$ (4.94 mL, 43.3 mmol) was added at −60 °C. The reaction mixture was warmed to room temperature over 12 h, aqueous NH_4Cl was added, and the mixture was extracted by hexane. The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The white solid thus obtained was recrystallized from hexane to afford $DmpGeCl_3$ as a white crystalline powder (18.6 g, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.67$ (t, $J = 7.6$ Hz, 1H, *p*-CH of Dmp), 7.17 (d, $J = 7.6$ Hz, 2H, *m*-CH of Dmp), 6.93 (s, 4H, *m*-CH of Mes; Mes = mesityl), 2.34 (s, 6H, *p*-CH_3 of Mes), 2.06 ppm (s, 12H , *o*-CH_3 of Mes); elemental analysis: calcd (%) for $C_{24}H_{25}Cl_3Ge$: C 58.54, H 5.12; found: C 57.75, H 5.01.

$DmpGeH_3$: $LiAlH_4$ (2.0 g, 52.7 mmol) was added to a solution of $DmpGeCl_3$ (6.5 g, 13.2 mmol) in THF (100 mL), and the mixture was stirred for 12 h at room temperature. After the mixture was quenched with dilute aqueous HCl, it was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, and all the solvent was removed under reduced pressure. The residue was recrystallized from CH_2Cl_2/EtOH to give $DmpGeH_3$ (4.97 g, 97% yield) as a white crystalline powder. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.64$ (t, $J = 7.6$ Hz, 1H, *p*-CH of Dmp), 7.07 (d, $J = 7.6$ Hz, 2H, *m*-CH of Dmp), 6.92 (s, 4H, *m*-CH of Mes), 3.23 (s, 3H, GeH_3), 1.98 (s, 6H, *p*-CH_3 of Mes), 1.97 ppm (s, 12H , *o*-CH_3 of Mes); elemental analysis: calcd (%) for $C_{24}H_{28}Ge$: C 74.09, H 7.25; found: C 74.00, H 7.01.

Sulfurization of $DmpGeH_3$: A mixture of $DmpGeH_3$ (3.0 g, 7.7 mmol) and elemental sulfur (7.0 g, 27 mmol as S_8) was heated to 200 °C for 1 h. Most of the excess sulfur was removed by recrystallization from chloroform. The residue was separated by GPC–HPLC (eluted by $CHCl_3$, 3.5 mL min^{-1}) to give two fractions in addition to that of elemental sulfur. The first fraction, which showed a retention time of 47 min, was trigermane **1**, which was recrystallized from CH_2Cl_2/EtOH to give light-yellow crystals in 9% yield. The second fraction, which showed a retention time of 50 min, was analyzed by TLC developed by hexane, which indicated three spots with small separation. Careful separation by silica-gel column chromatography eluted by hexane gave three bands that partly overlapped. The pure fractions for each band were collected to give 2,3,4,6,7-pentathia-1,5-digermabicyclo[3.1.1]heptane (**2**), 2,3,4,5,7,8-hexathia-1,6-digermabicyclo[4.1.1]octane (**3**), and 2,3,4,5,6,8,9-heptathia-1,7-digermabicyclo[5.1.1]nonane (**4**) in 15, 33, and 11% yield, respectively. **1**: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.40$ (t, $J = 7.6$ Hz, 2H, *p*-CH of Dmp), 7.38 (t, $J = 7.6$ Hz, 1H, *p*-CH of Dmp), 6.86 (d, $J = 7.6$ Hz, 4H, *m*-CH of Dmp), 6.85 (d, $J = 7.6$ Hz, 2H, *m*-CH of Dmp), 6.77 (br s, 4H, *m*-CH of Mes), 6.76 (s, 4H, *m*-CH of Mes), 6.74 (br s, 4H, *m*-CH of Mes), 2.33 (s, 12H, *p*-CH_3 of Mes), 2.13 (s, 6H, *p*-CH_3 of Mes), 2.05 (s, 12H, *o*-CH_3 of Mes), 1.91 (s, 12H, *o*-CH_3 of Mes), 1.82 ppm (s, 12H, *o*-CH_3 of Mes); elemental analysis: calcd (%) for $C_{72}H_{76}Ge_3S_5$: C 65.54, H 5.81, S 12.15; found: C 65.33, H 5.58, S 11.77. **2**: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.48$ (t, $J = 7.6$ Hz, 2H, *p*-CH of Dmp), 6.94 (d, $J = 7.6$ Hz, 4H, *m*-CH of Dmp), 6.85 (s, 8H, *m*-CH of Mes), 2.38 (s, 12H, *p*-CH_3 of Mes), 1.94 ppm (s, 24H , *o*-CH_3 of Mes); elemental analysis: calcd (%) for $C_{48}H_{50}Ge_2S_5$: C 61.83, H 5.40, S 17.19; found: C 60.27, H 5.04, S 17.35. **3**: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.49$ (t, $J = 7.6$ Hz, 2H, *p*-CH of Dmp), 6.95 (d, $J = 7.6$ Hz, 4H, *m*-CH of Dmp), 6.88 (s, 8H, *m*-CH of Mes), 2.41 (s, 12H, *p*-CH_3 of Mes), 2.03 ppm (s, 24H , *o*-CH_3 of Mes); elemental analysis: calcd (%) for $C_{48}H_{50}Ge_2S_6$: C 59.77, H 5.23, S 19.95; found: C 60.02, H 5.25, S 19.51. **4**: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.45$ (t, $J = 7.6$ Hz, 2H, *p*-CH of Dmp), 6.92 (d, $J = 7.6$ Hz, 4H, *m*-CH of Dmp), 6.85 (br s, 8H, *m*-CH of Mes), 2.39 (s, 12H, *p*-CH_3 of Mes), 1.94 ppm (s, 24H, *o*-CH_3 of Mes); elemental analysis: calcd (%) for $C_{48}H_{50}Ge_2S_8$: C 57.85, H 5.06, S 22.52; found: C 58.23, H 5.21, S 22.08.

5: $NaBH_4$ (220 mg, 5.8 mmol) was added to a solution of **3** (200 mg, 0.207 mmol) in THF/ethanol (10:1) at 0 °C. The mixture was stirred for 1 h at 0 °C and then for 10 h at room temperature. After treatment with 0.5 M HCl and extraction with CH_2Cl_2, the organic layer was dried over $MgSO_4$ and evaporated to dryness. The residue was recrystallized from CH_2Cl_2/ethanol to give *syn*-DmpGe(SH)(μ-S)$_2$Ge(SH)Dmp (**5**; 172 mg, 92% yield) as a white powder. Raman (solid, excitation; Nd:YAG laser, 1064 nm): $\tilde{\nu} = 2563$ cm^{-1} (S–H); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.47$ (t, $J = 7.6$ Hz, 2H, *p*-CH of Dmp), 6.93 (d, $J = 7.6$ Hz, 4H, *m*-CH of Dmp), 6.86 (s, 8H, *m*-CH of Mes), 2.37 (s, 12H, *p*-CH_3 of Mes), 2.02 (s, 24H, *o*-CH_3 of Mes), 1.49 ppm (s, 2H, GeSH); elemental analysis: calcd (%) for $C_{48}H_{52}Ge_2S_4$: C 63.89, H 5.81, S 14.21; found: C 63.70, H 5.98, S 13.88.

6: *n*BuLi (0.27 mL of a 1.5 M solution in hexane, 0.41 mmol) was added to a solution of **5** (170 mg, 0.188 mmol) in THF (20 mL) at −60 °C, and the mixture was stirred for 30 min. [Pd(dppe)Cl_2] (108 mg, 0.222 mmol) was added, and the mixture was stirred at 25 °C for 12 h to give an orange solution. The solvent was removed in vacuo, and the residue was treated with toluene (5 mL) and centrifuged to remove LiCl. The toluene solution was removed, and the residue was crystallized from CH_2Cl_2/hexane to give **6** as orange crystals in 94% yield. ^{1}H NMR (500 MHz, C_6D_6): $\delta = 7.53$–7.48 (m, 8H, dppe), 7.18 (t, $J = 7.6$ Hz, 2H, *p*-CH of Dmp), 7.18–7.12 (m, 12H, dppe), 6.90 (br s, 8H, *m*-CH of Mes), 6.88 (d, $J = 7.6$ Hz, 4H, *m*-CH of Dmp), 2.46 (s, 12H, *p*-CH_3 of Mes), 2.26 (s, 24H , *o*-CH_3 of Mes), 1.61 ppm (ABq, 4H, $J_1 = 29.7$ Hz, $J_2 = 10.1$ Hz, $(CH_2)_2$ of dppe); ^{31}P{^{1}H} NMR (168 MHz, C_6D_6): $\delta = 47.3$ ppm; elemental analysis: calcd (%) for $C_{74}H_{74}Ge_2P_2PdS_4$: C 63.25, H 5.31, S 9.13; found: C 63.18, H 5.35, S 8.71.

7: *n*BuLi (0.46 mL of a 1.5 M solution in hexane, 0.70 mmol) was added to a solution of **5** (300 mg, 0.332 mmol) in THF (20 mL) at −60 °C, and the mixture was stirred for 30 min. [Pd(PPh_3)$_2Cl_2$] (233 mg, 0.332 mmol) was added, and the mixture was stirred at 25 °C for 12 h to give a reddish-orange solution. The solvent was removed in vacuo, and the residue was treated with toluene (5 mL) and centrifuged to remove LiCl. The toluene solution was removed, and the residue was crystallized from hexane to give **7** as orange crystals in 58% yield. ^{1}H NMR (600 MHz, C_6D_6): $\delta = 7.67$–7.63 (m, 6H, PPh_3), 7.15 (t, $J = 7.6$ Hz, 2H, *p*-CH of Dmp), 7.12–7.07 (m, 3H, PPh_3), 7.05 (br s, 4H, *m*-CH of Mes), 7.04–7.00 (m, 6H, PPh_3), 6.84 (br s, 4H, *m*-CH of Mes), 6.83 (d, $J = 7.6$ Hz, 4H, *m*-CH of Dmp), 2.44 (s, 12H, *p*-CH_3 of Mes), 2.37 (br s, 12H, *o*-CH_3 of Mes), 2.21 ppm (br s, 12H, *o*-CH_3 of Mes); ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): $\delta = 39.4$ ppm (s); elemental analysis: calcd (%) for $C_{66}H_{65}Ge_2PPdS_4$: C 62.46, H 5.16, S 10.11; found: C 62.21, H 5.10, S 9.77.

Crystal-Structure Determination

Crystallographic data are summarized in Table 1. Crystals of **1**, **2**, **3**, **5**, **6**, and **7** were mounted on a loop with oil (immersion oil, type B or paraton, Hampton Research Corp.) and set on a Rigaku AFC-8 diffractometer equipped with an ADSC Quantum 1 CCD detector (for **6**) or a Mercury CCD detector (for **1**, **2**, **5**, **7**). The crystal of **3** was mounted on a quartz fiber with oil and set on a Rigaku AFC-7R diffractometer. Measurements were made by using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.710690$ Å) under a cold nitrogen stream. Frame data were integrated and corrected for absorption on an MSC d*TREK program package for **6** or a Rigaku/MSC CrystalClear package for **1**, **2**, **3**, **5**, and **7**. Structures were solved by direct methods and standard difference-map techniques and were refined by full-matrix least-square procedures on F^2 with a Rigaku/MSC CrystalStructure package. Anisotropic refinement was applied to all non-hydrogen atoms, but the disordered part and the CHCl$_3$ molecule for **1** were refined isotropically. For **1**, two DmpGe(SH) units are disordered in a 0.85:0.15 ratio. All the sulfur bridges are disordered for **2** in a 0.5:0.5 ratio. These ratios were refined freely while constraining the total occupancy of components to unity. All the hydrogen atoms were put at calculated positions. CCDC-664961 (**1**), -664962 (**2**), -664963 (**3**), -664960 (**5**), -664964 (**6**), and -664965 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

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