Synthesis and Reactivities of Dihydrosilanes Tethered with Two Thioether Moieties

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ABSTRACT: Dihydrosilanes tethered with two thioether moieties, $[2-(RSCH_2)C_6H_4]_2SiH_2(1a: R = t-$ Bu; 1b: R = i-Pr; 1c: R = Ph), were synthesized. Dihydrosilane 1b did not react with methanol, benzaldehyde, and carboxylic acids; this result may suggest very weak activation of the Si-H bonds in 1b. The corresponding dibromosilanes 4 and diiodosilanes 5 were synthesized by dihalogenation of 1 using N-bromosuccinimide and I_2 , respectively, whereas the dichlorosilanes 3 were synthesized by reaction of 2- $(RSCH_2)C_6H_4$ Li with SiCl₄. Reaction of **1b** with [PtCl₂] (cod) in the presence of Et_3N gave the corresponding bissilylplatinum complex, [Pt{SiH[2-(RSCH₂)- C_6H_4]₂]₂], the structure of which was determined by NMR and IR spectrometry and X-ray crystallography. © 2011 Wiley Periodicals, Inc. Heteroatom Chem 22:438-445, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20706

INTRODUCTION

Much attention has been focused on the chemistry of five- and six-coordinate silicon compounds

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due to their unique structures and reactivities as well as their application to organic synthesis [1,2]. As for five- and six-coordinate neutral silicon compounds intramolecularly coordinated by donors, there have been some compounds intramolecularly coordinated by nitrogen atoms; however, fiveand six-coordinate silicon compounds intramolecularly coordinated by thioether moieties are very few. For example, Jutzi and co-workers have reported the synthesis of some neutral five-coordinate hydrosilanes bearing thioether moiety such as (2- $MeSCH_2)C_6H_4SiHXY$ (X = Y = H; X = Ph, Y = OTf; X = H, Y = Cl [3]; however, the reactivities of such compounds are rarely known. In this paper, we present the synthesis and reactivities of dihydrosilanes **1a-c** tethered with two thioether moieties, [(2- $RSCH_2)C_6H_4]_2SiH_2$ (1a: R = t-Bu, 1b: R = i-Pr, 1c: R = Ph).

RESULTS AND DISCUSSION

Synthesis and Properties of Dihydrosilanes 1a-c

Synthesis of 1-bromo-2-(*tert*-butylthiomethyl) benzene **2a** and its derivatives were performed by modifying the reported synthetic method for **2a** [4]. Reaction of 1-bromo-2-bromomethylbenzene [5] with thiolates prepared from thiols and NaH gave the corresponding sulfides **2a–c** in good yields (Scheme 1).

Dihydrosilanes **1a–c** were synthesized by lithiation of **2a–c** with butyllithium in ether at $0^{\circ}C$ followed by treatment with SiHCl₃, and subsequent

Dedicated to Professor Kin-ya Akiba on the occasion of his 75th birthday.

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SCHEME 2 Synthesis of dihydrosilanes 1a-c.

hydrogenation with LiAlH₄ (Scheme 2). In this synthesis of **1a** from **2a**, a trisubstituted compound, $[2-(t-BuSCH_2)C_6H_4]_3$ SiH [6], was also obtained in 6% yield as a by-product. On the other hand, a similar reaction of **1a** in THF at -78° C resulted in the formation of an unidentifiable mixture along with *t*-BuSCH₂Ph (41%), which was probably formed by hydration of 2-(*t*-BuSCH₂)C₆H₄Li.

It has been known that six- and five-coordinate silicon compounds show up-field shifts of the ²⁹Si NMR resonances compared with the corresponding four-coordinate compounds [3]. For example, {2- $(Me_2NCH_2)C_6H_4$ NpSiH₂ (Np = naphthyl) and (8-Me₂N-1-C₁₀H₆)PhSiH₂, the X-ray structures of which indicate five-coordinate trigonal bipyramidal structures [7,8], show signals at -47.3 and -44.1 ppm, respectively, in the ²⁹Si NMR spectra, whereas the ²⁹Si NMR spectrum of PhNpSiH₂ indicates a resonance at -35.6 ppm [8,9]. The ²⁹Si NMR spectra of dihydrosilanes 1a-c showed slight up-field shifts $(\delta_{\rm Si} = -41.3 \text{ ppm for } \mathbf{1a}, -40.9 \text{ ppm for } \mathbf{1b}, \text{ and }$ -40.1 ppm for **1c**) compared with that of Ph₂SiH₂ $(\delta_{\rm Si} = -34.5 \text{ ppm})$ [10]. These values suggest weak or no interaction between silicon and sulfur atoms.

Reactivities of Dihydrosilane 1b as Reductant

It has been reported that Si–H bonds are activated by coordination of nucleophiles such as amines and fluorides [1]. For example, a five-coordinate dihydrosilane activated by intramolecular coordination of an amine moiety, (8-Me₂NCH₂-1-C₁₀H₆)PhSiH₂, reacts with ROH and RCOOH to give the corresponding alkoxysilanes and silyl carboxylates, respectively, together with the formation of H_2 [11]. In addition, it has been reported that thermolysis of the resulting silyl carboxylates affords the corresponding aldehydes and cyclotrisiloxanes [12]. This activated dihydrosilane also undergoes the addition of the Si–H bond to carbonyl moieties of arylaldehydes to afford benzyloxysilanes, hydration of which gives the corresponding benzylalcohol and disiloxane [11]. In this paper, we examined reaction of dihydrosilane **1b** with methanol, benzaldehyde, acetic acid, and 3-nitrobenzoic acid.

Thermolysis of **1b** in methanol at reflux for 13 h, reaction of **1b** with PhCHO in C_6D_6 at 150°C for 16 h in a sealed tube, reaction of 1b with CH_3CO_2H in C_6D_6 at 150°C for 1 h in a sealed tube, and reaction of **1b** with $3-NO_2C_6H_4COOH$ at $150^{\circ}C$ for 1 h, in every case, resulted in quantitative recovery of the starting material **1b**. These results are in sharp contrast to the reactions of the five-coordinate dihydrosilane activated by the intramolecular coordination of an amine moiety, (8-Me₂NCH₂-1-C₁₀H₆)PhSiH₂, giving the corresponding products [11,12]. The low reactivity of the Si-H bonds in 1b may suggest very weak or no coordination of thioether moieties to the silicon atom in 1b. These results do not contradict the slight up-field shift of the ²⁹Si NMR signal of **1b** compared with that of Ph₂SiH₂.

Dihalogenation of Dihydrosilanes **1a–c**

Attempted dichlorination of with 1b Nchlorosuccinimide (NCS) or trichloroisocyanuric acid (TCC) resulted in the formation of a complex mixture. Therefore, the synthesis of dichlorosilanes **3a, b** was examined by reaction of $2-(RSCH_2)C_6H_4Li$ with SiCl₄. Lithiation of **2a** and **2b** in ether at 0°C, followed by addition of 0.5 molar amounts of SiCl₄ at -40°C resulted in the formation of dichlorosilanes **3a**, **b** (Scheme 3). Although the isolation of **3a** was unsuccessful, dichlorosilane **3b**, which was unstable under the air, was purified by Kugelrohr distillation, to be isolated in 58% (for **3b**) yields.



SCHEME 3 Synthesis of dichlorosilanes 3a, b.



SCHEME 4 Synthesis of dibromosilanes **4a–c** and diiodosilanes **5a**, **b**.

The ²⁹Si NMR spectra of dichlorosilanes **3a**, **b** showed signals at -3.6 and -3.2 ppm, respectively, which are shifted to higher field by -10.1and -9.7 ppm, respectively, compared with the ²⁹Si NMR chemical shift of Ph₂SiCl₂ ($\delta_{Si} = 6.5$ ppm) [10]. Since the ²⁹Si NMR chemical shift of a five-coordinate dichlorosilane, [2-(Me₂NCH₂)C₆ H₄]₂SiCl₂, ($\delta_{Si} = -30.1$ ppm) [13] has reportedly shown the large up-field shift ($\Delta \delta_{Si} = -36.6$ ppm) compared with that of Ph₂SiCl₂, it may be suggested that the interaction between the silicon atom and thioether moieties in dichlorosilanes **3a**, **b** is absent or very weak.

Dibromosilanes **4a–c** and diiodosilanes **5a**, **b** were successfully synthesized from dihydrosilanes **1a–c**. Dihydrosilanes **1** were treated with *N*bromosuccinimide (NBS) and iodine to give the corresponding dibromosilanes **4** and diiodosilanes **5**, respectively, in good yields (Scheme 4). Dibromosilane **4b** and diiodosilane **5b** are highly sensitive to moisture to afford the corresponding silanediols, [2- $(i-PrSCH_2)C_6H_4]_2Si(OH)_2$.

The ²⁹Si NMR spectra of dibromosilanes 4a-c and diiodosilanes 5a and 5b showed signals at around -21 ppm (-21.4 ppm for **4a**, -21.3 ppm for **4b**, and -21.9 ppm for **4c**) and -40 ppm (-39.9 ppm for 5a and -39.5 ppm for 5b), respectively. Since examples for the measurement of ²⁹Si NMR spectra on diaryldibromosilanes and diaryldiiodosilanes are very few, it may be difficult to estimate the coordination number by their ²⁹Si NMR chemical shifts. However, the ²⁹Si NMR values of 4a-c are shifted to higher field by $\Delta \delta_{Si} = -24$ ppm as compared with that of a very bulky diaryldibromosilane, $Tbt(Dip)SiBr_2 [Tbt = 2,4,6-[(Me_3Si)_2CH]_3C_6H_2;$ Dip = $2,6-(i-Pr)_2C_6H_3$] (δ_{Si} = 3.0 ppm) [14], and the down-field shifts on dibromosilanes 4a-c $(\Delta_{\rm Si} = 19.9 \text{ ppm for 4a}, 19.6 \text{ ppm for 4b}, \text{ and}$ 18.2 ppm for **4c**) compared with the corresponding dihydrosilanes **1a–c** are much smaller than that on Tbt(Dip)SiBr₂ ($\Delta_{Si} = 67.0$ ppm); therefore, this dif-



SCHEME 5 Reaction of dihydrosilane 1b with [PtCl₂(cod)].

ference may suggest the five- or six-coordinate structure of **4a–c**. In addition, theoretical calculation for (2-MeSCH₂C₆H₄)₂SiBr₂ showed a four-coordinate structure as an optimized structure, where the calculated ²⁹Si NMR chemical shift (30.5 ppm) is similar to that of the optimized structure of Ph₂SiBr₂ (36.8 ppm), and very different from the observed values of **4a–c** ($\delta_{si} = -21.9$ to -21.3 ppm). These calculations may also support the five- or six-coordinate structure of **4a–c**.

Reaction of Dihydrosilane **1b** *with* [*PtCl*₂(*cod*)]

Hydrosilanes have been used for the synthesis of transition metal complexes bearing silyl ligands, and some examples for synthesis of silylplatinum(II) complexes by using hydrosilanes have been reported [15,16]. Tilley and a co-worker had reported a reaction of bis(8-quinolyl)methylsilane with [PtCl₂(cod)] in the presence of Et₃N, giving [PtCl{SiMe(8-quinolyl)₂}] [17], whereas we have recently reported that the reaction of [2-(*t*-BuSCH₂)C₆H₄]₃SiH with [PtCl₂(cod)] in the presence of Et₃N affords [PtCl{Si[2-(*t*-BuSCH₂)C₆H₄]₃}] [6]. We examined the reaction of dihydrosilane **1b** with [PtCl₂(cod)] in the presence of Et₃N.

When dihydrosilane 1b was allowed to react with 2.9 molar amounts of $[PtCl_2(cod)]$ in the presence of Et₃N in CH₂Cl₂ at room temperature, bissilylplatinum complex 6b was isolated in 5% yield (Scheme 5). The similar reaction of **1b** with 2.7 molar amounts and an equimolar amount of $[PtCl_2(cod)]$ resulted in the formation of complex mixtures in both cases. This result is in sharp contrast to the reaction of triarylsilanes, $[2-(RSCH_2)C_6H_4]_3SiH$ (R = t-Bu, i-Pr), with [PtCl₂(cod)], giving the corresponding square planar platinum(II) complexes [PtCl{Si[2-(RSCH₂)C₆H₄]₃}] with silvl ligand: Pt = 1:1 in good yields [6,18]. The isolation of bissilylplatinum 6b in low yield may be explained by the less hindered structure of dihydrosilane **1b** compared with the triarylsilane, that is, the 1:1 product of **1b** and [PtCl₂(cod)], [PtCl{SiH[2- $(i-\Pr{SCH_2})C_6H_4]_2$, can further react with **1b** or



FIGURE 1 ORTEP drawing of **6b** with thermal ellipsoids (50% probability). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Pt1–Si1, 2.3127(13); Pt1–S1, 2.4016(13); Si1–Pt1–S1, 94.52(5); Si1–Pt1–Si1*, 82.33(7); S1–Pt1–S1*, 88.69(7).

 $[PtCl_2(cod)]$ due to its less steric hindrance around the platinum and silicon atoms.

The structure of **6b** was determined by NMR and IR spectrometry and X-ray crystallography (Fig. 1). The ¹H NMR signal at 4.89 ppm and the IR absorption at 2052 cm⁻¹ indicated the presence of Si–H bonds, and the X-ray structure showed that the ratio of silyl ligand to metal is 2:1, and **6b** has a square planar structure around the platinum atom (sum of the bond angles around the Pt1 atom = 360°). The two silicon and two sulfur atoms on the platinum center are arranged in cis-form, and the isopropyl groups on the coordinated sulfur atoms and the 2-(isopropylthiomethyl)phenyl groups on the silicon atoms are situated in trans-configuration.

CONCLUSION

Dihydrosilanes tethered with two thioether moieties, [2-(RSCH₂)C₆H₄]₂SiH₂ (**1a**: R = t-Bu; **1b**: R = i-Pr; **1c**: R = Ph), were synthesized by reaction of 2-(RSCH₂)C₆H₄Li with SiHCl₃ followed by hydrogenation using LiAlH₄. The ²⁹Si NMR spectra of **1** showed slight up-field shifts compared with that of Ph₂SiH₂, and this result suggests very weak or no coordination of thioether moieties to the silicon atom. Dihydrosilane **1b** did not react with MeOH, PhCHO, CH₃CO₂H, and 3-NO₂C₆H₄COOH. These low reactivities of **1b** suggest very weak or no activation of the Si–H bonds in **1b**, probably due to very weak or no coordination of thioether moieties to the silicon atom. The corresponding dibromosilanes **4** and diiodosilanes **5** were synthesized by dihalogenation of **1** using NBS and I₂, respectively, whereas the dichlorosilanes **3** were synthesized by reaction of $2-(RSCH_2)C_6H_4Li$ with SiCl₄. Reaction of **1b** with [PtCl₂(cod)] in the presence of Et₃N gave the corresponding bissilylplatinum complex **6b**, the structure of which was determined by NMR and IR spectrometry and X-ray crystallography.

EXPERIMENTAL

General Procedures

All reactions were carried out under an argon atmosphere unless otherwise noted. Tetrahydrofuran (THF) and ether were purified by distillation from sodium diphenylketyl before use. All solvents used in the reactions were purified by the reported methods. Wet column chromatography (WCC) was performed with Merck Silica Gel 60 (70-230 mesh ASTM). The ¹H NMR (500 or 300 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL JNM- λ 500 or JEOL JNM-AL300 spectrometer using $SiMe_4$ (0 ppm) as internal standards. The ^{13}C NMR (126 MHz) and ^{29}Si NMR (99 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL JNM- λ 500 spectrometer using CDCl₃ (77.0 ppm) or C_6D_6 (128.0 ppm) as those for ${}^{13}C$ NMR spectroscopy and SiMe₄ (0 ppm) as internal standards for ²⁹Si NMR spectroscopy. Infrared spectra were recorded on a Shimadzu FTIR-8400S spectrometer. All melting points were determined on a Yanaco micro melting point apparatus MP-J3 and are uncorrected.

Synthesis of 1-Bromo-2-(tert-butylthiomethyl) benzene (**2a**) and Its Isopropyl and Phenyl Derivatives, **2b** and **2c**

A THF suspension (300 mL) of 2-methyl-2propanethiol (14 mL, 0.13 mmol) and sodium hydride (3.0 g, 0.13 mmol) was stirred at room temperature for 1 h. To the reaction mixture, a THF solution of 1-bromo-2-(bromomethyl)benzene [5] (30.0 g, 0.120 mol) was added and then the mixture was refluxed for 16 h. After addition of a saturated aqueous solution of NH₄Cl, the mixture was extracted with ether. The organic layer was dried with anhydrous Na₂SO₄, and the solvents were removed under reduced pressure. The residue was separated by WCC (SiO₂, hexane:ether = 4:1) to afford **2a** [4] (29.1g, 0.112 mol, 94%) as colorless oil.

1-Bromo-2-(isopropylthiomethyl)benzene (2b) and 1-bromo-2-(phenylthiomethyl)benzene (2c) were prepared in a manner similar to those for 2a described above, in the yields of 92% and 95%, respectively. 2b: colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 1.20 (d, ${}^{3}J_{HH} = 6.6$ Hz, 6H), 2.81 (sep, ${}^{3}J_{HH} = 6.6$ Hz, 1H), 3.77 (s, 2H), 7.00 (dd, ${}^{3}J_{HH} = 7.2$, 7.2 Hz, 1H), 7.16 (dd, ${}^{3}J_{HH} = 7.2$, 7.2 Hz, 1H), 7.31 (d, ${}^{3}J_{HH} = 7.2$ Hz, 1H), 7.45 (d, ${}^{3}J_{HH} = 7.2$ Hz, 1H); 13 C NMR (125 MHz, CDCl₃): δ 23.19 (q), 34.80 (d), 35.16 (t), 124.22 (s), 127.28 (d), 128.28 (d), 130.49 (d), 132.83 (d), 138.05 (s). **2c**: colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 4.11 (s, 2H), 6.99 (dd, ${}^{3}J_{HH} = 7.5$, 7.5 Hz, 1H), 7.20 (m, 6H), 7.22 (dd, ${}^{3}J_{HH} = 7.5$, 7.5 Hz, 1H), 7.45 (d, ${}^{3}J_{HH} = 7.5$ Hz, 1H); 13 C NMR (125 MHz, CDCl₃): δ 35.76 (t), 125.21 (d), 125.78 (d), 127.98 (d), 128.75 (d), 129.13 (d), 129.35 (d), 130.23 (d), 132.45 (s), 134.29 (s), 135.61 (d), 140.75 (s).

Synthesis of Bis[2-(tert-butylthiomethyl) phenyl]silane (**1a**) and Its Isopropyl and Phenyl Derivatives, **1b** and **1c**

To an ether solution (50 mL) of 2a (4.50 g, 18.3 mmol), a hexane solution of butyllithium (1.59 M, 11.5 mL, 18.3 mmol) was added at 0°C. After stirring the mixture at this temperature for 2 h, trichlorosilane (1.2 mL, 9.2 mmol) was added at -40° C, and the mixture was warmed to room temperature. LiAlH₄ (0.40 g, 11.7 mmol) was added to the mixture, and the mixture was stirred for 1 h. After addition of a saturated aqueous solution of NH₄Cl, the mixture was extracted with ether and the organic layer was dried with anhydrous Na2SO4. The solvents were removed under reduced pressure, and purification by Kugelrohr distillation (170°C, 0.3 mmHg) gave hydrosilane 1a (1.60 g, 68%). 1a: yellow oil; ¹H NMR (300 MHz, CDCl₃): δ 1.23 (s, 18H), 3.75 (s, 4H), 5.09 (s, ${}^{1}J_{\text{HSi}} = 204$ Hz, 2H), 7.12 (dd, ${}^{3}J_{\text{HH}} =$ 7.5, 7.5 Hz, 2H), 7.29 (dd, ${}^{3}J_{\text{HH}} = 7.5$, 7.5 Hz, 2H), 7.36 (d, ${}^{3}J_{\text{HH}} = 7.5$ Hz, 2H), 7.41 (d, ${}^{3}J_{\text{HH}} = 7.5$ Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 30.66 (q), 34.1 (t), 42.94 (s), 126.40 (d), 129.55 (d), 130.33 (d), 131.24 (s), 137.43 (d), 144.26 (s); ²⁹Si NMR (99 MHz, CDCl₃) δ -41.29.

Bis[2-(isopropylthiomethyl)phenyl]silane (**1b**) bis[2-(phenylthiomethyl)phenyl]silane (1c)and were prepared in a manner similar to those for 1a described above, in the yields of 59 and 55%, respectively. 1b: yellow oil; ¹H NMR (500 MHz, CDCl₃): δ 1.17 (d, ${}^{3}J_{\rm HH}$ = 6.5 Hz, 12H), 2.71 (sep, ${}^{3}J_{\rm HH}$ = 6.5 Hz, 2H), 3.78 (s, 4H), 5.13 (s, ${}^{1}J_{\text{SiH}}$ = 204 Hz, 2H), 7.23 (dd, ${}^{3}J_{\text{HH}} = 7.5$, 7.5 Hz, 2H), 7.35 (dd, ${}^{3}J_{\text{HH}}$ = 7.5, 7.5 Hz, 2H), 7.38 (d, ${}^{3}J_{HH}$ = 7.5 Hz, 2H), 7.52 (d, ${}^{3}J_{HH} = 7.5$ Hz, 2H); ${}^{13}C$ NMR (125 MHz, CDCl₃): δ 23.10 (q), 34.73 (d), 36.02 (t), 126.40 (d), 129.20 (d), 130.10 (d), 131.60 (s), 137.61 (d), 144.71 (s); ²⁹Si NMR (99 MHz, CDCl₃): δ –40.86. **1c**: ¹H NMR (500 MHz, CDCl₃): δ 4.14 (s, 4H), 5.11 (s, ${}^{1}J_{\text{SiH}} =$ 204 Hz, 2H), 7.22 (m, 12H), 7.30 (dd, ${}^{3}J_{HH} = 7.0$, 7.0 Hz, 2H), 7.30 (dd, ${}^{3}J_{\rm HH} =$ 7.0, 7.0 Hz, 2H), 7.51 (d, ${}^{3}J_{\rm HH} =$ 7.0 Hz, 2H); 13 C NMR (125 MHz, CDCl₃): δ 39.66 (t), 126.30 (d), 126.86 (d), 128.72 (d), 129.50 (d), 129.79 (d), 130.38 (d), 131.34 (s), 136.10 (s), 137.57 (d), 143.29 (s); 29 Si NMR (99 MHz, CDCl₃) δ -40.12.

Synthesis of Bis[2-(tert-butylthiomethyl)phenyl] dichlorosilane (**3a**) and Its Isopropyl Derivative **3b**

To an ether solution (100 mL) of **2b** (10.1 g, 40.8 mmol), a hexane solution of butyllithium (1.57 M, 26.0 mL, 40.8 mmol) was added at 0°C. After stirring the mixture at this temperature for 2 h, tetrachlorosilane (2.4 mL, 20.6 mmol) was added at -40° C and the mixture was warmed to room temperature. After stirring for 16 h, the reaction mixture was filtered and the solvents of the filtrate were removed under reduced pressure. Purification by Kugelrohr distillation (165°C, 0.3 mmHg) gave bis[2-(isopropylthiomethyl)phenyl]dichlorosilane3b (5.00 g, 58%). 3b: yellow oil; ¹H NMR (500 MHz, $C_6 D_6$): δ 0.93 (d, ${}^{3}J_{HH} = 7.0$ Hz, 12H), 2.42 (sep, ${}^{3}J_{HH}$ = 7.0 Hz, 2H), 3.83 (s, 4H), 6.99 (dd, ${}^{3}J_{\text{HH}} = 7.5$, 7.5 Hz, 2H), 7.12 (dd, ${}^{3}J_{\rm HH} =$ 7.5, 7.5 Hz, 2H), 7.49 (d, ${}^{3}J_{\text{HH}} = 7.5$ Hz, 2H), 8.07 (d, ${}^{3}J_{\text{HH}} = 7.5$ Hz, 2H); ²⁹Si NMR (99 MHz, C_6D_6): δ –3.2.

Dichlorosilane (**3a**) was prepared in a manner similar to those for **3b** described above, in the yields of ~20%, although the isolation of **3a** was unsuccessful. **3a**: yellow oil; ¹H NMR (300 MHz, C₆D₆): δ 1.15 (s, 18H), 3.81 (s, 4H), 6.86 (dd, ³J_{HH} = 7.5, 7.5 Hz, 2H), 7.04 (dd, ³J_{HH} = 7.5, 7.5 Hz, 2H), 7.42 (d, ³J_{HH} = 7.5 Hz, 2H), 8.01 (d, ³J_{HH} = 7.5 Hz, 2H); ²⁹Si NMR (99 MHz, C₆D₆): δ – 3.6.

Synthesis of Dibromobis[2-(tert-butylthiomethyl)phenyl]silane (**4a**) and Its Isopropyl and Phenyl Derivatives, **4b** and **4c**

A mixture of **1a** (257 mg, 0.66 mmol) and *N*bromosuccinimide (254 mg, 1.43 mmol) in benzene (3 mL) was stirred at room temperature for 30 min. After removal of the resulting succinimide by filtration under argon atmosphere, the solvent of the filtrate was evaporated under reduced pressure to give **4a** (340 mg, 0.62 mmol, 94%). **4a**: yellow oil; ¹H NMR (300 MHz, C₆D₆): δ 1.11 (s, 18H), 4.00 (s, 4H), 7.10 (dd, ³*J*_{HH} = 7.5, 7.5 Hz, 2H), 7.20 (dd, ³*J*_{HH} = 7.5, 7.5 Hz, 2H), 7.72 (d, ³*J*_{HH} = 7.5 Hz, 2H), 8.26 (d, ³*J*_{HH} = 7.5 Hz, 2H); ¹³C NMR (125 MHz, C₆D₆): δ 30.02 (q), 32.00 (t), 42.65 (s), 127.13 (d), 131.08 (d), 131.83 (d), 132.34 (s), 136.06 (d), 144.09 (s); ²⁹Si NMR (99 MHz, C₆D₆): δ –21.12.

Dibromobis[2-(isopropylthiomethyl)phenyl]silane (4b) and dibromobis[2-(phenylthiomethyl)phenyl]silane (4c) were prepared in a manner similar to those for 4a described above, in the yields of 96% and 95%, respectively. 4b: yellow oil; ¹H NMR (500 MHz, $C_6 D_6$): δ 0.91 (d, ${}^3J_{HH} = 7.0$ Hz, 12H), 2.40 (sep, ${}^{3}J_{\rm HH} = 7.0$ Hz, 2H), 3.85 (s, 4H), 7.01 (dd, ${}^{3}J_{\text{HH}} =$ 7.5, 7.5 Hz, 2H), 7.10 (dd, ${}^{3}J_{\text{HH}} =$ 7.5, 7.5 Hz, 2H), 7.50 (d, ${}^{3}J_{\text{HH}} = 7.5$ Hz, 2H), 8.19 (d, ${}^{3}J_{\text{HH}} = 7.5$ Hz, 2H); 13 C NMR (125 MHz, C₆D₆): δ 23.15 (q), 35.66 (d), 36.00 (t), 128.54 (d), 128.71 (d), 131.80 (d), 132.27 (s), 136.37 (d), 144.41 (s); ²⁹Si NMR (99 MHz, C_6D_6): δ –21.30. 4c: yellow oil; ¹H NMR (500 MHz, C₆D₆): δ 4.30 (s, 4H), 6.98 (m, 6H), 7.08 (m, 4H), 7.25 (m, 4H), 7.45 (d, ${}^{3}J_{\text{HH}} = 7.5$ Hz, 2H), 8.20 (d, ${}^{3}J_{\text{HH}} = 7.5 \text{ Hz}$, 2H); ${}^{13}\text{C}$ NMR (125 MHz, C_6D_6): δ 39.10 (t), 126.34 (d), 127.58 (d), 128.54 (d), 129.55 (d), 130.62 (d), 131.43 (s), 132.47 (d), 136.37 (d), 136.71 (s), 142.86 (s); ²⁹Si NMR (99 MHz, $C_6 D_6$): $\delta -21.28$.

Bis[2-(isopropylthiomethyl)phenyl]silanediol: ¹H NMR (500 MHz, CDCl₃): δ 1.04 (d, ³*J*_{HH} = 7.0 Hz, 12H), 2.62 (sep, ³*J*_{HH} = 7.0 Hz, 2H), 3.95(s, 4H), 5.37 (s, 2H), 7.09 (dd, ³*J*_{HH} = 7.5, 7.5 Hz, 2H), 7.15 (dd, ³*J*_{HH} = 7.5, 7.5 Hz, 2H), 7.23 (d, ³*J*_{HH} = 7.5 Hz, 2H), 8.04 (d, ³*J*_{HH} = 7.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 23.62 (q), 36.08 (d), 36.78 (t), 127.21 (d), 130.74 (d), 130.94 (d), 136.55 (s), 137.22 (d), 144.40 (s); ²⁹Si NMR (99 MHz, CDCl₃): δ -26.63.

Synthesis of Bis[2-(tert-butylthiomethyl)phenyl] diiodosilane (**5a**) and Its Isopropyl Derivative **5b**

A mixture of **1a** (152 mg, 0.391 mmol) and iodine (99 mg, 0.390 mmol) in benzene (3 mL) was stirred at room temperature for 12 h. Removal of the solvent under reduced pressure gave **5a** (237 mg, 0.370 mmol, 95%). **5a**: yellow oil; ¹H NMR (300 MHz, C_6D_6): δ 1.11 (s, 18H), 3.50 (s, 4H), 7.60 (m, 6H), 7.25 (d, ³J_{HH} = 7.5 Hz, 2H); ¹³C NMR (125 MHz, C_6D_6): δ 28.91 (q), 30.36 (t), 34.75 (s), 127.03 (d), 127.02 (d), 128.26 (d), 128.54 (s), 128.75 (d), 129.37 (s); ²⁹Si NMR (99 MHz, C_6D_6): δ – 39.91.

Bis[2-(isopropylthiomethyl)phenyl]diiodosilane (**5b**) was prepared in a manner similar to those for **5a** described above, in the yields of 96%. **5b**: yellow oil; ¹H NMR (500 MHz, C₆D₆): δ 0.91 (d, ³J_{HH} = 7.0 Hz, 12H), 2.38 (sep, ³J_{HH} = 7.0 Hz, 2H), 3.85(s, 4H), 6.97 (dd, ³J_{HH} = 7.5, 7.5 Hz, 2H), 7.08 (dd, ³J_{HH} = 7.5, 7.5 Hz, 2H), 7.46 (d, ³J_{HH} = 7.5 Hz, 2H), 8.39 (d, ³J_{HH} = 7.5 Hz, 2H); ¹³C NMR (125 MHz, C₆D₆): δ 23.31 (q), 35.77 (d), 35.97 (t), 127.24 (d), 128.19 (d), 131.29 (d), 131.89 (s), 137.54 (d), 143.67 (s); ²⁹Si NMR (99 MHz, C₆D₆): δ -39.50.

Reaction of **1b** *with* [*PtCl*₂(*cod*)]

A dichloromethane solution (6 mL) of **1b** (161 mg, 0.45 mmol), [PtCl₂(cod)] (57 mg, 0.15 mmol), and triethylamine (0.18 mL, 1.30 mmol) was stirred at room temperature for 3 d. After addition of a saturated aqueous solution of NH₄Cl and NaCl, the mixture was extracted with dichloromethane. The organic layer was dried with Na₂SO₄, and the solvent of the mixture was removed under reduced pressure. The resulting yellow solid (205 mg) was recrystallized from hexane/dichloromethane to give 6b (7 mg, 0.0077 mmol, 5%) as pale yellow crystals. 6b: pale yellow crystals; mp 127°C (decomp.); ¹H NMR (500 MHz, CDCl₃): δ 1.16 (d, ${}^{3}J_{\text{HH}} = 6.2$ Hz, 12H), 1.19 (d, ${}^{3}J_{\text{HH}} = 6.2$ Hz, 12H), 2.82 (m, 4H), 3.76 (d, ${}^{2}J_{\rm HH} = 13.3$ Hz, 4H), 4.10 (d, ${}^{2}J_{\rm HH} = 13.3$ Hz, 4H), 4.89 (s, 2H), 7.05–7.28 (m, 12 H), 7.85 (d, 4H); ²⁹Si NMR (99.3 MHz, CDCl₃): δ -7.82 (¹*J*_{SiPt} = 1465 Hz); IR (KBr) 2052 (Si-H stretch) cm⁻¹.

X-Ray Structural Analysis of 6b

Single crystals of 6b suitable for X-ray structural analysis were obtained by slow recrystallization from hexane/CH₂Cl₂. The crystal was mounted on a glass fiber. The intensity data were collected on Rigaku R-AXIS IV++ diffractometer with graphite monochromated Mo K α radiation (λ = 0.71070 Å). The structure was solved by direct methods (SHELXS-97 [19]) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97 [19]). All the non-hydrogen atoms were refined anisotropically, and all hydrogens were placed using AFIX instructions. The structural data are shown in Table 1. CCDC No. 790749 for 6b contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Theoretical Calculations

The geometries of $(2-\text{MeSCH}_2C_6H_4)_2\text{SiBr}_2$ and Ph_2SiBr_2 were optimized by using the Gaussian 03 program [20] with density functional theory at the B3LYP/6-31G(d) level. The ²⁹Si NMR chemical shifts were calculated by GIAO-B3LYP with the 6-311+G(2d,p) basis sets.

TABLE 1 Crystal Data and Refinement Details for 6b

6b Empirical formula C₄₀H₅₄PtS₄Si₂ Formula weight 914.34 Temperature 123(2) K Monoclinic Crystal system Space group $C_{2/c}$ (#15) a (Å) 13.721(2) b (Å) 14.4201(17) c (Å) 20.395(3) α (°) 90 98.576(2) β (°) γ (°) 90 $V(Å^3)$ 3990.1(10) Ζ 4 D_{calc} (Mg m⁻³) 1.522 Absorption coefficient (mm⁻¹) 3.814 Crystal size (mm³) $0.30\times0.20\times0.10$ 2.39-25.50° θ range Number of reflections 13,137 measured Number of independent 3705 reflections Rint 0.0226 Completeness 99.5% Data/restraints/parameters 3705 / 0 / 213 Goodness-of-fit on F^2 1.356 Final R indices $[I > 2\sigma(I)]^{a}$ $R_1 = 0.0425 \ wR_2 = 0.0815$ R indices (all data)^a $R_1 = 0.0434 \ wR_2 = 0.0819$ Largest difference peak and 0.842 and -1.208 hole (e $Å^{-3}$)

 ${}^{a}R_{1} = \Sigma \|F_{o}| - |F_{c}||/\Sigma |F_{o}|, wR_{2} = [(\Sigma w(F_{o}^{2} - F_{c}^{2})^{2}/\Sigma w(F_{o}^{2})^{2}]^{1/2}.$

SUPPORTING INFORMATION

¹H NMR spectra of **1a–c**, **3b**, **4a–c**, and **5a**, **b**, ¹³C NMR spectra of **1b**, **c**, **3b**, and **5a**, **b**, and atomic coordinates for the calculated molecules, $(2-\text{MeSCH}_2\text{C}_6\text{H}_4)_2\text{SiBr}_2$ and Ph_2SiBr_2 are available from the corresponding author (ntakeda@chembio.gunma-u.ac.jp) on request.

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