Studies on Construction and Photophysical Properties of π-Conjugated Compounds Containing Double Bonds of Heavier Group 14 Elements

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Contents

General Introduction ........................................................................................................... 1

Chapter 1

1.1 Introduction ................................................................................................................. 12

1.2 Result and Discussion

1.2.1. Synthesis of (E)-1,2-Bis(thiophen-2-yl)disilene (1) ........................................... 16

1.2.2. Synthesis of (E)-1,2-bis(2,2’-bithiophen-5-yl)disilene (2) ...................... 18

1.2.3. Molecular Structures of 1 and 2 ......................................................................... 19

1.2.4. Photophysical Properties of 1 and 2 ................................................................. 24

1.2.5. Theoretical Calculations of 1 and 2 ................................................................. 27

1.3 Conclusion .................................................................................................................. 31

1.4 Experimental Section

1.4.1. General Procedures ............................................................................................... 32

1.4.2. X-Ray Crystallographic Analysis ....................................................................... 35

1.5 References .................................................................................................................. 37

Chapter 2

2.1 Introduction ................................................................................................................ 40

2.2 Result and Discussion

2.2.1. Reactions of (Eind)BrSi=SiBr(Eind) (1a) with NHCs ..................................... 43

2.2.2. Reactions of (Eind)SiHBr₂ (4a) with NHCs ...................................................... 46

2.2.3. Reactions of (Eind)SiH₂Cl (5a) with NHCs ...................................................... 48

2.3 Conclusion .................................................................................................................. 51

2.4 Experimental Section

2.4.1. General Procedures .............................................................................................. 52
Chapter 3

3.1 Introduction........................................................................................................60

3.2 Result and Discussion

3.2.1. Synthesis of (E)-(Eind)XGe=GeX(Eind) [X = Br (1) and Cl (2)]...63
3.2.2. Molecular Structures of 1 and 2.................................................................65
3.2.3. Photophysical Properties of 1 and 2..........................................................67
3.2.4. Conversion to Halogermynoids.................................................................71
3.2.5. Synthesis of 1,2-Diphenyldigermene (7) .............................................73
3.2.6. Theoretical Studies of 7............................................................................75

3.3 Conclusion........................................................................................................76

3.4 Experimental Section

3.4.1. General Procedures....................................................................................77
3.4.2. X-Ray Crystallographic Analysis............................................................81
3.4.3. UV-Visible Measurements.......................................................................83

3.5 References.......................................................................................................84

Publication List.....................................................................................................88

Other Publication List..........................................................................................90

Acknowledgments
General Introduction

As shown in the periodic table (Figure 1), silicon is located just below carbon in the Group 14 elements. However, carbon and silicon have different roles and functions in nature. Carbon is a central element in the organic substances that constitute the body of all living things. Silicon is a key element of inorganic substances that constitute the earth’s crust. In our lives, silicon is widely used in glass, semiconductors, concrete, ceramics, etc. Interestingly, there is no organosilicon material with C–Si bonds in nature except for silicon carbide in meteorites. Accordingly, all organosilicon compounds are an artificial substance created by human technology.

![Figure 1 Periodic table.](image)

As shown in Figure 2, various allotropes of carbon, such as diamond, graphite, fullerenes, and carbon nanotubes, are known as a stable material, which consist of the $sp^3$- or $sp^2$-hybridized carbon atoms. In contrast, the stable form of silicon only possesses a diamond-type structure based on the formally $sp^3$-hybridized silicon atoms. An important question arises whether $sp^2$-hybridized silicon atoms can exist as a stable substance. Recently, the silicon analogue of graphene, *i.e.*, silicene, has attracted a lot of attention from both experimentalists and theoreticians, as a new two-dimensional allotrope of silicon.\(^1\)\(^-\)\(^3\) Theoretical investigations predict that repeating units in pure nanosheets of silicon do not exhibit a planar hexagonal geometry like graphene but a non-
classical propellane motif, which can be explained by the instability associated with $sp^2$-hybridized silicon atoms.\(^4\)

![Figure 2](image)

**Figure 2** Allotropes of carbon and silicon.

Generally, the Si–Si $\pi$-bond is much weaker than the C–C $\pi$-bond. This is essentially due to the less effective overlap of the two adjacent 3p orbitals relative to that of the 2p orbitals as shown in Figure 3, corresponding to the greater covalent atomic radius of silicon [$1.11(2)$ Å] than that of carbon [$sp^3$-C; 0.76(1), $sp^2$-C; 0.73(2), and $sp$-C; 0.69(1) Å].\(^5\)

![Figure 3](image)

**Figure 3** Size of s and p orbitals.
In 1981, West, Fink, and Michl demonstrated for the first time that disilene \((R_2Si=SiR_2)\) (A in Figure 4), the silicon analogue of alkene, can be created based on the concept of kinetic stabilization using sterically large substituents, protecting the highly reactive Si=Si double bond, which produced a significant change in the main group chemistry.\(^6\)–\(^{11}\)

![Figure 4](image)

**Figure 4** The disilene A.

After the finding of this isolatable disilene A, a variety of unsaturated silicon compounds have been successfully obtained by taking advantage of the steric effects of the bulky protecting groups.\(^{12}\)–\(^{22}\) Recent representative examples are shown in Figure 5. Since 2000, silaaromatics (B),\(^{23}\)–\(^{25}\) trisilaallenes (\(R_2Si=Si=SiR_2\)) (C),\(^{26}\)\(^{27}\) and disilynes (RSi=SiR) (D)\(^{28}\)–\(^{31}\) have been isolated using the appropriately designed bulky aryl, alkyl, and silyl substituents, respectively. Also, a tricyclic aromatic valence isomer of hexasilabenzene (E)\(^{32}\) and a disilicon(0) fragment stabilized by the \(N\)-heterocyclic carbenes (NHCs) (F)\(^{33}\) were synthesized as stable crystalline compounds. In 2011, Matsuo and Tamao reported the synthesis of a cyclobutadiene (CBD) silicon analog, i.e., tetrasilacyclobutadiene (G), with a planar rhombic charge-separated structure originating from the polar Jahn-Teller distortion.\(^{33}\) This is the first persila[n]annulene compound, (SiR)\(_n\) (\(n\) is an even number equal to or greater than 4), with a cyclic structure consisting of the formally \(sp^2\)-hybridized silicon atoms, which will open a new facet of silicon \(\pi\)-science.
Although the fundamental chemistry of unsaturated silicon compounds has been steadily established year-by-year, the functions and applications of the Si–Si π-bonds consisting of the 3pπ electrons on the formally sp²-hybridized silicon atoms have rarely been explored. In the main group element chemistry, recent synthetic efforts have been directed toward investigating the combination of the multiple bonds of the heavier main group elements and the carbon π-electron systems due to their unique electronic properties and potentially useful technological applications for organic electronics, which would offer a new avenue to functional organoelement materials. However, this chemistry always faces a formidable challenge. While the sufficient steric effects of the bulky substituents are crucial in protecting the highly reactive heavier multiple bonds, it may cause twisting of the π-framework, which prevents the preferred extension of the π-conjugation over the skeleton.

**Figure 5** Recent examples of unsaturated silicon compounds.
In order to further develop the chemistry of unsaturated silicon compounds toward advanced materials science and technology, Matsuo and Tamao have developed a new series of fused-ring bulky 1,1,3,3,5,5,7,7-octa-R-substituted s-hydrindacen-4-yl groups, called the “Rind” groups, as shown in Figure 6, where R denotes the initial of the substituents on the benzylic positions of the hydrindacene skeleton.46

Figure 6 Rind groups.

The Rind groups are giant aryl hydrocarbon substituents but can be easily prepared by organic synthetic methods, including the intramolecular Friedel-Crafts cyclization.47 Various R groups (R1, R2, R3, and R4 groups) can be introduced at the four benzylic positions of the hydrindacene skeleton. The peripheral R1 and R2 groups can control their physical properties such as crystallinity and solubility. The proximal R3 and R4 groups can directly change the steric effects of the Rind groups. The Rind groups have a rigid structure based on the fused-ring system and exhibit a high chemical stability due to the full substitution at all the benzylic positions.

The term “Rind” in English describes the thick outer skin of some types of fruits such as an orange and melon. This is fully in accordance with the research concept, i.e., Rind can keep the inside fresh. In fact, the Rind groups provided great opportunities to study a variety of low-coordinate compounds of the main group elements34,48–62 and coordinatively unsaturated transition metal complexes.63–71
This dissertation is concerned with the construction and photophysical properties of π-conjugated compounds containing double bonds of heavier group 14 elements.

In Chapter 1, the author has demonstrated that the Si=Si double bond can conjugate with thiophene rings by taking advantage of the steric effects using the fused-ring bulky Eind groups. The thienyl- and bithienyl-substituted disilenes can be isolated as air-stable orange and purple crystals, respectively, and their structural features have been thoroughly confirmed by X-ray crystallography. The photophysical properties and theoretical calculations provide clear evidence for the effective π-conjugation between the Si=Si chromophore and thiophene rings, originating from the essentially coplanar 1,2-bis(thienyl)disilene and 1,2-bis(bithienyl)disilene skeletons.

![Figure 7](image)

**Figure 7** 1,2-Bis(thienyl)disilene and 1,2-bis(bithienyl)disilene.

In Chapter 2, the author has synthesized the NHC-coordinated silicon species bearing the bulky Eind group. The mono-NHC adduct of the arylbromosilylene and the bis-NHC adduct of the formal arylsilyliumylidene cation have been obtained by two different synthetic procedures, i.e., the NHC-induced fragmentation of the 1,2-dibromodisilene and the dehydrobromination of the dibromohydrosilane with NHCs. The mono-NHC adducts of the arylhydrosilylenes have also been obtained by the dehydrochlorination of the arylchlorodihydrosilane with NHCs.

![Figure 8](image)

**Figure 8** NHC-coordinated silicon species bearing the bulky Eind group.
The availability of the three kinds of well-defined NHC-coordinated silicon compounds in quantity opens the door to the full experimental clarification of their electronic and bonding nature as well as their potential uses as new synthetic reagents and new building units in the field of advanced organosilicon materials.

In Chapter 3, the author has developed a novel synthetic procedure for the 1,2-dihalodigermenes, *i.e.*, a ligand redistribution reaction between a diaryldigermene and GeX₂·dioxane (X = Br, Cl). The 1,2-dihalodigermenes have a Ge=Ge double bond character in the crystalline state, but dissociate into halogermylenes in solution. The author has demonstrated the formation and isolation of the bromogermylenoids, which has been obtained by the addition of MBr (M = Li, K) to the THF solution of the bromogermylene. The author has also studied the synthesis, structure, and photophysical properties of the 1,2-diphenyldigermene as the first π-conjugated digermene compound.

![Synthesis and reactions of 1,2-dihalodigermenes](image)

**Figure 9** Synthesis and reactions of 1,2-dihalodigermenes.
References


Chapter 1

Synthesis, Structures, and Photophysical Properties of π-Conjugated Disilene Compounds with Thienyl- and Bithienyl Groups

1.1 Introduction

As described in the General Introduction, recently π-conjugated frameworks containing unsaturated bonds of the heavier main-group elements have attracted much attention from the viewpoints of their potentially useful properties and unique functions. In organosilicon chemistry, Scheschkewitz and Tamao reported the first model compounds of the disilene analogs of the oligo(p-phenylenevinylene) (Si–OPVs; A–C in Figure 1–1) in 2007. After that, a variety of π-electron systems comprising a Si=Si unit have been examined by taking advantage of kinetic stabilization using the appropriate bulky substituents. Especially, the fused-ring bulky Eind groups (Eind = 1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl) more efficiently protect the highly reactive Si=Si double bonds compared to the other protecting groups, producing a highly coplanar Si–OPV main chain owing to their perpendicular orientation and the interlocking proximate ethyl side chains above and below the π-skeletons. The resulting π-systems should be suitable for studying the intrinsic conjugation properties between the silicon-3pπ and carbon-2pπ electrons. Actually, the 1,4-bis(disilenyl)benzene C exhibits an orange fluorescence at ambient temperature because of the effective π-conjugation over the rigid framework.

Following the initial achievements of the model compounds of Si-OPVs (A and C), Matsuo and Tamao designed new π-conjugated disilenes having two π-extended aromatic groups on the Si=Si unit. The two regioisomers of 1,2-bis(naphthyl)disilenes, *i.e.*, (E)-1,2-bis(1-naphthyl)disilene (D) and (E)-1,2-bis(2-naphthyl)disilene (E) were obtained as red crystals, which were found to be air-stable in the solid state for more than several years, thus indicating the remarkable protection ability of the fused-ring Eind groups. The disilenes (D and E) exhibit a distinct absorption and emission at room temperature both in solution and solid state, which originate from the coplanar 1,2-dinaphthyl disilene π-skeletons. The density functional theory (DFT) calculations indicate
the substantial contribution of the $\pi^\ast(\text{Si} \cdots \text{Si}) \cdots \pi^\ast(\text{naphthalene})$ conjugation. The Si=Si moiety has higher highest occupied molecular orbital (HOMO) and lower lowest unoccupied molecular orbital (LUMO) levels compared to the C=C counterpart. Accordingly, the Si=Si unit exhibits a narrower HOMO–LUMO energy gap relative to that of the C=C fragment. Thus, the outstanding air and thermal stability of the disilene compounds would open up new opportunities for application in a range of organic electronic devices. Actually, the disilene E can emit light in an organic light-emitting diode (OLED), which is the first observation of electroluminescence (EL) from a disilene molecule in OLEDs, providing a new avenue to the applied chemistry of the main-group elements.

For the development of further $\pi$-extended disilene derivatives with polycyclic aromatic groups, Matsuo and Tamao examined the introduction of two pyrenyl groups to the Si=Si core. However, only the Z isomer of 1,2-bis(1-pyrenyl)disilene (F) could be isolated as purple crystals. The X-ray crystallography of F demonstrated that the two 1-pyrenyl groups and the two Eind groups fit together in a gear-like arrangement around the disilene unit; the two pyrene rings interact with an intramolecular $\pi$-$\pi$ stacking. The disilene F exhibits a distinct $\pi(\text{Si} \cdots \text{Si}) \rightarrow \pi^\ast(\text{pyrene})$ intramolecular charge-transfer (ICT) emission at room temperature, which may be based on the two pyrene rings twisted from the Si=Si fragment. In this context, Iwamoto and Kira reported a unique ICT absorption in the (9-anthryl)trialkyldisilene G, where the anthracene ring is orthogonal to the Si=Si double bond. In 2017, Iwamoto et al. reported the trialkyldisilenes with heteroaromatic rings such as thiophene, bithiophene, and acridine, one of which also displays a distinct ICT absorption. Also in 2017, Scheschkewitz et al. reported the synthesis and characterization of some new (oligo)aromatic species with one or two Si=Si double bonds.
In this chapter, the author describes a new type of $\pi$-conjugation between a Si=Si double bond and thiophene units. Previously, Matsuo and Tamao examined the synthesis and electronic properties of oligothiophenes ($\text{H-\text{J}}$) with the EMind groups (EMind = 1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-$s$-hydrindacen-4-yl) (Figure 1–2). The orthogonal arrangement of the EMind groups can produce a highly coplanar oligothiophene framework. These results prompted the author to study the possibility of constructing $\pi$-conjugated systems containing both disilene and thiophene units, incorporating the Rind groups. This chapter summarizes the results of the synthesis, characterization, and photophysical properties of ($E$)-1,2-bis(thiophen-2-yl)disilene (I).
and \((E)\)-1,2-bis(2,2'-bithiophen-5-yl)disilene (2), supported by the bulky Eind groups, as model compounds of disilene-thiophene copolymers. The theoretical studies of 1 and 2 using DFT calculations are also described.

**Figure 1–2** Oligothiophenes having EMind groups.
1.2 Results and Discussion

1.2.1 Synthesis of (E)-1,2-Bis(thiophen-2-yl)disilene (1).

Scheme 1–1 shows the synthesis of the disilene 1. The Eind-substituted tribromosilane, (Eind)SiBr₃ (3), is a starting material, which can be obtained by the bromination of the Si–H bonds of the Eind-substituted trihydrosilane, (Eind)SiH₃, with N-bromosuccinimide (NBS) in hexane. The reaction of 3 with 2-thienyllithium in THF afforded the 2-thienyl-substituted dibromosilane 4 as a colorless solid in 50% yield.

Scheme 1–1 Synthesis of 1.

The ¹H nuclear magnetic resonance (NMR) spectrum of 4 in C₆D₆ showed a set of three characteristic signals of the 2-thienyl group. Thus, one doublet of doublets at 6.66 ppm (J = 3.2 and 4.6 Hz) and two doublets at 7.05 (J = 4.6 Hz) and 7.28 ppm (J = 3.2 Hz) were found in the aromatic region, along with the singlet at 6.91 ppm due to the p-aryl proton of the Eind group. In the ²⁹Si NMR spectrum of 4 in C₆D₆, only one resonance appeared at −23.7 ppm. As shown in Figure 1–3, the structure of 4 was clearly determined by X-ray crystallography. In the crystal, the thiophene ring atoms (C29, C30, C31, C32, and S1) are disordered over the two positions with occupancy factors of ca. 0.86/0.14. Such a disordered thiophene fragment due to a 180° rotation about the exocyclic bond is often found in the crystal structure of the molecules containing a thiophene ring.

The reductive coupling of 4 with a slight excess amount (2.2 equiv) of lithium naphthalenide (LiNaph) in THF led to the isolation of an orange powder of 1,2-bis(thiophen-2-yl)disilene (1) in 37% yield. The characterization of 1 was based on NMR spectroscopy and high-resolution electrospray ionization mass spectrometry (HR-ESI-MS), as shown in Table 1–1. In the ¹H NMR spectrum of 1 in C₆D₆, one set of three signals of the 2-thienyl groups was observed similar to that of 4, appearing at 6.73 (doublet of doublets, J = 4.6 and 3.2 Hz), 7.01 (doublet, J = 4.6 Hz), and 7.14 ppm (doublet, J = 3.2 Hz), along with the signal due to the aryl proton of the Eind group at...
6.97 ppm (singlet). The $^{29}$Si NMR spectrum of 1 in C$_6$D$_6$ showed one signal at 51.5 ppm, comparable to that of (Eind)PhSi=SiPh(Eind) B (63.2 ppm),\textsuperscript{3} being in the range of those for typical aryl-substituted disilenes.\textsuperscript{7,14}

![Molecular structure of 4. The thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms and disordered C and S atoms are omitted for clarity. Selected distances (Å) and angles (deg): Si1–Br1 = 2.2390(13), Si1–Br2 = 2.2370(13), Si1–C1 = 1.890(4), Si1–C29 = 1.844(5), Br1–Si1–Br2 = 96.91(5), Br1–Si1–C1 = 122.98(13), Br1–Si1–C29 = 101.3(3), Br2–Si1–C1 = 116.14(13), Br2–Si1–C29 = 112.86(18), C1–Si1–C29 = 105.9(3).](image)

**Figure 1–3** Molecular structure of 4. The thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms and disordered C and S atoms are omitted for clarity. Selected distances (Å) and angles (deg): Si1–Br1 = 2.2390(13), Si1–Br2 = 2.2370(13), Si1–C1 = 1.890(4), Si1–C29 = 1.844(5), Br1–Si1–Br2 = 96.91(5), Br1–Si1–C1 = 122.98(13), Br1–Si1–C29 = 101.3(3), Br2–Si1–C1 = 116.14(13), Br2–Si1–C29 = 112.86(18), C1–Si1–C29 = 105.9(3).

**Table 1–1** X-ray Structural Parameters, NMR Spectroscopic Data, and HR-ESI-MS Data for 1 and 2, together with Compounds B and C.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>B\textsuperscript{a}</th>
<th>C\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si=Si/Å</td>
<td>2.1712(11)</td>
<td>2.1584(9)</td>
<td>2.1593(16)</td>
<td>2.156(2)</td>
</tr>
<tr>
<td>$\theta$/deg\textsuperscript{b}</td>
<td>19.12(12), 13.5(6)</td>
<td>5.44(10)</td>
<td>2.7(3)</td>
<td>0.7(3), 2.7(3)</td>
</tr>
<tr>
<td>$^{29}$Si(δ)/ppm</td>
<td>51.5</td>
<td>51.7</td>
<td>63.2</td>
<td>–</td>
</tr>
<tr>
<td>$M_{\text{ex}}$\textsuperscript{c}</td>
<td>984.6461</td>
<td>1148.6231</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$M_{\text{th}}$\textsuperscript{d}</td>
<td>984.6492</td>
<td>1148.6246</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Data from ref 3. \textsuperscript{b}Bent angle $\theta$ is defined as the angle between the axis through the Si=Si bond and C–Si–C plane. \textsuperscript{c}Experimental values. \textsuperscript{d}Theoretical values.
The author found that the disilene 1 is air-stable in the solid state for at least several months, which was confirmed by $^1$H NMR spectroscopy. A dilute THF solution of 1 (ca. $10^{-5}$ mol L$^{-1}$) gradually decomposed upon exposure to air with a half-lifetime of ca. 60–70 min as monitored by ultraviolet-visible (UV-vis) absorption spectroscopy. The observed half-lifetime (60–70 min) is longer than that of (Tip)$_2$Si=Si(Tip)$_2$ (Tip = 2,4,6-triisopropylphenyl; 17 min), but shorter than those of B, D, and E (ca. 2–4 h). Compound 1 is the first isolatable disilene compound bearing an aromatic heterocyclic group. The structure and electronic properties of 1 are described in the latter part of this chapter compared to those of 2.

1.2.2 Synthesis of (E)-1,2-Bis(2,2'-bithiophen-5-yl)disilene (2).

As described in the Introduction of this chapter, Matsuo and Tamao previously reported the synthesis of oligothiophenes up to the dodecamer (J) supported by the bulky EMind groups (Figure 1–2). The perpendicular orientation of the EMind group effectively induce a coplanar array of one or two neighboring thiophene rings. Based on these former results, the author set out to investigate the further π-extended disilene 2 having two bithiophene units on the Si=Si core (Scheme 1–2).

![Scheme 1–2 Synthesis of 2.](image)

Bithienyllithium was prepared by the reaction of 2,2'-bithiophene with $^+$BuLi in THF. The treatment of 3 with bithienyllithium resulted in the formation of the bithienyl-substituted dibromosilane (5). The crude 5 was obtained as a viscous pale yellow oil. In the $^1$H NMR spectrum of 5 in CD$_6$, five signals for the bithienyl group, i.e., one doublet of doublets at 6.53 ppm ($J = 5.0$ and 3.7 Hz) and four doublets at 6.62 ($J = 5.0$ Hz), 6.88
(J = 3.7 Hz), 6.90 (J = 3.7 Hz), and 7.15 ppm (J = 3.7 Hz), were observed. The aryl proton of the Eind group appeared at 6.91 ppm.

The author found that the isolation of 5 in the pure form was difficult due to its poor crystallinity. Thus, the crude 5 was used for the subsequent reaction without further purification. A solution of LiNaph in THF was added to a solution containing 5 in THF afforded a purple powder of 1,2-bis(2,2'-bithiophen-5-yl)disilene (2) in 12% yield. The disilene 2 was characterized by NMR spectroscopy and HR-ESI-MS (Table 1–1). The 1H NMR spectrum of 2 in C6D6 showed the characteristic five resonances due to the bithienyl groups in the aromatic region at 6.52 (doublet of doublets, J = 5.3 and 3.8 Hz), 6.57 (doublet, J = 5.3 Hz), 6.87 (doublet, J = 3.8 Hz), 6.91 (doublet, J = 3.8 Hz), and 7.03 ppm (doublet, J = 3.8 Hz), along with the signal for the aryl proton of the Eind group at 7.02 ppm (singlet). In the 29Si NMR spectrum of 2 in C6D6, one signal was found at 51.7 ppm, similar to that in 1 (51.5 ppm).

The purple powder of 2 did not change color in air for at least a few months. Thus, in the 1H NMR spectra, no detectable change was observed. The purple color of 2 in a dilute THF solution turned colorless within 1 hour even in the dark. According to these observations, the disilene 2 possesses similar or slightly lower air stability relative to 1.

1.2.3 Molecular Structures of 1 and 2.

The molecular structures of the disilenes 1 and 2 were clearly confirmed by a single-crystal X-ray diffraction analysis (Figures 1–4 and 1–5). Each molecule has an inversion center at the middle of the Si=Si double bond with an E configuration. For 1, the thiophene units are disordered over the two positions in the crystal with the occupancy factors of ca. 0.90/0.10. Thus, as shown in Figure 1–6, three rotational isomers, s-cis, s-cis (1a), s-cis, s-trans (1b), and s-trans, s-trans (1c),17 exist in the crystal with a ratio of ca. 0.81/0.18/0.01. In the crystal of 2, while the inner thiophene rings adopt an s-trans, s-trans conformation, the outer thiophene rings are disordered over the two orientations with the occupancy factors of ca. 0.76/0.24, which corresponds to the fact that three rotational isomers, anti-(s-trans, s-trans)-anti (2a), syn-(s-trans, s-trans)-anti (2b), and syn-(s-trans, s-trans)-syn (2c), exist in the crystal with a ratio of ca. 0.58/0.36/0.06 (Figure 1–7). It is noteworthy that all the NMR spectroscopic data for 1 and 2 suggest the free rotation around the Si1–C29 and C32–C33 bonds in solution at room temperature on the NMR time scale.
**Figure 1–4** Molecular structure of 1. The thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms and disordered C and S atoms are omitted for clarity. Selected distances (Å) and angles (deg): Si1–Si1* = 2.1712(11), Si1–C1 = 1.889(2), Si1–C29 = 1.851(2), C1–Si1–C29 = 109.27(11), C1–Si1–Si1* = 129.57(7), C29–Si1–Si1* = 116.63(9).

**Figure 1–5** Molecular structure of 2. The thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms, disordered C and S atoms, and benzene molecule are omitted for clarity. Selected distances (Å) and angles (deg): Si1–Si1* = 2.1584(9), Si1–C1 = 1.8884(17), Si1–C29 = 1.8466(17), C1–Si1–C29 = 120.29(8), C1–Si1–Si1* = 122.24(6), C29–Si1–Si1* = 117.17(6).
Figure 1–6 Rotational isomers of 1.

Figure 1–7 Rotational isomers of 2.
Figure 1–8 Molecular packing of 2; (a) top view, (b) side view. The hydrogen atoms, disordered C and S atoms, and benzene molecule are omitted for clarity.

Table 1–1 summarizes the selected structural parameters of 1 and 2. The disilene moiety of 1 exhibits a trans-bent structure. The trans-bent angles ($\theta$) between the Si–Si vector and the C–Si–C plane are 19.12(12)$^\circ$ (C1–Si1–C29 for 1a and 1b) and 13.5(6)$^\circ$ (C1–Si1–C29B for 1b and 1c). The Si–Si–C–C torsion angles are found to be 17.8(4)$^\circ$ (Si1*–Si1–C29–C30 for 1a and 1b) and −146.5(17)$^\circ$ (Si1*–Si1–C29B–C30B for 1b and 1c). The Si atoms have a somewhat pyramidal geometry; the sum of the bond angles around the Si atom ($\Sigma$Si) are ca. 355.5–357.5$^\circ$. The disilene 2 adopts a more coplanar arrangement compared to 1; the trans-bent angle ($\theta$) is 5.44(10)$^\circ$ and the Si1*–Si1–C29–
C30 torsion angle is –175.90(15)°. The Si atoms have an almost planar geometry; the sum of the bond angles around the Si atom (ΣSi) is 359.7°. The bithiophene moieties in 2 are slightly twisted; the dihedral angles between the inner and outer thiophene rings are 21.0(3)° (2a and 2b) and 28.6(10)° (2b and 2c). The Si=Si bond distances are 2.1712(11) Å for 1 and 2.1584(9) Å for 2, which are in the range of those for typical disilenes.7

Figure 1–8 shows the packing diagram of the disilene 2, where the bithiophene skeletons are arranged in a slipped-stack manner. Although the interlayer distances between the mean planes of the thiophene rings (ca. 3.35–3.47 Å) suggest a compact packing, the intermolecular atomic distances are not less than the sum of the van der Waals radii of the carbon (1.7 Å) and sulfur (1.8 Å) atoms [C31···C36 = 3.789(7), C32···C36 = 3.776(6), C32···S2 = 3.690(2), C33···S2 = 3.570(11), and S2···S2 = 3.729(2) Å].18 Thus, in the crystalline state of 2, there seems to be a very weak or almost no intermolecular thiophene-thiophene interaction. This is further supported by the solid-state emission of 2 (vide infra).
1.2.4 Photophysical Properties of 1 and 2.

The photophysical data of 1 and 2 are summarized in Table 1–2 together with those of B, C, and H for comparison. Figure 1–9 exhibits the absorption spectra of 1 and 2 in THF and the emission spectra of 2 both in THF and in the solid state. Figure 1–10 shows the photographs of 1 and 2 in THF, in which the absorption color changes from the yellow of 1 to the red-purple of 2. In the UV-vis spectrum of 1 in THF, a strong absorption was observed with the absorption maximum [$\lambda_{\text{max}}(\text{abs})$] at 459 nm ($\varepsilon = 1.1 \times 10^4$), which is similar to that of B [$\lambda_{\text{max}}(\text{abs}) = 461$ nm, $\varepsilon = 2.4 \times 10^4$]. This indicates the considerable $\pi$-conjugation between the Si=Si fragment and the two thiophene units. The absorption maximum of 2 [$\lambda_{\text{max}}(\text{abs}) = 530$ nm, $\varepsilon = 1.3 \times 10^4$] is 71 nm longer than that of 1 [$\lambda_{\text{max}}(\text{abs}) = 459$ nm] and comparable to that of C [$\lambda_{\text{max}}(\text{abs}) = 543$ nm]. This remarkable red-shift with the increasing number of the thiophene rings is most likely interpreted in terms of the extension of the $\pi$-conjugation over the bis(bithienyl)disilene framework. In addition, the $\lambda_{\text{max}}(\text{abs})$ value of 2 (530 nm) is 116 nm red-shifted from that of the quaterthiophene H [$\lambda_{\text{max}}(\text{abs}) = 414$ nm]. This suggests the insertion of the Si=Si bond into the quaterthiophene skeleton causes a considerable narrowing of the HOMO–LUMO gap.

The author found that the disilene 1 does not show any emission at ambient temperature. In contrast, the $\pi$-extended disilene 2 showed a weak but distinct emission both in solution and in the solid state, as shown in Figure 1–9. The emission maximum [$\lambda_{\text{max}}(\text{em})$] of 2 was observed at 688 nm in THF with a low quantum yield ($\Phi_F = 0.01$). The Stokes shift of 2 (4330 cm$^{-1}$) is larger than that of C (2080 cm$^{-1}$). These emission properties can be rationalized by the flexibility of the 1,2-bis(bithienyl)disilene skeleton compared to the 1,4-bis(disilanyl)benzene skeleton. The disilene 2 exhibits a relatively strong emission [$\lambda_{\text{max}}(\text{em}) = 691$ nm] in the solid state. The quantum yield ($\Phi_F = 0.11$) is about 10 times stronger than that in solution. Accordingly, there seems to be no fluorescence quenching of 2 in the solid state, thus suggesting no direct $\pi$–$\pi$ stacking interactions of the thiophene units. The weak emission of 2 in solution may be due to the free rotation of the bithienyl groups around the Si–C and the exocylic C–C bonds.
Figure 1–9 UV-vis absorption spectra of 1 and 2 in THF and emission spectra of 2 in THF, together with the solid-state emission spectrum of 2.

Figure 1–10 Photographs of 1 and 2; (a) solution of 1 in THF, (b) solution of 2 in THF, (c) solution of 2 in THF during irradiation at 365 nm.
Table 1–2 Photophysical Data of 1 and 2, together with Compounds B, C, and H

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>B&lt;sup&gt;a&lt;/sup&gt;</th>
<th>C&lt;sup&gt;a&lt;/sup&gt;</th>
<th>H&lt;sup&gt;b&lt;/sup&gt;</th>
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<tr>
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<td>THF</td>
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<td>hexane</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
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<tr>
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<td>530</td>
<td>461</td>
<td>543</td>
<td>414</td>
</tr>
<tr>
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<td>(1.3 \times 10^4)</td>
<td>(2.4 \times 10^4)</td>
<td>(3.0 \times 10^4)</td>
<td>(3.8 \times 10^4)</td>
</tr>
<tr>
<td>( \lambda_{\max} \text{(em)/nm} )</td>
<td>n.d.&lt;sup&gt;c&lt;/sup&gt;</td>
<td>688 (691)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>n.d.&lt;sup&gt;c&lt;/sup&gt;</td>
<td>612</td>
<td>460 (523)&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>( \Phi_F )</td>
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<td>0.01 (0.11)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>–</td>
<td>0.10</td>
<td>0.18 (0.18)&lt;sup&gt;d&lt;/sup&gt;</td>
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<tr>
<td>Stokes shift (/\text{cm}^{-1})</td>
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<td>4330</td>
<td>–</td>
<td>2080</td>
<td>2420</td>
</tr>
</tbody>
</table>

<sup>a</sup>Data from ref 3. <sup>b</sup>Data from ref 12. <sup>c</sup>Not detected. <sup>d</sup>Values in parentheses are measured in the solid state.
1.2.5 Theoretical Calculations of 1 and 2.

For the further elucidation of the structural and electronic properties of the disilenes 1 and 2, the author carried out DFT calculations at the B3LYP-D3/6-31G(d,p) level with the use of the Gaussian 09 program package. The DFT calculations indicated a flexible conformation around the disilene unit in 1. The optimized structures of 1a (s-cis, s-cis) (C₁ symmetry), 1b (s-cis, s-trans) (C₅ symmetry), and 1c (s-trans, s-trans) (C₁ symmetry) exhibit a highly coplanar dithienyldisilene framework (θ = 0.0–0.1°), which are different from the X-ray structure [θ = 19.12(12)° and 13.5(6)°]. These rotational isomers have almost the same energies with the relative energies of 0.00 (1a), 1.12 (1b), and 2.48 (1c) kcal mol⁻¹. On the other hand, the optimized structure of 2a (anti-(s-trans, s-trans)-anti) (C₁ symmetry) exhibits a more trans-bent structure (θ = 10.8°) compared to that observed in the crystals [θ = 5.44(10)°]. The calculated dihedral angles between the inner and outer thiophene units (17.8°) are smaller than those of the X-ray values [21.0(3)° and 28.6(10)°]. The conformational differences between the experimental X-ray and computational DFT structures are essentially arising from the flexibility of the skeletons consisting of the Si=Si double bond and the thiophene units, which may be readily affected by crystal packing forces.
The frontier molecular orbitals of 1a and 2a are shown in Figures 1–11 and 1–12. The HOMOs of 1a and 2a are represented by the \( \pi(\text{Si}-\text{Si}) \) orbital with some contribution of the \( \pi(\text{thiophene}) \) and \( \pi(\text{bithiophene}) \) orbitals. In contrast, the LUMOs of 1a and 2a delocalize over the 1,2-bis(thienyl)disilene and 1,2-bis(bithienyl)disilene skeletons. While the HOMO level of 2a (\(-4.211 \text{ eV}\)) is similar to that of 1a (\(-4.222 \text{ eV}\)), the LUMO level of 2a (\(-1.681 \text{ eV}\)) is much lower than that of 1a (\(-1.350 \text{ eV}\)), indicative of the entirely extended \( \pi^*(\text{Si–Si})-\pi^*(\text{bithiophene}) \) conjugation. The total HOMO–LUMO gap in 2a (2.530 eV) is narrower than that in 1a (2.871 eV), being in good agreement with the experimental absorption data. As shown in Figures 1–13 and 1–14, the time dependent (TD) DFT calculations well reproduce the absorption spectra with the absorption wavelengths at 466 nm \((f = 0.3462; \pi-\pi^*)\) for 1a and 558 nm \((f = 0.7595; \pi-\pi^*)\) for 2a, similar to the observed \( \lambda_{\text{max}}(\text{abs}) \) values (459 nm for 1 and 530 nm for 2), both of which are assignable to the allowed HOMO \( \rightarrow \) LUMO \( (\pi\rightarrow\pi^*) \) transitions.
Figure 1–13 Calculated transitions (vertical blue bars) and simulated UV-vis absorption spectrum (black line) of 1a using TD-B3LYP-D3/6-31G(d,p) method.
Figure 1–14 Calculated transitions (vertical blue bars) and simulated UV-vis absorption spectrum (black line) of 2a using TD-B3LYP-D3/6-31G(d,p) method.
1.3 Conclusion

In this chapter, the author has demonstrated for the first time that the Si=Si double bond can conjugate with thiophene rings by introducing the steric effects of the fused-ring bulky Eind groups. The resulting 1,2-di(thiophen-2-yl)disilene 1 and 1,2-bis(2,2'-bithiophen-5-yl)disilene 2 can be isolated as air-stable orange and purple crystals, respectively, and their structural characteristics have been thoroughly confirmed by X-ray crystallography. The photophysical properties and theoretical calculations provide clear evidence for the effective π-conjugation between the Si=Si chromophore and thiophene rings, arising from the essentially coplanar 1,2-bis(thienyl)disilene and 1,2-bis(bithienyl)disilene skeletons.
1.4 Experimental Section

1.4.1 General Procedures.

All manipulations of the air- and/or moisture-sensitive compounds were performed either using standard Schlenk-line techniques or in a glovebox under an inert atmosphere of argon. Anhydrous hexane, benzene, toluene, diethyl ether (Et₂O), and tetrahydrofuran (THF) were dried by passage through columns of activated alumina and a supported copper catalyst supplied by Hansen & Co., Ltd. Anhydrous pentane was purchased from Kanto Chemical Co., Inc., and used without further purification. Deuterated benzene (benzene-d₆, C₆D₆) was dried and degassed over a potassium mirror in vacuo prior to use. Tribromo(1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl)silane, (Eind)SiBr₃ (3), was prepared by the literature procedure.⁹ All other chemicals and gases were used as received.

Nuclear magnetic resonance measurements were carried out using a JEOL ECS-400 spectrometer (399.8 MHz for ¹H, 100.5 MHz for ¹³C, and 79.4 MHz for ²⁹Si). Chemical shifts (δ) are given by definition as dimensionless numbers and determined with respect to the residual solvent for ¹H (residual C₆D₅H in C₆D₆: ¹H(δ) = 7.15) and for ¹³C (C₆D₆: ¹³C(δ) = 128.0). The ²⁹Si NMR spectra were referenced using the external standard of tetramethylsilane (²⁹Si(δ) = 0.0). The absolute values of the coupling constants are given in hertz (Hz) regardless of their signs. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). The UV-vis spectra were obtained using a Shimadzu UV-3101(PC)S spectrometer. The fluorescence spectra were measured by a JASCO FP-6500 spectrofluorometer. The mass spectra were recorded by a JEOL JMS-T100LC AccuTOF LC-plus 4G mass spectrometer (ESI-MS) with a DART source. Melting points (mp) were determined by a Stanford Research Systems OptiMelt instrument. We were unable to obtain a satisfactory elemental analysis for the compounds (1, 2, and 4). For example, diffraction analysis quality single crystals afforded a rather lower-than-expected carbon analysis, even when combustion aids were used. On the basis of the NMR spectra and the X-ray crystal structures, the author believes that these compounds are authentic and analytically pure but that its lability on heating or incomplete combustion is responsible for the disappointing elemental analysis.

Synthesis of dibromo(1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl)-(thiophen-2-yl)silane [(Eind)SiBr₂(2-thiophene)] (4). To a solution of thiophene (0.30 mL, 3.71 mmol) in THF (7.5 mL) was dropwise added nBuLi (2.65 M in hexane, 1.30 mL, 3.39 mmol) at −78 °C. The mixture was stirred and allowed to warm to 0 °C. The
resulting solution was dropwise added to 3 (2.01 g, 3.09 mmol) in THF (18 mL) at −78 °C, and the mixture was stirred overnight. After the solvent was removed in vacuo, to the residue was added hexane (40 mL) and the resulting suspension was centrifuged to remove any insoluble materials. The supernatant was concentrated to dryness to give 4 as a colorless solid (1.02 g, 1.56 mmol, 50%): mp 103–108 °C (dec) (argon atmosphere in a sealed tube); 1H NMR (C6D6) δ 0.74 (t, J = 7.3 Hz, 12 H, CH2C3), 0.81 (t, J = 7.3 Hz, 12 H, CH2CH3), 1.54–1.69 (m, 8 H, 8 H, CH2CH3), 1.73 (s, 4 H, CH2), 2.10–2.25 (m, 8 H, CH2CH3), 6.66 (dd, J = 3.2 and 4.6 Hz, 1 H, CH), 6.91 (s, 1 H, ArH), 7.05 (d, J = 4.6 Hz, 1 H, CH), 7.28 (d, J = 3.2 Hz, 1 H, CH); 13C NMR (C6D6) δ 9.3, 10.3, 33.7 (× 2), 44.2, 47.8, 55.0, 124.5, 127.3, 133.8, 138.4, 143.3, 150.9, 157.2 (one aromatic peak is overlapped); 29Si NMR (C6D6) δ −23.7. DART- HRMS (positive-mode) Calcd for C32H48Br2SSi+H: 651.1691. Found: 651.1675.

Synthesis of (E)-1,2-bis(thiophen-2-yl)-1,2-bis(1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl)disilene (1). To a solution of 4 (1.51 g, 2.31 mmol) in THF (20 mL) was added a solution of lithium naphthalenide (5.05 mmol) in THF (7 mL) at −90 °C. After the reaction mixture was stirred overnight, the solvent was removed in vacuo. To the residue was added benzene (40 mL) and the suspension was centrifuged to remove any insoluble materials. The supernatant was concentrated, and the residual solid was washed with hexane and Et2O to afford 1 as an orange powder (410 mg, 0.42 mmol, 37%): mp 226–229 °C (dec) (argon atmosphere in a sealed tube); 1H NMR (C6D6) δ 0.84–0.97 (m, 48 H, CH2C3), 1.64–1.76 (m, 14 H, CH2CH3), 1.91 (s, 8 H, CH2), 2.42–2.56 (m, 18 H, CH2CH3), 6.73 (dd, J = 4.6 and 3.2 Hz, 2 H, CH), 6.97 (s, 2 H, ArH), 7.01 (d, J = 4.6 Hz, 2 H, CH), 7.14 (d, J = 3.2 Hz, 2 H, CH); 13C NMR (C6D6) δ 9.5, 9.6, 11.0, 11.2, 33.9 (× 3), 34.4, 41.0, 48.0, 54.4, 122.3, 122.5, 127.4, 131.1, 136.7, 137.9, 150.3, 156.9; 29Si NMR (C6D6) δ 51.5. UV-vis (THF) λmax (ε) = 459 nm (1.1 × 104). HRMS (ESI, positive) Caled for C64H96Si2Si2: 984.6492. Found: 984.6461.

Synthesis of dibromo(1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl)-(thiophen-2-yl)disilane [(Eind)SiBr2(2,2’-bithiophene)] (5). To a solution of 2,2'-bithiophene (308 mg, 1.85 mmol) in THF (7 mL) was dropwise added nBuLi (2.65 M in hexane, 0.71 mL, 1.86 mmol) at −78 °C. The mixture was stirred and allowed to warm to 0 °C. The resulting solution was dropwise added to 3 (1.21 g, 1.86 mmol) in THF (12 mL) at −78 °C, and the mixture was stirred overnight. After the solvent was removed in vacuo, to the residue was added hexane (40 mL) and the resulting suspension was centrifuged to remove any insoluble materials. The supernatant was concentrated to
dryness to give the crude 5 as a viscous pale yellow oil (1.31 g, crude yield 96%); \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 0.77 (t, \(J = 7.8\) Hz, 12 H, CH\(_2\)CH\(_3\)), 0.81 (t, \(J = 7.3\) Hz, 12 H, CH\(_2\)CH\(_3\)), 1.54–1.70 (m, 8 H, CH\(_2\)CH\(_3\)), 1.73 (s, 4 H, CH\(_2\)), 2.17–2.28 (m, 8 H, CH\(_2\)CH\(_3\)), 6.53 (dd, \(J = 5.0\) and 3.7 Hz, 1 H, CH\(_2\)), 6.62 (t, \(J = 5.0\) Hz, 1 H, CH\(_2\)), 6.88 (d, \(J = 3.7\) Hz, 1 H, CH\(_2\)), 6.90 (d, \(J = 3.7\) Hz, 1 H, CH\(_2\)), 7.15 ppm (d, \(J = 3.7\) Hz, 1 H, CH\(_2\)). \(^{13}\)C NMR (C\(_6\)D\(_6\)) \(\delta\) 9.3, 10.3, 33.8, 33.9, 44.3, 47.9, 55.1, 124.1, 124.5, 124.6, 125.0, 125.5, 127.0, 136.7, 139.1, 142.0, 146.0, 150.9, 157.3.

**Synthesis of \((E)-1,2\)-bis(2,2′-bithiophen-5-yl)-1,2-bis(1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl)disilene (2).** To a solution of the crude 5 (1.12 g, 1.52 mmol) in THF (10 mL) was added a solution of lithium naphthalenide (2.99 mmol) in THF (5 mL) at \(-90^\circ\)C. After the reaction mixture was stirred overnight, the solvent was removed in vacuo. To the residue was added benzene (40 mL) and the suspension was centrifuged to remove any insoluble materials. The supernatant was concentrated, and the residual solid was repeatedly washed with hexane and Et\(_2\)O to afford 2 as a purple powder (104 mg, 0.09 mmol, 12%): mp 320–322 °C (dec) (argon atmosphere in a sealed tube); \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 0.86–0.96 (m, 48 H, CH\(_2\)C\(_6\)H\(_3\)), 1.60–1.82 (m, 16 H, CH\(_2\)C\(_6\)H\(_3\)), 1.91 (s, 8 H, CH\(_2\)), 2.42–2.52 (m, 12 H, CH\(_2\)CH\(_3\)), 2.61–2.68 (m, 4 H, CH\(_2\)CH\(_3\)), 6.52 (dd, \(J = 5.3\) and 3.8 Hz, 2 H, CH\(_2\)), 6.57 (d, \(J = 5.3\) Hz, 2 H, CH\(_2\)), 6.87 (d, \(J = 3.8\) Hz, 2 H, CH\(_2\)), 6.91 (d, \(J = 3.8\) Hz, 2 H, CH\(_2\)), 7.02 (s, 2 H, ArH), 7.03 (d, \(J = 3.8\) Hz, 2 H, CH\(_2\)); \(^{13}\)C NMR (C\(_6\)D\(_6\)) \(\delta\) 9.5, 9.6, 11.2, 11.4, 33.5, 33.7, 33.9, 34.4, 41.1, 48.0, 54.4, 121.8, 122.6, 123.5, 124.2, 124.3, 137.5, 137.8, 137.9, 143.0, 150.5, 156.9 (one aromatic peak is overlapped); \(^{29}\)Si NMR (C\(_6\)D\(_6\)) \(\delta\) 51.7. UV-vis (THF) \(\lambda_{\text{max}}(\varepsilon) = 530\) nm \((1.3 \times 10^4)\). HRMS (ESI, positive) Calcd for C\(_{72}\)H\(_{100}\)S\(_4\)Si\(_2\): 1148.6246. Found: 1148.6231.
1.4.2 X-Ray Crystallographic Analysis

X-ray Crystallography.

Single crystals suitable for X-ray diffraction were obtained from benzene for 1 as orange blocks, from a mixture of THF and pentane for 2 as purple blocks, and from hexane for 4 as colorless blocks. Crystallographic data are summarized in Table 1–3.

The single crystals were immersed in oil (Immersion Oil, type B: code 1248, Cargille Laboratories, Inc.) and mounted on a Rigaku XtaLAB P200 with a PILATUS 200 K detector for 2, and a Rigaku AFC-10 diffractometer with a Saturn724+ CCD detector for 1 and 4. The diffraction data were collected using MoKα radiation (λ = 0.71073 Å), which was monochromated and focused by a curved graphite monochromator. The specimens were cooled at 100 K in a cold nitrogen stream during the measurements. The integration and scaling of the diffraction data were carried out using the programs of CrystalClear\textsuperscript{20} and CrysAlisPro.\textsuperscript{21} The Lorentz-polarization and absorption corrections were also performed. The structures were solved by a direct method with the programs of SIR97\textsuperscript{22} for 4, SIR2004\textsuperscript{23} for 1, and SIR2011\textsuperscript{24} for 2 and refined on $F^2$ by a full-matrix least-squares method using the programs of SHELXL-2016/6.\textsuperscript{25} Anisotropic atomic displacement parameters were applied to all the non-hydrogen atoms. The hydrogen atoms were placed at the calculated positions and refined by applying riding models.
Table 3–3 Crystallographic Data for 1, 2, and 4.

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<td>418</td>
<td>341</td>
</tr>
<tr>
<td><strong>GOF on F²</strong></td>
<td>1.119</td>
<td>1.027</td>
<td>1.045</td>
</tr>
<tr>
<td><strong>R1 [I &gt; 2σ(I)]</strong></td>
<td>0.0715</td>
<td>0.0587</td>
<td>0.0442</td>
</tr>
<tr>
<td><strong>wR2 (all data)</strong></td>
<td>0.1469</td>
<td>0.1774</td>
<td>0.1050</td>
</tr>
<tr>
<td><strong>Δρ_{max}, /e Å⁻³</strong></td>
<td>−0.313, 0.649</td>
<td>−0.948, 0.909</td>
<td>−0.894, 0.769</td>
</tr>
</tbody>
</table>

\[ R(F) = \Sigma |F_o| - |F_c| / |F_o| , \quad wR^2 = \left[ \Sigma \left( w(F_o^2 - F_c^2)^2 \right) / \Sigma \left( w(F_o^2)^2 \right) \right]^{1/2} \]
1.5 References


The Si=Si and C=C double bonds are *cis* or *trans* to each other based around the Si–C single bonds.


20 CrystalClear; Rigaku/MSC. Inc.: The Woodlands. TX, USA, 2005.
Chapter 2

N-Heterocyclic-Carbene-Coordinated Silicon Compounds with a Bulky Eind Group

2.1 Introduction

In recent decades, many unsaturated silicon species have been isolated by taking advantage of the complexation with metal ions and/or coordination of extra ligands, adding to the kinetic stabilization using sterically large substituents.\textsuperscript{1–10} Especially, the coordination chemistry of halogen-substituted divalent Si(II) species, \textit{i.e.}, halosilylenes, have attracted much interest, because they are considered as potentially valuable precursors for the development of various silicon-containing compounds.\textsuperscript{11–15} Recent examples of the coordination-stabilized arylhalosilylenes and their derivatives are shown in Figure 2–1.\textsuperscript{16–22} In 2010, the first \(N\)-heterocyclic carbene (NHC) adducts of arylchlorosilylenes with bulky \(m\)-terphenyl groups, (\textit{Im-Me}_\textit{4})→SiCl(Ar) (\(A\)) \([\text{Ar} = 2,6-(\text{Mes})_2\text{C}_6\text{H}_3 \text{(Mes = 2,4,6-\text{Me}_3\text{C}_6\text{H}_2}) \text{ (e)} \text{ and } 2,6-(\text{Tip})_2\text{C}_6\text{H}_3 \text{(Tip = 2,4,6-\text{iPr}_3\text{C}_6\text{H}_2}) \text{ (d)}]\) were reported by Filippou’s group.\textsuperscript{16} The NHC adducts \(A\) were obtained by the dehydrochlorination reaction of the aryldichlorohydrosilanes, (Ar)SiHCl\(_2\), with \textit{Im-Me}_\textit{4} (1,3,4,5-tetramethylimidazol-2-ylidene), concurrent with the formation of imidazolium chloride, [(\textit{Im-Me}_\textit{4})H][\text{Cl}]. The reaction of the NHC-arylchlorosilylene adduct \(A–d\) with [Li\(^+\)][\text{CpMo(CO)}\(_3\)]\(^–\) produced the molybdenum-arylsilylene-NHC complex, \text{Cp(CO)}\(_2\text{Mo=Si(Ar)(Im-Me}_\textit{4})\) (\(B–d\)), then the treatment with \text{B(C}_6\text{H}_4\text{-4-Me})\(_3\) afforded the molybdenum-arylsilylyne complex, \text{Cp(CO)}\(_2\text{Mo=Si(Ar)}\) (\(C–d\)).\textsuperscript{17,23}
In 2011, the 4-pyrrolidinopyridine (PPy) adducts of arylbromosilylenes having the bulky Rind groups, PPy→SiBr(Rind) (D) [Rind = 1,1,3,3,5,5,7,7-octa-R-substituted s-hydrindacen-4-yl; Eind (a: R1 = R2 = Et) and EMind (b: R1 = Et, R2 = Me)] were reported by Matsuo and Tamao. The PPy adducts D were formed by the addition of PPy to the 1,2-dibromodisilenes, (Rind)BrSi=SiBr(Rind) (1a and 1b). In 2012, Sasamori and Tokitoh reported the platinum complex of arylbromosilylene, (Bbt)BrSi=Pt(PCy3)2 (E–e) [Bbt = 2,6-{CH(SiMe3)2}2-4-C(SiMe3)3-C6H2 (e)], which was obtained by the reaction between the 1,2-dibromodisilene, (Bbt)BrSi=SiBr(Bbt) (1e), and Pt(PCy3)2. In 2014, Sasamori, Matsuo, and Tokitoh reported that the 1,2-dibromodisilenes (1b, 1e, and 1f) bearing the bulky EMind, Bbt, and Tbb groups [Tbb = 2,6-{CH(SiMe3)2}2-4-Bu-C6H2 (f)] reacted with Im-Me4 and Im′-Pr2Me2 (1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) to produce the mono-NHC adducts of the arylbromosilylenes, NHC→SiBr(Ar) (F–b′ and F–e), and the bromide salts of the bis-
NHC adducts of the formal arylsilylumylidene cations, [(NHC)$_2$→Si(Ar)]$^+$[Br$^-$] (G–b, G–b', and G–f). Also in 2014, Inoue’s group synthesized the chloride salts of the bis-NHC adducts of the formal arylsilylumylidene cations, [(Im-Me$_4$)$_2$→Si(Ar)]$^+$[Cl$^-$] (H–c and H–g) [Ar = Tip (g)]. Then, they reported the unique conversion of H–c and H–g to the silicon analogues of the acylium ions, [(Im-Me$_4$)$_2$→Si(=O)(Ar)]$^+$[Cl$^-$] (I–c and I–g), by treatment with CO$_2$.

Recently, Inoue also reported the chalcogen-atom transfer and exchange reactions of the NHC-coordinated heavier silaacylium ions, [(Im-Me$_4$)$_2$→Si(=E)(Ar)]$^+$[Cl$^-$] (E = S, Se, and Te).

In this chapter, the author describes the synthesis and characterization of the NHC-coordinated silicon species bearing the bulky Eind group, which can be regarded as potentially useful tools for the construction of a wide range of organosilicon compounds. The mono-NHC adduct of the arylbromosilylene and the bis-NHC adduct of the formal arylsilylumylidene cation have been obtained by two different synthetic procedures, i.e., the NHC-induced fragmentation of the Eind-based 1,2-dibromodisilene and the dehydrobromination of the Eind-based dibromohydrosilane with NHCs. The mono-NHC adducts of the arylhydrosilylenes have also been synthsized by the dehydrochlorination of the arylchlorodihydrosilane with NHCs.
2.2 Results and Discussion

2.2.1 Reactions of (Eind)BrSi=SiBr(Eind) (1a) with NHCs

The author first examined an NMR tube scale reaction of the Eind-substituted 1,2-dibromodisilene, (Eind)BrSi=SiBr(Eind) (1a), \(^{18}\) with 2 equivalents of the N-isopropyl-substituted NHC, Im-^Pr_2Me_2, in C_6D_6, which is bulkier than the N-methyl-substituted NHC, Im-Me_4. The course of the reaction was monitored by \(^1\)H NMR spectroscopy. After overnight heating at 70 °C, the mono-NHC adduct of the arylbromosilylene, (Im-^Pr_2Me_2)→SiBr(Eind) (2a'), was exclusively formed. The \(^{29}\)Si NMR spectrum showed only one signal at 18.0 ppm, similar to those of (Im-^Pr_2Me_2)→SiBr(EMind) (F–b') (13.1 ppm) and (Im-Me_4)→SiBr(Bbt) (F–e) (10.9 ppm).\(^{20}\) The \(^{13}\)C signal for 2a' was observed at 170.6 ppm, which is characteristic of a carbene carbon atom and close to those for F–b' (169.7 ppm) and F–e (167.5 ppm).\(^{20}\) Based on the NMR tube scale experiment, the mono-NHC adduct 2a' was obtained as an orange solid in 88% isolated yield, as shown in Scheme 2–1.

\[
\text{Scheme 2–1 Reaction of 1,2-dibromodisilene 1a with Im-}^\text{Pr}_2\text{Me}_2.
\]

The author also investigated the reaction of 1a using 4 equivalents of Im-^Pr_2Me_2. After a 1-day heating at 70 °C in C_6D_6, the \(^{29}\)Si NMR spectrum showed mainly two signals at 18.0 and –59.6 ppm, thus indicating the formation of a mixture containing the mono-
NHC adduct 2a’ (18.0 ppm) and the bis-NHC adduct of the arylsilyliumylidene cation, [(Im-iPr2Me2→Si(Eind)]+[Br–] (3a’) (~59.6 ppm). The latter 29Si resonance is comparable to those of the formal arylsilyliumylidene cations, [(NHC)2→Si(EMind)]+[Br–] (G–b and G–b’) (~60.8 and ~75.9 ppm) and [(Im-Me4→Si(Tbb)]+[Br–] (G–f) (~70.9 ppm). The author found that the reaction was not completed even after prolonged heating (longer than 1 week). This is probably due to the severe steric repulsion between the Im-iPr2Me2 molecules and the bulky Eind group. Although the author could not isolate 3a’ as a pure form, single red crystals were obtained from the reaction mixture. Thus, the molecular structure of 3a’ was confirmed by X-ray crystallography.

Figure 2–2 Molecular structure of 3a’. The thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms and benzene molecule are omitted for clarity.

Figure 2–2 shows a separated ion pair of 3a’ in the crystal with the closest Si···Br distance of 7.6669(6) Å, which is similar to that of G–b’ [7.732(3) Å]20 and much longer than the sum of the van der Waals radii of Si and Br (3.95 Å). The three-coordinate Si atom has a distorted pyramidal geometry due to the presence of a non-bonding pair of electrons. The sum of the surrounding angles around the Si atom (ΣSi) is estimated to be 327.3°, which is very close to that of G–b’ (ΣSi = 327.0°). The Si–C(Eind) bond distance in 3a’ is 1.9482(19) Å, which is similar to that in G–b’ [1.927(8) Å]20 and slightly longer than typical Si–C bonds (ca. 1.88 Å). This suggests the high s-character of the non-bonding pair of electrons on the Si atom and the high p-character of the Si–C(Eind) bond.
The Si→C(Im'-Pr₂Me₂) coordination distances in 3a' are 1.953(2) and 1.942(2) Å, comparable to those observed in G–b' [1.955(9) and 1.979(8) Å].

The author next examined the reaction of 1a with 2 equivalents of the less bulky NHC, Im-Me₄, in C₆D₆. After 1 day at room temperature, two ²⁹Si resonances were observed at 73.3 and -63.3 ppm, which are characterized as the unreacted dibromodisilene 1a and the bis-NHC adduct of the arylsilyliumylidene cation, [(Im-Me₄)₂→Si(Eind)][Br⁻] (3a). This result indicates that the possible intermediate, NHC-aryl bromosilylene adduct, (Im-Me₄)→SiBr(Eind) (2a), is more reactive with Im-Me₄ than 1a. As shown in Scheme 2–2, the dibromodisilene 1a reacted with 4 equivalents of Im-Me₄ in benzene to give the bis-NHC adduct 3a, which was isolated as an orange powder in 54% yield. The upfield-shifted ²⁹Si signal for 3a (-63.3 ppm) suggests the contribution of the charge-separated canonical form, i.e., bis(imidazolium) adduct of a silyl anion, whose electronic structure was supported by the theoretical calculations for G–b' and G–f. The ¹³C NMR spectrum of 3a in CD₃CN showed one NHC carbene signal at 162.0 ppm, which is similar to those for G–b (160.5 ppm), G–b' (162.4 ppm), and G–f (160.4 ppm).
2.2.2 Reactions of (Eind)SiHBr$_2$ (4a) with NHCs

The author studied another synthetic approach for the NHC-bound silicon species, i.e., the dehydrobromination reaction of the Eind-substituted dibromohydrosilane, (Eind)SiHBr$_2$ (4a), with NHCs. The precursor, (Eind)SiHBr$_2$ (4a), can easily be obtained as pale brown crystals by the dibromination reaction of the corresponding trihydrosilane, (Eind)SiH$_3$, with allyl bromide in the presence of PdCl$_2$ catalyst (Scheme 2–3). In this reaction, the dibromosilane 4a was exclusively produced; the tribromosilane, (Eind)SiBr$_3$, was not observed even using an excess amount of allyl bromide, presumably ascribed to the steric bulkiness of the Eind group. In this regard, Kunai and Ohshita previously reported the selective dibromination of some trihydrosilanes with CuBr$_2$ in the presence of Cul. The $^1$H NMR spectrum of 4a exhibited the Si–H signal at 6.89 ppm with satellite signals due to the $^{29}$Si nuclei [$^1J(^{29}$Si–$^1$H) = 288 Hz]. In the $^{29}$Si NMR spectrum, one signal was found at −28.7 ppm, which is analogous to that of (Bbt)SiHBr$_2$ (−28.47 ppm). In the infrared (IR) spectrum of 4a, the Si–H stretching band appeared at 2317 cm$^{-1}$. The molecular structure of 4a has been clearly confirmed by X-ray crystallography. The Si–H hydrogen atom was located on the difference Fourier maps and isotropically refined. As shown in Figure 2–3, the SiHBr$_2$ group is arranged in one conformation concerning the rotational isomer around the Si–C bond. A similar conformation was also found in the crystal of (Eind)PCl$_2$. The Si–C bond distance in 4a is 1.8746(18) Å, similar to those of typical Si–C bonds (ca. 1.88 Å).

Scheme 2–3 Synthesis of 4a.

Scheme 2–4 Reaction of 4a with Im–iPr$_2$Me$_2$.  

46
As shown in Scheme 2–4, the dibromohydrosilane 4a more smoothly reacted with 2 equivalents of Im–Pr₂Me₂ at room temperature compared to the reaction of 1a with Im–Pr₂Me₂ (Scheme 2–1). The resulting mono-NHC adduct 2a' was isolated in 59% yield. The dibromohydrosilane 4a also reacted with 3 equivalents of Im-Me₄ to produce the bis-NHC adduct 3a (Scheme 2–5). In these dehydrobromination reactions, the by-products, imidazolium bromides, [(NHC)H][Br⁻], were always formed. It is necessary to remove the by-products for the isolation procedure of the NHC-bound silicon products, which is a disadvantage when compared to the reaction using the dibromodisilene 1a as a precursor, essentially yielding no by-product (vide supra). In fact, the author found that the separation between 3a and [(Im-Me₄)H][Br⁻] met with difficulty. The dibromodisilene
1a, however, can be prepared by a two-step synthesis from the Eind-substituted trihydrosilane, (Eind)SiH$_3$. That is, the bromination of (Eind)SiH$_3$ with N-bromosuccinimide (NBS) first produces the tribromosilane, (Eind)SiBr$_3$, then the treatment of (Eind)SiBr$_3$ with two equivalents of lithium naphthalenide (LiNaph) affords 1a. Therefore, the dehydrobromination reaction of 4a with NHCs may be considered as a suitable short-step synthesis for the NHC-coordinated silicon derivatives.

2.2.3 Reactions of (Eind)SiH$_2$Cl (5a) with NHCs

The successful isolation of the mono-NHC adduct of the arylbromosilylene, (Im-'Pr$_2$Me$_2$)→SiBr(Eind) (2a'), further prompted the author to examine the synthesis of the mono-NHC adducts of the arylhydrosilylenes, NHC→SiH(Eind) (6). The coordination chemistry of highly reactive hydrogen-substituted divalent Si(II) species, i.e., hydrosilylenes, have attracted a lot of scientific attention for a long time. For example, Kato and Baceiredo reported the catalyst-free hydrosilylation of olefins using the phosphine-stabilized Si(II) hydride species.

Figure 2–4 shows the recent examples of coordination-stabilized arylhydrosilylenes and their derivatives. In 2016, Müller’s group reported the synthesis of the NHC adducts of the arylhydrosilylenes incorporating the bulky m-terphenyl groups, (Im-Me$_4$)→SiH(Ar) (J–c and J–d), which were obtained by the NHC-induced fragmentation reaction of the silanorbornadiene derivatives. The treatment of J–d with Fe$_2$(CO)$_9$ produced the iron complex, (CO)$_4$Fe→SiH(Ar)(Im-Me$_4$) (K–d), with the long Fe–Si bond. Also in 2016, Hashimoto and Tobita reported the synthesis of the tungsten-hydride-arylhydrosilylene complex, Cp*(CO)$_2$(H)W=SiH(Eind) (L–a), by the reaction of Cp*(CO)$_2$W(Py)Me with (Eind)SiH$_3$. The stepwise proton and hydride abstraction reaction of L–a led to the equilibrium mixture between the monomeric tungsten-aryl silylyne complex, Cp*(CO)$_2$W≡Si(Eind) (M–a), and its cyclic dimer (N–a) in solution.

![Figure 2–4 Examples of coordination-stabilized arylhydrosilylenes and their derivatives.](image-url)
For the synthesis of the NHC-aryldiyrosilylene adducts, NHC→SiH(Eind) (6), the author examined the dehydrochlorination reaction of the Eind-substituted chlorodiarylsilane, (Eind)SiH₂Cl (5a), with NHCs. The precursor, (Eind)SiH₂Cl (5a), was obtained as colorless crystals in 91% yield by the selective monochlorination of one of the three Si–H bonds in the Eind-substituted triarylsilane, (Eind)SiH₃, with trichloroisocyanuric acid (TCCA) in hexane, as shown in Scheme 2–6. Compound 5a was characterized by NMR spectroscopy and mass spectrometry. In the ¹H NMR spectrum of 5a, the Si–H signal was observed at 5.82 ppm with satellite signals due to the ²⁹Si nuclei [¹J(²⁹Si–¹H) = 233 Hz]. The ²⁹Si NMR spectrum showed one resonance at −30.2 ppm. Compound 5a reacted with (Eind)Li to produce a mixture of (Eind)₂SiH₂ and [(Eind)₂H₂Si₂]O and subsequent bromination with NBS afforded (Eind)₂SiBr₂ in 7% yield for 2 steps.

![Scheme 2–6 Synthesis of 5a.](image)

Scheme 2–6 Synthesis of 5a.

![Scheme 2–7 Reaction of 5a with Im-²Pr₂Me₂.](image)

Scheme 2–7 Reaction of 5a with Im-²Pr₂Me₂.

![Scheme 2–8 Reaction of 5a with Im-²Me₄.](image)

Scheme 2–8 Reaction of 5a with Im-²Me₄.
As shown in Scheme 2–7, the room-temperature dehydrochlorination reaction of 5a with 2 equivalents of Im-Me$_4$ produced the mono-NHC adduct of the arylhydrosilylene, (Im-Me$_4$)$\rightarrow$SiH(Eind) (6a), along with the formation of imidazolium chloride, [(Im-Me$_4$)H][Cl$^-$]. Similarly, 5a smoothly reacted with 2 equivalents of Im-$i$Pr$_2$Me$_2$ at room temperature to afford (Im-$i$Pr$_2$Me$_2$)$\rightarrow$SiH(Eind) (6a') and [(Im-$i$Pr$_2$Me$_2$)H][Cl$^-$] (Scheme 2–8). The NHC adducts 6a and 6a' have been characterized by NMR spectroscopy. The $^1$H signal due to the Si–H group appeared at 5.23 (6a) and 5.29 (6a') ppm with satellite signals due to the $^{29}$Si nuclei [$^{1}J$($^{29}$Si–$^{1}$H) = 102 (6a) and 102 (6a') Hz], which are comparable to those of J–c [4.00 ppm and $^{1}J$($^{29}$Si–$^{1}$H) = 103 Hz] and J–d [3.88 ppm and $^{1}J$($^{29}$Si–$^{1}$H) = 105 Hz].$^{32}$ In the $^{29}$Si NMR spectra, one signal was found at –77.8 (6a) and –81.7 (6a') ppm, similar to those of J–c (–87.6 ppm) and J–d (–80.5 ppm). The molecular structure of 6a' was determined by a single-crystal X-ray diffraction analysis (Figure 2–5). The hydrogen atom on the silicon atom was definitely located based on the difference Fourier map and isotropically refined. The three-coordinate Si atom has a highly distorted trigonal pyramidal structure. The sum of the bond angles around the silicon atom ($\Sigma$Si) is estimated to be 310.3°, which is larger than those of J–c ($\Sigma$Si = 289.8°) and J–d ($\Sigma$Si = 293°). The Si–C(Eind) bond distance in 6a' [Si1–C1 = 1.9430(9) Å] is similar to those observed in 3a' [1.9482(19) Å] and G–b' [1.927(8) Å],$^{20}$ which again suggests the high $p$-character of the Si–C(Eind) bond. The Si←C(Im-$i$Pr$_2$Me$_2$) coordination distance in 6a' [Si1–C29 = 1.9726(9) Å] are comparable to those of 3a' [1.953(2) and 1.942(2) Å] and G–b' [1.955(9) and 1.979(8) Å].$^{20}$

![Figure 2–5 Molecular structure of 6a'.](image-url)
2.3 Conclusion

In this chapter, the author has synthesized the mono-NHC adduct of the arylbromosilylene, (Im-′Pr₂Me₂)→SiBr(Eind) (2a'), and the bis-NHC adduct of the formal arylsilyliumylidene cation, [(Im-Me₄)₂→Si(Eind)]⁺[Br⁻] (3a), by two methods; one is the reactions of the stable diaryldibromodisilene, (Eind)BrSi=SiBr(Eind) (1a), with NHCs, and the other is the dehydrobromination of the arylbromohydrosilane, (Eind)SiHBr₂ (4a), with NHCs. In both synthetic pathways, the author has mainly obtained the mono-NHC adduct of the arylbromosilylene, (Im-′Pr₂Me₂)→SiBr(Eind) (2a'), and the bis-NHC adduct of the formal arylsilyliumylidene cation, [(Im-Me₄)₂→Si(Eind)]⁺[Br⁻] (3a), depending on the steric bulk of the NHCs (Im-′Pr₂Me₂ vs. Im-Me₄). The author has also obtained the mono-NHC adducts of the arylhydrosilylenes, NHC→SiH(Eind) (6a and 6a'), by the dehydrochlorination of the arylchlorodihydrosilane, (Eind)SiH₂Cl (5a), with NHCs. The availability of the three kinds of well-defined NHC-coordinated silicon compounds in quantity opens the door to the full experimental clarification of their electronic and bonding nature as well as their potential uses as new synthetic reagents and new building units in the field of functional organosilicon materials.
2.4 Experimental Section

2.4.1 General Procedures.

All manipulations of the air- and/or moisture-sensitive compounds were performed either using standard Schlenk-line techniques or in a glove box under an inert atmosphere of argon. Anhydrous hexane, benzene, and toluene were dried by passage through columns of activated alumina and supported copper catalyst supplied by Hansen & Co., Ltd. Anhydrous pentane and acetonitrile were purchased from Wako Pure Chemical Industries, Ltd., and used without further purification. Deuterated benzene (C\(_6\)D\(_6\), benzene-\(d_6\)) was dried and degassed over a potassium mirror in vacuo prior to use. Deuterated acetonitrile (CD\(_3\)CN, acetonitrile-\(d_3\)) was dried and distilled over calcium hydride (CaH\(_2\)) prior to use. (Eind)SiH\(_3\)\(^{29,30}\), (Eind)BrSi=SiBr(Eind) (1a)\(^{18}\), 1,3,4,5-tetramethylimidazol-2-ylidene (Im-Me\(_4\))\(^{57}\) and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (Im-\(^{iPr}_2Me_2\))\(^{57}\) were prepared by the literature procedures. All other chemicals and gases were used as received.

Nuclear magnetic resonance (NMR) measurements were carried out using a JEOL ECS-400 spectrometer (399.8 MHz for \(^1\)H, 100.5 MHz for \(^{13}\)C, and 79.4 MHz for \(^{29}\)Si) or JEOL JNM AL-300 spectrometer (300 MHz for \(^1\)H, 75 MHz for \(^{13}\)C, and 59 MHz for \(^{29}\)Si). Chemical shifts (\(\delta\)) are given by definition as dimensionless numbers and relative to \(^1\)H chemical shifts of the solvents (residual C\(_6\)D\(_5\)H in C\(_6\)D\(_6\), \(^1\)H(\(\delta\)) = 7.15, residual CD\(_2\)HCN in CD\(_3\)CN, \(^1\)H(\(\delta\)) = 1.94), and residual solvent for \(^{13}\)C (C\(_6\)D\(_6\): \(^{13}\)C(\(\delta\)) = 128.0 and CD\(_3\)CN: \(^{13}\)C(\(\delta\)) = 1.32). The signal of tetramethylsilane [\(^{29}\)Si(\(\delta\)) = 0.0] was used as an external standard in the \(^{29}\)Si NMR spectra. The absolute values of the coupling constants are given in Hertz (Hz) regardless of their signs. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). The mass spectra were recorded by a JEOL JMS-T100LC AccuTOF LC-plus 4G mass spectrometer (ESI-MS) with a DART source. The elemental analyses were performed in the Microanalytical Laboratory at the Institute for Chemical Research (Kyoto University). Melting points (mp) were determined by a Stanford Research Systems OptiMelt instrument.

Synthesis of dibromo(1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl)silane [(Eind)SiHBr\(_2\)] (4a). To a solution of (Eind)SiH\(_3\) (4.09 g, 9.91 mmol) in toluene (30 mL) was added PdCl\(_2\) (38.0 mg, 0.21 mmol) and allyl bromide (4.2 mL, 48.5 mmol). The reaction mixture was heated at 80 °C for 8 days. After the solvent was removed in vacuo, the residue was dissolved in hexane and the resulting mixture was centrifuged to remove
the insoluble materials. The supernatant was concentrated to dryness and the resulting residue was recrystallized from pentane to afford 4a as pale brown crystals in 81% yield (4.58 g, 0.08 mmol): mp 102–105 °C (argon atmosphere in a sealed tube); 1H NMR (CDCl3) δ 0.78 (t, J = 7.3 Hz, 12 H, CH2CH3), 0.80 (br. s, 12 H, CH2CH3), 1.48–1.65 (m, 8 H, CH2CH3), 1.76 (s, 4 H, CH2), 1.90–2.50 (br. m, 8 H, CH2CH3), 6.89 (s, 1 H, satellite, JSi-H = 288 Hz, SiH), 7.01 (s, 1 H, ArH). 13C NMR (CDCl3) δ 9.3, 10.5 (br), 33.5, 34.2 (br), 42.6 (br × 1), 44.8 (br × 1), 47.9 (br × 2), 54.7 (× 2), 123.6, 125.1, 150.8 (one aromatic peak is overlapped); 29Si NMR (CDCl3) δ −28.7 (d, J = 288 Hz). IR (KBr, cm−1) ν 2317 (Si–H). DART-HRMS (positive-mode) Calcd for C28H46Br2Si+H: 569.1814. Found: 569.1820. Anal. Calcd. for C28H46Br2Si: C, 58.94; H, 8.13. Found: C, 59.41; H, 8.19.

**Synthesis of (Im-Pr2Me2)→SiBr(Eind) (2a')**

(Method A) Reaction of (Eind)BrSi=SiBr(Eind) (1a) with Im-Pr2Me2.

A mixture of 1a (158 mg, 0.16 mmol) and Im-Pr2Me2 (63.0 mg, 0.35 mmol) was dissolved in benzene (5 mL). The reaction mixture was heated overnight at 70 °C. After the solvent was removed in vacuo, the residue was washed with pentane to afford 2a' as an orange solid in 88% yield (190 mg, 0.28 mmol): mp 152–156 °C (dec) (argon atmosphere in a sealed tube); 1H NMR (CDCl3) δ 0.81–1.00 (m, 24 H, CH2CH3), 1.12 (br, s, 6 H, CH(CH3)2–(Im-Pr2Me2)), 1.19 (d, J = 7.0 Hz, 6 H, CH(CH3)2–(Im-Pr2Me2)), 1.61 (s, 6 H, CH3–(Im-Pr2Me2)), 1.62–1.95 (m, 20 H, CH2 + CH2CH3), 5.00–5.27 (m, 2 H, CH(CH3)2–(Im-Pr2Me2)), 6.71 (s, 1 H, ArH). 13C NMR (CDCl3) δ 9.3, 9.4, 9.9, 10.0, 10.5 (Im-Pr2Me2), 20.7 (×2), 21.4, 24.6, 33.7 (br, Im-Pr2Me2), 42.8, 48.4, 51.1 (Im-Pr2Me2), 54.5, 119.9, 125.9 (Im-Pr2Me2), 147.2, 148.5, 153.7, 170.6 (Im-Pr2Me2); 29Si NMR (CDCl3) δ 18.0. HRMS (ESI, positive) Calcd for C39H65BrN2Si+H: 669.4179. Found: 669.4211. Anal. Calcd. For C39H65BrN2Si: C, 69.92; H, 9.78; N, 4.18. Found: C, 66.97; H, 9.83; N, 6.77. It was difficult to obtain satisfactory analytical data for 2a', probably due to its extremely high air- and moisture-sensitivity.

(Method B) Reaction of (Eind)SiHBr2 (4a) with Im-Pr2Me2.

A mixture of 4a (476 mg, 0.97 mmol) and Im-Pr2Me2 (352 mg, 1.95 mmol) was dissolved in benzene (7 mL). After stirring overnight at room temperature, the resulting orange suspension was filtered through a polytetrafluoroethylene (PTFE) syringe filter to remove the insoluble materials. The filtrate was concentrated to dryness and the resulting residue was washed with pentane to afford 2a' as an orange solid in 59% yield (197 mg, 0.29 mmol).
Synthesis of [(Im-Me$_4$)$_2$→Si(Eind)]$^+$$[\text{Br}]^-$ (3a).

(Method A) Reaction of (Eind)BrSi=SiBr(Eind) (1a) with Im-Me$_4$.

A mixture of 1a (102 mg, 0.11 mmol) and Im-Me$_4$ (54 mg, 0.43 mmol) was dissolved in benzene (6 mL). After stirring for 1 day at room temperature, the resulting orange solid was separated and washed with a mixture of hexane and benzene to afford 3a as an orange powder in 54% yield (85.2 mg, 0.12 mmol): mp 169–174 °C (dec) (argon atmosphere in a sealed tube); $^1$H NMR (CD$_3$CN) δ 0.79 (br. t, $J = 6.3$ Hz, 12 H, CH$_2$C$_6$H$_3$), 0.98 (t, $J = 7.3$ Hz, 12 H, CH$_2$CH$_3$), 1.70–1.88 (m, 8 H, C$_6$H$_2$ + CH$_2$CH$_3$), 2.11–2.15 (m, 12 H, CH$_2$CH$_3$), 2.34 (s, 12 H, CH$_3$–(Im-Me$_4$)), 3.43 (br. s, 12 H, CH$_3$–(Im-Me$_4$)), 6.93 (s, 1 H, ArH). $^{13}$C NMR (CD$_3$CN) δ 9.2, 9.4, 10.0 (br, Im-Me$_4$), 34.1 (br, overlapped, Im-Me$_4$), 42.8, 48.1, 54.2, 121.8, 128.5 (Im-Me$_4$), 136.5, 150.8, 162.0 (Im-Me$_4$) (one aromatic peak is overlapped). $^{29}$Si NMR (CD$_3$CN) δ −63.3. DART-HRMS (positive-mode) Calcd for C$_{42}$H$_{69}$BrN$_4$Si+H: 737.4553. Found: 737.4562. Anal. Calcd. For C$_{42}$H$_{69}$BrN$_4$Si: C, 68.35; H, 9.42; N, 7.59. Found: C, 66.87; H, 9.61; N, 6.41. It was difficult to obtain satisfactory analytical data for 3a, probably due to its extremely high air- and moisture-sensitivity.

(Method B) Reaction of (Eind)SiHBr$_2$ (4a) with Im-Me$_4$.

A mixture of 4a (447 mg, 0.12 mmol) and Im-Me$_4$ (413 mg, 0.41 mmol) was dissolved in benzene (6 mL). After stirring for 1 day at room temperature, an orange suspension was formed. An insoluble orange solid was collected by filtration, whose $^1$H NMR spectrum indicated the formation of a mixture of 4a and [(Im-Me$_4$)H]$^+$$[\text{Br}]^-$.

Synthesis of (Im-Me$_4$)→SiH(Eind) (6a) A mixture of 5a (10.3 mg, 23.0 µmol) and Im-Me$_4$ (6.8 mg, 54.8 mmol) was dissolved in C$_6$D$_6$ (0.6 mL). The reaction mixture was stirred for overnight at room temperature. After the solvent was removed in vacuo, the residue was washed with pentane to afford 6a as an orange solid.

$^{29}$Si NMR (C$_6$D$_6$): δ −77.8 (d, $J = 102$ Hz).

Synthesis of (Im-Pr$_2$Me$_2$)→SiH(Eind) (6a') A mixture of 5a (447 mg, 1.00 mmol) and Im-Pr$_2$Me$_2$ (413 mg, 2.29 mmol) was dissolved in benzene (30 mL). The reaction mixture was stirred for 1 day at room temperature. After the solvent was removed in vacuo, the residue was washed with pentane to afford 6a' as an orange solid.

$^{29}$Si NMR (C$_6$D$_6$) δ −81.7 (d, $J = 102$ Hz).
2.4.2 X-Ray Crystallographic Analysis

**X-ray Crystallography.**

Single crystals suitable for X-ray diffraction measurements were obtained from benzene for 3a' and from hexane for 4a. Intensity data were collected using a Rigaku XtalLAB P200 with a PILATUS200 K detector for 3a' and 6a', and a Rigaku AFC-8 with Saturn 70 CCD detector for 4a. All the measurements were carried out using MoKα radiation (λ = 0.71073 Å). The integration and scaling of the diffraction data were carried out using the programs of CrysAlisPro for 3a' and 4a, and CrystalClear for 6a'. Lorentz, polarization, and absorption corrections were also performed. The structures were solved by an iterative method with the program of SHELXT for 3a' and 4a, and a direct method with the program of SIR2011 for 6a' and refined by a full-matrix least-squares method on $F^2$ for all the reflections using the program of SHELXL-2017/1. The non-hydrogen atoms were refined by applying anisotropic temperature factors. Positions of all the hydrogen atoms were geometrically calculated, and refined as riding models. The Si–H hydrogen atom was located on difference Fourier maps and isotropically refined.
### Table 2–1 Crystallographic Data for 3a', 4a and 6a'.

<table>
<thead>
<tr>
<th></th>
<th>3a'</th>
<th>4a</th>
<th>6a'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₅₀H₈₅Br₃Si·C₆H₆</td>
<td>C₂₉H₄₆Br₂Si</td>
<td>C₃₀H₆₆N₂Si</td>
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<tr>
<td>FM</td>
<td>928.32</td>
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<td>100</td>
<td>100</td>
</tr>
<tr>
<td>wavelength/Å</td>
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<td>0.71073 (MoKa)</td>
<td>0.71073 (MoKa)</td>
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<td>orange</td>
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<tr>
<td>crystal size, mm</td>
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<td>triclinic</td>
<td>triclinic</td>
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<tr>
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<td>P1 (# 2)</td>
<td>P1 (# 2)</td>
</tr>
<tr>
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<td>7.972(3)</td>
<td>8.91806(9)</td>
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<tr>
<td>b/Å</td>
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<td>11.070(4)</td>
<td>13.87480(17)</td>
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<tr>
<td>c/Å</td>
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<td>16.621(5)</td>
<td>14.74310(19)</td>
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<td>89.972(5)</td>
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<td>3198.5(8)</td>
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<td>397</td>
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<td>1.016</td>
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<td>R1 [I &gt; 2σ(I)] a</td>
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<td>0.0298</td>
<td>0.0402</td>
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<tr>
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<td>0.0803</td>
<td>0.1084</td>
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<tr>
<td>Δρ_min, max / e Å⁻³</td>
<td>-0.755, 1.692</td>
<td>-0.44, 0.69</td>
<td>-0.50, 0.53</td>
</tr>
</tbody>
</table>

| a | \( R(F) = \Sigma ||F_o|| - |F_c|| / \Sigma |F_o| \) |
| b | \( wR(F^2) = [\Sigma (w(F_o^2-F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2} \) |
2.5 References

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Chapter 3

1,2-Dihalodigermenes with Bulky Eind Groups: Synthesis, Characterization, and Conversion to 1,2-Diphenyldigermene

3.1 Introduction

As already described in General Introduction, sterically-demanding substituents provide kinetic stabilization to a large variety of unsaturated compounds of the heavier main group elements. In organogermanium chemistry, since Lappert’s and Masamune’s groups independently reported the synthesis of Ge=Ge doubly bonded species, i.e., digermenes, many low-coordinate germanium compounds have been isolated by the introduction of the appropriate bulky groups. Especially, the halogen-substituted digermenes, i.e., 1,2-dihalodigermenes, have found to be very useful and versatile compounds for the synthesis of unique unsaturated compounds of germanium, as shown in Figure 3–1.

Figure 3–1 Examples of stable 1,2-dihalodigermenes.
The synthesis of a series of sterically large \( m \)-terphenyl-substituted 1,2-dichlorodigermenes, \((\text{Ar})\text{ClGe=GeCl(\text{Ar}) [Ar = 2,6-(\text{Mes})_2\text{C}_6\text{H}_3 (\text{Mes} = 2,4,6-\text{Me}_3\text{C}_6\text{H}_2) (\text{A}), 2,6-(\text{Tip})_2\text{C}_6\text{H}_3 (\text{Tip} = 2,4,6-\text{iPr}_3\text{C}_6\text{H}_2) (\text{B}), and 2,6-(\text{Dip})_2\text{C}_6\text{H}_3 (\text{Dip} = 2,6-\text{iPr}_2\text{C}_6\text{H}_3) (\text{C})] \) were firstly reported by Power’s group.\(^5\) Subsequently, the overcrowded 1,2-dibromodigermene, \((\text{Bbt})\text{BrGe=GeBr(Bbt) (D)}\), bearing the bulky Bbt groups (Bbt = 2,6-[CH(SiMe\(_3\))\(_2\)]-4-C(SiMe\(_3\))\(_3\)-C\(_6\)H\(_2\)) was synthesized by Tokitoh’s group.\(^6\) Although the X-ray crystallographic analyses of these 1,2-dihalodigermenes exhibit a dimer structure in the crystals,\(^7\) they behave as a monomeric halogen-substituted divalent Ge(II) species, \( i.e.\), halogermylenes,\(^8\) in solution with the cleavage of the Ge=Ge double bond. Thus, these germanium halide compounds are much reactive and could be used as an appropriate precursor for the preparation of substituted digermenes,\(^5\)\(^c\)\(^,\)\(^9\) digermylenes,\(^5\)\(^d\)\(^,\)\(^10\) and transition-metal germylene and germylyne complexes.\(^\)\(^11\) Recently, Tokitoh and Sasamori also reported another 1,2-dibromodigermene, \((\text{Tbb})\text{BrGe=GeBr(Tbb) (E)}\), with the bulky Tbb groups (Tbb = 2,6-[CH(SiMe\(_3\))\(_2\)]-4-tBu-C\(_6\)H\(_2\)). This compound can also be converted into the corresponding digermyne, and the subsequent treatment with acetylene afforded the digermabenzene as a new member of the germaaromatic species.\(^6\)\(^b\)\(^,\)\(^6\)\(^c\)

As described in the General Introduction, our group has continuously studied the low-coordinate compounds of the heavier main group elements employing the rigid fused-ring bulky Rind groups (Rind = 1,1,3,3,5,5,7,7-octa-R-substituted \( s \)-hydrindacen-4-yl).\(^\)\(^12\)\(^,\)\(^13\) Previously, Matsuo and Tamao reported the synthesis and dynamic behavior of the 1,2-dibromodisilenes, \((\text{Rind})\text{BrSi=SiBr(Rind) [Rind = Eind (R}^1\text{= R}^2\text{= Et) (F–a) and EMind (R}^1\text{= Et, R}^2\text{= Me) (F–b)]}, \) as shown in Figure 3–2. The addition of 4-pyrrolidinopyridine (PPy) to the dibromodisilenes (F) produced the PPy-bromosilylene adducts (G) in solution via the dissociation of the Si=Si double bond.\(^\)\(^14\)\(^,\)\(^15\) As already described in the Chapter 2, the author demonstrated that the 1,2-dibromodisilenes (F) reacted with \( N \)-heterocyclic carbenes (NHCs), producing the NHC-bromosilylene adducts (H) and the formal bis-NHC adducts of the silylmylidene cations (I).\(^\)\(^16\)\(^,\)\(^17\) These results further prompted the author to study the reactivities of halogen-substituted ditetrenes (heavier alkene analogues) and their related compounds of the heavier group 14 elements. Especially, the author is much interested in the construction and photophysical properties of \( \pi \)-conjugated compounds containing a Ge=Ge double bond.

In this chapter, the author describes the synthesis and characterization of the 1,2-dihalodigermenes, \((\text{Eind})\text{XGe=GeX(Eind) [X = Br (1) and Cl (2)]}, \) with the bulky Eind groups. Although the Eind-substituted 1,2-dihalodigermenes have a dimeric structure in the crystalline state, their Ge=Ge double bonds are totally cleaved in solution. The
unique conversions to the halogermyleenoids and 1,2-diphenylgermene, (Eind)PhGe=GePh(Eind) (7), are also described.

**Figure 3–2** Examples of stable 1,2-dihalodisilenes and their related compounds.
3.2 Results and Discussion

3.2.1 Synthesis of \((E)-(E\text{Ind})XGe=GeX(E\text{Ind})\) [\(X = Br\) (1) and \(Cl\) (2)].

The author first examined the salt metathesis reaction between the bulky aryllithium, \((E\text{Ind})Li\), and a commercially available \(GeCl_2\cdot\text{dioxane}\) complex, based on the general procedure (Scheme 3–1).\(^5,6,8\) Normally, aryl bromides can react with one equivalent of \(^{n}BuLi\) to yield aryl lithiums (lithium-halogen exchange reaction). However, the treatment of two equivalents of \(^{n}BuLi\) is very effective for the quick conversion of \((E\text{Ind})Br\)\(^{13}\) into \((E\text{Ind})Li\).\(^{12c}\) The resulting bulky aryl lithium, \((E\text{Ind})Li\), was found to be not very thermally stable; the decomposition of \((E\text{Ind})Li\) took place in solution and even in the solid state at ambient temperature. Nevertheless, single colorless crystals of the \(LiBr\) adduct of \((E\text{Ind})Li\), \([(E\text{Ind})Li(THF)(LiBr)]_2\), could be obtained from a THF solution of the reaction mixture. As shown in Figure 3–1, the dimeric structure was characterized by the X-ray crystallography. The two lithium atoms (Li1 and Li2) are bonded to the ipso carbon atom (C1) of the Eind group with the almost equal C–Li distances \([C1–Li1 = 2.147(7)\text{ Å} \text{ and } C1–Li2 = 2.137(7)\text{ Å}]\), adopting a distorted trigonal planar geometry. While the Li1 atom is coordinated to the C1, Br1, and Br1* atoms, the Li2 atom is bound to the C1 and Br1 atoms and one THF molecule. The solution containing \((E\text{Ind})Li\) and \(LiBr\) was treated with \(GeCl_2\cdot\text{dioxane}\) to afford not the expected chlorine-substituted digermene, \((E\text{Ind})ClGe=GeCl(E\text{Ind})\) (2), but bromine-substituted digermene, \((E\text{Ind})BrGe=GeBr(E\text{Ind})\) (1), which was isolated as yellow-orange crystals in 31% yield. Based on these experimental results, a halogen-exchange reaction may take place between the 1,2-dihalodigermenes, \((E\text{Ind})XGe=GeX(E\text{Ind})\), and lithium halides, \(LiX\) (\(X = Br, Cl\)), in THF, presumably through the formation of lithium halogermylenoids, \([Li^+][(E\text{Ind})GeX_2]^–\).\(^{18}\) The obtained 1,2-dibromodigermene 1 was analytically pure as confirmed by elemental, spectral, and fluorescence X-ray analyses. However, the contamination by a trace amount of \(LiX\) could not always be ruled out, having an effect on the reaction chemistry of 1.\(^{15b}\)

These experimental results involving a halogen-exchange process prompted the author to look for a “lithium-salt-free” synthetic strategy for the 1,2-dihalodigermenes. As shown in Scheme 3–2, the author next investigated the ligand redistribution reaction between the Eind-substituted diarylgermylene, \((E\text{Ind})_2Ge\): (3),\(^{19}\) and \(GeX_2\cdot\text{dioxane}\) complexes.\(^{5a,20}\)
Scheme 3–1 Reaction between \( \text{[(Eind)Li(THF)(LiBr)]}_2 \) with GeCl\(_2\)·dioxane.

Figure 3–3 Molecular structure of \( \text{[(Eind)Li(THF)(LiBr)]}_2 \). The thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1–Li1 = 2.147(7), C1–Li2 = 2.137(7), Br1–Li1 = 2.558(7), Br1–Li1* = 2.475(7), Br1–Li2 = 2.456(7), O1–Li2 = 1.877(7), C1–Li1–Br1 = 107.8(3), C1–Li1–Br1* = 149.5(3), Br1–Li1–Br1* = 102.7(3), C1–Li2–Br1 = 111.9(3), C1–Li2–O1 = 121.3(4), Br1–Li2–O1 = 125.9(4), Li1–C1–Li2 = 76.4(3), Li1–Br1–Li2 = 63.8(2), Li1–Br1–Li1* = 75.3(2), Li1*–Br1–Li2 = 136.5(2).

Scheme 3–2 Reaction between \( \text{(Eind)Ge: (3)} \) and GeX\(_2\)·dioxane \((X = \text{Br, Cl})\).
The diarylgermylene 3 gradually reacted with GeBr₂-dioxane\(^{21}\) in toluene at 50 °C leading to a color change in the solution from deep blue to brown. After the reaction mixture was heated for 2 days, 1,2-dibromodigermene 1 was obtained as yellow-orange crystals in 43% isolated yield. In this ligand redistribution reaction, a trace amount of Ge(IV) species, (Eind)₂GeBr₂, could also be isolated, whose structure was determined by a preliminary single-crystal X-ray diffraction analysis. The treatment of 3 with GeCl₂-dioxane resulted in the formation of the 1,2-dichlorodigermene 2 as yellow-orange crystals in 58% yield. In these thermal reactions, the Ge–C and Ge–X bond cleavage and recombination processes take place in solution, providing 1 and 2 as the main products without any halogen-contamination.

### 3.2.2 Molecular Structures of 1 and 2.

As depicted in Figure 3–4, the molecular structures of the Eind-substituted 1,2-dihalodigermenes 1 and 2 were confirmed by X-ray crystallography. The crystal structures of 1 and 2 are mutually isostructural with a center of symmetry at the middle of their Ge=Ge double bonds. Table 3–1 summarizes the selected structural parameters of 1 and 2, together with those of A–E and F–a for comparison.\(^5,6,14\) Both digermene moieties bearing the electronegative halogen atoms show a highly trans-bent geometry with an E configuration. The trans-bent angles (θ) between the Ge1–Ge1* vector and the X1–Ge1–C1 plane are estimated to be 43.29(4)° (1) and 44.34(7)° (2), being larger than those of the dibromodisilene [29.0° (F–a)]\(^{14}\) and dichlorodigermenes [39.0° (A), 36.8° (B) and 38.8° (C)]\(^5\) and similar to those of the dibromodigermenes [44.57(8)° (D) and 46.00(12) and 45.35(12)° (E)].\(^6\) The Ge=Ge double bond lengths [2.4145(3) (1) and 2.4119(5) (2) Å] are in the range of those reported for the dihalodigermenes A–E [2.363(2)–2.5087(7) Å].\(^5,6\) The central Ge atoms in 1 and 2 adopt a pyramidal geometry; the sum of the bond angles around Ge atoms (ΣGe) are 337.1° (1) and 335.9° (2), which are comparable to those of A–E (ΣGe = 327.8–346.6°)\(^5,6\) and smaller than that of F–a (ΣSi = 350.8°).\(^14\) The optimized structures of 1 and 2 at the B3PW91-D3/6-311G(3df) (Ge, Br, Cl), 6-311G(d) (C, H) level reproduced the structural parameters found in the crystals (Table 3–1).\(^22\) The somewhat more pyramidalized Ge atoms in 2 compared to those of 1 could be rationalized considering the higher electronegativity of Cl than Br.
Figure 3–4 Molecular structures of 1 (a) and 2 (b). The thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms and disordered chlorine and germanium atoms in 2 are omitted for clarity. Selected bond lengths (Å) and angles (deg) for 1: Ge1–Ge1* = 2.4145(3), Ge1–Br1 = 2.3622(2), Ge1–C1 = 1.9830(13), C1–Ge1–Br1 = 107.48(4), C1–Ge1–Ge1* = 125.38(4), Br1–Ge1–Ge1* = 104.276(9). Selected bond lengths (Å) and angles (deg) for 2: Ge1–Ge1* = 2.4119(5), Ge1–Cl1 = 2.2124(15), Ge1–C1 = 1.9783(19), C1–Ge1–Cl1 = 106.85(7), C1–Ge1–Ge1* = 125.05(6), Cl1–Ge1–Ge1* = 103.96(5).
3.2.3 Photophysical Properties of 1 and 2.

With pure 1 and 2 in hand, the author investigated their spectroscopic properties in solution. The yellow-orange crystals of 1 and 2 were dissolved in common organic solvents such as hexane, benzene, and toluene, giving transparent yellow color solutions. In the \(^1\)H and \(^{13}\)C NMR spectra of both 1 and 2 in C\(_6\)D\(_6\) at 25 °C, only one set of signals of the Eind groups were observed with a high symmetry [one peripheral (R\(^1\)) and one proximate (R\(^2\)) ethyl groups] (Figure 3−2). These spectral features of 1 and 2 are quite different from those of the dibromodisilene F–a, which display two peripheral (R\(^1\)) and two proximate (R\(^2\)) ethyl groups of the Eind groups.\(^{14}\) Based on these NMR data, while the Si=Si double bond in F–a is retained in solution within the NMR time scale, the Ge=Ge double bonds in 1 and 2 may be dissociated in solution to yield the corresponding halogermynes, (Eind)XGe:.

In the UV-vis spectra of 1 and 2 in toluene at 25 °C, the absorption maxima were observed at 406 nm (ε = 3,400) for 1 and at 390 nm (ε = 2,100) for 2 (Figure 3−5a), which are weaker than that of the 1,2-dibromodisilene F–a (\(\lambda_{\text{max}} = 401\) nm, ε = 12,000; π–π*).\(^{14}\) On the other hand, as shown in Figure 3−5b, the UV-vis spectra of 1 and 2 in a microcrystalline powder film showed the absorption maxima at 450 nm for 1 and 443 nm for 2. In addition, the absorption intensity and wavelength of 1 in a dilute toluene solution (3.4 × 10\(^{-4}\) M) were observed to be almost independent in the temperature range of 10–70 °C (Figure 3−5c), which indicate no significant dynamic equilibrium between the 1,2-dibromodigermene 1 and the bromogermylene, (Eind)BrGe: (4), in solution. The absorption intensity and wavelength of 1 in a dilute THF solution (7.6 × 10\(^{-4}\) M) were also observed to be almost independent in the temperature range of 25–55 °C (\(\lambda_{\text{max}} = 406\) nm).
Figure 3–5 (a) UV-vis spectra of 1 and 2 in toluene at 25 °C. (b) UV-vis spectra of 1 and 2 in a microcrystalline powder film. (c) Variable-temperature UV-visible spectra of 1 in toluene (3.4 × 10⁻⁴ M). (d) Variable-temperature UV-visible spectra of 1 with LiBr in THF (3.3 × 10⁻⁴ M).
The TD-DFT computations were performed to elucidate the electronic nature of 1 and 4 at the TD-B3PW91-D3/6-311G(3df) (Ge, Br) and 6-311G(d) (C, H) level of theory including the solvation effect by the conductor-like polarized continuum model (CPCM)\textsuperscript{23} with a dielectric constant of 2.3741 (toluene). The calculations suggest the absorption maxima at 456 nm ($\epsilon = 0.3273$; $\pi-\pi^*$) for 1 and at 413 nm ($\epsilon = 0.0278$; n–p) for 4, being in good agreement with the observed absorption maxima (450 and 406 nm). These experimental and computational results clearly indicate that the Ge=Ge double bond of 1 dissociates to afford 4 in solution. The author found that the yellow-orange solids of dihalodigermenes 1 and 2 can be regenerated by the removal of the solvents through the Ge=Ge double bond formation. Thus, the dibromodigermene 1 exists as the bromogermylene 4 in solution, in contrast to the case of the Bbt-substituted dibromodigermene, (Bbt)BrGe=GeBr(Bbt) D, which is in an equilibrium state between the dibromodigermene and bromogermylene in solution.\textsuperscript{6a} This different association-dissociation event between 1 and D could be explained by the dispersion effect of the bulky substituents. Thus, the estimated dissociation energies ($\Delta G$) of the Ge=Ge double bond in 1 and 2 ($C_i$ symmetry; 7.8 and 9.8 kcal mol$^{-1}$) were somewhat smaller than that in D ($C_i$ symmetry; 15.3 kcal mol$^{-1}$) at the B3PW91-D3/6-311G(3df) (Ge, Br), 6-311G(d) (Si, C, H) level of theory (including the dispersion effect).\textsuperscript{24}
Table 3–1 Structural parameters of 1, 2, 6, and 7, together with A–E, F–a, and J.

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<td>1.9783(19)</td>
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</table>

a Data from ref 5(a). b Data from ref 5(c). c Data from ref 5(d). d Data from ref 6(a). e Data from refs 6(b) and 6(c). f Data from ref 14. g Data of [(Eind)GeBr₂]⁻ (counterion-free). h Data from ref 12(a).
3.2.4 Conversion to Halogermylenoids.

Based on the experimental evidence that the dibromodigermene 1 exists as the bromogermylene 4 in solution at room temperature, the author next examined the possibility for the complexation between 4 and LiBr to afford a bromogermylenoid, [Li⁺][(Eind)GeBr₂]⁻ (5) (Scheme 3–3).¹⁸,²⁵ When a large excess amount of LiBr (108 equiv.) was added to a solution of 1 in THF at room temperature, a new shoulder peak was observed at 347 nm in the UV-vis spectrum with the decreasing absorption intensity at 406 nm for 4, as shown in Figure 3–5d (blue). The shoulder peak at 347 nm decreased with the increasing absorption intensity at 406 nm, as the temperature increased from 25 to 55 °C.²⁶ This absorption spectral change with an isosbestic point at 386 nm strongly suggests the reversible formation of the bromogermylenoid 5 in THF through the complexation between 4 and LiBr. The NMR spectra of the mixture of 1 and LiBr (9 equiv.) in THF-d₈ also indicated the formation of 5.

The author also found that the Eind-substituted bromogermylenoid could be obtained as a crystalline material by the reaction of 1 with KBr in THF in the presence of [2.2.2]-cryptand. The molecular structure of a cryptand-separated potassium ion pair, [K⁺(crypt-222)][(Eind)GeBr₂]⁻ (6), is shown in Figure 3–6, in which the closest K···Ge distance is 6.738(1) Å. The central three-coordinate Ge atom has a distorted pyramidal geometry owing to the presence of a lone pair of electrons. Thus, the sum of the surrounding angles around the Ge atom (ΣGe) is 308.3°. The Ge–C and Ge–Br bond distances in 6 [Ge1–C1 = 2.097(5), Ge1–Br1 = 2.4772(9), and Ge1–Br2 = 2.5580(8) Å] are longer than those of 1 [Ge1–C1 = 1.9830(13) and Ge1–Br1 = 2.3622(2) Å] (Table 3–1). These structural characteristics can be explained by the high s-character of the lone pair of electrons on the Ge atom and the high p-character of the Ge–C and Ge–Br bonds.¹⁸ The germylenoid 6 is a rare example of isolatable tetrylenoids clearly confirmed by X-ray crystallography.¹⁸,²⁵,²⁷ In addition, the THF solution of 6 showed the unique absorption maxima at 347 nm in the UV-vis spectrum, being almost identical to that of 1 with LiBr [Figure 3–5d (blue)], which indicates that the absorption may be due to the chromophore of the [(Eind)GeBr₂]⁻ moiety.²⁶ This synthetic methodology for stable halogermylenoids can be applicable toward other 1,2-dihalodigermenes.
Scheme 3–3 Reactions of 1 with MBr (M = Li and K).

Figure 3–6 Molecular structure of 6. The thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms, disordered carbon atoms of the ethyl groups in 6 is omitted for clarity. Selected bond lengths (Å) and angles (deg) for 6: Ge1–Br1 = 2.4772(9), Ge1–Br2 = 2.5580(8), Ge1–C1 = 2.097(5), C1–Ge1–Br1 = 98.59(13), C1–Ge1–Br2 = 98.59(13), C1–Ge1–Br1 = 96.59(13), C1–Ge1–Br2 = 96.60(3).
3.2.5 Synthesis of 1,2-diphenyldigermene (7).

The synthetic route to the 1,2-diphenyldigermene, (Eind)PhGe=GePh(Eind), (7) is outlined in Scheme 3–4. For the introduction of phenyl groups to the digermene core, the author examined the reaction of 1 with phenyllithium in the mixture of Et₂O and hexane. The 1,2-diphenyldigermene 7 was obtained as an air-stable orange powder in 23% yield. This orange powder of 7 did not change color in air for at least several months; no detectable change was found in the ¹H NMR spectra.

![Scheme 3–4 Synthesis of 7.](image)

Figure 3–7 Molecular structure of 7. The thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms and disordered carbon atoms in 7 are omitted for clarity. Selected bond lengths (Å) and angles (deg) for 7: Ge1–Ge1* = 2.2955(5), Ge1–C1 = 1.983(2), Ge1–C29 = 1.959(3), C1–Ge1–C29 = 105.34(12), C1–Ge1–Ge1* = 125.54(7), C29–Ge1–Ge1* = 114.59(9).
As shown in Figure 3–7, the molecular structure of 7 was determined by X-ray crystallography. The digermene core of 7 has a highly trans-bent structure; the trans-bent angles ($\theta$) between the Ge–Ge vector and the C–Ge–C plane is 34.00(12)$^\circ$ (Table 3–1). The Ge–Ge–C–C torsion angles are estimated to be 31.3(2)$^\circ$. The Ge atoms have a pyramidal geometry with the sum of the bond angles around the Ge atom ($\Sigma$Ge) of 345.5$^\circ$. These structural features in 7 are quite different from those observed in 1,2-diphenyldisilene, (Eind)PhSi=SiPh(Eind) (J), which has a highly coplanar diphenyldisilene skeleton [$\theta = 2.7(3)$].\textsuperscript{12a} These structural differences between the diphenyldigermene 7 and the diphenyldisilene J may be ascribed to the delicate balance between the steric congestion of the bulky Eind groups and the less effective hybridization of the heavier group 14 elements and/or the crystal packing configuration.

Figure 3–8 shows the UV-vis spectrum of 7 in hexane at room temperature. The absorption maximum ($\lambda_{\text{max}}$(abs)) of 7 was observed at 448 nm with a large molar extinction coefficient ($\varepsilon = 1.7 \times 10^4$), which can be assigned to the allowed $\pi-\pi^*$ electronic transition. The $\lambda_{\text{max}}$(abs) value of 7 (448 nm) is blue-shifted about 13 nm compared to that of J ($\lambda_{\text{max}} = 461$ nm).\textsuperscript{12a} This absorption data indicates that the Ge=Ge double bond of 7 is maintained in solution, thus participating in $\pi$-conjugation.

![Figure 3–8 UV-vis spectrum of 7 in hexane at 25 °C.](image-url)
3.2.6 Theoretical Studies of 7.

To elucidate the nature of the bonding in the 1,2-diphenyldigermene, DFT computations were carried out for 7 at the B3LYP-D3/6-311G(3df) (Ge), 6-311G(d,p) (C, H) level by using the Gaussian 09 program package. The optimized structure well reproduces the X-ray molecular structure found in the crystals.

The frontier molecular orbitals of 7 are depicted in Figure 3–9. While the HOMO is mainly represented by the π(Ge–Ge) orbital, the LUMO involves the substantial contribution of the π*(Ge–Ge)−π*(phenyl) conjugation. Both the HOMO and LUMO levels of 7 (−4.586 and −1.608 eV) are slightly lower than those of the 1,2-diphenyldisilene J (−4.253 and −1.330 eV). The total HOMO–LUMO gap in 7 (2.978 eV) is somewhat larger than that in J (2.923 eV), being in agreement with the experimental data, i.e., a blue-shifted absorption maximum in 7 (λ_max = 448 nm) relative to that in 7 (λ_max = 461 nm). The TD-DFT calculations of 7 reproduce the experimental absorption spectrum with the absorption wavelengths at 459 nm (f = 0.3001; π−π*), comparable to the observed λ_max(abs) values (448 nm), which is assignable to the HOMO → LUMO (π→π*) transition. The experimental and computational studies of 7 indicate the unique conjugation properties between the germanium–4pπ and carbon–2pπ electrons.

![Frontier molecular orbitals of 7 (top view).](image)

**Figure 3–9** Frontier molecular orbitals of 7 (top view).
3.3 Conclusion

In this chapter, the author has developed a novel synthetic procedure for the “lithium-salt-free” 1,2-dihalodigermenes, \textit{i.e.}, a ligand redistribution reaction between a diaryldigermene and GeX$_2$·dioxane (X = Br, Cl). The pure 1,2-dihalodigermenes were found to form the halogermylenes in solution at room temperature with the dissociation of the Ge=Ge double bond. The author has demonstrated the formation and isolation of the bromogermylenoids, which has been obtained by the addition of MBr (M = Li, K) to the THF solution of the bromogermylene. The author has also studied the synthesis, structure, and photophysical properties of the 1,2-diphenyldigermene as the first $\pi$-conjugated digermene compound.
3.4 Experimental Section

3.4.1 General procedures.

All manipulations of the air- and/or moisture-sensitive compounds were performed either using standard Schlenk-line techniques or in a glove box under an inert atmosphere of argon. Anhydrous benzene, toluene, and tetrahydrofuran (THF) were dried by passage through columns of activated alumina and supported copper catalyst supplied by Hansen & Co., Ltd. Deuterated benzene (C\textsubscript{6}D\textsubscript{6}, benzene-\textit{d}\textsubscript{6}) and deuterated THF (C\textsubscript{4}D\textsubscript{8}O, THF-\textit{d}\textsubscript{8}) were dried and degassed over a potassium mirror in vacuo prior to use. 4-Bromo-1,1,3,3,5,5,7,7-octaethyl-s-hydrindacene, (Eind)Br,\textsuperscript{13} (Eind)\textsubscript{2}Ge:,\textsuperscript{19} GeBr\textsubscript{2}-dioxane\textsuperscript{21} were prepared by the literature procedures. Other chemicals and gases were used as received.

The nuclear magnetic resonance (NMR) measurements were carried out using a JEOL ECS-400 spectrometer (399.8 MHz for \textsuperscript{1}H, 155.4 MHz for \textsuperscript{7}Li, and 100.5 MHz for \textsuperscript{13}C) or JEOL JNM AL-300 spectrometer (300 MHz for \textsuperscript{1}H, 120 MHz for \textsuperscript{7}Li and 75 MHz for \textsuperscript{13}C). Chemical shifts (\(\delta\)) are given by definition as dimensionless numbers and relative to \textsuperscript{1}H chemical shifts of the solvents (residual C\textsubscript{6}D\textsubscript{5}H in C\textsubscript{6}D\textsubscript{6}, \textsuperscript{1}H(\(\delta\)) = 7.15, residual C\textsubscript{4}D\textsubscript{7}HO in THF-\textit{d}\textsubscript{8}, \textsuperscript{1}H(\(\delta\)) = 3.58), external LiCl in D\textsubscript{2}O for \textsuperscript{7}Li (\textsuperscript{7}Li(\(\delta\)) = 0.0) residual solvent for \textsuperscript{13}C (C\textsubscript{6}D\textsubscript{6}: \textsuperscript{13}C(\(\delta\)) = 128.0 and C\textsubscript{4}D\textsubscript{8}O: \textsuperscript{13}C(\(\delta\)) = 67.21). The absolute values of the coupling constants are given in Hertz (Hz), regardless of their signs. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br).

The UV-visible spectra were obtained using a Shimadzu UV-1700 pharmaSpec UV-Vis spectrophotometer with an S-1700 Thermoelectric Single Cell Holder for \textbf{1} and a Shimadzu UV-3101(PC)S spectrometer for \textbf{2}. The elemental analyses were performed at the Materials Characterization Support Unit, RIKEN Center for Emergent Matter Science and the Microanalytical Laboratory at the Institute for Chemical Research (Kyoto University). Melting points (mp) were determined by a Stanford Research Systems OptiMelt instrument and a Yazawa BY-2 instrument.

\textbf{Synthesis of (E)-(Eind)BrGe=GeBr(Eind) (1)}

\textbf{(Method A)} Reaction of (Eind)Li with GeCl\textsubscript{2}-dioxane

To a suspension of (Eind)Br (1.87 g, 4.04 mmol) in THF (40 mL) was dropwise added \textsuperscript{2}BuLi (2.65 M in hexane, 3.2 mL, 8.48 mmol) at –78 °C. The resulting pale yellow solution was allowed to warm to 0 °C to give a yellow solution. This yellow solution was dropwise added to a colourless solution of GeCl\textsubscript{2}-dioxane (937 mg, 4.05 mmol) in THF (20 mL) to give an orange solution. After stirring overnight at room temperature, the
solvents were removed under reduced pressure to provide an orange solid. To the residue was added benzene (100 mL) and the resulting mixture was centrifuged to remove the insoluble materials. The supernatant was concentrated to dryness and recrystallized from THF at –30 °C to afford 1 as orange-yellow crystals, which were isolated by filtration in 31% yield (671 mg, 0.63 mmol): mp (argon atmosphere in a sealed tube) 150–152 °C (dec.); 1H NMR (399.8 MHz, C6D6, 25 °C) δ 0.82 (t × 2, J = 7.4 Hz, 48 H, CH2CH3), 1.13–1.40 (br.s, 8 H, CH2CH3), 1.50–1.69 (m, 16 H, CH2CH3), 1.59 (s, 8 H, CH2), 1.92–2.12 (br.s, 8 H, CH2CH3), 6.76 (s, 2 H, ArH); 13C NMR (155.4 MHz, C6D6, 25 °C): δ 9.45, 9.84, 33.5, 37.9, 51.3, 121.3, 147.9, 156.0, 161.3; 1H NMR (399.8 MHz, THF-d8, 25 °C) δ 0.85 (t, J = 7.6 Hz, 24 H, CH2CH3), 0.90 (t, J = 7.0 Hz, 24 H, CH2CH3), 1.29–1.34 (m, 8 H, CH2CH3), 1.59–1.71 (m, 16 H, CH2CH3), 1.80 (s, 8 H, CH2), 2.01–2.11 (m, 8 H, CH2CH3), 6.76 (s, 2 H, ArH). Anal. Calcd for C56H90Ge: C, 62.96; H, 8.49. Found: C, 62.81; H, 8.55. UV-vis (toluene) λmax (ε) = 406 nm (3400).

(Method B) Reaction of (Eind)2Ge: with GeBr2·dioxane

A mixture of (Eind)2Ge: (680 mg, 0.81 mmol) and GeBr2·dioxane (276 mg, 0.86 mmol) was dissolved in toluene (15 mL). The reaction mixture was heated at 50 °C for 2 days. After the solvent was removed in vacuo, the residue was dissolved with THF and filtered to remove the insoluble materials. The filtrate was concentrated and recrystallized from a mixture of THF and pentane at –30 °C to afford 1 as yellow-orange crystals, which were isolated by filtration in 43% yield (373 mg, 0.35 mmol). We also obtained a trace amount of (Eind)2GeBr2 from the reaction mixture, whose structure was confirmed by a preliminary single-crystal X-ray diffraction analysis.

Synthesis of (E)-(Eind)ClGe=GeCl(Eind) (2) A mixture of (Eind)2Ge: (681 mg, 0.82 mmol) and GeCl2·dioxane (183 mg, 0.79 mmol) was dissolved in toluene (15 mL). The reaction mixture was heated at 50 °C for 2 days. The solution was concentrated to dryness and recrystallized from THF at –30 °C to afford 2 as orange-yellow crystals, which were isolated by filtration in 58% yield (452 mg, 0.46 mmol): mp (argon atmosphere in a sealed tube) 130–134 °C (dec.); 1H NMR (399.8 MHz, C6D6, 25 °C) δ 0.82 (t × 2, J = 7.2 Hz, 48 H, CH2CH3), 1.18–1.42 (br.s, 8 H, CH2CH3), 1.49–1.67 (m, 16 H, CH2CH3), 1.59 (s, 8 H, CH2), 1.94–2.04 (m, 8 H, CH2CH3), 6.77 (s, 2 H, ArH); 13C NMR (155.4 MHz, C6D6, 25 °C): δ 9.45, 9.79, 33.4, 38.5, 39.7, 51.2, 53.2, 121.1, 147.8, 155.9, 161.2. Anal. Calcd for C56H90Ge: C, 68.67; H, 9.26; Cl, 7.24. Found: C, 68.30; H, 9.26; Cl, 7.12. UV-vis (toluene) λmax (ε) = 390 nm (2100).
Formation of [Li⁺][([Eind]GeBr₂)⁻] (5) In a J-Young NMR tube, a mixture of 1 (8.5 mg, 7.96 μmol) and LiBr (6.5 mg, 74.9 μmol) was dissolved in THF-d₈ (0.5 mL). The formation of 5 was confirmed by NMR spectroscopy. 1H NMR (399.8 MHz, THF-d₈, 25 °C): δ 0.83 (t, J = 6.0 Hz, 12 H, CH₂CH₃), 0.86 (t, J = 5.8 Hz, 12 H, CH₂CH₃), 1.57–1.73 (m, 8 H, CH₂CH₃), 1.78 (s, 4 H, CH₂), 2.07–2.13 (m, 8 H, CH₂CH₃), 6.68 (s, 1 H, ArH); ⁷Li NMR (100.5 MHz, THF-d₈, 25 °C): δ 2.78; ¹³C NMR (155.4 MHz, THF-d₈, 25 °C): δ 9.4, 10.2, 33.8, 37.0, 41.4, 50.5, 54.1, 119.7, 147.9, 155.5, 161.7.

Synthesis of [K⁺(crypt-222)][([Eind]GeBr₂)⁻] (6) In a J-Young NMR tube, a mixture of 1 (21.0 mg, 19.7 μmol), KBr (7.4 mg, 62.2 μmol), and [2.2.2]-cryptand (23.7 mg, 62.9 μmol) was dissolved in THF (0.5 mL). The colour of the solution changed from yellow to colourless within 60 min. Volatiles were removed under reduced pressure, and the residue was recrystallized from hexane to afford 6 as colourless crystals in 82% yield (33.3 mg, 32.3 μmol): mp (argon atmosphere in a sealed tube) 131–132 °C (dec.); ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 0.93 (t, J = 7.5 Hz, 12 H, CH₂C₃), 1.10 (t, J = 7.5 Hz, 12 H, CH₂C₃), 1.63–1.84 (m, 4 H, C₃H₂C₃), 1.86 (s, 4 H, CH₂), 2.17 (t, 12 H, J = 4.5 Hz, cryptand), 2.26–2.38 (m, 8 H, CH₂CH₃), 2.40–2.56 (m, 4 H, CH₂CH₃), 3.20 (t, 12 H, J = 4.5 Hz, cryptand), 3.32 (s, 12 H, cryptand), 6.83 (s, 1 H, ArH); ¹³C NMR (120 MHz, C₆D₆, 25 °C): δ 9.64, 11.1, 33.9, 35.7, 43.0, 49.0, 54.0 (cryptand), 54.5, 67.7 (cryptand), 70.6 (cryptand), 119.7, 147.8, 154.9, 160.8. Anal. Calcd for C₄₆H₈₁Br₂GeKN₂O₆: C, 53.66; H, 7.93. Found: C, 53.59; H, 7.95. UV-vis (THF) λₘₐₓ (ε) = 347 nm (1400, sh).

Synthesis of [(E)-(Eind)PhGe=GePh(Eind)] (7) To a solution of 1 (153 mg, 0.16 mmol) in mixture of Et₂O (13 mL) and Hexane (6.5 mL) was dropwise added PhLi (1.9 M in Bu₂O, 0.16 mL, 0.31 mmol) at –50 °C. The resulting pale yellow solution was allowed to warm to room temperature to give a red solution. After stirring overnight at room temperature, the solvents were removed under reduced pressure to provide an orange solid. To the residue was added toluene (30 mL) and the resulting mixture was centrifuged to remove the insoluble materials. The supernatant was concentrated to dryness and washed with pentane. The residue was recrystallized from THF at –30 °C to afford 1 as orange-yellow crystals, which were isolated by filtration in 23% yield (671 mg, 0.63 mmol); ¹H NMR (399.8 MHz, C₆D₆, 25 °C) δ 0.80 (t × 2, J = 7.2 Hz, 12 H, CH₂CH₃), 0.87 (t × 2, J = 7.3 Hz, 12 H, CH₂CH₃), 0.92 (t × 2, J = 7.4 Hz, 12 H, CH₂CH₃), 0.98 (t × 2, J = 7.4 Hz, 12 H, CH₂CH₃), 1.58–1.94 (m, 16 H, CH₂CH₃), 1.88 (s, 8 H, CH₂), 2.10–2.20 (m, 4 H, CH₂CH₃), 1.28–2.39 (m, 8 H, CH₂CH₃), 2.45–2.54 (m, 4 H, CH₂CH₃),
6.92 (t, $J = 7.3$ Hz, 2 H, ArH), 6.95 (s, 2 H, ArH), 7.00 (t, $J = 7.3$ Hz, 2 H, ArH), 7.49 (d, $J = 6.9$ Hz, 4 H, ArH); $^{13}$C NMR (155.4 MHz, C$_6$D$_6$, 25 °C): $\delta$ 9.52, 9.58, 10.9, 11.2, 33.7, 33.8, 34.3, 41.5, 48.2, 54.2, 120.8, 133.7, 135.0, 147.3, 150.7, 154.5 (two aromatic peaks are overlapped); Anal. UV-vis (hexane) $\lambda_{max}$ ($\varepsilon$) = 448 nm (1.7×10$^4$).
3.4.2 X-Ray Crystallographic Analysis

X-ray Crystallography.

Single crystals suitable for X-ray diffraction measurements were obtained from THF for [(Eind)Li(THF)(LiBr)]$_2$, 1, 2 and 7 and from hexane for (Eind)$_2$GeBr$_2$, and 6. Intensity data were collected using a Rigaku AFC-10 with Saturn 724+ CCD detector for [(Eind)Li(THF)(LiBr)]$_2$, a Rigaku XtaLAB P200 with a PILATUS200 K detector for 1, 2 and (Eind)$_2$GeBr$_2$, RIGAKU AFC-10 with Saturn70 CCD detector for 6, and RIGAKU AFC-8 with Saturn70 CCD detector for 7. All the measurements were carried out using MoK$\alpha$ radiation ($\lambda = 0.71073$ Å). Crystal data are summarized in Table 5–2. The integration and scaling of the diffraction data were carried out using the programs of CrystalClear$^{28}$ for [(Eind)Li(THF)(LiBr)]$_2$ and 7, CrysAlisPro$^{29}$ for 1, 2 and (Eind)$_2$GeBr$_2$, and HKL2000$^{30}$ for 6. Lorentz, polarization and absorption corrections were also performed. The structures were solved by direct methods with the program of SIR2002$^{31}$ for [(Eind)Li(THF)(LiBr)]$_2$, SIR2011$^{32}$ for 1, 2 and (Eind)$_2$GeBr$_2$ and SIR2004$^{33}$ for 7, and intrinsic phasing method with the program of SHELT$^{34}$ for 6, refined by a full-matrix least squares method on $F^2$ for all the reflections (SHELXL-2013$^{35}$ for 1, SHELXL-2014$^{35}$ for 2, and 6, SHELXL-2016$^{35}$ for [(Eind)Li(THF)(LiBr)]$_2$ and (Eind)$_2$GeBr$_2$ and SHELXL-97$^{36}$ for 7). The non-hydrogen atoms were refined by applying anisotropic temperature factors. Positions of all hydrogen atoms were geometrically calculated, and refined as riding models.
Table 3–2 Crystallographic data for [(Eind)Li(THF)(LiBr)]$_2$, 1, 2, (Eind)$_2$GeBr$_2$, and 6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>[(Eind)Li(THF)(LiBr)]$_2$</th>
<th>1</th>
<th>2</th>
<th>(Eind)$_2$GeBr$_2$</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C$<em>{32}$H$</em>{53}$BrLiO</td>
<td>C$<em>{98}$H$</em>{156}$BrClGe$_2$</td>
<td>C$<em>{98}$H$</em>{156}$BrGe$_2$</td>
<td>C$<em>{98}$H$</em>{156}$BrGeK$_2$Ge$_2$</td>
<td>C$<em>{98}$H$</em>{156}$Ge$_2$</td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>547.56</td>
<td>1068.32</td>
<td>979.35</td>
<td>995.68</td>
<td>1029.63</td>
<td>1062.66</td>
</tr>
<tr>
<td>λ (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal size / mm$^3$</td>
<td>0.52 x 0.37 x 0.29</td>
<td>0.11 x 0.07 x 0.06</td>
<td>0.08 x 0.07 x 0.04</td>
<td>0.11 x 0.09 x 0.05</td>
<td>0.08 x 0.07 x 0.04</td>
<td>0.07 x 0.09 x 0.10</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pbcn (#60)</td>
<td>P-1 (#2)</td>
<td>P-1 (#2)</td>
<td>Cc (#9)</td>
<td>P-1 (#2)</td>
<td>P-1 (#2)</td>
</tr>
<tr>
<td>$a$ / Å</td>
<td>19.486(5)</td>
<td>10.43530(14)</td>
<td>10.4792(3)</td>
<td>10.6306(9)</td>
<td>11.2880(9)</td>
<td>9.7901(13)</td>
</tr>
<tr>
<td>$c$ / Å</td>
<td>17.324(4)</td>
<td>12.12440(14)</td>
<td>12.0496(3)</td>
<td>18.0740(14)</td>
<td>18.9434(17)</td>
<td>16.1645(17)</td>
</tr>
<tr>
<td>$α$º</td>
<td>90</td>
<td>97.1732(10)</td>
<td>97.829(2)</td>
<td>90</td>
<td>104.562(4)</td>
<td>108.141(7)</td>
</tr>
<tr>
<td>$β$º</td>
<td>93.3651(10)</td>
<td>97.2483(11)</td>
<td>93.325(2)</td>
<td>104.562(4)</td>
<td>101.352(8)</td>
<td>96.164(5)</td>
</tr>
<tr>
<td>$γ$º</td>
<td>90</td>
<td>93.3651(10)</td>
<td>97.2483(11)</td>
<td>93.325(2)</td>
<td>107.936(5)</td>
<td>100.768(7)</td>
</tr>
<tr>
<td>$V$ / Å$^3$</td>
<td>6490(3)</td>
<td>1306.38(3)</td>
<td>1297.30(6)</td>
<td>5044.7(7)</td>
<td>2471.7(3)</td>
<td>1510.9(3)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>μ(MoKα) mm$^{-1}$</td>
<td>1.290</td>
<td>2.718</td>
<td>1.296</td>
<td>2.226</td>
<td>2.366</td>
<td>1.033</td>
</tr>
<tr>
<td>$D_{\text{calcd}}$ / g cm$^{-3}$</td>
<td>1.121</td>
<td>1.358</td>
<td>1.254</td>
<td>1.311</td>
<td>1.383</td>
<td>1.168</td>
</tr>
<tr>
<td>$θ_{\text{max}}$</td>
<td>27.423</td>
<td>30.000</td>
<td>29.999</td>
<td>26.000</td>
<td>25.999</td>
<td>30.06</td>
</tr>
<tr>
<td>Refl./restr./para m.</td>
<td>7382/0/333</td>
<td>7611/0/279</td>
<td>7495/18/292</td>
<td>9587/97/548</td>
<td>9641/0/566</td>
<td>8831/2/355</td>
</tr>
<tr>
<td>Completeness</td>
<td>99.8</td>
<td>99.9</td>
<td>99.0</td>
<td>99.6</td>
<td>99.3</td>
<td>99.6</td>
</tr>
<tr>
<td>GOF</td>
<td>1.139</td>
<td>1.053</td>
<td>1.158</td>
<td>1.026</td>
<td>1.097</td>
<td>1.106</td>
</tr>
<tr>
<td>$R_{1}$ ($I&gt;2\sigma(I)$)</td>
<td>0.757</td>
<td>0.0234</td>
<td>0.0428</td>
<td>0.1165</td>
<td>0.0506</td>
<td>0.0585</td>
</tr>
<tr>
<td>w$R_{1}$ ($I&gt;2\sigma(I)$)</td>
<td>0.1489</td>
<td>0.0616</td>
<td>0.0980</td>
<td>0.2987</td>
<td>0.1184</td>
<td>0.1431</td>
</tr>
<tr>
<td>$R_{1}$ (all data)</td>
<td>0.1061</td>
<td>0.0276</td>
<td>0.0515</td>
<td>0.1382</td>
<td>0.0697</td>
<td>0.0707</td>
</tr>
<tr>
<td>w$R_{1}$ (all data)</td>
<td>0.1649</td>
<td>0.0631</td>
<td>0.1003</td>
<td>0.3214</td>
<td>0.1323</td>
<td>0.1538</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.548, –0.318</td>
<td>0.949, –0.514</td>
<td>0.953, –0.619</td>
<td>1.726, –1.265</td>
<td>1.303, –0.610</td>
<td>0.943, –0.658</td>
</tr>
</tbody>
</table>
3.4.3 UV-Visible Measurements

The UV-visible spectra were obtained using a Shimadzu UV-1700 pharmaSpec UV-Vis spectrophotometer with S-1700 Thermoelectric Single Cell Holder for 1 and 6, and a Shimadzu UV-3101(PCS) spectrometer for 2 and 7. Dry toluene, THF and Hexane (purchased from Kanto Chemical Co., Inc.) were used for the sample solution. A 1 cm square quartz cell was used for the measurements. The variable-temperature UV-vis spectra of 1 were recorded at 10 °C, 30 °C, 50 °C, and 70 °C for toluene solution (3.4 × 10^{-4} M) and at 25 °C, 40 °C, and 55 °C for THF solution (7.6 × 10^{-4} M). The variable-temperature UV-vis spectra of the mixture of 1 ([1]₀ = ca. 3.3 × 10^{-4} M) and LiBr ([LiBr] = ca. 3.7 × 10^{-2} M) in THF were recorded at 25 °C, 40 °C, and 55 °C. Absorption spectra in a microcrystalline powder film were measured by using a Leica DMLP polarizing microscope connected with a Hamamatsu PMA-11 photodetector.
3.5 References


Compound II can exist in the solid state in either the monomeric or dimeric form, see: 5(b) and 5(c).


26 CPCM models (THF); TD-B3PW91-D3/6-311G(3df) (Ge, Br) and 6-311G(d) (C, H). 4: \( \lambda_{\text{max}} = 408 \text{ nm} \left( f = 0.0269 \right) \) \([\text{Eind}GeBr}_2^-\) (counterion-free): \( \lambda_{\text{max}} = 367 \left( f = 0.0210 \right) \), \( 310 \text{ nm} \left( f = 0.0958 \right) \).


Publication List

Chapter 1

π-Conjugation between a Si=Si double bond and thiophene rings: synthesis, structural characteristics, and photophysical properties of 1,2-bis(thiophen-2-yl)disilene and 1,2-bis(2,2′-bithiophen-5-yl)disilene


Chapter 2

Synthesis and structures of sterically congested diarylsilanes bearing two bulky Rind groups

N. Hayakawa, T. Morimoto, A. Takagi, T. Tanikawa, D. Hashizume, T. Matsuo


Synthesis and characterization of N-heterocyclic-carbene-coordinated silicon(II) species bearing a fused-ring bulky Eind group


Chapter 3

1,2-Dihalodigermenes bearing bulky Eind groups: synthesis, characterization, and conversion to halogermynoids

Other Publication List

1. π-Electron systems containing Si=Si double bonds
   T. Matsuo, N. Hayakawa

2. Cleavage of a P=P double bond mediated by N-heterocyclic carbenes
   N. Hayakawa, K. Sadamori, S. Tsujimoto, M. Hatanaka, T. Wakabayashi, T. Matsuo

3. A silylyne tungsten complex having an Eind group on silicon: its dimer–monomer equilibrium and cycloaddition reactions with carbodiimide and diaryl ketones
   T. Yoshimoto, H. Hashimoto, N. Hayakawa, T. Matsuo, H. Tobita,

4. Synthesis and structural characteristics of discrete organoboron and organoaluminum hydrides incorporating bulky Eind groups

5. Synthesis and structural characterization of lithium and titanium complexes bearing a bulky aryloxide ligand based on a rigid fused-ring s-hydrindacene skeleton
   S. Kanazawa, T. Ohira, S. Goda, N. Hayakawa, T. Tanikawa, D. Hashizume, Y. Ishida, H. Kawaguchi, T. Matsuo

6. (Z)-1,2-Di(1-pyrenyl)disilene: synthesis, structure, and intramolecular charge-transfer emission
7. Reactions of diaryldibromodisilenes with N-heterocyclic carbenes: formation of formal bis-NHC adducts of silyliumylidene cations

8. Highly coplanar (*E*)-1,2-di(1-naphthyl)disilene involving a distinct CH–π interaction with the perpendicularly oriented protecting Eind group

9. A stable free tetragermacyclobutadiene incorporating fused-ring bulky EMinl groups
Acknowledgement

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Naoki Hayakawa

2018