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Room-Temperature Dissociation of 1,2-Dibromodisilenes to Bromosilylenes

Katsunori Suzuki,[†] Tsukasa Matsuo,*[,†,§] Daisuke Hashizume,[‡] and Kohei Tamao*[,†]

[†]Functional Elemento-Organic Chemistry Unit and [‡]Advanced Technology Support Division, RIKEN Advanced Science Institute, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
[§]PRESTO, JST.

S Supporting Information

ABSTRACT: A room-temperature dynamic equilibrium between dibromodisilenes and bromosilylenes has been demonstrated by taking advantage of the steric protection using the fused-ring bulky 1,1,3,3,5,5,7,7-octa-R-*s*-hydrindacen-4-yl (Rind) groups. Although the bromosilylenes cannot be directly observed by spectroscopic methods, the thermal homolytic cleavage of the Si═Si double bond has been confirmed by a pseudo-first-order kinetics for the trapping with bis(trimethylsilyl)acetylene and a crossover reaction using two kinds of Rind-substituted dibromodisilenes. The addition of 4-pyrrolidinopyridine (PPy) to the dibromodisilene leads to an equilibrium mixture between the dibromodisilene and a PPy adduct of bromosilylene, the latter being isolated and characterized. The substitution of the bromine atom in the dibromodisilene by the Grignard reagent is significantly accelerated by the addition of PPy.

Over the past three decades, many unsaturated silicon compounds have been extensively developed using bulky substituents based on the concept of kinetic stabilization, which enable us to study their fundamental chemistry and potential properties as functional materials.[1,2] Theoretical studies suggest that the nature of the bonding in disilenes ($R_2Si═SiR_2$) significantly depends on the singlet−triplet energy difference (ΔE_{ST}) of the corresponding silylene fragment ($R_2Si:$).[3−5] Thus, the bond dissociation energy (BDE) for the Si═Si double bond tends to decrease with the increasing electronegativity of the R-substituents on silicon due to the greater stabilization of the corresponding singlet silylenes; disilenes with alkoxy and amino groups or halogen atoms are predicted to be highly distorted disilenes or to readily dissociate into the corresponding silylenes, which are stabilized by the formation of the R-bridged silylene dimer.[6,7] Experimentally, a reversible disilene-silylene equilibrium has been observed for some sterically overcrowded disilenes[8,9] and amino-substituted disilenes.[10−12]

Whereas halogen-substituted silylenes and disilenes are regarded as valuable precursors for the construction of unique unsaturated silicon frameworks,[13−16] such as disilynes[15,16] and substituted disilenes,[16] the dynamic equilibrium between halo-disilenes and halo-silylenes through cleavage of the Si═Si bond has not yet been reported.[17]

We now present the facile thermal dissociation of 1,2-dibromodisilenes **1**, stabilized by the fused-ring bulky 1,1,7,7-tetraethyl-3,3,5,5-tetra-R-substituted *s*-hydrindacen-4-yl (Rind) groups, into the corresponding highly reactive bromosilylenes **2**, which can be isolated and characterized as Lewis base adducts **3** (Scheme 1). We also report some substitution reactions of the dibromodisilenes by organolithium and magnesium reagents in the presence or absence of a Lewis base.

As shown in Scheme 1, the dibromodisilenes **1a** and **1b** were readily prepared by the reduction of the tribromosilane precursors $(Rind)SiBr_3$ with 2 equiv of lithium naphthalenide (LiNaph)[18] and isolated as air- and moisture-sensitive yellow crystals in moderate yields. The formation of the Si═Si bond was clearly confirmed by the ^{29}Si NMR spectra, in which the characteristic signal was observed at 74.6 (**1a**) and 73.2 (**1b**) ppm, respectively. Compounds **1a** and **1b** are stable at room temperature in the solid state for months under a dry argon atmosphere with no detectable change as confirmed by the ^1H NMR spectra.

Figure 1A shows the molecular structure of **1b** determined by X-ray crystallography. This molecule has an inversion center at the midpoint of the Si═Si bond. The disilene core adopts a *trans*-bent geometry with an *E* configuration; the *trans*-bent angle between the Si1−Si1′ vector and the Si1−Br1−C1 plane is 29.0°. The Si atoms are pyramidal with the sum of the surrounding angles of 350.8°. These structural features of **1b** found in the crystal are distinct from those of the Eind-substituted 1,2-diphenyldisilene (Eind)PhSi═SiPh(Eind), which adopts an almost planar geometry around the Si═Si bond with the *trans*-bent angle of 2.7°.[19] The Si═Si bond length of **1b** [2.1795(9) Å] is comparable to that of the diphenyldisilene [2.1593(16) Å][19] and in the range of those for the typical disilenes.[2]

The thermolysis of **1** at 100 °C overnight in bis(trimethylsilyl)acetylene (BTMSA) afforded a cycloadduct, i.e., the silacyclopropenes **4** as the sole product, isolated in moderate yields (Scheme 2),[20] indicative of the formation of the bromosilylenes (Rind)BrSi: (**2**) as a reactive intermediate through the homolytic cleavage of the Si═Si bond of **1**.[8,9] Kinetic studies of the thermal reaction of **1** with BTMSA (ca. 1000 equiv vs **1**) in toluene follow the pseudo-first-order kinetics with $\Delta H^\ddagger = 26.64 \pm 0.19$ kcal mol^{-1} and $\Delta S^\ddagger = 9.32 \pm 0.59$ cal mol^{-1} K^{-1},[20] which are comparable to the previously reported kinetic data for the thermolysis of the overcrowded disilenes,[8b] thus suggesting the facile dissociation of **1** into **2**.

In fact, equilibrium between **1** and **2** in solution was confirmed even at room temperature by a crossover reaction between the

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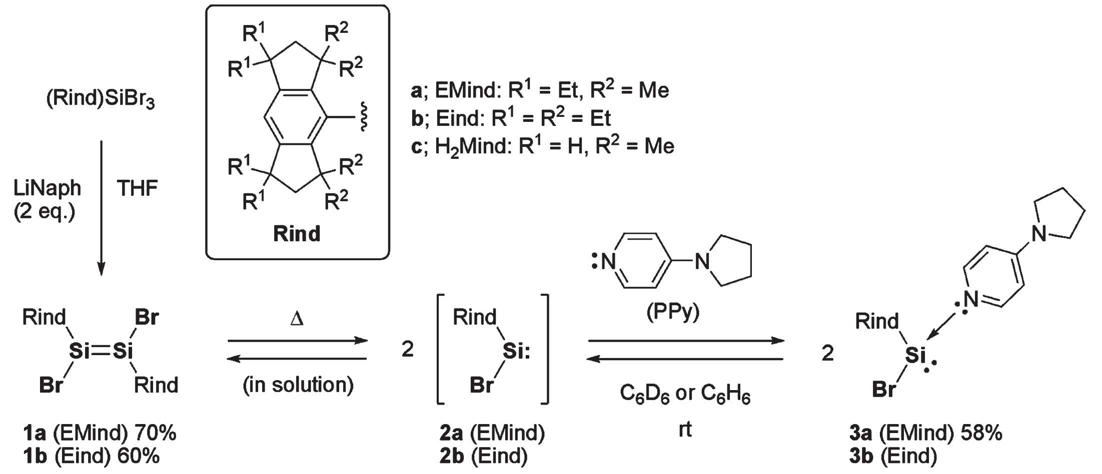
Scheme 1. Dynamic Equilibrium between Dibromodisilenes and Bromosilylenes



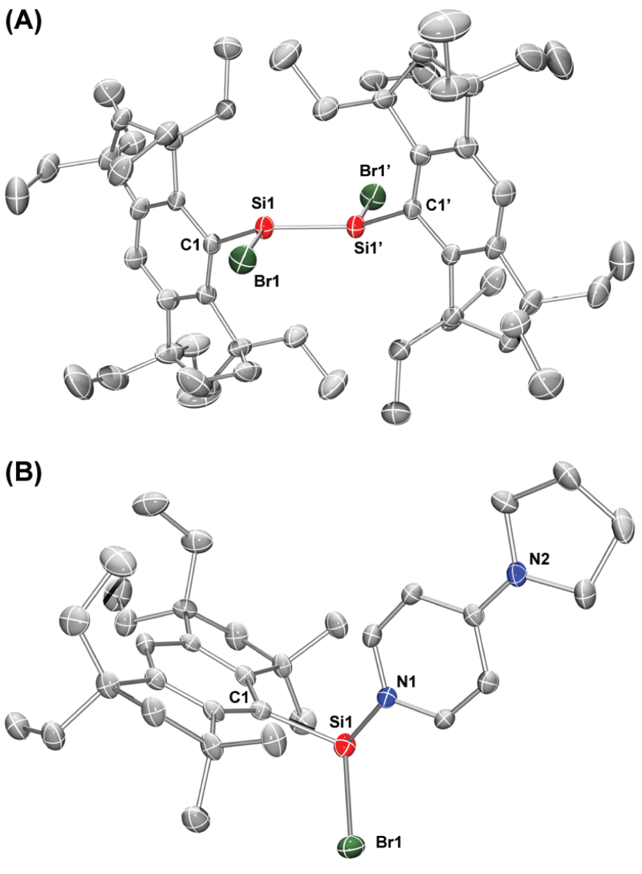
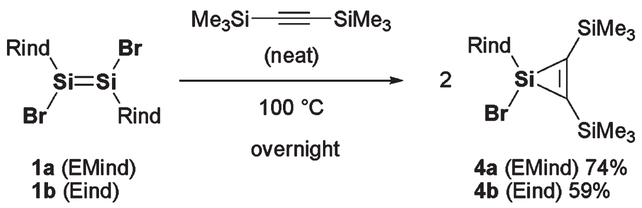
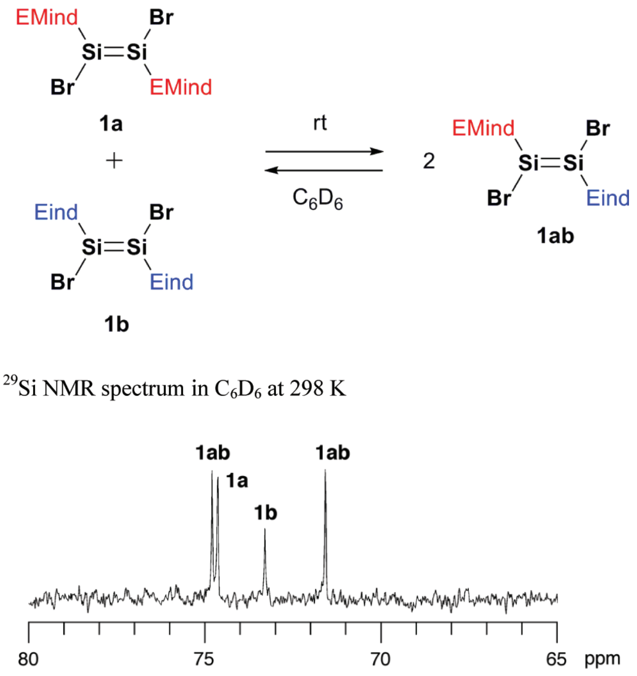


Figure 1. (A) Molecular structure of **1b** (50% probability ellipsoids). Hydrogen atoms and disordered ethyl group are not shown. Selected atomic distances (Å) and bond angles (deg): Si1−Si1′ = 2.1795(9), Si1−C1 = 1.8875(16), Si1−Br1 = 2.2279(6), C1−Si1−Si1′ = 126.86(6), C1−Si1−Br1 = 115.35(5), Br1−Si1−Si1′ = 108.59(3). (B) Molecular structure of **3a** (50% probability ellipsoids). Hydrogen atoms and solvent molecule are not shown. Selected atomic distances (Å) and bond angles (deg): Si1···N1 = 1.939(2), Si1−Br1 = 2.3922(9), Si1−C1 = 1.960(3), Br1−Si1−N1 = 96.23(7), Br1−Si1−C1 = 109.92(9), N1−Si1−C1 = 97.48(10).

Scheme 2. Thermolysis of 1 in BTMSA



Scheme 3. Crossover Reaction between 1a and 1b



EMind-substituted **1a** and the Eind-substituted **1b** (Scheme 3). Thus, a mixture of **1a** and **1b** in C_6D_6 gradually changed at room temperature into an equilibrium mixture containing a new disilene **1ab** bearing both the EMind and Eind groups, as monitored by ^{1}H NMR. After 24 h at room temperature, a dynamic equilibrium was attained in the ratio of **1a**:**1b**:**1ab** = 1:1:2.9, judging from integration of the aromatic signals in the ^{1}H NMR spectrum.[20] The ^{29}Si NMR spectrum, reproduced in Scheme 3, shows a pair of new signals at 71.6 and 74.8 ppm for **1ab**, in addition to the signals due to **1a** and **1b**. The equilibrium lies somewhat to the right, probably due to the release of the steric repulsion between the two bulkier Eind groups in **1b**.

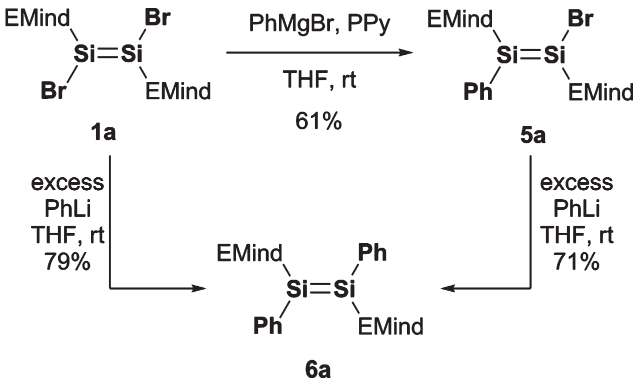
The facile dissociation of **1** into **2** is supported by the DFT computations at the B3LYP/6-31G(d,p) level using the Gaussian 03W program package,[21] performed for a set of model compounds having H_2Mind (see Scheme 1) groups. The BDE of the Si═Si double bond in the dibromodisilene $(H_2Mind)BrSi{=}SiBr(H_2Mind)$ (**1c**) is estimated to be 19.2 kcal mol^{-1}, which is much lower than that of the corresponding diphenyldisilene $(H_2Mind)PhSi{=}SiPh(H_2Mind)$ (34.0 kcal mol^{-1}) and between $(Me_5C_5)\{(Me_3Si)_2N\}Si{=}Si\{N(SiMe_3)_2\}(C_5Me_5)$ (23.2 kcal mol^{-1})[11] and $(i\text{-}Pr_2N)_2Si{=}Si(i\text{-}Pr_2N)_2$ (3−8 kcal mol^{-1}).[10c] The ΔE_{ST} value for the bromosilylene $(H_2Mind)BrSi$: (**2c**) (46.4 kcal mol^{-1}) is larger than that for the phenylsilylene $(H_2Mind)PhSi$: (38.2 kcal mol^{-1}) and again between that for $(Me_5C_5)\{(Me_3Si)_2N\}Si$: (39.6 kcal mol^{-1})[11] and $(i\text{-}Pr_2N)_2Si$: (54.3 kcal mol^{-1}).[10c]

The bromosilylenes **2** could not be directly observed by spectroscopic methods, but the equilibrium became observable in the presence of a strong Lewis base (Scheme 1). The addition of 4-pyrrolidinopyridine (PPy) to a solution of **1** in C_6D_6 immediately afforded an equilibrium mixture of **1** and the bromosilylene-PPy adducts **3**, as monitored by ^{1}H NMR.[20] In the ^{29}Si NMR spectra, one new resonance appears at 59.3 (**3a**) and 63.1 (**3b**) ppm, respectively. The equilibrium constants K_{eq} = 350 M^{-1} for **3a** and 0.64 M^{-1} for **3b** at 25 °C are quite different from each other.[20] Thus, the steric bulkiness of the Rind groups significantly affects the coordination of PPy to the Si center of the bromosilylene **2**. The negative enthalpy values of $\Delta H = -15.6$ (**3a**) and -10.3 (**3b**) kcal mol^{-1} were derived from the respective van't Hoff plots of the equilibrium between **1** and **3**,[20] which suggest that the PPy adducts **3** are favored at low temperatures.

Orange crystals of **3a** were isolated in 58% yield by crystallization from the equilibrium mixture of **1a** and **3a** in benzene at 6 °C. The dissolution of the pure crystals of **3a** in C_6D_6 again afforded the mixture of **1a** and **3a**. The X-ray structural analysis of **3a** demonstrates that the coordination of PPy forms a trigonal pyramidal geometry around the Si center with the sum of the bond angles of 303.6°, as shown in Figure 1B. The Si···N atomic distance of **3a** [1.939(2) Å] is much longer than the typical Si−N single bond length with the tetracoordinate Si(IV) center (1.74 Å)[22] but shorter than that observed in the $SiBr_4$−pyridine (Py) adduct ($SiBr_4Py_2$) [1.981(3) Å].[23] The Si−Br and Si−C bond lengths in **3a**, 2.3922(9) and 1.960(3) Å, respectively, are elongated relative to those, 2.2279(6) and 1.8875(16) Å, in **1b**, because of the increased p character of the silicon atomic orbitals directed to the bromine atom and the aryl group.[13,24] The solid state ^{29}Si CP-MAS NMR spectrum of **3a** shows a strong signal at 62.4 ppm, which is close to that observed in C_6D_6 (59.3 ppm), indicative of a solution structure of **3a** similar to the structure found in the crystal.

The substitution reactions of **1a** have also been examined in the presence or absence of PPy (Scheme 4). Although **1a** did not show any sign of reaction with PhMgBr in THF at room temperature, the addition of PPy (2 equiv) to the reaction mixture resulted in the facile, selective formation of a monophenylated product **5a**, which was isolated in 61% yield.

Scheme 4. Reactions of 1a with Organometallic Reagents



The resulting monobromodisilene **5a** is thermally stable, in contrast to the dibromodisilene **1a**, both in solution and in the solid state; the Si═Si bond dissociation was not observed in C_6D_6 even in the presence of excess PPy, as confirmed by the NMR monitoring. A possible mechanism for the PPy-promoted monophenylation of **1a** is proposed as follows: The bromosilylene-PPy complex **3a**, less hindered than **1a**, readily reacts with PhMgBr to give the phenylsilylene (EMind)PhSi: as a reactive intermediate, which is immediately trapped by **3a** to produce **5a**. At the moment, an alternative addition−elimination mechanism[16] is not ruled out; thus the PPy coordination to the Mg center may enhance the reactivity of the PhMgBr that causes a direct attack on the dibromodisilene **1a** to form **5a** via an addition−elimination mechanism. While the detailed mechanism remains to be clarified by further studies, the synthetic potentials of dibromodisilene **1a** are noteworthy. Thus, both **1a** and **5a** readily react with PhLi to form the diphenylated disilene **6a** in high yields, suggesting a useful general route to a variety of diaryldisilenes, including the unsymmetrical or heteroaryl-substituted diaryldisilenes, which are hardly accessible by the existing methods. Further synthetic investigations using **1** for the construction of unique π-conjugated disilene frameworks are currently in progress and will be reported shortly.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, crystallographic data for **1b**, **3a**, and **4a** in CIF format, details of the calculations, and complete ref 21. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

matsuo@riken.jp; tamao@riken.jp

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