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Synthesis of Kinetically Stabilized 1,2-Dihydrodisilenes

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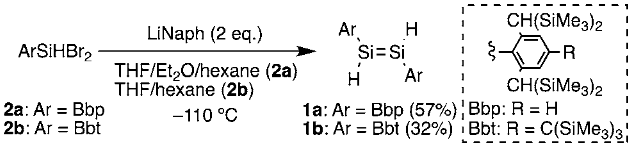
Supporting Information

ABSTRACT: Kinetically stabilized 1,2-dihydrodisilenes were successfully synthesized and isolated by the introduction of sterically protecting bulky aryl groups. These 1,2-dihydrodisilenes exhibit distinct Si═Si double-bond character in both solution and the solid state. The Si−H bonds in these 1,2-dihydrodisilenes exhibit higher s character than those of typical σ^4,λ^4-hydrosilanes. Moderate heating of these 1,2-dihydrodisilenes in solution resulted in their isomerization to the corresponding trihydrodisilanes, with an intramolecular hydrogen migration as the rate-determining step.

The high reactivity of the Si−H bond in σ^4,λ^4-hydrosilanes ($R_3Si{-}H$) and its versatility in organic and organometallic transformations have made these compounds one of the most attractive classes of chemical feed stock among organosilicon compounds.[1] However, the structurally closely related σ^3,λ^4-hydrosilanes $R_nE{=}Si(R){-}H$ (E = main-group element) remain an exotic and underdeveloped class of hydrosilanes. The severely changed coordination environment around the silicon atom in σ^3,λ^4-hydrosilanes relative to that in σ^4,λ^4-hydrosilanes is expected to result in significant differences in the properties and reactivity of σ^3,λ^4-hydrosilanes. Only a few examples of σ^3,λ^4-hydrosilanes, such as mono- and dihydrosilenes[2] as well as monohydrodisilenes [e.g., lithiodisilene $R^1(H)Si{=}Si(Li)R^1$ (**I**) (R^1 = $Si(i\text{-}Pr)Dis_2$, Dis = $CH(SiMe_3)_2$)] have been reported to date.[3] Despite the recent progress in the chemistry of kinetically stabilized multiply bonded silicon compounds, stable disilenes bearing more than one hydrogen substituent [e.g., 1,2-dihydrodisilenes $R(H)Si{=}Si(H)R$][4] still remain elusive.[5] Synthetically, the key challenge for the successful isolation of such multiply hydrogen-substituted disilenes lies in the effective stabilization of the sterically exposed H−Si═Si−H moiety. Wiberg et al.[6] have suggested the intermediate formation of 1,2-dihydrodisilene $R^2(H)Si{=}Si(H)R^2$ (**II**) (R^2 = $SiH[Si(t\text{-}Bu)_3]_2$) on the basis of NMR data of the crude reaction mixture. However, because of its facile thermal decomposition, **II** could not be isolated, and the structure of **II** was assigned by analysis of the decomposition product. Regardless of the synthetic challenges involved, 1,2-dihydrodisilenes are desirable targets for two important reasons: (i) the H−Si═Si moiety is expected to exhibit characteristics distinctly different from those of σ^4,λ^4-hydrodisilanes [$H{-}Si(R)_2{-}SiR_3$], and (ii) the H−Si═Si−H moiety represents a powerful model for the parent disilene, $H_2Si{=}SiH_2$, allowing fundamental insights into the intrinsic nature of the bonding situation in $H_2Si{=}SiH_2$. The successful application of the bulky aryl groups Bbp and Bbt in the kinetic stabilization of a variety of compounds containing low-coordinated heavier main-group elements[7] prompted us to investigate their potential for the steric protection of the labile H−Si═Si−H moiety. Herein we report the synthesis, structure, spectroscopic properties, and thermal isomerization of kinetically stabilized 1,2-dihydrodisilenes **1a** and **1b**.

Scheme 1. Synthesis of 1,2-Dihydrodisilenes 1a and 1b



Reduction of dibromosilanes **2a** and **2b** with 2 equiv of lithium naphthalenide (LiNaph) at −110 °C in THF/Et_2O/hexane (**2a**) or THF/hexane (**2b**) afforded 1,2-dihydrodisilenes **1a** and **1b** as pale-yellow solids in yields of 57 and 32%, respectively (Scheme 1). Both in the solid state and in solution (C_6D_6), **1a** and **1b** did not show any susceptibility toward decomposition below 25 °C.

Structural parameters of **1a** in the solid state were determined by X-ray diffraction analysis (Figure 1a).[8] Disilene **1a** has a crystallographic center of symmetry at the middle of the Si−Si bond. Hydrogen atom H1 was located on the difference Fourier maps and refined isotropically. The Si−Si bond length in **1a** [2.1708(6) Å] is contracted by 8% relative to that in the tetrahydrodisilane $Bbp(H)_2Si{-}Si(H)_2Bbp$ (**3**) [2.3633(2) Å] and comparable to those in previously reported

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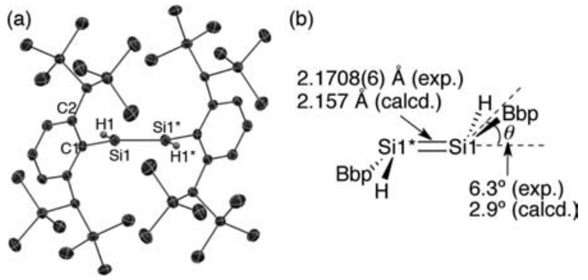


Figure 1. (a) Molecular structure of **1a**. Thermal displacement ellipsoids are drawn at the 50% probability level. H atoms except for H1 and H1* have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Si1* = 2.1708(6), Si1–C1 = 1.8843(10), Si1–H1 = 1.45(2), Si1*–Si1–C1 = 126.87(4), C1–Si1–H1 = 114.5(9), H1–Si1–Si1* = 118.1(9), Si1*–Si1–C1–C2 = 81.85(9)°. (b) Experimental and calculated Si═Si bond lengths and *trans*-bent angles (θ) in **1a**.

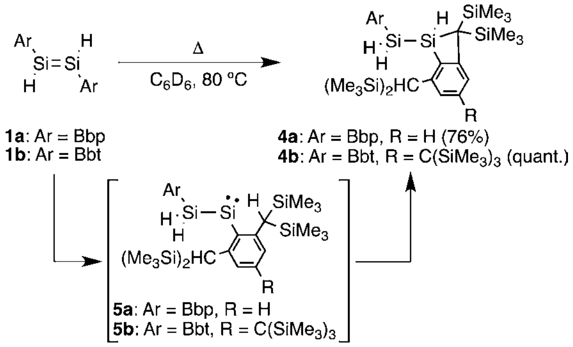
disilenes (2.138–2.360 Å),[9] indicating significant Si═Si double-bond character for **1a** in the crystalline state. In addition, **1a** exhibits a *trans*-bent structure, with a *trans*-bent angle (θ) of 6.3° around the Si1 atom. The molecular structure of **1a** was reproduced by density functional theory (DFT) calculations,[10] and the calculated Si1–Si1* bond length (2.157 Å) and *trans*-bent angle (2.9°) were in good agreement with those observed experimentally.

The ^{29}Si NMR spectra of **1a** and **1b** in C_6D_6 showed signals in the low-field region (**1a**, δ_{Si} = 63.3 ppm; **1b**, δ_{Si} = 61.8 ppm), characteristic of disilenes with adjacent carbon substituents. In the ^{1}H NMR spectra of **1a** and **1b** (C_6D_6), the hydrogen nuclei attached to the low-coordinated silicon atoms resonated at 6.04 and 6.11 ppm respectively. Both these values are low-field shifted relative to those of σ^4,λ^4-hydrosilanes (e.g., δ_H = 4.83 ppm for **3** in C_6D_6), reflecting the magnetic anisotropy effect of the Si═Si π electrons.[11] The observed $^1J_{SiH}$ values of the H–Si═Si–H moieties in **1a** (216 Hz) and **1b** (210 Hz) are larger than those in σ^4,λ^4-hydrosilanes such as **3** (188 Hz), suggesting increased s character of the Si–H bonds. In contrast, previously reported hydrogen-substituted disilenes **I** and **II** exhibited much smaller $^1J_{SiH}$ values (**I**, 155 Hz;[3a] **II**, 149.8 Hz[6]), suggesting a decrease in the s character of the Si–H bonds due to the presence of the electropositive silyl groups.[12] Similarly, the observed $^2J_{SiH}$ values for the H–Si═Si–H moieties in **1a** (16 Hz) and **1b** (16 Hz) were larger than those in **3** (6.5 Hz) and **II** (0.9 Hz), corroborating the increased s character of the Si–H bonds in **1a** and **1b**. Independently, natural bond orbital (NBO) calculations supported the greater s character of the Si–H bonds in **1a** [σ_{SiH} = 0.6591Si(sp$^{2.50}$) + 0.7520H(s)] relative to those in **3** [σ_{SiH} = 0.6557Si(sp$^{3.12}$) + 0.7550H(s) and 0.6506Si(sp$^{3.20}$) + 0.7594H(s)].[10]

The UV–vis spectra of **1a** and **1b** in hexane exhibited lowest-energy absorption maxima λ_{max} at 411 nm (ε = 2.1 × 10^4 M^{-1} cm^{-1}) and 421 nm (ε = 2.0 × 10^4 M^{-1} cm^{-1}) respectively, which can be assigned to π–π* electron transitions in the Si═Si moiety. The almost identical λ_{max} values for **1a** (412 nm) and **1b** (423 nm) in THF would exclude coordination of THF to these disilenes. In the solid-state Raman spectra, **1a** and **1b** exhibited Raman lines at 566 and 575 cm^{-1}, respectively. Theoretical calculations for **1a** estimated the Si═Si vibrational frequency to be 588 cm^{-1},[10] which is in good agreement with the experimentally observed values. The Si═Si stretching frequencies for previously reported carbon-substituted disilenes are known to be observed in the range from 500 to 600 cm^{-1},[13] indicating that **1a** and **1b** contain distinct Si═Si double bonds in the solid state. The IR spectra of **1a** and **1b** in a KBr disk showed Si–H vibrational frequencies at ν_{SiH} = 2160 cm^{-1} (**1a**) and 2151 cm^{-1} (**1b**). The observed values are again in good conformity with the calculated value for **1a** (2168 cm^{-1}) and slightly larger than those for σ^4,λ^4-hydrosilanes (e.g., 2122 cm^{-1} for Ph_3SiH).[2a]

Moderate heating of solutions of **1a** and **1b** in C_6D_6 to 80 °C resulted in the isomerization of these disilenes into the corresponding disilanes **4a** and **4b** (Scheme 2).[14] The formation of **4a** and **4b** can be logically explained by a mechanism proceeding via an initial 1,2-hydrogen migration to form intermediate silylsilylenes **5a** and **5b**, followed by a subsequent insertion of the silylene moiety into the benzylic C–H bonds of the sterically demanding $CH(SiMe_3)_2$ groups.[15] A similar mechanism was proposed for the decomposition of transient disilene **II**.[6,16]

Scheme 2. Thermolysis of 1a and 1b



Kinetic studies of the thermolysis of **1b** in hexane or THF by UV–vis spectrometry revealed that the isomerization is a first-order, unimolecular reaction. For hexane solutions, the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were estimated to be 20.6(5) kcal mol^{-1} and −15(2) cal K^{-1} mol^{-1}. The negative value of $\Delta S^\ddagger$ indicates a considerable conformational change of **1b** during the rate-determining step. For THF solutions, the activation parameters were determined to be $\Delta H^\ddagger$ = 23.6(7) kcal mol^{-1} and $\Delta S^\ddagger$ = −6(2) cal K^{-1} mol^{-1}. The small negative value of $\Delta S^\ddagger$ does not support any involvement of THF molecules during the rate-determining step. The isomerization mechanism of **1b** was further investigated using DFT calculations.[10] Figure 2 shows the computationally generated energy profile for the thermal isomerization of **1b**. The terminal hydrogen atom H2 in **1b** initially moves via transition state **TS1** toward a bridging position above the Si═Si π plane, resulting in the formation of intermediate **6b**. The calculated activation parameters for this step ($\Delta H^\ddagger$ = 19.4 kcal mol^{-1}, $\Delta S^\ddagger$ = −2.4 cal K^{-1} mol^{-1}) are in close agreement with the experimentally estimated values, suggesting that this step is rate-determining. Although the transition state between **6b** and **5b** (**TS2**) could not be located, the necessary activation barrier was estimated to be sufficiently low to allow fast interconversion between **5b** and **6b** prior to the intramolecular cyclization.[17,18] The final step (**5b** → **4b**) proceeds via **TS3** with a large exothermicity (−36.2 kcal mol^{-1}), suggesting that the isomerization from **1b** to **4b** should proceed readily. The activation barrier for this step ($\Delta H^\ddagger$ = 16.3 kcal mol^{-1}) was found to be smaller than that for the first step. Moreover, the activation entropy of this step was

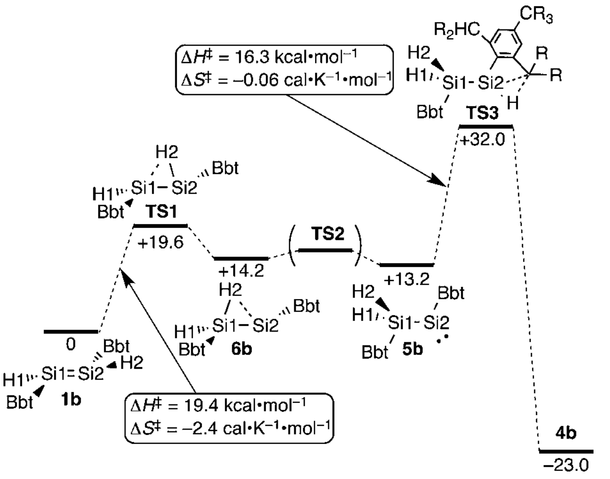


Figure 2. Calculated reaction path for the isomerization of **1b**. Values beneath the energy levels represent the SCF energies relative to **1b** (in kcal mol^{-1}); R = $SiMe_3$. The activation parameters in the boxes were calculated with zero-point vibrational energy corrections.

calculated to be close to zero (−0.06 cal K^{-1} mol^{-1}), suggesting that this final step, intramolecular cyclization, is not the experimentally observed rate-determining step. In conclusion, the computational results support the assumption that a gradual isomerization of 1,2-dihydrodisilenes **1a** and **1b** via a 1,2-hydrogen shift is what was observed in solution.

In summary, we have reported the synthesis, structure, and spectroscopic properties of kinetically stabilized 1,2-dihydrodisilenes **1a** and **1b**. Both in the solid state and in solution, **1a** and **1b** retain a pronounced Si═Si double bond, and their Si−H bonds have higher s character than those of σ^4,λ^4-hydrosilanes. Heating **1a** and **1b** resulted in isomerizations via intramolecular hydrogen migrations, resembling the hydrogen-shift equilibrium suggested for the parent disilene $H_2Si{=}SiH_2$.[18]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, analytical data for new compounds, computational results, and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 2000.

(2) (a) Ozaki, S.; Sasamori, T.; Tokitoh, N. *Organometallics* **2008**, *27*, 2163. (b) Tanaka, H.; Ichinohe, M.; Sekiguchi, A. *Chem. Lett.* **2008**, *37*, 1246.

(3) (a) Kinjo, R.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2007**, *129*, 26. (b) Takeuchi, K.; Ikoshi, M.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2010**, *132*, 930.

(4) A 1,2-dihydrodigermene was synthesized as a stable species. See: (a) Richards, A. F.; Phillips, A. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 3204. (b) Spikes, G. H.; Fettinger, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232.

(5) (a) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (b) Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 2001; Vol. 3, p 391. (c) Kira, M.; Iwamoto, T. *Adv. Organomet. Chem.* **2006**, *54*, 73. (d) Sasamori, T.; Tokitoh, N. In *Encyclopedia of Inorganic Chemistry*, 2nd ed.; King, R. B., Ed.; Wiley: Chichester, U.K., 2005; p 1698. (e) Lee, V. Y.; Sekiguchi, A. *Organometallic Compounds of Low-Coordinated Si, Ge, Sn, and Pb: From Phantom Species to Stable Compounds*; Wiley: Chichester, U.K., 2010; Chapter 5. (f) Fischer, R. C.; Power, P. P. *Chem. Rev.* **2010**, *110*, 3877.

(6) Wiberg, N.; Niedermayer, W.; Nöth, H.; Warchhold, M. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1717.

(7) (a) Sugiyama, Y.; Sasamori, T.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 1023. (b) Sasamori, T.; Mieda, E.; Nagahora, N.; Sato, K.; Shiomi, D.; Takui, T.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 12582. (c) Sasamori, T.; Hironaka, K.; Sugiyama, Y.; Takagi, N.; Nagase, S.; Hosoi, Y.; Furukawa, Y.; Tokitoh, N. *J. Am. Chem. Soc.* **2008**, *130*, 13856.

(8) The Si−Si bond length of **1b** was estimated to be in the range of 2.16−2.18 Å on the basis of a preliminary X-ray crystallographic analysis.

(9) The range of the Si═Si bond lengths of disilenes was taken from the Cambridge Crystallographic Data Centre database (82 examples).

(10) These calculations were performed at the B3PW91/6-311+G(2df)[Si]:6-31G(d)[C,H] level of theory.

(11) The calculated ^{29}Si and ^{1}H chemical shifts of **1a** and **1b** (δ_{Si} = 72.6 ppm, δ_H = 6.06 ppm for **1a**; δ_{Si} = 66.7, 68.7 ppm, δ_H = 6.27, 6.28 ppm for **1b**) were comparable to the experimentally observed values (HCTH407/6-311+G(2df)[Si]:6-31G(d)[C,H]). For Gauge-Independent Atomic Orbital (GIAO) calculations on disilenes, see: Karni, M.; Apeloig, Y.; Takagi, N.; Nagase, S. *Organometallics* **2005**, *24*, 6319.

(12) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

(13) (a) Leites, L. A.; Bukalov, S. S.; Mangette, J. E.; Schmedake, T. A.; West, R. *Spectrochim. Acta, Part A* **2003**, *59*, 1975. (b) Yuasa, A.; Sasamori, T.; Hosoi, Y.; Furukawa, Y.; Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 793.

(14) Thermolysis of **1a** afforded small amount of unidentified byproducts, resulting in a moderate yield of **4a**, while disilene **1b** isomerized quantitatively to **4b**.

(15) A transient silylene Tbt(Mes)Si: (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) undergoes facile cyclization in a fashion similar to that of **5b**. See: Suzuki, H.; Tokitoh, N.; Okazaki, R.; Harada, J.; Ogawa, K.; Tomoda, S.; Goto, M. *Organometallics* **1995**, *14*, 1016.

(16) Although a direct pathway from disilene **1** to cyclic disilane **4** via a [1,5]-H shift of the benzylic proton along with intramolecular cyclization (as in the case of $Mes_2Si{=}SiMes_2$) can be proposed for the isomerization of **1**, the mechanism shown here is considered to be the most reasonable because the results of the theoretical calculations reproduced well those obtained in the experimental kinetic study. See: (a) Nguyen, T.-L.; Scheschkewitz, D. *J. Am. Chem. Soc.* **2005**, *127*,

10174. (b) Fink, M. J.; De Young, D. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 1070.

(17) As for the isomerization of model disilenes R(H)Si═Si(H)R (R ═ H, Me, *t*-Bu), transition states corresponding to **TS2** were found in the DFT calculations, and the activation barrier was estimated to be <1 kcal mol^{-1}. See the Supporting Information for details.

(18) The isomerization among **1b**, **6b**, and **5b** resembles the hydrogen-shift equilibrium of the parent disilene $H_2Si{=}SiH_2$. See: (a) Trinquier, G. *J. Am. Chem. Soc.* **1990**, *112*, 2130. (b) Dolgonos, G. *Chem. Phys. Lett.* **2008**, *466*, 11. (c) Sari, L.; McCarthy, M. C.; Schaefer, H. F. III; Thaddeus, P. *J. Am. Chem. Soc.* **2003**, *125*, 11409.