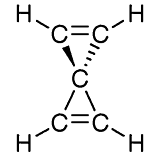
A Stable Bicyclic Compound with Two Si=Si Double Bonds

Takeaki Iwamoto, Makoto Tamura, Chizuko Kabuto, Mitsuo Kira*

In contrast to carbon, silicon does not readily form double bonds, and compounds containing silicon-silicon double bonds can usually be stabilized only by protection with bulky substituents. We have isolated a silicon analog of spiropentadiene 1, a carbon double-ring compound that has not been isolated to date. In the crystal structure of tetrakis[tri(*t*-butyldimethylsilyl)silyl]spiropentasiladiene 2, a substantial deviation from the perpendicular arrangement of the two rings is observed, and the silicon-silicon double bonds are shown to be distorted. Spectroscopic data indicate pronounced interaction between two remote silicon-silicon double bonds in the molecule. Silicon-silicon bonds may be more accessible to synthesis than previously assumed.

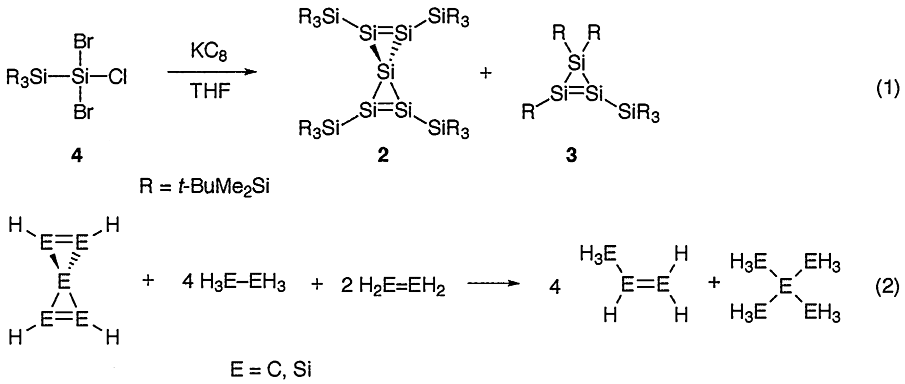
In contrast to alkenes, Si=Si doubly bonded compounds (disilenes) are usually unstable and can only be isolated when the double bonds are protected effectively by bulky substituents. Since the first isolation of tetramesityldisilene by West *et al.* in 1981 (*1*), a number of stable disilenes have been prepared, but the types of isolated disilenes remain very limited (*2–4*). The chemistry of disilenes cannot be compared to the extensive alkene chemistry, even though very recently a few silicon analogs of cycloalkenes (*5–9*) and butadienes (*10*) have been synthesized. We report the isolation of a silicon analog of spiropentadiene 1, which is a fascinating type of compound because of the possible through-space interaction between the two perpendicular double bonds, but it has not been isolated to date (*11*). Parent spiropentadiene **1** and 1,1′-dichlorinated spiropentadiene have been generated in solution but decompose within a few minutes even below −100°C; their structures were identified only by nuclear magnetic resonance (NMR) spectroscopy and by product analyses of a few chemical-trapping reactions (*12*, *13*). The present results demonstrate that the chemistry of Si=Si double bonds is not as limited as had been assumed, and it may even have comparable importance to organic alkene chemistry.

Compound 1.



1

We have found that tetrakis[tri(*tert*-butyldimethylsilyl)silyl]spiropentasiladiene (**2**) forms as a by-product during the preparation of cyclotrisilene **3** (Eq. 1) (*7*). The reaction of **4** with potassium graphite at −78°C and subsequent work-up resulted in a brownish red solid, which contained spiropentasiladiene **2** and cyclotrisilene **3** at a ratio of 1:8, as determined by ^{1}H NMR spectroscopy. Crystallization from hexane gave dark red crystals of **2** in 3.5%



Equations.

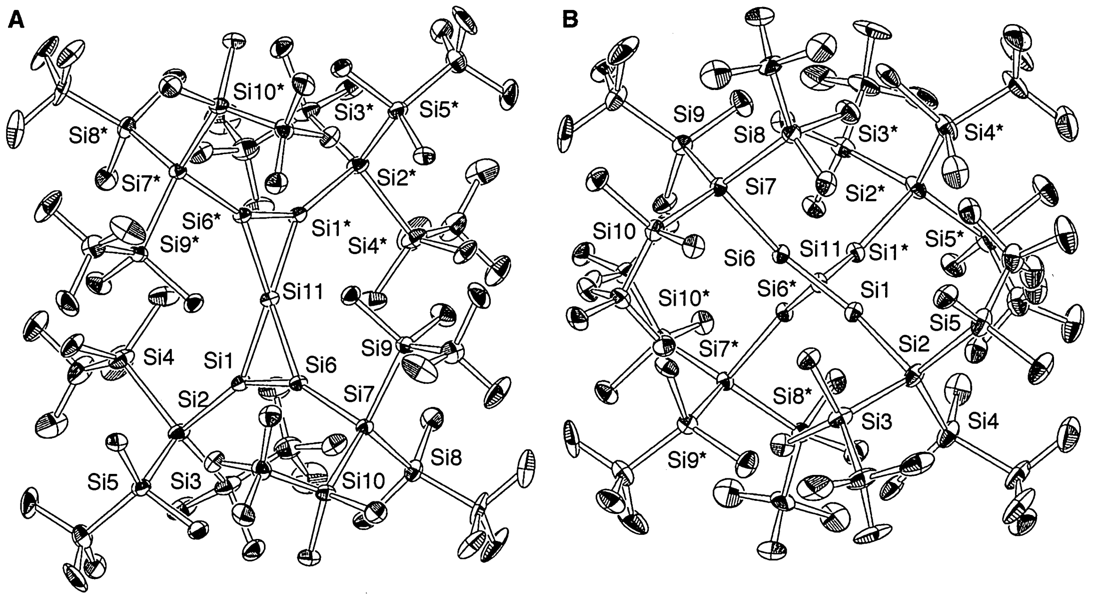


Fig. 1. Molecular view of tetrakis[tri(*t*-butyldimethylsilyl) silyl]spiropentasiladiene **2** in the solid state. Selected bond lengths (Å), angles (degrees), and dihedral angles (degrees): Si1-Si6 2.186(3), Si1-Si11 2.320(2), Si6-Si11 2.323(2), Si1-Si2 2.393(3), Si6-Si7 2.396(3), Si11-Si1-Si6 61.99(9), Si11-Si6-Si1 61.82(9), Si1-Si11-Si6 56.19(7), Si11-Si1-Si2 148.1(1), Si11-Si6-Si7 144.1(1), Si2-Si1-Si6 148.8(1), Si7-Si6-Si1 152.1(1), Si2-Si1-Si6-Si7 30.0(5), and plane 1 (Si11-Si1-Si6)–plane 2 (Si11-Si1*-Si6*) 78.26(0).

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan.

*To whom correspondence should be addressed. E-mail: mkira@si.chem.tohoku.ac.jp

yield. The structure of **2** was determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and x-ray crystallography (*14*). Although spiropentasiladiene **2** is sensitive to air, it is thermally very stable, in contrast to spiropentadiene itself; **2** melts at 216° to 218°C without decomposition (Eq. 1).

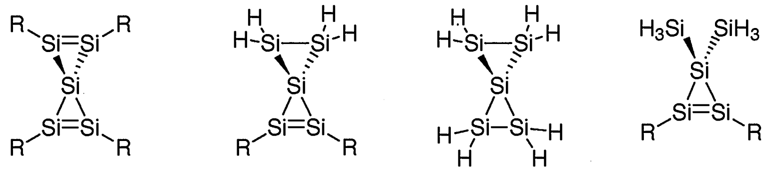
X-ray single-crystal analysis (*15*) shows that the two three-membered rings in **2** are not perpendicular to each other but are slightly twisted with a dihedral angle (θ) of 78.26(0)° (standard deviation is in parentheses) (Fig. 1). The geometry around the Si=Si bonds in **2** is not planar but substantially twisted; the dihedral angle Si2-Si1-Si6-Si7 (ϕ) is 30.0(5)°, and the sums of the bond angles are 358.9° at Si1 and 358.0° at Si6, respectively. The Si=Si double bonds in **2** are 0.05 Å longer, and the Si–Si single bonds in the three-membered ring are 0.03 to 0.04 Å shorter, than the corresponding bonds in tetrakis(di-*tert*-butylmethylsilyl)cyclotrisilene **5** (*8*). The geometry of a model spiropentasiladiene **6** was optimized by ab initio molecular orbital (MO) calculations at the B3LYP/6-31G(*d*) level with the Gaussian 98 program (*16*, *17*). Spiropentasiladiene **6** was found to be a minimum in D_{2d} symmetry, suggesting that the substantial deformation from D_{2d} to D_2 in **2** is due to the severe steric hindrance between bulky tris(trialkylsilyl)silyl groups. The lengths of the Si=Si bonds and the ring Si–Si bonds in **6** (D_{2d}) were found to be longer and shorter, respectively, than the corresponding bond lengths in cyclotrisilene **11** (C_{2v}). The reason for the modification of the bond distances in **2** [and **6** (D_{2d})] may be electronic and attributed to the effective interaction between the bonding π-orbital of a Si=Si bond and the low-lying Walsh-type σ* orbitals of Si–Si bonds in the other three-membered ring (σ*–aromaticity) (*18–20*) (Figs. 1 and 2).

Spiropentasiladiene **2** is kinetically stabilized as a result of steric protection by four bulky tri(*t*-butyldimethylsilyl)silyl groups, but isolation of **2** as the first spiropentadiene in the chemistry of group-14 elements is mainly due the relatively small strain energy (SE) of the ring systems. The SE value of parent spiropentasiladiene Si_5H_4 **7** with D_{2d} symmetry was calculated to be 61.1 kcal/mol as the heat of reaction of the following homodesmotic reaction (Eq. 2; E = Si) at the B3LYP/6-311++G(3*df*,2*p*)//B3LYP/6-31G(*d*) level (*17*, *21*). This SE value is much smaller than that of the corresponding spiropentadiene **1** (D_{2d}, 114.2 kcal/mol) calculated with the same equation (Eq. 2; E = C) at the same level (*22*).

The ultraviolet (UV)-visible spectral features of **2** in 3-methylpentane at room temperature were quite different from those of the monocyclic cyclotrisilenes **3** and **5** (*16*). Four major absorption bands in the longer wavelength region {absorption maxima (λ_{max}, in nanometers) [molar absorption coefficient (ε)/10^4]: 560 (0.253), 500 (0.364), 428 (1.17), and 383 (1.81)} were observed for **2**. The longest absorption maximum was highly red-shifted relative to those for **3** (*7*) and **5** (*8*), which show π→π* absorption maxima at 482 and 466 nm, respectively.

High-lying occupied and low-lying unoccupied molecular orbitals and their energy levels of cyclotrisilene **12** (C_{2v}), parent spiropentasiladiene **7** (D_{2d}), and a distorted spiropentasiladiene **7** (D_2), where the ring structure is fixed to a geometry similar to that of **2**, calculated at the HF/6-311++G(3*df*,2*p*) level are schematically shown in Fig. 3. In **7** (D_{2d}), there are two highly split π* orbitals (b_1 and a_2) and two degenerate π orbitals (e) of the Si=Si double bonds in addition to a low-lying σ* orbital (a_1). The large splitting of the π* orbitals is probably a result of the effective through-space interaction between the two remote π* orbitals, as suggested in parent spiropentadiene **1** (*22–24*). In the distorted spiropentasiladiene **7** (D_2), the degeneracy of the bonding π orbitals in **7** (D_{2d}) is removed efficiently by the through-space interaction between the π orbitals. The pronounced through-space interactions between π orbitals as well as between π* orbitals found in a distorted D_2 spiropentasiladiene may be the origin of the splitting of the low-energy transition bands and the red-shift of the longest wavelength band as observed experimentally in **2** (*25*) (Fig. 3).

The ^{29}Si NMR resonance due to the unsaturated silicon nuclei (Si$_u$) in **2** appeared at +154.0 parts per million, shifted to a lower field by ~60 ppm compared with the corre-



6, R = SiH_3
7, R = H

8, R = SiH_3
9, R = H

10, R = H

11, R = SiH_3
12, R = H

Fig. 2. Compounds **6** through **12**.

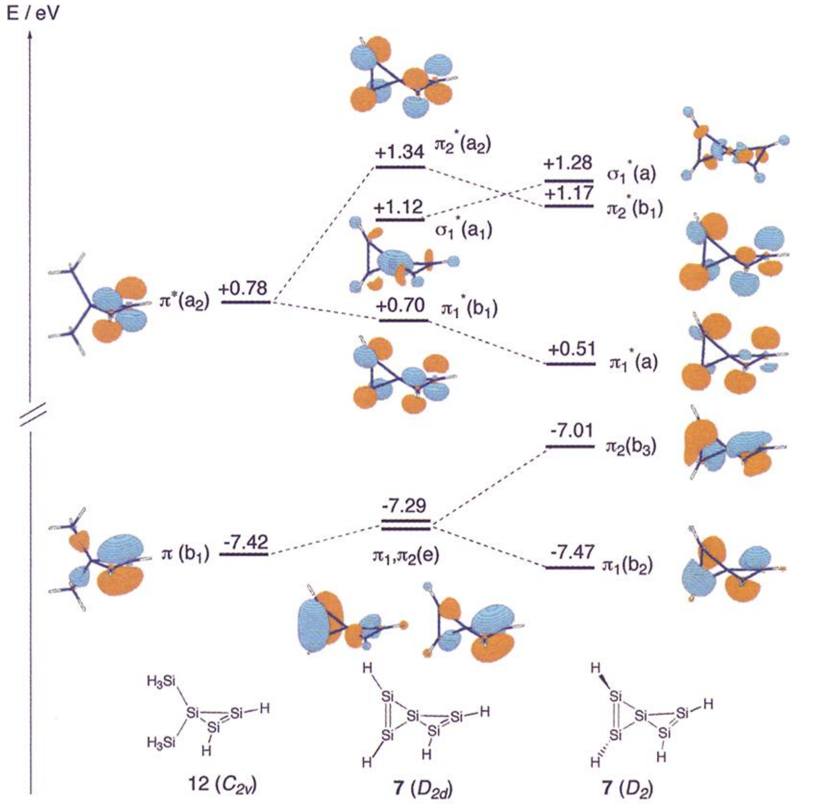


Fig. 3. Schematic molecular orbitals and energy levels for 3,3-bis(trihydrosilyl)cyclotrisilene **12** (C_{2v}), spiropentasiladiene **7** (D_{2d}), and distorted spiropentasiladiene **7** (D_2) at the HF/6-311++G(3*df*,2*p*) level. Structures of **12** (C_{2v}) and **7** (D_{2d}) were optimized at the B3LYP/6-31G(*d*) level. The structure of **7** (D_2) was fixed to a similar ring structure to **2**. The highest σ orbitals (b_2) in **7** (D_{2d}) and **7** (D_2), which are located at 8.73 and 8.66 eV, respectively, are omitted.

sponding resonances for **3** (+81.9 and +99.8 ppm) (*7*) and **5** (+97.7 ppm) (*8*). The Si_u resonances were well reproduced in the pertinent model compounds by ab initio MO calculations; the resonances were +178.3, +105.3, and +110.1 ppm for **6** (D_{2d}), spiropentasilene **8** (C_{2v}), and cyclotrisilene **11** (C_{2v}) at the GIAO/B3LYP/6-311+G(2*df*,*p*)//B3LYP/6-31G(*d*) level. Because the Si_u resonances in various disilenes are related to the reciprocal of the energy difference between σ and π* orbitals of the Si=Si bond (*26*), the remarkable lower-field shift of the Si_u resonance in **2** may be taken as another indication for the pronounced through-space interaction between π* orbitals. Unfortunately, the resonance due to the central ^{29}Si nucleus in **2** was not observed, probably as a result of the large spin-lattice relaxation time; the corresponding resonance in **6** was found at −45.9 ppm by the GIAO calculations (*16*).

The successful isolation of a spiropentasiladiene encourages us to make new types of silicon unsaturated compounds with new properties. Studies of the chemistry of these compounds may be an important innovation in the theory of chemical bonding and reactivity.

References and Notes

1. R. West, M. J. Fink, J. Michl, *Science* **214**, 1343 (1981).
2. G. Raabe, J. Michl, in *The Chemistry of Organic Silicon Compounds*, S. Patai, Z. Rappoport, Eds. (Wiley, New York, 1989), part 2, chap. 17.
3. T. Tsumuraya, S. A. Batcheller, S. Masamune, *Angew. Chem. Int. Ed. Engl.* **30**, 902 (1991).
4. R. Okazaki, R. West, *Adv. Organomet. Chem.* **39**, 231 (1996).
5. M. Kira, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **118**, 10303 (1996).
6. N. Wiberg, H. Auer, H. Nöth, J. Knizek, K. Polborn, *Angew. Chem. Int. Ed. Engl.* **36**, 2869 (1998).
7. T. Iwamoto, C. Kabuto, M. Kira, *J. Am. Chem. Soc.* **121**, 886 (1999).
8. M. Ichinohe, T. Matsuno, A. Sekiguchi, *Angew. Chem. Int. Ed. Engl.* **37**, 2194 (1999).
9. A. Grybat, S. Boomgaaden, W. Saak, H. Marsmann, M. Weidenbruch, *Angew. Chem. Int. Ed. Engl.* **38**, 2010 (1999).
10. M. Weidenbruch, S. Willms, W. Saak, G. Henkel, *Angew. Chem. Int. Ed. Engl.* **36**, 2503 (1997).
11. A saturated spiropentasilane has been reported [P. Boudjouk, R. Sooriyakumaran, *J. Chem. Soc. Chem. Commun.* 777 (1984)].
12. W. E. Billups, M. M. Haley, *J. Am. Chem. Soc.* **113**, 5084 (1991).
13. R. K. Saini, V. A. Litosh, A. D. Daniels, W. E. Billups, *Tetrahedron Lett.* **40**, 6157 (1999).
14. The detailed formation mechanism for **2** is currently under investigation. **2**: oxygen- and moisture-sensitive dark red crystals; melting point, 216° to 218°C; ^{1}H NMR (C_6D_6, δ): 0.68 (*s*, 72 H), 1.18 (*s*, 108 H); ^{13}C NMR (C_6D_6, δ): 2.5, 20.4, 29.5; ^{29}Si NMR (C_6D_6, δ): −100.6, 6.7, 154.2 (the resonance for the central silicon was not observed); UV-visible (3-methylpentane) λ_{max} (in nanometers) ($\varepsilon/10^4$): 560 (0.253), 500 (0.364), 428 (1.17), 383 (1.81), 304 (8.70), 265 (6.61, *sh*), 250 (8.63, *sh*), 235 (7.78, *sh*).
15. A single crystal of **2** used for the collection of x-ray diffraction involved two hexane molecules as a cosolvent for each spiropentasiladiene. Crystal data for **2**: $[C_{72}H_{180}Si_{21}\cdot(C_6H_{14})_2]$, formula weight = 1808.36; dark red plate; orthorhombic; space group = I_{bca}; cell constants, a = 27.510(3) Å, b = 29.461(1) Å, c = 29.830(1) Å; V (cell volume) = 24175(2) Å^3; number of molecules per unit cell (Z) = 8; calculated density (D_{calcd}) = 0.994 g/cm^3. Intensities of reflections were collected on a Rigaku/MSC Mercury charge-coupled device diffractometer with a graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) at 150 K. Of the 79,057 reflections that were collected, 14,416 were unique. The structure was solved by direct methods and refined anisotropically for nonhydrogen atoms. Hydrogen atoms and carbon atoms of a solvent were included but not refined. The final cycle of full-matrix least-squares refinement was based on 4943 observed reflections [$I > 2.00\sigma(I)$, where I is the observed reflection intensity] and 420 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.066$, $R_w = 0.078$, and GOF (goodness of fit) = 1.51. All calculations were performed with the teXsan crystallographic software package of Molecular Structure Corporation. Coordinates and other crystallographic information will be deposited in the Cambridge Crystallographic Database (*16*).
16. Supplementary data are available at *Science* Online at www.sciencemag.org/feature/data/1052253.shl.
17. M. J. Frisch *et al.*, *GAUSSIAN 98 (Revision A.7)* (Gaussian, Pittsburgh, PA, 1998).
18. L. Nyulászi, P. v. R. Schleyer, *J. Am. Chem. Soc.* **121**, 6872 (1999).
19. A. Goller, H. Heydt, T. Clark, *J. Org. Chem.* **61**, 5840 (1996).
20. For a recent example of the σ*-aromaticity in silacyclopropenes, see S. Tsutsui, K. Sakamoto, C. Kabuto, M. Kira, *Organometallics* **17**, 3819 (1998).
21. A homodesmotic reaction is defined as a reaction in which (i) there are equal numbers of C (or Si) atoms in their various states of hybridization in reactants and products and (ii) there are equal numbers of C (or Si) atoms with zero, one, two, and three H atoms attached in reactants and products (*27*). A homodesmotic reaction is arbitrarily chosen, but SE was almost independent of the choice. Several authors have calculated SE values for the parent spiropentadiene. Typically, the SE value was reported to be 117.7 kcal/mol when the same Eq. 2 at the 4-31G level was used (*22*). The SE values for spiropentadiene and related compounds calculated at the B3LYP/6-311++G(3*df*,2*p*)//B3LYP/6-31G(*d*) level are given in the supplementary material (*16*). As expected, the SE values of the spiro compounds are approximately equal to the sums of those of the component three-membered ring compounds. The SE value of the parent cyclotrisilene (34.5 kcal/mol) is similar to that of cyclotrisilane (35.5 kcal/mol), whereas the SE value of cyclopropene (55.5 kcal/mol) is 20 kcal/mol larger than that of cyclopropane (25.5 kcal/mol). Thus, the SE values of the parent spiropentasilane [10 (D_{2d})], spiropentasilene [9 (C_{2v})], and spiropentasiladiene [7(D_{2d})] are similar (60 to 70 kcal/mol) to each other, whereas those of the corresponding carbon compounds depend notably on the number of double bonds; the SE values are 55.5, 85.7, and 114.2 kcal/mol for spiropentane, spiropentene, and spiropentadiene, respectively.
22. J. Kao, L. Radom, *J. Am. Chem. Soc.* **100**, 766 (1978).
23. H. E. Simmons, T. Fukunaga, *J. Am. Chem. Soc.* **89**, 5208 (1967).
24. R. Hoffmann, A. Imamura, G. D. Zeiss, *J. Am. Chem. Soc.* **89**, 5215 (1967).
25. The CIS (configuration interaction, singlet) calculations for **7** (D_{2d}) [CIS/6-311++G(3*df*,2*p*)//B3LYP/6-31G(*d*)] predicted two degenerate π→π* bands at 358 and 293 nm, in addition to two π→σ* (a_1) and other transitions with negligible intensities in the UV-visible region; the π→π* band maximum for cyclotrisilene 12 (C_{2v}) was calculated to be 344 nm. As expected, the CIS calculations predicted that the distortion of **7** (D_{2d}) to **7** (D_2) caused the splitting of the degenerate two π→π* bands as well as the remarkable red shift of the longest wavelength band. For **7** (D_2), four band maxima of 422, 353, 288, and 283 nm with moderate intensities were found in the UV-visible region, where three of them were π→π* bands, but the 288-nm band showed a strong π→σ* nature (*16*). More sophisticated calculations on the real molecule are desirable for the convincing assignment of the absorption bands of **2**.
26. R. West *et al*, *J. Am. Chem. Soc.* **119**, 4972 (1997).
27. P. George, M. Trachtman, C. W. Bock, A. M. Brett, *Tetrahedron* **32**, 317 (1976).
28. We thank an anonymous reviewer for helpful discussion. Supported by the Ministry of Education, Science, Culture, and Sports of Japan [Grants-in-Aid for Scientific Research on Priority Areas (A) "The Chemistry of Inter-element Linkage" No. 09239101 (M.K.), Scientific Research (B) No.11440185 (M.K. and T.I.), and Encouragement of Young Scientists No. 12740336 (T.I.)].

16 May 2000; accepted 13 September 2000

Dimer Preparation That Mimics the Transition State for the Adsorption of H_2 on the Si(100)-2 × 1 Surface

Emily J. Buehler and John J. Boland*

A chemically induced dimer configuration was prepared on the silicon (Si) (100) surface and was characterized by scanning tunneling microscopy (STM) and spectroscopy (STS). These prepared dimers, which are essentially untilted and differ both electronically and structurally from the dynamically tilting dimers normally found on this surface, are more reactive than normal dimers. For molecular hydrogen (H_2) adsorption, the enhancement is about 10^9 at room temperature. There is no appreciable barrier for the H_2 reaction at prepared sites, indicating the prepared configuration closely approximates the actual dimer structure in the transition state. This previously unknown ability to prepare specific surface configurations has important implications for understanding and controlling reaction dynamics on semiconductor surfaces.

The reaction of H_2 with the Si(100)-2 × 1 surface is perhaps the best characterized and most important adsorbate-semiconductor system (*1*), but even the dynamics of H_2 on Si(100)-2 × 1 are poorly understood. Repeated experiments have shown that the barrier to the recombination of H atoms and subsequent desorption of H_2 is 2.5 eV (*2*), whereas the bond energies of the Si-H reactants and H-H product are ~3.5 and 4.5 eV (*3*), respectively. Together,