Organometallics **1984**, *3*, 1267–1272

13.45. Found: C, 69.64; H, 6.90; N, 13.37.

When the reaction mixture, as described above, in the 125-mL Erlenmeyer flask was exposed to direct sunlight at 25–35 °C, the reaction was complete after 4 h. Standard isolation provided 90 mg (60%) of imino ether **2**, 10 mg (5%) of (dimethylamino) imino ether, and 25 mg (8%) of 1,3-diazetidinone **8**.

4-Methoxy-4-methyl-1-(4-nitrophenyl)-2-phenyl-1,2-diazetidin-3-one (9). Carbene complex **1** (1.5 mmol, 375 mg) and 4-nitroazobenzene (1 mmol, 227 mg) were combined in the usual manner in a 125-mL Erlenmeyer flask, in ether (100 mL). The flask was placed in direct sunlight at 25–35 °C. After 4 days the reaction mixture was dark brown and heterogeneous. TLC showed still starting material; however, the reaction was worked up in the usual manner. Purification by Chromatotron (1-mm Al$_2$O$_3$ plate, hexane/ether, 10:1) afforded 20 mg (10%) of nitro imino ether and 9 mg (3%) of 1,2-diazetidinone **9** that was still contaminated with imino ether: ^{1}H NMR (60 MHz, CCl$_4$) δ 1.41 (s, 3 H, CCH$_3$), 3.50 (s, 3 H, OCH$_3$), 6.5–8.3 (m, 9 H, Ph); mass spectrum, *m/e* 313 (parent), 285 (P − CO), 227 (NO$_2$PhN=NPh); IR (CCl$_4$) 1805 (C=O) cm^{-1}. There was insufficient material to permit further purification and elemental analysis.

Azobenzene-*d*$_5$. The reaction with azobenzene-*d*$_5$ and the carbene complex **1** was carried out as described for azobenzene. The 85:15 mixture of 1,3-diazetidinone-*d*$_5$ **4** and 1,2-diazetidinone-*d*$_5$ **3**, synthesized by irradiation with Vitalite at 0 °C, gave a single parent peak at *m/e* 273 in the mass spectrum. No scrambling was observed. Purified azobenzene-*d*$_5$ recovered from an incomplete reaction (Vitalite, 25 °C, ~4 h), gave a single parent peak at *m/e* 187. Also the 1:1 mixture of **3**-*d*$_5$ and **4**-*d*$_5$ as well as pure 1,2-diazetidinone-*d*$_5$, synthesized by sunlight irradiation at 0 °C, gave no scrambling in the mass spectrum.

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Registry No. 1, 20540-69-6; 2, 24433-81-6; 3, 90742-54-4; *d*$_5$-3, 90742-52-2; 4, 90742-55-5; *d*$_5$-4, 90742-56-6; 5, 90742-57-7; 6, 90742-58-8; 7, 90742-59-9; 8, 90742-60-2; 9, 90742-53-3; PhN=NPh, 103-33-3; PhN=N(*p*-MeOPh), 2396-60-3; PhN=N(*p*-Me$_2$NPh), 60-11-7; PhN=N(*p*-NO$_2$PH), 2491-52-3; azobenzene-*d*$_5$, 90742-61-3.

Decomposition Channels of Chemically Activated Disilane. The π Bond Energy of Disilene and Its Derivatives

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The Hg (^{3}P$_1$) sensitized photolysis of an H$_2$/SiH$_4$ mixture not only yields Si$_2$H$_6$ but also Si$_3$H$_8$ and Si$_4$H$_{10}$. The formation of the latter two products as well as parts of the Si$_2$H$_6$ yield is explained by the decomposition of chemically activated disilane, formed by the combination of two silyl radicals. The activated disilane decomposes mainly into SiH$_2$ + SiH$_4$ which finally reacts to Si$_2$H$_6$ and to a lesser extent into H$_2$ + H$_3$SiSiH: and H$_2$ + H$_2$SiSiH$_2$. The silylsilylene inserts into SiH$_4$ yielding Si$_3$H$_8$, while disilene is thought to be scavenged successively by two SiH$_3$ radicals, the main reactive species under the given conditions. From the relative rate constants of the three decomposition channels, ΔH_f(H$_3$SiSiH:) = 273 ± 11 kJ/mol can be calculated. Also a lower bound to the π bond energy of disilene B_π(H$_2$SiSiH$_2$) ≥ 69 ± 11 kJ/mol is obtained. Ab initio CI calculations give B_π(H$_2$SiSiH$_2$) = 93 ± 8 kJ/mol. A substituted disilene is shown to have a probable π bond energy of 108 ± 20 kJ/mol from a thermochemical analysis of literature data.

Introduction

In a previous publication we showed^1 that in the H atom induced decomposition of SiH$_4$ disilane is formed by two parallel pathways: (i) recombination of the primarily formed silyl radicals leading to a chemically activated disilane (eq 1) which is either stabilized or decomposes according to (eq 2); (ii) direct disproportionation of two silyl radicals leading also to silylene and silane (eq 3). Silylene inserts into SiH$_4$ yielding ultimately Si$_2$H$_6$.

$$2\mathrm{SiH_3} \rightarrow \mathrm{Si_2H_6(v)} \qquad (1)$$

$$\mathrm{Si_2H_6(v)} \rightarrow \mathrm{SiH_2} + \mathrm{SiH_4} \qquad (2)$$

$$2\mathrm{SiH_3} \rightarrow \mathrm{SiH_2} + \mathrm{SiH_4} \qquad (3)$$

However, there must be other processes taking place as well. In their investigation of the 147-nm photolysis of SiH$_4$, Lampe and co-workers^2 observed Si$_3$H$_8$ also as a primary product. They proposed an additional decomposition channel for Si$_2$H$_6$(v), namely, the decomposition to silylsilylene and hydrogen (eq 4). Silylsilylene will

$$\mathrm{Si_2H_6(v)} \rightarrow \mathrm{H_3SiSiH{:}} + \mathrm{H_2} \qquad (4)$$

insert into SiH$_4$ yielding trisilane.^{3} Hydrogen elimination from both silicon atoms under formation of disilene was also considered (eq 5), but volatile products that might

$$\mathrm{Si_2H_6(v)} \rightarrow \mathrm{H_2SiSiH_2} + \mathrm{H_2} \qquad (5)$$

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(1) Reimann, B.; Matten, A.; Laupert, R.; Potzinger, P. *Ber. Bunsenges. Phys. Chem.* **1977**, *81*, 500–504.

(2) Perkins, G. G. A.; Austin, E. R.; Lampe, F. W. *J. Am. Chem. Soc.* **1979**, *101*, 1109–1115.

(3) Sefcik, M. D.; Ring, M. A. *J. Am. Chem. Soc.* **1973**, *95*, 5168–5173.

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have originated from disilene were not found. Lampe et al.[2] suggested that disilene might be a source of the polymer observed at the walls. O'Neal, Ring, and co-workers[4] found molecular hydrogen elimination as an important process in the shock tube decomposition of disilane but attributed it, in contrast to Lampe, solely to reaction 4.

In view of the newer findings[2,4] we have reinvestigated the H/SiH_4 system with special emphasis on the quantitative characterization of higher silane products with the aim of extracting kinetic and thermochemical information on decomposition channels eq 4 and 5. This information and other data, extracted from experiments described in the literature, will provide a first estimate of the π bond energy of the Si=Si double bond. Ab initio calculations of the rotational energy barrier of the Si=Si bond in disilene, taking into account correlation energy, will also be presented.

Experimental Results

The silyl radicals were generated by hydrogen abstraction from SiH_4 (eq 6). The hydrogen atoms, in turn, were

$$H + SiH_4 \rightarrow SiH_3 + H_2 \qquad (6)$$

formed by mercury-sensitized photolysis of H_2. Almost all experiments were performed in a 4-L spherical photoreactor where only an 800-mL volume of cylindrical shape was illuminated by the partially collimated beam of a low-pressure mercury resonance lamp (Graentzel, Karlsruhe, type 5). In this way surface effects were kept to a minimum. A few experiments were performed in a 10-L vessel as well as in a 200-mL cell, in order to investigate the importance of wall reactions. While with the 10-L vessel no changes in the product yields were found, the 200-mL cuvette did give appreciably smaller Si_4H_{10} yields.

The reaction mixture consisted of 260 Pa of silane, 2.6 × 10^4 Pa of H_2, and mercury vapor. Silane (Air Liquide) was semiconductor grade, SiD_4 was prepared by standard procedures,[5] and hydrogen (Messer Griesheim) had a specified purity of 99.999%. The absorbed intensity of the mercury resonance radiation was measured by propane actinometry. A value of 1.2×10^{13} cm^{-3} s^{-1} was obtained for the illuminated volume. Product analysis was performed by mass spectrometry (MAT 311A). Authentic samples of Si_2H_6, Si_3H_8, n-Si_4H_{10}, and i-Si_4H_{10} were available for calibration purposes.[6] The recorded spectra of these substances are in good agreement with literature data.[7] After photolysis the reaction mixture was cooled to liquid-nitrogen temperature and the hydrogen pumped off. The mass spectra of the condensable substances were measured in the mass range m/e 30–125.

With the help of the calibration spectra, the mole fractions of the various constituents and their standard deviations were extracted by multiple regression analysis[8] using all the fragment peaks up to m/e 122.

Besides the expected products Si_2H_6 and Si_3H_8, Si_4H_{10} was also found and at higher conversions Si_5H_{12}, as documented by the appearance of m/e 120. (Because of the similarity of the mass spectra for i- and n-Si_4H_{10} no distinction could be made between these two substances.) To check whether Si_3H_8 and Si_4H_{10} have the character of primary products, i.e., that they are not formed from Si_2H_6 by further attack of H atoms or SiH_2, we have studied the product yields as a function of irradiation time (Figure 1). The error bars refer to single standard deviation of the product concentrations obtained from the regression analysis. The smallest irradiation time corresponds to a conversion of 0.2% with respect to SiH_4. There exists a good linear relationship between conversion and irradiation up to 5–10% conversion. Then the curve levels off, indicating that products not included in our analysis are gaining in importance (Figure 2). The linear increase of the product yields with dose is an indication that besides Si_2H_6, also Si_3H_8 and Si_4H_{10} are primary products. However, such graphs are not very sensitive to the behavior of the rate at low photolysis times. A better resolution can be achieved by differentiating the curves in Figure 1 with respect to time; such a time dependence of product rates has been approximated by dividing the product yields by the irradiation time and plotting this ratio vs. irradiation time (Figure 3). Due to the large uncertainties in the experiments secondary formation of Si_4H_{10} and especially Si_3H_8 cannot be excluded with certainty. We have

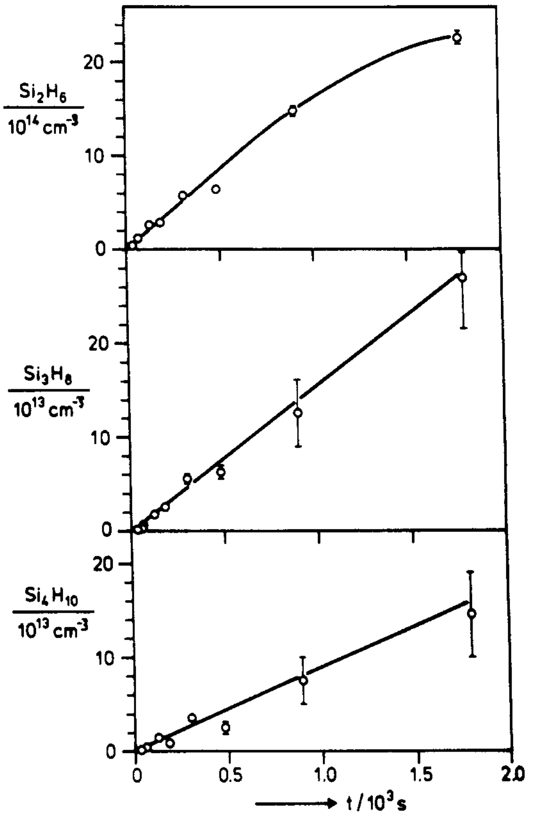

Figure 1. Product yields as a function of irradiation time.

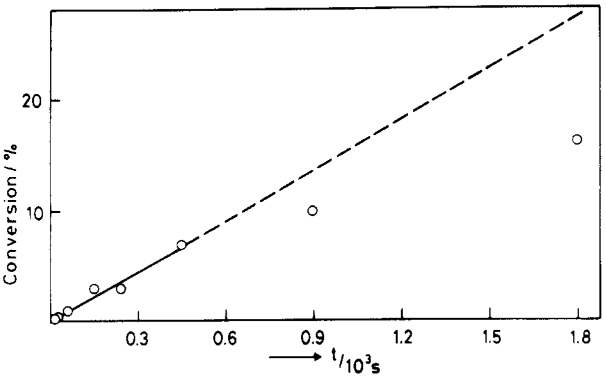

Figure 2. Conversion calculated from the products measured as a function of irradiation time.

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(5) Jolly, W. L. *Inorg. Synth.* **1968**, *11*, 170–181.

(6) We are grateful to Prof. Feher, Universität Köln, for providing these substances.

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(8) Efroymson, M. A. In: "Mathematical Methods for Digital Computers"; Ralston, A., Wilf, H. S., Eds.; Wiley: New York, 1966; Vol. 1, pp 191–203.

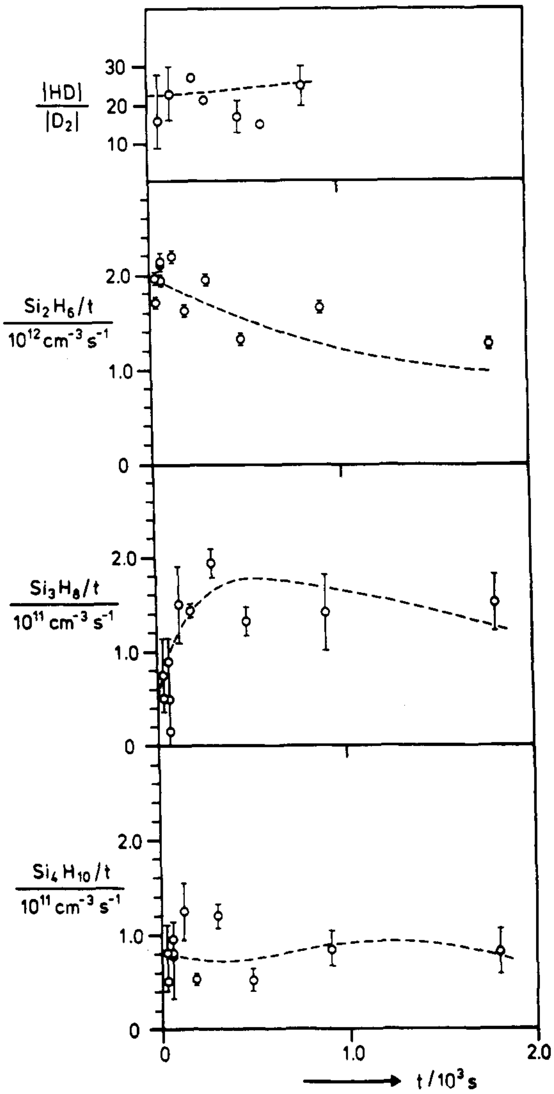

Figure 3. HD/D_2 product ratio as a function of irradiation time and Si_2H_6, Si_3H_8, and Si_4H_{10} product yields divided by irradiation time as a function of irradiation time (see text).

therefore investigated the system H/SiD_4 and measured the ratio HD/D_2 as a function of photolysis time (Figure 3). In this case the error bars represent single standard deviations of a series of measurements. This experiment confirms the results of Perkins et al.[2] and Dzarnoski et al.[4] that processes 4 and/or 5 are competing with (2) in the decomposition of the chemically activated disilane.

While the reactions leading to Si_3H_8 are well established,[3] the question arises as to how an Si_4 entity can be built up from H/SiH_4 without secondary reactions. The only pathway we can think of is via the formation of disilene which in the present system can be formed in reaction 5. An alternative path to H_2SiSiH_2 formation suggested by Dzarnoski et al.,[4] namely, the combination reaction of two silylene radicals, can be excluded under our experimental conditions in view of the fast scavenging of SiH_2 by SiH_4. Another alternative, the interconversion of H_3SiSiH: into H_2SiSiH_2 cannot be excluded but would not affect seriously the thermochemical inferences made below. If the silicon analogue of ethylene behaves similar to silaethylene, which has been shown to undergo rapid radical addition,[9,10] then reaction with SiH_3, the radical with by far the largest steady-state concentration, leads to Si_3H_7 (eq 7) and further to Si_4H_{10} (eq 8). A quantitative fit of

$$Si_2H_4 + SiH_3 \rightarrow Si_3H_7 \quad (7)$$

$$Si_3H_7 + SiH_3 \rightarrow Si_4H_{10} \quad (8)$$

the dependence of the product yields on photolysis time by numerical solution of the appropriate set of coupled differential equations would require the knowledge of reaction modes of higher silyl radicals and the pertinent rate constants. At present, these data are not available. However, a qualitative understanding can be achieved.

Three reactions lead to the decrease of the rate of Si_2H_6 formation with time: abstraction (eq 9) and displacement

$$H + Si_2H_6 \rightarrow H_2 + Si_2H_5 \quad (9)$$

$$H + Si_2H_6 \rightarrow SiH_4 + SiH_3 \quad (10)$$

$$SiH_2 + Si_2H_6 \rightarrow Si_3H_8 \quad (11)$$

(eq 10) reactions of H atoms[11,12] with and insertion (eq 11) of SiH_2[13] into Si_2H_6. These three reactions primarily lead to an increasing rate of Si_3H_8 formation via eq 12 and 13.

$$Si_2H_5 + SiH_3 \rightarrow Si_3H_8 \quad (12)$$

$$Si_2H_5 + SiH_3 \rightarrow SiH_4 + H_3SiSiH: \quad (13)$$

As the photolysis proceeds, Si_3H_8 itself will be attacked by the same species (H and SiH_2) as Si_2H_6, and its rate of formation will decrease again. The variation of the corresponding rate of Si_4H_{10} with photolysis time is less pronounced due to the low concentration of the direct precursor Si_3H_8. The dashed lines in Figure 3 illustrate these considerations.

From the intercept of the H/SiD_4 experiments (see top of Figure 3) one calculates the contribution of reactions 4 and/or 5 to the total product yield to be about 10%. From this and from the intercepts of the other products of Figure 3 one may extract the following product mole fractions in the limit of zero conversion:

$$x(Si_2H_6) = 0.93 \pm 0.07$$

$$x(Si_3H_8) = 0.03 \pm 0.015$$

$$x(Si_4H_{10}) = 0.04 \pm 0.015$$

Discussion

The present results confirm that decomposition channel (eq 2), investigated in an earlier study,[1] is the most important decomposition process of the activated disilane. At the same time they prove it is not the only decomposition process. Reaction 4 and, if our interpretation concerning the primary formation of Si_4H_{10} is correct, also reaction 5 both contribute to the decomposition of $Si_2H_6(v)$. These results are important in that they put us in a position to take a first look at the thermochemistry of disilene. Intermediates containing $p_\pi - p_\pi$ bonded silicon atoms have been postulated to an ever increasing extent and molecules with a Si=C double bond are nowadays quite well characterized both experimentally and theoretically.[14] No quantitative data are available for Si_2H_4, the simplest representative with an Si=Si double bond, except from quantum mechanical calculations (e.g., ref 15 and literature cited therein). The calculations of Lischka and Köhler[15] being the most elaborate ones predict equal

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Table I

model	Si_2H_6	.H. $[H_2Si\cdots SiH_3]^\ddagger$	.H···H. $[H_2Si\cdots SiH_2]^\ddagger$	.H $[H_3SiSiH.\dot{H}]^\ddagger$
freq, cm^{-1}	2150 (6)	2150 (5)	2150 (5)	2150 (5)
	940 (2)	900 (6)	900 (6)	900 (6)
	929 (2)	625 (2)	625 (2)	625 (2)
	909	560 (2)	600 (2)	380 (2)
	844	380 (2)	380 (2)	350
	625 (2)			200
	434			
	380 (2)			
	200			
symmetry number	18	1	2	3

stability for disilene and silylsilylene. The equilibrium bond length in disilene is calculated to be shorter than an Si–Si single bond, and a larger force constant is evaluated for this bond than in disilane. These findings argue in favor of an Si═Si double bond, and a nonzero π bond energy is therefore expected.

An experimental estimate of the heat of formation of silylsilylene and disilene can be obtained from the ratio of $k(4)/k(2)$ and $k(5)/k(2)$, respectively. From the mechanism given in ref 1 involving the eq 1–3 and the stabilization of $Si_2H_6(v)$, augmented by the steps 4 and 5, we can derive the expression shown in eq 14 for the mole fraction

$$x(Si_2H_6) = \frac{\dfrac{k(3)}{k(1)} + \dfrac{w + k(2)}{w + k(2) + k(4) + k(5)}}{k(3)/k(1) + 1} \qquad (14)$$

of Si_2H_6, where w stands for the product of the collision frequency Z, the pressure p, and the collisional deactivation efficiency λ. From Figure 1 in ref 1 we deduce the following values: $k(3)/k(1) = 0.7$ and $k(2)/w = 1.35$. Together with $k(5)/k(4) \simeq 1.5$ we obtain $k(5)/k(2) \simeq 0.14$ and $k(4)/k(2) \simeq 0.1$. In this calculation it has been assumed that all Si_2H_4 formed reacts to give Si_4H_{10}.

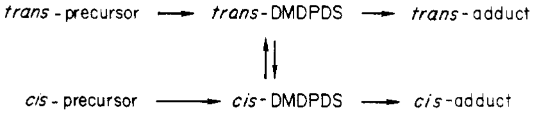
An estimate of the activation energies for reactions 4 and 5 can be obtained from RRKM calculations. Within this model the ratio of rate constants is given by eq 15, where

$$\frac{k(n)}{k(2)} = \frac{\sigma^*(2)}{\sigma^*(n)} \frac{W(E_v^*(n))}{W(E_v^*(2))} \qquad (15)$$

$$n = 4, 5$$

$W(E_v^*)$ is the number of states and σ^* is the symmetry number of the activated complex. Vibrational assignments of the complexes, shown in Table I, were made to be broadly consistent with the observed A factors, viz., $A(2)$ and that for the total H_2 formation, obtained by Dzarnowski et al.[4] The required energies for reaction 2 are known: the total nonfixed energy of the activated disilane molecule $E^*(2)$ amounts to 310 kJ/mol (the Si–Si bond dissociation energy[16]) while the critical energy (obtained from the measured, thermal, activation energy[4]) is 200 kJ/mol leading to a nonfixed energy, $E_v^*(2) = 110$ kJ/mol. $E_v^*(4)$ and $E_v^*(5)$ have been varied to reproduce the experimentally obtained rate constant ratios using eq 15. The values obtained were $E_v^*(4) = 84$ kJ/mol and $E_v^*(5) = 96$ kJ/mol. These values represent in our view the best compromises between different possible complex structures and the need to reconcile thermal H_2 formation from the shock tube[4] with very minor formation from earlier static bulb studies.[17] The existing uncertainties (mainly in thermal A factors) correspond to energy uncertainties of ±11 kJ/mol. The E_v^* values correspond to $E_A(4) = 233 \pm 11$ kJ/mol and $E_A(5) = 218 \pm 11$ kJ/mol. These figures may be compared with the activation energy estimate for total H_2 formation of Dzarnowski et al.[4] of 231 ± 9 kJ/mol.

Scheme I



If we consider first the thermochemistry of reaction 4, the following analogy suggests a nonzero activation energy for the reverse reaction. For reaction 16 O'Neal, Ring, and

$$SiH_4 \rightarrow SiH_2 + H_2 \qquad (16)$$

co-workers[18] measured an activation energy $E_A(16) = 249$ kJ/mol. $\Delta H(16)$ is estimated to be 209 kJ/mol,[13,16] leading to $E_A(-16) = 40$ kJ/mol. The assumption of a similar insertion barrier for $SiH_3SiH:$ into H_2 (i.e., $E_A(-4) = 40$ kJ/mol) leads to

$$\Delta H(4) = (233\text{–}40) \text{ kJ/mol} = \Delta H_f(SiH_3SiH:) - \Delta H_f(Si_2H_6)$$

From $\Delta H_f(Si_2H_6) = 80$ kJ/mol[16] hence $\Delta H_f(SiH_3SiH:) = 273 \pm 11$ kJ/mol. This value is in reasonable agreement with a published value of 270 ± 15 kJ/mol of Vanderwielen et al.,[19] but this latter is based on an old value of $\Delta H_f(Si_3H_8)$ and should be amended to 292 ± 15 kJ/mol. It should be pointed out that these values rule out the formation of $SiH_3SiH:$ (via step 4) from the less vibrationally excited $Si_2H_6(v')$ produced by reaction 17 as suggested by Longeway and Lampe.[20]

$$SiH_2 + SiH_4 \rightarrow Si_2H_6(v') \qquad (17)$$

For reaction 5 nothing is known about the back-reaction, and therefore $E_A(5)$ can only be used to set an upper limit on $\Delta H_f(H_2SiSiH_2)$, viz.

$$\Delta H(5) = \Delta H_f(H_2SiSiH_2) - \Delta H_f(Si_2H_6) < 218 \pm 11 \text{ kJ/mol}$$

From $\Delta H_f(Si_2H_6)$ cited above hence $\Delta H_f(H_2SiSiH_2) < 298 \pm 11$ kJ/mol. With this figure we are able to calculate a lower bound to the π bond energy of H_2SiSiH_2 with the help of eq 18. The enthalpy of reaction 18 can be written

$$H_2SiSiH_2 + H_2 \rightarrow Si_2H_6 \qquad (18)$$

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$$\Delta H(18) = B_\pi + \mathrm{DH(H{-}H)} - 2\mathrm{DH(Si{-}H)}$$

$$B_\pi \geq -E_A(5) - \mathrm{DH(H{-}H)} + 2\mathrm{DH(Si{-}H)} = -218 - 435 + 2 \times 361 \text{ kJ/mol} = 69 \text{ kJ/mol}$$

where the figures are based on known bond dissociation energies.[16] However, it is likely that reaction 5 would have an activation energy at least as large as that for (−4). This would imply a π-bond energy of $\geq 109 \pm 11$ kJ/mol.

These considerations hint that possibly H_2SiSiH_2 is more stable than SiH_3SiH:. However the figures are not sufficiently clear-cut to contest the conclusions of the elaborate calculations of Köhler and Lischka[15] that disilene and silylsilylene are of almost equal stability. If the latter is accepted together with the above estimate of ΔH_f(SiH_3SiH:), then $B_\pi = 94$ kJ/mol.

Ab Initio Calculation of $B_\pi(H_2SiSiH_2)$

In order to provide a theoretical comparison, we have also undertaken a direct quantum chemical calculation of the π bond energy in disilene as the difference in the energies of the planar molecule and the configuration twisted by 90° around the Si=Si double bond. The structure of disilene was determined by Lischka and Köhler.[15] According to their calculations the ^1A_g ground state is planar or only slightly bent; for the triplet state they found a twisted bent structure as the most stable one. This geometry was used in our calculations on the twisted ^1A state, while the planar geometry was employed for the ^1A_g state.

The basis set for silicon consisted of the [6s4p] contraction as given by McLean and Chandler[21] and a (5s/3s) set for hydrogen,[22] together with one d set ($\alpha = 0.51$) on the Si atoms and one p set ($\alpha = 0.43$) on the hydrogens. The calculations were performed with the MRD-CI method,[23] the reference configurations were determined by preliminary calculations, and a configuration selection threshold of 5 μHartree was employed together with energy extrapolation.[23] In both cases one natural orbital iteration was performed; the final energies are −580.337 205 and −580.300 862 au for the ^1A_g and the twisted ^1A state, respectively.

To assess a possible error due to a nonoptimized geometry for the twisted ^1A state, an attempt was made to vary the Si–Si bond length by using a somewhat smaller basis. However, only a negligible improvement of 0.0009 A was found. From this result it is concluded that the error due to geometry should be less than 2 kJ/mol. From our calculations we estimate the error in the energy difference between the two states to be about 4 kJ/mol. With the zero-point corrections given by Lischka and Köhler[15] for the ^1A_g ground state of 84.9 kJ/mol and for the ^3B state of 82.4 kJ/mol and assuming an error of 2 kJ/mol in these corrections, we arrive at an estimate of 92.8 ± 8.0 kJ/mol for the calculated π bond energy in disilene. This rotational energy barrier is only slightly higher than the energy difference between the ^1A_g ground state and the ^3B state.[15] Therefore, an energetically more favorable pathway for the internal rotation about the Si=Si bond via intersystem crossing to the triplet state does not seem to exist.

The π Bond Strength in a Derivative of Disilene

Another estimate for the π bond energy in a disilene may be obtained from a thermochemical analysis of cis–trans isomerization of 1,2-dimethyl-1,2-diphenyldisilene, DMDPDS, which has been plausibly observed as an intermediate by Sakurai and co-workers.[24] The reaction system consisted of mixtures of *either* the *cis-* *or* the *trans*-DMDPDS precursor with anthracene, A, in benzene solution that were heated in sealed tubes. The anthracene served as a Diels–Alder trapping agent for DMDPDS and was used to indicate the extent of stereo retention. The reaction scheme may be represented as shown in Scheme I. Experiments were carried out under conditions of predominant trapping, e.g., from the *trans*-precursor, 96% *trans*-adduct, and 4% *cis*-adduct were observed at 300 °C after 17 h. Similar results were observed starting from a *cis*-precursor. Somewhat greater stereo mutation occurred at higher temperatures.

Under these conditions, starting, say, from the trans-precursor, product ratios are governed by a simple stationary state treatment that gives

$$[\text{cis-adduct}]/[\text{trans-adduct}] = k_i/k_t[\mathrm{A}]$$

where k_i and k_t are the rate constants for isomerization and trapping, respectively. Making the reasonable assumption of an approximately 0.1 M solution the results indicate that k_i/k_t is ca. 0.0042 mol dm^{-3}. This result may be turned into an activation energy difference by means of the following *A* factor estimates: $A_i = 10^{13.5}$ s^{-1} and $A_t = 10^6$ dm^3 mol^{-1} s^{-1}. These figures are obtained from the reasonable precedents of known *A* factors for analogous cis–trans isomerization[25,26] and Diels–Alder processes.[27] At 300 °C these figures give $E_i - E_t = 108$ kJ/mol. Making allowance for uncertainties in our estimates this energy should be within ±20 kJ/mol of the true value.

In a cis–trans isomerization the π bond energy is closely related to the isomerization activation energy E_i.[25,26] E_t is unknown but likely to be small (the analogous silenes, with C=Si double bonds, are fairly efficiently trapped by dienes[28,29]). These arguments suggest that B_π in DMDPDS is $\geq 108 \pm 20$ kJ/mol. Since neither methyl nor phenyl substituents substantially affect Si–H bond strengths or therefore silyl radical stability,[16] it is not expected that the substituted disilenes should possess π bond strengths significantly different from the parent disilene itself. The figures presented here bear this out.

In a further recent study Sakurai and co-workers[30] have observed the reaction 19. This is the first clear-cut example of a silylsilylene to disilene rearrangement. Wulff, Goure, and Barton[31] have previously presented strong evidence for the reaction 20. This is an example of a

$$\mathrm{Me_3SiSiMe_2SiMe{:}} \rightarrow \mathrm{Me_2Si{=}SiMeSiMe_3} \qquad (19)$$

$$\mathrm{Me_2Si{=}SiMe_2} \rightarrow \mathrm{Me_3SiSiMe{:}} \qquad (20)$$

disilene to silylsilylene rearrangement, the reverse process. These results suggest that while disilenes and silylenes may

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not have identical stabilities, they are at least fairly close in energy.

The π bond energy of disilene as estimated from the experimental data and obtained from the calculations is much lower than the π bond energy in the Si=C double bond that is found to be in the range of 180 ± 20 kJ/mol.[16,32-35] Such a result is not unreasonable because as was shown theoretically,[35] the rather large value for the Si=C double bond is caused mainly by bond polarization, an effect which cannot operate in the case of disilene.

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Registry No. SiH_4, 7803-62-5; Si_2H_6, 1590-87-0; Si_3H_8, 7783-26-8; Si_4H_{10}, 7783-29-1; H_2SiSiH_2, 15435-77-5.

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Stereochemistry of the Insertion of Manganese into Si–H and Ge–H Bonds. Complexes Containing a Two-Electron, Three-Center Mn···H···Si (or Ge) Interaction

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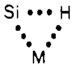
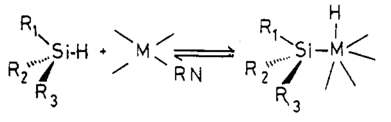
A crystallographic study of the complex (−)-(η^5-$CH_3C_5H_4$)$(CO)_2$(1-NpPhMeSi)(H)Mn (1, 1-Np = 1-$C_{10}H_7$, Ph = C_6H_5, Me = CH_3) reveals that the oxidative addition of (+)-1-NpPhMeSiH on methylcymantrene takes place with retention of configuration at silicon. The germyl complexes (η^5-$CH_3C_5H_4$)$(CO)_2$(R_3Ge)(H)Mn are prepared either by oxidative addition of R_3GeH (R = Ph) on (η^5-$CH_3C_5H_4$)$(CO)_3$Mn or by protonation of the related anions $[(\eta^5\text{-}CH_3C_5H_4)(CO)_2(R_3Ge)Mn]^-$ (R_3 = Ph_3, 1-NpPhMe, Cl_3). Only the cis isomers are obtained. Complex 2 (R = Ph) exhibits a higher acidity than the silyl analogue. This acidity is close to that of HCl. However both 1 and 2 undergo easy elimination of R_3SiH or R_3GeH when treated with PPh_3. The Mn–Ge bond is cleaved by H_2O, CH_3OH, Cl_2, and CCl_4; this behavior contrasts with that of 1 since Cl_2 or CCl_4 lead to elimination. These observations are in agreement with a two-electron, three-center bond between manganese, silicon (or germanium), and hydrogen.

Introduction

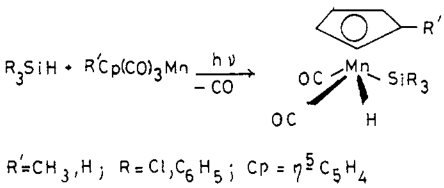
Oxidative addition of a Si–H bond to a transition-metal center is a key step in catalytic hydrosilylation reactions.[1,2] The addition–elimination process is a fast equilibrium.[3] This process takes place with retention of configuration (RN) at silicon, as deduced from the catalytic SiH/SiD exchange[4,5] rather than with a double inversion (INV) that seems less probable since the Si–H bond is always displaced with retention of configuration (Scheme I).

The mechanism of the oxidative addition of a Si–H bond to a transition metal has been suggested to proceed via a three-center transition state.[6-8] In order to understand thoroughly the  bonding, we have studied the complexes formed by oxidative addition of silanes to (η^5-methylcyclopentadienyl)tricarbonylmanganese, first described by Graham et al.[9] (Scheme II).

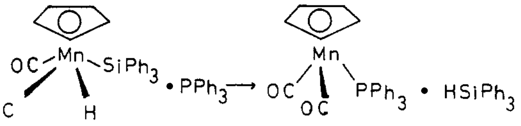
Scheme I



Scheme II



Scheme III



Indeed, X-ray structure determinations are in agreement with a close contact (≤2.0 Å) between the silicon and the

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