

# Kinetics and mechanisms of the reactions of transient silylenes with amines

Svetlana S. Kostina<sup>a</sup>, Tishaan Singh<sup>a</sup> and William J. Leigh<sup>a\*</sup>



The N–H insertion reactions of dimethyl-, diphenyl-, and dimesitylsilylene (SiMe<sub>2</sub>, SiPh<sub>2</sub>, and SiMes<sub>2</sub>, respectively) with *n*-butylamine (BuNH<sub>2</sub>) and diethylamine (Et<sub>2</sub>NH) were studied in hexanes by steady-state and laser photolysis methods. The process begins with the formation of the corresponding Lewis acid–base complexes, which decayed with second-order kinetics at rates that show modest sensitivity to silylene and amine structures. The complexation process, which was also studied using triethylamine (Et<sub>3</sub>N), proceeds at rates close to the diffusion limit, but the rate constants vary systematically with steric bulk in the amine. Equilibrium constants were determined for the complexation of Et<sub>2</sub>NH and Et<sub>3</sub>N with SiMes<sub>2</sub>, which proceeds reversibly. The complexes of SiMe<sub>2</sub> and SiPh<sub>2</sub> with BuNH<sub>2</sub> and Et<sub>2</sub>NH decayed with pseudo-first-order rate coefficients in the 10<sup>4</sup>–10<sup>5</sup> s<sup>-1</sup> range. This is consistent with upper limits of about 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup> for the rate constants for amine-catalyzed H-migration, which is thought to be the dominant mechanism for product formation from the complexes. The results are compared to published kinetic data for the O–H insertion reactions of these silylenes with alcohols, which also proceeds via initial complexation followed by catalytic proton transfer. The results indicate that catalyzed H-transfer in the amine complexes is at least 10<sup>4</sup> times slower than the analogous process in silylene–MeOH complexes. The experimental data are compared to the results of theoretical calculations of the SiMe<sub>2</sub>+NH<sub>2</sub>Me and SiMe<sub>2</sub>+MeOH potential energy surfaces, carried out at the Gaussian-4 and B3LYP/6-311+G(d,p) levels of theory. Copyright © 2011 John Wiley & Sons, Ltd.

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**Keywords:** complexation; kinetics; N–H insertion; O–H insertion; silylene

## INTRODUCTION

Silylenes, the silicon analogues of (singlet) carbenes, have been studied extensively over the past few decades in the gas phase, in solution, and in solid matrixes at low temperatures, and have also been the subject of numerous theoretical studies.<sup>[1–6]</sup> The parent silylene, SiH<sub>2</sub>, has received particular attention,<sup>[5]</sup> both because of its fundamental importance and because it is a critical intermediate in the thermal breakdown of hydrosilanes and the chemical vapor deposition of solid silicon.<sup>[7]</sup> There have also been great advances made in the synthesis and study of isolable silylene derivatives, rendered so by some combination of steric and electronic stabilization of the intrinsically reactive divalent Si(II) center by substituents,<sup>[3,8–11]</sup> and in catalytic applications involving silylene–transition metal complexes.<sup>[12]</sup>

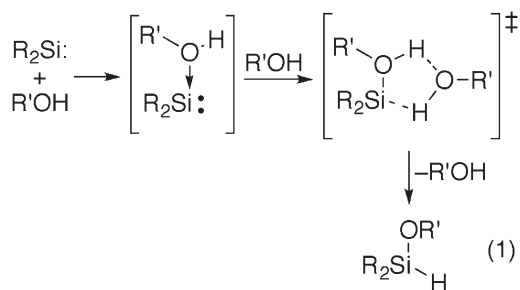
One particularly well-known class of reactions that these species share with their Group 14 homologues, (singlet) carbenes and gerylenes, is their insertion into the X–H bonds of alcohols and amines. These reactions have been well-studied theoretically,<sup>[13–19]</sup> and as a result are generally considered to proceed with the initial rapid formation of a Lewis acid–base complex between the silylene and the substrate, followed by rate-controlling migration of hydrogen from oxygen or nitrogen to silicon to form the net insertion product. Indeed there is abundant experimental evidence that, in general, silylenes are ardent participants in complexation processes with Lewis bases<sup>[20–23]</sup> and that complexation with the basic site in the substrate is the first step in the reactions with water<sup>[19,24,25]</sup> and alcohols,<sup>[24–29]</sup> as well as ammonia<sup>[30]</sup> and alkylamines.<sup>[31]</sup> In the case of the oxygenated substrates, this

proceeds at rates close to the encounter-controlled limit in both the gas phase and in solution, for both SiH<sub>2</sub> and the dimethyl-derivative (SiMe<sub>2</sub>) in the gas phase<sup>[18,19,24–26]</sup> and for SiMe<sub>2</sub> and simple (transient) arylalkyl- and diarylsilylenes in solution.<sup>[27–29]</sup> On the other hand, we have recently shown that the unimolecular H-transfer process presumed to occur next is in fact too slow, at least in solution, to compete with a catalytic pathway involving a second molecule of alcohol as catalyst.<sup>[29]</sup> Evidence for catalysis has also been reported by Becerra *et al.* for the reactions of SiH<sub>2</sub> with water<sup>[18]</sup> and methanol<sup>[26]</sup> in the gas phase. In hexane solutions at 25 °C, catalytic H-transfer proceeds at the diffusion-controlled rate for both the SiMe<sub>2</sub>- and SiPh<sub>2</sub>-MeOH reactive complexes.<sup>[29]</sup> Kinetic deuterium isotope effects are consistent with a mechanism involving the simultaneous transfer of two protons in the catalytic step, as shown in Eqn (1). In contrast, complexation is reversible in the case of the sterically hindered silylene dimesitylsilylene (SiMes<sub>2</sub>),<sup>[29]</sup> which reduces the corresponding complexes to the status of steady-state intermediates in solution at ambient temperatures and prevents them from building up to high enough concentrations to be

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detected. The situation changes at very low temperatures, where the complexes of  $\text{SiMe}_2$  with some secondary alcohols have been directly detected.<sup>[21]</sup>



The primary goal of the present work is to elucidate the mechanism(s) of the analogous reactions of primary and secondary amines with these three silylenes in hydrocarbon solvents, and probe the role of catalysis in the second, product-forming step of the sequence. The complexation of  $\text{SiMe}_2$  and  $\text{SiMe}_2$  with amines and various other donors was studied in solution and low temperature matrixes in several early seminal studies of the chemistry of these prototypical silylene derivatives,<sup>[20,21,31,32]</sup> and one study in particular explored the effects of donor-complexation on the rates of several representative silylene reactions.<sup>[32]</sup> However, the mechanisms of the uni- and bimolecular reactions of the complexes have only been studied theoretically.<sup>[13,16,30,33,34]</sup> The actual course of the reactions of  $\text{SiMe}_2$  with  $\text{Et}_2\text{NH}$  and other (primary and secondary) amines was reported in the early 1980s by Gu and Weber.<sup>[35]</sup>

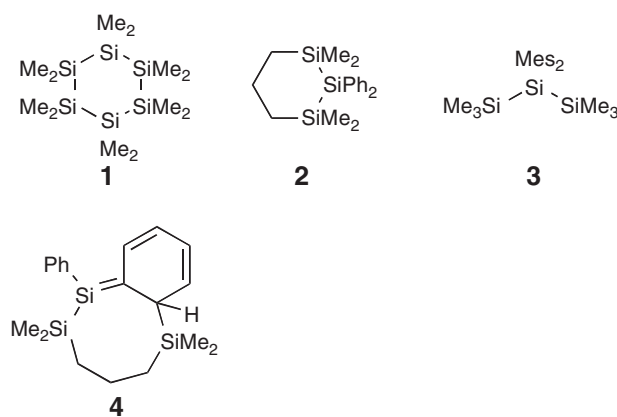
In the present paper, we report the results of fast kinetics studies of the reactions of  $\text{SiMe}_2$ ,  $\text{SiPh}_2$ , and  $\text{SiMe}_2$  with *n*-butylamine ( $\text{BuNH}_2$ ), diethylamine ( $\text{Et}_2\text{NH}$ ), and triethylamine ( $\text{Et}_3\text{N}$ ) in hydrocarbon solvents, in the interest of making comparisons to the analogous reactions of these species with alcohols. We have also carried out a computational study of the complexation of  $\text{SiMe}_2$  with ammonia, the methylamines ( $\text{MeNH}_2$ ,  $\text{Me}_2\text{NH}$ , and  $\text{Me}_3\text{N}$ ), and  $\text{MeOH}$ , including characterization of the unimolecular and catalytic H-transfer processes involving the complexes, at the B3LYP/6-311+G(d,p) and Gaussian-4 (G4) levels of theory.

## RESULTS AND DISCUSSION

As in our earlier studies on  $\text{SiMe}_2$ ,  $\text{SiPh}_2$ , and  $\text{SiMe}_2$  in solution,<sup>[27,29,36]</sup> laser flash photolysis experiments were carried out with rapidly flowed, deoxygenated solutions of **1** (ca.  $4 \times 10^{-4}$  M), **2** (ca.  $6 \times 10^{-5}$  M), and **3** (ca.  $6 \times 10^{-5}$  M), respectively, in anhydrous hexanes at  $25 \pm 1^\circ\text{C}$  using the pulses from a KrF excimer laser (248 nm, 90–105 mJ, ca. 20 ns) for excitation. The silylenes are observed as promptly formed transients with UV–Vis absorption bands centered at  $\lambda_{\text{max}}=465$  nm ( $\text{SiMe}_2$ ;  $\tau \approx 500$  ns),  $\lambda_{\text{max}}=300$  and 515 nm ( $\text{SiPh}_2$ ;  $\tau \approx 2$   $\mu\text{s}$ ), and  $\lambda_{\text{max}}=290$  and 580 nm ( $\text{SiMe}_2$ ;  $\tau \approx 20$   $\mu\text{s}$ ) in the absence of added substrates under these conditions. They decay with the concomitant formation of longer-lived UV–Vis absorptions due to the corresponding disilenes,  $\text{Si}_2\text{Me}_4$  ( $\lambda_{\text{max}}=360$  nm,  $\tau \approx 20$   $\mu\text{s}$ ),  $\text{Si}_2\text{Ph}_4$  ( $\lambda_{\text{max}}=290$  and 460 nm,  $\tau \approx 100$   $\mu\text{s}$ ), and  $\text{Si}_2\text{Me}_4$  ( $\lambda_{\text{max}}=420$  nm,  $\tau > 20$  s), respectively.<sup>[27,29,36]</sup>

Silylene formation from **2** is accompanied by the formation of minor amounts (about 3%) of silene **4**, which gives rise to long-lived residual absorptions centered at 460 nm on which the spectra of  $\text{SiPh}_2$  and  $\text{Si}_2\text{Ph}_4$  are superimposed.<sup>[36,37]</sup> This species exhibits much lower reactivity than  $\text{SiPh}_2$  towards most substrates, so

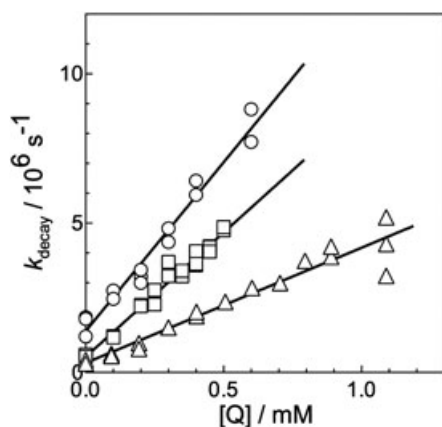
its presence in the photolysis mixture does not compromise the determination of rate constants or the characterization of transient products from the reactions of the silylene with added substrates. Trisilane **3** also affords a long-lived minor side product, which gives rise to an absorption band centered at  $\lambda_{\text{max}}=440$  nm, underlying the spectrum of  $\text{Si}_2\text{Me}_4$ , its identity is also unknown, but it too is relatively unreactive towards most substrates and does not interfere with kinetic measurements.



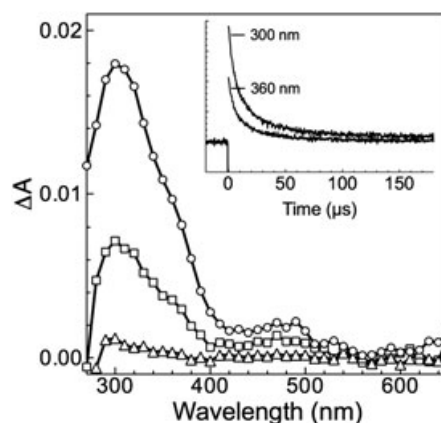
Addition of submillimolar concentrations of  $\text{BuNH}_2$ ,  $\text{Et}_2\text{NH}$ ,  $\text{Et}_2\text{ND}$ , or  $\text{Et}_3\text{N}$  to hexane solutions of **1** and **2** led to closely analogous results: the lifetimes of the silylene absorptions were reduced, the formation of the corresponding disilene absorptions was quenched, and new transient absorptions centered at shorter wavelengths were observed to grow at rates similar to those of the silylene decays, all to an increasing extent with increasing amine concentration. Plots of the pseudo-first-order decay rate coefficients ( $k_{\text{decay}}$ ) versus [amine] according to Eqn (2), where  $k_0$  is the hypothetical pseudo-first-order decay coefficient of the silylene in the absence of the amine (Q) and  $k_Q$  is the second-order rate constant for the reaction, exhibited good linearity in every case. Figure 1 shows the plots obtained for the quenching of  $\text{SiPh}_2$  by  $\text{BuNH}_2$ ,  $\text{Et}_2\text{NH}$ , and  $\text{Et}_3\text{N}$ , while the second-order rate constants given by the slopes are listed in Table 1.

$$k_{\text{decay}} = k_0 + k_Q[\text{Q}] \quad (2)$$

The transient products of these reactions are assigned to the corresponding silylene-amine Lewis acid–base complexes, the spectra of which were recorded in the presence of sufficiently high concentrations of amine to reduce the lifetimes of the corresponding free silylenes to undetectable levels. Those of the complexes of  $\text{SiMe}_2$  with  $\text{BuNH}_2$  and  $\text{Et}_2\text{NH}$  are centered at  $\lambda_{\text{max}} \approx 280$  nm in both cases, in good agreement with the spectra reported by Yamaji *et al.* for the complexes of  $\text{SiMe}_2$  with pyrrolidine and *N*-methylpyrrolidine in cyclohexane at  $20^\circ\text{C}$ <sup>[31]</sup> and with various tertiary amines in hydrocarbon matrixes at 77 K by Gillette *et al.*<sup>[21]</sup> The spectrum of the  $\text{SiMe}_2$ – $\text{Et}_3\text{N}$  complex ( $\lambda_{\text{max}} \leq 270$  nm) is blue-shifted somewhat relative to the low-temperature matrix spectrum,<sup>[21]</sup> as reported previously by Levin *et al.*<sup>[32]</sup> The spectra of the  $\text{SiPh}_2$ – $\text{BuNH}_2$  and  $\text{SiPh}_2$ – $\text{Et}_2\text{NH}$  complexes are also quite similar to one another, exhibiting  $\lambda_{\text{max}} \approx 300$  nm with a discernible shoulder absorption at about 360 nm in both cases. Figure 2 shows the spectrum of the  $\text{SiPh}_2$ – $\text{Et}_2\text{NH}$  complex, recorded with a solution of **2** in hexanes containing 5 mM  $\text{Et}_2\text{NH}$ . A spectrum recorded with **2** in the presence of 1.5 mM  $\text{Et}_3\text{N}$



**Figure 1.** Plots of the first-order rate coefficients for decay ( $k_{\text{decay}}$ ) of  $\text{SiPh}_2$  versus  $[\text{Q}]$ , for the complexation reactions with  $\text{BuNH}_2$  ( $\circ$ ),  $\text{Et}_2\text{NH}$  ( $\square$ ), and  $\text{Et}_3\text{N}$  ( $\triangle$ ) in hexanes at  $25^\circ\text{C}$



**Figure 2.** Transient absorption spectra recorded 1.0–2.2  $\mu\text{s}$  ( $\circ$ ), 11.8–13.4  $\mu\text{s}$  ( $\square$ ), and 107.8–109.4  $\mu\text{s}$  ( $\triangle$ ) after the laser pulse, by laser photolysis of a deoxygenated hexanes solution of **2** containing 5.0 mM  $\text{Et}_2\text{NH}$ . The inset shows transient decay profiles recorded at monitoring wavelengths of 300 and 360 nm

exhibited broad absorptions ( $\tau \approx 80 \mu\text{s}$ ) throughout the 300–500 nm range with an apparent maximum at approximately 330 nm, superimposed on a very long-lived absorption ( $\lambda_{\text{max}} = 290 \text{ nm}$ ) whose lifetime exceeded 1 ms. Both the above experiments with  $\text{Et}_3\text{N}$  also showed strong, short-lived absorptions in the 280–320 nm range ( $\tau \approx 2 \mu\text{s}$ ) due to transient products arising from photolysis of the amine,<sup>[38]</sup> which absorbs significantly more strongly at the excitation laser wavelength than the others. These complications precluded more extensive studies with this amine, so we limited the maximum concentration employed for rate constant determinations to 1.0 mM or less.

The rate constants for the complexation of  $\text{SiMe}_2$  with the three amines are all quite close to the diffusional rate constant in hexanes at  $25^\circ\text{C}$  ( $k_{\text{diff}} \approx 2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ), and are thus consistent with the values reported previously by Yamaji *et al.* for quenching of  $\text{SiMe}_2$  by pyrrolidine and *N*-methylpyrrolidine in cyclohexane at  $20^\circ\text{C}$  ( $k_{\text{Q}} \approx 9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ),<sup>[31]</sup> given the differences in solvent viscosity and temperature. On the other hand, the corresponding values for  $\text{SiPh}_2$  vary modestly but systematically with substitution on the amine, increasing by a factor of about three throughout the series  $\text{Et}_3\text{N} < \text{Et}_2\text{NH} < \text{BuNH}_2$ . The rate constants appear to correlate with the degree of steric bulk at nitrogen and run opposite to what would be expected on the

basis of gas phase basicities,<sup>[39]</sup> which seems the most appropriate predictor of relative basicities in a solvent such as hexanes. No isotope effect is detectable for the quenching of either silylene by  $\text{Et}_2\text{NH(D)}$ , as expected for a simple complexation process.

The effects of added amine were markedly different for the sterically hindered silylene,  $\text{SiMe}_2$ . Somewhat surprisingly given the indication above that complexation of  $\text{SiPh}_2$  is at least modestly sensitive to steric factors, the complexation of  $\text{SiMe}_2$  with  $\text{BuNH}_2$  proceeds equally as rapidly as in the case of the less-hindered diarylsilylene,  $\text{SiPh}_2$ . In the presence of 4.8 mM  $\text{BuNH}_2$  the silylene lifetime is reduced to  $< 50 \text{ ns}$ , the formation of the silylene dimer is eliminated, and there is a new absorption band present centered at 300 nm with a shoulder absorption at  $\sim 380 \text{ nm}$  that can be assigned to the  $\text{SiMe}_2\text{-BuNH}_2$  complex.<sup>[20]</sup> The complex decays with mixed-order kinetics and an apparent lifetime of about 30  $\mu\text{s}$ .

A different behavior was observed with the secondary amine,  $\text{Et}_2\text{NH}$ . The addition of small amounts of the substrate caused the absorptions due to  $\text{SiMe}_2$  to decay with bimodal kinetics, the traces consisting of a fast initial decay and a much slower-decaying residual component. The initial decay accelerated as the amine concentration was increased, and the intensity of

**Table 1.** Absolute rate constants ( $k_{\text{Q}}$ , in units of  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) and equilibrium constants ( $K_{\text{eq}}$ ,  $\text{M}^{-1}$ ) for Lewis acid–base complexation of  $\text{SiMe}_2$ ,  $\text{SiPh}_2$ , and  $\text{SiMes}_2$  with *n*-butyl amine ( $\text{BuNH}_2$ ), diethylamine ( $\text{Et}_2\text{NH}$ ), and triethylamine ( $\text{Et}_3\text{N}$ ), in hexanes at  $25 \pm 1^\circ\text{C}$

Quencher	$\text{SiMe}_2^{\text{a}}$	$\text{SiPh}_2^{\text{a}}$	$\text{SiMes}_2$	
	$k_{\text{Q}} / 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{\text{Q}} / 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$k_{\text{Q}} / 10^9 \text{ M}^{-1} \text{ s}^{-1}$	$K_{\text{eq}} (\text{M}^{-1})$
<i>n</i> - $\text{BuNH}_2$	$17 \pm 2$	$11 \pm 3$	$10 \pm 3$	<sup>a</sup>
$\text{Et}_2\text{NH}$	$16 \pm 3$	$8.3 \pm 0.7$	$3.5 \pm 0.5$	$6300 \pm 600$
$\text{Et}_2\text{ND}$	$18 \pm 2$	$9.1 \pm 0.9$	<sup>b</sup>	<sup>b</sup>
$\text{Et}_3\text{N}$	$9.8 \pm 0.8$	$3.9 \pm 0.4$	<sup>c</sup>	$\leq 1000^{\text{c}}$

<sup>a</sup>The silylene absorptions decayed with clean pseudo-first-order kinetics completely to baseline at all amine concentrations studied. This is consistent with a lower limit of  $K_{\text{eq}} > 25,000 \text{ M}^{-1}$  for the equilibrium constant.

<sup>b</sup>Not determined.

<sup>c</sup>No effect on the decay kinetics or intensity of the  $\text{SiMes}_2$  absorption was observed over the 0–1 mM concentration range in added  $\text{Et}_3\text{N}$ ; see text.

the residual absorption diminished. Such behavior is consistent with a reversible reaction, with the forward rate and equilibrium constants being of an appropriate magnitude to allow both the approach to equilibrium and the free silylene remaining after equilibrium has been achieved to be resolved.<sup>[40]</sup> The forward rate constant is given by the slope of a plot of  $k_{\text{decay}}$  versus  $[Q]$  according to Eqn (2) (the intercept in this case is approximately equal to the reverse rate constant,  $k_{-Q}$ ), while the equilibrium constant is given by the slope of a plot of the ratios of the residual signal intensities relative to the initial signal intensity recorded in the absence of the substrate ( $\Delta A_0/\Delta A_{\text{res},Q}$ ) versus  $[Q]$  (Eqn (3)). Both plots showed good linearity (see Fig. 3(a)), and are characterized by slopes of  $k_Q=(3.5\pm 0.5)\times 10^9\text{M}^{-1}\text{s}^{-1}$  and  $K_{\text{eq}}=6,300\pm 600\text{M}^{-1}$ , respectively. In the presence of 4.7mM  $\text{Et}_2\text{NH}$  the silylene lifetime is decreased to  $<50\text{ns}$  and the formation of  $\text{Si}_2\text{Mes}_4$  is again completely suppressed (Fig. 3(b)). A new transient is formed with the laser pulse, which exhibits a spectrum centered at 320nm and decays with approximate first-order kinetics ( $\tau\approx 40\mu\text{s}$ ). The spectrum is in good agreement with the low-temperature spectra of other  $\text{SiMe}_2$ -amine complexes reported by Gillette *et al.*<sup>[21]</sup> and Ando *et al.*<sup>[20]</sup> In the experiments employing  $\text{Et}_3\text{N}$  as the substrate, no evidence of an effect on the silylene signal could be obtained other than that expected from screening of the excitation light by the substrate. Given the behavior observed in the presence of the secondary amine, we interpret the result as indicative of a fast reversible reaction characterized by an equilibrium constant smaller than about  $1000\text{M}^{-1}$ .<sup>[40]</sup> A lower limit of  $k_Q > 10^8\text{M}^{-1}\text{s}^{-1}$  for the forward rate constant is consistent with the behavior observed.

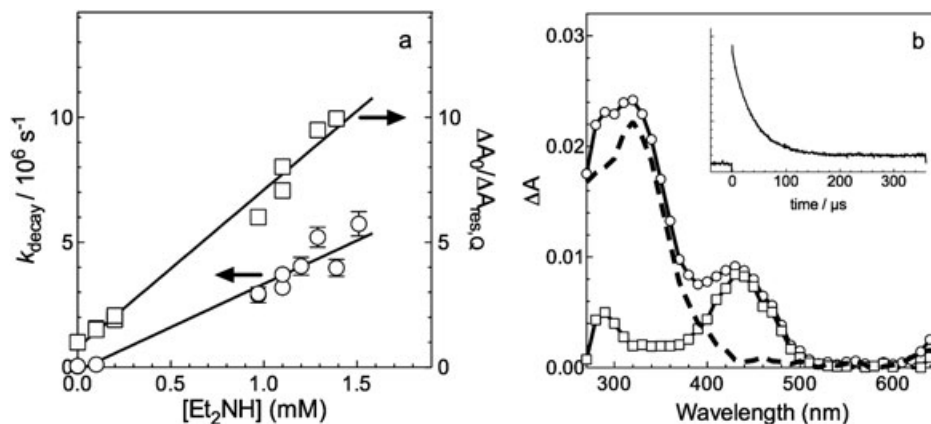
$$\Delta A_0/\Delta A_{\text{res},Q} = 1 + K_{\text{eq}}[Q] \quad (3)$$

The experimental data indicate that the complexation of  $\text{SiMe}_2$  with  $\text{BuNH}_2$  and  $\text{Et}_2\text{NH}$  proceeds at close to the diffusion-controlled rate in hexanes at  $25^\circ\text{C}$ , and thus the intrinsic free energy barrier for complexation is on the order of  $3.5\text{kcalmol}^{-1}$  or less for both the primary and secondary amines. A small but significant decrease in the rate constant occurs with  $\text{Et}_3\text{N}$ , which may be due to the introduction of a small sterically-induced barrier to complexation in the case of the tertiary amine. Replacing the methyl groups in  $\text{SiMe}_2$  with phenyl groups is expected to

lead to increased Lewis acidity,<sup>[38,40–42]</sup> and thus result in more stable complexes based on electronic considerations alone. This is not reflected in the rate constants, which are somewhat smaller for  $\text{SiPh}_2$  in every case. With  $\text{SiPh}_2$  they decrease modestly but in a regular manner with increasing substitution in the amine, indicating that steric effects associated with the amine substituents are relatively small. Steric factors clearly dominate the situation with  $\text{SiMe}_2$ , systematically destabilizing both the transition state and the resulting complexes with increasing substitution in the amine. Here the complexation energies vary from an upper limit of  $\Delta G_{298\text{K}}\leq -4.2\text{kcalmol}^{-1}$  for  $\text{BuNH}_2$  to a lower limit of  $\Delta G_{298\text{K}}\geq -2.1\text{kcalmol}^{-1}$  for  $\text{Et}_3\text{N}$ , with that for  $\text{Et}_2\text{NH}$  ( $\Delta G_{298\text{K}}\approx -3.3\text{kcalmol}^{-1}$ ) falling almost exactly midway between the two extremes. The fact that the rate constants for complexation of  $\text{SiPh}_2$  and  $\text{SiMe}_2$  with  $\text{BuNH}_2$  are the same within the uncertainty limits indicates that steric factors have minimal effects on the barrier for complexation with the primary amine, and are introduced only with the addition of the second amine substituent. The slightly smaller rate constant for the complexation of  $\text{SiPh}_2$  with  $\text{BuNH}_2$ , relative to that for  $\text{SiMe}_2$  is typical of most of the reactions of these two silylenes with common substrates<sup>[27,29]</sup> and clearly cannot be attributed simply to steric factors associated with the silylene substituents.

### The N–H insertion step in the reactions of silylenes with 1° and 2° amines

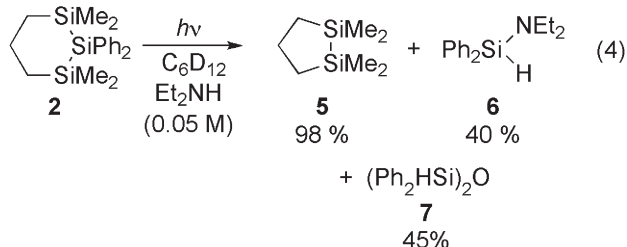
Gu and Weber studied the course of the reactions of  $\text{SiMe}_2$  with *tert*-butylamine,  $\text{Et}_2\text{NH}$ , and 2,2-dimethylaziridine by photolysis of deoxygenated solutions of **1** in the neat amines with a medium-pressure mercury lamp at  $5^\circ\text{C}$ , and found the corresponding hydridosilanamines corresponding to N–H insertion to be formed in yields of about 85% in every case.<sup>[35]</sup> In the present study, we examined the course of the reaction of  $\text{SiPh}_2$  with  $\text{Et}_2\text{NH}$  as a dilute solution in cyclohexane- $d_{12}$ , as to our knowledge the analogous reaction involving this silylene has not been previously characterized. The experiment involved photolyzing a deoxygenated solution of **2** (0.05M) in  $\text{C}_6\text{D}_{12}$  containing the amine (0.05M) and 1,4-dioxane (0.01M) as internal standards,<sup>[43]</sup> and monitoring the course of the (254nm) photolysis by  $^1\text{H}$  NMR



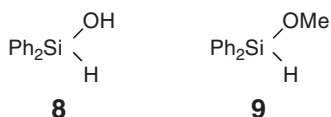
**Figure 3.** (a) Plots of  $k_{\text{decay}}$  (○) and  $\Delta A_0/\Delta A_{\text{res},Q}$  (□) versus  $[Q]$  for the reversible quenching of  $\text{SiMe}_2$  by  $\text{Et}_2\text{NH}$  in hexanes at  $25^\circ\text{C}$ . (b) Transient absorption spectra recorded 3.8–6.4  $\mu\text{s}$  (○) and 193.3–196.5  $\mu\text{s}$  (□) after the laser pulse, by laser photolysis of **3** in hexanes containing 4.7mM  $\text{Et}_2\text{NH}$ ; the dashed line shows the difference spectrum calculated from the two spectra, while the inset shows a transient decay profile recorded at 320nm



spectroscopy up to about 20% conversion of **2**. Inspection of the spectrum at the end of the photolysis period revealed that the reaction produced disilane **5**, the expected silanamine **6**, and 1,1,3,3-tetraphenyldisiloxane (**7**) in yields of about 98%, 40%, and 45%, respectively, relative to consumed **2** (Eqn 4); the identities of **6**<sup>[44]</sup> and **7**<sup>[45,46]</sup> were confirmed by <sup>29</sup>Si NMR spectroscopy, carried out on the crude reaction mixture at the end of the experiment.



While the concentration versus time plots for **2** and **5** were both uniformly linear throughout the experiment, those for Et<sub>2</sub>NH and **6** exhibited clear signs of an induction period. This encompassed roughly the first half of the photolysis period, which was dominated by the formation of **7** via (formal) condensation of diphenylsilanol (**8**). The silanol was tentatively detected as well by NMR ( $\delta$  5.47)<sup>[46]</sup> during the initial few minutes of the photolysis, its concentration reaching a maximum at 4 min and then decreasing thereafter until it disappeared altogether at roughly the point in the experiment where consumption of the amine and the concomitant formation of **6** began; as expected, the rate of formation of **7** also slowed detectably at this point. A liberal estimate of the maximum concentration of water present in the sample at the beginning of the experiment is about 5 mM.



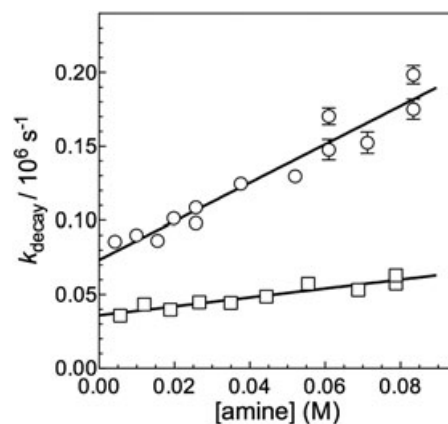
Addition of 0.01 M MeOH to the photolyzate from above resulted in the quantitative conversion of silanamine **6** to methoxydiphenylsilane (**9**), within a time period of less than about 5 min at room temperature.

The results of the steady state photolysis experiment show that the reaction of SiPh<sub>2</sub> with Et<sub>2</sub>NH proceeds in the manner expected based on previous studies with other silylene derivatives, provided the amine is the only prototypic substrate present in solution. It also demonstrates that the reaction with water is significantly more efficient than that with the amine, even when the latter is present in substantial excess. It is the reaction with water that is responsible for the induction period described above, in which **2** (and hence SiPh<sub>2</sub>) is consumed while the amine is not. It is not possible to comment on how the hydrolysis product is likely to be formed, whether on the short time scale via reaction of the silylene-amine complex with water, or on a longer time scale (i.e. several seconds to a few minutes) via secondary hydrolysis of the silanamine after it is formed, or both. The rapidity with which **6** is converted to the corresponding alkoxysilane (**9**) in the presence of only 0.01 M MeOH shows that we cannot discriminate between these two possibilities on the basis of product studies, at least not under the conditions employed in our experiments. Problems caused by adventitious water do not arise in laser photolysis

experiments, where much more rigorous procedures are employed for the drying of solvents and the apparatus.

The complexes of both silylenes with BuNH<sub>2</sub> and Et<sub>2</sub>NH are relatively long-lived, and decay with predominant second-order kinetics at the typical laser intensities employed in our laser photolysis experiments. Modest increases in laser power caused both the SiMe<sub>2</sub>-Et<sub>2</sub>NH and SiPh<sub>2</sub>-Et<sub>2</sub>NH complexes to decay with clean second-order kinetics, giving rate coefficients of  $2k/\epsilon_{290\text{-nm}} = (7.4 \pm 0.2) \times 10^6 \text{ cm}^2 \text{ s}^{-1}$  for the complex with SiMe<sub>2</sub> and  $2k/\epsilon_{370\text{-nm}} = (8.3 \pm 0.4) \times 10^6 \text{ cm}^2 \text{ s}^{-1}$  for that with SiPh<sub>2</sub>. No significant difference in either rate coefficient could be detected in similar experiments using Et<sub>2</sub>ND in place of the protiated amine. Values of  $2k/\epsilon_{280\text{-nm}} = (1.3 \pm 0.2) \times 10^7 \text{ cm}^2 \text{ s}^{-1}$  and  $2k/\epsilon_{370\text{-nm}} = (1.4 \pm 0.2) \times 10^7 \text{ cm}^2 \text{ s}^{-1}$  were obtained in similar experiments with the two silylenes in the presence of BuNH<sub>2</sub>. The outcome of the second-order decay pathway cannot be ascertained easily with the methods we have available; certainly, the lack of an isotope effect makes it doubtful that H-transfer is involved. *Inter alia*, the data are compatible with a mechanism for the second-order decay process that leads to the formation of the corresponding disilene, formed as a steady-state intermediate because of a rapid subsequent reaction with the substrate.

Reducing the laser intensity caused the decays of the complexes to lengthen, consistent with the presence of a first-order or pseudo-first-order pathway for their decay. The lifetimes of the complexes were found to be in the range of 10–30 μs in all cases, with consistently smaller values obtained for the complexes with BuNH<sub>2</sub> compared to those with the secondary amine. The lifetimes of the SiMe<sub>2</sub>-amine complexes varied modestly with amine concentration over the 4–85 mM range and plots of  $k_{\text{decay}}$  versus [amine] were linear (see Fig. 4). The slopes may be associated with the rate constants for catalytic H-transfer in the complexes by a second molecule of amine,  $k_{\text{cat}} = (1.3 \pm 0.2) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and  $(3.0 \pm 0.7) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  for the SiMe<sub>2</sub>-BuNH<sub>2</sub> and SiMe<sub>2</sub>-Et<sub>2</sub>NH complexes, respectively. However, we note that these should be considered as upper limits of the true values, as it is difficult to rule out contributions from adventitious impurities in the amine samples. Lifetimes of a similar magnitude were measured for the SiPh<sub>2</sub> complexes, but they showed no systematic variation with amine concentration. The upper limit estimates of the catalytic rate constants for H-transfer in the SiMe<sub>2</sub>-amine complexes correspond to free energy barriers in



**Figure 4.** Plots of the pseudo-first-order rate coefficients for decay ( $k_{\text{decay}}$ ) of the SiMe<sub>2</sub>-BuNH<sub>2</sub> (○) and SiMe<sub>2</sub>-Et<sub>2</sub>NH (□) complexes versus [amine] in hexanes at 25 °C

the range of 9–10 kcal mol<sup>-1</sup>, where the standard state is the gas phase at 25 °C and 101.325 kPa pressure. This contrasts sharply with the energetics of catalytic proton transfer in the SiMe<sub>2</sub>– and SiPh<sub>2</sub>–MeOH complexes by MeOH, which proceeds at close to the diffusional limit in hexanes under similar conditions.<sup>[29]</sup> Thus, with the silylene–alcohol complexes catalysis proceeds with free energy barriers of about 3 kcal mol<sup>-1</sup> or less.

The intercepts of the plots gave values of  $k_{\text{decay}} = (7 \pm 1) \times 10^4 \text{ s}^{-1}$  and  $(3.6 \pm 0.4) \times 10^4 \text{ s}^{-1}$ , respectively, and define the upper limits of the rate constants for unimolecular H-migration in the complexes. These values are indicative of free energy barriers in excess of 11 kcal mol<sup>-1</sup> at 25 °C, which can be compared to the theoretically-predicted values of 33–38 kcal mol<sup>-1</sup> for the corresponding process in the SiH<sub>2</sub>–NH<sub>3</sub> complex.<sup>[13,30]</sup>

### Computational studies of the reactions of SiMe<sub>2</sub> with amines and MeOH

The thermochemistry of the complexation of SiMe<sub>2</sub> with ammonia (NH<sub>3</sub>) and the methylamines (MeNH<sub>2</sub>, Me<sub>2</sub>NH, and Me<sub>3</sub>N) was studied computationally at the B3LYP<sup>[47]</sup>/6-311+G(d,p) and Gaussian-4<sup>[48]</sup> (G4) levels of theory, along with the reaction pathways associated with the ensuing unimolecular and catalytic N–H migration/transfer processes in the cases of the SiMe<sub>2</sub>–MeNH<sub>2</sub> complex. We also characterized the complexation and corresponding reaction pathways of SiMe<sub>2</sub> with MeOH using the same methods, to allow comparisons to be made with the experimentally better-characterized O–H insertion reaction. Transition states were confirmed to be first-order saddle points on the basis of their vibrational frequencies, and their connections to reactants and products were established by internal reaction coordinate calculations carried out in both the forward and reverse directions. The calculated (G4) thermochemical data for complexation of SiMe<sub>2</sub> with NH<sub>3</sub> and the three amines and the Si–N bond distances in the complexes are summarized in Table 2, while the thermochemical data associated with the formal N–H and O–H insertion reactions of SiMe<sub>2</sub> with MeNH<sub>2</sub> and MeOH, respectively, are summarized in Table 3. The various stationary points located in the latter calculations are shown in Fig. 5 along with selected geometric parameters from the G4 calculations. Figure 6 shows the calculated (G4) standard free energy surfaces for the two processes, while the corresponding enthalpy surface and the results obtained at the B3LYP/6-311+G(d,p) level of theory are shown in the Supplementary Information. The latter calculations led to a different order of stabilities of the amine complexes compared with the G4 method, but similar free energy barriers for the H-transfer processes for both systems. Only the more accurate G4 results will be discussed.

The calculated complexation energies of the four SiMe<sub>2</sub>–NRR'R'' complexes vary in an irregular fashion as the hydrogen atoms in ammonia are replaced successively with methyl groups throughout the series, but the overall trend reflects the counterbalancing effects of increasing amine basicity (as measured by gas phase proton affinities<sup>[39]</sup>) and increasing steric bulk with increasing methyl substitution. Thus, the increase in stability of about 4 kcal mol<sup>-1</sup> that results from replacing the first H in ammonia with Me is followed by additional stabilization of only 2 kcal mol<sup>-1</sup> upon replacing the second, and a decrease in stability of about 1 kcal mol<sup>-1</sup> upon replacing the third. The calculated enthalpy of complexation of SiMe<sub>2</sub> with ammonia (–19.5 kcal mol<sup>-1</sup>) can be compared to the G3-value of –25.3 kcal mol<sup>-1</sup> reported by Becerra

**Table 2.** Electronic energies, enthalpies (298.15 K), and free energies (298.15 K) of the Lewis acid–base complexes of SiMe<sub>2</sub> with NH<sub>3</sub>, MeNH<sub>2</sub>, Me<sub>2</sub>NH, and Me<sub>3</sub>N, calculated at the G4 level of theory relative to the isolated reactants (in kcal mol<sup>-1</sup>)

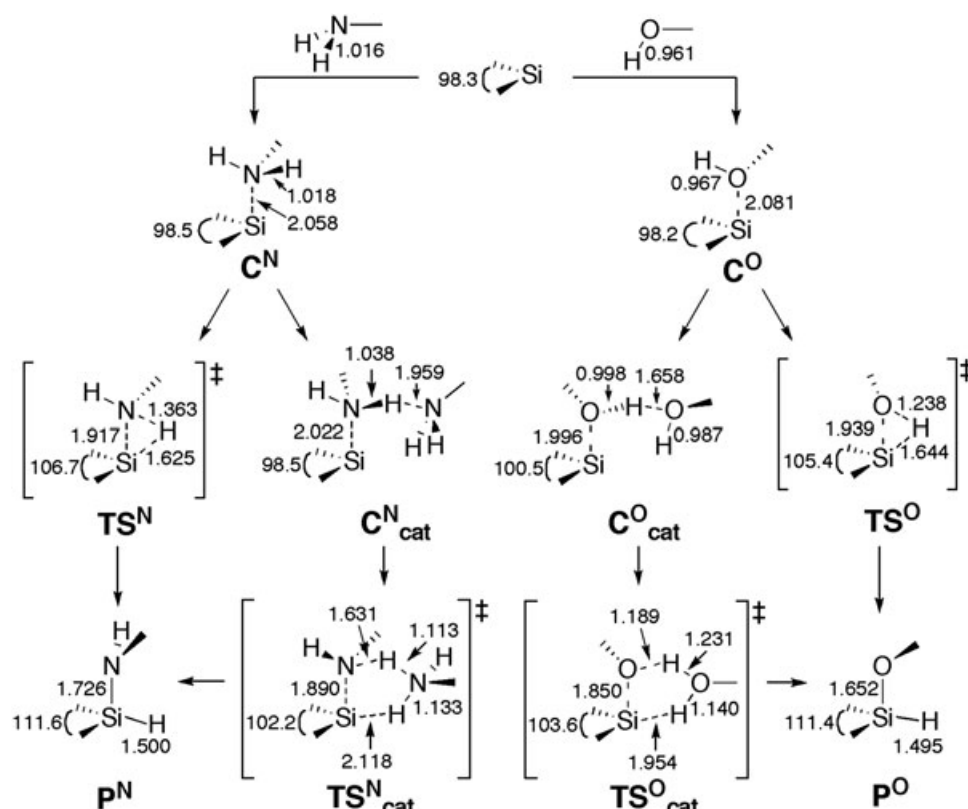
Species	$\Delta E_{\text{elec}}$	$\Delta H_{298 \text{ K}}$	$\Delta G_{298 \text{ K}}$	$r_{\text{Si-X}}$ (Å)
Me <sub>2</sub> Si–NH <sub>3</sub>	–22.1	–19.5	–8.0	2.073
Me <sub>2</sub> Si–NH <sub>2</sub> Me	–26.9	–24.2	–12.1	2.058
Me <sub>2</sub> Si–NHMe <sub>2</sub>	–29.7	–27.0	–14.1	2.067
Me <sub>2</sub> Si–NMe <sub>3</sub>	–28.6	–25.7	–13.2	2.142

**Table 3.** Electronic energies, enthalpies (298.15 K), and free energies (298.15 K) of stationary points in the reactions of SiMe<sub>2</sub> with methylamine and methanol, calculated at the G4 level of theory relative to the isolated reactants (in kcal mol<sup>-1</sup>)

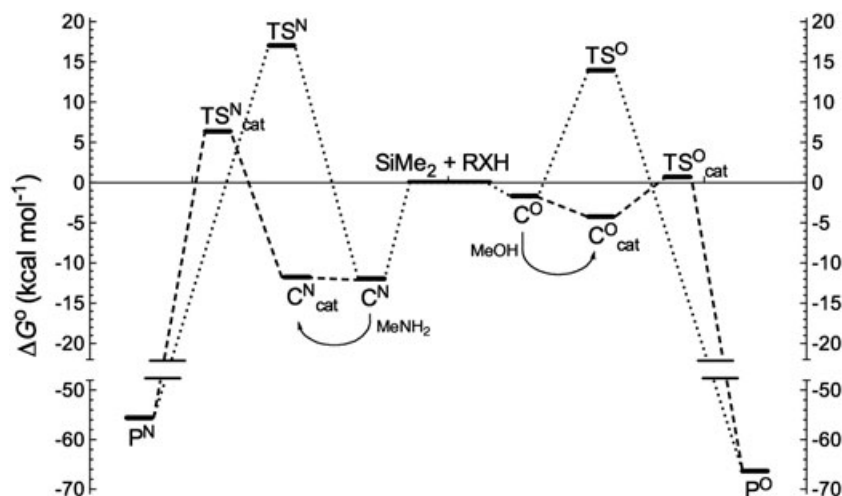
Species	$\Delta E_{\text{elec}}$	$\Delta H_{298 \text{ K}}$	$\Delta G_{298 \text{ K}}$
Me <sub>2</sub> Si–NH <sub>2</sub> Me (C <sup>N</sup> )	–26.9	–24.2	–12.1
TS <sub>uni</sub> (TS <sup>N</sup> )	+6.3	+4.7	+17.1
(Me <sub>2</sub> Si–NH <sub>2</sub> Me) – NH <sub>2</sub> Me (C <sup>N</sup> <sub>cat</sub> )	–37.4	–33.2	–11.8
TS <sub>cat</sub> (TS <sup>N</sup> <sub>cat</sub> )	–17.9	–17.7	+6.4
Me <sub>2</sub> Si(H)NHMe (P <sup>N</sup> )	–67.5	–67.2	–55.4
Me <sub>2</sub> Si–O(H)Me (C <sup>O</sup> )	–15.1	–13.0	–1.8
TS <sub>uni</sub> (TS <sup>O</sup> )	+3.5	+2.1	+14.1
(Me <sub>2</sub> Si–O(H)Me) – MeOH (C <sup>O</sup> <sub>cat</sub> )	–29.5	–26.0	–4.3
TS <sub>cat</sub> (TS <sup>O</sup> <sub>cat</sub> )	–21.4	–22.6	+0.7
Me <sub>2</sub> Si(H)OMe (P <sup>O</sup> )	–78.9	–78.2	–66.2

*et al.* for the SiH<sub>2</sub>+NH<sub>3</sub> system.<sup>[30]</sup> The difference is similar to those reported for other reactions of SiH<sub>2</sub> and SiMe<sub>2</sub> with common substrates.<sup>[5,6]</sup>

The noncatalytic components of the calculated pathways for the reaction of SiMe<sub>2</sub> with MeNH<sub>2</sub> and MeOH are generally analogous to those reported in previous theoretical studies of the reactions of SiH<sub>2</sub> with ammonia,<sup>[13,30]</sup> water,<sup>[13,15,17–19,49]</sup> and MeOH.<sup>[17,50]</sup> This aspect of the results for the SiMe<sub>2</sub>+MeOH system is also in reasonable agreement with those reported by Su from calculations at the CCSD(T)/LANL2DZdp//B3LYP/LANL2DZ level of theory,<sup>[51]</sup> but the G4 method predicts a greater stabilization of the SiMe<sub>2</sub>–MeOH complex (C<sup>O</sup>) and the transition state for unimolecular H-migration (TS<sup>O</sup>) by 2–3 kcal mol<sup>-1</sup>, and of the net insertion product by about 6 kcal mol<sup>-1</sup>, compared to the earlier calculations. The free energy barrier for unimolecular H-migration in the SiMe<sub>2</sub>–MeOH complex is predicted to be  $\Delta G^\ddagger = 15.9 \text{ kcal mol}^{-1}$  at the G4 level of theory, which can be compared to the value of  $\Delta G^\ddagger = 29.2 \text{ kcal mol}^{-1}$  predicted for the corresponding process in the SiMe<sub>2</sub>–NH<sub>2</sub>Me complex. Similar values were predicted for the enthalpic barriers ( $\Delta H^\ddagger = 15.1$  and  $28.9 \text{ kcal mol}^{-1}$ , respectively, see Table 3). The latter are somewhat smaller than those predicted for the corresponding SiH<sub>2</sub>–H<sub>2</sub>O and SiH<sub>2</sub>–NH<sub>3</sub> complexes at the G3 level of theory,<sup>[19,30]</sup> but the difference between them is quite similar to that found for the parent systems. It should be noted that a free energy barrier of 16 kcal mol<sup>-1</sup> corresponds to a rate constant of about 1 s<sup>-1</sup>, leading to the conclusion that the net X–H



**Figure 5.** Calculated (G4) structures and selected geometric parameters of stationary points on the  $\text{SiMe}_2+2\text{MeNH}_2$  and  $\text{SiMe}_2+2\text{MeOH}$  potential energy surfaces



**Figure 6.** Standard free energy surfaces for the X-H insertion reactions of  $\text{SiMe}_2$  with  $\text{MeNH}_2$  (left) and  $\text{MeOH}$  (right), calculated at the G4 level of theory

insertion is unlikely to proceed *at all* in the condensed phase under ambient conditions *unless* a catalytic pathway for the H-migration process exists; the barriers are simply too high to compete with other reaction channels that are available, such as dimerization in the case of  $\text{SiMe}_2$ .

Indeed, the calculations indicate that, with both  $\text{MeOH}$  and  $\text{MeNH}_2$ , catalysis by a second molecule of the substrate should provide a significantly lower energy pathway for reaction of the initially formed complex than unimolecular H-migration. The

process begins with the formation of a second complex, held together by a hydrogen bond between (one of) the acidic proton (s) in the initially formed complex and the basic site in the second molecule of the substrate, which then proceeds to form the X-H insertion product via a cyclic 5-membered transition state in which two protons are transferred together. The structures of the termolecular complex and transition state for the O-H insertion reaction of  $\text{SiMe}_2$  with  $\text{MeOH}$  are analogous to those reported by Becerra *et al.* in their studies of the  $\text{SiH}_2 + 2\text{H}_2\text{O}$ <sup>[18]</sup> and  $\text{SiH}_2 + 2\text{MeOH}$ <sup>[26]</sup>

systems at the G3 level. The present calculations indicate that the (per)methylated system possesses a similar complexation energy as the parent ( $\text{SiH}_2 + 2\text{H}_2\text{O}$ ) system, but a lower enthalpic barrier for the H-transfer step by 5–7 kcal mol<sup>-1</sup>.<sup>[18]</sup> The similar complexation energies appear to result from a near-cancellation of a stabilizing effect of Me-for-H substitution in the Lewis base (by 5–6 kcal mol<sup>-1</sup>)<sup>[18,19,26]</sup> and a destabilizing effect of Me-for-H substitution in the silylene. The same is true for the bimolecular complexes as well,<sup>[52]</sup> and most likely reflects the lower Lewis acidity of  $\text{SiMe}_2$  compared to  $\text{SiH}_2$ <sup>[5,6]</sup> and the higher gas phase basicity of methanol compared to water.<sup>[39]</sup> In any event, the predicted (G4) free energy barrier of  $\Delta G^\ddagger = 2.4$  kcal mol<sup>-1</sup> for catalyzed proton transfer in the  $\text{SiMe}_2$ -MeOH complex corresponds to a catalytic rate constant of  $k_{\text{cat}} \approx 10^{11} \text{M}^{-1} \text{s}^{-1}$ , in good agreement with the experimentally determined value of  $k_{\text{cat}} = (1.5 \pm 0.1) \times 10^{10} \text{M}^{-1} \text{s}^{-1}$ .<sup>[29]</sup>

In the case of the  $\text{SiMe}_2 + \text{MeNH}_2$  system, enthalpic stabilization of the bimolecular complex by hydrogen bonding to a second molecule of the substrate is somewhat less than with the alcohol complex, and is approximately free energy neutral. This is presumably because of the lower acidity of the N-H protons in the silylene-amine complex compared to that of the O-H proton in the silylene-alcohol complex. The barrier for catalytic H-transfer ( $\Delta G^\ddagger \approx 18.5$  kcal mol<sup>-1</sup>, again starting from the bimolecular complex) is considerably higher than that for the alcohol system, and significantly higher than what would be expected ( $\Delta G^\ddagger \approx 9$  kcal mol<sup>-1</sup>) based on a rate constant in the order of  $k_{\text{cat}} \approx 10^6 \text{M}^{-1} \text{s}^{-1}$ , the approximate upper limit determined above for the  $\text{SiMe}_2$ -BuNH<sub>2</sub> complex in hexanes at 25 °C. We thus conclude that the experimental rate constant is very likely overestimated, probably because of the presence of adventitious quenching impurities in our amine samples, and probably by a considerable amount. The theoretically predicted barrier for catalytic H-transfer in the  $\text{SiMe}_2$ -MeNH<sub>2</sub> complex by a second molecule of amine is consistent with a lifetime in the order of several seconds in solution in the presence of 0.05 M amine. This could well be the case under the typical conditions employed in steady-state photolysis experiments.

## SUMMARY AND CONCLUSIONS

The transient silylenes  $\text{SiMe}_2$ ,  $\text{SiPh}_2$ , and  $\text{SiMes}_2$  react with primary, secondary, and tertiary amines at close to the diffusion-controlled rate in hexanes solutions, to produce long-lived Lewis acid-base complexes that are easily detected by time-resolved UV-Vis absorption spectroscopy. For each of the silylenes that were studied, the rate constants for complexation vary modestly as a function of amine structure, with those for  $\text{SiPh}_2$  following the expected trend based on the variation in steric bulk in the amines, and opposite to what might be predicted based on gas phase basicities. Although quite rapid, the complexation of the sterically bulky diarylsilylene,  $\text{SiMes}_2$ , with  $\text{Et}_2\text{NH}$  and  $\text{Et}_3\text{N}$  is also quite rapid, but proceeds reversibly on the microsecond time scale. The data afford the first equilibrium constants to be reported for a silylene reaction in solution. The rate constant for complexation of  $\text{SiMes}_2$  with  $\text{BuNH}_2$  ( $k = (1.0 \pm 0.3) \times 10^{10} \text{M}^{-1} \text{s}^{-1}$ ) is the same as that determined for  $\text{SiPh}_2$ , making this the fastest reaction known for the prototypical, sterically stabilized diarylsilylene derivative.

Though both  $\text{SiMe}_2$  and  $\text{SiPh}_2$  react with primary and secondary amines to produce the corresponding silanamines

derived from N-H insertion and theory suggests that the reaction proceeds via the initially formed complexes, the formal N-H migration required to transform the complexes to the final products is too slow to be accurately characterized under the conditions typically employed in laser flash photolysis experiments in solution. A catalytic pathway for the process is implicated by the observation of modest variations in the pseudo-first-order decay rate constants of the  $\text{SiMe}_2$ -BuNH<sub>2</sub> and  $\text{SiMe}_2$ -Et<sub>2</sub>NH complexes, and apparent catalytic rate constants in the range of  $10^5$ – $10^6 \text{M}^{-1} \text{s}^{-1}$  were measured. Catalysis is thus at least four orders of magnitude slower than that exhibited by the  $\text{SiMe}_2 + \text{MeOH}$  system under similar conditions. Theoretical calculations at the G4 level of theory for the  $\text{SiMe}_2 + \text{MeNH}_2$  system suggest that the free energy barrier for amine-catalyzed N-H migration in the complex is too high for the process to be observable under typical laser photolysis conditions, indicating these values should be viewed as upper limits of the rate constants for catalyzed H-transfer by a second molecule of amine. Calculations at the same level of theory were carried out for the analogous reaction of  $\text{SiMe}_2$  with MeOH, and the results were benchmarked against the experimentally determined catalytic rate constant for this system in hexanes solution at 25 °C. The agreement between experiment and theory in this case is excellent and lends credence to our conclusions with regard to the experimental data for the  $\text{SiMe}_2$ -amine systems. The calculations for  $\text{SiMe}_2 + \text{MeNH}_2$  predict pseudo-first-order lifetimes on the order of seconds for the complexes of  $\text{SiMe}_2$  with primary and secondary amines in solution at ambient temperatures in the presence of low concentrations of amine.

The discovery that experimental thermodynamic data could be obtained for the complexation of  $\text{SiMe}_2$  with  $\text{Et}_2\text{NH}$  and  $\text{Et}_3\text{N}$  in solution under ambient conditions suggests that similar measurements might also be possible for the complexation of this silylene with other heteroatom donors under similar conditions. Experiments directed at this goal are in progress.

## EXPERIMENTAL SECTION

<sup>1</sup>H NMR spectra were recorded on a Bruker AV600 spectrometer in cyclohexane-*d*<sub>12</sub> and were referenced to the residual solvent protons. <sup>29</sup>Si spectra were recorded using the Heteronuclear Multiple Bond Correlation (HMBC) pulse sequence and were referenced either to an external solution of tetramethylsilane or (internal) bis(trimethylsilyl)methane (<sup>29</sup>Si δ 0.16, <sup>1</sup>H δ -0.27 (s, 2H), 0.028 (s, 18H)). Gas chromatography/mass spectrometry (GC/MS) analyses were carried out on a Varian Saturn 2200 GC/MS/MS system equipped with a VF-5ms capillary column (30 m × 0.25 mm; 0.25 mm; Varian, Inc.).

Dodecamethylcyclohexasilane (**1**) was synthesized as reported previously<sup>[53]</sup> and recrystallized six times from ethanol : THF (7:1). 1,1,3,3-Tetramethyl-2,2-diphenyl-1,2,3-trisilacyclohexane (**2**)<sup>[36]</sup> and 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane (**3**)<sup>[54]</sup> were synthesized as reported previously and purified by column chromatography on silica gel with hexanes as eluent. All three compounds were judged to be >97% pure by GC/MS analysis and <sup>1</sup>H NMR spectroscopy. *n*-Butylamine, diethylamine and triethylamine (Sigma-Aldrich) were refluxed over solid NaOH for 12 h and distilled under nitrogen. Methanol (Sigma-Aldrich) was refluxed over sodium and distilled. Bis(trimethylsilyl)methane (Sigma-Aldrich) was refluxed for 24 h over calcium hydride and distilled. Hexanes (EMD OmniSolv) were dried by passage through



activated alumina under nitrogen using a Solv-Tek solvent purification system (Solv-Tek, Inc).

### Laser flash photolysis experiments

Laser flash photolysis experiments were carried out using a Lambda Physik Compex 120 excimer laser filled with F<sub>2</sub>/Kr/Ne (248nm, 20ns, 98–110mJ/pulse) and a Luzchem Research mLFP-111 laser flash photolysis system, modified as described previously.<sup>[55]</sup> The solutions were prepared in deoxygenated anhydrous hexanes such that the absorbance at 248nm was between 0.4 and 0.7. The solutions were flowed rapidly through a 7 × 7mm Suprasil flow cell connected to a calibrated 100mL or 250mL reservoir, which contained a glass frit to allow bubbling of argon gas through the solution for 40min prior to and throughout the experiment. The flow cell was connected to a Masterflex™ 77390 peristaltic pump fitted with Teflon tubing (Cole-Parmer Instrument Co.), which pulled the solution through the cell at a constant rate of 2–3mL/min. The glassware, sample cell, and transfer lines were dried in a vacuum oven (65–85°C) before use. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple inserted into the thermostatted sample compartment in close proximity to the sample cell. Substrates were added directly to the reservoir by a microliter syringe as aliquots of standard solutions. Transient absorbance–time profiles were recorded by signal-averaging of data obtained from 10–40 individual laser shots, using neutral density filters as necessary to reduce the laser intensity to achieve first order decay kinetics. Decay rate constants were calculated by nonlinear least squares analysis of the transient absorbance–time profiles using the PRISM 5.0 software package (GraphPad Software, Inc.) and the appropriate user-defined fitting equations, after importing the raw data from the LUZCHEM mLFP software. Rate constants were calculated by linear least-squares analysis of decay rate–concentration data that spanned as large a range in transient decay rate as possible. Errors are quoted as twice the standard error obtained from the least-squares analyses.

### Steady-state photolysis experiments

In a typical steady-state photolysis experiment, nonvolatile reagents were placed in a 1mL volumetric flask, filled to the mark with cyclohexane-*d*<sub>12</sub>, and deoxygenated for about 5min with a stream of dry argon. Volatile reagents were added as neat liquids using a glass syringe and the solution was placed in an argon-filled quartz NMR tube, which was then sealed with a rubber septum. The solution was photolyzed in a Rayonet photochemical reactor (Southern New England Ultraviolet Co.) equipped with two RPR-2537 lamps and a merry-go-round apparatus, monitoring the course of the photolysis at selected time intervals by <sup>1</sup>H NMR and <sup>29</sup>Si HMBC spectroscopy. The products were identified based on the following spectroscopic data:

**Diphenylsilanol (7)**,<sup>[46]</sup> <sup>1</sup>H NMR δ 7.57 (d, <sup>3</sup>J=7.38Hz, 4H), 5.47 (s, 1H), (the expected 6H multiplet at about 7.2ppm is obscured by the resonances due to **2**).

**Tetraphenyldisiloxane (8)**,<sup>[45,46]</sup> <sup>1</sup>H NMR, δ 7.47 (d, <sup>3</sup>J=7.56 Hz, 8H), 7.20 (m, 12H), 5.58 (s, 2H) <sup>29</sup>Si NMR δ 19.2 (<sup>1</sup>J<sub>Si-H</sub>=219.6Hz).

**N,N-diethyl-1,1-diphenylsilanamine (6)**,<sup>[44]</sup> <sup>1</sup>H NMR, δ 7.53 (d, <sup>3</sup>J=7.44Hz, 4H), 7.25 (m, 6H), 5.30 (s, 1H), 2.94 (q, 4H, <sup>3</sup>J=7.0), 0.67 (t, 6H, <sup>3</sup>J=7.0), <sup>29</sup>Si NMR δ 14.0 (<sup>1</sup>J<sub>Si-H</sub>=205Hz).

**Methoxydiphenylsilane (9)**,<sup>[36]</sup> <sup>1</sup>H NMR, δ 7.54 (dd, <sup>3</sup>J=1.38, <sup>2</sup>J=7.86), 7.25 (m, 6H), 5.36 (s, 1H), 3.52 (s, 3H), <sup>29</sup>Si NMR δ 9.7 (<sup>1</sup>J<sub>Si-H</sub>=212Hz).

**Theoretical calculations** were carried out using the GAUSSIAN09 suite of programs.<sup>[56]</sup>

## Acknowledgement

We wish to thank the Natural Sciences and Engineering Research Council of Canada for financial support, and congratulate Professor Bob Moss on the occasion of his 70<sup>th</sup> birthday.

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