

# Fast Kinetics Study of the Reactions of Transient Silylenes with Alcohols. Direct Detection of Silylene-Alcohol Complexes in Solution

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The kinetic behavior of dimethyl-, diphenyl-, and dimesitylsilylene in hexanes solution in the presence of methanol (MeOH), tert-butanol (t-BuOH), and the respective O-deuterated isotopomers has been studied, with the goal of elucidating a detailed mechanism for the formal O-H insertion reaction of transient silvlenes with alcohols in solution. The data are in all cases consistent with a mechanism involving the intermediacy of the corresponding silylene-alcohol Lewis acid-base complexes, which have been detected directly for each of the SiMe2-ROL and  $SiPh_2$ -ROL (L = H or D) systems that were studied. Complexation proceeds effectively irreversibly  $(K_{eq} \ge 2 \times 10^5 \,\mathrm{M}^{-1})$  and at close to the diffusion-controlled rate in these cases. In contrast, the kinetic and spectroscopic behavior observed for SiMes<sub>2</sub> in the presence of these alcohols indicates the SiMes<sub>2</sub>-ROL complexes are involved as steady-state intermediates, formed reversibly and 10-100 times more slowly than is the case with SiMe<sub>2</sub> and SiPh<sub>2</sub>. Product formation from the silvlene-alcohol complexes is shown to proceed via catalytic proton transfer by a second molecule of alcohol, the rate of which exceeds that of unimolecular intracomplex H-migration in all cases, even at submillimolar alcohol concentrations. The catalytic rate constants range from  $10^9$  to  $10^{10}$  M<sup>-1</sup> s<sup>-1</sup> for the SiMe<sub>2</sub>-ROH and SiPh<sub>2</sub>-ROH complexes, sufficiently fast that the isotope effect ranges from ca. 2.5 to close to unity for all but the  $SiPh_2-t$ -BuOL complex, where it is remarkably large ( $k_{\rm HH}/k_{\rm DD} = 10.8 \pm 2.4$ ). The value is consistent with a mechanism for catalysis involving double proton transfer within a cyclic five-membered transition state. The isotope effects on the ratio of the rate constants for catalytic proton transfer and dissociation of the SiMes<sub>2</sub>-MeOH and SiMes<sub>2</sub>-t-BuOH complexes suggest that a different mechanism for catalytic proton transfer is involved in the case of the sterically hindered diarylsilylene.

## Introduction

Insertion into the O-H bonds of simple alcohols is one of the best-known reactions of singlet carbenes and their heavier group 14 homologues, silylenes and germylenes.<sup>1-3</sup> While most singlet carbenes react with alcohols by initial protonation followed by nucleophilic capture of the resulting carbenium ion,<sup>4,5</sup> silylenes and germylenes react with these substrates via the initial formation of the corresponding Lewis acid-base complex followed by H-transfer from oxygen to the group 14 heteroatom (eq 1).<sup>1,3,6,7</sup> In carbene chemistry, the analogous mechanism is thought to be preferred over that involving initial protonation only with

pp 651-715. (4) Kirmse, W. In Advances in Carbene Chemistry; Brinker, U. H., Ed.;

(6) Gaspar, P. P.; Jones, M., Jr.; Moss, R. A. In Reactive Intermediates, Vol. 3; John Wiley & Sons: New York, 1985; pp 333-427

(7) Becerra, R.; Walsh, R. Phys. Chem. Chem. Phys. 2007, 9, 2817.

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particularly electrophilic carbenes such as <sup>1</sup>CH<sub>2</sub> and the dihalocarbenes.8,9



In the cases of simple silvlenes and germylenes, the mechanism of eq 1 is supported by the results of theoretical calculations,<sup>10–19</sup> low-temperature spectroscopic studies,<sup>20,21</sup>

(13) Schoeller, W. W.; Schneider, R. Chem. Ber. 1997, 130, 1013.

(14) Su, M. D.; Chu, S. Y. J. Phys. Chem. A 1999, 103, 11011.

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<sup>(1)</sup> Gaspar, P. P.; West, R. In The Chemistry of Organic Silicon Compounds, Vol. 2; Rappoport, Z., Apeloig, Y., Eds.; John Wiley and Sons: New York, 1998; pp 2463-2568.

Tokitoh, N.; Okazaki, R. Coord. Chem. Rev. 2000, 210, 251.
 Tokitoh, N.; Ando, W. In Reactive Intermediate Chemistry; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; John Wiley & Sons: New York, 2004;

Elsevier: Amsterdam, 2001; Vol. 3, pp 1-51.

<sup>(5)</sup> Keeffe, J. R.; More O'Ferrall, R. A. ARKIVOC 2008, 193.

<sup>(8)</sup> Gonzalez, C.; Restrepo-Cossio, A.; Marquez, M.; Wiberg, K. B. J. Am. Chem. Soc. 1996, 118, 5408.

<sup>(9)</sup> Pliego, J. R., Jr.; De Almeida, W. B. J. Phys. Chem. A 1999, 103, 3904.

<sup>(10)</sup> Raghavachari, K.; Chandrasekhar, J.; Gordon, M. S.; Dykema, K. J. J. Am. Chem. Soc. 1984, 106, 5853.

<sup>(11)</sup> Su, S.; Gordon, M. S. Chem. Phys. Lett. 1993, 204, 306.
(12) Lee, S. Y.; Boo, B. H. J. Mol. Struct. (THEOCHEM) 1996, 366, 79.

and kinetic studies in both the gas phase<sup>7,17,18,22-24</sup> and solution.<sup>25-30</sup> The intermediate Lewis acid-base complexes of alcohols with several silvlenes<sup>21,27,29</sup> and germylenes<sup>20,28,30</sup> have been detected directly in low-temperature matrixes and in solution, where their kinetic behavior has been found to be qualitatively consistent with theoretical results for the reactions of the parent MH<sub>2</sub> (M = Si or Ge) and MMe<sub>2</sub> species with water or methanol.<sup>10–19</sup> The calculations predict the initial complexation step to be barrierless and of similar, moderate exothermicity for both the silvlene and germylene; the barrier occurs in the H-migration step, which is substantially higher for germylenes than silvlenes of otherwise identical structures. In keeping with these predictions, the complexes of SiMe<sub>2</sub> and SiPh<sub>2</sub> with simple alcohols are short-lived reaction intermediates, detectable in hydrocarbon solvents only at submillimolar alcohol concentrations,<sup>27,29</sup> while those of GeMe<sub>2</sub> and GePh<sub>2</sub> are sufficiently stable to be observable in hexanes solution as discrete species in equilibrium with the free reactants.<sup>28</sup> The complexes of GeMe2 and GePh2 with methanol (MeOH) are remarkably long-lived even in neat alcohol as solvent, where they have lifetimes in the  $4-50 \,\mu s$  range.<sup>30</sup>

The kinetic results obtained for the GeMe<sub>2</sub>-MeOH complex indicate that the barrier for unimolecular H-migration in the complex is sufficiently high that it cannot compete with a catalytic proton-transfer pathway involving one or more alcohol molecules as catalyst in neutral solution. Even the latter process is remarkably slow, as evidenced by the ca. 4 µs lifetime of the GeMe<sub>2</sub>-MeOH complex in MeOH solution at 25 °C.<sup>30</sup> This leads to an estimated upper limit of  $k \le 10^4 \text{ M}^{-1} \text{ s}^{-1}$  for the rate constant for catalysis by a single solvent molecule; that for the corresponding process in the case of the GePh<sub>2</sub>-MeOH complex is roughly an order of magnitude smaller.<sup>30</sup> In contrast, the SiPh<sub>2</sub>-MeOH complex exhibits a lifetime of ca. 400 ns in *hexanes* solution containing 0.15 mM MeOH.<sup>29</sup> Under these conditions, the complex can be observed as a weakly absorbing transient with UV-vis spectrum centered at  $\lambda_{\rm max} \approx 370$  nm, which grows in with a rise time of ca. 40 ns and then decays on a time scale just slightly longer than that of the free silvlene under the same conditions. The species is undetectable at

- (15) Heaven, M. W.; Metha, G. F.; Buntine, M. A. J. Phys. Chem. A 2001, 105, 1185.
- (16) Heaven, M. W.; Metha, G. F.; Buntine, M. A. Aust. J. Chem. **2001**, *54*, 185.
- (17) Alexander, U. N.; King, K. D.; Lawrance, W. D. J. Phys. Chem. A 2002, 106, 973.
- (18) Becerra, R.; Goldberg, N.; Cannady, J. P.; Almond, M. J.; Ogden, J. S.; Walsh, R. J. Am. Chem. Soc. **2004**, *126*, 6816.
- (19) Su, M. D. Chem. Eur. J. 2004, 10, 6073.
- (20) Ando, W.; Itoh, H.; Tsumuraya, T. Organometallics 1989, 8, 2759.
- (21) Gillette, G. R.; Noren, G. H.; West, R. *Organometallics* **1989**, *8*, 487.
- (22) Baggott, J. E.; Blitz, M. A.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. Int. J. Chem. Kinet. 1992, 24, 127.
- (23) Alexander, U. N.; King, K. D.; Lawrance, W. D. Phys. Chem. Chem. Phys. 2003, 5, 1557.
- (24) Becerra, R.; Cannady, J. P.; Walsh, R. J. Phys. Chem. A 2003, 107, 11049.
- (25) Steele, K. P.; Weber, W. P. Inorg. Chem. 1981, 20, 1302.
- (26) Steele, K. P.; Tzeng, D.; Weber, W. P. J. Organomet. Chem. 1982, 231, 291.
- (27) Levin, G.; Das, P. K.; Bilgrien, C.; Lee, C. L. Organometallics 1989, 8, 1206.
- (28) Leigh, W. J.; Lollmahomed, F.; Harrington, C. R.; McDonald, J. M. Organometallics **2006**, *25*, 5424.
- (29) Moiseev, A. G.; Leigh, W. J. Organometallics 2007, 26, 6268.
- (30) Lollmahomed, F.; Huck, L. A.; Harrington, C. R.; Chitnis, S. S.; Leigh, W. J. Organometallics **2009**, *28*, 1484.

higher (1-3 mM) MeOH concentrations, in experiments on the nanosecond time scale. Similar observations were mentioned by Levin et al. in their kinetic study of the reactions of SiMe<sub>2</sub> with aliphatic alcohols in cyclohexane solution, but were evidently not pursued.<sup>27</sup>

The mechanism of the fast proton-migration/transfer process in silylene-alcohol complexes-whether by unimolecular H-migration or the catalyzed pathway, or bothremains to be established. Becerra et al. reported kinetic and computational evidence for a mechanism, for the gas-phase reaction of SiH<sub>2</sub> with water, involving two molecules of the substrate in the rate-determining step for consumption of silvlene;<sup>18</sup> an analogous mechanism has been proposed for singlet carbene O-H insertions on the basis of computational studies of the reaction of dichlorocarbene with water. It is difficult to predict what this means for the reactions of alcohols with substituted silylenes in solution, as theory predicts that the complexation of water with SiMe<sub>2</sub> is less exothermic than that with SiH<sub>2</sub>, and (unimolecular) H-migration within the silylene-water complex proceeds via a (slightly) lower enthalpic barrier.<sup>11</sup> The preliminary kinetic behavior reported earlier for the SiPh2-MeOH complex in hexanes is consistent with either the unimolecular or catalytic H-transfer pathway, or a combination of both, for decay of the species in the presence of submillimolar concentrations of MeOH.29

In this paper, we report the results of more detailed kinetic studies of the reactions of alcohols with  $SiMe_2$ ,  $SiPh_2$ , and dimesitylsilylene ( $SiMes_2$ ) in hexanes solution, focusing on the direct detection and characterization of their reactive Lewis acid-base complexes with MeOH, *tert*-butanol (*t*-BuOH), and the O-deuterated isotopomers of the two alcohols. As in our previous study,<sup>29</sup> the three silylenes were generated and detected directly by laser flash photolysis of the oligosilane derivatives **1**–**3**, respectively.



## **Results and Discussion**

Diphenylsilylene (SiPh<sub>2</sub>). Laser flash photolysis of deoxygenated solutions of 1 (ca. 0.05 mM) in anhydrous hexanes, with the pulses from a KrF excimer laser (248 nm; ca. 20 ns; ca. 100 mJ/pulse), affords the characteristic transient absorptions due to SiPh<sub>2</sub> ( $\lambda_{max} = 290$  and 515 nm;  $\tau \approx 1.7 \,\mu$ s), which decay with second-order kinetics with the concomitant growth of the longer-lived absorptions due to the silvlene dimerization product, tetraphenyldisilene  $(Si_2Ph_4; \lambda_{max} = 460 \text{ nm}; \tau > 50 \,\mu\text{s}).^{31}$  The absorptions due to SiPh<sub>2</sub> and Si<sub>2</sub>Ph<sub>4</sub> are superimposed on the much longer-lived ones due to a minor transient coproduct ( $\lambda_{max} = 460 \text{ nm}; \tau > 100 \text{ nm}$ 50  $\mu$ s), which we have assigned previously to the transient silene 4.<sup>29</sup> Representative transient spectra and decays are shown in Figure 1a. It should be noted that the spectra of Figure 1a lack the weak transient absorption centered at ca. 360 nm that was present in our earlier published spectra from laser photolysis of 1 in hexanes;<sup>29</sup> we believe this absorption

<sup>(31)</sup> Moiseev, A. G.; Leigh, W. J. J. Am. Chem. Soc. 2006, 128, 14442.



**Figure 1.** Transient absorption spectra from laser flash photolysis of deoxygenated solutions of 1 (ca. 0.05 mM) in hexanes: (a) in the pure anhydrous solvent, recorded 96–128 ns ( $\Box$ ), 1.52–1.58  $\mu$ s ( $\bigcirc$ ), and 8.56–8.62  $\mu$ s ( $\oplus$ ) after the laser pulse; and (b) after addition of 0.3 mM *t*-BuOH, recorded 32–64 ns ( $\Box$ ), 0.38–0.45  $\mu$ s ( $\bigcirc$ ), and 4.00–4.07  $\mu$ s ( $\oplus$ ) after the laser pulse. The insets show transient decay/growth profiles recorded at monitoring wavelengths of 350, 460, and 530 nm. The solid line through the 530 nm decay in (a) is the best nonlinear least-squares fit of the data to second-order kinetics ( $2k/\epsilon = (3.9 \pm 0.6) \times 10^7 \text{ cm}^{-1} \text{ s}^{-1}$ ), while that in (b) is the best fit to first-order kinetics ( $k_{decay} = (4.3 \pm 0.3) \times 10^6 \text{ s}^{-1}$  (errors as  $\pm 2\sigma$ )).

was due to the SiPh<sub>2</sub>-H<sub>2</sub>O complex, arising from inadequate drying of the solvent and(or) sample-handling system in our earlier study.



Addition of small amounts of methanol or *tert*-butanol as either the protiated or O-deuterated isotopomers (MeOL and *t*-BuOL, respectively; L = H or D) caused the decay of the SiPh<sub>2</sub> absorptions to accelerate and quenched the formation of Si<sub>2</sub>Ph<sub>4</sub>, both to an increasing extent with increasing concentration of added alcohol. The decay of the silylene signal obeyed clean pseudo-first-order kinetics in the presence of alcohol, and plots of the first-order decay rate coefficients ( $k_{decay}$ ) versus [ROL] were linear in each case. Least-squares analysis of the data according to eq 3, where  $k_0$  is the hypothetical pseudo-first-order decay rate coefficient in the absence of ROL and  $k_Q$  is the second-order rate constant for reaction of the monitored species (the silylene, in this case) with the alcohol, afforded values of  $k_Q$  (= $k_{ROL}$ ) that varied over the range (1.1–1.8) × 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>, as summarized in Table 1.

$$k_{\text{decay}} = k_0 + k_Q[\text{ROL}] \tag{3}$$

The measured rate constants are all within a factor of 2 of the diffusional rate constant ( $k_{diff} = 2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  in hexane at 25 °C)<sup>32</sup> and do not vary appreciably as a function of alcohol structure. Similarly, there is little variation in the rate constant with isotopic substitution for either alcohol

Table 1. Absolute Rate Constants (in units of  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) for Reaction of SiMe<sub>2</sub> and SiPh<sub>2</sub> with Alcohols in Deoxygenated Hexanes at 25 °C ( $k_{ROL}$ ) and for Quenching of the Transient Absorptions Due to the Corresponding Silylene-ROL Complexes by ROL ( $k_{-1}$ )<sup>a</sup>

Cor	nplexes	by .	ROL	$(k_{cat})^{a}$

	SiMe <sub>2</sub>		SiPh <sub>2</sub>	
ROL	$/10^9 \mathrm{M}^{-1} \mathrm{s}^{-1}$	$/10^9 {{M^{-1}} \over {M^{-1}}} {{\rm s}}^{-1}$	$k_{\rm ROL}^{\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $	$/10^9 {{k_{\rm cat}}^e \over {\rm M}^{-1}} {\rm s}^{-1}$
MeOH MeOD t-BuOH t-BuOD	$21 \pm 3$ $20 \pm 3$ $14 \pm 2$ $13 \pm 1$	$15 \pm 3 \\ 17 \pm 5 \\ 8.1 \pm 1.2 \\ 7.2 \pm 0.9$	$18 \pm 2 \\ 14 \pm 2 \\ 14 \pm 1 \\ 11 \pm 1$	$18 \pm 1 \\ 8.6 \pm 1.2 \\ 1.4 \pm 0.1 \\ 0.13 \pm 0.02$

<sup>*a*</sup> Rate constants are the mean of two independent measurements in each case, while errors are listed as the standard deviation of the average value. <sup>*b*</sup> Monitored at 470 nm. <sup>*c*</sup> Monitored at 310 nm. <sup>*d*</sup> Monitored at 520–530 nm. <sup>*e*</sup> Monitored at 350 nm.



**Figure 2.** (a) Transient decay traces recorded at 350 nm, from laser photolysis of **1** in hexanes containing 0, 0.2, and 1.0 mM *t*-BuOH. (b) Transient absorption spectra from laser photolysis of **1** in hexanes containing 0.05 M *t*-BuOD, recorded 90–102 ns ( $\Box$ ), 205–218 ns ( $\bigcirc$ ), and 742–755 ns ( $\bigcirc$ ) after the laser pulse; the insets show transient decay traces recorded at monitoring wavelengths of 350 and 460 nm.

within the error limits of our measurements, not unexpectedly considering that those for reaction of SiPh<sub>2</sub> with the protiated substrates are so close to the diffusion-limiting value. The value of  $k_{\text{MeOH}}$  obtained in the experiments with MeOH ( $k_{\text{MeOH}} = (1.8 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) is in reasonable agreement with our previously reported values.<sup>29,31</sup>

The primary products of these reactions could be detected as transients with distinct absorption bands centered at  $\lambda_{max}$  $\approx$  360 nm, in the wavelength range characteristic of the complexes of SiPh2 with other O-donors such as tetrahydrofuran (THF) and methoxytrimethylsilane.33 These absorptions grew in over a time scale similar to that of the decay of the silvlene signal at a given ROL concentration, increasing in maximum signal intensity with increasing ROL concentration, and then decayed with lifetimes in the 0.2–1.5  $\mu$ s range. For example, Figure 1b shows a series of timeresolved spectra obtained from laser photolysis of a solution of 1 in hexanes containing 0.3 mM t-BuOH, conditions under which free SiPh<sub>2</sub> could still be detected ( $\tau \approx 230$  ns). The weak transient absorption centered at 460 nm contains contributions from both Si<sub>2</sub>Ph<sub>4</sub>, whose formation is incompletely quenched at this alcohol concentration, and the longlived transient coproduct (silene 4). We assign the 360 nm transients to the corresponding SiPh2-ROL complexes and the process(es) responsible for their decay to proton migration and(or) transfer, which transforms them to the final reaction product, the corresponding alkoxydiphenylsilane.

<sup>(32)</sup> Espenson, J. H. Chemical Kinetics and Reaction Mechanisms; McGraw-Hill, Inc.: New York, 1995; pp 15–45.

<sup>(33)</sup> Moiseev, A. G.; Leigh, W. J. Organometallics 2007, 26, 6277.



**Figure 3.** Plots of the pseudo-first-order decay rate coefficients ( $k_{decay}$ ) of the SiPh<sub>2</sub>-ROL complexes (L = H ( $\blacksquare$ ) or D ( $\Box$ )) vs [ROL] for (a) R = Me and (b) R = *t*-Bu, in hexanes at 25 °C. The solid lines are the best linear least-squares fits of the data to eq 3.

The maximum intensities of the signals due to the complexes, their lifetimes (at the same ROL concentration), and the range of alcohol concentrations over which they could be detected all increased in the order MeOH < MeOD <t-BuOH < t-BuOD, indicating a significant dependence of their decay kinetics on alcohol structure and isotopic substitution. Figure 2a illustrates the observed variation in the growth/decay profiles associated with the SiPh2-t-BuOH complex as a function of t-BuOH concentration in a typical experiment. The signals due to the  $SiPh_2 - t$ -BuOH complex could be detected over the 0.2-5 mM concentration range in added alcohol, above which they were too short-lived for precise kinetic analysis to be carried out. In the low concentration (0.2-1 mM) range, the signals exhibited a rapid growth, of rise time similar to that of the decay of the free silvlene absorption at the same *t*-BuOH concentration. This was followed by a two-component decay, consisting of a fast component that accelerated with increasing t-BuOH concentration and a much slower component whose overall intensity decreased with increasing concentration. The fastdecay component of the absorption, which intensified with increasing alcohol concentration over the 0.2-1 mM range, is assigned to the silvlene-alcohol complex. First-order rate coefficients for decay of these absorptions were estimated by fitting the fast component of the decays to single exponentials and treating the slow component as a nondecaying residual absorption. The SiPh<sub>2</sub>-t-BuOD complex exhibited similar spectral characteristics at low t-BuOD concentrations, but its lifetime was much less responsive to changes in alcohol concentration. The complex remained detectable even in the presence of 50 mM t-BuOD, where it exhibited a lifetime  $\tau \approx 165$  ns. The absorption due to the deuterated complex was monitored over the 3-50 mM concentration range in added t-BuOD, conditions under which it was formed within the duration of the laser pulse and decayed completely to baseline. Figure 2b shows the transient UV-vis spectrum of the SiPh2-t-BuOD complex, obtained by laser photolysis of 1 in hexanes containing 0.05 M t-BuOD. Under these conditions the complex is the only silylene-derived species detectable in solution. The spectrum consists of an intense short-wavelength band centered below 300 nm with a long-wavelength shoulder at ca. 360 nm; the apparent maximum at 300 nm in the spectrum of Figure 1b is the result of spectral distortion due to bleaching of the precursor, whose absorption onset is in the 290-300 nm range.



The signals due to the SiPh<sub>2</sub>-MeOH and SiPh<sub>2</sub>-MeOD complexes were weaker than those of the SiPh<sub>2</sub>-t-BuOL complexes, and their apparent lifetimes were considerably more sensitive to MeOL concentration; they were, however, always significantly longer than the lifetime of the free silylene under the same conditions. First-order decay rate coefficients were estimated over the 0.1-0.4 mM concentration range in added MeOH or MeOD, using a similar procedure to that used for the SiPh<sub>2</sub>-t-BuOL complexes.

Figure 3 shows plots of  $k_{decay}$  versus ROL concentration for the four SiPh<sub>2</sub>-ROL complexes studied in this work; the solid lines represent the best linear least-squares fits of the data to eq 3. The intercepts of these plots should correspond (in principle) to the first-order rate constants for unimolecular proton migration in the complexes to yield the corresponding alkoxysilane (i.e.,  $k_1 = k_0$  of eq 3), and the slopes to the absolute rate constants for catalytic proton transfer by a second molecule of ROL ( $k_{cat} = k_Q$  of eq 3), as shown in Scheme 1. In practice however, the values of the intercepts varied considerably from experiment to experiment with a given alcohol, so we can place no significance on them beyond noting that they are characteristically small; a reasonable upper limit in the case of the SiPh<sub>2</sub>-MeOH complex is  $k_1 \leq 10^5 \text{ s}^{-1}$ . Kinetic simulations established an upper limit of  $k_{-\text{MeOH}} \approx 10^5 \text{ s}^{-1}$  for the rate constant for reversion of the SiPh<sub>2</sub>-MeOH complex to the free reactants and thus a lower limit of  $K_{eq} \ge 2 \times 10^5 \,\mathrm{M}^{-1}$  for the equilibrium constant for complexation of SiPh<sub>2</sub> with MeOH.<sup>34</sup> Table 1 summarizes the second-order rate constants for both the primary reaction of the free silvlene with ROL (i.e.,  $k_{ROL}$ ) and the

<sup>(34)</sup> Kinetic simulations, employing the  $k_{\text{MeOH}}$  and  $k_{\text{cat}}^{\text{MeOH}}$  values of Table 1 showed that a value of  $k_{-\text{MeOH}} = 1 \times 10^5 \text{ s}^{-1}$  or less is required to reproduce the experimentally observed lifetimes of free SiPh<sub>2</sub> and the SiPh<sub>2</sub>-MeOH complex at the lowest MeOH concentration studied (0.06 mM).



**Figure 4.** (a) Plots of the pseudo-first-order decay rate coefficients ( $k_{decay}$ ) vs [*t*-BuOL] of free SiMe<sub>2</sub> ( $\lambda_{max} = 465 \text{ nm}$ ; L = H ( $\bullet$ ) and D ( $\bigcirc$ )) and of the SiMe<sub>2</sub>-*t*-BuOL complex ( $\lambda_{max} = 300 \text{ nm}$ ; L = H ( $\bullet$ ) and D ( $\square$ )). (b) Transient absorption spectra from a deoxygenated solution of **2** in anhydrous hexanes containing 1.16 mM *t*-BuOD, recorded 16–26 ns ( $\bigcirc$ ) and 138–150 ns ( $\square$ ) after the laser pulse; the insets show transient decay traces recorded at monitoring wavelengths of 310 and 470 nm.

catalytic rate constants ( $k_{cat}$ ) obtained from analysis of the first-order rate coefficients for decay of the complexes as a function of ROL concentration.

The data indicate that the formation of the SiPh<sub>2</sub>-MeOH complex and its catalytic transformation to the final (alkoxysilane) product by a second molecule of MeOH both proceed with rate constants approaching the diffusion limit. Interestingly, in spite of the rapidity of the catalytic process it exhibits a primary kinetic isotope effect of  $k_{\rm HH}/k_{\rm DD} \approx 2$ . Catalysis is roughly an order of magnitude slower in the case of the SiPh<sub>2</sub>-t-BuOH complex, consistent with a marked sensitivity of the catalytic process to increased steric hindrance in the alcohol. The process exhibits a kinetic isotope effect of  $k_{\rm HH}/k_{\rm DD} = 10.8 \pm 2.4$ , which too seems quite remarkable given the value of  $k_{\rm cat} \approx 10^9 \text{ M}^{-1} \text{ s}^{-1}$  that characterizes the protiated species. While proton transfers involving sterically hindered reactants frequently exhibit abnormally large isotope effects due to tunneling,<sup>35</sup> especially in nonpolar solvents,<sup>36</sup> the value is also consistent with a mechanism involving a simultaneous double proton transfer such as that shown in eq 4; the net isotope effect should be given (in principle) by the product of the isotope effects associated with the individual protons in flight in the transition state.<sup>37</sup>

$$\begin{array}{ccc} & & & & & & & \\ & & & & & \\ R^{\vee} & & & & \\ & & & \\ R^{\vee} & & & \\ & & & \\ H = & & \\ & & & \\ & & \\ & & \\ & & \\ \end{array} \end{array} \xrightarrow{ \begin{array}{ccc} & & & Ph \\ & & & \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} } \xrightarrow{ \begin{array}{ccc} & & Ph \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} } \xrightarrow{ \begin{array}{ccc} & & Ph \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} } \xrightarrow{ \begin{array}{ccc} & & Ph \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} } \xrightarrow{ \begin{array}{ccc} & & Ph \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} } \xrightarrow{ \begin{array}{ccc} & & Ph \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} } \xrightarrow{ \begin{array}{ccc} & & Ph \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} } \xrightarrow{ \begin{array}{ccc} & & Ph \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \xrightarrow{ \begin{array}{ccc} & & Ph \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \xrightarrow{ \begin{array}{ccc} & & Ph \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \xrightarrow{ \begin{array}{ccc} & & Ph \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \xrightarrow{ \begin{array}{ccc} & & Ph \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \xrightarrow{ \begin{array}{ccc} & & Ph \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \xrightarrow{ \begin{array}{ccc} & & Ph \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \xrightarrow{ \begin{array}{ccc} & & Ph \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \xrightarrow{ \begin{array}{ccc} & & Ph \\ & & \\$$

The intercepts of the plots of Figure 3b afford upper limits of  $k_1 \le 1 \times 10^6 \text{ s}^{-1}$  and  $k_1 \le 5 \times 10^5 \text{ s}^{-1}$  for the rate constants for unimolecular H(D) migration in the SiPh<sub>2</sub>-*t*-BuOH and SiPh<sub>2</sub>-*t*-BuOD complexes, respectively.

**Dimethylsilylene** (SiMe<sub>2</sub>). The kinetics of the reactions of SiMe<sub>2</sub> with MeOL and *t*-BuOL were studied using dodecamethyl-cyclohexasilane (2) as the silylene precursor.<sup>27,29,33,38–40</sup>

(38) Levin, G.; Das, P. K.; Lee, C. L. Organometallics 1988, 7, 1231.

(39) Shizuka, H.; Tanaka, H.; Tonokura, K.; Murata, K.; Hiratsuka, H.; Ohshita, J.; Ishikawa, M. *Chem. Phys. Lett.* **1988**, *143*, 225.

Laser photolysis of ca. 0.5 mM hexanes solutions of 2 afforded the characteristic transient absorptions due to SiMe<sub>2</sub> ( $\lambda_{max} = 465$  nm;  $\tau \approx 500$  ns), which decayed with apparent first-order kinetics with the concomitant growth of the longer-lived absorptions due to  $Si_2Me_4$  ( $\lambda_{max} = 290$  and 360 nm;  $\tau \approx 20 \,\mu$ s), as reported previously.<sup>29,33,40</sup> Addition of 0.1-1.0 mM t-BuOH resulted in reductions in the lifetime of the silylene absorptions and quenched the formation of the disilene, and a plot of  $k_{deccay}$  for the silylene versus [t-BuOH] was linear with slope  $k_{t-BuOH} = (1.3 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . Similar results were obtained with MeOH ( $k_{MeOH} = (2.1 \pm$  $0.3) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) and with the O-deuterated alcohols as substrates. As with SiPh<sub>2</sub>, the rate constants for silylene quenching by the deuterated alcohols were the same as those obtained with the protiated analogues in both cases. The values of  $k_{MeOH}$  and  $k_{t-BuOH}$  determined in these experiments (see Table 1) are in good agreement with the previously reported values in hexanes or cyclohexane solution.<sup>27,29,38,39</sup>

Inspection of transient growth/decay profiles at 300-310 nm, in the range characteristic of SiMe<sub>2</sub>-O-donor complexes, 21,27,33,40 revealed the presence of new transient absorptions that behaved similarly to those due to the SiPh<sub>2</sub>-ROH complexes, increasing in both maximum intensity and decay rate with increasing alcohol concentration until they became too short-lived to be detected. These absorptions, which we assign to the corresponding SiMe<sub>2</sub>-ROL complexes, were superimposed on a longer-lived component ( $\lambda_{max} = 290$  nm) whose contribution to the overall decay diminished as the alcohol concentration was increased; this is due most likely to Si<sub>2</sub>Me<sub>4</sub> and(or) a higher oligomerization product, whose yield decreases with increasing efficiency of silvlene trapping by the added alcohol. The absorptions due to the complexes exhibited apparent lifetimes longer than those of the free silvlene under the same conditions in every case; the SiMe2-MeOL complexes were detectable over the 0.08-0.5 mM alcohol concentration range, while the corresponding t-BuOL complexes were detectable over the 0.1-2 mM concentration range. They were too short-lived at higher alcohol concentrations to be accurately resolved from the negative-going signal due to sample fluorescence.

Figure 4a shows the plots of  $k_{decay}$  versus [*t*-BuOL] that resulted from the experiments with that alcohol, while Figure 4b shows transient absorption spectra and representative absorption-time profiles recorded with a solution of **2** 

<sup>(35)</sup> Bell, R. P. The Tunnel Effect in Chemistry; Chapman and Hall: London, 1980.

<sup>(36)</sup> Jarczewski, A.; Hubbard, C. D. J. Mol. Struct. 2003, 649, 287.

<sup>(37)</sup> Gerritzen, D.; Limbach, H. H. J. Am. Chem. Soc. 1984, 106, 869.

<sup>(40)</sup> Yamaji, M.; Hamanishi, K.; Takahashi, T.; Shizuka, H. J. Photochem. Photobiol. A: Chem. 1994, 81, 1.

in hexanes containing ca. 1.2 mM of the deuterated substrate at 25 °C. The lifetime of SiMe<sub>2</sub> under the conditions of Figure 4b was ca. 70 ns, while that of the SiMe<sub>2</sub>-*t*-BuOD complex ( $\lambda_{max} = 300$  nm) was ca. 130 ns; the formation of Si<sub>2</sub>Me<sub>4</sub> is almost completely quenched at this concentration, as evidenced by the weak shoulder on the long-wavelength edge of the absorption band due to the complex ( $\lambda_{max} \approx$ 300 nm). The analogous plots of  $k_{decay}$  versus [MeOL] from the experiments with MeOH and MeOD as substrate are shown in Figure S2 of the Supporting Information. The various rate constants determined in these experiments are listed in Table 1 along with the corresponding values for SiPh<sub>2</sub>.

Again, the lifetimes of both free SiMe<sub>2</sub> and the SiMe<sub>2</sub>-MeOH complex responded in parallel fashion to variations in MeOH concentration, with the lifetime of the complex being roughly twice longer than that of the free silylene at the same alcohol concentration throughout the range studied. Similar results were obtained in experiments using MeOD as substrate. The intercepts of the plots of  $k_{decay}$  versus [ROH] for the SiMe<sub>2</sub>-MeOH and SiMe<sub>2</sub>-t-BuOH complexes were both indistinguishable from zero, establishing an upper limit of  $k_1 \le 10^5$  s<sup>-1</sup> for the rate constant for unimolecular H-migration within the complex in both cases. Thus, catalysis by a second molecule of alcohol provides the only detectable proton-transfer pathway for product formation from the intermediate complexes, as was found to be the case for the corresponding SiPh<sub>2</sub>-ROH complexes. In contrast to the SiPh<sub>2</sub>-ROH complexes, however, the catalytic process exhibits an isotope effect of approximately unity for both the SiMe<sub>2</sub>-MeOH and SiMe<sub>2</sub>-t-BuOH complexes.

It is unclear to what extent we should expect the present kinetic data to correlate with the relative rate data published in the early studies by Steele and Weber of the reactions of SiMe<sub>2</sub> with aliphatic alcohols in cyclohexane solution.<sup>25,41</sup> The early data, which were derived from competitive trapping experiments, afford a value of  $k_{\text{MeOH}}/k_{t-\text{BuOH}} \approx 2.1$  for the relative rates of product formation from reaction of SiMe<sub>2</sub> with the two alcohols in cyclohexane at ambient temperatures, which agrees well with the ratio of the catalytic rate constants ( $k_{cat}^{MeOH}/k_{cat}^{t-BuOH} = 1.9 \pm 0.6$ ) determined in the present work. However, our data indicate kinetic isotope effects of approximately unity for both steps in the reactions of SiMe<sub>2</sub> with MeOH and t-BuOH, which is at odds with the values of  $k_{\rm H}/k_{\rm D} \approx 2$  established by Steele and Weber, for the reactions of EtOH(D) and t-BuOH(D) with SiMe<sub>2</sub>, on the basis of relative product yields.<sup>25</sup> The disagreement may be due to the vastly different experimental conditions used in the early experiments compared to the present ones. The competition experiments were all carried out in cyclohexane containing molar concentrations of the alcohols,<sup>25</sup> where the substrates exist largely in (hydrogenbonded) oligomeric form rather than the monomeric form that dominates alcohol speciation at the submillimolar concentrations employed in our kinetic experiments.<sup>42,43</sup> Furthermore, the early isotope effect experiments were carried out using mixtures of the protiated and deuterated alcohols, and hence the measured isotope effect contains contributions from a minimum of four isotopomeric reaction pathways, in addition





to the (probably greater) contributions from other pathways involving alcohol oligomers. Our experiments were carried out with isotopically pure substrates at relatively low alcohol concentrations where the monomeric form of the alcohol is essentially the only species present. The results indicate that under these conditions the isotope effects on both the complexation and catalytic proton-transfer steps are approximately unity within experimental error for both MeOH and *t*-BuOH.

**Dimesitylsilylene** (SiMes<sub>2</sub>). Our preliminary kinetic study of the reaction of SiMes<sub>2</sub> with MeOH in hexanes afforded a linear plot of  $k_{\text{decay}}$  versus [MeOH] ( $k_{\text{Q}} = (8.2 \pm 0.3) \times$  $10^8 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>29</sup> consistent with a reaction mechanism leading to overall second-order kinetics (first-order in SiMes<sub>2</sub>; firstorder in MeOH) over the alcohol concentration studied (1-8 mM). However, the plot exhibited a negative intercept, which suggests a higher order dependence on alcohol concentration that functions only at low (< 2 mM) concentrations. The simplest change to the mechanism of Scheme 1 that could result in this behavior is the introduction of reversibility in the first step of the reaction. The resulting working mechanism, with the additional provision that the rate constant for unimolecular H-transfer within the complex is vanishingly small (i.e.,  $k_1 \ll k_{cat}[ROL]$  at all ROL concentrations studied), is shown in Scheme 2. The predicted dependence of the pseudo-first-order rate coefficient for silvlene decay, assuming the steady-state approximation holds for the intermediate complex (vide infra), is given in eq 5. It should be noted that this expression predicts a linear dependence of  $k_{decay}$  on [ROL] (with slope equal to the complexation rate constant,  $k_{ROL}$ ) in the high concentration range, where  $k_{\text{cat}}[\text{ROL}] \gg k_{-\text{ROL}}$ , and a gradual change to a squared dependence on [ROL] as [ROL]  $\rightarrow 0$ , where catalytic proton transfer involving the complex takes over as the ratecontrolling step for silvlene decay.

$$k_{\text{decay}} = k_0 + k_{\text{ROL}} k_{\text{cat}} [\text{ROL}]^2 / (k_{-\text{ROL}} + k_{\text{cat}} [\text{ROL}])$$
(5)

Thus, information on the magnitudes of  $k_{cat}$  and  $k_{-ROL}$ should be accessible (in principle) from analysis of the concentration dependence of the pseudo-first-order rate constants for silylene decay in the low concentration range where the nonlinear behavior prevails. Such an analysis is made potentially difficult by the fact that as [ROL]  $\rightarrow 0$ , dimerization takes over as the main reaction channel available to the silylene, which should result in decay profiles that follow mixed pseudo-first- and second-order kinetics and are hence more difficult to analyze quantitatively. In principle, it should be possible to reduce the contribution of the secondorder component due to silylene dimerization by working at low excitation laser intensities, but we have little flexibility in this regard because the silylene absorptions are relatively weak. Nevertheless, the presence of a primary isotope effect

<sup>(41)</sup> Steele, K. P.; Weber, W. P. J. Am. Chem. Soc. 1980, 102, 6095.

<sup>(42)</sup> Landeck, H.; Wolff, H.; Goetz, R. J. Phys. Chem. 1977, 81, 718.

<sup>(43)</sup> Griller, D.; Liu, M. T. H.; Scaiano, J. C. J. Am. Chem. Soc. 1982, 104, 5549.



**Figure 5.** Plots of the pseudo-first-order rate constants for the decay of  $SiMes_2$  vs [MeOL] (L = H, ( $\bullet$ ) or D ( $\odot$ )) in hexanes at 25 °C. The solid lines are the nonlinear least-squares fits of the data to eq 6.

on the catalytic proton-transfer process should be at least qualitatively evident in the resulting  $k_{decay}$  versus [ROL] plots, as an extension of the concentration range over which the curvature is displayed for the deuterated alcohol compared to that of the protiated isotopomer. The result should be a displacement of the linear portion of the plot to higher concentrations for the deuterated alcohol, with the extent of the displacement depending on the magnitude of the isotope effect on  $k_{cat}$ .

Laser photolysis of deoxygenated hexanes solutions of the SiMes<sub>2</sub> precursor (3) afforded the characteristic absorptions due to free SiMes<sub>2</sub> ( $\lambda_{max} = 290$  and 580 nm), which decayed with second-order kinetics with the concomitant growth of the long-lived absorption due to the dimerization product, tetramesityldisilene (Si<sub>2</sub>Mes<sub>4</sub>;  $\lambda_{max} = 420 \text{ nm}$ ;  $\tau_0 > 20 \text{ s}$ ), as reported previously.<sup>29,44</sup> Addition of as little as 0.2 mM MeOH to the solutions caused a noticeable shortening of the silylene decay (monitored at 580 nm) and suppression of the characteristic growth of the disilene absorption at 420 nm. As anticipated, the silylene absorptions decayed with mixed-order kinetics in the presence of the alcohol over the 0.2 to ca. 1.3 mM concentration range, above which the decay profiles fit well to first-order kinetics. First-order decay rate coefficients over the lower range in [MeOH] were estimated by fitting the data to two first-order exponentials (i.e., treating the second-order component, which dominates the earliest portion of the decay profile, as a first-order decay) and taking the slower of the two decay coefficients as that due to reaction with the alcohol; those at higher concentrations were obtained from fits to simple first-order kinetics. Decay rate coefficients were measured at a total of 12-15 different alcohol concentrations, up to that required for the silvlene lifetime to be reduced to 150 ns or less. A similar procedure was followed using MeOD, t-BuOH, and t-BuOD as substrates. Figure 5 shows the resulting plots of  $k_{\text{decay}}$  versus [ROL] for MeOH and MeOD; the corresponding ones for t-BuOL (Figure S4, Supporting Information) show similar curvature, except they span a ca. 10-fold higher range in alcohol concentration. It should be noted that the alcohol concentration ranges studied in these experiments are well above the range where exchange of the deuterated

 Table 2. Kinetic Data for the Reaction of SiMes<sub>2</sub> with Alcohols in Deoxygenated Hexanes at 25 °C<sup>a</sup>

ROL	$k_{\rm ROL}/10^9 {\rm ~M^{-1}~s^{-1}}$	$(k_{\rm cat}/k_{-\rm ROL})/{\rm M}^{-1}$
MeOH	$1.01 \pm 0.09$	$550 \pm 150$
MeOD	$1.26 \pm 0.25$	$220 \pm 100$
t-BuOH	$0.136 \pm 0.005$	$36 \pm 7$
t-BuOD	$0.136\pm0.009$	$64 \pm 5$

<sup>*a*</sup> From analysis of  $k_{\text{decay}}$  vs [ROL] data according to eq 6; listed as the average  $\pm$  standard deviation of three independent determinations in each case. The silylene decay was monitored at 580 nm.

substrates with adventitious water in the solvent might be a problem (below ca. 0.1 mM), yet below the ranges where oligomerization effects begin to seriously complicate alcohol speciation (above ca. 0.01 M for MeOH; above ca. 0.08 M for t-BuOH).<sup>42,43,45</sup>

As expected, the plots reveal a nonlinear dependence of  $k_{\text{decay}}$  on [ROL] in the low alcohol concentration ranges, which changes to a linear dependence at intermediate alcohol concentrations and above. The kinetic behavior at MeOH concentrations higher than 1.0 mM is in excellent agreement with our earlier study;29 linear least-squares analysis of the present data, excluding those data points below 1.5 mM MeOH, affords a slope of  $(8.6 \pm 0.3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . As expected, the linear portion of the plot for MeOD is displaced to higher concentrations compared to that for MeOH; this is consistent with a normal kinetic isotope effect on the catalytic rate constant  $(k_{cat})$ , although the effect is apparently quite small. Interestingly, the linear portion of the plot for t-BuOD is displaced to lower concentrations compared to that for t-BuOH, consistent with an inverse kinetic isotope effect on  $k_{cat}$  for the bulkier alcohol.

Attempts to fit the data to eq 5 failed to yield unambiguous values for  $k_{-ROL}$  and  $k_{cat}$ , so the expression was recast in the analytically more tractable form of eq 6. The results of fitting the data to the latter equation are shown as the solid lines in the plots of Figures 5 and S4, while the  $k_{ROL}$  and  $k_{cat}/k_{-ROL}$  values afforded by the analyses are listed in Table 2. Each of the values listed is the average of three independent determinations.

$$k_{\text{decay}} = k_{\text{ROL}} (k_{\text{cat}}/k_{-\text{ROL}}) [\text{ROL}]^2 / (1 + (k_{\text{cat}}/k_{-\text{ROL}}) [\text{ROL}])$$
(6)

The use of the steady-state approximation in the derivation of eqs 5 and 6 can be justified by the fact that transient spectra recorded in the presence of MeOH (3.9 mM; Figure S4a, Supporting Information) or t-BuOH (0.05 M; Figure S4c, Supporting Information), where the lifetime of the silvlene is reduced to ca. 10% of its value in the absence of added alcohol, showed only short-lived absorptions due to free SiMes<sub>2</sub> and no evidence of new transient absorptions in the 300-420 nm range that might be assigned to the corresponding SiMes<sub>2</sub>-ROH complexes;<sup>21</sup> lifetimes measured in this spectral range were nearly identical to those measured at 570-580 nm, as was also the case in the absence of added alcohol. Analogous results were obtained in experiments carried out at both lower and higher concentrations of MeOH. We measured transient spectra from a hexanes solution of 3 containing 0.6 M THF (Figure S4b, Supporting Information) in order to determine how the expected spectra of SiMes<sub>2</sub>-ROH complexes should appear in fluid solution,

<sup>(44)</sup> Conlin, R. T.; Netto-Ferreira, J. C.; Zhang, S.; Scaiano, J. C. Organometallics 1990, 9, 1332.

<sup>(45)</sup> Valero, J.; Gracia, M.; Gutierrez Losa, C. J. Chim. Phys. Phys.-Chim. Biol. 1980, 77, 65.

assuming that the appearance of the spectrum should be roughly independent of structural differences in the O-donor, as has been shown previously for SiMe<sub>2</sub> and SiPh<sub>2</sub>.<sup>33</sup> The spectrum of the SiMes<sub>2</sub>-THF complex in hexanes at 25 °C was found to consist of a strong band centered at  $\lambda_{max}$  = 300 nm coupled with a shoulder centered at ca. 400 nm. This appears to be different from the reported UV/vis spectrum of a photolyzed sample of 3 in a 95:5 3-methylpentane-THF matrix at 77K ( $\lambda_{max}$  = 328 nm), which was assigned to the SiMes<sub>2</sub>–THF complex.<sup>21</sup> It is, however, quite similar to the spectrum of the SiPh<sub>2</sub>-t-BuOD complex (Figure 2) under similar conditions, the main difference being a 30-40 nm shift of the spectrum to longer wavelengths. Comparison of the spectrum of the SiMes<sub>2</sub>-THF complex to that of free SiMes<sub>2</sub> suggests that the putative SiMes<sub>2</sub>-ROH complexes, if they were present in appreciable concentrations, should be detectable selectively in the 380-390 nm monitoring wavelength range. None of the spectra recorded for solutions of 3 containing MeOH or t-BuOH exhibited discrete transient absorptions within this spectral window, suggesting that the concentrations of the complexes do not grow to detectable levels. The mechanistic situation contrasts that for SiMe<sub>2</sub> and SiPh<sub>2</sub>, where the rates of product formation from the complex far exceed those of its dissociation to the free reactants even at very low alcohol concentrations, and as a result the complexes can be detected within limited concentration ranges.

The data of Table 2 indicate that the steric bulk afforded by the mesityl substituents in SiMes<sub>2</sub> has a pronounced effect on the rate constant for the initial complexation step in the reaction with MeOH, which is more than an order of magnitude smaller for SiMes<sub>2</sub> than for SiPh<sub>2</sub>. Increasing the steric bulk in the alcohol further reduces the complexation rate constant, as evidenced by the ca. 7-fold lower value of  $k_{t-BuOH}$  compared to  $k_{MeOH}$ . As we found for the more reactive silylenes, the complexation rate constants for both alcohols exhibit isotope effects indistinguishable from unity, as expected considering that they should be secondary effects and hence quite small. Surprisingly, the isotope effects on the  $k_{\rm cat}/k_{\rm -ROH}$  ratios are also quite small and appear to vary between a small normal effect for MeOH and an inverse effect for t-BuOH. Since we can reasonably expect at most a small (potentially inverse) secondary isotope effect on  $k_{-ROL}$ , we conclude that the isotope effects on  $k_{cat}$  must be quite small for both alcohols.

The data for the protiated complexes indicate that product formation is ca. 10 times more *efficient* for the MeOH complex compared to the bulkier *t*-BuOH complex, which is consistent with faster catalysis and(or) slower reversion to free reactants in the former compared to the latter. The very modest kinetic isotope effect on the  $k_{cat}/k_{-MeOH}$  ratio, which transforms to an inverse isotope effect in the case of *t*-BuOH, argues for a different mechanism for the catalytic protontransfer process in the complexes with the bulkier silylene, compared to the concerted double proton-transfer process that may be operable for the SiPh<sub>2</sub>-ROH complexes. A reasonable possibility is a sequential deprotonation/protonation process, which would be expected to be less sterically demanding than the concerted double proton transfer proposed for the SiPh<sub>2</sub>-ROL complexes.

#### **Summary and Conclusions**

The well-known O-H insertion reaction of dialkyl- and diarylsilylenes with alcohols proceeds via the initial formation

of the corresponding silylene–alcohol Lewis acid–base complex, which proceeds to the corresponding alkoxysilane via catalyzed proton transfer from oxygen to silicon, with a second molecule of the alcohol acting as catalyst. Complex formation is effectively irreversible with sterically unhindered silylenes such as SiMe<sub>2</sub> and SiPh<sub>2</sub> and proceeds at or close to the diffusioncontrolled rate in hexanes solution. As a result, the corresponding silylene–alcohol complexes can be detected directly at low alcohol concentrations as short-lived reaction intermediates with their own distinctive UV/vis spectra. A lower limit of  $K_{eq} \ge 2 \times 10^5 \text{ M}^{-1}$  has been estimated for the equilibrium constant for formation of the SiPh<sub>2</sub>–MeOH complex, corresponding to a free energy difference of  $\Delta G \approx -7.2$  kcal mol<sup>-1</sup> for the complex relative to the free reactants in hexanes solution at 25 °C.

The involvement of catalysis in the mechanism for the transformation of the complexes to product is revealed by a dependence of the lifetimes of the complexes on alcohol concentration and isotopic substitution; this process is also extremely rapid, proceeding with a rate constant similar to that of the initial complexation step. The large deuterium kinetic isotope effect exhibited by t-BuOH catalyzed proton transfer in the SiPh2-t-BuOH complex, for which a value of  $k_{\rm HH}/k_{\rm DD}$  = 10.8 ± 2.4 has been determined in hexanes at 25 °C, is consistent with a mechanism involving concerted, double proton transfer within a cyclic five-membered transition state. An upper limit of  $k_1 \le 10^5 \text{ s}^{-1}$  has been established for the rate constants for unimolecular H-migration in the complexes of SiMe2 and SiPh2 with MeOH, consistent with a free energy of activation of  $\Delta G^{\ddagger} \approx 11 \text{ kcal mol}^{-1}$  or greater at 25 °C. Thus, of the two unimolecular decay channels available to the silylene-alcohol complex, H-migration to produce the alkoxysilane product must surmount a significantly higher free energy barrier than reversion to the free reactants, in agreement with earlier theoretical studies of the reactions of SiH<sub>2</sub> with water and alcohols.<sup>11,15,18</sup>

The reactions of MeOH and t-BuOH with sterically protected diarylsilylenes such as dimesitylsilylene exhibit much different kinetic behavior compared to that of the parent diarylsilylene, SiPh<sub>2</sub>. The difference arises because of a substantially lower equilibrium constant for silvlenealcohol complexation in the case of the sterically hindered silvlene compared to those exhibited by the less hindered derivatives, which leads to kinetics consistent with reversible complexation in the first step of the reaction followed by alcohol-catalyzed proton transfer in the second step. As a result, the corresponding silylene-alcohol complexes are involved as steady-state intermediates and cannot be detected in fluid solution. The rates of alcohol-catalyzed proton transfer relative to those for dissociation of the complexes exhibit small deuterium isotope effects, which vary between normal and inverse depending on the alcohol. This suggests that a different mechanism for catalysis may operate in the case of the sterically hindered silvlene, such as a stepwise process involving sequential protonation/ deprotonation or deprotonation/protonation. Interestingly, of the three silvlenes studied in the present work, SiMes<sub>2</sub> exhibits kinetic characteristics that are qualitatively most similar to those reported by Walsh and co-workers for the gasphase reaction of the parent silylene (SiH<sub>2</sub>) with water.<sup>18</sup> The similarity is due to the fact that in both systems dissociation of the intermediate silvlene-ROH complex back to the free reactants is competitive with the catalytic proton-transfer process that transforms it to the final product.

Further mechanistic studies of the reactions of transient silylenes and their germanium homologues are in progress.

#### **Experimental Section**

1,1,3,3-Tetramethyl-2,2-diphenyl-1,2,3-trisilacyclohexane (1),<sup>29</sup> dodeccamethylcyclohexasilane (2),<sup>27</sup> and 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane ( $\mathbf{3}$ )<sup>46</sup> were prepared and purified by the reported methods and exhibited spectral and analytical data similar to those published previously. Hexanes (EMD OmniSolv) was dried by passage through activated alumina under nitrogen using a Solv-Tek solvent purification system (Solv-Tek, Inc.). Methanol and *tert*-butanol (anhydrous), methanol-Od (99 atom % D), and *tert*-butanol-Od (99 atom % D) were used as received from Sigma-Aldrich Chemical Co. Tetrahydrofuran (Caledon Reagent) was refluxed for several days over sodium metal and distilled.

Laser flash photolysis experiments employed the pulses from a Lambda Physik Compex 120 excimer laser filled with  $F_2/K_T/$  Ne mixtures (248 nm; *ca*. 20 ns; 90–120 mJ/pulse) and a Luzchem Research mLFP-111 laser flash photolysis system, modified as described previously.<sup>47</sup> Solutions of **1–3** in anhydrous hexanes were prepared at concentrations (0.06–0.5 mM)<sup>29</sup> such that the absorbance at the excitation wavelength (248 nm) was ca. 0.7 and were flowed (ca. 3 mL/min) through a 7 × 7 mm Suprasil

flow cell from a calibrated 250 mL reservoir, fitted with a glass frit to allow bubbling of argon gas through the solution for at least 30 min prior to and then throughout the duration of each experiment, using a Masterflex 77390 peristaltic pump fitted with Teflon tubing (Cole-Parmer Instrument Co.). The sample cell and transfer lines were dried before use in a vacuum oven at 65-85 °C, while the reservoir was flame-dried and allowed to cool under an argon atmosphere. Reagents were added directly to the reservoir by microliter syringe as aliquots of standard solutions. Transient decay rate constants were calculated by nonlinear least-squares analysis of the absorbance-time profiles using the Prism 4.0 or 5.0 software packages (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 rateconcentration data (8-15 points). Errors in absolute second-order rate constants are quoted as twice the standard error obtained from the least-squares analyses or as the standard deviation of 2-3 replicate determinations.

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**Supporting Information Available:** Plots of  $k_{decay}$  vs [ROL] and transient absorption spectra from laser photolysis of **3** in hexanes containing MeOH, *t*-BuOH, and THF. This material is available free of charge via the Internet at http://pubs.acs.org.

<sup>(46)</sup> Tan, R. P.; Gillette, G. R.; Yokelson, H. B.; West, R. Inorg. Synth. 1992, 29, 19.

<sup>(47)</sup> Leigh, W. J.; Harrington, C. R.; Vargas-Baca, I. J. Am. Chem. Soc. 2004, 126, 16105.