

ulations remain constant at 0.264 for the smaller basis and at 0.280 for the larger basis. A detailed analysis of individual elements of the Mulliken overlap population matrix indicates that π -interactions between Ta and Si are insignificant. Si d functions primarily affect σ Ta-Si bonding. Most of the non-Ta contributions in 1's LUMO and 2's HOASO belong to Cl p functions that interact in a π -antibonding sense with Ta's d_{xy} functions.

An important portion of the present analysis concerns Mulliken charges, which can provide a rough summary of the electronic distribution. In all calculations, the silyl group, the phosphine, and the Cp ring have charges that are close to zero. Only the chlorine ligands are unambiguously anionic, with charges of about -0.4 for 1 and 2. Increasing the d electron count will reduce Coulomb attractions between Ta and the Cl's.

Upon changing from d^0 to d^1 , a combination of electrostatic repulsions and Ta-Cl antibonding character in 2's HOASO causes the elongation of the average Ta-Cl separation from 2.343 Å in A to 2.405 Å in B. As the Ta is now less crowded in the latter structure, it is possible for Si to approach Ta more closely. (For the same reasons, the observed Ta-Cp(centroid) distance is 0.03 Å less in B). The expense of these calculations prevents a full optimization of the Ta-Si distance as a function of Ta-Cl distance or other geometric parameters. It is nonetheless possible to state how occupation of the Ta d_{xy} -like MO affects the Ta-ligand separations. Antibonding Ta-Cl character causes the Ta-Cl separation to increase, allowing the Ta-Si distance to decrease. Mulliken charges on the ligands also disclose the electrostatic origin of 2's longer Ta-Cl separation and the consequent decrease in the Ta-Si distance.

Registry No. (η^5 -Cp)TaCl₃(SiH₃), 113748-18-8; (η -Cp)-TaCl₂(PH₃)(SiH₃), 113748-19-9.

Dimethylsilylene: Spectroscopy, Reactivity, and Complexation in Fluid Solutions¹

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Summary: Upon 266-nm laser flash photolysis, cyclohexane solutions of dodecamethylcyclohexasilane give rise to a transient species ($\lambda_{\text{max}} = 465$ nm) that is best assigned as dimethylsilylene. This species exhibits unusually high reactivity toward alcohols and reagents con-

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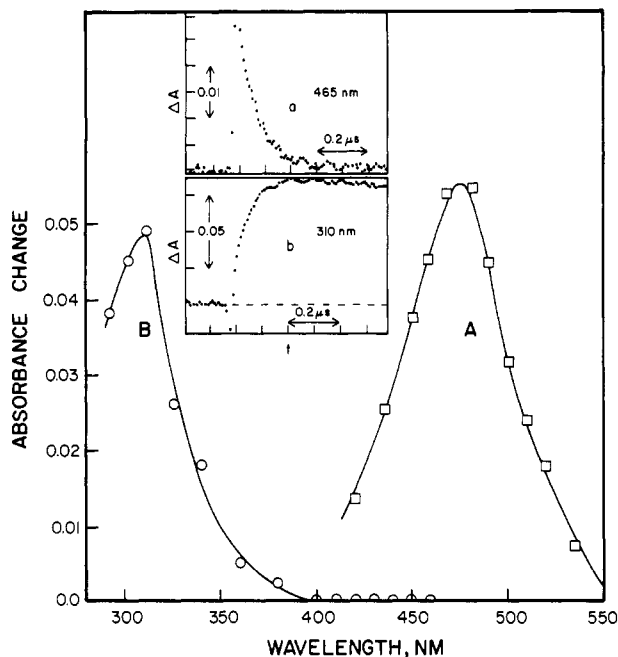


Figure 1. Transient absorption spectra following 266-nm laser flash photolysis of dodecamethylcyclohexasilane solution in cyclohexane: A, in the absence of THF and at 0.1 μ s following the laser flash, and B, in the presence of 0.8 mM THF and at 1.3 μ s following laser flash. Note that the two spectra were taken under different conditions of laser intensity and ground-state absorbance. Insets: kinetic traces showing (a) the enhanced decay of the 465-nm species in the presence of 0.8 mM THF and (b) the concomitant formation of transient absorption at 310 nm.

taining Si-H, C=C, and C \equiv C bonds (with rate constants in the limit of diffusion control) and readily forms complexes with lone-pair containing molecules (ethers, triethylamine, and acetonitrile), the latter showing considerably reduced reactivity relative to the "free" silylene.

Currently, considerable interest is being shown in divalent silicon intermediates, i.e., second-row analogues of carbenes.³ In particular, dimethylsilylene (1) has been at the center of controversy for a number of years.⁴⁻⁶ This species is claimed to be formed as a bright yellow product ($\lambda_{\text{max}} = 430$ -470 nm) of photolysis of various precursors (e.g., dodecamethylcyclohexasilane, 2) in low-temperature inert gas or hydrocarbon matrices⁴ as well as in the course of flash pyrolysis of suitable substrates followed by isolation in low-temperature N₂ or Ar matrices.⁵ In contrast, laser flash photolysis (308-nm) experiments with 2 in fluid hydrocarbon solutions at room temperature have been negative regarding the observation of the 450-nm species;

(3) (a) Gaspar, P. P.; Holten, D.; Konieczny, S.; Corey, J. Y. *Acc. Chem. Res.*, in press. (b) Gaspar, P. P.; Boo, B.-H.; Chari, S.; Ghosh, A. K.; Holten, D.; Kirmaier, C.; Konieczny, S. *Chem. Phys. Lett.* 1984, 105, 153-157. (c) Gaspar, P. P. In *Reactive Intermediates*; Jones, M.; Moss, R. A., Eds.; Wiley-Interscience: New York, 1981; Vol. 2, pp 335-385.

(4) (a) Vancik, H.; Raabe, G.; Michalczuk, M. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* 1985, 107, 4097-4098. (b) Drahnak, T. J.; Michl, J.; West, R. *Ibid.* 1981, 103, 1845-1846; 1979, 101, 5427-5428. (c) Arrington, C. A.; West, R.; Michl, J. *Ibid.* 1983, 105, 6176-6177. (d) Arrington, C. A.; Klingensmith, K. A.; West, M.; Michl, J. *Ibid.* 1984, 106, 525-530.

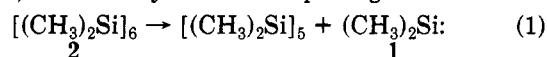
(5) (a) Maier, G.; Mihm, G.; Reisenauer, H. P.; Littmann, D. *Chem. Ber.* 1984, 117, 2369-2381. (b) Reisenauer, H. P.; Mihm, G.; Maier, G. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 854-855.

Table I. Reactivity of Uncomplexed and Complexed Dimethylsilylene in Cyclohexane at 296 K

complexing agent	λ_{\max} , nm	τ , μs	reagent	$10^9 k$, ^a $\text{M}^{-1} \text{s}^{-1}$
none	465	0.4	oxygen	2.2
			ethanol	3.9
			2-butanol	10.1
			2-methyl-2-propanol	10.2
			tri- <i>n</i> -propylsilane	2.9
			1-hexene	7.3
			trimethylvinylsilane	5.9
			trimethylacetylenylsilane	8.0
			THF	12.7
			THF	310
tri- <i>n</i> -propylsilane	~0.001			
2-methyl-2-propanol	0.044			
1-hexene	0.0024			
trimethylvinylsilane	0.0026			
diethyl ether	305	4.0	ethanol	0.98
triethylamine	~270	29	ethanol	0.033
acetonitrile	340	2.3	ethanol	0.11

^aMaximum deviation, $\pm 20\%$ (from 2σ of least-squares linear fits).

instead, a transient characterized by λ_{\max} at 350 nm and lifetime (τ) of 8 μs in 3-methylpentane and cyclopentane has been noted.⁶ We have carried out a 266- and 248-nm laser flash photolysis study of **2** in cyclohexane solution at 296 K; this clearly shows the photogeneration of a



transient intermediate with absorption spectrum, kinetic behavior, and reactivity that fit very well the description of dimethylsilylene, **1**. Interestingly, this species reacts with suitable organic Lewis bases (e.g., ethers and tertiary amines) forming complexes characterized by blue-shifted absorption spectra and significantly subdued reactivity (relative to "naked" dimethylsilylene).

The 266-nm laser pulse excitation⁷ of deoxygenated cyclohexane solutions of **2** leads to the formation of a transient species characterized by a broad absorption spectrum ($\lambda_{\max} = 465$ nm, see Figure 1A) and a typical lifetime⁸ of 400 ns. A similar transient is also produced upon 248-nm laser flash photolysis. Oxygen sensitive, the decay of the 465-nm species is enhanced in the presence of millimolar concentrations of reagents that are recognized to react with silylene intermediates (namely, alcohols and compounds containing Si-H and C-C multiple bonds). The plots of pseudo-first-order rate constants for decay against reagent concentrations were linear in each case. The bimolecular rate constants (k) obtained from the slopes of the plots are given in Table I. Steady-state

competition experiments in which **2** was photolyzed⁹ in the presence of varying concentrations of ethanol and tri-*n*-propylsilane (in cyclohexane) and the corresponding insertion products were analyzed⁹ gave a value of 2.1 for the ratio of the reactivity of the two reagents. This value is close to the observed ratio of 1.4 for the absolute rate constants for the two reagents (Table I).

The 465-nm species derived from **2** under 266-nm laser flash photolysis is readily quenched by reagents containing lone pairs of electrons, namely, tetrahydrofuran (THF), diethyl ether, triethylamine, and acetonitrile. In each case, as a result of the interaction, the long-wavelength absorption spectrum is replaced by one that is considerably blue-shifted. This is illustrated by the transient absorption spectrum (Figure 1B, $\lambda_{\max} = 310$ nm) in the presence of THF and by concurrent decay/formation kinetics of absorption (see insets of Figure 1). Upon complexation, **1** becomes longer lived than when it is "free". At the same time, its reactivity becomes considerably reduced as shown by the bimolecular rate constants (k) measured for the complexes and typical reagents (Table I). Specifically, the relative decrease in k upon complexation with THF is higher by several orders of magnitude for tri-*n*-propylsilane than for ethanol; this is supported by the results of competition experiments under steady-state irradiation in the presence of THF.

On the basis of our results, the following observations can be made. First, the 465-nm phototransient in fluid solutions, best described as "free" dimethylsilylene, is spectrally similar to the 430–470 nm photoproduct observed by Michl and co-workers⁴ in low-temperature matrices. Theoretical calculations^{10,11} predict singlet–singlet absorption maxima in a similar spectral region. Second, "free" dimethylsilylene is unusually reactive. The bimolecular rate constants (Table I) are in the limit of diffusion control and are significantly higher than those obtained by Gaspar and co-workers^{3a} for related systems. On the other hand, the k value for tri-*n*-propylsilane (Table I) agrees well with that measured by Baggott et al.¹² for trimethylsilane in the gas phase at 295 K. Interestingly, the alcohols behave as nucleophiles interacting with the vacant p orbital of the silylene, as evident from the increase in k on going from ethanol to 2-butanol or *tert*-butyl alcohol. Third, lone-pair donors form well-defined complexes with dimethylsilylene. The reduced reactivity of these complexes underlines the importance of the vacant p orbital of "free" silylene in rendering insertion reactions facile.

Registry No. **1**, 6376-86-9; **1**-THF, 113686-61-6; **1**-diethyl ether, 113686-62-7; **1**-triethylamine, 113686-63-8; **1**-acetonitrile, 113686-64-9; **2**, 4098-30-0; THF, 109-99-9; $[(\text{CH}_3)_2\text{Si}]_5$, 13452-92-1; oxygen, 7782-44-7; ethanol, 64-17-5; 2-butanol, 78-92-2; 2-methyl-2-propanol, 75-65-0; tri-*n*-propylsilane, 998-29-8; 1-hexene, 592-41-6; trimethylvinylsilane, 754-05-2; trimethylacetylenylsilane, 1066-54-2.

(9) Static photolysis was carried out in quartz tubes in a Rayonet photochemical assembly (Model RPR-100) equipped with 16 RPR-3000 Å lamps. The products were analyzed in a H.P. 5890 gas chromatograph attached to a H.P. 5970 mass spectrometer.

(10) Apeloig, Y.; Karni, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1048–1049.

(11) Grev, R. S.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1986**, *108*, 5804–5808.

(12) Baggott, J. E.; Blitz, M. A.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. *Chem. Phys. Lett.* **1987**, *135*, 39–45.

(6) (a) Nazran, A. S.; Hawari, J. A.; Griller, D.; Alnaimi, I. S.; Weber, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 7267–7268. (b) Hawari, J. A.; Griller, D. *Organometallics* **1984**, *3*, 1123–1124. (c) Nazran, A. S.; Hawari, J. A.; Griller, D.; Alnaimi, I. S.; Weber, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5041.

(7) (a) The fourth harmonic (266 nm, 6 ns, 10–20 mJ) of the output from a Quanta-Ray Nd-YAG laser source and laser pulses at 248 nm (20 ns, ≤ 50 mJ) from a Lambda-Physik EMG 101 MSC system were used for laser photolysis of solutions either in 1 cm \times 1 cm quartz cells in right-angle geometry or in 0.2 cm \times 1 cm quartz cells in front-face configuration. For details, see: Nagarajan, V.; Fessenden, R. W. *J. Phys. Chem.* **1985**, *89*, 2330–2335. (b) Special care was exercised to purify **2**, namely, by crystallization (3 \times) from methanol and sublimation (3 \times) at low temperature (60–70 $^\circ\text{C}$) under vacuum. Freshly prepared solutions were used in all experiments.

(8) Shorter lifetimes (first order) as well as longer ones (mixed with second order) were also noted in some of the measurements. We believe that the lack of reproducibility of τ is due to adventitious impurities.