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Kinetic Study of Dimesitylsilylene by Laser Flash Photolysis†

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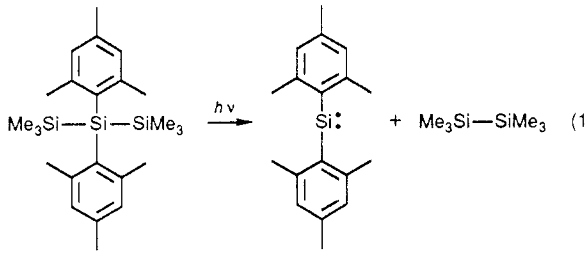
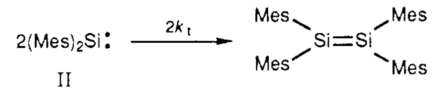
Summary: The rate constants for the self-reaction of dimesitylsilylene as well as for representative quenchers have been measured with laser flash photolysis techniques. Decay of the silylene, generated from 266-nm photolysis of the corresponding trisilane in cyclohexane, was monitored at 580 nm. Among the various quenchers used, the rate of reactivity with the silylene is ketone > silyl hydride > oxygen > diene > alkene > alkoxysilane. Kinetic and product studies indicate no significant deuterium isotope effect for the insertion into the Si–H(D) bond of triethylsilane.

Dimerization of silylenes[1] to transient disilenes has been invoked to account for mechanisms of product formation in reactions spanning temperatures >1000 °C and culminating in the first successful synthesis of a stable disilene.[2] It was suggested that dimesitylsilylene (II), produced by the photolysis of 2,2-dimesitylhexamethyltrisilane (I), was the intermediate responsible for the dimerization leading to tetramesityldisilene (III) (reactions 1 and 2).



(1)

I II



$$2(\mathrm{Mes})_2\mathrm{Si}\!: \xrightarrow{2k_t} (\mathrm{Mes})_2\mathrm{Si}{=}\mathrm{Si}(\mathrm{Mes})_2 \quad (2)$$

II III

Dimesitylsilylene has been characterized in matrices at low temperature, where it shows an absorption maximum at 580 nm. While several of its reactions have been characterized with use of the trisilane and other precursors, no time-resolved kinetic studies have been reported. Herein we report a kinetic study of the self-reaction of II leading to the disilene III, as well as hallmark reactions with representative quenchers including triethylsilane, oxygen, ketones, cyclohexene, and 2,3-dimethylbutadiene.

Laser flash photolysis of I (10^{-4} M in dry, deoxygenated, and acetone-free[3] cyclohexane) at 298 K with 266-nm pulses (~12 ns, ≤40 mJ/pulse) from a Nd-YAG laser[4] produced a transient with an absorption maximum at 580 nm (see Figure 1) that has been well characterized as dimesitylsilylene (II)[5] and that within the time resolution of the instrument appeared to be formed "instantaneously". In the absence of added scavengers, II decayed with second-order kinetics. This decay was accompanied by the growth of an easily detectable signal at 420 nm, which can be readily identified as III on the basis of its known absorption spectrum. The inserts in Figure 1 show traces monitored at 580 and 420 nm, and the main part of the figure shows the spectrum reported for II. Kinetic analysis of the data leads to the ratio $2k_t/\epsilon_\lambda$, where ϵ_λ is the extinction coefficient for II at the monitoring wavelength. Thus, at 580 nm we obtained the value 9×10^6 cm^{-1} s^{-1}, which, combined with the extinction coefficient[6] of 1.96×10^3 M^{-1} cm^{-1}, led to a value for $2k_t$ of 1.7×10^{10} M^{-1} s^{-1}. Therefore, the rate constant for combination of the two divalent silicon atoms was essentially the same as the encounter control limit in cyclohexane, and thus, the four *o*-methyl groups do not significantly impede dimerization. Naturally, in the case of singlet silylenes there are no spin restrictions to self-reactions. In contrast, (2,4,6-triisopropylphenyl)(1,2,3-tri-*tert*-butylcyclopropenyl)silylene has been recently reported to be stable at temperatures up to 200 K.[7]

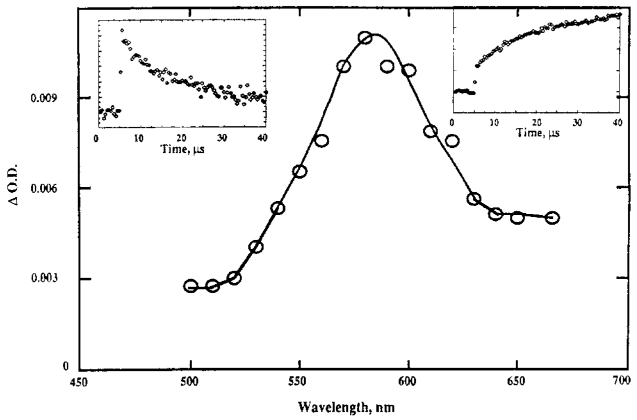


Figure 1. Transient spectrum for dimesitylsilylene in cyclohexane. Inserts show the decay of the silylene at 580 nm (left) and growth of the dimer at 420 nm (right) following the 266-nm excitation of I in cyclohexane.

We have also determined rate constants for reactions of II with various substrates. While the silylene decays by second-order kinetics, in the presence of scavengers the decay follows pseudo-first-order kinetics. In principle the

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§ National Research Council of Canada.

[1] For earlier references to silylene dimerization to transient disilenes, see: (a) Nakadaira, Y.; Kobayashi, T.; Otsuka, T.; Sakurai, H. *J. Am. Chem. Soc.* **1979**, *101*, 486. (b) Margrave, J. L.; Perry, K. L. *Inorg. Chem.* **1977**, *16*, 1820. (c) Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 868.

[2] West, R.; Fink, M. J.; Michl, J. *Science* (*Washington, D.C.*) **1981**, *214*, 1343.

[3] When the cell glassware was cleaned with acetone and dried overnight, the 580-nm signal attributed to the silylene was not observed. Hence, all glassware was washed with hexane prior to drying. Quenching agents were dried and distilled immediately prior to each experiment.

[4] The laser system uses a Lumonics Hyperyag-750 Nd-YAG laser for excitation. The monitoring system and detector are similar to those employed in a laser system already described in the literature (Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747). Briefly, a pulsed xenon lamp provides the analyzing beam, while a CVI Digikrom 240 monochromator, an RCA-4840 photomultiplier, and a Tektronix 7912-AD digitizer were used to capture the transient signals. A PDP-11/55 computer controlled the experiment and provided suitable storage, processing, and hardcopy facilities.

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[6] Values of ϵ_{580} were measured at 77 K in a 3-MP matrix from complete photolysis of I at several concentrations.

[7] Puranik, D. P.; Fink, M. *J. Am. Chem. Soc.* **1989**, *111*, 5951.

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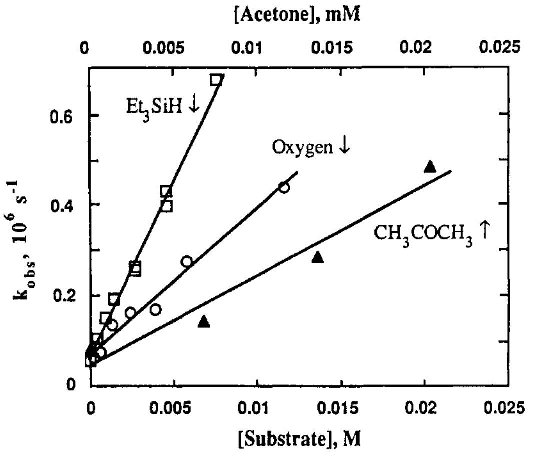


Figure 2. Silylene quenching plots for triethylsilane (□), oxygen (○), and acetone (▲).

Table I. Rate Constants for the Reactions of Various Substrates with Dimesitylsilylene in Cyclohexane

substrate	k_r/M^{-1} s^{-1}
triethylsilane	$(7.9 \pm 0.4) \times 10^7$
triethylsilane-*Si-d*	$(7.1 \pm 0.7) \times 10^7$
acetone	$(2.5 \pm 0.5) \times 10^{10}$
1,1,3,3-tetramethyl-2-indanone	$(1.6 \pm 0.2) \times 10^9$
cyclohexene	$(2.8 \pm 0.3) \times 10^6$
2,3-dimethylbutadiene	$(8.8 \pm 0.7) \times 10^6$
methoxytrimethylsilane	$<1 \times 10^6$
oxygen	$(3.2 \pm 0.4) \times 10^7$

decay will be given by eq 3a. In practice the first term

$$\frac{d[Mes_2Si]}{dt} = 2k_t[Mes_2Si]^2 + k_r[Mes_2Si][substrate] \quad (3a)$$

is very small compared with the substrate-mediated decay and the equation reduces to eq 3b such that the observable

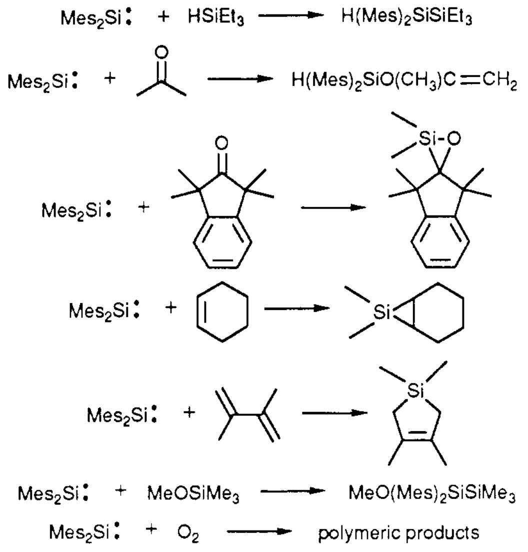
$$k_{obs} \approx k_r[substrate] \quad (3b)$$

rate constant is related to the scavenging rate constant (k_r). This treatment is illustrated for three examples in Figure 2, and the data are summarized in Table I. A summary of these reactions and their products is given in Scheme I.

Several aspects of the data in Table I are worth comment. The rate constant for insertion in the Si–H bond indicates that the reaction is quite rapid; for comparison, a rate constant of 2.9×10^9 M^{-1} s^{-1} for the reaction of Me$_2$Si: with tri-*n*-propylsilane has been recently reported.[8] Similarly, Shizuka reported a rate constant of 3.6×10^9 M^{-1} s^{-1} for reaction of Me$_2$Si: with triethylsilane.[9] These numbers contrast with a value of 1.54×10^3 M^{-1} s^{-1} recently reported for the reaction of diphenylsilylene and ethyldimethylsilane.[10] The reasons for this discrepancy are not obvious to us.

Surprisingly, the 580-nm signal from Mes$_2$Si: was not quenched within the time frame of this experiment by methoxytrimethylsilane, a reagent frequently employed as a diagnostic for the presence of silylenes in mechanistic studies.[11,12] In our product studies, however, the product from insertion into the Si–O bond, methoxydimesityl-2,2,2-trimethyldisilane, was formed cleanly in high yield. The reaction with oxygen[13] is fast, 3.2×10^7 M^{-1} s^{-1}, but in fact is substantially slower than similar reactions in the case of carbenes; for example, for the triplet dimesitylcarbene, the rate constant[14] was 3.4×10^8 M^{-1} s^{-1} and it is faster for all other triplet carbenes examined. The slower rates in the case of silicon may reflect spin restrictions, similar to those for *singlet* carbenes, which do not react with oxygen in the short time scales examined by laser flash photolysis.[15] Just as in the case of carbenes, the rates for the dimesityl derivative are smaller than for the less hindered silylenes.

Scheme I. Expected Products from 254-nm Photolysis of Trisilane in Cyclohexane Solutions Containing a Trapping Agent[a,26]



[a] See text for details.

Formation of strong silicon–oxygen bonds[16] contributes a thermodynamic driving force to reactions between electron-deficient silicon and the multiply bonded oxygen of ketones. Addition of II to the sterically hindered but polar carbonyl bond of 1,1,3,3-tetramethyl-2-indanone, known to afford an isolable oxasilirane,[17] was rapid; $k_r = 1.6 \times 10^9$ M^{-1} s^{-1}. In cyclohexane solvent at room temperature, however, no evidence was found for the silacarbonyl ylide previously reported at 610 nm in a low-temperature 3-methylpentane matrix. Given that the decay lifetime of for Mes$_2$Si: was 1.6 μs at the highest indanone concentration employed (0.27 mM),[18] this implies that the ylide lifetime must be <2 μs at room temperature, assuming that its spectral properties do not change substantially. The scavenging by acetone[19] was remarkably fast, 2.5×10^{10} M^{-1} s^{-1}.

The measured kinetic isotope effect for insertion in triethylsilane was only 1.12, which approaches our experimental uncertainty and suggests a nonlinear transition

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(18) Higher concentrations of indanone could not be employed because this ketone competes with the trisilane for 266-nm laser photons.

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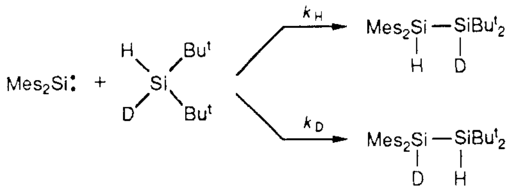
state for insertion.[20] Included in this mechanistic picture is possible complexation between the divalent silicon and the tetravalent silicon atom of the hydride prior to insertion.[21] This possibility has been investigated by NMR analysis of the products from insertion into the Si–H(D) bonds of di-*tert*-butyldeuteriosilane. The product isotope effect, 1.25, obtained from the H/D ratio on the mesityl-labeled silicon atom is similar to that reported for insertion of diphenylsilylene into the Si–H and Si–D bonds of triethylsilane.[22]



Cycloaddition of divalent silicon to organic π-electrons has provided an efficient synthesis of a variety of substituted siliranes. The rate constant for the dimesitylsilylene reaction with cyclohexene,[23] $k_r = 2.8 \times 10^6$ M^{-1} s^{-1}, is less, as might be anticipated from product studies, than that observed for addition to the conjugated 2,3-dimethylbutadiene, 8.8×10^6 M^{-1} s^{-1}. A more revealing comparison is between the rates of insertion into a silicon–hydrogen σ bond of a trialkylsilane and of addition to the π system of a diene. Triethylsilane is 9 times more reactive than the 2,3-disubstituted diene, in quite reasonable agreement with a factor of 6 reported by Walsh and co-workers[24,25] for kinetic studies of gas-phase reactions of dimethylsilylene.

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Registry No. II, 79184-71-7; III, 80785-72-4; HSiEt$_3$, 617-86-7; DSiEt$_3$, 1631-33-0; CH$_3$C(O)CH$_3$, 67-64-1; CH$_2$═C(CH$_3$)C(CH$_3$)═CH$_2$, 513-81-5; MeOSiMe$_3$, 1825-61-2; O$_2$, 7782-44-7; H(Mes)$_2$SiSiEt$_3$, 88957-30-6; (Mes)$_2$Si(H)Si(H)(*t*-Bu)$_2$, 100327-82-0; Mes$_2$Si(CH[CH$_2$]$_4$CH), 125610-64-2; Mes$_2$Si(CH$_2$CCH$_3$═CCH$_3$CH$_2$), 109853-00-1; Mes$_2$Si(H)OC(Me)═CH$_2$, 75529-59-8; Mes$_2$Si(Me$_3$Si)OMe, 125610-65-3; 1,1,3,3-tetramethyl-2-indanone, 5689-12-3; cyclohexene, 110-83-8.

Supplementary Material Available: A description of the laser system and previously unreported NMR data (6 pages). Ordering information is given on any current masthead page.

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[21] Walsh, R. *Organometallics* **1989**, *8*, 1973.

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[23] The measurement of the rate constant with cyclohexene proved difficult. An initial value of 1.4×10^8 M^{-1} s^{-1} was obtained from a sample dried over sodium and freshly distilled. Further purification, by passing of the cyclohexene through an alumina column and treating with molecular sieves, led to the value in Table I. Naturally, given the large difference, one may wonder if the second treatment provided sufficient purification or if the true rate constant is even lower. In this sense the error limits quoted for cyclohexene may be open to question.

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[26] Reaction products were characterized by NMR spectroscopy (^{1}H, ^{13}C, and ^{29}Si), but the assignments must be regarded as tentative until full characterization.

Synthesis and Characterization of the First Example of Insertion by Platinum(II) into a Tetrasubstituted Cyclopropane

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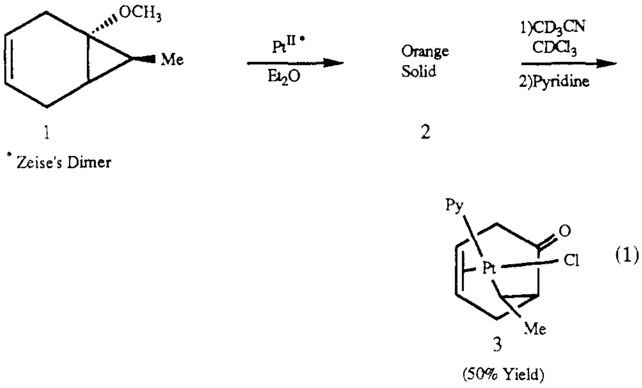
Summary: Methodology for the preparation and characterization of insertion of Pt^{II} into a tetrasubstituted cyclopropane is established. In this case, the insertion of Pt^{II} was accomplished with use of 7-methyl-1-methoxybicyclo[4.1.0]hept-3-ene. A unique rearrangement involving a platinacyclobutane as an intermediate is suggested.

Metallacyclobutanes may be involved as intermediates in various processes such as isomerization of alkenes, alkene metathesis, polymerization, and also strained-ring rearrangements.[1-5] Platinacyclobutanes were the first such compounds to be prepared and studied.[6] Formation of platinacyclobutanes is often accomplished by the insertion (oxidative addition) of platinum into a cyclopropane. To date, mono-, di-, and trisubstituted cyclopropanes[1,7] have shown insertion of platinum(II) while tetrasubstituted examples have failed to react.[8]

Earlier work has shown that the bicyclo[4.1.0] system reacts with Pt(II) to form platinacyclobutanes.[9] It has also been observed that electron-releasing groups facilitate the reaction.[10,11] Reaction of a cyclopropane[12] encompassing both of these principles resulted in the first example of insertion of Pt(II) into a tetrasubstituted cyclopropane (eq 1).



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[12] **1** was synthesized by reaction of 1-methoxy-1,4-cyclohexadiene (Aldrich) with 1,1-diiodoethane and Zn–Cu couple (60%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 5.4 (m, 2 H), 3.3 (s, 3 H), 2.6–2.1 (m, 4 H), 1.25 (m, 1 H), 1.2 (d, 3 H), 0.8 (dq, 1 H), J_{HH} = 6.0 Hz). ^{13}C NMR (125 MHz, CDCl$_3$): δ 123.5 (d), 124.1 (d), 63.3 (s), 54.2 (q), 27.3 (t), 25.5 (t), 23.9 (q), 19.8 (d), 11.8 (d).

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