McGlynn and Smith (S. P. McGlynn and J. K. Smith, *J. Mol. Spectrosc.*, **6**, 164 (1961)) have suggested that the lowest absorption between 20 500 and 30 000 cm^{-1} results from a singlet-triplet transition. They also noted that the excited uranyl complex is weakly paramagnetic.

(7) For example, see K. A. McLauchlan, R. C. Sealy, and J. M. Wittman, *Mol. Phys.*, **36**, 1397 (1978), and references therein.

(8) We thank a referee who reminded us that the large spin orbit interaction is probably responsible for the fast relaxation.

J. W. M. deBoer, K. S. Chen
Y. C. Chan Chung, J. K. S. Wan*
Department of Chemistry, Queen's University
Kingston, Ontario, Canada K7L 3N6

Received April 20, 1979

Dimethylsilylene, $(CH_3)_2Si$

Sir:

Dimethylsilylene, $(CH_3)_2Si$, has been frequently postulated as an organosilicon reaction intermediate[1] but has never been observed. We now report the preparation and spectroscopic characterization of this elusive species in hydrocarbon glasses and inert gas matrices at low temperatures. It is noteworthy that dimethylsilylene is stable indefinitely in hydrocarbon glasses at 77 K, permitting its use as a preformed reagent.

Irradiation of solutions of dodecamethylcyclohexasilane (**1**) is well known to produce decamethylcyclopentasilane (**2**). The $(CH_3)_2Si$ residue appears as a polymer, $[(CH_3)_2Si]_n$, or can be transferred to suitable trapping agents.[2] We find that irradiation of **1** in rigid hydrocarbon glasses (3-methylpentane (3-MP), methylcyclohexane, or decalin) at 77 K or in an argon matrix at 10 K produces **2**, characterized by comparison of its UV and IR spectra with those of an authentic sample, and a new bright yellow species (**3**).

$$\underset{\mathbf{1}}{[(CH_3)_2Si]_6} \xrightarrow[254\ nm]{h\nu} \underset{\mathbf{2}}{[(CH_3)_2Si]_5} + \underset{\mathbf{3}}{(CH_3)_2Si}$$

In 3-methylpentane glass **3** shows a broad electronic absorption band at 453 nm ($\epsilon \approx 1500$) and a weak fluorescence peaking at 655 nm, depicted in Figure 1. In argon matrix, the absorption peak is shifted to 445 nm. The fluorescence excitation spectrum follows the shape of the absorption band. A characteristic infrared absorption is found for **3** at 1220 cm^{-1}, in a region free of absorption by **1** and **2**. The visible and infrared absorptions both disappear when the glass or matrix is warmed to its softening point.

The spectroscopic data are compatible with assignment of **3** as $(CH_3)_2Si$. The electronic absorption band for **3** lies near those for SiH_2 (480–650 nm)[3a] and SiHCl (500 nm),[3b] and the infrared band may be assigned to a methyl symmetrical deformation vibration.[4a]

Convincing evidence for the identification of **3** as $(CH_3)_2Si$ is provided by the results of chemical trapping experiments. Trapping agents used were triethylsilane (**4**), bis(trimethylsilyl)ethyne (**5**), and 1-hexene (**6**). Typically, 0.3 mL of trapping agent and 6 mg of **1** were dissolved in 1.7 mL of 3-MP, cooled to 77 K, and irradiated for ~10 min at 254 nm, producing the deep yellow color of **3**. When the mixture was warmed to melt the matrix, the color disappeared. The procedure was repeated several times until irradiation no longer produced a yellow color. The expected[2a] product from **4**, 1,1,1-triethyl-2,2-dimethyldisilane (**7**), was isolated by preparative GC and identified by its ^1H NMR and mass spectra. The initial product from the reaction of **5** with **3** was treated with methanol, yielding 1,2-bis(trimethylsilyl)vinyldimethylmethoxysilane,[5] identified by GC–mass spectrometry. The initial product from the reaction of **6** with **3** was treated with ethanol, yielding hexyldimethylethoxysilane,[6] again identified by GC–MS. These are the products expected[7] from alcoholysis of the primary adducts of dimethylsilylene to the multiple bonds. Yields in all three reactions were ~60% (by GC).

In the absence of a trapping agent, $[(CH_3)_2Si]_n$ polymer was formed when the hydrocarbon matrix containing **3** was melted. The same result was obtained when dimethyldimethoxysilane was present as a potential trapping agent. The fact that little or no 1,2-dimethoxytetramethyldisilane was produced is of interest, because dimethyldimethoxysilane is believed[2a] to trap efficiently dimethylsilylene photogenerated in lower concentrations in fluid solutions at higher temperatures.

Significantly, when the irradiation of **1** is performed in 2-methyltetrahydrofuran glass at 77 K, conversion into **2** is observed in the UV spectrum, but the absorption band of **3** does not appear and the glass remains colorless. We believe that **3** is still generated but reacts with the solvent. In the presence of the trapping agent, **4**, we detect only a few percent of the trapping adduct **7**, in contrast to the 60% formed in a hydrocarbon solvent under otherwise similar conditions. This result confirms our assignment of the yellow species as the one which is being trapped in hydrocarbon solvents, i.e., as **3**.

The rigid solutions of **3** have no ESR signal, indicating that **3** is a ground-state singlet, similar to known inorganic silylenes.[3,8] The huge Stokes shift between the maxima for the absorption and fluorescence bands (Figure 1) suggests a large change of geometry upon excitation, presumably a large increase of the C–Si–C angle. This difference is analogous to that established for inorganic silylenes.[3]

Irradiation of the rigid solutions of **3** with visible light slowly bleached the yellow color and caused the disappearance of the visible and IR absorption bands attributed to **3**. A new electronic absorption appeared at 260 nm, and several new IR bands emerged. One of these, at 2186 cm^{-1}, is attributable to a Si–H stretching mode.[4b] Its appearance and position, which is high for a simple alkylsilane, are particularly significant and suggest that the photochemical process is a 1,2-hydrogen shift leading to 2-silapropene. This interesting transformation is

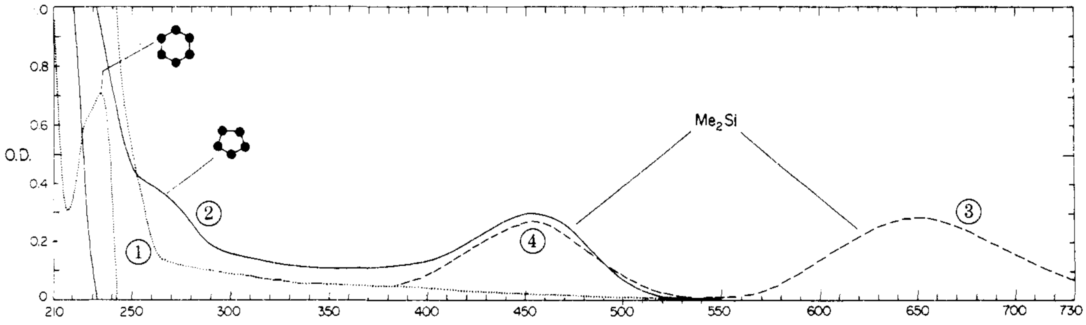


Figure 1. Absorption spectrum of **1** (1). Absorption (2), fluorescence (3), and excitation (4) spectra of a mixture of **2** and **3** obtained from **1** by UV irradiation (2 min), 77 K, 3-MP. Attribution of structural formulas to spectral bands is shown (a dark dot stands for the $(CH_3)_2Si$ unit).

0002-7863/79/1501-5427$01.00/0

being further investigated, as is the extension of the present work to other organic silylenes.

Acknowledgment. We thank Dr. R. T. Conlin for helpful discussions. Support of this work by Grants CHE-76-02446 from the National Science Foundation and AF-AFOSR-74-2644 from the Air Force Office of Scientific Research is gratefully acknowledged.

References and Notes

(1) For reviews, see: (a) Atwell, W. H.; Weyenberg, D. R. *Intra-Sci. Chem. Rept.* **1973**, *7*, 139–145. (b) Hengge, E. *Top. Curr. Chem.* **1974**, *51*, 58–66. (c) Chernyshev, E. A.; Komalenkova, N. G.; Bashkirova, S. A. *Russian Chem. Rev.* (*Engl. Transl.*) **1976**, *45*, 913–930. (d) Gaspar, P. P. In "Reactive Intermediates", Jones, M., Jr., and Moss, R. A., Eds.; Wiley: New York, 1978; Vol 1, pp 229–277.

(2) (a) Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* **1972**, *42*, 325–332. (b) Kumada, M. *Ibid.* **1975**, *100*, 127–138.

(3) Burger, H.; Eujen, R. *Top. Curr. Chem.* **1974**, *50*, (a) 19, (b) 26–27.

(4) Bellamy, L. J. "The Infra-red Spectra of Complex Molecules", 3rd ed.; Wiley: New York, 1975; (a) p 377, (b) pp 380–381.

(5) Seyferth, D.; Annarelli, D. C.; Vick, S. C. *J. Am. Chem. Soc.* **1976**, *98*, 6382–6384.

(6) Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* **1974**, *81*, C3–C6.

(7) Conlin, R. T.; Gaspar P. P. *J. Am. Chem. Soc.* **1976**, *98*, 3715–3716.

(8) Margrave, J. L.; Wilson, P. W. *Acc. Chem. Res.* **1971**, *4*, 145–151. Kasdan, A.; Herbst, E.; Lineberger, W. C. *J. Chem. Phys.* **1975**, *62*, 541–548.

(9) (a) University of Wisconsin; (b) University of Utah.

Timothy J. Drahnak,[9a] Josef Michl,*[9b] Robert West[9a]
Departments of Chemistry
University of Wisconsin, Madison, Wisconsin 53706
University of Utah, Salt Lake City, Utah 84112
Received February 6, 1979

Kinetics and Mechanism of the Reaction of Palladium(II) Complexes of *o*-Diphenylphosphinothioanisole and *o*-Diphenylphosphinoselenoanisole with the Nucleophiles Thiocyanate and Iodide

Sir:

The conversion of methyl thioether complexes into thiolato metal compounds by the loss of a methyl group has been reported for a range of compounds.[1] The reaction with nonfluorinated ligands is commonly found to occur under high temperature conditions, and in only a few cases has an attempt been made to determine the fate of the alkyl group. The reaction has received attention because of its possible similarity to the demethylation of *S*-adenosylmethionine.[2] Mechanistically there has been a suggestion that an ionic pathway is involved with the reaction resembling the Zeisel ether cleavage.[1f] More recently, however, Shaw has found that the addition of halide ion had minimal effect on the dealkylation of $PtCl_2[PPh_2(o\text{-}MeOC_6H_4)]_2$ to *cis*-$Pt[PPh_2(o\text{-}OC_6H_4)]_2$.[3] There has hitherto been no kinetic investigations published on these demethylation reactions, and, in view of current interest in methylsulfonium and similar complexes,[4] we have decided to investigate more fully one of these reactions.

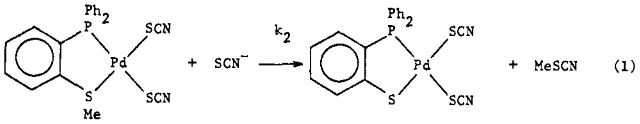
The first aim was to try to effect the reaction under more controlled conditions in order to compare the data obtained with that from the demethylation of *S*-adenosylmethionine and methylsulfonium compounds.[5] Previously the conversion of methyl thioether into thiolato complexes of palladium(II) has been carried out in refluxing DMF. We have now found that the reaction proceeds readily at temperatures above 55 °C in the presence of a nucleophile such as thiocyanate or iodide.[6] We have therefore made a kinetic study of the reaction between $(o\text{-}Ph_2PC_6H_4SMe)Pd(SCN)_2$ and $(o\text{-}Ph_2PC_6H_4SMe)PdI_2$ with their respective nucleophiles SCN^- and I^-.

Table I. Rate Data for the Reaction of $(o\text{-}Ph_2PC_6H_4SMe)$-$Pd(SCN)_2$ (0.020 M) with SCN^- in CD_3CN Solvent

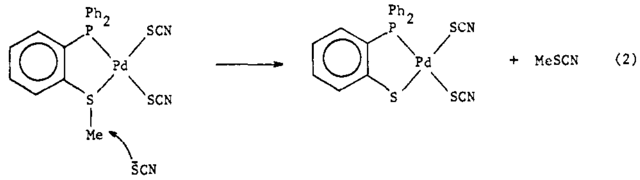
temp, °C	$[NaSCN]_0$, M	k_2(obsd), s^{-1}
75	0.213	3.25×10^{-4}
75	0.420	4.15×10^{-4}
75	0.635	5.79×10^{-4}
65	0.222	1.21×10^{-4}
55	0.222	0.38×10^{-4}

Table II. Rate Data for the Demethylation of $(o\text{-}Ph_2PC_6H_4SeMe)$-$Pd(SCN)_2$ (0.023 M) with SCN^- in $CD_3CN\text{-}CH_2Cl_2$ (3:1) Solvent

temp, °C	$[NaSCN]_0$, M	k_2(obsd), s^{-1}
55	0.225	2.51×10^{-3}
45	0.225	1.05×10^{-3}
35	0.231	0.353×10^{-3}



The reaction between $(o\text{-}Ph_2PC_6H_4SMe)Pd(SCN)_2$ and SCN^- follows the rate law rate = k_2[complex][SCN^-][(eq 1). The rate has been measured by following the decrease in size of the ^1H NMR methyl peak in the complex.[7] The compound MeSCN is formed during the reaction. This was identified by comparison of its ^1H NMR chemical shift and its gas chromatographic retention time against those authentic samples. The kinetics has also been followed by measuring the increase in MeSCN concentration, and the same rate constant found. This isomer MeSCN appears to be the one formed directly in the reaction since initially added MeNCS is recovered unchanged at the end. These data are in agreement with a mechanism involving direct nucleophilic attack by the thiocyanate sulfur at the methyl carbon of the coordinated ligand (eq 2). The data are shown in Table I. It is apparent that a plot of k_2(obsd) against [NaSCN] is not linear. This deviation for ionic reactions in nonaqueous solvents has been observed before and arises because effects such as ion pairing cause the activity of the thiocyanate ion to be less than that obtained simply by using the value for [NaSCN].[8] The degree of dissociation has previously been related to both the dielectric constant and donor number of the particular solvent, and is roughly proportional to both these quantities. From these data it is apparent that there will be considerable ion pairing of NaSCN in this solvent. For the solvent Me_2SO, however, dissociation should be more complete, and this is borne out by the ^{23}Na chemical-shift data for NaSCN in this solvent.[9] At 77.6 ± 0.2 °C the respective rate constants k_2(obsd) in $Me_2SO\text{-}d_6$-CH_2Cl_2 (3:1) solvent are 2.26×10^{-4} and 4.06×10^{-4} for NaSCN concentrations of 0.222 and 0.387 M. Using the approximation that [SCN^-] = [NaSCN], the rate constants k_2 are 1.02×10^{-3} and 1.05×10^{-3} M^{-1} s^{-1}, showing the ion pairing effect to be negligible in this solvent. From an Eyring plot of the data in Table I the values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 22.9 ± 1.0 kcal/mol and −9.2 ± 2.1 cal/mol, respectively.



We have measured the rate of the reaction of the selenium analogue $(o\text{-}Ph_2PC_6H_4SeMe)Pd(SCN)_2$ with SCN^- (Table II). These data confirm the previous suggestion that the rate

0002-7863/79/1501-5428$01.00/0