The First Spectroscopic Detection of Silaylides in the Reaction of Dimesitylsilylene with P, S, and N Heteroatom-Containing Substrates. The Stability of Silaylides

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Summary: UV spectra of silaylides formed in the reaction of dimesitylsilylene with heteroatom-containing (P, S, N) substrates were observed at 77 K in a soft matrix. Under these conditions the silaylides were stable, and the relative stabilities of the silaylides are discussed.

Spectroscopic studies of silylenes in various glass matrices have been actively studied in recent years.[1,2] With the advancement of these techniques, the reactivities and structures of silylenes have gradually become evident. One notable topic in silylene chemistry is whether a silylene forms complexes with heteroatom-containing molecules. A silylene–ether complex was first proposed by Weber and Steel in 1980,[3] and 2 years later, the complex involving (HO)HSi: and H_2O was observed by Margrave in an infrared spectroscopic experiment.[4] The existence and nature of silylene–Lewis base complexes was theoretically predicted by Gordon;[5] but the nature of such complexes still is obscure. Recently, we showed with a low-temperature soft-matrix technique that dimesitylsilylene reacts with electron-pair donors of type C=O and C=S to form silacarbonyl and silathiocarbonyl ylides (eq 1).[6]

(1)

Here we report the results of recent investigations of the reaction of dimesitylsilylene with heteroatom-containing (P, S, N) substrates in isopentane (IP) and 3-methylpentane (3MP) soft matrices, leading to the first spectroscopic detection of silaylides.

In IP/3MP (4:1) at 77 K 2,2-dimesitylhexamethyltrisilane (**1**) was photolyzed with a low-pressure mercury lamp to produce the absorption bands due to dimesitylsilylene (**2**) (573 nm) and tetramesityldisilene (**3**) (420 nm), which had been observed earlier.[2,7] When similar photolysis of **1** was carried out in an IP/3MP (4:1) glass matrix at 77 K containing *N*-methylpyrrolidine (**4a**), only an intense band with λ_{max} = 324 nm was observed and no bands were observed at 420 and 573 nm, indicating that neither the silylene nor the disilene is present. The new band grew in intensity with irradiation time (Scheme I and Figure 1) and persisted for several hours after the light was interrupted; when the matrix was annealed, the band disappeared and the band due to the disilene appeared. The matrix was warmed to room temperature, and the products were analyzed by mass spectrometry. The spectrum is dominated by a large *m/e* at 351 (M^+) and *m/e* 308 ($M^+ - 43$) and 266 ($M^+ - 85$) together with dimesitylsilane; the signal of *m/e* 308 probably corresponding to $[Mes_2Si(CH_2)_3]^+$ indicates the formation of the insertion product of dimesitylsilylene into the ring C–N bond.[8] All of these data are consistent with the assignment of the 324-nm absorption band to silaammonium ylide **5a**.

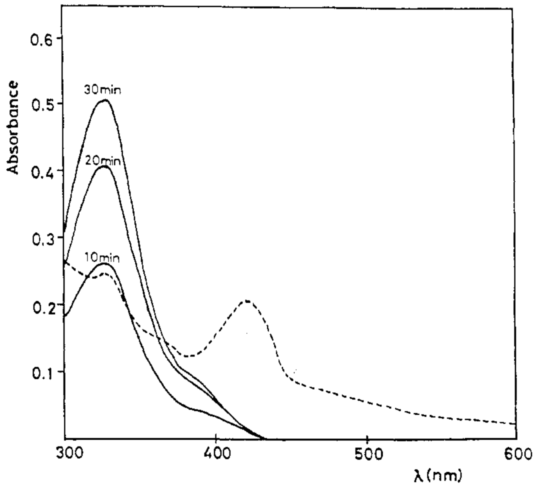
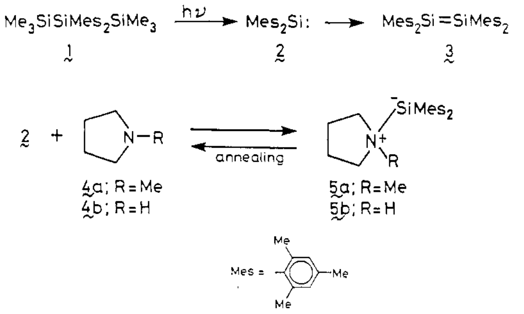


Figure 1. The time course of the UV spectrum observed in the photolysis of **4a** in an isopentane/3-methylpentane (4:1) glass matrix at 77 K (—). The spectrum observed after annealing (---).

Scheme I



The reaction of **2** with pyrrolidine **4b** in the IP/3MP matrix at 77 K produces products that show three bands with λ_{max} at 334, 420, and 573 nm. These are assigned to silaylide **5b**, the disilene, and the silylene, respectively. The silaylide **5b** is stable at 77 K on prolonged standing but is less stable than **5a**, suggesting an equilibrium between the silaylide and (silylene + pyrrolidine).

The reaction of dimesitylsilylene (**2**) with piperidine in the IP/3MP matrix showed a band with λ_{max} at 328 nm, but quite weak and broad. In contrast, the presence of quinuclidine as the donor molecule led to an intense band with λ_{max} at 330 nm, probably due to stable silaylide formation.

The reaction of **2** with tetrahydrofuran and tetrahydrothiophene also give products that show broad and

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(6) Ando, W.; Hagiwara, K.; Sekiguchi, A. *Organometallics* **1987**, *6*, 2270.

(7) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343. West, R. *Science (Washington, D.C.)* **1984**, *225*, 1109.

(8) The C–N insertion product was observed only in the matrix reaction.

(9) One reviewer pointed out that if the ylide formation is reversible, the absorption spectrum of the glass should gradually approach that of the pure disilene. However, under the conditions of this work the concentration of substrate is very much higher than that of the free silylene, so the intensity of their absorptions did not change for a few hours.

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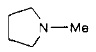
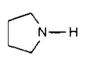
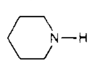
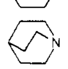
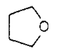
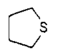
Table I. The UV Absorption Maxima of Silaylides and Their Relative Intensities[a]

substrate	λ_{max}, nm	rel intensities[b] silaylide	silylene	disilene
			0.1	0.9
	324	1		
	334	0.6	<0.1	<0.1
	328	0.2	<0.1	<0.1
	330	1.3		
n-Bu_3P	338	2.7 3.7[c]	0.4	0.2 0.6[c]
	320[d]	<0.1	<0.1	<0.1
	315	<0.1	<0.1	<0.1
PhCl			0.1	0.9

[a] The values in the isopentane/3-methylpentane (4:1) glass matrix at 77 K. [b] The relative values to 1 for the intensity of the absorption of **5a**. [c] The value after the light was interrupted for 1 h. [d] The growth of new band was observed at 385 nm, after the light was interrupted.

weak absorption bands in IP/3MP at low temperature. These are indicative of the instability and high reactivity of the silaylides formed (e.g. C–O or C–S insertion of the silylene).

When a similar photolysis of **1** was carried out in the presence of n-Bu_3P in IP/3MP at 77 K, a intense band with λ_{max} at 338 nm due to silaphosphorus ylide was observed, together with the band due to tetramesityldisilene. The silaphosphorus ylide is significantly more stable under these conditions. The formation of a solution with no bands corresponding to the silylene indicates that formation of the silaphosphorus ylide competes with the dimerization of the silylene.

The observed relative stabilities of silaylides showed a similar trend as complexation energies of the silylene–Lewis base complexes calculated by Gordon ($NH_3 > PH_3 > H_2O > H_2S > HCl$) show.[5]

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Novel Peroxo- and Oxo-Alkyl Complexes of (Pentamethylcyclopentadienyl)tungsten

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Summary: Alkylation of Cp^*WO_2Cl with RMgCl (R = Me, CH_2SiMe_3) provides a synthetic route to alkyl–dioxo tungsten and trialkyl–oxo tungsten complexes. The Cp^*WO_2R complexes are readily converted to the novel $Cp^*WO(O_2)R$ peroxy–alkyl complexes.

There have been rapid developments in higher oxidation state organometallic chemistry which have demonstrated substantial stabilities for complexes containing oxo as well as alkyl, olefinic, or acetylenic substituents.[1] Current interest in transition-metal oxo and peroxo complexes as oxidizing agents and for oxygen atom transfer to substrates[2] prompts our report of $Cp^*WO(O_2)CH_2SiMe_3$ and $Cp^*WO(O_2)CH_3$, which may serve as models for intermediates or as O-atom transfer agents themselves.

Cp^*WO_2Cl and $(Cp^*WO_2)_2O$ are readily available via oxidation of $[Cp^*W(CO)_2]_2$[3] and are very useful starting materials in synthesizing oxo–alkyl tungsten complexes. Cp^*WO_2Cl reacts at −70 °C with excess methylmagnesium chloride to yield 30% of Cp^*WOMe_3 (**1**) and 5% of Cp^*WO_2Me (**2**), respectively.[4] However, the reaction of Cp^*WO_2Cl with Me_3SiCH_2MgCl affords only $Cp^*WO_2CH_2SiMe_3$.[3] We did not observe $Cp^*WO(CH_2SiMe_3)_3$ in the product, although its formation may have been anticipated by analogy with the reactions with methyl Grignard or the known stability of its cyclopentadienyl analogue which was obtained by oxidation of nitrosyl complexes.[5] Our Grignard route to Cp^*WO_2R

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(2) Mimoun, H. *The Chemistry of Functional Groups, Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; p. 465.

(3) Reflux of a chloroform solution of $[Cp^*W(CO)_2]_2$ under an atmosphere of oxygen for 24 h yields a brown solution. Ether extraction of the brown residue obtained upon evaporation of the chloroform provides a 27% yield of pale yellow Cp^*WO_2Cl. [Faller, J. W.; Ma, Y. *J. Organomet. Chem.*, in press.]

(4) (a) **Preparations of $Cp^*WO(Me)_3$ (1) and Cp^*WO_2Me (2).** Cp^*WO_2Cl (120 mg, 0.31 mmol) was dissolved in 50 mL of diethyl ether and treated with 3 equiv of 2 M MeMgCl in THF at −70 °C for 1 h. The solvent was concentrated, and the residue was extracted with 150 mL of diethyl ether in three fractions. The combined extracts were concentrated to give a light yellow residue that contained both compounds **1** and **2** in addition to some yellow impurities. This mixture was then separated and purified by means of thin-layer chromatography on a 0.25-mm silica gel plate with diethyl ether as an eluent. The yields of **1** and **2** were 34 mg (29%) and 4.5 mg (4%), respectively. Preliminary X-ray results indicate that complex **1** has a four-legged piano-stool structure, but there is disorder between a methyl group and the oxygen. **1**: ^1H NMR ($CDCl_3$, 25 °C, 250 MHz) δ 1.88 (s, 15 H, C_5Me_5), 1.06 (m, 6 H, cis-CH_3, J_{W-H} = 6 Hz), 0.17 (m, 3 H, trans-CH_3, J_{W-H} = 6 Hz); IR (CS_2, $\nu_{W=O}$) 948 cm^{-1} (s). Anal. Calcd for $WOC_{13}H_{24}$: C, 41.07; H, 6.36. Found: C, 41.06; H, 6.38. **2**: ^1H NMR ($CDCl_3$, 25 °C, 250 MHz) δ 2.08 (s, 15 H, C_5Me_5), 0.99 (s, 3 H, J_{W-H} = 10.8 Hz); IR (CS_2, $\nu_{W=O}$) 950, 907 cm^{-1} (s). Anal. Calcd for $WO_2C_{11}H_{18}$: C, 36.09; H, 4.96. Found: C, 36.13; H, 5.00. (b) If more Cp^*WO_2Me is desired, using 1.5 equiv of MeMgCl gives about 20% of **1** and 15% of **2** in the final products. (c) **$Cp^*WO(O_2)Me$ (3).** Compound **2** (20 mg, 0.055 mmol) was dissolved in 15 mL of diethyl ether that tested positive for peroxide, and the solution was stirred for 10 h. The product was purified by TLC in a similar fashion to compounds **1** and **2** to yield 16 mg of compound **3** (76%): ^1H NMR ($CDCl_3$, 25 °C, 250 MHz) δ 2.05 (s, 15 H, C_5Me_5), 1.32 (s, 3 H, J_{W-H} = 8.4 Hz); IR (CS_2) $\nu_{W=O}$ 951 (s), ν_{O-O} 864 (m), ν_{W-O} 588 (w), 572 (s) cm^{-1}. Anal. Calcd for $WO_3C_{11}H_{18}$: C, 34.57; H, 4.75. Found: C, 34.63; H, 4.79. (d) **$Cp^*WO(O_2)CH_2SiMe_3$ (4).** Following that for **3** but with R = CH_2SiMe_3 gave **4** in 80% yield: ^1H NMR ($CDCl_3$, 25 °C, 250 MHz) δ 2.03 (s, 15 H, C_5Me_5), 0.97 (d, 1 H, CH′, $J_{H-H'}$ = 12.6 Hz, J_{W-H} = 10.0 Hz, J_{Si-H} = 7.3 Hz), 0.40 (d, 1 H, CH, $J_{H-H'}$ = 12.6 Hz, J_{W-H} = 7.0 Hz, J_{Si-H} = 7.0 Hz), 0.09 (s, 9 H, $SiMe_3$, J_{Si-H} = 6.6 Hz); IR (CS_2) $\nu_{W=O}$ 945 (s), ν_{O-O} 868 (m), ν_{W-O} 585 (w), 567 cm^{-1}. Anal. Calcd for $WSiO_3C_{14}H_{26}$: C, 37.01; H, 5.77. Found: C, 37.08; H, 5.80. (e) Using *tert*-butyl hydroperoxide as an oxidizing agent was far less effective in giving complexes **3** and **4** over a 10-h period. As (EtO)(Me)HCOOH decomposes upon chromatography and **3** and **4** do not, the potential hazards of evaporating solutions to dryness can be avoided by passing solutions through a short column of alumina before concentration.

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