Organometallics 1994, 13, 424–425

A Silathiirane and a Silaselenirane from a Stable Silene

A. G. Brook,* Rajkumar Kumarathasan, and Alan J. Lough

Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario M5S 1A1, Canada

Received October 19, 1993[●]

Summary: A stable silathiirane and a modestly stable silaselenirane were isolated from the reaction of the stable silene Mes(Me_3Si)Si=C($OSiMe_3$)Ad with elemental sulfur or selenium. A crystal structure of the sulfur compound confirmed the structural assignment.

Attempts to add sulfur or selenium across the ends of the silicon–carbon double bonds of silenes have not been reported to date, and our attempts to add sulfur to members of the family of silenes $(Me_3Si)_2Si{=}C(OSiMe_3)R$ gave very complex mixtures. However, disilenes have been reported to add sulfur,[1] selenium,[2] and tellurium[2] to give stable three-membered-ring adducts. Also, silathiiranes were reported by Ando[3] as the products of reaction of a silylene with thioketones, indicating that the silathiirane ring is inherently stable. We have now successfully isolated the sulfur and selenium adducts to the *E* geometric isomer of the silene Mes(Me_3Si)Si=C($OSiMe_3$)Ad as crystalline materials and have obtained the crystal structure of the sulfur adduct.

The silathiirane **3** was prepared by cophotolysis of a mixture of the parent acylsilane **1** with 1 equiv of sulfur in deuteriotoluene (see Scheme 1). Alternatively, if the silene **2** was preformed by photolysis, it reacted overnight in the dark with sulfur to give the same material in a somewhat purer state. Spectroscopic and other details are given in ref 4.

The *E* geometric isomer is the predominant species formed on the photolysis of **1**,[5] so that the isolation of material with the structure **3** was anticipated. Since the NMR spectra indicated the presence of small amounts of other species in the crude reaction mixture, it is possible that a small amount of the corresponding adduct of the *Z* silene isomer was also formed, but this was removed in the isolation–purification procedure.

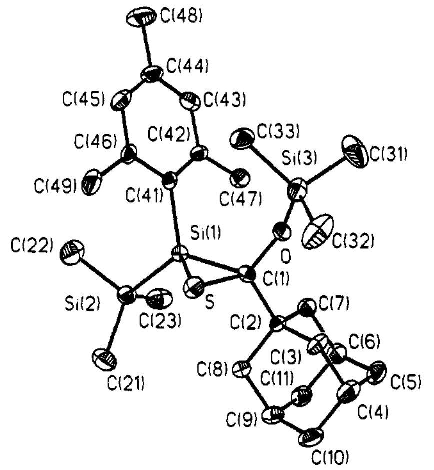
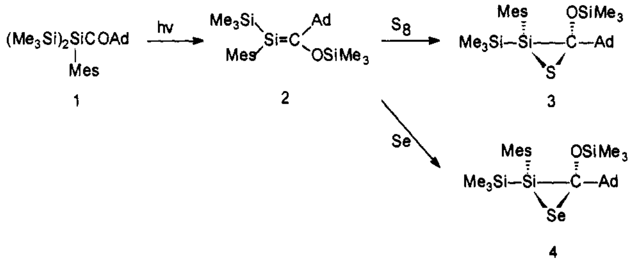


Figure 1. View of **3** showing the atomic labeling scheme. Thermal ellipsoids are at the 25% probability level. For the sake of clarity, hydrogen atoms have been omitted.

Scheme 1



The crystal structure of the silathiirane **3** was obtained on the colorless material, and the ORTEP diagram is shown in Figure 1. Details of the crystal structure analysis are given in Table 1 and ref 6. The ring bond length of 2.129(2) Å for the Si–S bond is slightly longer than the value of 2.093 Å (no esd's reported) found by Ando but shorter than the 2.161(2) Å found by West, the C–S bond length of 1.902(5) Å is not significantly different from the length of 1.905 Å found by Ando, and the Si–C ring bond length of 1.880(6) Å was similar to the 1.903 Å reported by Ando. The ring bond angles at S, Si, and C are 55.2(2), 56.2(2), and 68.5(2)°, respectively, compared to values of 56.6, 56.7, and 66.7° reported by Ando for his silathiirane. West's disilathiirane had angles at S and Si of 64.0(1) and 58.0(1)°, respectively. Despite the very acute angles in the ring, the angles between the other substituents at the ring carbon and silicon atoms are relatively tetrahedrally

---

[●] Abstract published in *Advance ACS Abstracts,* January 1, 1994.

(1) West, R.; De Young, D. J.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 4942.

(2) Tan, R. P.-K.; Gillette, G. R.; Powell, D. R.; West, R. *Organometallics* **1991**, *10*, 546.

(3) Ando, W.; Hamada, Y.; Sekiguchi, A.; Ueno, K. *Tetrahedron Lett.* **1983**, *24*, 4033.

(4) Properties of **3**: Compound **3** was prepared by photolyzing under argon a solution of acylsilane **1** (50 mg, 0.11 mmol) and sulfur (4 mg, 0.11 mmol) in 0.5 mL of deuteriotoluene for 0.5 h in an NMR tube using three PAR 38 ultraviolet lamps ($\lambda > 360$ nm). The solution was run through a short column of silica gel that had been pretreated with trimethylchlorosilane. Removal of the solvent and recrystallization from hexane gave pure **3** in 70% yield. Mp: 148–150 °C. ^{1}H NMR: δ –0.03, 0.18 (each 9 H, s, Me_3Si), 1.68–2.03 (15 H, m, Ad), 2.09 (3 H, s, *p*-Me), 2.62, 2.63 (each 3H, s, *o*-Me), 6.75 (1 H, s, CH Mes). ^{13}C NMR: δ –0.27 (Me_3Si), 2.09 ($OSiMe_3$), 21.21 (*p*-Me), 23.04, 24.93 (*o*-Me), 29.36 (CH Ad), 37.53, 41.53 (CH_2Ad), 42.61 (quat C Ad), 91.96 (ring C), 128.56, 129.22 (CH sp^2 Mes), 129.64, 139.55, 142.94, 145.69 (C sp^2 Mes). ^{29}Si NMR: δ –57.66 (ring Si), –14.36 (Me_3Si), 13.28 ($OSiMe_3$). Anal. Calcd for $C_{26}H_{44}OSSi_3$: C, 63.86, H, 9.08. Found: C, 64.64; H, 9.16. HR-MS: calcd for M^+ 488.2420, found 488.2412.

(5) Brook, A. G.; Baumegger, A.; Lough, A. J. *Organometallics* **1992**, *11*, 3088.

(6) X-ray Structural Determination: Intensity data were collected on a Siemens P4 diffractometer at room temperature, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The ω-scan technique was applied using variable scan speeds (5–30° min^{-1} in ω). The intensities of three standard reflections measured every 2 h showed no decay. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods. Non-hydrogen atoms were refined with anisotropic thermal parameters by least squares to minimize $\sum w(F_0 - F_c)^2$, where $w^{-1} = \sigma^2(F) + gF^2$. Hydrogen atoms were positioned on geometric grounds and included in the refinement as riding atoms (C–H = 0.96 Å, U_{iso} = 0.092(4) Å^2). There were no chemically significant features in the final difference Fourier map. Crystal data, data collection, and least-squares parameters are listed in Table 1. All calculations were performed and graphics created using SHELXTL PC[8] on a 486-66 personal computer. Atomic coordinates and other data concerning the crystal structures are given in the supplementary material.

0276-7333/94/2313-0424$04.50/0

Table 1. Summary of Crystal Data, Details of Intensity Collection, and Least-Squares Refinement Parameters

empirical formula	$C_{26}H_{44}OSSi_3$
M_r	488.9
cryst size, mm	0.25 × 0.20 × 0.15
cryst class	monoclinic
space group	$P2_1/n$
a, Å	11.476(1)
b, Å	9.567(1)
c, Å	26.931(4)
β, deg	99.72(1)
V, Å^3	2914.4(6)
Z	4
D_{calcd}, g cm^{-3}	1.114
μ(Mo Kα), cm^{-1}	2.50
F(000)	1064
range θ collected, deg	2–50
indices collected	h, −1 to +13; k, 0–11; l, −32 to +31
total no. of rflns	5982
no. of unique rflns	5142
R_{int}	0.094
no. of obsd data ($F > 6\sigma(F)$)	1908
R	0.049
R_w	0.045
weighting g	0.0001
goodness of fit	1.33
largest/mean Δ/σ	0.02/0.00
no. of params refined	281
max/min density in ΔF map, e Å^{-3}	+0.28/−0.23

normal, being 110.0(4)° for O–C(1)–C(2) and 109.9(2)° for Si(2)–Si(1)–C(41), suggesting little steric interaction between the substituents.

The analogous silaselenirane **4** was prepared by reaction overnight of the preformed silene with 1 equiv of selenium dissolved in deuteriobenzene in the dark at room temperature. It was isolated in 60% yield after chromatography on Me_3SiCl-treated silica gel followed by recrystallization from hexane. Spectroscopic and other properties are given in ref 7. Over some weeks the original colorless crystals became violet, indicating decomposition.

Both the silathiirane **3** and the silaselenirane **4** decomposed to a complex mixture of products either when heated to 100 °C for 2 h or when photolyzed overnight with $\lambda >$ 360 nm radiation. These were not further investigated.

It is evident that relatively stable adducts of sulfur and selenium can be made by direct addition to silenes, provided that the latter bear appropriate substituents. Silenes with a mesityl group and a trimethylsilyl group on silicon and adamantyl and trimethylsiloxy groups on carbon have been found to be particularly useful in these and other addition reactions[5] in yielding stable adducts.

Acknowledgment. This research was supported by the Natural Science and Engineering Research Council of Canada.

Supplementary Material Available: Tables of atomic coordinates, all bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **3** (5 pages). Ordering information is given on any current masthead page.

OM930721P

---

(7) Compound **4** was prepared by photolyzing 0.10 g (0.22 mmol) of **1** in 0.5 mL of C_6D_6 for 45 min to yield the silenes **2**. To this solution was added 17 mg (0.22 mmol) of Se, and this mixture was left in the dark overnight and then worked up as above. Mp: 146–148 °C. ^{1}H NMR: δ −0.05, 0.21 (each 9 H, s, Me_3Si), 1.63–2.08 (15 H, m, Ad), 2.09 (3 H, s, *p*-Me), 2.62, 2.70 (each 3 H, s, *o*-Me), 6.75 (2 H, s, CH Mes). ^{13}C NMR: δ −0.29, 1.71 (Me_3Si), 21.13, 23.07, 25.77 (Me Mes), 29.24 (CH Ad), 37.34, 41.97 (CH_2 Ad), 42.25 (quat C Ad), 99.50 (ring C), 128.75, 129.00 (CH sp^2 Mes), 128.63, 139.46, 142.87, 145.95 (C sp^2 Mes). ^{29}Si NMR: δ −48.59 (ring Si), −15.55 (Me_3Si), 14.94 ($OSiMe_3$). ^{77}Se NMR: δ 48.84. Anal. Calcd for $C_{26}H_{44}OSeSi_3$: C, 58.21; H, 8.21. Found: C, 58.42; H, 8.36. HR-MS: calcd for M$^+$ 536.1865, found 536.1833.

(8) Sheldrick, G. M. SHELXTL PC; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1989.