Spectroscopic observation of silylene-ether complexes

Gregory R. Gillette, George H. Noren, and Robert. West

Organometallics, **1987**, 6 (12), 2617-2618• DOI: 10.1021/om00155a033 • Publication Date (Web): 01 May 2002

and C2–C3–C4–C5, respectively. The five pentadienyl carbon atoms are coplanar to within 0.01 Å and the pentadienyl plane makes a dihedral angle of 28.9° with the equatorial plane Re/P1/P2/P3/C22. The projection of pentadienyl vector C1–C2 onto the equatorial plane falls between carbonyl ligand C22–O22 and phosphine ligand P3; plane Re/C1/C2 makes a dihedral angle of 23.3° with plane C1/Re/C22. A clear alternation in pentadienyl C–C bond lengths is again observed: C1–C2 = 1.51 (3) Å; C2–C3 = 1.27 (2) Å; C3–C4 = 1.39 (2) Å; C4–C5 = 1.29 (2) Å.

In solution, the η^1-*trans*-pentadienyl ligand in **3** gives rise to a ^{1}H NMR spectrum that closely resembles those of **1b** and **2b**. Particularly diagnostic are the large J_{H2-H3} coupling constant (14.6 Hz) and the upfield chemical shift of H4 (δ 6.74), which is comparable to that of H2.

We have begun to study the reactivity of these unusual (η^1-pentadienyl)rhenium complexes toward heat, light, and electrophilic reagents. Results of these investigations will be reported in future communications.

Acknowledgment. Support from the National Science Foundation (Grant CHE-8520680) is gratefully acknowledged. Washington University's High resolution NMR Service Facility was funded in part by National Institutes of Health Biomedical Research Support Instrument Grant 1 S10 RR02004 and by a gift from Monsanto Co. We thank Monica Meckfessel (a participant in Washington University's Summer Undergraduate Research Program) for synthetic help.

Supplementary Material Available: Synthesis and spectroscopic characterization of **2** and listings of final atomic coordinates, thermal parameters, bond lengths, bond angles, torsional angles, and significant least-squares planes including subtended dihedral angles for **1a** and **3** (16 pages); listings of observed and calculated structure factor amplitudes for **1a** and **3** (17 pages). Ordering information is given on any current masthead page.

Spectroscopic Observation of Silylene–Ether Complexes

Gregory R. Gillette, George H. Noren, and Robert West*

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received September 4, 1987

Summary: The ultraviolet photolysis of linear trisilanes in 2-MeTHF at 77 K has led to the first spectroscopic detection of silylene ether complexes. The complexes are also formed during the annealing of mixed 3-MP/2-MeTHF glasses. Chemical evidence for complexed silylenes based on competitive trapping studies as well as evidence that the silylene–ether complexes have a significant lifetime in solution at low temperatures is presented.

The isolation of silylenes in argon or hydrocarbon matrices has in recent years contributed greatly to the knowledge of these reactive species.[1,2] Here we report the results of recent investigations of diorganosilylenes in pure 2-methyltetrahydrofuran (2-MeTHF) glasses and in 3-methylpentane (3-MP) matrices containing ether dopants, leading to the first spectroscopic observation of silylene–ether complexes.

Table I. Absorption Maxima for Silylenes and Their Annealing Products in 2-MeTHF and 3-MP Matrices at 77 K

		2-MeTHF		3-MP	
R	R′	λ_{max}	annealed λ_{max}	λ_{max}	annealed λ_{max}
Mes	*t*-Bu	510, 350	350	505	335, 390
Mes	OAr	430	330	425	350, 390, 430
Mes	Ad	526, 530	350	526	338, 392
Mes	Mes	350	350	577	420

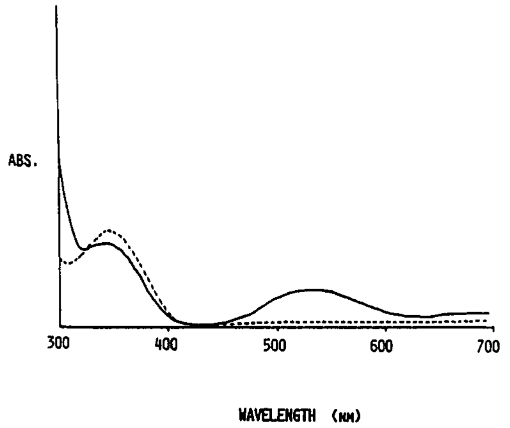


Figure 1. UV spectrum obtained in photolysis of **1c** in 2-MeTHF at 77K (—). Spectrum observed after annealing of the matrix (- - -).

Ether-stabilized silylenes were first proposed as intermediates by Weber and Steele in 1980.[3] In these studies dimethylsilylene was observed to react with increased selectivity in ether solvents leading the authors to postulate an "electron-pair donor complex with the solvent"[3] as the cause of the observed selectivity. Silylene complexes with Lewis bases have also been proposed on theoretical grounds.[4] However, no spectroscopic evidence for such complexes has been reported.[5]

In our experiments, trisilanes **1a–d** were photolyzed to give the corresponding silylenes.[6] In 3-MP at 77 K compounds **1a–d** behave similarly to other trisilanes whose photolyses have been studied earlier.[2] Initially, absorption bands due to the silylene are observed; upon annealing of the matrix these disappear and bands of the disilene appear (Table I). For **1a**,**c**,**d** the disilenes are stable and can be isolated.

When a similar photolysis of **1a** or **1c** was carried out in a matrix composed of 95:5 3-MP/2-MeTHF, initially only bands due to the silylene were observed, but upon annealing these disappeared and a new band was formed with λ_{max} = 350 nm. After further warming, this band diminished and the band associated with the disilene grew in. The disilene was stable to room temperature and was detected by GC–MS as the 1,3-cyclodisiloxane following the addition of O_2 to the solution.[7]

---

(1) Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Ed.; Wiley, New York, 1985; Vol. 3, p 333.

(2) Michalczyk, M. J.; Fink, M. J.; De Young, D. J.; Carlson, C. W.; Welsh, K. M.; West, R. *Silicon, Germanium, Tin Lead Compds.* **1986**, *1*, 75–80.

(3) Steele, K. P.; Weber, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6095–6097.

(4) Ragharachari, K.; Chandrasekhar, J.; Gordon, M. S.; Dykema, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 5853–5859.

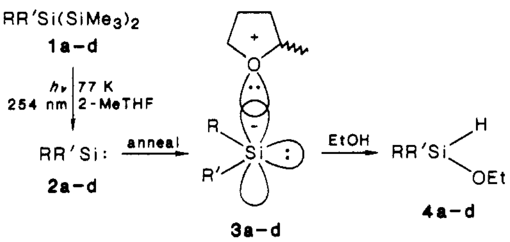
(5) Recently Ando et al. have reported the observation of a silacarbonyl ylide from the reaction of dimesitylsilylene with tetramethyl-2-indanone. Ando, W.; Hagiwara, K.; Sekiguchi, A. *Organometallics* **1987**, *6*, 2270–2271.

(6) Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* **1972**, *42*, 325–332.

(7) Similar results are obtained by using diethyl ether as the Lewis base; the new band is also observed to have λ_{max} = 350 nm.

0276-7333/87/2306-2617$01.50/0 © 1987 American Chemical Society

Scheme I



a, R = mesityl, R′ = *t*-Bu; **b**, R = mesityl, R′ = 2,6-diisopropylphenoxy; **c**, R = mesityl, R′ = 1-adamantyl; **d**, R = R′ = mesityl

Table II. Product Ratios for Competitive Trapping of Silylene 2a at Room Temperature

	MeOH/EtOH	MeOH/IPA	EtOH/IPA
pentane	1.2	2.0	1.8
Et_2O	1.4	5.4	3.0
2-MeTHF	1.6	6.4	4.4

Quite different results were obtained when **1a–d** were irradiated in pure 2-MeTHF. For **1c**, the electronic spectra are shown in Figure 1. Photolysis again produces a band at 530 nm,[8] assigned to free silylene, as well as a band at 350 nm. When the matrix is annealed, the 530-nm band diminishes as the 350-nm band grows. Similar behavior was observed for trisilanes **1a,b,d** (for **1d** only the band at 350 nm was observed). All of the samples showed only the band at 350 nm after the matrix was annealed (Table I).

Melting of the matrix gave, in each case, a solution with no bands having $\lambda_{max} > 300$ nm, indicating that no disilene was formed. Analysis of the photolysate by GC–MS showed the only volatile products to be four different isomers of a compound with a molecular ion corresponding to (RR′Si + 2-MeTHF)$^+$.[9] When ethanol was present as a silylene trap,[10] the O–H insertion compounds **4a–d** were produced. All of these data are consistent with the assignment of the 350-nm absorption bands to silylene–2-MeTHF complexes **3a–d** (Scheme I).

To provide further evidence for silylene complexes a series of competitive trapping experiments similar to those described by Weber[3] were done utilizing **1a** as the silylene precursor. In these studies methanol, ethanol, and 2-propanol, present in 20-fold molar excess, were used as trapping reagents in the solvents pentane, diethyl ether, and 2-MeTHF. All of the trapped products were characterized by GC–MS and by comparison to authentic samples.[11] The selectivity for insertion of silylene **2a** into the O–H bond of the less hindered alcohol increases in ether solvents (Table II). These results agree with those obtained by Weber and Steele; moreover the selectivity is distinctly greater for **2a** than for dimethylsilylene, probably reflecting the larger steric bulk of **2a**.

A final experiment indicates that silylene–ether complexes may also have a reasonable lifetime in solution at low temperatures. Irradiation of **1c** in 2-MeTHF solution at −135 °C for 2 h followed by freezing in liquid N_2 yielded a matrix whose UV spectrum contained only the band at 350 nm. Addition of ethanol to the matrix after the UV spectrum was obtained gave a small yield of the insertion product **4c**. The complex therefore has a short, but significant lifetime in solution, estimated to be 1 min based on measurement of the decay rate of the 350-nm band at −135 °C.

Acknowledgment. Research was sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Contract No. F49620-86-0010 and National Science Foundation Grant No. CHE-8318820-02. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation thereon.

Registry No. **1a**, 88526-27-6; **1b**, 111060-23-2; **1c**, 111060-24-3; **1d**, 79184-72-8; **2a**, 89486-28-2; **2b**, 111060-25-4; **2c**, 111060-26-5; **2d**, 79184-71-7; **3a**, 111060-27-6; **3b**, 111060-28-7; **3c**, 111060-29-8; **3d**, 111060-30-1; **4a**, 111060-31-2; **4b**, 111060-32-3; **4c**, 111060-33-4; **4d**, 51525-38-3; 2-MeTHF, 96-47-9; 3-MP, 96-14-0; MeOH, 67-56-1; IPA, 67-63-0; EtOH, 64-17-5; Mes(*t*-Bu)SiHCl, 111060-34-5.

---

(8) The 4-nm shift of the silylene absorption maximum in going from 3-MP to 2-MeTHF is probably due to a matrix effect.

(9) Attempts to isolate these compounds as single isomers have been unsuccessful. These compounds are probably the products of insertion into the C–O bond of 2-MeTHF. Each regioisomer would have two stereoisomers, leading to the observation of four isomers by GC–MS. Data from a high-resolution mass spectrometry study of the mixture of isomers are consistent with this assignment.

(10) Gu, T-Y.; Weber, W. P. *J. Organomet. Chem.* **1980**, *184*, 7–11.

(11) Authentic samples of the products of silylene insertion into alcohols were prepared by reacting Mes(*t*-Bu)SiH(Cl) with the desired alcohol in dry hexane in the presence of triethylamine as an HCl scavenger. The average yield of these reactions was 85%. Mes(*t*-Bu)SiH(OMe): ^{1}H NMR ($CDCl_3$) δ 1.21 (s, *t*-Bu), 2.42 (s, para Me), 2.69 (s, ortho Me), 3.66 (s, OMe) 5.22 (s, SiH), 6.99 (s, ArH); ^{29}Si NMR ($CDCl_3$) δ +3.40, +5.54 (J_{Si-H} = 213.4 Hz); MS, *m/e* (relative intensity) 239 (M$^+$, 17.2), 179 (M$^+$ − *t*-Bu, 100). Mes(*t*-Bu)SiH(OEt): ^{1}H NMR ($CDCl_3$) δ 1.25 (s, *t*-Bu), 1.43 (t, CH_3), 2.48 (s, para Me), 2.69 (s, ortho Me), 3.94 (q, OCH_2), 5.30 (s, SiH), 6.98 (s, ArH); ^{29}Si NMR ($CDCl_3$) δ −0.39, 1.63 (J_{Si-H} = 200.4 Hz); MS, *m/e* (relative intensity) 250 (M$^+$, 6.6), 193 (M$^+$ −*t*-Bu, 100). Mes(*t*-Bu)SiH(O-iPr): ^{1}H NMR ($CDCl_3$) δ 1.26 (s, *t*-Bu), 1.45 (d, CH_3CH), 2.49 (s, para Me), 2.74 (s, ortho Me) 4.2 (sep, OCH), 5.37 (s, SiH), 7.05 (s, ArH); ^{29}Si NMR ($CDCl_3$) δ −3.91, −1.94 (J_{Si-H} = 196.7 Hz); MS, *m/e* (relative intensity) 264 (M$^+$, 6.0), 207 (M$^+$ − *t*-Bu, 100). Satisfactory analyses were obtained for all three compounds.

Intermediates in the Direct Synthesis of Rhenium Carbide Clusters from Rhenium Carbonyl. Crystal Structure of $[Et_4N]_2[HRe_5(\mu_5\text{-}C)(CO)_{16}]$

Timothy J. Henly, Scott R. Wilson, and John R. Shapley*

School of Chemical Sciences and Materials Research Laboratory
University of Illinois, Urbana, Illinois 61801

Received September 9, 1987

Summary: The reaction of $Re_2(CO)_{10}$ with a 1.2:1 mole ratio of sodium in triglyme at 200 °C yields the new rhenium carbido clusters $[HRe_6C(CO)_{18}]^{3-}$ and $[HRe_5C(CO)_{16}]^{2-}$. The latter cluster consists of a square-based pyramid of rhenium atoms with a μ_5-carbido atom 0.10 Å below the basal plane and a semibridging carbonyl on one basal–apical edge. This compound is the first example of such a M_5C complex outside of the iron triad elements.

The reduction of $Re_2(CO)_{10}$ with sodium at elevated temperatures in glyme solvents is an efficient synthetic pathway to the high-nuclearity clusters $[H_2Re_6C(CO)_{18}]^{2-}$, $[Re_7C(CO)_{21}]^{3-}$, and $[Re_8C(CO)_{24}]^{2-}$.[1,2] These clusters have been prepared by different routes and crystallographically characterized by Ciani et al.[3-5] In order to probe for

---

(1) Hayward, C. M. T.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3816.

(2) (a) Hayward, C. M. T. Ph.D. Thesis, University of Illinois, Urbana, 1984. (b) Hayward, C. M. T.; Shapley, J. R. *Organometallics*, accepted for publication.

0276-7333/87/2306-2618$01.50/0