Cyclosilaselenanes. Photochemical and Thermal Precursors of Silaneselones, Reactive Intermediates with a Silicon–Selenium Double Bond[1]

Philip Boudjouk,* Steven R. Bahr, and Dennis P. Thompson

Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105

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Several cyclodi- and cyclotrisilaselenanes $(R_2SiSe)_n$ (n = 2, 3) were prepared from in situ generated Na_2Se and R_2SiCl_2. The properties of the cyclosilaselenanes depend on the groups attached to silicon, ranging from thermally unstable and air-sensitive yellow oils (R = Me, Et) to green crystals (R = Me_3Si) that can be exposed to air for several days and withstand temperatures of 250 °C under nitrogen. $(R_2SiSe)_n$ will generate silaneselones, $R_2Si{=}Se$, which are easily trapped with hexamethylcyclotrisiloxane, thermally and photolytically when R = Me, Et and n = 3 but only thermally when R = Me, Et and n = 2. For R = Ph, only the six-membered ring (n = 3) was isolated, which produced modest yields of $Ph_2Si{=}Se$ under thermal conditions but gave a complex mixture upon photolysis. Silylene extrusion is not an important reaction of cyclodi- and cyclotrisilaselenanes.

Introduction

Pyrolysis of cyclic compounds of the type $(R_2E{-}X)_n$ (n = 2–4) is a well-known route to reactive intermediates of the type $R_2E{=}X$ (eq 1).[2] This approach has been used to generate reactive intermediates for E = C and X = S,

$$(R_2E-X)_n \xrightarrow{\Delta} [R_2E=X] \qquad (1)$$

R = Alkyl, H, Halogen; E = C, Si, Ge; X = O, S, Se

Se such as thiocarbonyl fluoride,[3] thioacetaldehyde and thioacetone,[4] thioformaldehyde,[5] and selenoacetaldehyde[6] as well as for some of the heavier analogues like dimethylsilathione (R = Me, E = Si, X = O)[7,8] and diethylgermathione (R = Et, E = Ge, X = S).[9]

The first cyclosilaselenanes were prepared by Schmidt and Ruf in 1963,[10] but no attempts to generate silaneselones from these compounds, with the exception of our own,[1] have been reported. Recently, we described a convenient procedure for the synthesis of alkali-metal selenides and diselenides in THF from an alkali metal and selenium in the presence of a catalytic amount of naphthalene.[11] Using sodium selenide produced by this technique we prepared tetraethylcyclodisilaselenane and hexaethylcyclotrisilaselenane and found that photolysis (254 nm) of the latter generated diethylsilaneselone, a reactive intermediate containing the silicon–selenium double bond.[1] We have prepared several new cyclosilaselenanes and investigated some of their photochemical and thermal reactions. The results of these studies are presented in this paper.

Scheme I. Synthesis of Cyclosilaselenanes

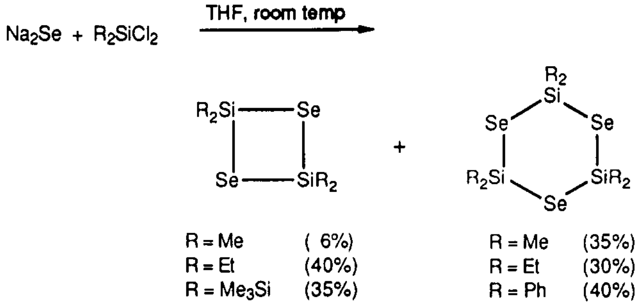

Table I. Ring Contractions of $(Me_2SiSe)_3$ and $(Et_2SiSe)_3$

$$(R_2SiSe)_3 \longrightarrow (R_2SiSe)_2$$

entry	R	conditions	time, h	% yield[a] of $(R_2SiSe)_2$	% conversion[b]
1	Me	254 nm/hexane	23	68	95
2	Me	150 °C/decane	48	~3	~3
3	Me	225 °C/decane	70	39	46
4	Me	225 °C/decane	94	35	48
5	Et	254 nm/hexane	18	90	100
6	Et	225 °C/decane	40	80	100
7	Et	155 °C/decane	40	15	16

[a] Yields determined by GC. [b] Percent cyclotrisilaselenane reacted.

Results and Discussion

When R_2SiCl_2 (R = Et, Me) is added to sodium selenide, generated in situ from selenium and sodium in the presence of a catalytic amount of naphthalene in THF, cyclodi- and cyclotrisilaselenanes are produced (Scheme I). Tetramethylcyclodisilaselenane is a solid in pentane at −78 °C and a light yellow oil at room temperature. Although it only slowly decomposes in solution, isolated samples will decompose in minutes even under a nitrogen atmosphere. Hexamethylcyclotrisilaselenane, tetraethylcyclodisilaselenane, and hexaethylcyclotrisilaselenane were isolated as yellow oils in >90% purity by molecular distillation. These compounds are unstable in air but withstand room temperature under nitrogen for several hours and can be stored in a hydrocarbon solvent at 0 °C for months. The only isolated product of the reaction of sodium selenide with diphenyldichlorosilane is hexaphenylcyclotrisilaselenane. This compound is a col-

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[1] A preliminary account of this work has appeared: Thompson, D. P.; Boudjouk, P. *J. Chem. Soc., Chem. Commun.* **1987**, 1466.

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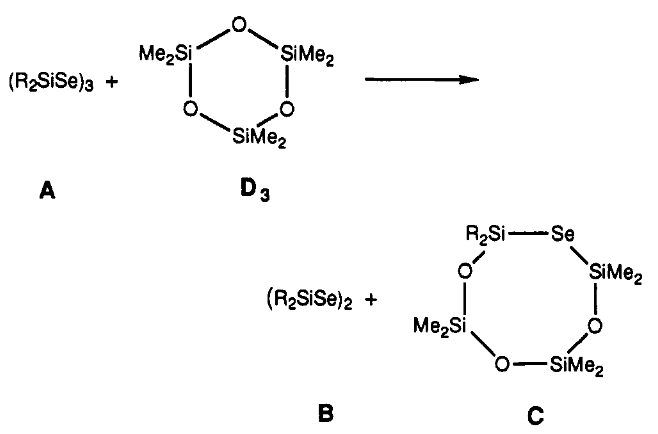
Table II. Ring Contractions in the Presence of D_3



expt[a]	R	D_3A	conditions	C/B	% recovered Se as B and C
1	Me	20/1	254 nm/hexane	2.40/1	80
2	Me	100/1	254 nm/hexane	>100/1	60
3	Me	20/1	225 °C/decane	3.00/1	65
4[b]	Me	100/1	225 °C	>100/1	70
5	Et	8/1	254 nm/hexane	0.33/1	81
6	Et	20/1	254 nm/hexane	0.55/1	85
7	Et	100/1	254 nm/hexane	3.00/1	85
8	Et	30/1	225 °C/decane	0.65/1	84
9[b]	Et	100/1	225 °C	2.70/1	72

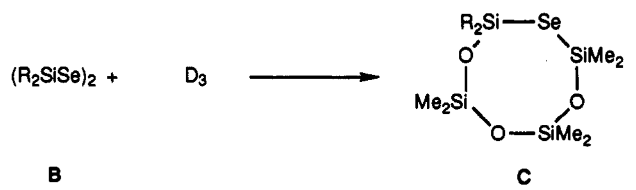
[a] All reactions showed complete consumption of starting material. [b] Experiments run without solvent.

orless, crystalline solid that is stable for several hours in the presence of dry air. The reaction of bis(trimethylsilyl)dichlorosilane with sodium selenide produces tetrakis(trimethylsilyl)cyclodisilaselenane, isolated as light green needles that are stable in dry air for several days.

Ring Contractions of Cyclotrisilaselenanes. $(Me_2SiSe)_3$ and $(Et_2SiSe)_3$ undergo ring contraction photochemically and thermally to form $(Me_2SiSe)_2$ and $(Et_2SiSe)_2$ respectively (Table I). The UV spectra of $(Me_2SiSe)_3$ and $(Et_2SiSe)_3$ show absorbances at 254 nm, while the absorbances of $(Me_2SiSe)_2$ and $(Et_2SiSe)_2$ but off at 220 nm. Photolysis (Rayonet, 254-nm lamps, hexane) of $(Et_2SiSe)_3$ produces $(Et_2SiSe)_2$ in 90% yield and is the only product observed by GC (Table I, entry 5). In a separate experiment, it was shown that $(Et_2SiSe)_2$ is essentially inert to photolysis (254 nm, 48 h, 93% recovery, no evidence of $(Et_2SiSe)_3$). Photolysis of $(Me_2SiSe)_3$ produces $(Me_2SiSe)_2$ in 68% yield (Table I, entry 1). Decomposition was observed in the form of discharged elemental selenium in all reactions, photochemical and thermal.

Replacing methyl groups with ethyl groups significantly alters the chemistry of the ring systems. For example, $(Me_2SiSe)_2$ has a $t_{1/2}$ of 60 h at 69 °C (refluxing hexane) producing a 22% yield of $(Me_2SiSe)_3$, whereas $(Et_2SiSe)_2$ is stable indefinitely at that temperature and, even after 32 h at 250 °C, 80% can be recovered (no $(Et_2SiSe)_3$ was detected). For the six-membered rings, the stabilities are reversed: $(Me_2SiSe)_3$ is stable to 110 °C, is only 3% converted to $(Me_2SiSe)_2$ at 150 °C, and is less than 50% converted at 225 °C even after 94 h (Table I, entries 1, 6, and 7). The ethyl analogue $(Et_2SiSe)_3$, on the other hand, shows much higher conversion rates to $(Et_2SiSe)_2$ thermally and photochemically (Table I, entries 2–4). Photolysis of $(Me_2SiSe)_3$ at 254 nm in hexane produces a mixture of $(Me_2SiSe)_2$ and $(Me_2SiSe)_3$ in an 11:1 ratio. This mixture was then transferred to a sealed tube and heated to 225 °C. After 36 h, the ratio changes to about 5.3:1, but significant quantities of elemental selenium were also produced.

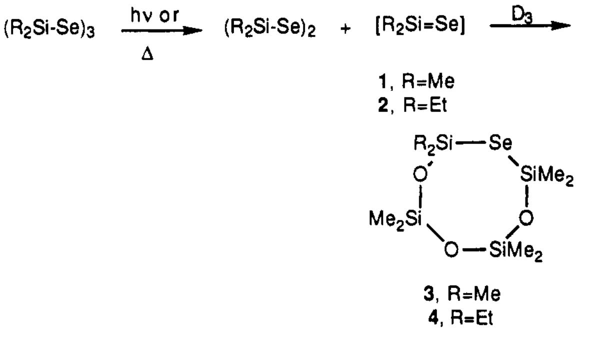
Table III. Thermolysis of $(R_2SiSe)_2$ with D_3



R	D_3	conditions	% yield of C	% conversion of B
Me	12/1	225 °C/decane/48 h	70	90
Et	12/1	250 °C	5	9

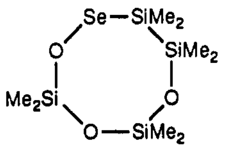
Thus only for the methyl case does there appear to be an equilibrium between the four- and six-membered rings and then only under thermal conditions. Accurate determination of an equilibrium constant is prevented by the accompanying side reactions. An equilibrium under our photochemical conditions is not possible because $(Me_2SiSe)_2$ and $(Et_2SiSe)_2$ do not absorb at 254 nm.

Ring Contraction in the Presence of D_3. Evidence for Silaneselones. Photolysis or thermolysis of $(Me_2SiSe)_3$ (or $(Et_2SiSe)_3$) in the presence of D_3 gives $(Me_2SiSe)_2$ and 2,2,4,4,6,6,8,8-octamethyl-1,5,7,2,4,6,8,3-trioxatetrasilaselenocane (**3**) (or $(Et_2SiSe)_2$ and 4,4,6,6,8,8-hexamethyl-2,2-diethyl-1,5,7,2,4,6,8,3-trioxatetrasilaselenocane (**4**)), in good yields (Table II). By analogy to known two-atom insertion reactions observed for other $R_2Si{=}X$ species ($X = CR_2$, NR, O, S),[7,12] we postulate the intermediacy of silaneselones **1** and **2** (eq 2).



(2)

The structures of **3** and **4** can be assigned unambiguously on the basis of ^{13}C NMR data. For example, the carbon spectrum of **3** exhibits two singlets at 6.79 and 1.14 ppm, respectively. The alternative structure, **5**, would have four absorptions. The data in Table II illustrate important differences in the chemistries of $(Me_2SiSe)_3$ and $(Et_2SiSe)_3$. While $(Me_2SiSe)_3$ is more stable with respect to ring contraction than $(Et_2SiSe)_3$ (Table I), $(Me_2SiSe)_3$ is a far better



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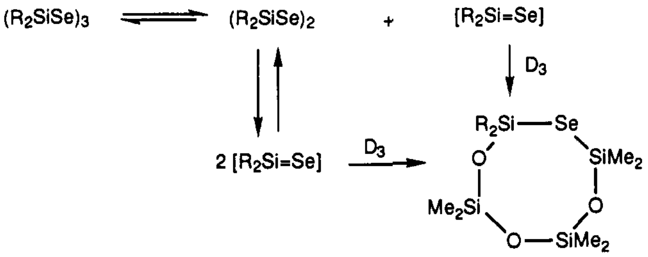
Scheme II



source of a silaneselone than is $(Et_2SiSe)_3$. The experiments with D_3 affect overall silaneselone production. For example, when the ratio of D_3 to $(Me_2SiSe)_3$ is 100:1, <1% of $(Me_2SiSe)_2$ is detected (experiments 2 and 4). On the other hand, when a D_3:$(Et_2SiSe)_3$ ratio of 100:1 is used, the product mixture contains >30% $(Et_2SiSe)_2$ (experiments 7 and 9). While the product distribution may be affected by relative trapping efficiencies, i.e., the smaller dimethylsilaneselone (**1**) probably reacts faster with D_3 than diethylsilaneselone (**2**), the reactivities of the cyclodisilaselenanes play a key role because they are sources of silaneselones. When $(Me_2SiSe)_2$ and a 12-fold excess of D_3 is refluxed in hexane for 60 h, no selenocane is observed, but $(Me_2SiSe)_3$ is obtained in 22% yield. This suggests that $(Me_2SiSe)_2$ is a better trap for the silaneselone than D_3 but $(Me_2SiSe)_2$ is approximately 10 times more reactive than $(Et_2SiSe)_2$ (Table III). In these reactions, cyclodisilaselenanes are not traps of chemical consequence, since any six-membered ring which is formed should fragment to give silaneselone.

We propose the following pathways for the thermal (>200 °C) reactions of hexaalkylcyclotrisilaselenanes in the presence of D_3 (Scheme II). The reaction begins with the extrusion of dialkylsilaneselone by the cyclotrisilaselenane. The silaneselone once formed may dimerize and insert into D_3 giving the selenocane or insert into newly formed cyclodisilaselenane reforming starting material. We see no evidence of insertion of silaneselone into cyclotrisilaselenane to produce cyclotetrasilaselenane (in similar experiments with cyclotrisilathianes no cyclotetrasilathianes were observed[7,8]). Cyclodisilaselenane formed in the reaction is also capable of extruding silaneselone (e.g., $(Me_2SiSe)_2$ is a more efficient source of silaneselone than $(Me_2SiSe)_3$).

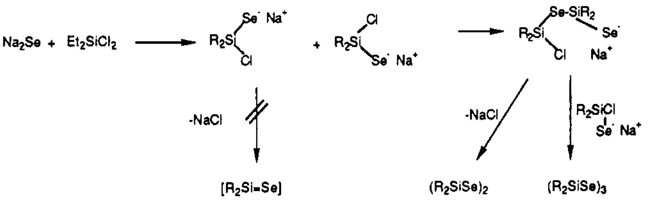
When $(Et_2SiSe)_3$ is photolyzed or thermolyzed in the presence of triethylsilane, no Si–H insertion is observed. The only observable product is $(Et_2SiSe)_2$ in 90% yield. This indicates that the silaneselone does not readily insert into Si–H bonds under these conditions and is further evidence that silylene formation is not an important pathway in the decomposition of alkylated cyclotrisilaselenanes.

No cycloaddition reactions between silaneselones and dienes or alkenes were observed. When $(Et_2SiSe)_3$ is photolyzed in a 12-fold excess of cyclohexene, or heated (225 °C) in a 12-fold excess of anthracene, the only product observed is $(Et_2SiSe)_2$ in approximately 90% yield.

We also investigated the possibility that silaneselones might be intermediates in the synthesis of cyclosilaselenanes by treating Et_2SiCl_2 with sodium selenide in the presence of D_3. No selenocanes were detected. This suggests that ring formation occurs primarily through bimolecular reactions involving ionic intermediates (Scheme III).

Thermolysis and Photolysis of $(Ph_2SiSe)_3$ and $[(Me_3Si)_2SiSe]_2$. The photolysis of hexaphenylcyclotrisilaselenane in D_3 is more complex than $(Me_2SiSe)_3$ and $(Et_2SiSe)_3$, presumably because the initial photoproducts absorb at 254 nm. When a 20:1 mixture of D_3 and $(Ph_2SiSe)_3$ was photolyzed in methylene chloride at 254 nm for 24 h, six products were detected. Only one could be fully characterized: 4,4,6,6,8,8-hexamethyl-2,2-diphenyl-1,5,7,2,4,6,8,3-trioxatetrasilaselenocane (**6**), which was about 20% of the product mixture and is probably the result of insertion of diphenylsilaneselone, $Ph_2Si{=}Se$, into D_3. When a decane solution of $(Ph_2SiSe)_3$ was heated to 275 °C in a sealed tube for 90 h, only starting material was recovered. However, when a mixture of $(Ph_2SiSe)_3$ and a 20-fold excess of D_3 was heated in decane (275 °C, 72 h), $(Ph_2SiSe)_3$ and **6** (30%) were isolated. No tetraphenylcyclodisilaselenane was observed. This implies that, at 275 °C in the absence of a trap, $(Ph_2SiSe)_3$ is fragmenting to produce tetraphenylcyclodisilaselenane and diphenylsilaneselone but the four-membered ring is either converted back to $(Ph_2SiSe)_3$ or decomposed to the silaneselone. We pyrolyzed $(Ph_2SiSe)_3$ in the presence of Et_3SiH in an effort to trap diphenylsilylene. We were unable to detect the insertion product, Et_3Si–$SiPh_2$–H, by GC–MS.

Scheme III



A mixture of tetrakis(trimethylsilyl)cyclodisilaselenane and a 12-fold excess of D_3 in decane were heated in a sealed tube at 250 °C. After 5 days, analysis of the reaction mixture indicated no volatile products and >95% recovery of starting material. Photolysis produced similar results.

Experimental Section

Sodium selenide was produced from selenium powder and sodium pellets that had been cut into chips. Tetrahydrofuran was distilled from sodium benzophenone ketyl immediately before use. Commercially available dichlorosilanes (Petrarch) were used without further purification.

Melting points were obtained by using a Thomas capillary melting point apparatus and are uncorrected. NMR spectra were obtained from Varian Model EM-390, JEOL Model FX90Q, and JEOL GSX400 NMR spectrometers. ^{77}Se NMR spectra were recorded at 76.10 MHz with a 5-mm broad-band probe and temperature control at 25 °C. A sweep width of 130000 Hz (about 1700 ppm) was used, and the spectra were proton decoupled. Samples were prepared as 20–25% by volume solutions in $CDCl_3$. Chemical shifts are reported relative to 25% Me_2Se in $CDCl_3$ (0 ppm).[13] Mass spectra were obtained on Hewlett-Packard 5992 GC-MS, MAT CH-5DF, and MAT CH-7 spectrometers operating at 70 eV. UV spectra were obtained by using a Hewlett-Packard 8451A spectrophotometer. Elemental analyses were done by Galbraith Laboratories (Knoxville, TN). Photolyses were performed in a Rayonet Model RPR reactor.

Synthesis. Tetraethylcyclodisilaselenane and Hexaethylcyclotrisilaselenane. Into a clean, dry, three-necked round-bottomed flask equipped with condenser and nitrogen inlet were charged selenium powder (6.20 g, 0.078 mol), THF (50 mL), sodium chips (3.61 g, 0.156 mol), and naphthalene (2.01 g, 0.016 mol). The mixture was stirred overnight to ensure complete consumption of the sodium, producing a white solid. A rubber septum was placed on the flask, and the flask was cooled to 0 °C. Diethyldichlorosilane (12.3 g, 0.078 mol) was added slowly, with stirring, via syringe. The mixture was warmed to room temperature and stirred for 3 days, eventually turning a dark gray. The mixture was washed with hexane. The hexane wash was

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[13] The ^{77}Se shifts reported here correct those reported earlier,[1] where the use of 20000 Hz sweep widths led to aliasing of the ^{77}Se peaks.

filtered under nitrogen, and the filtrate stripped of solvent. The yellow oil which remained contained naphthalene, $(Et_2SiSe)_2$, and $(Et_2SiSe)_3$. The cyclic silaselenanes were brought to approximately 95% purity by molecular distillation in 40% and 30% yields, respectively. Analytically pure samples of $(Et_2SiSe)_2$ were obtained by preparative GC.

$(Et_2SiSe)_2$. MS: *m/z* 332 (M^+, 27.1%), 303 ($M^+ - Et$, 100%) with correct isotope distribution for two Se atoms. ^1H NMR, 90 MHz (CCl_4): δ 1.00 (s, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 24.4 (CH_2), 7.4 (CH_3). ^{29}Si NMR ($CDCl_3$): δ 8.7. ^{77}Se NMR ($CDCl_3$): δ −330. UV(cyclohexane): λ_{max} 222, $\epsilon = 3.98 \times 10^4$. Anal. Calcd for $C_8H_{20}Se_2Si_2$: C, 29.08; H, 6.10. Found: C, 29.37; H, 6.16.

$(Et_2SiSe)_3$. MS: *m/z* 495 (M^+, 14.3%), 467 ($M^+ - Et$, 6.1%), 303 ($Et_3Si_2Se_2^+$, 100%) with correct isotope distribution for three Se atoms. ^1H NMR, 90 MHz (CCl_4): δ 1.05 (s, CH_2CH_3, signal begins to separate in C_6D_6). ^{13}C NMR ($CDCl_3$): δ 13.4 (CH_2), 7.6 (CH_3). ^{29}Si NMR ($CDCl_3$): δ 25.7. ^{77}Se NMR ($CDCl_3$): δ −334. UV (cyclohexane): λ_{max} 220, $\epsilon = 4.12 \times 10^4$; λ_{max} 254, $\epsilon = 1100$.

Hexamethylcyclotrisilaselenane. Into a clean, dry, three-necked round-bottomed flask equipped with condenser and nitrogen inlet was placed selenium powder (6.0 g, 0.075 mol), sodium chips (3.50 g, 0.15 mol), THF (40 mL), and naphthalene (1.94 g, 0.015 mol). The reactants were stirred overnight to ensure complete consumption of the sodium, producing a white solid. The mixture was cooled to 0 °C, and dimethyldichlorosilane (9.68 g, 0.075 mol) added slowly with stirring via syringe. The mixture was warmed to room temperature and stirred for 3 days. The dark gray mixture was stripped of solvent and washed with hexane. An aliquot of the yellow hexane solution indicated two products. The hexane wash was filtered under nitrogen and stripped of solvent. Molecular distillation was used to obtain **2** (3.6 g, 35% yield) in >93% purity. Attempts to purify **2** by preparative GC led to decomposition. Elemental selenium was observed as a product at the GC exit port. All samples of **2** showed significant decomposition within 3 h at room temperature. MS: *m/z* 411 (M^+, 14.8%), 397 ($M^+ - Me$, 11%), 259 ($Me_3Si_2Se_2$, 37.9%), 73 (100%) with correct isotope distribution for three Se atoms. ^1H NMR ($CDCl_3$): δ 0.91. ^{13}C NMR ($CDCl_3$): δ 8.74. ^{29}Si NMR ($CDCl_3$): δ 15.0. ^{77}Se NMR ($CDCl_3$): δ −236. UV (cyclohexane): λ_{max} 220, $\epsilon = 3.92 \times 10^4$; λ_{max} 254, $\epsilon = 1250$. $(Me_2SiSe)_2$ was also produced in small quantities (6%, GC yield).

Hexaphenylcyclotrisilaselenane and Tetrakis(trimethylsilyl)cyclodisilaselenane. Into a clean, dry, three-necked round-bottomed flask equipped with condenser and nitrogen inlet was placed selenium powder (2.4 g, 0.030 mol), THF (30 mL), sodium pellets (1.4 g, 0.60 mol), and naphthalene (0.80 g, 0.006 mol, 10 mol % with respect to sodium). The mixture was stirred at room temperature for approximately 10 h to ensure complete consumption of the sodium. An addition funnel was placed on the flask and charged with diphenyldichlorosilane (7.5 g, 0.030 mol) dissolved in 20 mL of THF. The flask was cooled to 0 °C, and the dichlorosilane was added dropwise with stirring. After addition was complete, the flask was brought to room temperature and stirred for 3 days. The flask was stripped of solvent, leaving a light yellow semisolid, which, upon analysis by capillary GC showed only naphthalene and a single product. The yellow solid was washed with hexane to give a white solid, which was recrystallized from benzene/hexane. The colorless prismatic crystals (2.5 g, 40%) obtained were identified as **5** (mp 195–7 °C). MS: *m/z* 784 (M^+, 2%), 522 ($Ph_4Si_2Se_2^+$, 8.0%), 259 (Ph_2SiSe^+, 100%) with correct isotope distribution for three Se atoms. ^1H NMR ($CDCl_3$): δ 7.18–7.50 (C_6H_5). ^{13}C NMR ($CDCl_3$): δ 134.8, 134.4, 129.5, 127.5 (C_6H_5). ^{29}Si NMR ($CDCl_3$): δ 3.7. ^{77}Se NMR ($CDCl_3$): δ −287. Anal. Calcd for $C_{36}H_{30}Se_3Si_3$: C, 55.17; H, 3.86. Found: C, 55.27; H, 3.84.

A similar experiment using bis(trimethylsilyl)dichlorosilane produced **6** in 35% yield upon recrystallization from pentane (mp 105–8 °C). MS: *m/z* 506 (M^+, 11.7%), 433 ($M^+ - Me_3Si$, 19.6%), 73 (100%). ^1H NMR ($CDCl_3$): δ 0.2. ^{13}C NMR ($CDCl_3$): δ −2.5. ^{29}Si NMR ($CDCl_3$): δ −0.82 ($-SiMe_3$), −16.38 (Se–Si–Se). ^{77}Se NMR ($CDCl_3$): δ −614. Anal. Calcd for $C_{12}H_{36}Se_2Si_6$: C, 28.44; H, 7.16. Found: C, 28.66; H, 7.19.

Photolysis of Cyclotrisilaselenanes in the Absence of a Trap. Hexaethylcyclotrisilaselenane. A clean, dry, three-necked round-bottomed flask was charged with hexane (5 mL), decane (0.4 mL, used as an internal standard), and $(Et_2SiSe)_3$. The reaction mixture was degassed by bubbling nitrogen through the solution for 5–10 min and then syringed into a clean, dry 25-mL quartz Erlenmeyer flask with condenser. The quartz Erlenmeyer was then placed within a Rayonet photochemical reactor equipped with 254-nm lamps and photolyzed. The reaction was monitored by GC analysis of aliquots removed from the reaction mixture. After approximately 12 h, a black solid discharge appeared on the walls of the quartz Erlenmeyer, and the reaction mixture had turned yellow. After 48 h, all of $(Et_2SiSe)_3$ was consumed, and the only observed product was $(Et_2SiSe)_2$ (90%, calculated from GC analysis).

Hexamethylcyclotrisilaselenane. A solution of $(Me_2SiSe)_3$ (220 mg, 0.49 mmol), in hexane was degassed and photolyzed in the usual manner. Usually, reactions involving photolysis of methylated rings were accompanied by a greater discharge of black solid than reactions involving ethylated rings. After 30 h of photolysis, no cyclotrisilaselenane remained, and only one product was observed. The reaction mixture was cooled to −78 °C in dry ice/acetone producing a light yellow solid. The hexane was removed by syringe at −78 °C and the solid warmed to room temperature, where it became a yellow oil. In order to remove hexane completely without decomposing the product, pentafluorobromobenzene was added to permit exhaustive pumping. This permitted unambiguous NMR assignments of proton peaks. The unstable oil was identified as tetramethylcyclodisilaselenane (100 mg, or 50% yield). ^1H NMR (C_6F_5Br): δ 1.0 (s, $SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 12.5. ^{29}Si NMR (hexane): δ −8.0. ^{77}Se NMR (hexane): δ −199. *m/z* 272 (M^+, 4.0%), 257 ($M^+ - Me$, 8.5%) with appropriate isotope distribution for two selenium atoms, 73 (100%). The compound is stable for approximately 1 day in solution at room temperature. Upon removal of solvent, the oil deposits a red solid, presumably selenium, within a few minutes.

Photolysis of Cyclotrisilaselenanes and Cyclodisilaselenanes in the Presence of D_3. Hexaethylcyclotrisilaselanane. In a typical experiment, a clean, dry round-bottomed flask equipped with nitrogen inlet was charged with $(Et_2SiSe)_3$ (200 mg, 0.40 mmol), D_3 (1.80 g, 5 mmol, 20-fold excess), and hexane (5 mL) producing a colorless solution. The reaction mixture was degassed and photolyzed in the usual manner, leading to the discharge of black solid and yellow solution. The progress of the reaction was monitored by GC analysis of aliquots removed from the reaction mixture. After 28 h, $(Et_2SiSe)_3$ was consumed and two new products were formed. One product was identified as $(Et_2SiSe)_2$. The other product was isolated by preparative GC and was identified as 4,4,6,6,8,8-hexamethyl-2,2-diethyl-1,5,7,2,4,6,8,3-trioxatetrasilaselenocane (**4**). MS: *m/z* 388 (M^+, 2.3%), 373 ($M^+ - Me$, 6.1%), 359 ($M^+ - Et$, 100%) with appropriate isotope distribution. ^1H NMR, 300 MHz ($CDCl_3$): δ 1.05–0.8 (m, 10 H, CH_2Me), 0.5 (s, 6 H, Se–$SiMe_2$), 0.12 and 0.11 (2 s, 12 H, O–$SiMe_2$). ^{13}C NMR ($CDCl_3$): δ 11.7 (CH_2), 7.0 and 6.8 ($-CH_2CH_3$ and Se–$SiCH_3$), 9.1 and 8.8 (O–$SiCH_3$). ^{29}Si NMR ($CDCl_3$): δ 3.1, −2.4, −23.0, −23.3. ^{77}Se NMR ($CDCl_3$): δ −292. Anal. Calcd for $C_{10}H_{28}O_3SeSi_4$: C, 30.98; H, 7.28. Found: C, 31.40; H, 7.37.

Hexamethylcyclotrisilaselenane. Photolysis of $(Me_2SiSe)_3$ under the above conditions gave octamethyl-1,5,7,2,4,6,8,3-trioxatetrasilaselenocane (**3**). MS: *m/z*: 360 (M^+, 18.5%), 345 ($M^+ - Me$), 100%). ^1H NMR ($CDCl_3$): δ 0.6 (s, $Me_2SiSeSiMe_2$), 0.1 (s, $Me_2SiOSiMe_2$). ^{13}C NMR ($CDCl_3$): δ 6.79 ($Me_2SiSeSiMe_2$), 1.14 ($Me_2SiOSiMe_2$). ^{29}Si NMR ($CDCl_3$): δ 9.3, −21.9. ^{77}Se NMR ($CDCl_3$): δ −245. Anal. Calcd for $C_8H_{24}O_3SeSi_4$: C, 26.72; H, 6.73. Found: C, 26.71; H, 6.85.

Sealed Tube Thermolyses of Cyclotri- and Cyclodisilaselenanes. In a typical experiment, a benzene solution of $(Ph_2SiSe)_3$ (250 mg, 0.31 mmol) and D_3 (1.38 g, 6.20 mmol, 20-fold excess) was degassed in the usual manner and then syringed into a Pyrex tube under nitrogen, which was sealed with a Teflon stopcock. The tube was placed in a sand bath at 250 °C and the reaction monitored by GC analysis of aliquots removed from the reaction mixture. After 24 h, the reaction mixture began to turn green. After 72 h, the tube was removed from the reaction mixture and cooled. An aliquot of the reaction mixture was analyzed by GC, and two products were observed. The reaction mixture was stripped of solvent and washed with pentane, leaving a white solid, which was identified as $(Ph_2SiSe)_3$. Pentane was stripped from the wash, leaving a solid (90% purity), which was identified as

4,4,6,6,8,8-hexamethyl-2,2-diphenyl-1,5,7,2,4,6,8,3-trioxatetrasilaselenocane (**6**). MS: *m/z* 484 (M^+, 32.2%), 469 (M^+ - Me, 40.24%), 407 (M^+ - Ph, 14%), 251 ($Me_6Si_4O_3^+$, 100%) with appropriate isotope distribution. ^{1}H NMR ($CDCl_3$): δ 7.1 (s, broad, C_6H_5), 0.2 (s, broad, Si-Me). ^{13}C NMR ($CDCl_3$): δ 137.4, 134.1, 130.0, 127.8 ($-C_6H_5$), 1.0 ($-CH_3$). ^{29}Si NMR ($CDCl_3$): δ 3.3, -16.6, -17.1, -17.7. ^{77}Se NMR ($CDCl_3$): δ -234. An analytically pure sample was obtained by preparative GC. Anal. Calcd for $C_{18}H_{28}O_3SeSi_4$: C, 44.71; H, 5.84. Found: C, 45.07; H, 5.98.

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Insertion of Acetylenes into Carbon–Hydrogen Bonds Catalyzed by Rhodium–Trimethylphosphine Complexes

William T. Boese and Alan S. Goldman*

Department of Chemistry, Rutgers—The State University of New Jersey,
New Brunswick, New Jersey 08903

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The insertion of terminal acetylenes ($RC{\equiv}CH$) into benzene C—H bonds has been found to be photochemically ($\lambda > 350$ nm) catalyzed by $Rh(PMe_3)_2(CO)Cl$. Chemical yields (e.g. R = *t*-Bu, 58%; R = *p*-$MeOC_6H_4$–, 95%) and turnover numbers (>200/Rh) are fairly good, although the quantum efficiency is low (e.g. $\lambda = 366$ nm, R = *p*-$MeOC_6H_4$, $\varnothing = 3.6 \times 10^{-3}$). Crossover experiments reveal that both the H atom and Ph group added to the triple bond are derived from the same molecule of benzene. The orientation of addition is dependent upon the R group; for R = aryl, exclusively 1,1-substituted (branched) olefins are produced, while for R = *n*-propyl or *tert*-butyl a mixture of 1,1- and 1,2-substituted (linear) olefins is formed. The linear olefins are those resulting from exclusively syn addition across the C≡C bond. These results are consistent with a mechanism that involves a concerted addition across a triple bond; in particular addition of the Rh—H bond of a hydridophenylrhodium species is suggested. Additional results consistent with such a pathway include a primary isotope effect ($k_{C_6H_6/C_6D_6} = 1.4$) and a reactivity order among alkynes (and olefins) that is inconsistent with a variety of nonconcerted pathways such as transfer of hydrogen atom or hydride. Labeling experiments reveal that the stereochemistry of the branched olefinic products is that resulting from anti addition across the triple bond; possible mechanistic implications are discussed. In a nonphotochemical reaction, $[(Rh(PMe_3)_2Cl]_2$ efficiently catalyzes the dimerization of terminal acetylenes by insertion into the acetylenic C—H bond. Similar reactivity patterns are found between this reaction and the $Rh(PMe_3)_2(CO)Cl$-catalyzed reaction with benzene. All products from the dimerization result from syn addition.

A large body of reactions of hydrocarbons with low-valent soluble transition-metal complexes has been developed in the past decade.[1] Progress toward the goal of *catalytic* functionalization has also been made in this field but has been considerably more limited.[2-6] Notably, several such examples have been revealed by complexes of the form $RhL_2(CO)Cl$ (L = PPh_3,[7] PMe_3[8-13]). These have been found to photochemically catalyze a variety of C—H bond functionalization reactions including arene[7,8] and alkane[8] carbonylation, aldehyde decarbonylation,[7,8] alkane[9,13] and arene[10] dehydrogenation and transfer dehydrogenation, and the insertion of isocyanides into benzene C—H bonds.[11] The insertion of olefins into C—H bonds with very low yields (<5%)[14] has also been reported.[12] Herein

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