Thermal and Photochemical $[2+2]$ Cycloreversion of a 1,2-Disilacyclobutane and a 1,2-Digermacyclobutane

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Abstract: Upon heating of the highly sterically congested 1,1,2,2-tetakis(trimethylsilyl)dispiro[3,3′,4,4′-biadamantane-1,2-disilacyclobutane] (2) in solution in the presence of trapping reagents, such as 1,3-butadienes, styrene, phenylacetylene, and methanol, the trapping products of the silene bis(trimethylsilyl)adamantylidenesilene (1) are formed with high regioselectivity and good yields. Photolysis of 2 at $-196 \, ^\circ \text{C}$ in anhydrous THF in the absence of trapping agents produces tetrakis(trimethylsilyl)disilene (3). Photolysis of 2 in solution in the presence of 1,3-butadiene leads to a 2:1 mixture of 1,1,2,2-tetakis(trimethylsilyl)-1,2-disilacyclobutane (10) and 2,2′-bis(trimethylsilyl)-1,2-disilacyclobutane-3-ene (11). The trapping product of bis(trimethylsilyl)silylene (4) and one 1,2-disilacyclobutane (2) with 2,2′-biadamantylidene. The results of laser flash photolysis and additional trapping experiments suggest that the sole primary product in the photoysis of 2 is the silene 3, which dissociates under further irradiation to produce the silylene 4. Heating of 1,1,2,2-tetakis(trimethylsilyl)dispiro[3,3′,4,4′-biadamantane-1,2-digermacyclobutane] (14) in solution results in the quantitative formation of 2,2′-biadamantylidene and of germanium-containing oligomers, while neither bis(trimethylsilyl)adamantylidene (15) nor tetrakis(trimethylsilyl)germylene (16) could be trapped. Upon photolysis of 14 behaves similarly to 2, leading to 16 and 17, which could be trapped by 1,3-butadiene.

1. Introduction

The chemistry of small rings containing silicon is a fast growing area of organosilicon chemistry.1 Many novel compounds of this type were recently synthesized, providing access to many novel compounds, especially to derivatives with low-coordinated silicon, e.g., silenes ($Si=CR_2$), disilenes ($R_2Si=SiR_2$), and silylenes ($RSi_3$).1,2

Recently we found that the reaction of (Me$_3$Si)$_2$SiLi:3THF with 2-adamantane leads via a Peterson-type reaction to the novel silene, bis(trimethylsilyl)adamantylidenesilene (1), which is the absence of trapping agents spontaneously dimerizes in a head-to-head fashion to give 1,1,2,2-tetakis(trimethylsilyl)-dispiro[3,3′,4,4′-biadamantane-1,2-disilacyclobutane] (2).3

The X-ray analysis of the molecular structure of 2 reveals extremely congested ring. The sterically congested ring exists in a very substantial elongation of the ring bonds, i.e., $r(C-C) = 1.647(5)$ Å, $r(C-Si) = 2.008(3)$ Å, and in strong puckering of the central 1,2-disilacyclobutane ring (the ring C-Si=Si dihedral angle is 39.6°).3 The extreme steric congestion in 2 can be relieved by fragmentation along two pathways to produce (i) two molecules of the silene 1 (Scheme 1, path a) or (ii) the disilene 3 and/or the silylene 4 and 2,2′-biadamantylidene (5) (Scheme 1, path b).

It is known that 1,2-disilacyclobutanes with bulky substituents easily dissociate thermally to yield silenes.2,4 For example, 1,1,2,2-tetakis(trimethylsilyl)-3,4-di-tert-butyl-1,3,4-bis(trimethylsilyloxy)-1,2-disilacyclobutane was found to be in equilibrium in solution with the corresponding silene.4 We have suggested

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recently that the thermal [2+2] cycloreversion of a 1,2-disilacyclobutane, similar to 2, leads to the disilene \((\text{Me}_3\text{Si})_2\text{Si} \equiv \text{Si}(\text{SiMe}_3)_2\).\(^5\)

The presence of a chain of four silicon atoms in 2 suggests that like other oligosilanes\(^6\) 2 may also undergo photolytic reactions, such as a photolytic [2+2] cycloreversion reaction. This idea is supported by the fact that numerous small cyclic polysilanes yield under both thermal and photolytic conditions disilenes and silylenes.\(^1,2\) The above considerations led us to believe that the 1,2-disilacyclobutane 2 might undergo [2+2] cycloreversion reactions according to both path a and path b in Scheme 1, depending on the reaction conditions. The results of our thermal and photolysis experiments are reported below.

2. Results and Discussion

a. Thermal Reactions of 2. Heating of 2 in hexane at 60–100 °C in the absence of trapping reagents leads to slow decomposition, but specific attempts to detect the presence of 1, 3, or 4 in the reaction mixture by NMR or UV/vis spectroscopy failed. However, in the presence of trapping reagents, known to react with silenes, such as methanol, styrene, phenylacetylene, and 1,3-butadienes (e.g., 1-methoxy-1,3-butadiene),\(^2\) the expected trapping products of the silene 1, 6–9, respectively, are formed\(^7\) (Scheme 2). Interestingly these reactions are highly regioselective, leading to only one out of the two possible regiosomeric cycloadducts. Trapping products of the disilene 3 or of the silylene 4 could not be detected under these conditions. We conclude that the thermal [2+2] cycloreversion of 2 leads exclusively to two molecules of the silene 1 (Scheme 1, path a).

b. Photolytic Reactions of 2. Continuous photolysis of 2 at 254 nm in degassed hexane or methylcyclohexane was studied both in the presence and in the absence of trapping agents. Photolysis of 2 at \(-196{\circ}\text{C}\) in methylcyclohexane in the absence of trapping agents produces a green glass whose spectrum shows a maximum at 415 nm and a weaker band at 346 nm (Figure 1). This spectrum is identical to that previously reported for \((\text{Me}_3\text{Si})_2\text{Si} \equiv \text{Si}(\text{SiMe}_3)_2\) (3)\(^8d\) and is very close to those of other known tetrakis(trialkylsilyl)disilenes.\(^8\) Upon annihilation of the matrix the green color disappears and the solution becomes colorless.

When the photolysis of 2 is carried out in hexane at \(-78{\circ}\text{C}\) the solution becomes violet and its spectrum shows a very broad maximum at 538 nm (Figure 1). The violet color due to the 538 nm absorption is persistent for several hours at \(-78{\circ}\text{C}\). If 5% of THF is added the solution turns red, the absorption peak at 538 nm disappears, and a weak broad absorption in the range of 550–650 nm remains. These observations are consistent with the interpretation that the violet solution contains a silylene(s) absorbing at around 540 nm, which upon addition of THF form(s) a silylene–THF complex. The formation of the complex results in a bathochromic shift of the absorption (unfortunately, we could not identify the exact location of the absorption peak within the broad absorption range of 550–650 nm), as has been previously observed for other silylenes.\(^9\) The identity of the species absorbing at 538 nm (denoted as X) could not be determined but we can exclude several possibilities. X cannot be dimethylsilylene or other simple alkyl silylenes because these silylenes absorb around 450–470 nm.\(^1b\) It is also unlikely that X is \((\text{Me}_3\text{Si})\text{MeSi}\), which was calculated to absorb

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\(^{(7)}\) For data on the trapping products of 1 with 1,3-butadienes (e.g. 9) see ref 3. The other trapping products are described in the Experimental Section.

Scheme 3

around 680 nm, or (Me₃Si)₂Si (4), which is predicted to absorb at an even longer wavelength of 987 nm (this absorption lies beyond the lower measurement limit of our spectrophotometer). In agreement with the theoretical predictions of a strong “red-shift” of the silylene absorption by silyl substitution, Kira et al. have reported that the longest wavelength absorption band of Mes(Me₃Si)Si is at 760 nm.

Our tentative explanation for the 538 nm absorption is that in the absence of trapping agents (Me₃Si)₂Si: (4), which is formed in the reaction mixture (see below), undergoes re-arrangements (possibly with silicon chain degradation) to other silylenes having bulky alkyl substituents attached to the silylene center. Such silylenes were reported to absorb in the range of 530–550 nm, i.e., in the region of the observed peak in the photolysis of 2. Thermolytic degradation of (Me₃Si)₂Si: (4) to produce other silylenes has been described previously by other researchers. Another possibility is that the 538 nm absorption is due to radicals. The violet solution shows a peak (without fine structure) with g ~ 2.0 G, in the ESR spectrum. This supports the presence of radicals in the photolysis reaction mixture, but these are probably not silyl-centered radicals which are known to absorb in the range of 210–430 nm. As the trapping experiments of the violet solution with butadiene, Et₃SiH, or Bu₃SnH gave only trapping products of 3 and 4 and as these species do not absorb at 538 nm, it is clear that X is either not trapped by the above-mentioned reagents or is present in very low concentrations and therefore its trapping products elude detection. Further studies are required to determine the identity of all the species which are involved in the continuous photolysis of 2, and in particular of the species which is responsible for the 538 nm absorption.

Continuous photolysis of 2 in the presence of trapping reagents confirmed the presence of both the disilene 3 and the silylene 4 in the reaction mixture. In the presence of 1,3-butadiene the photolysis of 2 in hexane (at both −78 °C and at room temperature) leads to a 2:1 mixture of 1,2-disilacyclopentene 10 (the trapping product of the disilene 3) and of silacyclopentene 11 (formally the trapping product of the silylene 4), together with 2,2-biadamantylidene (5) (Scheme 3). However, we also found that the photolysis of isolated 10 produces 11. We therefore conclude that 11 probably results mostly from secondary photolysis of 10 as its concentration builds up, and not from direct trapping of 4. This conclusion is consistent with the flash-photolysis experiments described below. However, the presence of (Me₃Si)₂Si: in the photolysis product mixture is supported by the results of photolysis of 2 in the presence of Et₃SiH or Bu₃SnH (the latter does not serve as a trap for the disilene 3), which yielded the expected insertion products of 4, i.e., 12 and 13, respectively (Scheme 4). We did not find even traces of the trapping products of the disilene 3 by Et₃SiH or Bu₃SnH. This finding is consistent with the known much higher reactivity of Et₃SiH and Bu₃SnH with silylenes than with disilenes, this differentiation being more significant for Et₃SiH. At this point, we do not have information about the efficiency of the photodisociation of the disilene 3 to the silylene 4, or about the contribution of other processes to the generation of 4. Trapping products of the silene 1 were also not detected under these photolytic conditions. Thus, we conclude that the continuous photolytic [2+2] cycloreversion of 2 follows exclusively path b in Scheme 1.

From the results of the continuous photolysis experiments it is impossible to differentiate unambiguously between the following mechanistic possibilities: (a) the silylene (Me₃Si)₂Si: (4) is formed in an extrusion process from 2 and then it dimerizes to the disilene 3; (b) 3 and 4 are formed in parallel processes; or (c) the disilene 3 is the primary product and...
(Me₂Si)₂Si is produced by its subsequent photodissociation. The observed photolysis spectrum at −196 °C (see above) seems to support the idea that the disilene 3 is formed first and that the silylene 4 results from its subsequent photodissociation.

To probe further the mechanism of the photolysis of 2, a series of nanosecond laser flash photolysis experiments were carried out, using a KrF excimer laser (248 nm) as the excitation source. Flash photolysis of deoxygenated, 0.001 M solutions of 2 in cyclohexane or isooctane gave rise to readily detectable, long-lived transient absorptions which decayed with mixed first- and second-order kinetics. The spectrum, recorded in point-by-point fashion 10–20 µs after the laser pulse, is shown in Figure 2 along with a typical transient decay profile. The spectrum shows the presence of a peak at 410 nm. In extensively deoxygenated solution and with low laser intensities, the transient decays with pseudo-first-order kinetics and exhibits a lifetime of ~750 ms, a value that probably reflects quenching by residual oxygen in the solvent (vide infra). The above lifetime value rules out the formation of the silylene 4 at the initial stage of photolysis, since silylenes generally have a much shorter lifetime at room temperature (e.g., 200–380 ns for Me₃Si;³⁸ 40–50 ns for i-Pr₂Si;³⁸ 8a and t-BuMeSi;³⁸ all in methylcyclohexane). The decay

![Scheme 4](image-url)
kinetics were identical throughout the 250–430 nm spectral range, suggesting that the spectrum shown in Figure 2 is due to a single transient species. The growth of the signal at 410 nm could not be resolved from the laser pulse (~15 ns full width), indicating that the species is formed as a primary photoproduct. The spectrum in Figure 2 is similar to that reported previously for the product of photolysis of octakis-(trimethylsilyl)cyclotetrasilane and assigned to disilene 3. It is identical to the spectrum observed on photolysis of 2 at 77 K (Figure 1).

Addition of methanol, 2,3-dimethyl-1,3-butadiene (DMB), or oxygen to isooctane solutions of 2 resulted in a shortening of the lifetime of the transient and a change to clean pseudo-first-order decay kinetics. Quenching rate constants (k_q) were determined from plots of the decay rate constant (k_{decay}) versus quencher concentration according to eq 1, where k_o is the pseudo-first-order decay rate constant in the absence of quencher Q.

\[ k_{\text{decay}} = k_o + k_q [Q] \]  

These plots were linear in each case, and afforded the following second-order quenching rate constants (in units of M^{-1} s^{-1}): MeOH, (3.0 ± 0.1) × 10^5; O_2, (1.1 ± 0.1) × 10^6; 2,3-dimethylbutadiene, (4.0 ± 0.2) × 10^4. Comparison of the rate constant for quenching of the disilene 3 by MeOH to those reported previously for the addition of ethanol to PhMeSi=SiMe_2 (k = 1.7 × 10^3 M^{-1} s^{-1}) and PhMeSi=SiMePh (k = 1.9 × 10^8 M^{-1} s^{-1}) in methycyclohexane suggests that disilene 3 exhibits significantly greater kinetic stability than alkyl- or aryl-substituted disilenes.

The results of the flash-photolysis experiments suggest that the sole primary product of the photolysis of 2 is tetrakis-(trimethylsilyl)disilene (3), which can be trapped by 1,3-butadiene to yield the cycloadduct 10. In the absence of trapping agents the disilene disappears (the resulting silicon containing products were not identified) following (at high laser intensities) second-order decay kinetics. The second-order decay may suggest that the disilene polymerizes, but additional studies are required to support this conclusion. No evidence for the primary formation of silylene 4 could be obtained in these experiments, although as noted above, its absorption spectrum may lie outside of our limits of detection. However, the steady-state trapping experiments with Et_3SiH and Bu_3SnH described above strongly support the intermediacy of silylene 4 in the photolysis of 2. If 4 is not a primary product, then it must be formed by secondary photolysis of disilene 3 or its butadiene trapping product (10). We believe that 3 is indeed photolyzed in solution at room temperature to produce 4, but instrumental limitations have prevented us from verifying this point, and this is the subject of future investigations. The entire photolytic reaction sequence as we believe it occurs is shown in Scheme 4.

c. Thermal and Photolytic [2+2] Cycloreversion Reactions of the 1,2-Digermaryclobutane 14. We have recently reported that in analogy to the reaction of (Me_3Si)_2SiLi:3THF with 2-adamantanone, the reaction of (Me_3Si)_2GeLi:3THF with 2-adamantanone leads to the corresponding germene, bis-(trimethylsilyl)adamantylidenegermene (15). Like 1, 15 also spontaneously dimerizes in a head-to-head fashion to give 1,1,2,2-tetrakis(trimethylsilyl)dispiro[3,3,3,8b] adamantane-1,2,3-digermaryclobutane (14), the first known 1,2-digermaryclobutane. Upon heating, 14 exhibits an entirely different behavior from that of its silicon analogue 2 (see Scheme 1, path a). Thus, heating of 14 to 60 °C in degassed benzene or hexane leads to the quantitative formation of 2,2′-diamantylidenelignane (5) and a mixture of germene-containing compounds which were not fully characterized. Attempts to obtain trapping products of the germene (Me_3Si)_2Ge=2-Ad (15) by heating 14 in hexane in the presence of suitable concentrations of various trapping reagents (e.g., 1,3-butadienes, methanol) failed. We therefore suggest that 14 (in contrast to 2) does not revert upon heating to the corresponding germene 15, but instead undergoes cleavage of the C−Ge bonds to give the dimerene (Me_3Si)_2Ge=Ge-Si(Me_3) (16), which at 60 °C polymerizes before it can be trapped (Scheme 5).

In contrast to the thermolysis, the photolysis at 254 nm of the digermacyclobutane 14 proceeds in close analogy to the photolysis of the disilacyclobutane 2. At ~196 °C in methycyclohexane, in the absence of trapping agents, a green glass showing a spectrum with a maximum at 410 nm and a weaker band at 352 nm was observed. This spectrum is almost identical to that described above for (Me_3Si)_2Si=Si(Me_3) (3) and very close to those of other known tetrakis(trialkylsilyl)digermenes. Furthermore, the 410 nm peak is slightly blue-shifted, by ca. 5 nm, relative to that in 3 (in methycyclohexane), as was observed for other pairs of digermenes and disilenes, and we therefore suggest that it corresponds to the, previously unknown, dimerene (Me_3Si)_2Ge=Ge(SiMe_3) (16).

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The photolysis of 14 at −78 °C in the presence of 1,3-butadiene (0.2 M) produces, in addition to 2,2′-biadamantylidene (5), the expected trapping products of the digermene 16 and of the germene (Me3Si)2Si (17), i.e., the 1,2-digermacyclobutene 18 and the germacyclopentene 19, respectively (Scheme 6), in a ratio of ca. 5:1. By analogy to the photolysis of 2 we suggest that also in the photolysis of the 1,2-digermacyclobutane 14, the primary product of the [2+2] photocycloreversion is the digermene 16, which under further irradiation dissociates to produce the bis(trimethylsilyl)germylene (17).

3. Conclusions

We have found an unusual dual [2+2] cycloreversion behavior of the 1,2-disilacyclobutane, which in solution readily undergoes both thermal and photolytic [2+2] cycloreversion reactions. Under thermal conditions the silene (Me3Si)2Si (2-Ad) is produced. Photolysis yields the disilene (Me3Si)2Si (14), which undergoes subsequent photodissociation to produce the silylene (Me3Si)2Si (2-Ad) (4). The analogous 1,2-digermacyclobutane 14 undergoes both thermal and photolytic [2+2] cycloreversion to give the previously unknown digermene (Me3Si)2Ge=Ge(SiMe3)2 (16), whose photodissociation produces the germene (Me3Si)2Ge (17).

4. Experimental Section

Instruments and Procedures. NMR spectra were measured at room temperature in CDCl3 or C6D6 solutions with Bruker EM-200 or Bruker-400 MHz instruments. MS measurements were performed on a Finnigan MAT TSQ 45 triple stage quadrupole mass spectrometer. UV-visible spectra were measured in hexane on a Hewlett-Packard 8451A Diode-Array UV/vis spectrophotometer, using standard or evaporated 10 mm cells. Nanosecond laser flash photolysis experiments employed the pulses (248-nm, ~15 ns, 80~120 mJ) from a KrF excimer laser and a microcomputer controlled detection system.20 The spectral beam consisted of the focused output from a 150-W high-pressure Xe arc lamp (Oriel), and was not pulsed. Solutions were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was ca. 0.7 (0.001 M) and were flowed continuously through a 3 × 7 mm Suprasil flow cell connected to a calibrated 100 mL reservoir. Nitrogen or nitrogen–oxygen mixtures were bubbled continuously through the reservoir throughout the experiments. Quenchers were added directly to the reservoir by microliter syringe as aliquots of standard solutions or the neat liquids. Rate constants were calculated by linear least-squares analysis of decay rate–concentration data (6~10 points) which spanned at least a factor of 5 (usually more than 1 order of magnitude) in the transient decay rate. Errors are quoted as twice the standard deviation obtained from the least-squares analysis in each case. Transient absorption spectra were recorded in point-by-point fashion over selected time windows after the laser pulse.

Trapping under Thermal Conditions. A typical procedure is as follows: 1.25 g (2 mmol) of 2 and 6 mmol of a trapping agent in 30 mL of dry hexane were placed in a Schlenk flask under vacuum. The solution was heated at 60 °C for 24 h. Hexane was evaporated and the residue was washed with 2 × 20 mL of methanol. Methanol was evaporated and the crude product was further purified by column chromatography on silica gel with a 10:1 hexane/ether mixture as eluent.

2-[Bis(trimethylsilyl)methoxyethyl]adamantane (6). Yield after purification 92%.1 H NMR (CDCl3): δ 0.147 (18H, s, Me3Si); 1.65~2.10 (15H, m, Ad); 3.44 (3H, s, OMe). 13C NMR (CDCl3): δ 126.08, 127.41, 127.61, 128.34, 132.77 (Mä). CI-MS: m/z 341 (M+ + 1, 100), 325 (M+ + Me, 60), 267 (M+ + SiMe3, 5). EI-MS: m/z 325 (M+ + Me, 100), 267 (M+ + SiMe3, 45). Anal. Calcd for C17H36Si3: C, 59.93; H, 10.65. Found: C, 59.41; H, 10.98.

1,1-Bis(trimethylsilyl)-3-phenylspiro[2,2-adamantane-1-silacyclobutene (7). Yield after purification 87%.1 H NMR (CDCl3): δ 0.364 (18H, s, Me3Si); 0.832 (1H, d, J = 6.4 Hz, CH2-ring); 1.085 (1H, d, J = 7.0 Hz, CH2-ring); 1.32~2.29 (14H, m, Ad); 3.62 (1H, t, CH-ring); 7.18~7.39 (5H, m, Ph). 13C NMR (CDCl3): δ 121.33 (Mä); 122.57 (Mä); 127.92 (Mä); 132.77 (Mä); 147.60 (Ph). 

13Si NMR (CDCl3): δ −14.78, −15.18 (SiMe3, 24.00 (Si-ring). CI-MS: m/z 412 (M+ + 97); 397 (M+ + Me, 18); 335 (M+ + Ph, 59); 308 (M+ + PhCH=CH2, 100). EI-MS: m/z 412 (M+ + 2); 308 (M+ + PhCH=CH2, 100); 235 (M+ + PhCH=CH2-SiMe3, 7). Anal. Calcd for C17H36Si: C, 69.82; H, 9.77. Found: C, 69.10; H, 9.35.

1,1-Bis(trimethylsilyl)-3-phenylspiro[2,2-adamantane-1-silacyclo-3-butene (8). Yield after purification 76%.1 H NMR (CDCl3): δ 0.180 (18H, s, Me3Si); 1.36~2.14 (14H, m, Ad); 6.06 (1H, t, CH); 7.13~7.20 (5H, m, Ph). 13C NMR (CDCl3): δ 0.48 (Me3Si); 28~41 (Ad); 126.08, 127.41, 127.61, 128.34, 132.77 (CH=CH2, 172.99 (Ph=Cä). CI-MS: m/z 411 (M+ + 11, 100); 395 (M+ + Me, 17); 337 (M+ + MeSi, 18); 333 (M+ + Ph, 21). HR-MS: m/z 410.2266; C17H36Si requires 410.2268. Anal. Calcd for C17H36Si: C, 70.17; H, 9.32. Found: C, 70.45; H, 9.67.

Trapping under Photolytic Conditions. A typical procedure is as follows: 1.25 g (2 mmol) of 2 and 6 mmol of a trapping agent in 30 mL of dry hexane were placed in a quartz ampule under vacuum. The solution was irradiated (254 nm) at −78 °C or at room temperature for 2 h. Hexane was evaporated, the residue was washed with 2 × 20 mL of methanol, the methanol was evaporated, and the products were separated by column chromatography on silica gel with a 10:1 hexane/ether mixture as eluent.

In the photolysis of 2 in the presence of Et3SiH analysis of the reaction mixture by GC-MS showed 15% of triethylsilylbutyryl-1,1-bis(trimethylsilyl)adamantane (12). EI-MS: m/z 290 (M+, 10); 275 (M+ + Me, 35); 216 (M+ + Me3Si, 32); 188 (M+ + Me3SiCH=CH2, 31); 160 (M+ + Me3Si, 2-CH=CH2, 100). The other products were not identified.

In a similar photolysis experiment of 2 in the presence of Bu3SnH we observed by GC-MS the formation of 10% of tributylstannylbis-
(trimethylsilyl)silane (13). EI-MS: \( m/z \) 409 (M\(^+\) – C\(_2\)H\(_5\)CH\(_2\) – 10); 353 (M\(^+\) – 2C\(_2\)H\(_5\)CH\(_2\)); 353 (M\(^+\) – 2C\(_2\)H\(_5\)CH\(_2\) – CH\(_3\)); 353 (M\(^+\) – 3C\(_2\)H\(_5\)CH\(_2\) – Me\(_3\)Si, 15); 73 (M\(^+\) – Me\(_3\)Si(H)SiSnBu\(_3\), 100). The other products were not identified.

**Photolysis of 2 in the Presence of Butadiene.** (a) 1,1,2,2-Tetrakis(trimethylsilyl)-1,2-disilacyclohex-4-ene (10). Yield after purification 54%. \(^1\)H NMR (CDCl\(_3\)): \( \delta \) 0.167 (36H, s, Me\(_3\)Si); 1.51 (4H, d, \( J = 4 \) Hz, CH\(_2\)-ring); 5.67 (2H, m, HC\(_{22}\)CH). \(^13\)C NMR (CDCl\(_3\)): \( \delta \) 1.35 (Me\(_3\)Si); 7.76 (CH\(_2\)-ring); 127.5 (C\(_d\)C). \(^29\)Si NMR (C\(_6\)H\(_6\)): \( \delta \) -12.425 (Me\(_3\)Si); -81.955 (Si-ring). EI-MS: \( m/z \) 402 (M\(^+\), 5); 387 (M\(^+\) – Me, 3); 348 (M\(^+\) – C\(_2\)H\(_5\)CH\(_2\)-CH\(_2\), 40), 329 (M\(^+\) – Me\(_3\)Si, 60). HR-MS: 402.1916, C\(_{16}\)H\(_{42}\)Si\(_6\) requires 402.1902. Anal. Calcd for C\(_{16}\)H\(_{42}\)Si\(_6\): C, 47.68; H, 10.50. Found: C, 47.94; H, 10.83.

(b) 1,1-Bis(trimethylsilyl)-1-silacyclopent-3-ene (11). Yield after purification 22%. \(^1\)H NMR (CDCl\(_3\)): \( \delta \) 0.089 (18H, s, Me\(_3\)Si); 1.60 (4H, s, CH\(_2\)-ring); 5.86 (2H, m, HC\(_{22}\)CH). \(^13\)C NMR (CDCl\(_3\)): \( \delta \) -1.14 (Me\(_3\)Si); 13.44 (CH\(_2\)-ring); 131.8 (HC\(_{22}\)CH). EI-MS: \( m/z \) 228 (M\(^+\), 15); 213 (M\(^+\) – Me, 3); 154 (M\(^+\) – Me\(_3\)Si, 100). HR-MS: 228.1191, C\(_{10}\)H\(_{24}\)Si\(_3\) requires 228.1186. Anal. Calcd for C\(_{10}\)H\(_{24}\)Si\(_3\): C, 42.55; H, 10.50. Found: C, 42.22; H, 10.40.

**Photolysis of 14 in the Presence of Butadiene.** (a) 1,1,2,2-Tetrakis(trimethylsilyl)-1,2-digermacyclohex-4-ene (18). A 1.42 g (2 mmol) sample of 14 and 0.32 g (6 mmol) of 1,3-butadiene in 30 mL of dry hexane were placed in a quartz ampule under vacuum. The solution was irradiated at \(-78^\circ\)C or at room temperature for 2 h. Hexane was evaporated and the residue was washed with 2 \( \times \) 20 mL of methanol. Methanol was evaporated and the products was separated by column chromatography on silica gel with a 10:1 hexane/ether mixture as eluent. Yield of 18 after separation 45%. \(^1\)H NMR (CDCl\(_3\)): \( \delta \) 0.217 (36H, s, Me\(_3\)Si); 1.60 (4H, d, \( J = 14 \) Hz, CH\(_2\)-ring); 5.58 (2H, m, HC\(_{22}\)CH). \(^13\)C NMR (CDCl\(_3\)): \( \delta \) 2.27 (Me\(_3\)Si); 9.95 (CH\(_2\)-ring); 126.6 (C\(_{22}\)C). \(^29\)Si NMR (CDCl\(_3\)): \( \delta \) -5.243 (Me\(_3\)Si). EI-MS: \( m/z \) 494 (M\(^+\), 1); 479 (M\(^+\) – Me, 5); 440 (M\(^+\) – CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_2\), 20), 421 (M\(^+\) – Me\(_3\)Si, 5). HR-MS: 494.0752, C\(_{16}\)H\(_{42}\)Ge\(_2\)Si\(_4\) requires 494.0787. Anal. Calcd for C\(_{16}\)H\(_{42}\)Ge\(_2\)Si\(_4\): C, 39.06; H, 8.60. Found: C, 39.82; H, 8.51.

(b) 1,1-Bis(trimethylsilyl)-1-germacyclopent-3-ene (19). Yield after separation 10%. \(^1\)H NMR (CDCl\(_3\)): \( \delta \) 0.137 (18H, s, Me\(_3\)Si); 1.67 (4H, s, CH\(_2\)-ring); 5.88 (2H, s, HC\(_{22}\)CH). \(^13\)C NMR (CDCl\(_3\)): \( \delta \) -0.286 (Me\(_3\)Si); 14.78 (CH\(_2\)-ring); 132.3 (C\(_{22}\)C). \(^29\)Si NMR (CDCl\(_3\)): \( \delta \) -9.124 (Me\(_3\)Si). EI-MS: \( m/z \) 274 (M\(^+\), 10); 259 (M\(^+\) – Me, 15); 220 (M\(^+\) – CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_2\), 50). HR-MS: 274.0667, C\(_{10}\)H\(_{24}\)Ge\(_2\)Si\(_3\) requires 274.0628. Anal. Calcd for C\(_{10}\)H\(_{24}\)Ge\(_2\)Si\(_3\): C, 43.99; H, 8.86. Found: C, 44.11; H, 8.81.

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