Reactivity of the Isolable Disilene R*PhSi=SiPhR* (R* = Si*t*Bu$_3$)[**]

Nils Wiberg,*[a] Wolfgang Niedermayer,[a] Kurt Polborn,[a, b] and Peter Mayer[a, c]

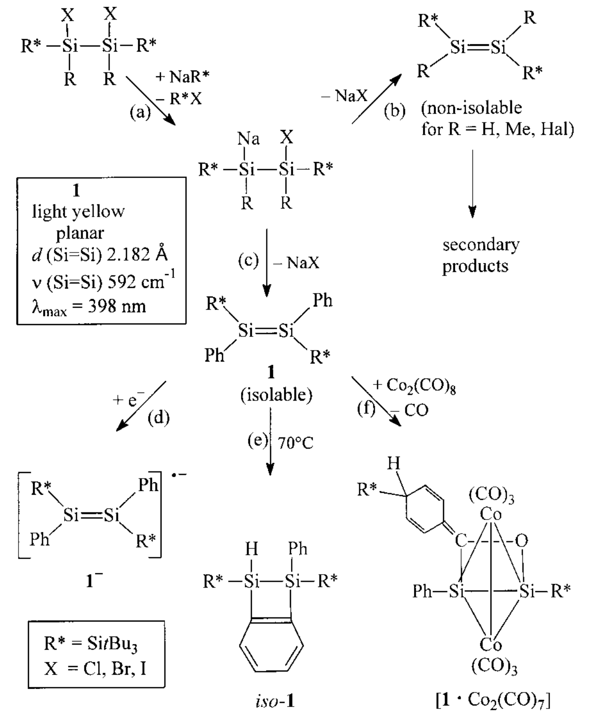
Dedicated to Professor Wolfgang Beck on the occasion of his 70th birthday

Abstract: The disilene R*PhSi=SiPhR* (R* = supersilyl = Si*t*Bu$_3$), which can be quantitatively prepared by dehalogenation of the disilane R*PhClSi–SiBrPhR* with NaR* (yellow, water- and air-sensitive crystals; decomp at ca. 70 °C; Si=Si distance 2.182 Å), is comparatively reactive. It transforms 1) with Cl_2, Br_2, HCl, HBr, and HOH under *1,2-addition* into disilanes R*PhXSi–SiX′PhR* (X/X′ = Hal/Hal, H/Hal, H/OH), 2) with O_2, S_8, and Se_n under *insertion* into 1,3-disiletanes R*PhSi(–Y–)$_2$SiPhR* (Y = O, S, Se), 3) with $Me_2C{=}CH_2$ under *ene reaction* into the disilane R*PhRSi–SiHPhR* (R = CH_2-CMe=CH_2), 4) with N_2O, Te_n, *t*BuN≡C, and $Me_3SiN{=}N{=}N$ under *[2+1] cycloaddition* into disiliranes –R*PhSi–Y–SiPhR*– (Y = O, Te, C=N*t*Bu, $NSiMe_3$; P_4 adds 2 molecules of disilene), 5) with CO_2, COS, PhCHO, and Ph_2CS under *[2+2] cycloaddition* into disiletanes –R*PhSi–SiPhR*–Y–CO– (Y = O, S) as well as –R*PhSi–SiPhR*–Y–CRPh– (Y/R = O/H, S/Ph), 6) with CS_2 and CSe_2 under *[2+3] cycloaddition* into ethenes $R^*{}_2Ph_2Si_2Y_2C = CY_2Si_2Ph_2R^*{}_2$ (Y = S, Se), and 7) with $CH_2{=}CMe{-}CMe{=}CH_2$ and Ph_2CO under *[2+4] cycloaddition* into "Diels–Alder adducts". X-ray structure analyses of seven of these compounds are presented.

Keywords: addition · cycloaddition · disilenes · ene reaction · silicon · structure eluciation

Introduction

We have shown recently,[1, 2] that supersilyl sodium NaR* (R* = supersilyl = Si*t*Bu$_3$) in tetrahydrofuran (THF) acts as an excellent dehalogenating agent for disilanes R*RHal-Si–SiHalRR*. The first step of these reactions at −78 °C consists of an exchange of halogen for sodium to form disilanides (see Scheme 1, path a), which then eliminate NaHal at about −50 °C or higher with formation of *trans*-configured disilenes R*RSi=SiRR* (Scheme 1 paths b or c). For R equal to hydrogen, methyl, halogen, these exist only as short lived intermediates and transform into secondary products or may be trapped by suitable reagents,[1] but for R equal to more bulky substituents, the disilenes become isolable. In fact, we could isolate *trans*-diphenyldisupersilyldisilene (R*PhSi=SiPhR*, **1**) as light yellow crystals[2] and characterize it spectroscopically, by X-ray structure analysis, by reduction with alkali metals in tetrahydrofuran (formation of the radical anion **1**$^-$, Scheme 1, path d), and by thermolysis (formation of the product *iso*-**1** with *cis*-configured R* groups, Scheme 1, path e).[2]



Scheme 1. Formation, characterization and some reactions of the disilene R*PhSi=SiPhR*.

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X-ray structure analyses of compounds **5b**, **6**, **13**, **16a**.

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X-ray structure analysis of compound **12b**.

[**] Compounds of Silicon, Part 155. Unsaturated silicon compounds, Part 62. For parts 154 and 61 see ref. [2].

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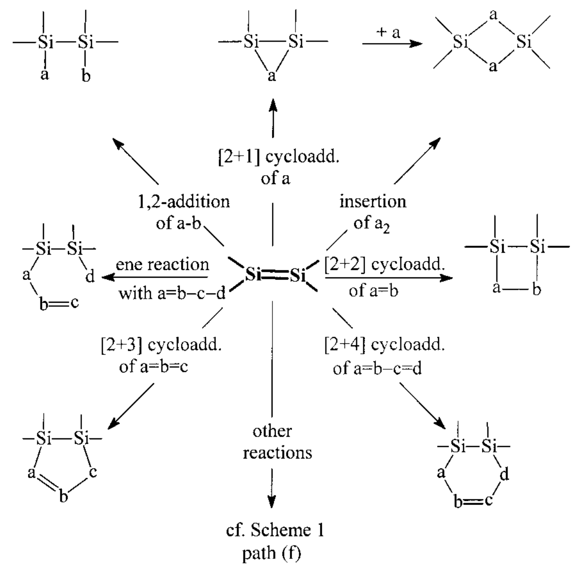
Syntheses, geometric as well as electronic structures, and reactions of disilenes are reported in review articles.[3–10] To date, approximately 40 acyclic disilenes and several cyclic disilenes have been isolated. In addition, many disilenes have been indicated as intermediates. Among the more thoroughly investigated stable acyclic disilenes, the following are worth mentioning: tBu$_2$Si=SitBu$_2$, Mes$_2$Si=SiMes$_2$, (tBuMe$_2$Si)$_2$-Si=Si(SiMe$_2t$Bu)$_2$, and the disilene R*PhSi=SiPhR* (**1**), discussed here. Due to its sterical overcrowdedness, **1** is comparatively thermostable, first decomposing at about 70 °C (Scheme 1), but nevertheless rapidly combines with a great variety of reactants if they are not too bulky.

Among typical reactions of disilenes, additions, insertions, ene reactions, and cycloadditions of **1** have been summarized in Scheme 2 (cf. refs. [10, 11]). Certainly, other reactions than those realized in Scheme 2 are also possible. For example, [Co$_2$(CO)$_8$] reacts with **1** to form [**1**·Co$_2$(CO)$_7$] (X-ray structure analysis,[12] Scheme 1, path f).

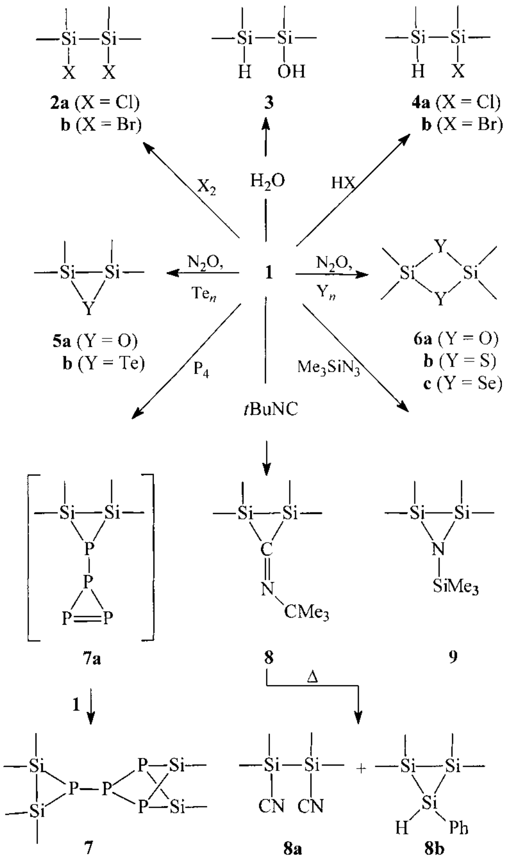


Scheme 2. Reactivity of disilenes.

As will be demonstrated hereafter, the reactivity of **1** is partly analogous, but also partly different from those of other disilenes.[5–9] Altogether, it is noticeable that the reactions of disilenes occur in most cases with preservation of the disilene moiety. Exceptions are, for example, the reactions of **1** with chalcogens or phosphorus (cf. Scheme 3).

Results and Discussion

1,2-Additions: Additions of small molecules like halogens, hydrogen halides, water, or alcohols to the Si=Si bond were among the first reactions of disilenes R$_2$Si=SiR$_2$ to be studied.[5–9] In fact, **1** rapidly adds Cl$_2$, Br$_2$, H$_2$O, HCl, and HBr according to Scheme 3 with formation of disilanes R*PhXSi–SiX′PhR* (X/X′ = Cl/Cl: **2a**; Br/Br: **2b**; H/OH: **3**; H/Cl: **4a**; and H/Br: **4b**). Thereby, as reported for other disilenes RR′Si=SiR′R,[13] only one of two thinkable diastereomers—namely the one which results from *syn*-addition—is formed in each case (evidently *syn*-additions are preferred to *anti*-additions[14]). As a result of the rapid reaction of **1** with water, the treatment of the disilene with moist air leads exclusively to the H$_2$O addition product.



Scheme 3. 1,2-Additions, insertions, and [2+1] cycloadditions of **1** (reactions of **1** with nonmetals, thermolysis of **8**).

Insertions: The chalcogens O$_2$, S$_8$, and Se$_n$ react with **1** at room temperature according to Scheme 3 with insertion into the Si=Si bond and formation of 1,3-dichalcogena-2,3-disiletanes (1,3-dichalcogena-2,4-disilacyclobutanes), R*PhSi(–Y–)$_2$SiPhR* (Y = O: **6a**; S: **6b**; and Se: **6c**). Certainly, reaction with oxygen leads not only to **6a**, but also to hitherto unidentified products. However, excess N$_2$O transforms **1**—by way of the oxadisilirane **5a** (Scheme 3)—quantitatively into the dioxadisiletane **6a**. Disilenes other than **1** react in most of the cases with oxygen exclusively to dioxadisiletanes,[15–19] but give with the oxygen homologues chalcogenadisiliranes (cf. [2+1] cycloadditions, below).[20–22] This last reaction pathway is also observed when **1** is treated with Te$_n$ (see below).

The isolated disiletanes are colorless, water-sensitive in the case of **6a**, oxygen- and thermostable solid substances. Figure 1 shows the structures of **6** (the crystals **6b** and **6c** have one molecule of benzene per molecule of **6**) together with selected bond lengths and angles.

The central structural elements of **6** consist of planar SiYSiY rings (sum of bond angles in the quadrangles 360°) with *trans*-configured Ph and R* groups at the Si atoms (SiSiC and C$_6$H$_5$ planes at angles of 90° and 67°, respectively, with regard to the SiYSiY plane). Whereas the SiOSiO ring in **6a** is

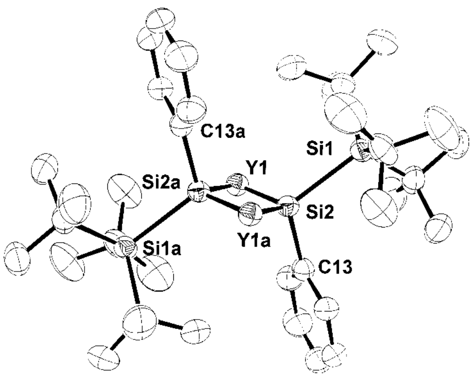


Figure 1. View of the molecule **6a** (Y = O) in the crystal (H atoms excluded). This view is taken as representative also for **6b** (Y = S) and **6c** (Y = Se), regardless of the reduced symmetry in the latter cases due to the additional benzene molecules in the crystal. Selected bond lengths [Å] and angles [°] of **6a**/**6b**/**6c** (for **6b** and **6c** mean values without standard deviations are given for bond lengths and angles): Si1–Si2 2.422(1)/2.418/2.412, Si1–C13 1.863(4)/1.882/1.879, Si1–Y1 1.683(2)/2.169/2.301, Si1–Y1A 1.690(2)/2.167/2.318, Si1–Si1A 2.419(1)/2.881/3.039, Y1–Y1A 2.354(1)/3.238/3.476, Si–C (mean values) 1.938/1.930/1.944; Si2-Si1-C13 113.0(1)/115.2/116.0, Si2-Si1-Y1 119.1(1)/114.7/114.5, Si2-Si1-Y1A 116.4(1)/114.6/113.7, C13-Si1-Y1 108.0(1)/106.9/106.9, C13-Si1-Y1A 109.3(1)/106.9/106.4, Y1-Si1-Y1A 88.43(10)/96.7/97.6, Si1-Y1-Si1A 91.57(10)/83.3/82.4, C-Si-C (mean values) 111.7/111.7/111.8; Si2-Si7 ··· Si1A-Si2A and C13-Si1 ··· Si1A-C13A 180.00 in each case.

centrosymmetric, the same does not hold for the SiSSiS and SiSeSiSe rings in **6b** and **6c**; this is due to a symmetry reduction by means of the disordered benzene molecules. As expected, these compounds have structures that are analogous to other dioxadisiletanes prepared from disilenes and O_2,[15–19] as well as other disulfa- and diselenadisiletanes prepared by special procedures[20–22] (certainly, the SiYSiY rings in Mes(Tbt)Si(–Y–)$_2$Si(Tbt)Mes with Y = O, S and Tbt = 2,4,6-[$(Me_3Si)_2CH$]C_6H_2 are non-planar[18, 20]). Whereas the SiOSiO ring in **6a** is nearly rectangular (angles at O 91.57°, at Si 88.43°), the SiSSiS and SiSeSiSe rings in **6b** and **6c** are distorted rhombic (angles at S and Si 83.19/83.43° and 96.65/96.74°, at Se and Si 82.69/82.05° and 98.09/97.18°).

As was noticed, the Si ··· Si distance in the SiOSiO ring of $Mes_2Si(–O–)_2SiMes_2$, the first isolated molecule of dioxadisiletanes[15] (1,3-cyclodisiloxanes; higher cyclosiloxanes and polysiloxanes have been known for a long time[23]), is just as short (2.390 Å) as a typical Si–Si single bond (2.32–2.34 Å[23]). It is even shorter (2.349 Å) in *cis*-MesRSi=SiRMes with R = N$(SiMe_3)_2$,[16] but longer in **6a** (2.419 Å). Possibly, the repulsive interactions of the two ring oxygens are the main reason for the small Si ··· Si separations.[8, 24] As a consequence of the larger radii and smaller electronegativities of sulfur and selenium, the Si ··· Si distances in **6b** and **6c** are distinctly longer (2.880 Å, 3.039 Å) than in **6a**.

The reactions of disilenes with chalcogens occur more or less rapidly (e.g., **1** in solution is unstable in the presence of oxygen even at low temperatures, whereas Mes(Tbt)-Si=Si(Tbt)Mes is oxygen-stable at room temperature[18]). As has been proved in the case of other disilenes,[8, 25] and may be correct also for **1**, their reactions with O_2 occur initially under *syn*-addition of oxygen (cf. halogens, above) to form 1,2-dioxa-3,4-disiletanes. The latter then transform with retention of configuration by an intramolecular process into 1,3-dioxadisiletanes (transition state with a tetrahedro-Si_2O_2 moiety?), and—very seldom (e.g., reaction of O_2 with $Tip_2Si{=}SiTip_2$ (Tip = 2,4,6-$i\mathrm{Pr}_3C_6H_2$)[16, 17] or with **1**, see above)—into other products (radical processes?). Sulfur and selenium may react with **1** to give 1,3-dichalcogenadisiletanes as does oxygen by way of 1,2-dichalcogenadisiletanes (*syn*-addition of S_2 or Se_2 moieties), or—more probable—by way of chalcogenadisiliranes (*syn*-addition of S or Se atoms). In fact, telluradisilirane **5b** is the final product of the action of Te_n on **1** (see below). It should also be noted that oxadisiliranes are transformed into 1,3-dioxadisiletanes in the presence of O_2.[25]

[2+1] Cycloadditions: Whereas chalcogens Y_n react with $Mes_2Si{=}SiMes_2$ with formation of chalcogenadisiliranes $–Mes_2Si–Y–SiMes_2–$ (Y = O, S, Se, Te; the oxadisilirane is formed as a minor product besides the dioxadisiletane, see above),[16, 26] we obtained a [2+1] cycloadduct –R*PhSi–Y–SiPhR*– (**5b**; light green, partially oxygen- and water-stable) as a result of the action of chalcogens on the disilene **1** (Scheme 3) with $Y_n = Te_n$. On the other hand, the relevant cycloadduct with Y = O (**5a**; light yellow, oxygen-, water-, and light-sensitive, m.p. at 175 °C with decomp) is formed (besides N_2) by the action of equimolar amounts of N_2O on **1**.

Phosphorus P_4 transforms **1** (described in more detail in a forthcoming publication[27]) possibly by way of the [2+1] cycloadduct **7a** as a reactive intermediate (*syn*-addition of P_4) into the tetraphosphane **7** (colorless, m.p. 180 °C with decomp; see also Scheme 3). In fact, Mes(*t*Bu)Si=Si(*t*Bu)Mes gives an analogous product when treated with P_4.[28] The intermediate formation of **7a** is strongly supported not only by the reaction of **1** with N_2O and Te_n (see above), but also with the isonitrile *t*BuNC and the silyl azide Me_3SiN_3, which give the disilirane **8** and the azadisilirane **9**, respectively (Scheme 3), as [2+1] cycloadducts [bright orange **8** is thermolabile and slowly (over several weeks) decomposes according to Scheme 3 into the disilane **8a** and the cyclotrisilane **8b** along with the formation of supersilane R*H and isobutene $Me_2C{=}CH_2$; colorless **9** is formed along with N_2 and decomposes at 160 °C]. To date, only two other reactions are known to proceed analogously under formation of [2+1] cycloadducts with an isonitrile ($R_2Si{=}SiR_2$ + RNC; R = 2,6-$Me_2C_6H_3$[29]) or a silylazide ($Mes_2Si{=}SiMes_2$ + Me_3SiN_3[30]).

The proposed structures of the disiliranes **5**, **8**, and **9** (for **7** see ref. [27]) are consistent with the NMR spectra of the compounds, which resemble those of other disiliranes $–R_2Si–ER'–SiR_2–$ (see the Experimental Section and ref. [8]). Figure 2 shows in addition the structure of the telluradisilirane **5b** in the crystal together with selected bond lengths and angles (a preliminary X-ray structure analysis proves the structure of the oxadisilirane **5a**).

The central structural element of **5b** consists of a SiTeSi ring with *trans*-configured Ph and R* groups at the Si atoms. The ring is slightly disordered with regard to the Si positions in a ratio of 0.793/0.207. The Si–Si distance (2.343 Å), like the distances in other disiliranes (2.23–2.34 Å),[8, 9] is relatively short even with bulky substituents (for comparison: Si–Si

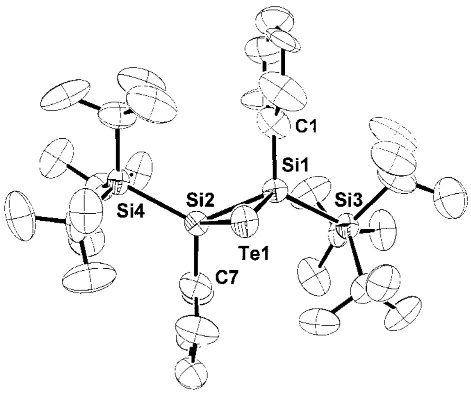


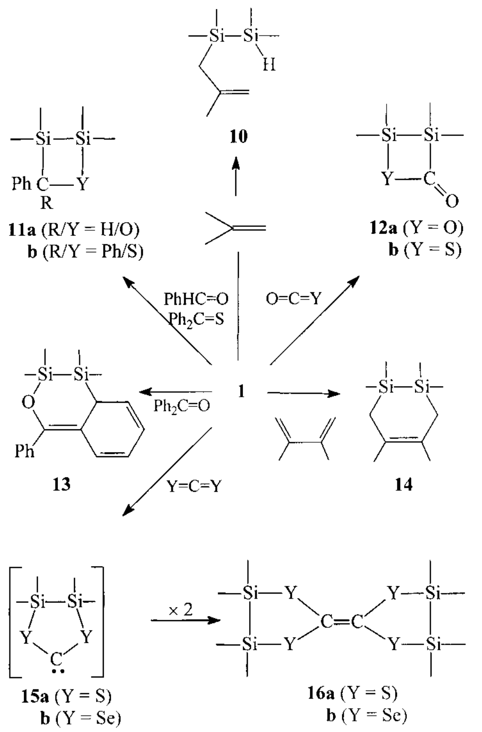
Figure 2. View of the molecule **5b** in the crystal (H atoms excluded). Selected bond lengths [Å] and angles [°]: Si1–Si2 2.343(8), Si1–Si3 2.405(7), Si2–Si4 2.455(7), Si1–Te1 2.536(6), Si2–Te1 2.532(5), Si1–C1 1.87(2), Si2–C2 1.88(2), Si–*t*Bu (mean value) 1.94; Si1-Te1-Si2 55.1, Si1-Si2-Te1 62.5(2), Si2-Si1-Te1 62.4(2), Si3-Si1-Te1/C1/Si2 115.5(2)/115.4(7)/130.0, Si4-Si2-Te1/C7/Si1 113.2(2)/115.7(7)/129.6(3), C1-Si1-Te1/Si2 109.0(6)/111.1(7), C7-Si2-Te1/Si1 111.1(6) 111.4(7).

distance in R*PhClSi–SiHPhR* 2.414 Å;[31] the Si–Si distance in **5a** amounts to ca. 2.27 Å). The bond angles sum around the ring silicon atoms, excluding Te, amounts to 356.5°. Indeed, the short Si–Si bond length and the nearly planar geometry of the central framework of the disilane moiety in **5b** resembles the bonding situation in olefin complexes of transition metals.[23] The unusual configuration which also is found in other disiliranes $-R_2Si-ER'-SiR_2-$[8, 9] points to a bonding situation half way between a three-membered ring and a π-complex of **1** with Te.

In fact, disilenes react with various types of reagents to afford disiliranes $-R_2Si-ER'-SiR_2-$ that are otherwise inaccessible.[8, 9] Thereby the three-membered rings may form, with retention of configuration, by [2+1] cycloadditions, as possibly is true for the action of chalcogens (see above), nitrogen oxide, isonitriles, or silyl azides on disilenes.[8] Certainly, alkyl azides $AlkN_3$ at first react with disilenes through [2+1] cycloaddition of the terminal N atom with formation of azadisiliranes $-R_2Si-NR'SiR_2-$ (N = NAlk as substitutent R′) from which N_2 subsequently is eliminated to leave the azadisilirane with R′=Alk.[8] On the other hand, the thus formed [2+1] cycloadducts must not result mechanistically from [2+1] cycloadditions as has been shown for aryl azides ArN_3, which by way of [2+3] cycloadducts transform finally at higher temperatures into azadisiliranes[8] (the same may be valid for N_2O).

Ene reactions: The disilene **1** reacts with isobutene to form the ene reaction product **10** (Scheme 4). This is in agreement with reactions of the tetrasilyldisilene $(tBuMe_2Si)_2Si{=}Si(SiMe_2tBu)_2$ with various alkenes that contain allylic hydrogen atoms.[32] On the other hand, ene reactions of tetraaryldisilenes are not known to date.

[2+2] Cycloadditions: The addition of disilenes to compounds that contain double or triple bonds such as C=C, C≡C, C=N, C≡N, C=O, C=S, N=N, N=O and the formation of four-membered-ring compounds belongs to the most typical reactions of the >Si=Si< groups.[8, 9] Indeed, these [2+2] cycloadducts are difficult to synthesize otherwise.



Scheme 4. Ene reaction and [2+*n*] cycloadditions (*n* = 2, 3, 4) of **1**.

The disilene **1** reacts, for example, with PhCH=O and $Ph_2C{=}S$ to give the oxadisiletane **11a** or thiadisiletane **11b** (Scheme 4), but gives unexpectedly a [2+4] cycloadduct with $Ph_2C{=}O$ ($Mes_2Si{=}SiMes_2$ reacts both with $Ph_2C{=}S$ and $Ph_2C{=}O$ with [2+2] cycloaddition[33]). Analogous to PhCH=O and $Ph_2C{=}S$, the heterocumulenes O=C=O and O=C=S react with **1** with formation of the oxa- and thiadisiletanes **12a** and **12b** (see Scheme 4; reactions of disilenes with carbon dichalcogenides are not reported), but with S=C=S and Se=C=Se only [2+3] cycloadducts are formed.

The isolated disiletanes are colorless, and oxygen-, water- and thermostable compounds (m.p. for **11a**/**11b**/**12a**/**12b** 250 (decomp)/301/230 (decomp)/217 °C (decomp)), whereas the thiadisiletane **11b** is light sensitive, as is the adduct of $Mes_2Si{=}SiMes_2$ with $Ph_2C{=}S$.[32] The latter compound decomposes slowly in daylight with formation of the dithiadisiletane **6b** among others (see Experimental Section).

Figure 3 shows the crystal structure of the thiadisiletane (thiadisilacyclobutanone) **12b** along with selected bond lengths and angles. The central structural element of **12b** consists of a nearly planar four-membered CSiSiS ring (bond angles sum in the quadrangle 358.0°) with *trans*-configured Ph and R* groups at the Si atoms. The angle between a C_6H_5 plane and the plane of the ring as well as the plane of the second C_6H_5 ring amounts to 72.3° (mean value) and 2.8°. The Si–Si distance is somewhat longer (2.413 Å) than normal Si–Si single bonds (2.32–2.34 Å[23]). The sum of bond angles around the ring carbon amounts to 360°.

[2+3] Cycloadditions: Further examples of less known and hitherto less studied[8, 9] [2+3] cycloadditions of disilenes are

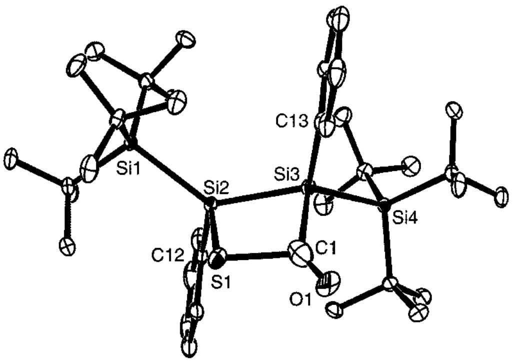


Figure 3. View of the molecule **12b** in the crystal (H atoms excluded; the crystal contains 0.5 moles benzene per mole of **12b**). Selected bond lengths [Å] and angles [°]: Si1−Si2 2.436(1), Si2−Si3 2.413(1), Si3−Si4 2.428(1), Si2−S1 2.168(2), Si2−C12 1.895(3), Si3−C1 1.919(2), Si3−C13 1.887(3), Si−*t*Bu (mean value) 1.939; Si1-Si2-Si3/S1/C12 130.60(4)/109.33(5)/111.75(9), Si4-Si3-Si4/C1/C13 129.92(4)/110.28(7)/112.32(9), C12-Si2-Si3/S1 111.61(9)/103.29(13), C13-Si3-Si2/C1 111.16(8)/101.94(1), Si3-Si2-S1 82.29(5), Si2-Si3-C1 83.39(6), Si3-C1-S1 98.2(1), Si2-S1-C1 94.1(1), O1-C1-Si3/S1 141.1(3)/120.7(3), *t*Bu-Si-*t*Bu (mean value) 111.6; Si1-Si2-Si3-Si4/C13 130.30/18.44, Si1-Si2-S1-C1 141.02, Si2-Si1-C1-O1/Si3 169.55/12.35, Si2-Si3-C1-Si1/O1 11.13/171.48, Si4-Si3-C1-O1/S1 41.24/110.28.

the reactions of **1** with the cumulenes S=C=S and Se=C=Se to give at first the carbenes **15a** and **15b**, respectively (Scheme 4). These compounds stabilize with dimerization and formation of the ethenes **16a** and **16b**, respectively . In fact, cyclic carbenes of the type **15a** with C−C as well as C=C instead of Si−Si groups and NR instead of S atoms (imidazolin- as well as imidazol-2-ylidenes) were isolated some years ago.[34] Since thiazol-2-ylidenes (one NR group substituted by S in imidazol-2-ylidenes) are in equilibrium with their dimers,[34] a dimerization of the intermediately formed carbenes **15a** and **15b** seems very reasonable (for an analogous reaction of an alkyne with CS_2, see ref. [35]).

The isolated ethenes **16** are colorless and water- and thermostable compounds, whereas **16b** transforms slowly in the air with formation of the diselenadisiletane **6c** among others. Figure 4 shows the crystal structure of the ethene **16a** along with selected bond lengths and angles.

The central structural element of **16a** consists of a nearly planar (SiS)SC=CS(SSi) moiety. A further Si atom lies each above and below this plane and forms together with one Si, two S and one C atom a nonplanar five-membered Si_2S_2C ring (half-chair) with nearly *trans*-configured Ph and R* substituents at the Si atoms (torsion angles R*−Si−Si−R*/Ph−Si−Si−Ph 173.2/173.6°). The two Si_2S_2C half-chairs are *trans* to each other. The angles between the SiSiS or C_6H_5 planes and the SiSCS plane of the five-membered rings amount to 50.5° and 89.3°, respectively. The C=C distance (1.334 Å) is as long as expected for a double bond,[23] the C−S distances (1.766/1.777 Å) are shorter, and the Si−S distances (2.172/2.167 Å) as well as the Si−Si distances (*endo*: 2.417 Å; *exo*: 2.456 Å) are longer than expected for single bonds.[23]

As mentioned above (Scheme 3), CO_2 and COS react with **1** under [2+2] cycloaddition which indeed is the expected way that disilenes combine with unsaturated compounds, but, unexpectedly, **1** gives with CS_2 and CSe_2 [2+3] cycloadducts. In fact, the former additions must occur in two steps, whereas the latter may take place synchronously in one step (according to non-retention or retention of orbital symmetry, concerted reactions are forbidden and non-forbidden in the first and second cases, respectively).[36] Evidently, the tendency for concerted reactions is more pronounced with **1** than with many other disilenes.

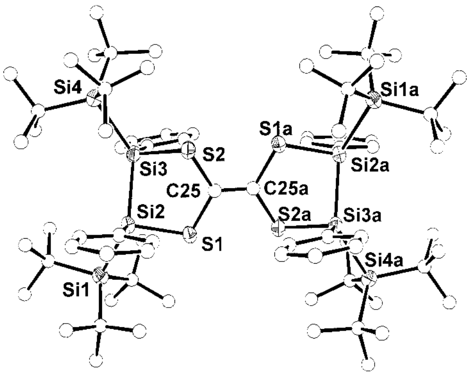


Figure 4. View of the molecule **16a** in the crystal (H atoms excluded; the crystal contains one mole benzene per mole of **16b**). Selected bond lengths [Å] and angles [°]: Si2−Si3 2.417(2), Si1−Si2 2.456(2), Si4−Si3 2.456(2), Si2−S1 2.172(1), Si3−S2 2.167(2), S2−C25 1.766(3), S1−C25 1.771(3), C25−C25A 1.334(5), Si2−C13 1.903(3), Si3−C19 1.902(3), Si−*t*Bu (mean value) 1.948; Si1-Si2-Si3/S1/C13 131.51(6)/99.90(6)/112.23(11), Si4-Si3-Si2/S2/C19 130.16(6)/102.34(6)/112.29(11), C13-Si2-Si3/S1 107.85(11)/106.54(11), C19-Si3-Si2/S2 108.81(11)/106.41(11), Si2-Si3-S2 91.71(7), Si3-Si2-S1 93.66(6), Si2-S1-C25 105.72(11), Si3-S2-C25 102.22, S2-C25-S1/C25A 120.1(2)/120.9(3), S1-C25-C25A 119.0(3), *t*Bu-Si-*t*Bu (mean value) 111.0; S1-C25-C25A-S1A/S2A 0.29/180.00, C25A-C25-S1-Si2/Si3 179.43/144.92, Si2-S1-C25-S2 0.86, Si3-S2-C25-S1 35.38, Si3-Si2-S1-C25 29.40, S2-Si3-Si2-S1 43.04, Si2-Si3-S2-C25 46.87, C13-Si2-Si3-C19 173.62, Si1-Si2-Si3-Si4 173.22.

[2+4] Cycloadditions: There were reports on reactions of disilenes with organic 1,3-dienes under [2+4] cycloaddition (Diels–Alder reactions) in 1983 (*t*Bu_2Si=Si*t*Bu_2 + 2,3-dimethylbutadiene DMB),[37] in 1995 (*t*Bu_2Si=Si*t*Bu_2 + cyclopentadiene),[38] in 1997 (**1** + DMB → **14**; see Scheme 4),[10] and in 1998 ((*t*$BuMe_2Si)_2Si$=$Si(SiMe_2$*t*$Bu)_2$ + DMB).[32] On the other hand, a large number of [2+4] cycloadditions of disilenes with heterodienes are known.[8, 9] As an example, the disilene **1** combines with Ph_2C=O to form the [2+4] cycloadduct **13** (Scheme 4).

The Ph_2CO adduct **13** is yellow and both water and air sensitive, but thermally stable (m.p. 180 °C with decomp), whereas the DMB adduct **14** is colorless and water-, air-, and thermostable (m.p. 207 °C). Figure 5 shows the crystal structure of **13** along with selected bond lengths and angles.

The central structural element of **13** consists of a nonplanar six-membered O1-Si1-Si2-C3-C2-C1 ring (angle between the planes O1-C1-C2-C3 and O1-Si1-Si2-C3 42.0°) with *gauche*-configured Ph and R* substituents at the Si atoms (torsion angles R*-Si-Si-R*/Ph-Si-Si-Ph 146.6/121.4°). This last fact indicates a certain rotation of the R*PhSi halves around the Si=Si bond in the course of cycloaddition of **1** and DMB. The angle between the planes of the C_6H_5 groups at Si amounts to 5.2°. The C1−C2 distance (1.328 Å) lies in between the distances of a single and a double carbon bond; the Si1−Si2

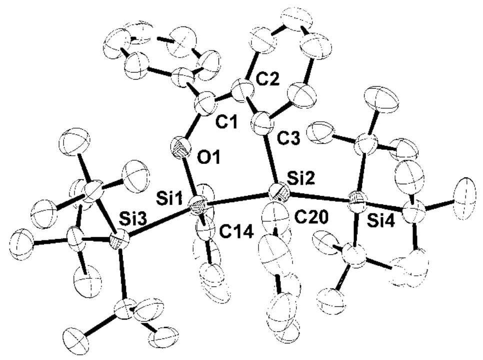


Figure 5. View of the molecule **13** in the crystal (H atoms excluded; the crystal contains one mole Ph_2CO per mole of **13**). Selected bond lengths [Å] and angles [°]: Si1–Si2 2.426(4), Si1–Si3 2.477(4), Si2–Si4 2.500(4), Si1–C14 1.90(1), Si2–C20 1.92(1), Si1–O1 1.663(7), Si2–C3 1.98(1), C1–O1 1.40(1), C1–C2 1.33(1), C1–C8 1.50(2), C2–C3 1.51(1), Si–*t*Bu (mean value) 1.951; O1-Si1-Si2 99.5(3), Si1-Si2-C3 92.7(3), Si2-C3-C2 115.7(7), C3-C2-C1 123.2(9), C2-C1-O1 121.0(9), C1-O1-Si1 133.6(6), Si3-Si1-C14/Si4-Si2-C20 109.2(3)/109.3(3); Si3-Si1-Si2-Si4 146.6, C14-Si1-Si2-C20 121.4, O1-Si1-Si2-C3 19.3, Si1-Si2-C3-C2 53.6, Si2-C3-C2-C1 52.4, C3-C2-C1-O1 2.4, C2-C1-O1-Si1 48.7, C1-O1-Si1-Si2 26.8.

distance (2.426 Å) is longer than a normal Si–Si single bond.[23]

As mentioned above (Scheme 4), PhHC=O and $Ph_2C{=}S$ react with **1** under [2+2] cycloaddition, but $Ph_2C{=}O$ unexpectedly gives a [2+4] cycloadduct, whereas other disilenes such as $Mes_2Si{=}SiMes_2$ add $Ph_2C{=}O$ in the normal [2+2] way.[8, 33] In addition, unlike some other disilenes **1** reacts with DMB rapidly with [2+4] cycloaddition. In fact, this may take place—like [2+3] cycloadditions (see above)—synchronously in one step. Again, the results speak for a marked tendency of **1** to enter into concerted reactions.

Experimental Section

All experiments were carried out in flame-dried glass apparatus with standard Schlenk techniques under dry argon or nitrogen. Air and moisture were strictly excluded. The solvents (pentane, benzene, [D$_6$]benzene, tetrahydrofuran (THF), carbon tetrachloride, acetone) were distilled from sodium/lead or sodium/benzophenon. Available for use: Cl_2, Br_2, O_2, Se_n, Te_n, P_4, HCl, HBr, H_2O, Me_3SiN_3, CO_2, COS, CS_2, PhCHO, Ph_2CO, *t*BuNC, $Me_2C{=}CH_2$, $CH_2{=}CMe{-}CMe{=}CH_2$ (DMB). The following compounds were synthesized according to literature procedures: **1**,[2] Ph_2CS,[39] CSe_2.[40] NMR spectra: Jeol GX-270 ($^1H/^{13}C/^{29}Si/^{31}P/^{77}Se/^{125}Te$: 270.17/67.94/53.67/109.37/51.43/85.24 MHz), Jeol EX-400 ($^1H/^{13}C/^{29}Si/^{31}P$: 399.78/100.54/79.43/161.84 MHz). Standards: $\delta(^1H/^{13}C/^{29}Si)$: int./int./ext. TMS; $\delta(^{31}P)$: ext. H_3PO_4 (85%); $\delta(^{77}Se)$: ext. $SeMe_2$ in C_6D_6; $\delta(^{125}Te)$: ext. $TeMe_2$ in C_6D_6. The NMR spectra were recorded with the INEPT as well as DEPT pulse sequence using empirically optimized parameters for the mentioned groups. MS spectra: Varian Atlas CH7; Jeol MStation JMS 700.

Reaction of 1 with Cl_2—formation of 2a: Cl_2 (0.080 mmol) in CCl_4 (3 mL) was condensed into a solution of **1** (0.039 g, 0.064 mmol) in THF (5 mL) at −78 °C. According to NMR spectroscopy, the reaction mixture (heated to RT; decolorized) then contained the *gauche*-diastereomer **2a** only (cf. reaction of **1** with H_2O, remarks). After evaporation of volatile products in an oil pump vacuum, *gauche*-**2a** remained as a colorless substance (identification by comparison with an authentic sample, the isomer of which (*trans*-**2a**) has been studied by X-ray crystallography[31]).

Reaction of 1 with Br_2—formation of 2b: Br_2 (0.018 g, 0.23 mmol) in pentane (3 mL) was added dropwise to a solution of **1** (0.139 g, 0.230 mmol) in pentane (10 mL) at −5 °C. According to NMR spectroscopy, the reaction mixture (heated to RT; decolorized) then contained one diastereomer of **2b** only, that is, the *gauche*-isomer (cf. reaction of **1** with H_2O, remarks). After evaporation of volatile products in an oil pump vacuum, *gauche*-**2b** remained as a colorless substance (identification by comparison with an authentic sample[31]).

Reaction of 1 with H_2O—formation of 3: H_2O (0.019 g, 1.04 mmol) was condensed into a solution of **1** (0.072 g, 0.119 mmol) in C_6H_6 (5 mL) at −78 °C. According to NMR spectroscopy, the reaction mixture (heated to RT, decolorized) then contained one diastereomer of **3** only. After evaporation of volatile products in an oil pump vacuum **3** remained as a colorless substance. M.p. 228–229 °C; elemental analysis calcd (%) for $C_{36}H_{66}OSi_4$ (627.3): C 68.93, H 10.61; found: C 68.26, H 10.79; ^1H NMR (C_6D_6): $\delta = 1.110/1.167$ (s/s, 27H/27H; Si*t*Bu$_3$ at SiH and at SiOH), 4.737 (s, 1H; SiH), 7.03–8.11 (m, 10H; 2Ph); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 23.90/24.34$ (3C/3C; 3*C*Me$_3$/3*C*Me$_3$), 31.54/31.80 (9C/9C; 3C*Me*$_3$/3C*Me*$_3$) 125.1/128.7/135.4/140.5 (2C/C/2C/C; *m-/p-/o-/i*-C of Ph), (125.1 + 126.5)/129.5/(136.3 + 140.5)/142.8 (2C/C/2C/C; *m-/p-/o-/i*-C of Ph; splitting of signals because of hindrance of rotation); $^{29}Si\{^1H\}$ NMR (C_6D_6): δ = -58.72 (d, $^1J(Si,H)$ = 164.1 Hz, 1Si; SiH), 1.46 (1Si; SiOH), 10.53/20.62 (1Si/1Si; Si*t*Bu$_3$/Si*t*Bu$_3$); IR (KBr): $\tilde{\nu} = 2082\ cm^{-1}$ (SiH); MS (70 eV): *m/z* (%): 626 (9) [M^+], 611 (6) [$M^+ - Me$], 569 (60) [$M^+ - t$Bu], 549 (67) [$M^+ - Ph$], 513 (7) [$M^+ - t$Bu $- C_4H_8$], 493 (19) [$M^+ - Ph - C_4H_8$], 427 (36) [$M^+ -$ Si*t*Bu$_3$], 409 (9) [$M^+ -$ Si*t*Bu$_3 - H_2O$], 385 (11) [$M^+ -$ Si*t*Bu$_3 - C_3H_6$], 371 (6) [$M^+ -$ Si*t*Bu$_3 - C_4H_8$], 321 (100) [$M^+ -$ Si*t*Bu$_3$ − PhSiOH].

Remarks: 1) Disilanes of type R*PhXSi–SiX′PhR* (X equal or unequal X′) exist as *gauche*- and *trans*-diastereromers, whereby *gauche* and *trans* are related to the configuration of the phenyl groups[31] (the R* groups are, for steric reasons, always *trans*-configured). 2) According to NMR spectra, the reactions of **1** and Hal_2, H_2O, or HHal leads only to one diasteromer, which in case of **2a** and **4a** is definitively the *gauche* isomer[31] (comparison with authentic samples). By analogy, and as indiciated from NMR spectroscopic insights as well as results with other disilenes,[8, 9] compounds **2b**, **3**, and **4b** also probably exist as the *gauche*-isomer. 3) Moist air reacts with **1** exclusively under formation of **3**.

Reaction of 1 with HCl—formation of 4a: HCl (0.070 mmol) was condensed into a solution of **1** (0.037 g, 0.061 mmol) in THF (5 mL) at −78 °C. According to NMR spectroscopy, the reaction mixture (heated to RT; decolorized) then contained the *gauche*-diasteromer **4a** only (cf. reaction of **1** with H_2O, remarks). After evaporation of volatile products in an oil pump vacuum *gauche*-**4a** was obtained as a as colorless substance (identification by comparison with an authentic sample which itself has been studied by X-ray structure analysis[31]).

Reaction of 1 with HBr—formation of 4b: Compound **1** (0.072 g, 0.12 mmol) in C_6D_6 (0.4 mL) was stirred under an atmosphere of HBr (fast decolorization). According to NMR spectroscopy, the reaction mixture then contained one diastereomer **4b** only, which is evidently is the *gauche*-isomer (cf. reaction of **1** with H_2O, remarks). After evaporation of volatile products in an oil pump vacuum *gauche*-**4b** remained as a colorless substance (identification by comparison with an authentic sample[31]).

Reaction of 1 with N_2O and O_2—formation of 5a and 6a *Method 1*: N_2O (0.048 mmol) was condensed into a solution of **1** (0.029 g, 0.048 mmol) in C_6D_6 (0.5 mL) at −196 °C. According to NMR spectroscopy, the reaction mixture in a closed NMR tube (after heating to RT; decolorized) then contained **5** (30%), **6a** (30%), and unreacted **1**. From the solution the oxadisilirane **5a** precipitated after two weeks as air-sensitive, light-yellow crystals. ^1H NMR (C_6D_6): $\delta = 1.064$ (s, 54H; 2Si*t*Bu$_3$), 7.03–8.12 (m, 10H; 2Ph); $^{29}Si\{^1H\}$ NMR (C_6D_6): $\delta = -3.25$ (2Si; 2SiPh), 16.65 (2Si; 2Si*t*Bu$_3$); X-ray structure analysis: The structure could not be solved exactly (operator: K. Polborn), but the constitution of **5a** is beyond doubt.

Method 2: N_2O (0.19 mmol) was condensed into a solution of **1** (0.046 g, 0.076 mmol) in C_6D_6 (0.5 mL) at −196 °C. According to NMR spectroscopy, the reaction mixture in a closed NMR tube (after heating to RT; decolorized) then contained **6a** only. After concentration of the solution to 0.1 mL the dioxadisiletane **6a** (0.040g, 0.284 mmol; 92%) was obtained as colorless crystals. M.p. 186 °C (decomp); elemental analysis calcd (%) for $C_{36}H_{64}O_2Si_4$ (641.2): C 67.43, H 10.06; found: C 66.84, H 10.14; ^1H NMR (C_6D_6): $\delta = 1.053$ (s, 54H; 2Si*t*Bu$_3$), 7.12–7.96 (m; *o-*, *p-*, *m*-H of 2Ph); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 23.24/31.48$ (6C/18C of 6*C*Me$_3$/6C*Me*$_3$); $^{29}Si\{^1H\}$ NMR (C_6D_6): $\delta = -13.70$ (2Si; 2SiPh), 5.92 (2Si; 2Si*t*Bu$_3$); MS (70 eV): *m/z* (%): 640 (1) [M^+], 625 (1) [$M^+ - Me$], 583 (100) [$M^+ - t$Bu], 541 (4)

$[M^+ - t\text{Bu} - C_3H_6]$, 527 (6) $[M^+ - t\text{Bu} - C_4H_8]$, 471 (3) $[M^+ - t\text{Bu} - 2C_4H_8]$, 441 (12) $[M^+ - \text{Si}t\text{Bu}_3]$, 385 (2) $[M^+ - \text{Si}t\text{Bu}_3 - C_4H_8]$, 199 (21) $[\text{Si}t\text{Bu}_3]$; X-ray structure analysis: see Figure 1 (colorless prisms of **6a** from benzene)

Method 3: Compound **1** (0.038 g, 0.062 mmol) in C_6D_6 was stirred under an atmosphere of water-free oxygen, which immediately lead to a decolorization of the solution. According to NMR, the dioxadisiletane **6a** (56%) was formed besides unidentified products with δ(^{1}H, Si*t*Bu$_3$) = 1.077, 1.090, 1.124, 1.159, 1.279 (ratio of areas of signals ca. 1:1:2:1.5:1.5); δ(^{29}Si, Si*t*Bu$_3$) = 5.64, 6.57, 7.80, 7.98, 9.40.

Reaction of 1 with S_8—formation of 6b: S_8 (0.011 g, 0.044 mmol) was added to a solution **1** (0.082 g, 0.135 mmol) in C_6D_6 (0.5 mL) at RT, whereby the solution decolorized rapidly. According to NMR spectroscopy, the reaction mixture then contained **6b** only. After concentration to 0.1 mL the 1,3-dithiadisiletane **6b** (0.082 g, 0.108 mmol, 80%) was obtained as colorless crystals that contained one mole C_6D_6 per mole **6b**. M.p. 294–295 °C; elemental analysis calcd (%) for $C_{36}H_{64}S_2Si_4$ (673.4): C 64.21, H 9.58, S 9.52; found: C 63.84, H 9.86, S 9.32; ^{1}H NMR (C_6D_6): $\delta = 1.068$ (s, 54H; 2Si*t*Bu$_3$), 7.07–8.10 (m, 10H; 2Ph); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 24.75/31.34$ (6C/18C; 6*C*Me$_3$/6C*Me$_3$*), 127.0/128.8/130.9/135.4 (4C/2C/4C/2C; *m-/p-/o-/i*-C of 2Ph); ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = 5.48$ (2Si; 2SiPh), 15.94 (2Si; 2Si*t*Bu$_3$); MS (70 eV): *m/z* (%): 672 (1) $[M^+]$, 657 (1) $[M^+ - \text{Me}]$, 615 (100) $[M^+ - t\text{Bu}]$, 559 (2) $[M^+ - t\text{Bu} - C_4H_8]$, 473 (11) $[M^+ - \text{Si}t\text{Bu}_3]$; X-ray structure analysis: see Figure 1 (colorless prisms of **6b** · C_6D_6 from C_6D_6).

Reaction of 1 with Se$_n$—formation of 6c: Se$_n$ (0.029 g, 0.365 mmol Se) was added to a solution of **1** (0.103 g, 0.170 mmol) in C_6D_6 (0.5 mL) at RT, whereby the solution decolorized rapidly. According to NMR spectroscopy, the reaction mixture then contained **6c** only. After filtration of insoluble parts and concentration of the solution to 0.1 mL the diselenadisiletane **6c**)(0.116 g, 0.136 mmol, 80%) was obtained as colorless crystals, which contained one mole C_6D_6 per mole **6c**. M.p. 320 °C (decomp); elemental analysis calcd (%) for $C_{36}H_{64}Se_2Si_4 \cdot C_6D_6$ (851.3): C 59.26, H 9.00; found: C 58.39, H 8.90; ^{1}H NMR (C_6D_6): $\delta = 1.140$ (s, 54H; 2Si*t*Bu$_3$), 7.10–8.18 (m, 10H; *o-*, *p-*, *m*-H of 2Ph); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 25.45/31.69$ (6C/18C; (6*C*Me$_3$/6C*Me$_3$*), 127.0/128.8/130.9/135.4 (4C/2C/4C/2C; *m-/p-/o-/i*-C of 2Ph); ^{29}Si{^{1}H} NMR (C_6D_6): δ = not observed (2SiPh), 21.50 (2Si; 2Si*t*Bu$_3$); ^{77}Se NMR (C_6D_6): $\delta = -947.89$ (2Se, 2SiSe); MS (70 eV): *m/z* (%): 764/766/768 (8) $[M^+]$, 707/709/711 (79) $[M^+ - t\text{Bu}]$, 651/653/655 (2) $[M^+ - t\text{Bu} - C_4H_8]$; X-ray structure analysis: see Figure 1 (colorless needles of **6c** · C_6D_6 from C_6D_6).

Reaction of 1 with Te$_n$—formation of 5b: Compound **1** (0.187 g, 0.307 mmol) in C_6D_6 (0.5 mL) was treated for several hours with Te$_n$ (0.040 g, 0.314 mmol Te). According to NMR spectroscopy, the reaction mixture then contained **5b** only. After concentration to 0.1 mL the telluradisilirane **5b** (0.209 g, 0.284 mmol, 92%) was obtained as light-sensitive, light green crystals; M.p. 175 °C (decomp); elemental analysis calcd (%) for $C_{36}H_{64}Si_4Te$ (736.9): C 58.68, H 8.75; found: C 57.71, H 8.64; ^{1}H NMR (C_6D_6): $\delta = 1.083$ (s, 54H; 2Si*t*Bu$_3$), 7.00–8.21 (m, 10H; *o-*, *p-*, *m*-H of 2Ph); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 25.02/31.92$ (6C/18C; 6*C*Me$_3$/6C*Me$_3$*), (126.3 + 128.2)/128.9/(133.6 + 138.1)/142.9 (2C + 2C/2C/2C + 2C/2C; *m-/p-/o-/i*-C of 2Ph; splitting of signals because of hindrance of rotation); ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = -81.09$ [2Si; 2SiPh; satellites from coupling with Te: ^1J(Si,Te) = 173.9/179.4 Hz (for comparison –Mes$_2$Si-Te-SiMes$_2$-: δ(Si) = –90/^1J(Si,Te) = 166 Hz[26]); t, ^3J(Si,H) = 5.9 Hz; 2SiPh], 21.34 (2Si; 2Si*t*Bu$_3$); ^{125}Te NMR (C_6D_6): $\delta = -1285.4$ (br, 1Te; SiTe); MS (70 eV): *m/z* (%): 734/736/738 (100) $[M^+]$, 705/707/709 (9) $[M^+ - C_2H_5]$, 677/679/681 (26) $[M^+ - t\text{Bu}]$, 621/623/625 (4) $[M^+ - t\text{Bu} - C_4H_8]$, 579/581/583 (7) $[M^+ - t\text{Bu} - C_4H_8 - C_3H_6]$, 535/537/539 (24) $[M^+\text{-Si}t\text{Bu}_3]$, 479/481/483 (15) $[M^+ - \text{Si}t\text{Bu}_3 - C_4H_8]$; X-ray structure analysis: see Figure 2 (colorless needles of **5b** from C_6D_6)

Remark: Excess Te$_n$ does not transform **5b** into a ditelluradisiletane.

Reaction of 1 with P_4—formation of 7: See ref.[27]

Reaction of 1 with *t*BuNC—formation of 8: Compound **1** (0.081 g, 0.133 mmol) in C_6D_6 (0.5 mL) was treated with *t*BuNC (0.035 g, 0.417 mmol) at RT. According to NMR spectroscopy, the reaction mixture then contained **8** only. After evaporation of all volatile products in an oil pump vacuum, the disilirane **8** (0.083 g, 0.121 mmol; 91%) was obtained as water- and oxygen-sensitive as well as thermolabile bright orange substance; M.p. > 80° (decomp); elemental analysis calcd (%) for $C_{41}H_{73}NSi_4$ (692.4): C 71.12, H 10.63; found: C 70.66, H 10.56; ^{1}H NMR (C_6D_6): $\delta = 1.089/1.108$ (s/s, 27H/27H; Si*t*Bu$_3$/Si*t*Bu$_3$), 1.705 (s, 9H; N*t*Bu), 7.10–8.33 (m, 10H; *o-*, *p-*, *m*-H of 2Ph); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 24.33/24.86$ (3C/3C; (3*C*Me$_3$/3*C*Me$_3$), 31.90/31.99 (9C/9C; (3C*Me$_3$*/3C*Me$_3$*), 34.43/64.13 (C/3C; N*C*Me$_3$/NC*Me$_3$*), (127.3 + 128.6)/128.8/(137.6 + 138.6)/140.1 (2C + 2C/2C/2C + 2C/2C; *m-/p-/o-/i*-C of 2Ph; splitting of signals because of hindrance of rotation); ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = -60.88$ (t, ^3J(Si,H) = 5.3 Hz, 2Si; 2SiPh), 24.97/27.67 (Si/Si; Si*t*Bu$_3$/Si*t*Bu$_3$; non-equivalent); MS (70 eV): *m/z* (%): 691 (4) $[M^+]$, 676 (3) $[M^+ - \text{Me}]$, 634 (100) $[M^+ - t\text{Bu}]$, 592 (11) $[M^+ - t\text{Bu} - C_3H_6]$, 578 (23) $[M^+ - t\text{Bu} - C_4H_8]$, 492 (30) $[M^+ - \text{Si}t\text{Bu}_3]$, 450 (15) $[M^+ - \text{Si}t\text{Bu}_3 - C_3H_6]$.

Thermolysis of 8--formation of 8a and 8b: Compound **8** (0.115 g, 0.166 mmol) in C_6D_6 (0.5 mL) was thermolized for three weeks at RT, whereby the orange solution decolorized. According to NMR spectroscopy, the reaction mixture then contained **8a**, **8b**, R*H,[41] and isobutene in the mole ratio of approximately 3:2:6:6.

*Disilane **8a***: Colorless substance with m.p. 220 °C; ^{1}H NMR (C_6D_6): $\delta = 1.071$ (s, 2Si; 2Si*t*Bu$_3$), 6.97–8.21 (m, 10H; 2Ph); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 25.32/31.89$ (6C/18C; 6*C*Me$_3$/6C*Me$_3$*), 122.3 (2C; 2CN), 127.2/135.8/137.9/141.8 (4C/2C/4C/2C; *m-/p-/o-/i*-C of 2Ph); ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = -62.91$ (t, ^3J(Si,H) = 8.2 Hz, 2Si; 2SiPh), 24.79 (2Si; 2Si*t*Bu$_3$); MS (EI): *m/z* (%): 660 (22) $[M^+]$, 634 (43) $[M^+ - \text{CN}]$, 603 (37) $[M^+ - t\text{Bu}]$, 578 (95) $[M^+ - \text{CN} - C_4H_8]$, 547 (33) $[M^+ - t\text{Bu} - C_4H_8]$, 522 (31) $[M^+ - \text{CN} - 2C_4H_8]$, 500 (100) $[M^+ - \text{CN} - C_4H_8 - C_6H_6]$; X-ray structure analysis: K. Polborn, unpublished results (*gauche*-diastereomer, Si–Si distance 2.421(4) Å, Si-Si-Si-Si/C-Si-Si-C torsion angles 154.17/65.77°; see ref. [31]).

*Cyclotrisilane **8b***: Colorless substance; ^{1}H NMR (C_6D_6): $\delta = 1.052$ (s, 54H; 2Si*t*Bu$_3$), 4.778 (s, 1Si; SiH), 6.97–8.21 (m, 15H; 3Ph); ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = -60.38$ (dt, *J*(Si,H) = very small, 2Si; 2SiPh), –56.26 (dt, ^1J(Si,H) = 168.9 Hz, ^3J(Si,H) = 5.6 Hz, 1Si;, SiHPh), 24.79 (2Si; 2Si*t*Bu$_3$); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 24.30/31.69$ (6C/18C; 6*C*Me$_3$/6C*Me$_3$*), (129.5 + 129.8)/134.1/(138.7 + 140.8)/139.2 (2C + 2C/2C/2C + 2C/2C; *m-/p-/o-/i*-C of 2Ph; splitting of signals because of hindrance of rotation), 127.2/135.6/136.7/140.1 (2C/C/2C/C; *m-/p-/o-/i*-C of 1Ph); MS (70 eV): *m/z* (%): 637 (100) $[M^+ - \text{Ph}]$, 581 (43) $[M^+ - \text{Ph} - C_4H_8]$.

Reaction of 1 with Me_3SiN_3—formation of 9: Compound **1** (0.194 g, 0.318 mmol) in C_6D_6 (0.5 mL) was treated with Me_3SiN_3 (0.039 g, 0.341 mmol) at RT, whereby the solution decolorized under production of N_2. According to NMR spectroscopy, the reaction mixture then contained **9** only. After evaporation of volatile products in an oil pump vacuum, the azadisilirane **9** (0.217 g, 0.312 mmol; 98%) was obtained as colorless crystals. M.p. > 160 °C (decomp); elemental analysis calcd (%) for $C_{39}H_{73}NSi_5$ (696.4): C 67.26, H 10.56; found: C 66.37, H 10.62; ^{1}H NMR (C_6D_6): $\delta = 0.636$ (s, 9H; SiMe$_3$), 1.091 (s, 54H; 2Si*t*Bu$_3$), 7.11–8.02 (m, 10H; *o-* ,*p-*, *m*-H of 2Ph); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 6.14$ (3C; SiMe$_3$), 24.32/32.13 (6C/18C; 6*C*Me$_3$/6C*Me$_3$*), (126.8 + 127.3)/128.6/(135.8 + 137.6)/142.6 (2C + 2C/2C/2C + 2C/2C; *m-/p-/o-/i*-C of 2 Ph; splitting of signals because of hindrance of rotation); ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = -61.51$ (2Si; 2SiPh), –10.01 (Si; SiMe$_3$), 19.33 (2Si; 2Si*t*Bu$_3$, equivalent!); MS (CI): *m/z* (%): 695 (100) $[M^+]$.

Reaction of 1 with $Me_2C{=}CH_2$—formation of 10: A solution of **1** (0.131 g, 0.215 mmol) in C_6H_6 (5 mL) was stirred for 12 h under an atmosphere of $Me_2C{=}CH_2$. According to NMR spectroscopy, the reaction mixture then contained **10** only. After removing all volatile components in an oil pump vacuum and recrystallization of the residue from acetone (2 mL) the ene product **10** (0.083 g, 0.125 mmol; 58%) was obtained as colorless substance. ^{1}H NMR (C_6D_6): $\delta = 0.900/1.191$ (br/br, 27H/27H, Si*t*Bu$_3$/Si*t*Bu$_3$), 1.211 (br, 5H; CH$_2$, CH$_3$), 5.016 (s, 1H; SiH), 5.001/5.120 (br/br, H/2H; CH=CH$_2$), 6.76–8.14 (m, 10H; 2Ph); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 24.17$ (1C; 1CH$_3$), 31.83 (1C; SiCH$_2$), 24.84/25.28 (3C/3C; 3*C*Me$_3$/3*C*Me$_3$), 32.26/32.64 (9C/9C; 3C*Me$_3$*/3C*Me$_3$*), 111.8 (1C; =CH$_2$) 138.8 (1C; >C=), (127.2 + 127.5)/(136.6 + 136.6)/(139.8 + 139.9)/(141.8 + 142.7) (2C + 2C/C + C/2C + 2C/C + C; *m-/p-/o-/i*-C of 2Ph); ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = -58.18$ (dm, ^1J(Si,H) = 158.0 Hz, 1Si; SiH), –28.40 (1Si; SiC), 18.23/26.35 (1Si/1Si; Si*t*Bu$_3$/Si*t*Bu$_3$); MS (70 eV): *m/z* (%): 664 (7) $[M^+]$, 607 (100) $[M^+ - t\text{Bu}]$, 565 (14) $[M^+ - t\text{Bu} - C_3H_6]$, 551 (6) $[M^+ - t\text{Bu} - C_4H_8]$, 465 (37) $[M^+ - \text{Si}t\text{Bu}_3]$.

Reaction of 1 with PhCHO—formation of 11a: PhCHO (0.033 g, 0.307 mmol) was added to as solution of **1** (0.133 g, 0.219 mmol) in C_6H_6 (5 mL) at RT, whereby the solution decolorized rapidly. According to NMR spectroscopy, the reaction mixture then contained **11a** only. After concentration to 0.4 mL, filtration of the insoluble parts and evaporation of all volatile components from the latter, the oxadisiletane **11a** (0.143 g, 0.200 mmol; 91 %) was obtained as colorless substance; M.p. 250 °C (decomp); $C_{43}H_{70}OSi_4$ (715.4): calcd. C 72.20, H 9.86; found C 71.94, H 9.82; ^{1}H NMR (C_6D_6): $\delta = 1.126/1.139$ (s/s, 27 H/27 H; Si*t*Bu$_3$/Si*t*Bu$_3$), 6.99–8.56 (m, *o*-, *p*-, *m*-H of 3 Ph); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 14.14$ (1 C; CH), 23.80/23.80 (3 C/3 C; 3 *C*Me$_3$/3 *C*Me$_3$), 31.57/31.97 (9 C/9 C; 3 C*Me*$_3$/3 C*Me*$_3$), (125.2 + 125.7 + 126.9)/(128.3 + 128.7 + 128.9/(134.6 + 137.0 + 138.0)/(140.6 + 144.0 + 146.7) (2 C + 2 C + 2 C/C + C + C/2 C + 2 C + 2 C/C + C + C; *m*-/*p*-/*o*-/*i*-C of 3 Ph); ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = -54.56$ (t, ^3J(Si,H) = 3.6 Hz, 1 Si; SiO), −52.52 (td, 1 Si; SiC), 15.55/24.54/1Si/1Si; Si*t*Bu$_3$/Si*t*Bu$_3$); MS (70 eV): *m/z* (%): 714 (10) [M^+], 657 (100) [$M^+ - t$Bu], 515 (26) [$M^+ -$ Si*t*Bu$_3$].

Reaction of 1 with Ph$_2$CS—formation of 11b: Ph$_2$CS (0.056 g, 0.284 mmol) was added to **1** (0.168 g, 0.276 mmol) in C_6H_6 (0.55 mL) at RT, whereby the solution decolorized rapidly. According to NMR spectroscopy, the reaction mixture then contained **11b** only. After concentration to 0.2 mL, filtration of the insoluble parts and evaporation of all volatile components from the latter, the thiadisiletane **11b** (0.193 g, 0.239 mmol, 87 %) was obtained as colorless substance. M.p. 301 °C; elemental analysis calcd (%) for $C_{49}H_{74}SSi_4$ (807.5): C 72.88, H 9.27; found: C 72.00, H 9.19; ^{1}H NMR (C_6D_6): $\delta = 1.085/1.286$ (s/s, 27 H/27 H; Si*t*Bu$_3$/Si*t*Bu$_3$), 6.76–8.15 (m, 20 H; *o*-, *p*-, *m*-H of 4 Ph); ^{13}C{^{1}H} NMR (C_6D_6, TMS): $\delta = 25.69/26.40$ (3 C/3 C; 3 *C*Me$_3$/3 *C*Me$_3$), 32.72/33.06 (9 C/9 C; 3 C*Me*$_3$/3 C*Me*$_3$), 72.56 (1 C; *C*Ph$_2$), (125.8 + 126.3 + 126.5 + 127.3)/(129.9 + 130.2 + 130.6 + 132.5)/(135.6 + 137.0 + 138.8 + 141.6)/(147.0 + 147.8 + 149.7 + 151.3) (2 C + 2 C + 2 C + 2 C/C + C + C + C/2 C + 2 C + 2 C + 2 C/C + C + C + C; *m*-/*p*-/*o*-/*i*-C of 4 Ph; splitting of signals because of hindrance of rotation); ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = -13.70/1.62$ (1 Si/1 Si; SiPh/SiPh), 25.38/27.61 (1 Si/1 Si; Si*t*Bu$_3$/Si*t*Bu$_3$); MS (CI): *m/z* (%): 806 (7) [M^+], 607 (100) [$\mathbf{1}^+ -$ H], 470 (1) [R*PhSi=CPh$_2^+$], 198 (20) [Ph$_2$CS$^+$].

Remark: Daylight transforms **11b** into **6** among others. Evidently, irradiation causes at first a [2+2] cycloreversion according to **11b**

Reaction of 1 with CO$_2$—formation of 12a: A solution of **1** (0.206 g, 0.338 mmol) in THF (10 mL) was stirred for 4 h under an atmosphere of CO$_2$ at RT. According to NMR spectroscopy, the reaction mixture then contained **12a** only. After removing all volatile compounds in an oil pump vacuum, the oxadisilacyclobutanone **12a** (0.220 g, 0.337 mmol, 100 %) remained as colorless needles. M.p. 230 °C (decomp); elemental analysis calcd (%) for $C_{37}H_{64}O_2Si_4$ (653.3): C 68.03, H 9.87; found: C 66.37, H 10.62; ^{1}H NMR (C_6D_6): $\delta = 1.010/1.014$ (s/s, 27 H/27 H; Si*t*Bu$_3$/Si*t*Bu$_3$), 7.07–8.21 (m, 10 H; *o*-, *p*-, *m*-H of 2 Ph); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 23.74/24.19$ (3 C/3 C; 3 *C*Me$_3$/3 *C*Me$_3$), 31.51/31.72 (9 C/9 C; 3 C*Me*$_3$/3 C*Me*$_3$), (127.2 + 127.5 + 128.5 + 128.5)/(129.5 + 133.9)/(134.6 + 135.6 + 136.9 + 137.1)/(137.7 + 139.8) (each 1 C; *m*-/*p*-/*o*-/*i*-C of 2 Ph; splitting of signals because of hindrance of rotation), 185.9 (1 C; CO); ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = 8.43/11.75$ (1 Si/1 Si; SiO/SiCO), 17.66/23.47 (1 Si/1 Si; Si*t*Bu$_3$/Si*t*Bu$_3$); IR (KBr): $\tilde{\nu} = 1713$ cm^{-1} (C=O); MS (70 eV): *m/z* (%): 652 (77) [M^+], 567 (100) [$M^+ - t$Bu − CO], 511 (17) [$M^+ - t$Bu − CO − C_4H_8], 455 (5) [$M^+ - t$Bu − CO − 2 C_4H_8].

Reaction of 1 with COS—formation of 12b: COS (0.235 mmol) was condensed into a solution of **1** (0.142 g, 0.234 mmol) in C_6H_6 (10 mL) at −78 °C. According to NMR spectroscopy, the solution (after warming to RT; decolorized) then contained **12b** only. After removing all volatile components in an oil pump vacuum, dissolving the residue in C_6H_6 (2 mL), concentration to 0.5 mL, filtration of the insoluble parts, and evaporation of benzene from the latter, the thiadisilacyclobutanone **12b** (0.107 g, 0.160 mmol, 69 %) was obtained as colorless crystals. M.p. 217 °C (decomp); elemental analysis calcd (%) for $C_{37}H_{64}OSSi_4$ (669.3): C 66.40, H 9.64; found C 65.94, H 9.59; ^{1}H NMR (C_6D_6): $\delta = 1.017/1.037$ (s/s, 27 H/27 H; Si*t*Bu$_3$/Si*t*Bu$_3$), 7.04–8.21 (m, 10 H; *o*-, *p*-, *m*-H of 2 Ph); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 24.82/24.94$ (3 C/3 C; 3 *C*Me$_3$/3 *C*Me$_3$), 31.83/31.91 (9 C/9 C; 3 C*Me*$_3$/3 C*Me*$_3$), (126.6 + 127.2 + 127.8 + 128.7)/(129.4 + 129.5)/(136.3 + 136.7 + 137.0 + 137.1)/(138.3 + 139.5) (each 1 C; *m*-/*p*-/*o*-/*i*-C of 2 Ph; splitting of signals because of hindrance of rotation), 217.5 (1 C; CO); ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = 21.44/26.21$ (1 Si/1 Si; Si*t*Bu$_3$/Si*t*Bu$_3$), 1.52 (1 Si; SiCO), −70.65 (1 Si; SiS); X-ray structure analysis: see Figure 3 (colorless prisms of **12b** · 0.5 C_6D_6 from C_6D_6).

Reactions of 1 with Ph$_2$C=O—formation of 13: The reaction of **1** (0.289 g, 0.474 mmol) and Ph$_2$CO (0.154 g, 0.845 mmol) in C_6H_6 (5 mL) lead rapidly and (according to NMR spectroscopy) quantitatively to **13**. After evaporation of all volatile components in an oil pump vacuum and dissolving the residue in benzene (2 mL), the Ph$_2$CO adduct **13** (0.402 g, 0.413 mmol; 87 %) was obtained as yellow substance with one mole Ph$_2$CO per mole adduct. M.p. of **13** · Ph$_2$CO 180 °C (decomp); elemental analysis calcd (%) for $C_{40}H_{74}OSi_4$ (791.5): C 76.48, H. 8.70; found: C 76.01, H 8.76; ^{1}H NMR (C_6D_6): $\delta = 0.900/0.966$ (s/s, 27 H/27 H; Si*t*Bu$_3$/Si*t*Bu$_3$), 1.211 (br, 1 H; CH), 5.36–6.75 (m, 4 H; 4=CH), 7.00–8.20 (m, 15 H; *o*-, *p*-, *m*-H of 3 Ph); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 24.41$ (br, 7 C; 6 *C*Me$_3$ + 1 CH), 31.76/32.16 (9 C/9 C, 3 C*Me*$_3$/3 C*Me*$_3$), 118.1–146.7 (18 signals; 6 C + 18 C; CCCHCHCHCH + C of 3 Ph); ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = -14.16$ (1 Si; PhSiO), 6.22 (1 Si; PhSiC), 20.97/30.65 (1 Si/1 Si; Si*t*Bu$_3$/Si*t*Bu$_3$); UV/Vis (heptane): $\lambda_{\max}$ (ε) = 396.2 nm (1560); MS (70 eV): *m/z* (%): 790 (7) [M^+], 733 (3) [$M^+ - t$Bu], 713 (13) [$M^+ -$ Ph], 671(1) [$M^+ -$ Ph − C_3H_6], 657 (1) [$M^+ -$ Ph − C_4H_8], 608 (29) [$\mathbf{1}^+$], 591 (31) [$M^+ -$ Si*t*Bu$_3$], 551 (100) [$\mathbf{1}^+ - t$Bu], 495 (2) [$\mathbf{1}^+ - t$Bu − C_4H_8], 409 (17) [$\mathbf{1}^+ -$ Si*t*Bu$_3$]; X-ray structure analysis: see Figure 5 (yellow needles of composition **1** + Ph$_2$CO from benzene).

Reaction of 1 with DMB—formation of 14: The reaction of **1** (0.147 g, 0.241 mmol) and $CH_2{=}CMe{-}CMe{=}CH_2$ (0.041 g, 0.502 mmol) in C_6H_6 (0.5 mL) lead rapidly (decolorization) and, according to NMR spectroscopy, quantitatively to **14**. After evaporation of all volatile components in an oil pump vacuum and dissolving the residue in acetone (2 mL), the DMB adduct **14** (0.130 g, 0.188 mmol; 78 %) was obtained as colorless substance. M.p. 206–207 °C; elemental analysis calcd (%) for $C_{42}H_{74}Si_4$ (691.4): C 72.96, H 10.79; found: C 72.09, H 10.69; ^{1}H NMR (C_6D_6): $\delta = 1.096$ (s, 54 H; 2 Si*t*Bu$_3$), 1.953 (s, 6 H; 2 Me of DMB), 2.278/2.477 (d/d, ^2J(H,H) = 16.5/16.5 Hz, 2 H/2 H; 2 CH$_2$), 7.099–8.332 (m, 10 H; *o*-, *p*-, *m*-H of 2 Ph); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 24.65/25.81$ (2 C/2 C; 2 CH$_3$/2 CH$_2$ of DMB), 25.10/32.21 (6 C/18 C; 6 *C*Me$_3$/6 C*Me*$_3$), 126.7 (2 C, C=C of DMB), 128.5/139.4/140.10/145.8 (4 C/2 C/4 C/2 C; *m*-/*p*-/*o*-/*i*-C of 2 Ph); ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = -38.74$ (2 Si; 2 SiPh), 21.16 (2 Si; 2 Si*t*Bu$_3$); MS (70 eV): *m/z* (%): 690 (3) [M^+], 675 (2) [$M^+ -$ Me], 633 (9) [$M^+ - t$Bu], 577 (3) [$M^+ - t$Bu − C_4H_8], 491 (100) [$M^+ -$ Si*t*Bu$_3$], 435 (6) [$M^+ -$ Si*t*Bu$_3$ − C_4H_8].

Reaction of 1 with CS$_2$—formation of 16a: As a consequence of the reaction of **1** (0.076 g, 0.125 mol) and CS$_2$ (0.021 g, 0.269 mmol) in C_6D_6 (0.5 mL) deep green solution was formed (**15a**?), from which a colorless precipitate was obtained. After filtration of the insoluble parts and evaporation of all volatile components from the latter, the ethene **16a** (0.081 g, 0.055 mmol, 89 %) was obtained as colorless substance. M.p. > 350 °C; elemental analysis calcd (%) **16a** · C_6D_6: C 66.04, H 9.70; found: C 66.63, H 9.83; ^{1}H NMR (C_6D_6): $\delta = 1.95$ (s, 108 H; 4 Si*t*Bu$_3$), 7.01–8.14 (m, 20 H; *o*-, *p*-, *m*-H of 4 Ph); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 25.04/32.09$ (12 C/36 C; 12 *C*Me$_3$/12 C*Me*$_3$), 128.3/128.9/133.4/136.7 (8 C/4 C/8 C/4 C; *m*-/*p*-/*o*-/*i*-C of 4 Ph), not observed (2 C of C=C); ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = 26.00$ (4 Si; 4 Si*t*Bu$_3$), not observed (4 Si; 4 SiPh); MS (70 eV): *m/z* (%): 1370 (37) [M^+], 1313 (12) [$M^+ - t$Bu], 1171 (14) [$M^+ -$ Si*t*Bu$_3$], 1114 (3) [$M^+ -$ Si*t*Bu$_3$ − C_4H_8], 1057 (3) [$M^+ -$ Si*t*Bu$_3$ − -2 C_4H_8], 672 (2) [**1** · 2 S$^+$], 616 (28) [**1** · 2 S$^+$ − C_4H_8], 584 (100) [**1** · S$^+$ − C_4H_8], 528 (10) [**1** · S$^+$ − 2 C_4H_8], each peak with correct isotopic pattern; X-ray structure analysis: see Figure 4 (colorless plates of composition **16a** + C_6D_6 from C_6D_6 after 2 years).

Remark: According to the structure of **16a** (see Figure 4), one expects two different sorts of R* and Ph substituents. In fact, the latter are equivalent in the NMR spectrum. Evidently, the five-membered rings are not comformation-stable on the NMR timescale. On the other hand, **16b** gives the expected R* signals.

Reaction of 1 with CSe$_2$—formation of 16b: As a consequence of the reaction of **1** (0.120 g, 0.197 mmol) with CSe$_2$ (0.034 g, 0.197 mmol) in C_6D_6 (0.5 mL), a colorless precipitate was formed (in between, the reaction mixture turned black brown; **15b**?). After filtration of the insoluble parts and evaporation of all volatile components from the latter, the ethene **16b** (0.141 g, 0.091 mmol; 92 %) was obtained as colorless substance. M.p. 335 °C (decomp); elemental analysis calcd (%) for $C_{74}H_{128}Se_4Si_8$ (1558.35): C 57.04, H 8.28; found: C 56.81, H 8.41; ^{1}H NMR (C_6D_6): $\delta = 1.180/1.188$ (s/s, 54 H/54 H; 2 Si*t*Bu$_3$/2 Si*t*Bu$_3$), 6.90–8.52 (m, 20 H; *o*-, *p*-, *m*-H of 4 Ph); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 25.07/25.10$ (6 C/6 C; 6 *C*Me$_3$/6 *C*Me$_3$), 31.77/31.98 (18 C/18 C; 6 C*Me*$_3$/6 C*Me*$_3$), not observed (24 C of 4 Ph, 2 C of C=C); ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = 31.78/31.98$ (2 Si/2 Si; 2 Si*t*Bu$_3$/2 Si*t*Bu$_3$), not observed (4 Si of 4 SiPh); MS (70 eV): *m/z* (%): 1559 (6) [M^+], 1502 (2) [$M^+ - t$Bu], 1359 (2) [$M^+ -$ Si*t*Bu$_3$], 1303 (1) [$M^+ -$ Si*t*Bu$_3$ − C_4H_8], 1281 (1) [$M^+ -$ Si*t*Bu$_3$ − C_6H_6], 814 (5) [$M^+ -$ **1** · Se − C_4H_8], 792 (3) [$M^+ -$ **1** · 2 Se − C_4H_8], 759 (9) [$M^+ -$ **1** · Se − 2 C_4H_8], 712 (25) [**1** · 2 Se$^+$ − C_4H_8], 632

Table 1. Selected parameters of the X-ray structure analyses of **5b**, **6**, **12b**, **13**, **16a**.

	5b	**6a**	**6b**[a]	**6c**[a]	**12b**[a]	**13**[a]	**16a**[a]
formula	$C_{36}H_{64}TeSi_4$	$C_{36}H_{64}O_2Si_4$	$C_{36}H_{64}S_2Si_4$	$C_{36}H_{64}Se_2Si_4$	$C_{37}H_{64}OSSi_4$	$C_{59}H_{78}O_4Si_4$	$C_{72}H_{128}S_4Si_8$
M_r	736.83	641.23	673.36	767.15	669.31	915.57	1370.72
system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	Cc	Cc	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a [Å]	8.866(3)	8.885(1)	14.520(1)	14.579(3)	23.102(2)	17.791(4)	11.447(8)
b [Å]	20.910(6)	19.694(9)	19.937(4)	20.084(4)	8.6239(3)	26.691(7)	12.632(8)
c [Å]	21.468(6)	11.6209(9)	16.385(4)	16.301(2)	21.532(1)	12.169(5)	17.284(6)
β [°]	93.39(2)	106.505(8)	108.83(1)	108.12(1)	105.157(8)	99.52(3)	78.74(4)[b]
V [Å^3]	3973(2)	1949.7(4)	4490(1)	4537(1)	4141.1(4)	5699(9)	2202(2)
Z	4	2	4	4	4	4	1
ρ [Mg m^{-3}]	1.232	1.092	1.112	1.238	1.136	1.135	1.093
μ [mm^{-1}]	0.891	0.180	0.252	1.762	0.223	0.145	0.255
$F(000)$	1552	704	1640	1784	1548	2112	790
θ [°]	2.14–20.02	2.56–18.05	2.43–22.98	2.42–22.99	1.93–25.87	2.57–22.99	2.38–24.04
index ranges	$0 \leq h \leq 8$	$-9 \leq h \leq 9$	$-15 \leq h \leq 15$	$-14 \leq h \leq 16$	$-27 \leq h \leq 28$	$-19 \leq h \leq 19$	$-13 \leq h \leq 0$
	$\leq \leq k \leq 20$	$-21 \leq k \leq 0$	$-21 \leq k \leq 0$	$-22 \leq k \leq 0$	$-8 \leq k \leq \leq 0$	$-29 \leq k \leq 0$	$-14 \leq k \leq 13$
	$-20 \leq l \leq 20$	$0 \leq l \leq 12$	$-17 \leq l \leq 17$	$-17 \leq l \leq 16$	$-26 \leq l \leq 26$	$0 \leq l \leq 13$	$-19 \leq l \leq 19$
reflns measured	4022	2860	6228	7111	22097	8346	7268
independent reflns	3710	2711	6228	5496	7792	7910	6874
observed reflns[c]	2831	2215	4989	4567	4576	4727	5041
R_{int}	0.0756	0.0103	0.000	0.0004	0.0665	0.0345	0.0372
x/y[d]	0.1233/	0.0387/	0.0459/	0.0436/	0.0592/	0.0913/	0.0408/
	777.375	0.9851	36.365	64.188	0.000	651.956	12.815
$R1$[c]	0.0944	0.0374	0.0380	0.0316	0.0509	0.1365	0.0465
$wR2$[c]	0.2426	0.0861	0.0890	0.0802	0.1082	0.3189	0.0748
GOOF (F^2)	1.087	1.068	1.098	1.146	0.861	1.096	1.096
max./min. electron	1.247/	0.173/	0.296/	0.388/	0.981/	0.772/	0.279/
density [e Å^{-3}]	−1.229	−0.196	−0.188	−0.301	−0.645	−0.506	−0.210

[a] Composition of crystals: **6b** + C_6D_6, **6c** + C_6D_6, **12b** + $0.5\,C_6D_6$, **13** + Ph_2CO, **16a** + C_6D_6. [b] $\alpha = 73.99(4)°$, $\gamma = 70.53(5)°$. [c] $F > 4\sigma(F)$. [d] $w^{-1} = (\sigma^2 F_o^2 + (xP)^2 + yP)$ with $P = (F_o^2 + 2F_c^2)/3$.

(100) [**1** · $Se^+ - C_4H_8$], 608 (1) [**1**$^+$], 568 (55) [**1** · $2Se^+ - SitBu_3$]; each peak with correct isotopic pattern.

Remark: Compound **16b** (0.076 g) transforms in air in three weeks (according to NMR spectroscopy) quantitatively into the 1,3-diselenadisiletane **6c**.

X-ray structure determinations of 5b, 6, 12b, 13, 16a: Crystallographic data for compounds **5b**, **6**, **12b**, **13** and **16a** are given in Table 1. The intensities were measured with a CAD 4 of Enraf-Nonius (**5b**, **6**, **13**, **16a**) and a STOE IPDS with area detector (**12b**) ($Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $T = 293(2)$ K for **5b**, **6**, **13**, **16a** and 188(2) K for **12b**). The structures were solved by using direct methods and refined against F^2 for all observed reflections. All non-hydrogen atoms were refined anisotropically with a riding model and fixed U_i values.

CCDC-140135 (**5b**), CCDC-173753 (**6a**), CCDC-173754 (**6b**), CCDC-173755 (**6c**), CCDC-173758 (**12b**), CCDC-173756 (**13**) and CCDC-173757 (**16a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk).

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