Decamethylsilicocene Chemistry: Unprecedented Multistep Reactions of a Silicon(II) Compound with the Heterocumulenes CO_2, COS, CS_2, and RNCS (R = Methyl, Phenyl)

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In the reaction of the nucleophilic decamethylsilicocene, $((Me_5C_5)_2Si$ (**1**), with the electrophilic heterocumulenes CO_2, COS, CS_2, and RNCS, multistep processes are observed, which in most cases proceed via several highly reactive intermediates. In all reactions, the formal oxidation state of the silicon atom changes from +2 in **1** to +4, and the hapticity of the pentamethylcyclopentadienyl ligands changes from η^5 to η^1. In the reaction of **1** with CO_2, COS, or RNCS, double-bond species of the type $(Me_5C_5)_2Si{=}X$ (X = O, S) are formed, which are stabilized via different routes. Thus, reaction of **1** with CO_2 in toluene as solvent finally leads to the spiro compound $[(Me_5C_5)_2SiO_2]_2C$ (**4**), whereas in pyridine as solvent, the eight-membered heterocycle $[(Me_5C_5)_2SiO_2CO]_2$ (**5**) is formed. The dithiadisiletane $[(Me_5C_5)_2SiS]_2$ (**9**) results from the reaction of **1** with COS. Dithiasiletane derivates of the type $(Me_5C_5)_2SiS_2C{=}NR$ (**10, 11**) are the final products from the reaction of **1** with RNCS (R = CH_3, C_6H_5). Multistep rearrangement processes have to be postulated to explain the formation of the dithiadisiletane derivate **15** in the surprising reaction of **1** with CS_2; ligands that initially are bonded to the silicon (Me_5C_5) and to the carbon atom (S) have to be completely exchanged to build up the final product. The silaheterocycles **4**, **5**, **10**, and **15** and also some of the basic molecular framework have been unknown in the literature. The crystal strucutres of **4**, **5**, **10**, and **15** were determined by X-ray crystallography and are presented.

Introduction

Recent years have brought much progress in the attempts to synthesize stable monomeric compounds with divalent silicon. Species analogous to Arduengo's carbenes have been prepared[1] as well as a higher coordinated silicon(II) compound with two diphoshinomethanide ligands.[2] The first silicon(II) compound stable under ordinary conditions was decamethylsilicocene $((Me_5C_5)_2Si$ (**1**), in which two pentamethylcylcopentadienyl ligands are bonded in a η^5 fashion to the silicon atom.[3] The chemistry of **1** has already been investigated in some detail.[4] As a result of these investigations, **1** is regarded as a hypercoordinated electron-rich nucleophilic silylene, which reacts preferentially with electrophilic substrates and under oxidation of the silicon atom from the formal +2 to the +4 oxidation state. Heterocumulenes of the type X=C=Y are classified as electrophilic substrates. In this context, we have investigated the reaction of **1** with the heterocumulenes CO_2, COS, CS_2, and RNCS (R = Me, Ph). Some of these reactions were already communicated in an earlier publication.[5] In this paper, the structure of the product of the reaction of **1** with CS_2 was misinterpretated. Only now can we present an X-ray crystal structure analysis of the product and suggest a possible reaction pathway.

Results and Discussion

Decamethylsilicocene (**1**) reacts with carbon dioxide under mild conditions. Surprisingly, the products obtained depend on the solvent used. Bubbling CO_2 at room temperature for ~3 h through a solution of **1** in toluene led to the spiro heterocyclic **4** in ~70% yield, whereas in pyridine as solvent, the eight-membered cyclic **5** was formed in ~65% yield. The compounds **4** and **5** were characterized by spectroscopic and analytical data as well as by X-ray crystal structure analysis (Figures 1 and 2, vide infra). They showed good solubility in common organic solvents.

For the reaction of **1** with CO_2 we propose the following pathway (see Scheme 1). The first intermediate is a highly reactive [2 + 1] cycloaddition product or its ring-opened isomer, which easily loses carbon monoxide to give the silanone **2**. The formation of CO was proved by reaction with the iron complex (H_5C_5)-

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(1) Denk, U.; Lennon, R.; West, R.; Belgalov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Ketzler, H. *J. Am. Chem. Soc.* **1994**, *116*, 2691.

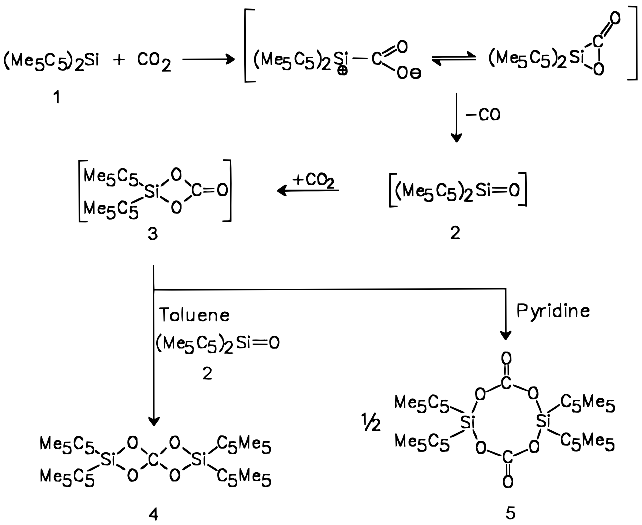
(2) Karsch, H. H.; Keller, U.; Gamper, S.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 295.

(3) Jutzi, P.; Holtmann, U.; Kanne, D.; Krüger, C.; Blohm, A.; Gleiter, R.; Hyla-Kryspin, I. *Chem. Ber.* **1989**, *122*, 1629.

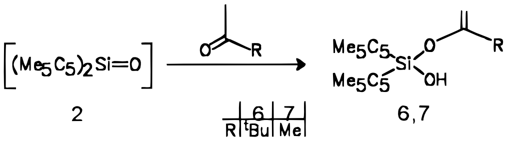
(4) (a) Jutzi, P.; Kanne, D.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 164. (b) Jutzi, P.; Möhrke, A.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1518. (c) Jutzi, P.; Bunte, E.-A.; Holtmann, U.; Neumann, B.; Stammler, H.-G. *J. Organomet. Chem.* **1993**, *446*, 139. (d) Jutzi, P.; Möhrke, A. *Angew. Chem., Int. Ed. Engl.* **1990**, *28*, 893. (e) Jutzi, P. In *Frontiers of organosilicon chemistry*; Bassindale, A. R., Gaspar, P. P., Eds.; Royal Society of Chemistry: Cambridge, England, 1991. (f) Jutzi, P.; Bunte, E.-A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1605.

(5) Jutzi, P.; Möhrke, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 762.

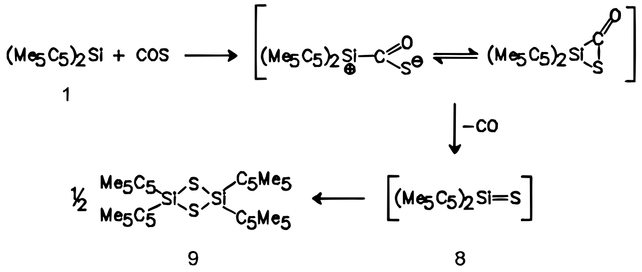
Scheme 1



Scheme 2



Scheme 3

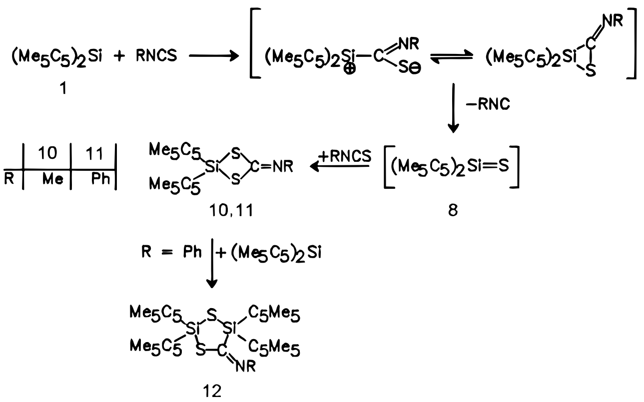


$Fe(SMe_2)_3{}^+BF_4{}^-$.[6] The silanone **2** is not stable under the reaction conditions and is transformed by the CO_2 present in solution to the [2 + 2] cycloaddition product **3,** which once more is a highly reactive intermediate. In toluene as solvent, **3** reacts with the silanone **2** present in the reaction mixture to give the final product **4** in a further [2 + 2] cycloaddition step. In pyridine as solvent, the intermediate silanone **2** is deactivated.[7] As a result, **3** does not react with **2**, but forms the dimerization product **5** after ring opening at one of the Si−O bonds.

The intermediate silanone **2** was derivatized by trapping reactions. In the presence of *tert*-butyl methyl ketone or acetone, the addition products **6** or **7** were formed in an ene-type reaction[8] (see Scheme 2).

1 reacts with carbon oxysulfide under very mild conditions: A toluene solution of **1** was added to liquid COS at −78 °C. The dithiadisiletane **9** was isolated in about 50% yield after a reaction time of 2 h at this temperature (see Scheme 3). **9**, already known in the literature as the reaction product of **1** with sulfur,[3b] was poorly soluble in organic solvents. It was characterized by NMR spectroscopic and mass spectrometric data.

Scheme 4



In analogy to the reaction of **1** with CO_2, an intermediate [2 + 1] cycloaddition product or its ring-opened isomer is formed, which loses CO; the resulting silathione **8** is unstable under the reaction conditions and dimerizes to the dithiadisiletane **9**. The first stable silathione, Tbt(Tip)Si=S (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl and Tip = 2,4,6-triisopropylphenyl), has been recently reported by Okazaki et al.[9]

In the reaction of **1** with methyl isothiocyanate, the dithiasiletane **10** was isolated in ~50% yield after a reaction time of 16 h at room temperature (see Scheme 4). Slightly more drastic conditions (5 h at 65 °C) were necessary for the reaction of **1** with phenyl isothiocyanate, which led to the corresponding dithiasiletane **11** in 65% yield. The formation of **10** and **11** was independent of the stoichiometry of the reactands. Under even more drastic conditions (20 h at 100 °C), the five-membered heterocycle **12** was formed in the reaction of **1** with PhNCS in ~65% yield. **10**, **11**, and **12** showed good solubility in common organic solvents. They were characterized by spectroscopic and analytical data. The solid state structure of **10** was determined by a single-crystal X-ray crystal structure analysis (Figure 3, vide infra).

The pathway of the reaction of **1** with isothiocyanates is discussed as follows (see Scheme 4): An intermediate [2 + 1] cycloaddition product or its ring-opened isomer loses the corresponding isonitrile RNC; the formation of phenylisonitrile was proved by ^{13}C-NMR spectroscopy.[10] The silathione **8** thus formed does not dimerize but is trapped by the respective isothiocyanate in form of the stable [2 + 2] cycloadditon product **10** or **11**. The formation of a dithiasiletane derivative is also observed by Okazaki et al. in the reaction of the stable silathione (Tbt(Tip)Si=S) with PhNCS.[9]

Under more rigorous conditions, **11** reacts with **1** still present in the reaction mixture to give the insertion product **12**.

The intermediate silathione **8** was derivatized with the trapping agent *tert*-butyl methyl ketone (see Scheme 5 and cf. Scheme 2): In a first step **8** is transformed to an addition product containing a thiol group, in a further step this species reacts with **1** in an oxidative

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[6] Reaction of CO with $[(C_5H_5)_2Fe(Me_2S)_3]$ BF_4 leads to a carbonyl complex IR(CsI): $\nu_{(CO)}$ = 1980, 1730 cm^{-1}.

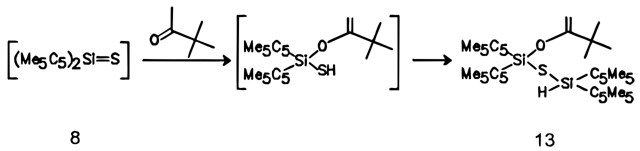
[7] Chult, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371.

[8] Wiberg, N.; Preiner, G.; Wagner, G. *Z. Naturforsch. B* **1987**, *B426*, 1062.

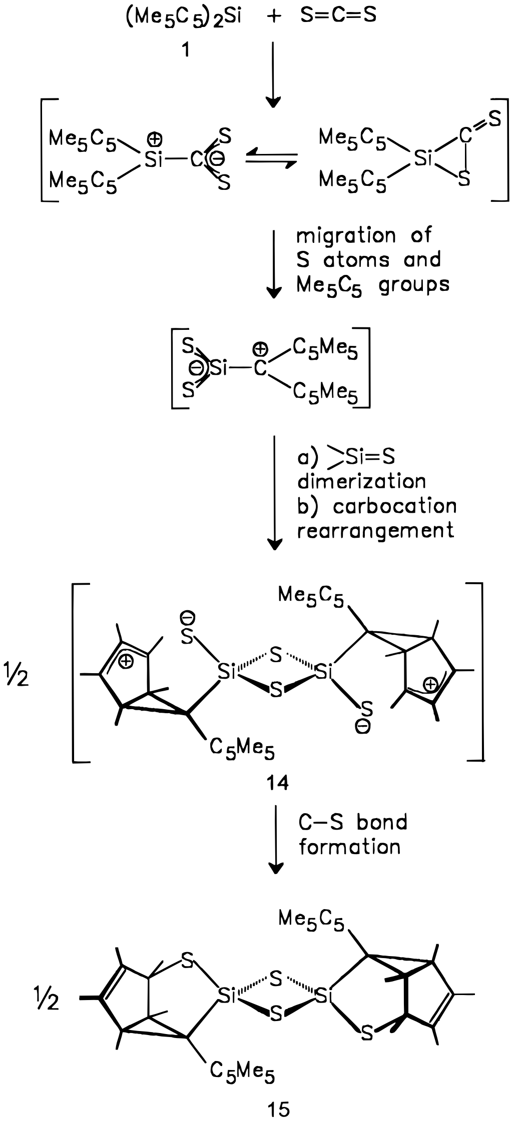
[9] Suzuki, H.; Tokitoh, N.; Nagase, S.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 11578.

[10] ^{13}C NMR of PhNC: δ = 165.5 ppm (*^{13}C-NMR-Spektroskopie*; Kalinowski, H. D., Burger, S., Braun, S., Eds.; Thieme: Stuttgart, 1984 (δ = 165.7 ppm)).

Scheme 5



Scheme 6



addition process to form the final product **13** (see Scheme 5 and cf. Scheme 2). **13** was characterized by spectroscopic and analytical data.

In the reaction of **1** with carbon disulfide, a highly surprising multistep reaction is observed. Excess CS_2 was added to a solution of **1**, and after 16 h at room temperature, the dithiadisiletane **15** was isolated in ~60% yield (see Scheme 6). **15** was characterized by spectroscopic and analytical data and by an X-ray crystal structure analysis (Figure 4, vide infra).[11]

The pathway of the underlying process is tentatively described as follows (see Scheme 6): A highly reactive [2 + 1] cycloaddition product or its ring-opened isomer is the first intermediate. In a subsequent multistep rearrangement, the ligands at carbon and at silicon have to be completely exchanged: two sulfur atoms migrate from carbon to silicon and two Cp* groups migrate from silicon to carbon. The resulting product is present in form of a strained three-membered ring system or in form of a dipolar ring-opened structure. This compound once more is highly reactive and gains stabilization by dimerization and by a rearrangement process transforming a classical carbenium ion into an allyl-type cation in the form of the intermediate **14**. Comparable rearrangement processes are described in the literature.[12] In a final step, **14** is transformed to **15** by carbon–sulfur bond formation. We have not been able so far to identify or trap one of the postulated intermediates in this reaction sequence.

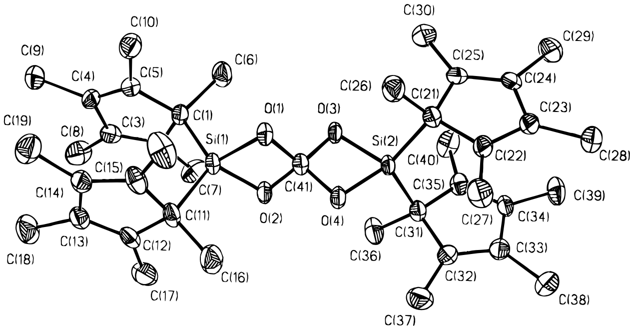


Figure 1. Molecular structure of **4**.

Structure Data of the Novel Silaheterocycles 4, 5, 10, and 15. To the best of our knowledge the silaheterocycles **4**, **5**, **10**, and **15** and also some of the basic molecular frameworks have been unknown in the literature. In the following we will discuss important structural parameters of these compounds on the basis of their X-ray crystal structure data.

The molecular structures of **4, 5**, **10**, and **15** are presented in Figures 1–4; bond lengths, interatomic nonbonded distances and bond angles are displayed in Tables 1–4. Crystallographic data are given in Table 6.

Common to the structures of **4**, **5**, and **10** is the presence of two Si-bonded σ-pentamethylcyclopentadienyl ligands, which adopt a nearly parallel sandwich-like orientation. The respective C(Cp*)SiC(Cp*) angles deviate drastically from the value expected for an sp^3-hybridized Si atom; furthermore, the Si–C(Cp*) distances are rather long (~1.89 Å). These data are consistent with the well-known effects of two σ-bonded Cp* ligands at silicon.[3c] Naturally, the steric requirements of the Cp^*_2Si group will influence the structural parameters of the basic molecular framework of the corresponding silaheterocycles.

The structure of **4** displays a tetraoxodisilaspiroheptane unit with nearly D_{2d} symmetry of the ring skeleton. Two planar four-membered rings, each containing one silicon, two oxygen, and one carbon atom, are cross-connected by a common carbon atom. Bonding parameters of the second ring of the molecule **4** are identical to those given for the first ring within the margin of error of the structure determination. A pronounced strain within the rings as well as the discussed Cp^*_2Si effects lead to rather small bonding angles (O1Si1O2 = 80.3°; O1C41O2 = 100.9°; Si1O1C41 = 89.3°). Rather

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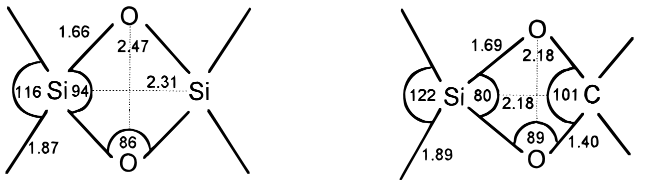
(11) The structure of **15** was misinterpretated in an earlier publication.[5]

(12) (a) Childs, R. F.; Sakai, M.; Parrington, B. D.; Winstein, S. *J. Am. Chem. Soc.* **1974**, *96*, 6403. (b) Childs, R. F; Winstein, S. *J. Am. Chem. Soc.* **1974**, *96*, 6409.

Chart 1



SiO$_2$Si skeleton in [Mes$_2$SiO]$_2$

SiO$_2$C skeleton in **4**

Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Interatomic Nonbonding Distances (Å) of 4

Bond Lengths			
Si1−O1	1.689(2)	O3−C41	1.404(4)
Si1−O2	1.686(2)	O4−C41	1.408(4)
Si2−O3	1.684(2)	Si1−C1	1.892(3)
Si2−O4	1.689(2)	Si1−C11	1.882(4)
O1−C41	1.411(4)	Si2−C21	1.891(4)
O2−C41	1.412(4)	Si2−C31	1.882(4)
Interatomic Nonbonding Distances			
Si1−C41	2.188(4)	O1−O2	2.177(4)
Si2−C41	2.177(4)	O3−O4	2.177(4)
Bond Angles			
O1−Si1−O2	80.35(12)	O2−C41−O3	113.1(3)
O1−Si1−C1	111.46(14)	O2−C41−O4	114.0(3)
O1−Si1−C11	112.53(14)	O3−C41−O4	101.5(2)
O2−Si1−C1	111.21(14)	C41−O3−Si2	89.2(2)
O2−Si1−C11	111.3(2)	C41−O4−Si2	88.9(2)
C1−Si1−C11	122.3(2)	O3−Si2−O4	80.41(11)
Si1−O1−C41	89.3(2)	O3−Si2−C21	110.08(14)
Si1−O2−C41	89.4(2)	O3−Si2−C31	113.61(14)
O1−C41−O2	100.9(2)	O4−Si2−C21	113.14(14)
O1−C41−O3	114.4(3)	O4−Si2−C31	119.14(14)
O1−C41−O4	113.5(3)	C21−Si2−C31	122.0(2)

long Si−O distances (1.69 Å) are noteworthy, too. Striking features of the structure of **4** are the rather short nonbonded O−O and Si−C distances. The O−O separation (2.18 Å) is markedly shorter than the sum of the van der Waals radii (2.80 Å); the Si−C separation (~2.18 Å) is longer than the sum of the covalence radii (1.94 Å), but much shorter than the sum of the van der Waals radii (3.85 Å). Thus, the nature of the bonding within the SiO$_2$C rings in **4** raises interesting questions very similar to those in connection with the unusual structure of tetramesityldisiloxane.[13] A comparison of structural data of these four-membered heterocycles is given in Chart 1.

The spiro silaheterocyclic ring system of **4** has so far not been described in the literature.

The structure of **5** shows a corrugated eight-membered ring system with two Cp*$_2$SiO$_2$ units bridged by two CO groups and with D_2 symmetry of the ring skeleton. The four oxygen atoms are located alternatively above and below a plane formed by the two silicon and the two carbon atoms. Bonding parameters of the second half of the molecule **5** are identical to those given for the first half within the margin of error of the structure determination. The O1C41O2 angles (113.7°) are smaller than expected (120°); the small O1Si1O4 angles (107.0°) are a consequence of the bulky exo-Cp* ligands. To the best of our knowledge, the ring system present in **5** has not yet been described in the literature.

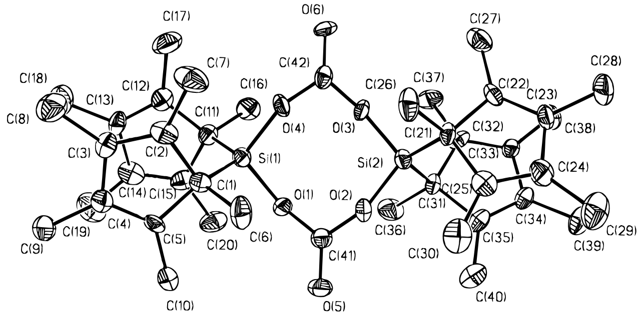


Figure 2. Molecular structure of **5**.

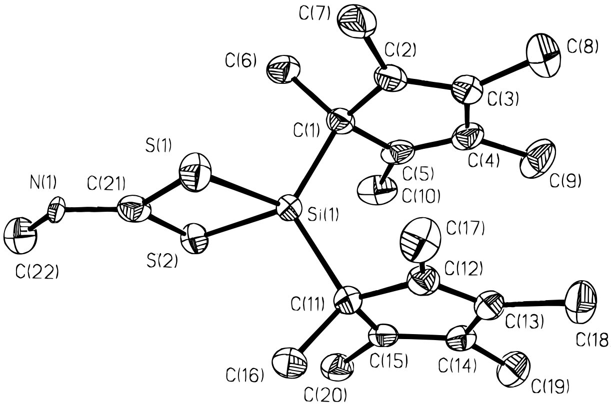


Figure 3. Molecular structure of **10**.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of 5

Bond Lengths			
C1−Si1	1.870(5)	C41−O2	1.344(6)
C11−Si1	1.889(5)	O2−Si2	1.672(4)
Si1−O1	1.672(4)	O3−Si2	1.663(4)
Si1−O4	1.669(4)	Si2−C21	1.887(5)
O1−C41	1.344(6)	Si2−C31	1.869(5)
O4−C42	1.325(6)	C41−O5	1.190(6)
C42−O3	1.349(6)	C42−O6	1.201(6)
Bond Angles			
C1−Si1−C11	122.6(2)	O4−C42−O6	122.8(5)
C11−Si1−O4	109.1(2)	O3−C42−O6	122.1(5)
C11−Si1−O1	103.9(2)	O2−C41−O5	123.0(5)
C1−Si1−O4	104.1(2)	C41−O2−Si2	133.6(4)
C1−Si1−O1	109.3(2)	C42−O3−Si2	134.4(4)
O1−Si1−O4	107.0(2)	O2−Si2−O3	107.0(2)
Si1−O4−C42	135.2(4)	O3−Si2−C21	109.6(2)
Si1−O1−C41	134.5(4)	O3−Si2−C31	104.7(2)
O1−C41−O2	113.7(5)	O2−Si2−C21	103.8(2)
O3−C41−O4	115.1(5)	O2−Si2−C31	108.4(2)
O1−C41−O5	123.3(5)	C21−Si2−C31	122.5(3)

The structure of **10** shows a planar 1,3-dithiasiletane ring system containing an sp^2-hybridized carbon atom. The molecular symmetry is C_s. The ring strain and the steric effects of the Cp*$_2$Si unit lead to rather small angles within the cycle (SSiS = 85.1°; SiSC = ~82.3°; SCS = 110.3°). The nonbonding S−S and Si−S distances in **10** are noteworthy. The S−S distance (2.95 Å) is markedly shorter than the sum of the van der

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Table 3. Selected Bond Lengths (Å), Bond Angles (deg), and Interatomic Nonbonding Distances (Å) of 10

Bond Lengths			
C1−Si1	1.904(3)	S1−C21	1.789(3)
C11−Si1	1.905(3)	S2−C21	1.803(3)
Si1−S1	2.193(1)	C21−N1	1.295(4)
Si1−S2	2.167(1)	C22−N1	1.385(4)
Interatomic Nonbonding Distances			
Si1−C21	2.633(3)	S1−S2	2.947(1)
Bond Angles‘			
C1−Si1−C11	120.60(13)	Si1−S1−C21	82.09(11)
C1−Si1−S1	111.73(10)	Si1−S2−C21	82.53(11)
C1−Si1−S2	111.04(10)	S1−C21−S2	110.3(2)
C11−Si1−S1	111.78(10)	S1−C21−N1	123.8(2)
C11−Si1−S2	111.10(10)	S2−C21−N1	125.9(2)
S1−Si1−S2	85.07(5)	C22−N1−C21	119.9(3)

Table 4. Selected Bond Lengths (Å), Bond Angles (deg), and Interatomic Nonbonding Distances (Å) of 15

Bond Lengths			
Si1−S1a	2.142(1)	C11−C12	1.505(4)
Si1−S1	2.141(1)	C12−C13	1.332(4)
Si1−S2	2.123(1)	C13−C14	1.518(4)
Si1−C21	1.919(3)	C14−C15	1.555(4)
C21−C11	1.562(4)	S2−C14	1.868(3)
C21−C15	1.553(4)	C21−C1	1.552(4)
C11−C15	1.502(4)		
Interatomic Nonbonding Distances			
Si1−Si1a	2.874(1)	S1−S1a	3.175(1)
Bond Angles			
S1−Si1−S1a	95.69(4)	Si1−C21−C1	113.3(2)
S1a−Si1−S2	117.30(5)	C12−C11−C21	116.7(2)
S1−Si1−S2	105.61(4)	C12−C11−C15	106.3(2)
S1a−Si1−C21	116.18(9)	C15−C11−C21	60.9(2)
S2−Si1−C21	97.94(9)	C14−C15−C21	114.0(2)
S1−Si1−C21	125.12(9)	C11−C15−C21	61.5(2)
Si1−S1−Si1a	84.31(4)	C14−C15−C11	106.2(2)
C11−C21−C1	123.9(2)	S2−C14−C15	109.6(2)
C15−C21−C1	126.4(2)	C13−C14−C15	103.9(2)
C11−C21−C15	57.7(2)	S2−C14−C13	106.9(2)
Si1−C21−C11	116.2(2)	C14−C13−C12	111.7(3)
Si1−C21−C15	108.1(2)	C13−C12−C11	111.2(2)

Waals radii (3.70 Å). Similarly, the Si−C distance (2.63 Å) is shorter than the sum of the van der Waals radii (3.85 Å).

The ring system of **10** has already been described in the literature, but no structural parameters have been specified.[9]

A planar 1,3-dithia-2,4-disiletane ring is the central unit in the polycyclic **15**. The central ring is cross-connected by the silicon atoms to a tricyclooctene ring system. The ring system consists of a heterocyclic five-membered ring containing one silicon, one sulfur, and three carbon atoms, of a condensed five-membered carbon ring and of a condensed cyclopropane ring. The molecular symmetry of **15** is C_i.

Some parameters in the structure of **15** are noteworthy. Within the planar dithiadisiletane cycle rather small SSiS and SiSSi angles (95.7° and 84.3°) are observed. Furthermore, the nonbonding S−S (3.17 Å) and Si−Si (2.87 Å) distances are shorter than the respective van der Waals radii (3.70 Å and 4.00 Å). In Table 5, bond angles and bonding and nonbonding distances in several compounds with 1,3-dithia-2,4-disiletane structures are compared. The similarity in these parameters indicates comparable bonding situations.

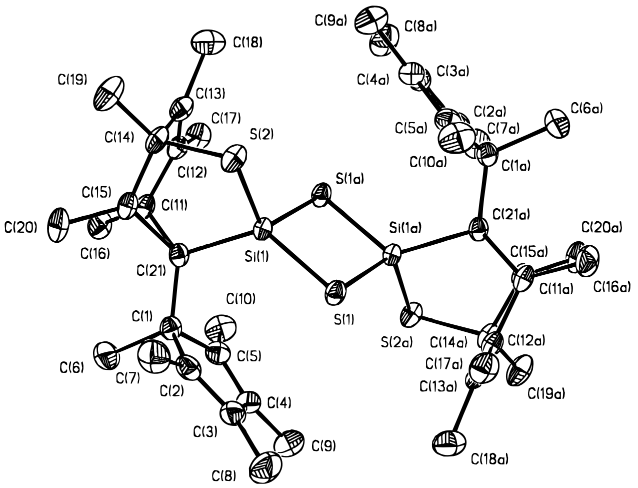

Figure 4. Molecular structure of **15**.

Table 5. Comparison of the Bond Angles (deg), Bond Lengths (Å), and Interatomic Nonbonding Si−Si and S−S Distances (Å) of Four-Membered Ring Systems of the Type $R_4Si_2S_2$

	15	Si_2S_2-$(O^tBu)_4$[14]	$Si_2S_2Cl_4$[15]	$Si_2S_2Br_4$[15]	$Si_2S_2Me_4$[16]	$(SiS_2)_n$[17]
Si−S−Si	84.3	82.2	80.2	81.1	82.5	81.2
S−Si−S	95.7	97.8	99.8	98.9	97.5	98.8
Si−S	2.14	2.14 2.131	2.11 2.117	2.10 2.123	2.15	2.13
Si−Si	2.87		2.72	2.74	2.84	2.78
S−S	3.17				3.33	3.24

The annellated polycyclic ring systems do not show any exceptional structural feature. A heterocycle of the type **15** has not been described in the literature so far.

Conclusion

This is the first time that the reaction of a silicon(II) compound (transient or stable) with heterocumulenes (X=C=Y) is described. The results obtained can be summerized as follows:

In all reactions, a change of hapticity of the pentamethylcyclopentadienyl ligands from η^5 in the starting compound decamethylsilicocene (**1**) to η^1 in the products and also a change of the oxidation state of silicon from Si(II) in **1** to Si(IV) in the products is observed. **1** reacts as a nucleophilic silylene, which is in accord with earlier observations.[3e]

In nearly all reactions, several highly reactive intermediates are formed, which are stabilized in sometimes unexpected multistep reactions to the final products. The reactions are highly specific and proceed under fairly mild conditions.

The first intermediates in the reaction of **1** with the heterocumulenes could neither be identified spectroscopically nor derivatized by trapping agents. These intermediates can be described as Lewis acid−Lewis base addition products of the type $Cp^*_2Si^+C(X)Y^-$ or as three-membered ring compounds. Compounds of this type are unknown in the literature. Their reactions depend on the atoms X and Y. In the case of CS_2 (X=Y=S), a highly surprising multistep rearrangement process finally leads to **15**; in the case of CO_2, COS, and RNCS, elimination of CO or RNC leads to the Cp*-substituted silanone $Cp^*_2Si{=}O$ (**2**, X = O) and the silathione $Cp^*_2Si{=}S$ (**8**, X = S), respectively.

Table 6. Crystallographic Data[a]

	4	**5**	**10**	**15**
empirical formula	$C_{41}H_{60}O_4Si_2$	$C_{42}H_{60}O_6Si_2$	$C_{22}H_{33}NS_2Si_2$	$C_{42}H_{60}S_4Si_2\cdot{}^4/_3$benzene (disordered)
cryst size , mm^3	0.50 × 0.40 × 0.10	0.60 × 0.50 × 0.15	0.80 × 0.50 × 0.40	0.50 × 0.30 × 0.30
fw	673.07	717.08	403.70	853.46
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/n$
lattice parameter				
a, Å	8.751(3)	16.474(4)	8.864(3)	7.988(2)
b, Å	14.939(4)	17.054(4)	14.421(5)	17.142(4)
c, Å	15.610(7)	16.320(6)	17.230(6)	17.069(4)
α, deg	74.12(3)	90	90	90
β, deg	81.87(3)	119.41(2)	95.19(3)	96.27(2)
γ, deg	86.56(2)	90	90	90
V, Å^3	1942.6(12)	3994(2)	2193.4(13)	2323.3(10)
Z	2	4	4	2
d_{calc}, g/cm^3	1.151	1.192	1.222	1.220
diffractometer	Siemens P2$_1$	Siemens P2$_1$	Siemens P2$_1$	Siemens P2$_1$
F(000)	732	1552	872	920
μ(Mo Kα), mm^{-1}	0.130	0.134	0.304	0.290
temp, °C	−100	−100	−100	−100
$2\Theta_{max}$, deg	3.38 to 55.12	3.70 to 55.12	3.68 to 55.12	4.78 to 55.12
no. of data collected	9573	9478	5377	5725
no. of params refined	444	471	246	316
no. of obsd data [$F > 4\sigma(F)$]	4509	3189	3633	3498
residuals: R_F, $wR_F{}^2$ for obsd data	0.0718, 0.1298	0.0987, 0.1148	0.0582, 0.1407	0.0517, 0.1126
largest peak in final diff map, e/Å^3	0.3	0.4	1.0	0.3
abs corr	none	none	none	semiempir from ψ scans

[a] X-ray structure determination: A single crystal was coated with a layer of hydrocarbon oil, attached to a glass fiber, and cooled to 173 K for data collection. Crystallographic programs used for structure solution and refinement were from SHELXTL PLUS and SHELXL-93. The structures were solved by using direct methods and were refined by using full-matrix least squares on F^2 of all unique reflections with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at the calculated positions with U(H) = $1.2U_{eq}$ for CH and CH$_2$ groups and U(H) = $1.5U_{eq}$ for CH$_3$ groups.

2 and **8** are too reactive to be isolated; this result is in accord with earlier findings. On the other hand, these compounds can be derivatized by trapping agents.

The chemical behavior of the intermediate **3**, resulting from the reaction of the silanone **2** with CO$_2$, depends on the solvent used. **3** dimerizes to form the eight-membered heterocycle **5** or reacts with **2** to form the spiro compound **4**.

The most surprising multistep pathway is observed in the reaction **1** with carbon disulfide, as explicitly described in Scheme 6. Ligands, which initially are bonded to the silicon atom (Cp*) or to the carbon atom (S) , finally have to be completely exchanged, presumably by a sequence of dyotropic rearrangments. This type of reaction is unprecedented and initiates further investigations with comparable substrates.

Experimental Section

General Considerations. Standard Schlenk techniques were used for all syntheses and sample manipulations. The solvents were dried by standard methods and destilled under argon prior to use. The reagents MeNCS, PhNCS, CO$_2$, COS, and CS$_2$ were procured commerially and used without further purification.

Physical Measurements. IR spectra were obtained from KBr or CsI pellets or from solution in hexane using a Mattson Perkin Polaris FTIR spectrophotometer. Mass spectra (EI) were run on a Varian 311 A mass spectrometer (70 eV, 300 μA emission), and NMR spectra were obtained using a Bruker AM 300 spectrometer (^{1}H, 300.13 MHz; ^{13}C, 75.47 MHz; ^{29}Si, 59.60 MHz). NMR spectra were referenced to the residual protic impurities of the deuteriated solvents C$_6$D$_6$, CDCl$_3$, and toluene-d_8. Elemental analyses were performed by the Microanalytical Laboratory of the University of Bielefeld. Melting points (uncorrected) were measured using a Büchi 510 melting point apparatus in sealed capillary tubes.

Synthesis of 2,2,6,6-Tetrakis(pentamethylcyclopentadienyl)-1,3,5,7-tetraoxa-2,6-disilaspiro[3,3]heptane (4). CO$_2$ was bubbled through a stirred solution of 1.07 g (3.60 mmol) of **1** in 25 mL of toluene at room temperature for 3 h. The reaction mixture was stirred for 16 h under an atmosphere of CO$_2$. The solvent was removed under reduced pressure; the residue was washed with 10 mL of *n*-pentane and dried in vacuo. The colorless powder was dissolved in toluene. Colorless crystals of **4** (mp: 179 °C dec) formed upon cooling this solution to −60 °C for 5 days (0.87 g, 72% yield). ^{1}H (C$_6$D$_6$): δ 1.78 (s, 60H, C$_5$(*CH*$_3$)$_5$). ^{13}C (C$_6$D$_6$): δ 12.8 (C$_5$(*C*H$_3$)$_5$; 136.8 (*C*$_5$(CH$_3$)$_5$); 141.8 (*C*O$_4$). ^{29}Si (C$_6$D$_6$): δ 11.2. Anal. Calcd for $C_{41}H_{60}O_4Si_2$: C, 73.18; H, 8.96. Found: C, 72.33; H, 8.69.[18] MS (*m*/*z*): 672 (M$^+$). IR (KBr): $\nu_{(C-O)}$ 1185 (s) cm^{-1}; $\nu_{(Si-O)}$ 1057 (s) cm^{-1}.

Synthesis of 2,2,6,6-Tetrakis(pentamethylcyclopentadienyl)-1,3,5,7-tetraoxa-2,6-disilacycloocta-4,8-dione (5). CO$_2$ was bubbled through a stirred solution of 1.14 g (3.82 mmol) **1** in 25 mL of pyridine at room temperature for 2 h. The reaction mixture was allowed to stir for 16 h under an atmosphere of CO$_2$. The solvent was removed under reduced pressure; the colorless residue was washed with 20 mL of *n*-hexane and dried in vacuo. The precipitate was dissolved in a mixture of *n*-hexane and toluene (3:1) and colorless crystals of **5** (mp: 222 °C dec) formed upon cooling this solution to −60 °C for 7 days (0.89 g, 65% yield). ^{1}H (CDCl$_3$): δ 1.13, 1.73, 1.87 (s, 12H:24H:24H, C$_5$(*CH*$_3$)$_5$). ^{13}C (CDCl$_3$): δ 11.5, 11.7 15.7 (C$_5$(*C*H$_3$)$_5$; 53.3 (allyl *C*$_5$(CH$_3$)$_5$); 136.1, 138.0 (vinyl *C*$_5$(CH$_3$)$_5$); 143.9 (*C*=O). ^{29}Si (CDCl$_3$): δ −28.3. Anal. Calcd for $C_{42}H_{60}O_6Si_2$: C, 70.34; H, 8.43. Found: C, 70.29; H, 7.90.[18] MS (*m*/*z*): 716 (M$^+$). IR (KBr): $\nu_{(C=O)}$ 1760 (vs) cm^{-1}; $\nu_{(C-O)}$ 1247 (s) cm^{-1}; $\nu_{(Si-O)}$ 1098 (s) cm^{-1}.

Synthesis of Bis(pentamethylcyclopentadienyl)-(2,2-dimethyl-1-methylene)propoxy(hydroxy)silane (6). CO$_2$ was bubbled through a solution of 1.22 g (4.09 mmol) of **1** in 15 mL of 2,3-dimethylbutadiene (containing 2% of *tert*-butyl methyl ketone (2.50 mmol)) at room temperature for 2 h. The reaction mixture was stirred for 16 h under an atmosphere of CO$_2$. The solvent was removed and the residue extracted with

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(18) NMR investigations indicated the present of low-volatility organic compounds.

n-hexane, which left **4** as a colorless powder. The hexane extract was reduced to dryness in vacuo leaving a colorless powder, which was crystallized in *n*-pentane. **6** (mp: 71−73 °C) was obtained as colorless crystals (0.47 g, 46% yield). ^{1}H ($CDCl_3$): δ 1.16 (s, 6H, allyl $C_5(CH_3)_5$); 1.24 (s, 9H, $C(CH_3)_3$); 1.74, 1.92, 1.98 (s, 12H:6H:6H, allyl $C_5(CH_3)_5$); 2.20 (s, 1H, O*H*); 4.28, 4.57 (s, 1H:1H, CH_2). ^{13}C ($CDCl_3$): δ 11.5, 12.1, 12.4, 12.6, 17.2 ($C_5(CH_3)_5$; 29.0 ($C(CH_3)_3$); 37.0 ($C(CH_3)_3$); 54.9 (allyl $C_5(CH_3)_5$); 87.1 (CH_2); 135.6, 135.8, 138.1 (vinyl $C_5(CH_3)_5$); 167.0 ($C{=}CH_2$). ^{29}Si ($CDCl_3$): δ −21.1. Anal. Calcd for $C_{26}H_{42}O_2Si$: C, 75.30; H, 10.21. Found: C, 74.67; H, 10.28.[18] MS (*m*/*z*): 414 (M^+). IR (hexane): $\nu_{(OH)}$ 3460−3150 (m) cm^{-1}.

Synthesis of Bis(pentamethylcyclopentadienyl)-(1-methylene)ethoxy(hydroxy)silane (7). CO_2 was bubbled through a solution of 1.59 g (5.36 mmol) **1** in 70 mL of acetone at room temperature for 1 h. The reaction mixture was stirred for 16 h under an atmosphere of CO_2. The mixture was reduced to dryness in vacuo. After purification by sublimation (0.01 bar, 90 °C), **7** (mp: 42 °C) was isolated as a colorless powder (1.83 g, 92% yield). ^{1}H ($CDCl_3$): δ 1.02, 1.72. 1.77 (s, 6H:12H:12H, $C_5(CH_3)_5$); 1.91 (s, 3H, CH_3); 2.36 (s, 1H, O*H*); 4.06, 4.31 (s, 1H:1H, CH_2). ^{13}C ($CDCl_3$): δ 11.3, 11.8, 11.9, 16.2 ($C_5(CH_3)_5$; 22.6 (CH_3); 54.4 (allyl $C_5(CH_3)_5$); 90.9 (CH_2); 136.4, 135.6, 137.4, 137.8 (vinyl $C_5(CH_3)_5$); 155.7 ($C{=}CH_2$). ^{29}Si ($CDCl_3$): δ −24.0. Anal. Calcd for $C_{23}H_{36}O_2Si$: C, 74.14; H, 9.74. Found C, 73.48; H, 9.76.[18] MS (*m*/*z*): 372 (M^+). IR (KBr): $\nu_{(OH)}$ 3600 (s) cm^{-1}.

Synthesis of 2.2,4,4-Tetrakis(pentamethylcyclopentadienyl)-1,3-dithia-2,4-disilaetane (9). A solution of 0.95 g (3.20 mmol) of **1** in 20 mL of toluene was added to liquid COS at −78 °C. The reaction mixture was stirred for 1 h at −78 °C and then allowed to warm slowly to room temperature. The solvent was removed in vacuo and the residue dissolved in THF. Cooling this solution to −60 °C yielded **9** (mp: >300 °C) as a colorless powder (0.53 g, 55% yield). ^{1}H ($CDCl_3$): δ 1.45 (s, 12H, allyl $C_5(CH_3)_5$); 1.69, 1.84 (s, 24H:24H, vinyl $C_5(CH_3)_5$). ^{13}C ($CDCl_3$): δ 11.5, 12.9 ($C_5(CH_3)_5$; 136.2,139.0 ($C_5(CH_3)_5$). ^{29}Si (toluene-d_8): δ −10.2. MS (*m*/*z*): 660 (M^+). IR (KBr): $\nu_{(Si-S)}$ 492 (s) cm^{-1}.

Synthesis of 2,2-Bis(pentamethylcyclopentadienyl)-4-(methylimino)-1,3-dithia-2-siletane (10). A solution of 0.86 g (11.80 mmol) of MeNCS in 10 mL of toluene was added at room temperature to a solution of 1.68 g (5.60 mmol) 1 in 15 mL of toluene over a period of 15 min. Then the mixture was allowed to stir for 16 h. The solvent was removed under reduced pressure; the residue was recrystallized in *n*-hexane. 10 (mp: 107 °C) was isolated as colorless crystals (1.17 g, 52% yield). ^{1}H (C_6D_6): δ 1.61 (s, 60H, $C_5(CH_3)_5$); 3.19 (s, 3H, CH_3). ^{13}C (C_6D_6): δ 12.8 ($C_5(CH_3)_5$); 40.8 (CH_3); 136.9 ($C_5(CH_3)_5$); 141.1 ($C{=}N$). ^{29}Si (C_6D_6): δ 13.1. Anal. Calcd for $C_{22}H_{33}NS_2Si$: C, 65.46; H, 8.18; N, 3.47. Found: C, 65.26; H, 8.04; N, 3.52. MS (*m*/*z*): 403 (M^+).

Synthesis of 2,2-Bis(pentamethylcyclopentadienyl)-4-(phenylimino)-1,3-dithia-2-siletane (11). A solution of 1.80 g (6.0 mmol) of **1** and 1.5 mL (12.5 mmol) of PhNCS in 15 mL of toluene was heated to 65 °C over a period of 5 h. Volatiles were removed and the residue was crystallized in *n*-pentane. **11** (mp: 118 °C dec) was obtained as pale yellow crystals (1.53 g, 55% yield). ^{1}H ($CDCl_3$): δ 1.66 (s, 30H, $C_5(CH_3)_5$); 7.03, 7.14, 7.36 (m, 2H:1H:2H, aryl *H*). ^{13}C ($CDCl_3$): δ 13.0 ($C_5(CH_3)_5$); 121.1, 124.6, 129.0 (aryl *C*); 137.4 ($C_5(CH_3)_5$); 148.5 (aryl *C*); 149.5 ($C{=}N$). ^{29}Si ($CDCl_3$): δ 12.0. Anal. Calcd for $C_{27}H_{35}NS_2Si$: C, 69.62; H, 7.57; N, 3.01. Found: C, 69.80; H, 7.67; N, 3.00. MS (*m*/*z*): 465 (M^+). IR (KBr) $\nu_{(C=N)}$ 1617 (s) cm^{-1}.

Synthesis of 2,2,5,5-Tetrakis(pentamethylcyclopentadienyl)-4-(phenylimino)-1,3-dithia-2,5-disilolane (12). A solution of 1.35 g (4.53 mmol) of **1** and 2.0 mL (19.0 mmol) of PhNCS in 15 mL of toluene was heated to 100 °C over a period of 20 h. Volatiles were removed, and the orange residue was crystallized in toluene. **12** (mp: 264 °C) was isolated as a pale yellow powder (2.27 g, 66% yield). ^{1}H ($CDCl_3$): δ 1.18, 1.38, 1.46, 1.65, 1.69, 1.82, 1.85, 2.05 (s, 6H:6H:6H:6H:12H:12H:12H:12H, $C_5(CH_3)_5$); 6.21, 6.68, 6.96 (m, 2H:1H:2H, aryl *H*). ^{13}C ($CDCl_3$): δ 10.7, 11.5, 12.7, 20.2, 21.8, 22.5 ($C_5(CH_3)_5$); 57.3, 67.0 (allyl ($C_5(CH_3)_5$); 115.6, 122.2, 126.6 (aryl *C*); 136.1, 136.6, 138.5, 140.4 (vinyl $C_5(CH_3)_5$); 150.7 (aryl *C*); 184.8 ($C{=}N$). ^{29}Si ($CDCl_3$): δ −0.4; +21.4. Anal. Calcd for $C_{47}H_{65}NS_2Si_2$: C, 73.86; H, 8.57; N, 1.83. Found: C, 72.39; H, 8.47; N, 1.80.[18] MS (*m*/*z*): 763 (M^+). IR (CsI): $\nu_{(C=N)}$ 1605 (m) cm^{-1}.

Synthesis of Bis(pentamethylcyclopentadienyl)[(2,2-dimethyl-1-methylene)propoxy]silylbis(pentamethylcyclopentadienyl)hydridosilyl Thioether (13). A solution of 0.29 g (4.00 mmol) of MeNCS in 10 mL of toluene was added to a solution of 1.08 g (3.60 mmol) of **1** and 0.36 g (3.60 mool) of *tert*-butyl methyl ketone in 15 mL of toluene at −78 °C. The reaction mixture was stirred for 3 h at −78 °C and then allowed to warm slowly to room temperature. After being stirred for a further 3 days at this temperature, the solvent was removed under reduced pressure and the residue was crystallized in toluene. **13** (mp: 205−206 °C) was isolated as colorless crystals (1.09 g, 42% yield). ^{1}H (C_6D_6): δ 1.28 (s, 9H, $C(CH_3)_3$); 1.38, 1.53, 1.74, 1.76, 1.78, 1.90, 2.01, 2.14, 2.18 (s, 6H:6H:12H:6H:6H:6H.6H:6H.6H, $C_5(CH_3)_5$); 4.61, 5.00 (s, 1H:1H, CH_2); 5.51 (s, 1H, Si*H*). ^{13}C (C_6D_6): δ 11.6, 13.2, 13.8, 14.2, 21.2, 22.1 ($C_5(CH_3)_5$); 29.3 ($C(CH_3)_3$); 37.0 ($C(CH_3)_3$); 55.1, 57.4 (allyl ($C_5(CH_3)_5$); 93.1 (CH_2); 135.4, 136.3, 137.8, 139.0 (vinyl $C_5(CH_3)_5$); 164.7 ($C{=}CH_2$). ^{29}Si (C_6D_6): δ 6.3 (d, $^{1}J_{SiH}$ = 217 Hz, *Si*H) 0.3. Anal. Calcd for $C_{46}H_{72}OSSi_2$: C, 75.80; H, 9.89. Found: C, 74.83; H, 9.84.[18] MS (*m*/*z*): 728 (M^+). IR (hexane): $\nu_{(Si-H)}$ 2179 (m) cm^{-1}.

Synthesis of the Dithiadisiletane Derivate (15). CS_2 (1.26 mL, 20.0 mmol) was added to a solution of 0.60 g (2.0 mmol) of **1** in 10 mL of benzene at room temperature. The reaction mixture was stirred for 16 h at this temperature. Volatiles were removed under reduced pressure; the green residue was washed with 20 mL of *n*-pentane leaving an almost colorless substance, which was crystallized in benzene. **15** (mp: 237 °C) was obtained as colorless crystals (0.45g, 60% yield). ^{1}H ($CDCl_3$): δ 0.98, 1.20, 1.32, 1.40, 1.58, 1.67, 1.86, 2.04, 2.10, 2.12 (s, 6H:6H:6H:6H:6H:6H:6H:6H:6H:6H, $C_5(CH_3)_5$). ^{13}C ($CDCl_3$): δ 11.5, 12.1, 12.5, 13.4, 16.4, 23.2, 27.3 ($C_5(CH_3)_5$); 48.3, 49.0, 50.3, 60.0, 72.3 (allyl *C*);134.6, 134.9, 136.1, 137.0, 144.1 (vinyl $C_5(CH_3)_5$). ^{29}Si ($CDCl_3$): δ 21.6. Anal. Calcd for $C_{42}H_{60}S_4Si_2$: C, 67.32; H, 8.07. Found: C, 67.29; H, 8.13. MS (*m*/*z*): 748 (M^+). IR (KBr): $\nu_{(Si-S)}$ 535 (s) cm^{-1}; $\nu_{(C=C)}$ 1652 (v) cm^{-1}.

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Supporting Information Available: Tables of crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles for **4**, **5**, **10**, and **15** (30 pages). Ordering information is given on any current masthead page.

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