Synthesis of 4-Silylcyclobut-2-enethiones and Their Use in Cyclobutadiene Generation

Martin Müller, Wolf-Rüdiger Förster, Andreas Holst, Arend J. Kingma, Ernst Schaumann,* and Gunadi Adiwidjaja

Abstract: Alkynyl silyl sulfides **2** reacted with ynamines **3** to give 1:1 adducts. The structure of 4-silylcyclobut-2-enethiones **4** was confirmed by X-ray analysis of **4a**. A cyclobutadiene intermediate is probably not involved in this reaction; we think that it is initiated by a silyl transfer from **2** to **3**, and that this is followed by a combination of the resulting ions to give the unsaturated thioketene **7**, which undergoes an electrocyclization to give products **4**. In the reaction of thiones **4** with trimethyloxonium tetrafluoroborate (Meerwein salt) selective methylation at sulfur was observed to give cyclobutenethionium ions **16**. Ions **16** underwent fluoride-induced desilylation with various fluoride sources to give cyclobutadienes **17**, which could not be isolated, but trapping of **17a–c** was possible with dimethyl acetylenedicarboxylate yielding regioisomeric benzene derivatives **20–23**. Similarly, **17a** and bis(methylthio)methylene malononitrile (**24**) led to hexatriene derivative **27** by a sequence of cycloaddition and two ring-opening reactions. In contrast, silyl-substituted cyclobutadienes **17d,e** dimerized even in the presence of trapping agents to *anti*-tricyclo-[4.2.0.0^{2,5}]octadienes **29**; this suggests that a two-step cycloaddition is taking place, rather than a concerted Diels–Alder reaction. Attempts to intercept **17d,e**, generated from **16d,e** with cyclopentadiene (**30**), gave deprotonation of **30** leading to substitution of the methylthio group in **16** and finally to formation of cyclobutenes **33** through a hydrogen shift.

Keywords
alkynyl sulfides · cyclobutadienes · cyclobutenethiones · desilylation · ynamines

Introduction

Because of their highly strained character and the adverse effect of internal resonance stabilization,[1] cyclobutadienes cannot normally be obtained by cycloaddition of electron-rich ynamines and electron-poor acetylenes.[2] The only successful transformation of this type was found for the reaction of alkynyl sulfones with ynamines to give cyclobutadienes,[3a] though formation of a four-membered ring in this reaction is controversial.[3b] Usually, product formation involves participation of a substituent of the triple bond[3b, 4] or incorporation of a third acetylene molecule leading to benzene derivatives.[5]

Alkynyl silyl sulfides **2**, which are readily available by thiolation of alkynides and subsequent silylation,[6a] have so far only been employed in reaction with amines, azomethines, or thioimidates[6b] where they display a thioketenoid behavior. However, alkynes **2** have so far not been tested in reactions with other types of nucleophiles. Herein, we report on the reaction of **2** with ynamines **3** as examples of electron-rich acetylenes and on the conversion of the resulting 4-silylcyclobutenethiones **4** into cyclobutadienes **17**.

[*] Prof. Dr. E. Schaumann, Dr. M. Müller, Dr. W.-R. Förster, Dr. A. Holst, Dr. A. J. Kingma
Institut für Organische Chemie der Technischen Universität Clausthal
Leibnizstr. 6, D-38678 Clausthal-Zellerfeld (Germany)
Fax: Int. code + (5323)72-2858
e-mail: ernst.schaumann@tu-clausthal.de
Dr. G. Adiwidjaja
Mineralogisch-Petrographisches Institut der Universität Hamburg
Grindelallee 48, D-20146 Hamburg (Germany)

Results and Discussion

Synthesis of 4-silylcyclobut-2-enethiones: Alkynyl silyl sulfides **2** and ynamines **3** were found to react at room temperature to give 1:1 adducts, which appear to be four-membered ring systems **4** on the basis of their spectroscopic properties (Scheme 1, Table 1). The conclusive structural evidence was obtained by X-ray crystal structure analysis of **4a**. This confirmed the presence of a cyclobutene ring (Fig. 1).[7] The remarkable feature in the product is that a silyl shift has taken place from sulfur to the β carbon of the original ynamine component (C4 in the cycloadduct). Since the bond lengths C1–C2 and C2–C3 are almost identical, extensive electron delocalization appears to occur within the vinylogous thioamide fragment S11-C1-C2-C3-N31, although the heteroatoms are twisted by 12.2 (S11) and 18.1° (N31) out of the plane defined by C1-C2-C3. This is in accord with previous work on *trans*-3-aminovinylthioketones.[8] On the basis of the ^{13}C NMR data, the same structure **4** can be assumed for all 1:1 products from **2** and **3** (Table 1).

The reaction was carried out under various conditions. The best yields based on ynamines **3** were obtained with inert solvents, like pentane or diethyl ether. Starting from the aryl- and alkyl-substituted acetylenes **1a–c**, a one-pot synthesis was pos-

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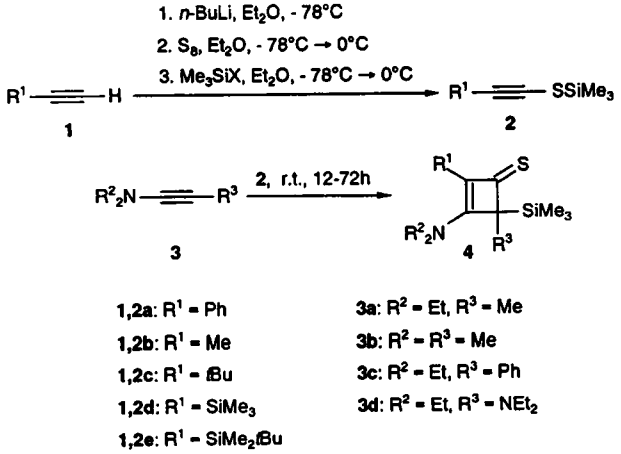
Table 1. Spectroscopic data and physical properties of cyclobutenethiones **4** and **14**.

	R^1	R^2	R^3	Yield [a] [%]	M.p. [°C]	IR (KBr) [cm^{-1} (C=C)]	^1H NMR [δ (4-CH_3)]	^{13}C NMR [δ (C1, C2, C3, C4)]	Elem. analysis
4a	Ph	Et	Me	94 (A) 63 (C)	123–4	1620	1.48	213.6, 126.3, 171.7, 55.4	calcd C 68.08, H 8.57, N 4.41, S 10.10 found C 68.07, H 8.67, N 4.36, S 9.85
4b	Ph	Me	Me	23 (C)	140	1655	1.53	213.5, 126.1, 172.7, 55.6	calcd C 66.38, H 8.01, N 4.84, S 11.07 found C 66.26, H 7.94, N 4.78, S 11.46
4c	*t*Bu	Et	Me	42 (A)	83–4	1610	1.32	212.2, 134.5, 171.5, 55.2	calcd C 64.58, H 10.50, N 4.71, S 10.77 found C 64.39, H 10.27, N 4.66, S 10.83
4d	Me	Me	Me	26 (A)	103	1640	1.38	215.9, 122.9, 174.3, 53.6	calcd C 58.12, H 9.32, N 6.17, S 14.08 found C 58.12, H 9.42, N 5.98, S 14.08
4e	Ph	Et	Ph	45 (A) 30 (C)	110–1	1630	–	210.0, 125.7, 168.8, 63.1	calcd C 72.77, H 7.70, N 3.69, S 8.45 found C 72.76, H 7.67, N 3.70, S 8.59
4f	$SiMe_3$	Et	Me	31 (C)	83	1590	1.41	224.6, 125.3, 179.8, 57.9	calcd C 57.44, H 9.96, N 4.47, S 10.22 found C 57.72, H 10.32, N 4.29, S 10.66
4g	$SiMe_2$*t*Bu	Et	Me	24 (B)	79–80	1585	1.43	226.7, 123.1, 181.2, 57.5	calcd C 60.78, H 10.48, N 3.94, S 9.01 found C 61.32, H 10.46, N 3.99, S 8.57
4h	$SiMe_2$thex [b]	Et	Me	70 (B)	40	1590	1.41	225.8, 124.9, 180.7, 57.3	calcd C 62.64, H 10.78, N 3.65, S 8.36 found C 62.79, H 10.86, N 3.68, S 9.06
4i	*t*Bu	Et	NEt_2	6 (A)	128	1550	–	not measured	calcd C 64.34, H 10.80, N 7.90, S 9.04 found C 64.37, H 10.76, N 7.99, S 9.43
14a	Ph	Et	Me	63	100–1	1620	2.03 4.40 (4-H)	210.2, 137.0, 170.1, 63.1	calcd C 73.42, H 7.80, N 5.71, S 13.07 found C 73.36 , H 7.90, N 5.60, S 13.30
14b	*t*Bu	Et	Me	79	69–70	1620	1.95 3.32 (4-H)	210.3, 132.3, 170.0, 67.3	calcd C 69.27, H 10.28, N 6.21, S 14.23 found C 69.48, H 10.30; N 6.28, S 14.02
14c	Ph	Et	Ph	93	115–6	1640	– 4.52 (4-H)	208.7, 133.4, 168.1, 63.5	calcd C 78.13, H 6.88, N 4.56, S 10.43 found C 78.05, H 6.82, N 4.60, S 10.53

[a] Yields are given for different purification methods of **2**: A) use of pure compounds, yields based on **2**; B) use of crude **2**, yields based on **1**; C) use of one-pot synthesis, yields based on **1**. [b] thex: 1,1,2-trimethylpropyl.



Scheme 1. The synthesis of 4-silylcyclobut-2-enethiones **4a–i**.

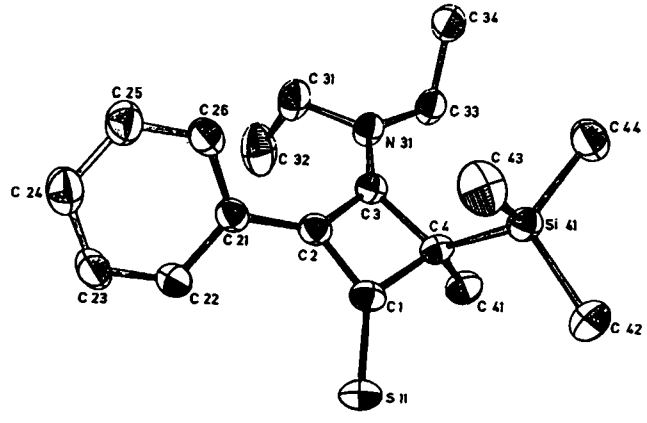


Fig. 1. ORTEP plot of the molecular structure of **4a** (ellipsoids at the 50% probability level, hydrogens omitted for clarity). Selected interatomic distances between non-hydrogen atoms [pm] and angles [°] with standard deviations of the last significant figure in parentheses: S11–C1 165.5(4), Si41–C4 189.7(4), N31–C3 133.5(5), C1–C2 140.8(5), C1–C4 155.3(6), C2–C3 140.3(5), C3–C4 153.5(5), C4–C41 152.6(6); S11-C1-C2 136.0(4), C2-C1-C4 93.8(5), C1-C2-C3 90.0(3), C1-C2-C21 131.8(4), N31-C3-C2 134.9(4), C2-C3-C4 94.8(3), C1-C4-C3 80.2(3), C3-C4-Si41 117.2(3), C3-C4-C41 117.3(4).

sible. Thus, the ynamines **3** were added to the alkynyl silyl sulfides **2a–c**, used as formed from **1** without workup, to give the products **4** with no or only a slight reduction in yield. Since the purification of silyl-substituted alkynyl silyl sulfides **2d,e** is usually difficult and tedious, crude **2d,e** were used. However, removal of the lithium salts formed in the synthesis of **2** from **1** was required, because they are weak Lewis bases and so favor dimerization of ynamines[9] in competition with the desired reaction. The reaction of ynediamine **3d** with **2c** provided only very little **4i**, and the major product was *N*,*N*-diethyl-3,3-dimethylthiobutanamide; this indicates that **3d** is decomposing and that the liberated diethylamine adds to sulfide **2c**. The reaction was found to fail when both components were deactivated by a bulky alkyl or a phenyl substituent. Thus, alkynyl sulfide **2c** and ynamine **3c** did not react.

A simple mechanistic explanation for the formation of products **4** is that they result from a 1,5-S → C silyl shift in cyclobutadienes of type **17** (Scheme 5, $SSiMe_3$ instead of SMe) formed as primary cycloadducts, but we think it highly improbable that these high-energy species are in fact intermediates. A more likely mechanism, by analogy with the aminolysis of **2**,[6a] is the transfer of the silyl group from the alkynyl silyl sulfide **2** to the ynamine **3** to give the ynethiolate **5** and the ketene immonium ion **6** (Scheme 2). These two ions then react with C–C bond formation to yield the unsaturated thioketene **7**. Finally, electrocyclization of **7** leads to products **4**. The ready cyclization of **7**, a heteroanalogue of vinylallene, is in line with the effect of silicon on the electrocyclization of the corresponding all-carbon species.[10] A mechanism involving a primary rearrangement of alkynyl silyl sulfides **2** to silyl thioketenes **8**

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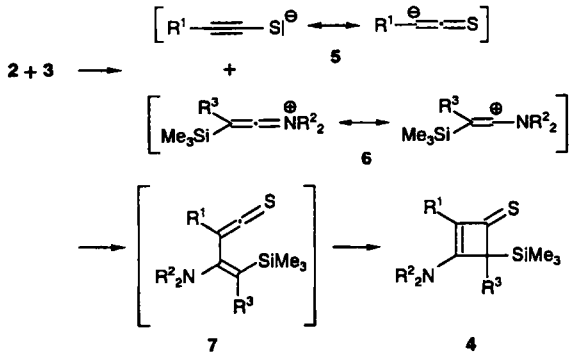
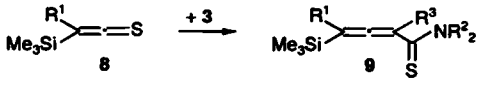


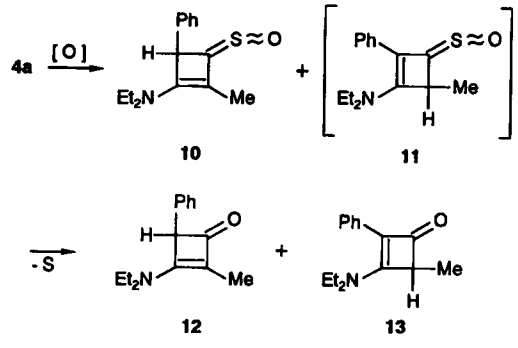
Scheme 2. Probable mechanism for the formation of 4.

can be ruled out, since control experiments showed that the reaction of **8** with **3** gives allenes **9** rather than cylobutenethiones **4** (Scheme 3).[11]



Scheme 3.

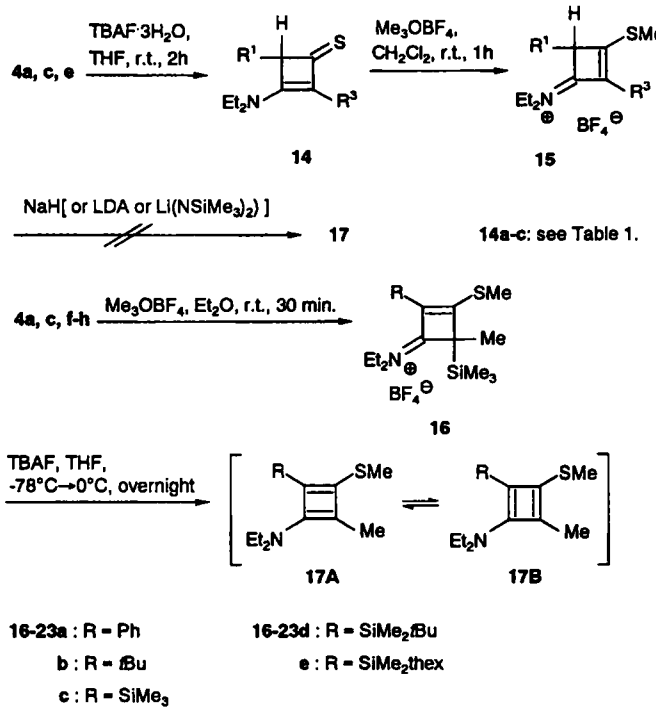
Desilylation of thione 4: Oxidation of cyclobutenethiones **4** was expected to provide the as yet unknown 4-silylcyclobutenones. However, oxidation of **4a** with various reagents invariably led to the protiodesilylated cyclobutenones **12** and **13** in moderate yields (Scheme 4). Astonishingly, in all oxidation reactions both



Scheme 4. Oxidation of **4a**.

tautomers **12** and **13** were formed. Even on oxidation with dimethyldioxirane, protiodesilylation was observed. However, in this case the sulfine **10** was isolated as one of the products.

Protiodesilylation of **4** with commercially available tetrabutylammonium fluoride led to cyclobutenethiones **14** (Scheme 5). As expected for an allylsilane, the proton attacks in an S_E2' fashion. This regiochemistry can be derived from the coupling constants between the added proton and the methyl group ($R^3 = CH_3$): the observed value of 2.4 Hz suggests allylic coupling. Although it was possible to regioselectively methylate **14** at sulfur with Meerwein salt, attempted deprotonation of the resulting immonium ions **15** did not give any conclusive evidence for the formation of cyclobutadienes **17**. This reaction probably failed owing to insufficient acidity of **15**.

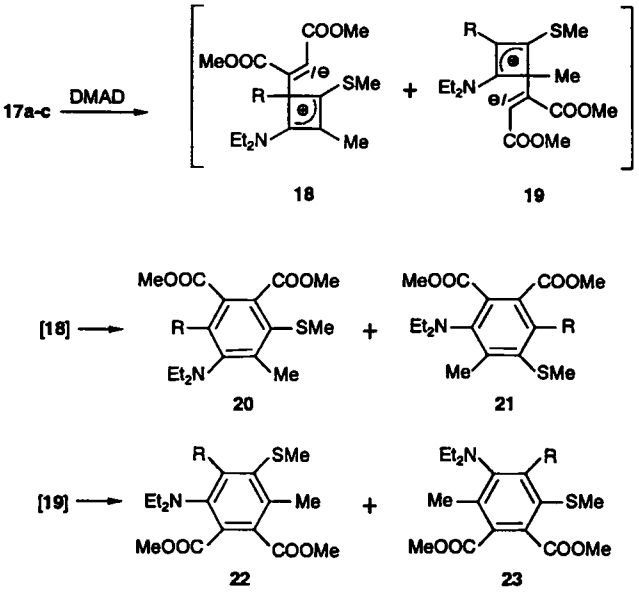


16-23a : R = Ph
b : R = *t*Bu
c : R = $SiMe_3$
16-23d : R = $SiMe_2$*t*Bu
e : R = $SiMe_2$thex

Scheme 5. Generation of cyclobutadienes **17** (thex = CMe_2*i*Pr, TBAF = tetrabutylammonium fluoride).

Generation and trapping of cyclobutadienes: Cyclobutenethiones **4** were readily methylated by the action of trimethyloxonium tetrafluoroborate (Meerwein salt) (Scheme 5). The regioselectivity of the methylation at sulfur to give **16** was established by means of the ^{1}H NMR spectrum [δ(SMe) = 2.19]. Ions **16** underwent fluoride-induced desilylation to give, at least formally, cyclobutadienes **17** at −78 °C in THF. The best results were obtained with anhydrous tetrabutylammonium fluoride, but potassium fluoride/[18]crown-6 or cesium fluoride also gave desilylation. Attempts to isolate the liberated cyclobutadienes **17** failed; this demonstrates that the push–pull effect of the diethylamino and the methylthio groups is not sufficiently strong to stabilize the cyclobutadiene system. We therefore turned our attention to the task of trapping of **17**.

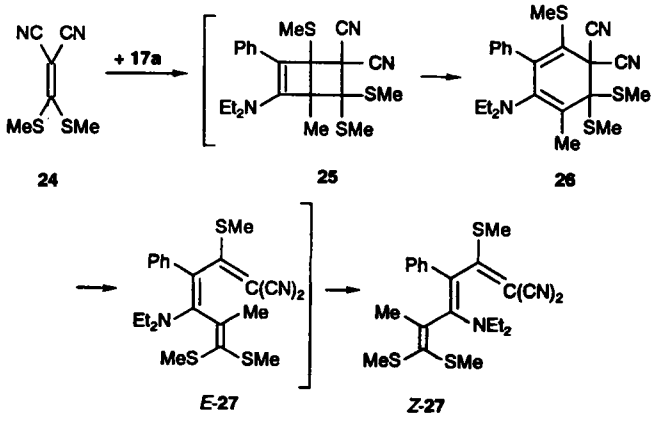
The trapping reaction of **17a–c** with dimethyl acetylenedicarboxylate (DMAD) led to a mixture of the regioisomeric benzenes **20–23** in moderate yields (Scheme 6). In accordance with the literature,[12] the alkynoate is a highly reactive trapping agent with low selectivity: attack of DMAD occurred on all four sides of **17**; the resulting Dewar benzene derivatives rearranged rapidly to the isomeric Kekulé structures **20–23**. With **17a** as starting material, the major isomer **20a** could be enriched by extended column chromatography. The structure of **20a** was established by applying a detailed NMR analysis. Thus, a COLOC-NMR spectrum allowed us to link the signals of the ring atoms in the ^{13}C NMR spectrum to their respective substituents on the basis of long-range C,H coupling constants. In combination with the detection of directly bound carbons in a 1D-INADEQUATE spectrum, structure **20a** could be unambiguously derived. Subsequently, structures **21a–23a** were established by analysis of the COLOC spectrum. The regioisomers obtained from **17b,c** and DMAD could not be separated. A control experiment confirmed that there is no reaction between **16a** and DMAD in the absence of fluoride; the reacting species is therefore desilylated **16**, that is, **17**.



Scheme 6. Trapping of cyclobutadienes **17** (for substituents R, see Scheme 5).

The formation of isomers **20–23** might be accounted for by [4+2] cycloaddition to the two valence tautomers **17A,B** or by parallel [2+2] and [4+2] cycloadditions to **17A** or **17B**. However, [2+2] cycloadditions to cyclobutadienes have been observed only in very few cases with carbon disulfide or azo compounds[13]. On the other hand, by analogy with the formation of formal [2+2] and [4+2] cycloadducts in the autoxidation of a stable cyclobutadiene,[14] zwitterionic intermediates **18** and **19** could lead to four ring-closure products through bond formation at both termini of the allyl moiety, and the intermediates could rearrange to **20,21** and **22,23**, respectively. In fact, the positive charge in **18** and **19** is efficiently stabilized by allyl resonance as well as by the electron-donating effect of the heteroatoms. Moreover, **18** and **19** may be looked upon as homoaromatic[15] homocyclopropenylium derivatives, and for **18c** and **19c**, the β-effect of silicon[16] provides additional stabilization of the positive charge. Similarly, the substituents will allow a low-energy transition of the corresponding Dewar benzene derivatives into **20–23**.[17, 18]

Reaction of **17a** with malononitrile derivative **24** (Scheme 7) led to a crystalline compound, which gave broadened NMR signals at the usual temperature of measurement, but sharp resonances were observed at 80 °C. As the spectroscopic data did not allow an unambiguous structural assignment, an X-ray



Scheme 7. Trapping of **17a** with malononitrile derivative **24**.

single-crystal analysis was carried out. This confirmed that the product has the structure **27**[7] (Fig. 2). Apparently, because of opposing steric effects, the C5=C6 bond is not in conjugation with the diene system of carbons C1 through C4, but for the

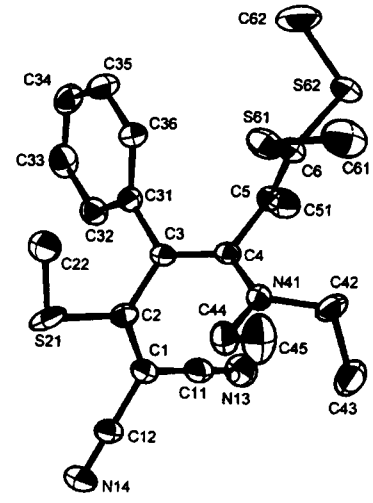


Fig. 2. ORTEP representation of the molecular structure of **27** (ellipsoids at the 50% probability level, hydrogens omitted for clarity). Selected interatomic distances between non-hydrogen atoms [pm] and angles [°] with standard deviations of the last significant figure in parentheses: S21–C2 174.5(3), S61–C6 177.3(3), S62–C6 177.2(3), N13–C11 114.3(4), N41–C4 136.2(3), C1–C2 136.3(4), C1–C11 143.2(4), C2–C3 146.4(3), C3–C4 137.7(4), C3–C31 148.7(3), C4–C5 150.5(3), C5–C6 132.7(4), C5–C51 150.8(4); C2-S22-C22 104.2(2), C2-C1-C11 121.1(2), S21-C2-C1 115.9(2), S21-C2-C3 122.1(2), C1-C2-C3 121.9(2), C2-C3-C4 122.1(2), C2-C3-C31 114.8(2), C3-C4-C5 118.7(2), C4-C5-C6 121.6(2), N13-C11-C1 178.6(3).

latter fragment the measured bond lengths suggest at least some electron delocalization in spite of twisting of the olefinic units by approximately 50°. To account for formation of **27**, we suggest a mechanism involving a—probably nonconcerted—[4+2] cycloaddition to give bicyclic adduct **25**. Subsequent consecutive electrocyclic ring-opening steps would first give the cyclohexadiene **26** and then the product **27**. However, neither this mechanism nor a direct [2+2] cycloreversion[19] of the cyclobutane unit in intermediate **25** account for the surprising (*Z*) configuration of the C3=C4 bond, which may therefore be the result of a thermodynamically favored isomerization of the primary product (*E*)-**27**.

Silyl-substituted cyclobutadienes **17d,e** showed a different reactivity. Attempts to obtain trapping products with dimethyl acetylenedicarboxylate or the activated alkene **24** failed. Instead, colorless crystals were isolated in all reactions. NMR spectroscopy confirmed the presence of all carbons and hydrogens of **17** and elementary analyses matched the values of **17**. However, X-ray analysis established that the structure of the product obtained from **17e** is **29b** (Scheme 8, Fig. 3),[7] that is, a dimer of **17** of a type known for cyclobutadienes.[1] A remarkable feature of the structure is a very long C33–C35 bond in the thexyl group. A similar effect has been observed before.[20] According to the literature,[21] the formation of *anti*-**29** probably excludes a concerted Diels–Alder reaction, since this would give products that would give rise to a *syn* orientation, but is consistent with a zwitterionic intermediate **28** in which, by analogy with **18**/**19**, the charges are efficiently stabilized. The low energy of the transition state in the formation of **28** may account for the marked preference shown by **17d,e** towards dimerization rather than cycloaddition with trapping agents.

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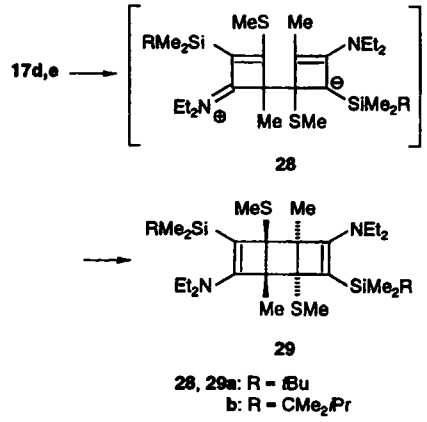


Scheme 8.

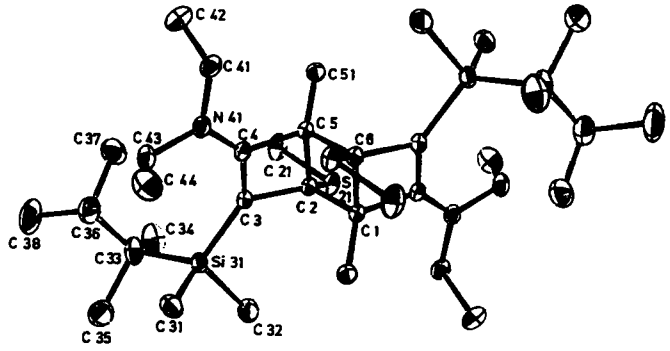
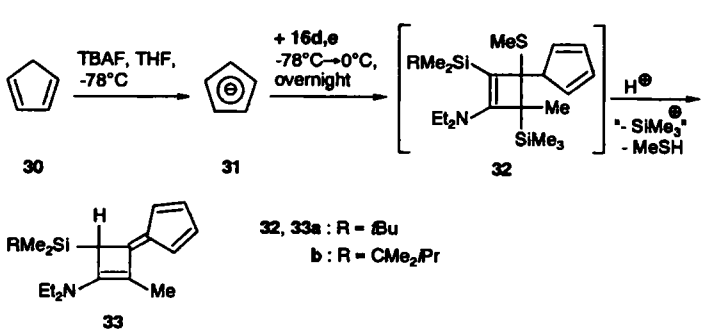


Fig. 3. ORTEP representation of the molecular structure of **29b** (ellipsoids at the 50% probability level; hydrogens omitted for clarity). Selected interatomic distances between non-hydrogen atoms [pm] and standard deviations of the last significant figure in parentheses: S21–C2 182.1(2), S21–C21 179.5(3), Si31–C3 187.7(2), Si31–C33 192.7(3), N41–C4 135.6(3), N41–C41 146.5(3), C2–C3 153.1(3), C2–C5 158.1(3), C2–C1 158.3(2), C3–C4 137.8(3), C4–C5 151.4(3), C5–C51 151.4(3), C5–C6 158.3(2), C33–C34 154.0(6), C33–C35 167.2(6), C33–C36 151.2(5), C36–C37 149.7(6), C36–C38 156.6(6), C41–C42 152.1(4); C2-S21-C2 1 103.4(2), S21-C2-C3 121.6(2), S21-C2-C1 112.6(1), C3-C2-C5 88.6(2), C3-C2-C1 115.8(2), C5-C2-C1 90.1(2), Si31-C3-C2 129.5(2), Si31-C3-C4 139.6(2), C2-C3-C4 90.3(2), N41-C4-C3 136.3(2), N41-C4-C5 126.2(2), C3-C4-C5 97.3(2), C2-C5-C4 83.7(2), C2-C5-C51 120.3(2), C2-C5-C6 89.9(1), C4-C5-C6 113.7(2), C51-C5-C6 119.1(2).

Attempts to generate **17d,e** under the usual conditions of desilylation in the presence of cyclopentadiene (**30**) gave a different type of product, namely, cyclobutenes **33a,b**, respectively (Scheme 9). The structure shown is based on an X-ray structural investigation of **33a** (Fig. 4).[7] Cyclobutenes **33** are probably formed as the result of an initial attack by the cyclopentadienyl anion (**31**) on unreacted cyclobutenium ion **16** followed by elimination of methanethiol and by acid-induced desilylation. In fact, fluoride is known to be a strong base under anhydrous conditions,[22] and a control experiment confirmed that fluoride



Scheme 9.

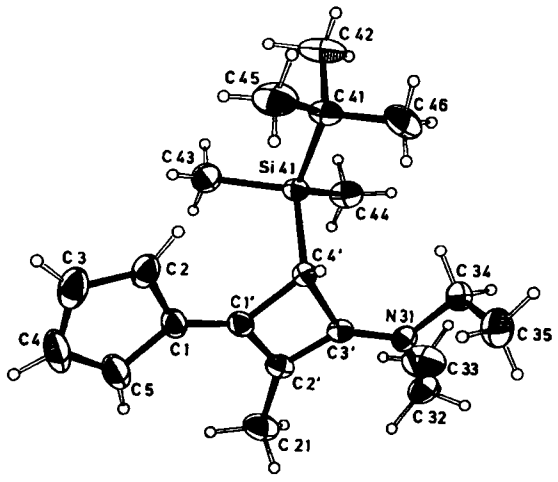


Fig. 4. ORTEP plot of the molecular structure of **33a** (ellipsoids at the 50% probability level). Selected interatomic distances between non-hydrogen atoms [pm] and angles [°] with standard deviations of the last significant figure in parentheses: Si41–C4′ 191.5(3), N31–C3′ 132.5(4), C1′–C1 136.6(5), C1′–C2 141.3(5), C1′–C4′ 154.3(4), C1–C2 144.3(6), C2′–C3′ 138.8(5), C2–C3 135.5(6), C3′–C4′ 152.7(4), C3–C4 140.8(9); C1-C1′-C2′ 138.0(4), C1-C1′-C4′ 129.8(3), C2′-C1′-C4′ 92.0(3), C1′-C2′-C3′ 91.8(3), C1′-C2′-C21 132.1(4), C3′-C2′-C21 135.7(4), N31-C3′-C2′ 136.9(3), N31-C3′-C4′ 129.4(3), C2′-C3′-C4′ 93.6(3), Si41-C4′-C1′ 115.9(2), Si41-C4′-C3′ 116.5(2), C1′-C4′-C3′ 81.8(2).

can replace sodium hydride in the formation of a ketene *S,S*-acetal from dimethyl trithiocarbonate and cyclopentadiene (**30**).[23] However, an alternative mechanism is possible in which **33** is formed by rearrangement of a cycloadduct of **17** and **30**.

Experimental Section

General: All temperatures are not corrected. NMR: Bruker ARX400 with $CDCl_3$ as solvent at 25 °C with TMS as internal standard unless otherwise indicated. Coupling constants (*J*) are given in Hz. IR: Pye-Unicam SP3-200. Low resolution mass spectra (MS) were recorded with a Hewlett Packard 5970 instrument coupled with a Perkin Elmer Sigma 1 gas chromatograph. Solvents were dried by conventional methods. Petroleum ether and ethyl acetate for chromatography were distilled prior to use. Preparative column chromatography: silica gel 60 (E. Merck, Darmstadt). Tetrabutylammonium fluoride (TBAF) was dried according to a literature procedure [24]. Acetylenes **1b** [25a], **1c** [25b], and **1d** [25c], and ynamines **3a** [26a], **3c** [26b], and **3d** [26c] were synthesized according to literature procedures. **3b** [26c] was obtained analogously to **3a** (yield 25%). Acetylene **1a** is commercially available.

General procedure for silylation of acetylene: The silyl chloride (125 mmol) was added rapidly at −50 °C under nitrogen to a solution of ethynylmagnesium bromide [25a] (0.125 mol) in dry THF (200 mL). Dry HMPA (50 mL) was then added. The solution was stirred under reflux for 8 h. Ice water (200 mL) was then added with cooling, followed by pentane (200 mL). The organic layer was separated, the solvents were evaporated under reduced pressure, and the residue was distilled in vacuo.

***tert*-Butylethynyldimethylsilane (1e)**: 7.18 g (41%) of a clear liquid. $B.p._{30}$ 40 °C; IR (neat): $\tilde{\nu}$ = 2020 cm^{-1} (C≡C), 1250 (Si–C); ^1H NMR (400 MHz): δ = 0.03 (s, 6H, $SiCH_3$), 0.86 (s, 9H, $SiCCH_3$), 2.21 (s, 1H, C≡CH); ^{13}C NMR (100 MHz): δ = −4.6 ($SiCH_3$), 16.2 (CCH_3), 26.8 (CCH_3), 88.3 (≡CSi), 93.6 (≡CH).

Ethynyldimethyl-1,2,2-trimethylpropylsilane (1f): 12.6 g (60%) of a clear liquid. $B.p._8$ 52 °C; IR (neat): $\tilde{\nu}$ = 2010 cm^{-1} (C≡C), 1250 (Si–C); ^1H NMR (400 MHz): δ = 0.20 (s, 6H, $SiCH_3$), 0.90 (s, 6H, $SiCCH_3$), 0.90 (d, 6H, *J* = 7 Hz, CH_3), 1.60 (m, 1H, $CHCH_3$), 2.40 (s, 1H, C≡CH); ^{13}C NMR (100 MHz): δ = −2.6 ($SiCH_3$), 18.4 ($CHCH_3$), 20.4 ($SiCCH_3$), 23.0 ($SiCMe_2$), 34.4 ($CHMe_2$), 89.7 (≡CSi), 93.8 (≡CH).

General procedure for the synthesis of alkynyl silyl sulfides 2 (modification of the literature procedure [6a]): To a solution of the acetylene **1** (0.1 mol) in dry diethyl ether (200 mL) was added dropwise a 1.6 M solution of *n*-butyllithium in hexane (59.4 mL, 0.095 mol) at −78 °C under nitrogen. After an additional 15 min of stirring, finely crushed sulfur (3.2 g, 0.1 mol) was added at −78 °C. The solution

was allowed to warm to 0 °C, and stirred for 30 min at this temperature. The resulting clear, yellow or red solution was cooled to −78 °C, and chlorotrimethylsilane (10.8 g, 0.1 mol; for **2a–c**) or bromotrimethylsilane (14.3 g, 0.1 mol; for **2d,e**) were added rapidly. The reaction mixture was allowed to warm to 0 °C and purified as described.

Method A: The solvent was evaporated in vacuo at 0 °C, and then hexane (50 mL) was added. The precipitate was separated under nitrogen, and the filtrate was rectified in vacuo to give pure **2**.

Method B: The solvent was evaporated in vacuo at 0 °C, and then hexane (50 mL) was added. The precipitate was separated under nitrogen, and the filtrate was used without further purification.

Caution: Alkynyl silyl sulfides **2** have a very unpleasant smell. Used glassware should be rinsed with acetone prior to further cleaning.

Phenylethynyl trimethylsilyl sulfide (2a): Method A: 10.6 g (51%) of a red liquid. B.p.$_1$ 105 °C; IR (neat): $\tilde{\nu}$ = 2170 cm^{-1} (C≡C). ^{1}H NMR (400 MHz): δ = 0.44 (s, 9H, $SiCH_3$), 7.17–7.33 (m, 5H, Ph).

1-Propynyl trimethylsilyl sulfide (2b): Method A: 10.0 g (69%) of an orange liquid. B.p.$_{15}$ 51–52 °C; IR (neat): $\tilde{\nu}$ = 2190 cm^{-1} (C≡C), 1242, 835 (C–Si), 750, 620; ^{1}H NMR (400 MHz): δ = 0.39 (s, 9H, $SiCH_3$), 1.84 (s, 3H, CH_3).

3,3-Dimethylbutynyl trimethylsilyl sulfide (2c): Method A: 12.0 g (64%) of a yellow liquid. B.p.$_{18}$ 64–66 °C; IR (neat): $\tilde{\nu}$ = 2172 cm^{-1} (C≡C), 1456, 1362, 1251 (C–Si); ^{1}H NMR (400 MHz): δ = 0.47 (s, 9H, $SiCH_3$), 1.21 (s, 9H, CCH_3).

Trimethylsilyl trimethylsilylethynyl sulfide (2d): Method A: 19.0 g (95%) of a colorless liquid, which rearranges within days at 0 °C to the corresponding thioketene. B.p.$_{0.1}$ 34 °C; IR (neat): $\tilde{\nu}$ = 2080 cm^{-1} (C≡C), 1242, 880, 825 (C–Si); ^{1}H NMR (400 MHz): δ = 0.14 (s, 9H, $SiCH_3$), 0.44 (s, 9H, $SSiCH_3$).

(*tert*-Butyldimethylsilyl)ethynyl trimethylsilyl sulfide (2e) and (1,1,2-trimethylpropyldimethylsilyl)ethynyl trimethylsilyl sulfide (2f): Method B: Distillation was not possible as the compounds rearrange to the corresponding thioketenes very quickly.

General procedure for the synthesis of 4-silylcyclobut-2-enethiones 4: To a solution of alkynyl silyl sulfide **2** (0.1 mol) in diethyl ether or pentane (100 mL) was added ynamine **3** (0.1 mol). The reaction mixture was stirred overnight at room temperature. Water-saturated ethyl acetate (50 mL) was added, and the solution was stirred for an additional 30 min to remove unreacted alkyne. The solvent was removed in vacuo, and flash chromatography (silica gel, ethyl acetate/petroleum ether 1:10) gave pure product **4**.

3-Diethylamino-4-methyl-2-phenyl-4-trimethylsilylcyclobut-2-enethione (4a): 20.0 g (63%, using pure **2a**) of yellow crystals [27]. M.p. 123–4 °C; IR (KBr): $\tilde{\nu}$ = 1620 cm^{-1} (C=C), 1590, 1500, 1430, 1250 (C–Si); ^{1}H NMR (400 MHz): δ = 0.22 (s, 9H, $SiCH_3$), 1.00 + 1.27 (2t, J = 7.2 Hz, 3 + 3H, $NCCH_3$), 1.48 (s, 3H, CH_3), 3.37 (q, J = 7.2 Hz, 4H, NCH_2), 7.22 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ = −2.0 ($SiCH_3$), 13.5 + 12.6 ($NCCH_3$), 16.7 (CH_3), 42.8 + 44.9 (NCH_2), 55.4 (C4), 126.3 (C2), 126.6 + 128.0 + 128.6 (Ph), 132.0 (Ph), 171.7 (C3), 213.6 (C1). Analysis calcd for: $C_{18}H_{27}NSSi$: C 68.08, H 5.87, N 4.41, S 10.10; found: C 68.07, H 8.67, N 4.36, S 9.85. For additional data and for further products **4** see Table 1.

General procedure for oxidation of 4a: The oxidation agent (3 mmol) was added to a solution of **4a** (952 mg, 3 mmol) in 5 mL of solvent at 0 °C. The reaction mixture was stirred for 1 h at 0 °C, and 3 h at room temperature. Ethyl acetate (50 mL) was added, and the solution was washed twice with saturated aqueous $NaHCO_3$ solution and finally with brine. The organic layer was dried ($MgSO_4$), and the solvents were removed in vacuo. Flash chromatography (silica gel, ethyl acetate/petroleum ether 1:1) provided the products.

mCPBA in dichloromethane: 286 mg (32%) of **12**, 143 mg (16%) of **13**.

mCPBA and $NaHCO_3$/$MgSO_4$ in dichloromethane: 220 mg (32%) of **12**, 100 mg (15%) of **13**.

tBuOOH in dichloromethane: 140 mg (21%) of **12**, 70 mg (10%) of **13**.

H_2O_2 in acetone: 260 mg (38%) of **12**, 140 mg (21%) of **13**.

Dimethyldioxirane in acetone: 240 mg (21%) of **10**, 150 mg (16%) of **12**, 75 mg (8%) of **13**.

3-Diethylamino-2-methyl-4-phenylcyclobut-2-enethione *S*-oxide (10): The compound decomposed completely within a couple of hours. Therefore neither a melting point nor an elemental analysis could be obtained. IR (KBr): $\tilde{\nu}$ = 2965 cm^{-1}, 2910, 1660, 1485, 1315, 1085, 700; ^{1}H NMR (400 MHz): δ = 0.92 + 1.33 (2t, J = 7.2 Hz, 3 + 3H, $NCCH_3$), 2.02 (d, J = 2.3 Hz, 3H, 2-CH_3), 3.12 + 3.14 + 3.50 + 3.51 (4dq, ^2J = 14.4 Hz, ^3J = 7.2 Hz, 1 + 1 + 1 + 1H, NCH_2), 7.22–7.35 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ = 10.2 (2-CH_3), 14.2 + 14.7 ($NCCH_3$), 44.2 + 45.6 (NCH_2), 63.1 (C4), 127.9 + 128.2 + 129.2 (Ph), 130.6 + 137.0 (Ph, C2), 170.1 (C3), 210.2 (C1).

3-Diethylamino-2-methyl-4-phenyl-2-cyclobutenone (12): The product was contaminated by a trace of **13**; m.p. 102–3 °C (ref. [28]: 113–115 °C), colorless crystals; IR (neat): $\tilde{\nu}$ = 3050 cm^{-1}, 3010, 2965, 2920, 1735, 1580, 1435, 1290, 990, 700; ^{1}H NMR (400 MHz): δ = 0.88 + 1.27 (2t, J = 7.1 Hz, 3 + 3H, $NCCH_3$), 1.78 (d, J = 2.3 Hz, 3H, 2-CH_3), 3.03 + 3.05 + 3.40 + 3.41 (4dq, ^2J = 14.2 Hz, ^3J = 7.1 Hz, 1 + 1 + 1 + 1H, NCH_2), 4.36 (q, J = 2.3 Hz, 1H, 4-H), 7.15–7.30 (m, 5H, Ph); ^{13}C NMR (100 MHz:) δ = 7.6 (2-CH_3), 14.1 + 14.2 ($NCCH_3$), 43.6 + 45.6 (NCH_2), 63.7 (C4), 109.7 (C2), 127.0 + 128.4 + 128.7 (Ph), 136.7 (Ph), 165.7 (C3), 182.9 (C1); Analysis calcd for $C_{15}H_{19}NO$: C 78.56, H 8.35, N 6.11; found C 78.20, H 8.36, N 6.00.

3-Diethylamino-4-methyl-2-phenyl-2-cyclobutenone (13): The compound could not be separated completely from **12**. IR (neat): $\tilde{\nu}$ = 3050 cm^{-1}, 3010, 2965, 2920, 1735, 1580, 1435, 1290, 990, 700; ^{1}H NMR (400 MHz): δ = 1.22 (t, J = 7.1 Hz, 6H, $NCCH_3$), 1.35 (d, J = 6.6 Hz, 3H, 4-CH_3), 3.40 (q, J = 7.1 Hz, 4H, NCH_2), 3.47 (q, J = 6.6 Hz, 1H, 4-H), 7.14–7.30 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ = 14.4 ($NCCH_3$), 20.7 (4-CH_3), 43.3 + 45.6 (NCH_2), 60.3 (C4), 112.2 (C2), 126.2 + 127.2 + 128.1 + 131.2 (Ph), 167.5 (C3), 185.2 (C1).

General procedure for protiodesilylation of 4: To a solution of **4** (3 mmol) in THF (30 mL) was added commercially available tetrabutylammonium fluoride trihydrate (3 mmol). The reaction mixture was stirred for 2 h at room temperature. The solvent was evaporated in vacuo. Flash chromatography (silica gel, ethyl acetate/petroleum ether 1:10) gave pure product **14**.

3-Diethylamino-2-methyl-4-phenylcyclobut-2-enethione (14a): 464 mg (63%) of colorless crystals. M.p. 100–101 °C; IR (KBr): $\tilde{\nu}$ = 1655 cm^{-1}, 1485, 1440, 1320, 1085, 990, 705; ^{1}H NMR (400 MHz): δ = 0.93 + 1.34 (2t, 3 + 3H, J = 7.2 Hz, $NCCH_3$), 2.03 (d, 3H, J = 2.4 Hz, CH_3), 3.13 + 3.51 (2m, 2 + 2H, NCH_2), 4.40 (q, 1H, J = 2.4 Hz, 4-H), 7.23–7.35 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ = 9.7 (CH_3), 13.8 + 14.4 ($NCCH_3$), 43.8 + 45.2 (NCH_2), 62.7 (C4), 127.5 + 127.8 + 128.8 (Ph), 130.2 (C2), 136.6 (Ph), 169.7 (C3), 209.8 (C1). For further data on **14a–c** see Table 1.

General procedure for the generation and trapping reactions of cyclobutadienes 17: To a solution of cyclobutenethione **1** (3 mmol) in dichloromethane (20 mL) was added trimethyloxonium tetrafluoroborate (Meerwein salt; 444 mg, 3 mmol) at room temperature. The reaction mixture was stirred, until the Meerwein salt had disappeared (ca. 1 h). The solvent was removed in vacuo, and the residue was dissolved in THF (10 mL). The solution was cooled to −78 °C, and the trapping agent (10 mmol) and dried tetrabutylammonium fluoride (3 mmol) were added. The reaction mixture was allowed to warm to room temperature overnight, and the solvent was removed in vacuo. The residue was purified by flash chromatography (silica gel, ethyl acetate/petroleum ether 1:4).

Trapping reaction of 1-diethylamino-2-methyl-3-methylthio-4-phenyl-1,3-cyclobutadiene (17a) with dimethyl acetylenedicarboxylate: 550 mg (45%) of a colorless oil, which was a mixture of 4 regioisomers; analysis calcd for $C_{22}H_{27}NO_4S$ (401.5): C 65.81, H 6.78, N 3.49, S 7.98; found C 65.31, H 6.84, N 3.36, S 8.22. The major product was enriched to 90% purity by column chromatography (silica gel, ethyl acetate/petroleum ether 1:40, 3 weeks); the structures were determined by NMR methods.

Dimethyl 6-diethylamino-5-methyl-4-methylthio-biphenyl-2,3-dicarboxylate (20a): ca. 23%; ^{1}H NMR (400 MHz): δ = 0.85 (t, J = 7.2 Hz, 6H, $NCCH_3$), 2.34 (s, 3H, SCH_3), 2.59 (s, 3H, CH_3), 2.70 (q, J = 7.2 Hz, 4H, NCH_2), 3.39 + 3.90 (2s, 3 + 3H, $2OCH_3$), 7.19–7.36 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ = 13.8 (NCH_3), 17.8 (CH_3, ^1J = 46.6), 19.4 (SCH_3), 46.7 (NCH_2), 52.0 + 52.5 ($2OCH_3$), 127.2 + 127.5 + 129.5 (Ph), 130.9 (C2, ^1J = 47.6, 58.6), 133.4 (C4, ^1J = 50.6, 59.5), 134.8 (C3, ^1J = 50.6, 58.6), 138.3 (C1'), 140.4 (C1, ^1J = 47.6, 61.0), 145.8 (C5, ^1J = 46.6, 59.5), 150.0 (C6), 168.0 + 168.6 (C=O); the coupling constants were derived from a 1D-INADEQUATE NMR spectrum. The assignment of the signals to the carbon atoms was possible by a COLOC-NMR spectrum. MS (70 eV, EI): m/z (%): 401 (M^+, 44%), 386 ($M^+ - CH_3$, 100%), 370 ($M^+ - OCH_3$, 22%), 354 ($M^+ - SCH_3$, 30%).

Dimethyl 4-diethylamino-5-methyl-6-methylthio-biphenyl-2,3-dicarboxylate (21a): ca. 3%; ^{1}H NMR (400 MHz): δ = 0.90 (t, J = 7.2 Hz, 6H, $NCCH_3$), 2.35 (s, 3H, SCH_3), 2.58 (s, 3H, CH_3), 2.83 (q, J = 7.2 Hz, 4H, NCH_2), 3.42 + 3.88 (2s, 3 + 3H, $2OCH_3$); MS (70 eV, EI): m/z (%): 401 (M^+, 44%), 386 ($M^+ - CH_3$, 100%), 370 ($M^+ - OCH_3$, 22%), 354 ($M^+ - SCH_3$, 30%). The structure was assigned by analysis of a COLOC-NMR spectrum.

Dimethyl 2-diethylamino-5-methyl-6-methylthiobiphenyl-3,4-dicarboxylate (22a): ca. 11%; ^{1}H NMR (400 MHz): δ = 1.08 (t, J = 7.2 Hz, 3H, $NCCH_3$), 1.98 (s, 3H, SCH_3), 2.64 (s, 3H, CH_3), 3.08 (q, J = 7.2 Hz, 4H, NCH_2), 3.41 + 3.87 (2s, 3 + 3H, $2OCH_3$); MS (70 eV, EI): m/z (%): 401 (M^+, 44%), 386 ($M^+ - CH_3$, 100%), 370 ($M^+ - OCH_3$, 22%), 354 ($M^+ - SCH_3$, 30%). The structure was assigned by analysis of a COLOC-NMR spectrum.

Dimethyl 6-diethylamino-5-methyl-2-methylthiobiphenyl-3,4-dicarboxylate (23a): ca. 11%; ^{1}H NMR (400 MHz): δ = 0.78 (t, J = 7.2 Hz, 3H, $NCCH_3$), 1.96 (s, 3H, SCH_3), 2.64 (s, 3H, CH_3), 2.72 (q, J = 7.2 Hz, 4H, NCH_2), 3.87 + 3.92 (2s, 3 + 3H, $2OCH_3$); MS (70 eV, EI): m/z (%): 401 (M^+, 44%), 386 ($M^+ - CH_3$, 100%), 370

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($M^+ - OCH_3$, 22%), 354 ($M^+ - SCH_3$, 30%). The structure was assigned by analysis of a COLOC-NMR spectrum.

Trapping reaction of 1-*tert*-butyl-2-diethylamino-3-methyl-4-methylthio-1,3-cyclobutadiene (17b) with dimethyl acetylenedicarboxylate: 200 mg (ca. 17%) of a red oil, which was a mixture of regioisomers **20b–23b** and could not be obtained completely free of impurities. MS (70 eV, EI): *m/z* (%): 366 ($M^+ - CH_3$, 58%), 334 ($M^+ - SCH_3$, 63%), 324 ($M^+ - C_4H_9$, 100%).

Trapping reaction of 1-diethylamino-2-methyl-3-methylthio-4-trimethylsilyl-1,3-cyclobutadiene (17c) with dimethyl acetylenedicarboxylate: 200 mg (33%) of a colorless oil, which was a mixture of four regioisomers as established by GLC/MS. The structure of the individual isomers **20c–23c** could not be assigned, since the oil could not be completely purified. ^{1}H NMR (400 MHz) of the enriched two main isomers: δ = 0.36 +0.42 (2s, $SiCH_3$), 0.92 +1.02 (2t, J = 7.2 Hz, $NCCH_3$), 2.20 +2.23 (2s, 2-CH_3), 2.55 (2s, SCH_3), 2.95 +3.04 (2q, J = 7.2 Hz, NCH_2), 3.82 +3.84 (2s, OCH_3); MS (70 eV, EI): *m/z* (%): 1st isomer: 397 (M^+, 33%), 382 ($M^+ - CH_3$, 43%), 366 ($M^+ - OCH_3$, 19%), 350 ($M^+ - SCH_3$, 19%), 338 ($M^+ - C_2H_3O_2$, 9%), 324 [$M^+ - Si(CH_3)_3$, 100%], 73 [$Si(CH_3)_3$, 17%]; 2nd isomer: 397 (M^+, 30%), 382 ($M^+ - CH_3$, 100%), 366 ($M^+ - OCH_3$, 19%), 350 ($M^+ - SCH_3$, 19%), 338 ($M^+ - C_2H_3O_2$, 9%), 324 [$M^+ - Si(CH_3)_3$, 30%], 73 [$Si(CH_3)_3$, 7%]; 3rd isomer: 397 (M^+, 15%), 382 ($M^+ - CH_3$, 30%), 366 ($M^+ - OCH_3$, 11%), 350 ($M^+ - SCH_3$, 19%), 338 ($M^+ - C_2H_3O_2$, 9%), 324 [$M^+ - Si(CH_3)_3$, 100%], 73 [$Si(CH_3)_3$, 11%]; 4th isomer: 382 ($M^+ - CH_3$, 100%), 366 ($M^+ - OCH_3$, 5%), 338 ($M^+ - C_2H_3O_2$, 5%), 324 [$M^+ - Si(CH_3)_3$, 44%], 73 [$Si(CH_3)_3$, 11%].

2-(3-Diethylamino-4-methyl-1,5,5-trimethylthio-2-phenyl-2,4-pentadienylidene)malononitrile (27) from 17a and 24: Desilylation was carried out by using KF (157 mg, 3 mmol)/[18]crown-6 (714 mg, 2.7 mol) instead of TBAF to give 300 mg (26%) of red crystals. M.p. 145–7 °C; IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1}, 2160, 1470, 1435, 1410, 1045, 855, 720, 680; ^{1}H NMR (400 MHz, DMSO, 350 K): δ = 1.16 (t, J = 6.4 Hz, 6H, $NCCH_3$), 2.04 (s, 3H, 4'-CH_3), 2.25 +2.30 +2.35 (3s, 3 + 3 + 3H, $3SCH_3$), 3.09 (q, J = 6.4 Hz, 4H, NCH_2), 7.20–7.33 (m, 5H, Ph); analysis calcd for $C_{22}H_{27}N_3S_3$ (429.7): C 61.50, H 6.33, N 9.78, S 22.39; found C 61.53, H 6.40, N 9.46, S 22.42.

3,7-Bis(diethylamino)-2,6-dimethyl-4,8-bis(*tert*-butyldimethylsilyl)-1,5-dimethylthiotricyclo[4.2.0.0^{2,5}]octa-3,7-diene (29a) from 17d: 300 mg (33%) of colorless crystals. M.p. 194–5 °C; IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2850, 1565, 1455, 1250, 1200, 1120, 815, 760, 650; ^{1}H NMR (400 MHz, C_6D_6): δ = 0.44 +0.47 (2s, 6+6H, 2 $SiCH_3$), 0.98 (t, J = 6.6 Hz, 12H, 4$NCCH_3$,), 1.16 (s, 18H, 2*t*Bu-CH_3), 1.57 (s, 6H, 2-CH_3 +6-CH_3), 1.96 (s, 6H, 2SCH_3), 3.05 +3.07 +3.29 +3.31 (4dq, ^2J = 13.2 Hz, ^3J = 6.6 Hz, 2+2+2+2H, 4 NCH_2); ^{13}C NMR (100 MHz, C_6D_6): δ = −0.7 +0.7 ($SiCH_3$), 13.8 (4 $NCCH_3$), 14.5 (2-CH_3 +6-CH_3), 16.8 (2SCH_3), 19.9 [2$C(CH_3)_3$], 30.3 [2$C(CH_3)_3$], 42.6 (4NCH_2), 60.6 (C2 +C6), 63.4 (C1 +C5), 96.9 (C4 +C8), 166.1 (C3 +C7); analysis calcd for $C_{32}H_{62}N_2S_2Si_2$ (595.15): C 64.58, H 10.50, N 4.71, S 10.77; found C 64.50, H 10.55, N 4.53, S 10.83.

3,7-Bis(diethylamino)-2,6-dimethyl-4,8-bis(dimethylthexylsilyl)-1,5-dimethylthiotricyclo[4.2.0.0^{2,5}]-octa-3,7-diene (29b) from 17e: 100 mg (10%) of colorless crystals. M.p. 201–2 °C; IR (KBr): $\tilde{\nu}$ = 2985 cm^{-1}, 2880, 1575, 1470, 1380, 1250, 1040, 820, 775, 660; ^{1}H NMR (400 MHz, C_6D_6): δ = 0.64 +0.66 (2s, 6+6H, 2 $SiCH_3$), 1.11 (d, J = 6.6 Hz, 12H, 2$CHCH_3$), 1.11 (t, J = 7.1 Hz, 12H, 4$NCCH_3$), 1.21 (s, 6H, 2$SiCCH_3$), 1.69 (s, 6H, 2-CH_3 +6-CH_3), 2.06 (sept, J = 6.6 Hz, 2H, 2CH), 2.08 (s, 6H, 2SCH_3), 3.15 +3.16 +3.40 +3.42 (4dq, ^2J = 14.2 Hz, ^3J = 7.1 Hz, 2+2+2+2H, NCH_2); ^{13}C NMR (100 MHz, C_6D_6): δ = 0.3 +0.5 ($SiCH_3$), 13.9 +14.3 (2$NCCH_3$), 17.0 (2$SiCCH_3$), 19.6 (2-CH_3, 6-CH_3), 19.7 (2$CHCH_3$), 23.4 (2SCH_3), 26.5 (2CCH_3), 35.0 (2CH), 42.6 (2NCH_2), 61.2 (C1 +C5), 63.0 (C2 +C6), 98.1 (C4 +C8), 165.5 (C3 +C7); analysis calcd for $C_{36}H_{70}N_2S_2Si_2$ (651.26): C 66.39, H 10.83, N 4.30; found C 66.25, H 11.16, N 4.24.

4-(*tert*-Butyldimethylsilyl)-3-cyclopentadienylidene-1-diethylamino-2-methylcyclobutene (33a) from 17d and 30: 300 mg (32%). IR (KBr): $\tilde{\nu}$ = 3094 cm^{-1}, 1639, 1542 (C=C), 1249, 840, 824, 811, 775; ^{1}H NMR (400 MHz): δ = 0.02 +0.05 (2s, 3+3H, $SiCH_3$), 0.72 (t, J = 7.7 Hz, 6H, $NCCH_3$), 0.95 (s, 9H, $SiCCH_3$), 1.86 (d, ^4J = 2.0 Hz, 3H, 2-CH_3), 2.59–2.66 +2.78–3.01 (2m, 2+2H, NCH_2), 3.95 (q, ^4J = 2.0 Hz, 1H, 4-H,), 6.70–7.08 (m, 4H, =CH); ^{13}C NMR (100 MHz): δ = −4.5 + −3.9 ($SiCH_3$), 12.3 (2-CH_3), 14.1 ($NCCH_3$), 18.3 (SiC), 27.4 ($SiCCH_3$), 28.0 (C4), 41.9 (CH_2), 106.7 (C2), 119.0 +119.6 +122.5 +124.7 (=CH), 123.1 (=C), 153.4 (C3), 158.5 (C1); MS (70 eV, EI): *m/z* (%): 315 (100%, M^+), 258 (55%), 230 (52%), 73 (38%).

3-Cyclopentadienylidene-1-diethylamino-2-methyl-4-dimethylthexylsilylcyclobutene (33b) from 17e and 30: 206 mg (20%). ^{1}H NMR (400 MHz): δ = 0.10 +0.12 (s, 6H, $SiCH_3$), 0.70 (m, 6H, $NCCH_3$), 0.86 +0.87 (2d, J = 7.0 Hz, 3+3H, $CHCH_3$), 0.90 +0.97 (2s, 3+3H, $SiCCH_3$), 1.77 (m, 1H, CH), 1.88 (d, ^4J = 2.0 Hz, 3H, 2-CH_3), 2.49–2.67 +2.75–3.02 (2m, 2+2H, NCH_2), 3.04 (q, ^4J = 2.0 Hz, 1H, 4-H), 6.66–7.11 (m, 4H, =CH); ^{13}C NMR (100 MHz): δ = −1.9 + −1.6 ($SiCH_3$), 12.3 (2-CH_3), 14.0 ($NCCH_3$), 21.6 +21.7 ($CHCH_3$), 25.1 (SiC), 34.3 (CH), 37.9 (C4), 41.8 (NCH_2), 107.4 (C2), 119.1 +119.6 +122.6 +124.7 (=CH), 123.2 (=C), 153.5 (C3), 158.5 (C1); MS (70 eV, EI): *m/z* (%): 343 (31%, M^+), 259 (51%), 230 (100%), 73 (30%).

Crystal structure determinations of 4a, 27, 29b, and 33a [7]: Rotating crystal (Weissenberg) and precession photographs of a crystal with the dimensions as shown in Table 2 gave approximate lattice constants and the preliminary space group. Refinement of the lattice constants led to the cell dimensions (Table 2). Intensity measure

Table 2. Crystallographic data of compounds **4a**, **27**, **29b**, and **33a**.

	4a	27	29b	33a
cryst. dimensions [mm]	0.21 × 0.28 × 0.25	0.21 × 0.24 × 0.45	0.28 × 0.22 × 0.37	0.33 × 0.45 × 0.52
a [pm]	791.6(1)	738.7(1)	1482.6(1)	1165.9(1)
b [pm]	1304.4(1)	940.0(1)	983.2(1)	1482.6(2)
c [pm]	1844.3(2)	1747.8(1)	1446.4(1)	1286.6(2)
α [°]	90	75.26(1)	90	90
β [°]	90	84.65(1)	107.21(1)	110.71
γ [°]	90	81.95(1)	90	90
V [× 10^9 pm^3]	1.904	1.16	2.014	2.08
space group	$P2_12_12_1$	$P1$	$P2_1/c$	$P2_1/c$
Z	4	2	2	4
ρ_{calcd} [gcm^{-3}]	1.11	1.25	1.07	1.01
I measured	2144	4759	3995	2923
I included	1939	4838	3547	1961
R 0.039	0.041	0.049	0.039	
R_w	0.036	0.040	0.049	0.037

ments were carried out with a CAD4-SDP (Fa. Entraf Nonius) diffractometer by using $Cu_{K\alpha}$ radiation monochromated with graphite by the θ–2θ scan technique with variable scan speed in the range of $2 \le \theta \le 70°$. The intensity data were corrected for absorption [29]. The measured intensities were reduced to the symmetry-independent reflexions [$I > 3\sigma(I)$]. The structures were solved by the direct-methods program MULTAN [30]. The E maps revealed the position of all the heavy atoms. After the refinement of these positions the H atoms were found from a Fourier synthesis [31] and refined to convergence. Interatomic distances and angles are included in Figures 1–4 [7].

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