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In Pursuit of an Acetylenedithiolate Synthesis

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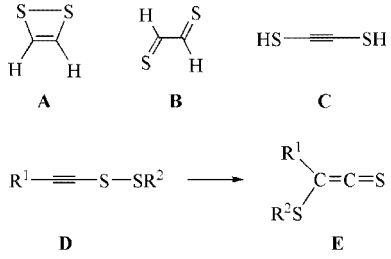
Acetylene disulfides RSC_2SR, which are furnished with typical thiol protection groups R, were synthesized, fully characterized, and tested with respect to the aimed cleavage of R. While the alkyne RSC_2SR with R = $C_2H_4SiMe_3$ is easily accessible, the corresponding disulfide with R = CPh_3 can be prepared only with difficulties, and attempts to use the $SiMe_3$ group lead to the isolation of a dithiacyclopentene derivative. The molecular structures of $Ph_3CSC_2SCPh_3$ and Ph_3CSC_2H, which were investigated by X-ray diffraction, show a remarkable combination of long and very short carbon–sulfur single bonds. However, removal of the trityl groups by sodium phenolate or methyllithium in THF led to intractable solutions. In contrast, removal of both trimethylsilylethyl groups in $Me_3SiC_2H_4SC_2SC_2H_4SiMe_3$ with $(Bu_4N)F$ in THF proceeded smoothly, if benzyl bromide as the trapping agent is present. Hence, the successful transfer of the $C_2S_2^{2-}$ synthon in solution was proven by isolation of $BnSC_2SBn$.

Introduction

Bis(alkylthio)acetylenes are interesting synthetic intermediates possessing a highly electron-rich triple bond. Thus, bis(alkylthio)acetylenes are efficient acetylene equivalents in cycloaddition reactions.[1] The polymerization of bis(alkylthio)acetylenes leads to poly[bis(alkylthio)acetylenes], which in turn can be doped with electron acceptors to produce semiconductors.[2] In addition, dithioalkyne units are the building blocks in remarkable cyclic diynes investigated by Gleiter[3] and in oligoacetylenes reported by Lee.[4] Our research program is devoted to the coordination chemistry of acetylenedithiolate.[5] Thereby, the instability of acetylenedithiolate is a major obstacle because it is prone to rapid oligomerization with the aid of Lewis acids. In the course of these studies we sought dithioalkynes, which are furnished with sulfur protection groups. However, the synthesis of bis(alkylthio)acetylenes, in which the alkyl groups can be cleaved under desirably mild conditions, turned out to be challenging. The choice of an appropriate sulfur protecting group is complicated by the fact that groups with too high lability might result in a conversion process of alkyne into thione bonds. Thus, a number of theoretical investigations uncovered the higher stability of the $C_2H_2S_2$ isomers 1,2-dithiete **A** and dithioglyoxal **B** relative to acetylenedithiol **C**.[6] Alkyne 1-disulfides **D**, for example, are known to transform rapidly into thioketenes **E**.[7]



In this contribution we report on the synthesis of dithioalkynes with triphenylmethyl and 2-trimethylsilylethyl protection groups. The removal of the trimethylsilylethyl groups under retention of the $(SC{\equiv}CS)^{2-}$ moiety is proven by successful *trans* alkylation experiments, bis(benzylthio)-acetylene serving as a test system. The successful reductive removal of the benzyl groups in alkyne complexes with bis(benzylthio)acetylene was already shown by us.[5] Furthermore, we report the molecular structures of ethynyl triphenylmethyl sulfide (**2c**) and bis(triphenylmethylthio)-acetylene (**3c**), which both combine a very short with a long carbon sulfur bond at individual sulfur atoms. Finally, an investigation with trialkylsilyl groups uncovers the unsuitability of these groups as protection groups for acetylenedithiolate.

Results

A variety of synthetic procedures leading to bis(alkylthio)acetylenes are known. While seeking for an appropriate and facile method, we checked some of the syntheses. Variable elimination reactions with bis(alkylthio)ethylenes[8]

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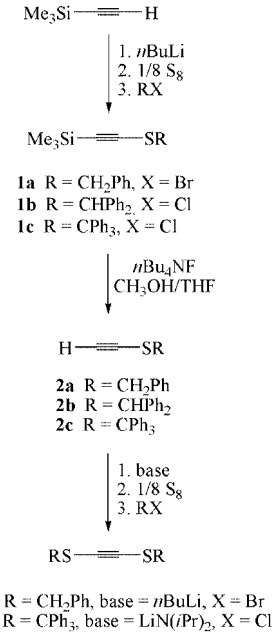
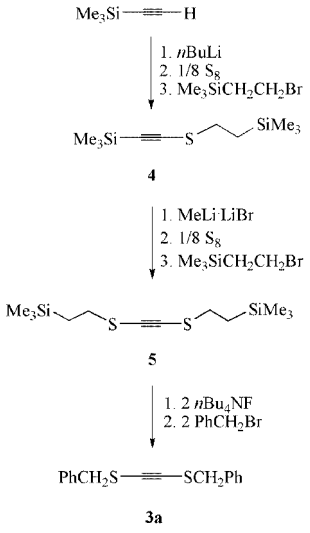
have not been considered because of the obvious expense transfer to the preparation of the corresponding ethylenes. A straightforward syntheses of bis(alkylthio)acetylenes succeeds by the reaction of various alkylthiocyanates with NaC_2H in liquid NH_3[9] or with Li_2C_2 in THF.[3a] Other methods are based on metathesis with reversed polarity. Thus, bis(alkylthio)acetylenes are obtained by reaction of dichloroacetylene with thiols in the presence of either KH[10] or LiHMDS[1f] and by treatment of bis(iodonium)-acetylenes with sodium thiolates.[11]

Finally we found the step-by-step procedure outlined in Scheme 1 the most convenient and, particularly, the only one that could be successfully adapted for the preparation of bis(triphenylmethylthio)acetylene (**3c**) and bis(2-trimethylsilylethylthio)acetylene (**5**) in reasonable yields. The synthesis is based on the long-known reaction of deprotonation of terminal alkynes with elemental sulfur.[12] Deprotonation of trimethylsilylacetylene with *n*BuLi, reaction with sulfur at –30 °C, and subsequent alkylation yielded **1a**–**c**. The consumption of sulfur, which is only sparingly soluble in diethyl ether, is remarkably clear and fast. Removal of the trimethylsilyl group with catalytic amounts of Bu_4NF in THF/methanol yielded **2a**–**c**, the reaction of **1c** was much slower than that of **1a**. Simple repetition of the sequence deprotonation, reaction with the sulfur, and alkylation with benzyl bromide yielded **3a**. However, this step is critical in the synthesis of bis(triphenylmethylthio)acetylene (**3c**). Nucleophilic bases like alkyllithium compounds presumably would rather attack the trityl group than deprotonate the alkyne. Alkyne **3c** can be isolated in moderate yields, if lithium diisopropylamide in a diethyl ether/THF solvent mixture is used. The addition of sulfur and alkylation with triphenylmethyl chloride must strictly be performed at low temperatures owing to side reactions. Bis(diphenylmethylthio)acetylene could not be obtained at all. Analytically pure samples of **3c** were obtained from toluene solutions, which tend conspicuously to supersaturation. Disulfide **3c** is less soluble in *n*-hexane and diethyl ether. Slow decomposition is observed in polar solvents and under daylight.



Scheme 1. Synthesis of acetylene disulfides.

The introduction of the trimethylsilylethyl protection group in acetylene disulfides required a variation in the synthetic procedure. Deprotonation of trimethylsilylacetylene with *n*BuLi, reaction with sulfur at –30 °C, and subsequent alkylation with trimethylsilylethyl bromide yielded **4** (Scheme 2). In the next step, the removal of the trimethylsilyl group at the alkyne cannot be performed with fluoride ions because of the presence of the second trimethylsilyl group in the molecule. However, reaction of **4** with 1 equiv. of MeLi·LiBr at 0 °C yielded, after 3 h, the intermediate $Me_3SiC_2H_4SC_2Li$. Subsequent addition of sulfur and alkylation with 2-trimethylsilylethyl bromide resulted in the formation of **5** in good yields. Alkyne **5** can be obtained in an analytically pure form by column chromatography.



Scheme 2. Synthesis and reactivity of bis(trimethylsilylethylthio)-acetylene.

The X-ray structure analyses of **2c** and **3c** confirm their identity as trityl alkynyl sulfides (Figure 1 and Table 1). In addition, the molecular structures of **2c** and **3c** are interesting because of the extreme ratio of the two carbon–sulfur bond lengths at the sulfide group. The sulfur–carbon bonds to the alkynyl carbon atoms are very short and amount to 1.682 Å in **2c** and to 1.661/1.662 Å in **3c**. The sulfur–carbon

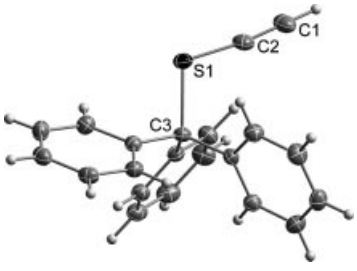


Figure 1. Molecular structure of **2c** (50% ellipsoid probability).

bonds to the tertiary carbon atom are very long and amount to 1.893 Å in **2c** and to 1.913/1.902 Å in **3c**. These bond lengths mark the whole range of carbon–sulfur single bonds in unstrained thioethers. A comparable ratio of the carbon–sulfur bond lengths was observed in cyclic poly(alkyne thioethers).[13] The remarkably short alkyne–sulfur bonds are in accordance with extensive structural data for alkynyl sulfides published by Gleiter[3a,13] and others.[14] Short C(sp)–X distances generally reflect the dependence of the bond length from the hybridization at the carbon center. However, the differences in the $R_nC–XR_m$ bond lengths, while changing from a C(sp^3) to a C(sp^2) and finally to a C(sp) center, are particularly pronounced with X = S compared to the corresponding C–P and C–Si bonds (Table 2). The structural features of disulfide **3c** emphasize the strong alkyne sulfur bond and the potential protection group character of the trityl group (Figure 2).

Table 1. Selected bond lengths [Å] and angles [°] of **2c** and **3c**.

	2c		**3c**
C1–C2	1.188(2)	C1–C2	1.205(2)
C2–S1	1.682(2)	C1–S1	1.661(2)
		C2–S2	1.662(2)
S1–C3	1.893(2)	S1–C3	1.913(2)
		S2–C22	1.902(2)
C1–C2–S1	173.1(2)	C1–C2–S2	178.7(2)
		C2–C1–S1	173.6(2)

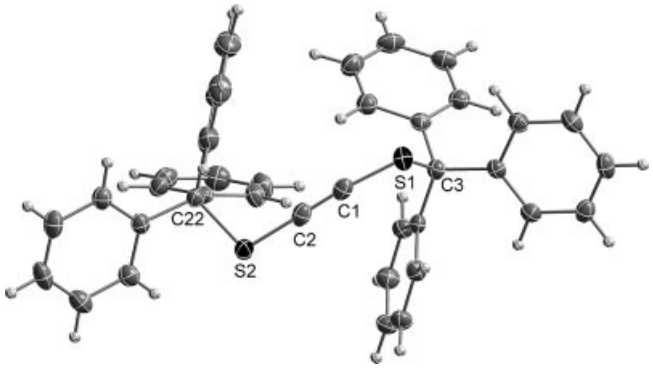


Figure 2. Molecular structure of **3c** (50% ellipsoid probability).

Our attempts to remove the trityl groups in **3c** under basic conditions turned out to be disappointing. Treatment of **3c** with MeLi·LiBr or sodium phenolate in THF resulted in highly colored solutions. However, independently of the reaction time or temperature, subsequent alkylation with benzyl bromide did not yield **3a**, whereas **3c** could not be recovered. In contrast, if colorless solutions of **5** in THF are treated with 2 equiv. of $(Bu_4N)F$ at ambient temperature, ethylene evolution is observed and a bright-yellow color appeared. This solution persists for circa one hour without any precipitation. However, at longer standing it turned slowly brown, and finally black solids formed. Both immediate addition of benzyl bromide after fluoride addition, and the reverse sequence, yielded straightforwardly bis(benzylthio)acetylene (**3a**) (Scheme 2). In turn, if **5** is treated at room temperature with benzyl bromide without the addition of fluoride ions, the formation of the corresponding sulfenium salts can be excluded by NMR spectroscopic evidence. Therefore, the formation of free alkynethiolate groups in solution is evident. However, the existence of acetylenedithiolate cannot be concluded because a stepwise removal of the trimethylsilylethyl groups is likely in consideration of the charge. Consistently, the addition of benzyl bromide 15 min after the fluoride addition at ambient temperature yielded only traces of **3a**. We attribute this observation to the protonation of the intermediary dianionic acetylenedithiolate and subsequent decomposition. The water content of commercial $(Bu_4N)F$ effectively renders HF_2^- ions the reactive species. The use of anhydrous $(Bu_4N)F$ is impeded by its poor solubility in THF, while the reaction of anhydrous $(Bu_4N)F$[19] with **5** in acetonitrile led to intractable reaction mixtures.

Trialkylsilyl groups form comparatively weak bonds with sulfur and therefore they are tested as an alternative protection group for acetylenedithiolate. As the procedures outlined in Schemes 1 and 2 cannot be adapted for the synthesis of bis(trialkylsilylthio)acetylenes we tried to ascertain the general utility of trialkylsilyl groups solely on one side of the alkyne. However, the reaction of benzyl ethynyl sulfide (**2a**) with *n*BuLi, sulfur, and Me_3SiCl under standard conditions resulted in crystalline product **6** in almost stoichiometric yield. Compound **6** displayed the double molecular mass in MALDI mass spectrometry, no alkyne resonances, and two resonances for both the trimethylsilyl and the benzyl group, respectively, in the NMR spectra. The identity of **6** as a thiafulvalene-like compound consisting of a dithiacyclopentene ring and an exocyclic C–C double bond was uncovered by X-ray structure analysis (Figure 3). The metric parameters of **6** are not discussed in detail be-

Table 2. Trends in the C–X single bond lengths [Å] (X = Si, P, S) depending on the hybridization at the carbon atom.[a]

	X = SiR_3[15]	X = PR_2[16]	X = SR[17,3b]
Alkyl–X	1,4-$(Me_3Si)_2C_6H_4$	1,2-$(MePhP)_2C_6H_4$	1,2-$(MeS)_2C_6H_4$
	1.864	1.842	1.800
Aryl–X	1.886	1.837	1.762
Alkenyl–X	$Ph_3SiC_2(H)_2SiHPh_2$[b]	$Ph_2PC_2(H)_2PPh_2$[b]	$C_2(SC_2H_4S)_2C_2(H)_2$[c]
	1.858	1.807	1.750[d]
Alkynyl–X	Ph_3SiC_2H	$Ph_2PC_2PPh_2$	$C_2(SC_2H_4S)_2C_2(H)_2$
	1.819	1.767	1.677[d]

[a] Representative examples with maximum similarity were chosen, bond lengths are mean values where applicable. [b] *trans*. [c] *cis*. [d] With R = Ph, the C–S bonds are slightly shorter: PhSC(H)C(CO_2Me)CHPh(OH): 1.741 Å,[18] $PhSC_2SPh$: 1.665 Å.[14b]

cause of a disorder problem in the structure solution. The dimerization of formal (benzylthio)(trimethylsilylthio)-acetylene can be rationalized by an equilibrium of (benzylthio)(trimethylsilylthio)acetylene and (benzylthio)(trimethylsilyl)thioketene in the silylation reaction as suggested in Scheme 3. Obviously, the Si–S bond is too weak to allow the stabilization of dithioalkyne systems. Furthermore, we were not successful in using alternative silyl groups like *tert*-$BuMe_2Si$ in the synthesis of the desired bis(trialkylsilylthio)alkynes.

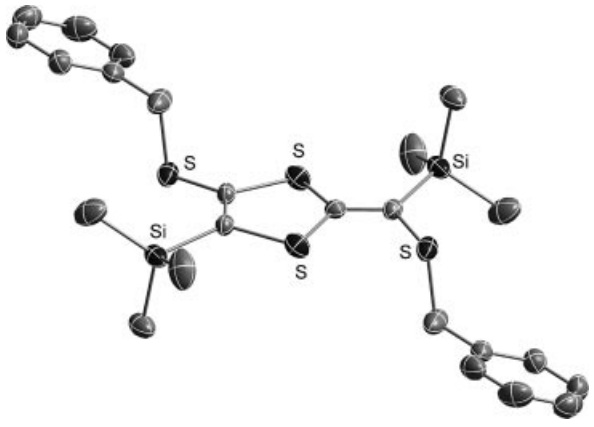
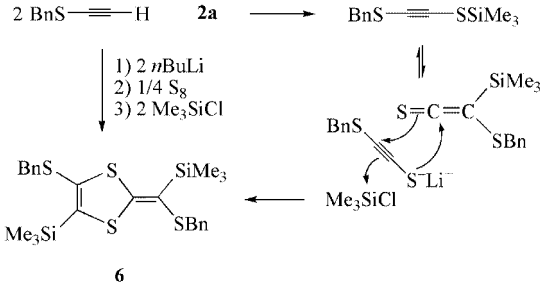


Figure 3. Molecular structure of **6** (50% ellipsoid probability); hydrogen atoms are omitted for clarity.



Scheme 3. Reactivity of alkynethiolate with a Me_3Si alkylating agent.

Conclusions

We pursued the synthesis of free acetylenedithiolate in solution because of its putative value as a building block in coordination chemistry and as a preparative synthon in organic synthesis. Primarily, we succeeded in the synthesis of acetylene disulfides, which are furnished with typical sulfur protection groups at the sulfur atoms. The synthesis of RSC_2SR is facile with R = $C_2H_4SiMe_3$, rather difficult with R = CPh_3, and not viable with R = $SiMe_3$. In addition, the subsequent removal of the triphenylmethyl groups in $Ph_3CSC_2SCPh_3$ led to intractable solutions. In contrast, the cleavage of both trimethylsilylethyl groups by treatment of $Me_3SiC_2H_4SC_2SC_2H_4SiMe_3$ with 2 equiv. of $(Bu_4N)F$ in THF and subsequent re-alkylation with benzyl bromide resulted in the formation of $BnSC_2SBn$ in good yields. Therefore the $(C_2S_2)^{2-}$ synthon can be transferred under mild conditions. However, the free dianion acetylenedithiolate turned out to be prone to decomposition in the presence of any sources of protons or even Lewis acids.

Experimental Section

General Procedures: All operations were carried out under a dry argon atmosphere by using standard Schlenk and glove box techniques. All solvents were dried and saturated with argon by standard methods and freshly distilled prior to use. $Me_3SiC_2H_4Br$ was prepared according to a literature procedure.[20] Trimethylsilylacetylene was purchased from Aldrich. ^1H and ^{13}C NMR spectra were recorded with a Bruker AC 200 and a Bruker Avance 400 NMR spectrometer. Elemental analyses were performed with a Vario EL III CHNS elemental analyzer. MALDI mass spectra were obtained with the use of a Bruker Reflex IV spectrometer with the matrix [(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enyliden]malononitrile (DCTB). Infrared spectra were recorded with a Bruker Vektor 22.

Benzyl Trimethylsilylethynyl Sulfide (1a): Trimethylsilylacetylene (36 mL, 0.255 mol) was dissolved in diethyl ether (250 mL) and cooled to –78 °C. *n*-Butyllithium (10 M solution in *n*-hexane, 25.5 mL) was added, and the solution was stirred at –78 °C for 15 min. Sulfur (8.16 g, 0.255 mol), which was dried in vacuo for 1 h, was added, and the mixture was stirred for 15 min at –78 °C. Upon warming to room temperature, the reaction was complete in the course of one hour, which was observed by the consumption of the sulfur. The resulting clear orange solution was treated with benzyl bromide (29.5 mL, 0.255 mol) at 0 °C, and the solution was stirred at room temperature overnight. After removal of the solvent in vacuo, the residue was extracted with *n*-hexane (150 mL and 3 × 20 mL) and filtered. The solvent of the filtrate was removed in vacuo and purified by distillation under reduced pressure (80 °C, 0.01 mbar), yielding **1a** (48.4 g, 0.22 mol, 86%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.39 (m, 5 H, Ph-*H*), 3.98 (s, 2 H, SCH_2), 0.25 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 136.2 (Ph-C_{ipso}), 128.9, 128.3, 127.6 (Ph-*C*), 102.0 (Si*C*≡C), 94.2 (C≡*C*S), 40.0 (S*C*H_2), –0.2 [Si(*C*H_3)$_3$] ppm. $C_{12}H_{16}SSi$ (220.41): calcd. C 65.39, H 7.32, S 14.55; found C 65.44, H 7.35, S 14.50.

Diphenylmethyl Trimethylsilylethynyl Sulfide (1b): Compound **1b** was prepared in a scale of 14 mmol (30 mL diethyl ether) as described for **1a** by using diphenylmethyl chloride (2.5 mL, 14.0 mmol) as the alkylating agent. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.4 (Ph-C_{ipso}), 128.5, 128.4, 127.6 (Ph-*C*), 103.2 (Si*C*≡C), 94.3 (C≡*C*S), 58.1 (S*C*H), –0.3 [Si(*C*H_3)$_3$] ppm.

Triphenylmethyl Trimethylsilylethynyl Sulfide (1c): Compound **1c** was prepared as described for **1a** using triphenylmethyl chloride (71 g, 0.255 mol) as alkylating agent. The addition of triphenylmethyl chloride was performed in a toluene solution (100 mL). After stirring for 12 h the solvents were removed in vacuo and the residue was subjected to Soxhlet extraction using 300 mL *n*-hexane. Finally the solution was cooled stepwise to –30 °C in order to complete precipitation of **1c** (58 g, 61%), which was isolated by filtration and dried in vacuo. $C_{24}H_{24}SSi$ (372.61): calcd. C 77.36, H 6.49, S 8.60; found C 77.43, H 6.53, S 8.47. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 144.0 (Ph-C_{ipso}), 129.9, 127.8, 127.2 (Ph-*C*), 106.0 (Si*C*≡C), 95.9 (C≡*C*S), 71.6 (S*C*Ph_3), –0.5 (Si-(*C*H_3)$_3$) ppm.

Benzyl Ethynyl Sulfide (2a): Pure **1a** (48.4 g, 0.22 mol) was dissolved in THF (120 mL). Methanol (40 mL) and tetrabutylammonium fluoride (400 mg) were added, and the mixture was stirred for 3 d at ambient temperature. After removal of the solvents in vacuo, the residue was dissolved in *n*-hexane (150 mL), dried with magnesium sulfate, and filtered. The residue was thoroughly washed with *n*-hexane (3 × 20 mL). After removal of the solvent in vacuo **2a** (32.2 g, 99%) was obtained as a light yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.29–7.20 (m, 5 H, Ph-*H*), 3.85 (s, 2 H, SCH_2), 2.75 (s, 1 H, *H*C≡C) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 136.2 (Ph-C_{ipso}), 128.8, 128.4, 127.6 (Ph-*C*), 83.4 (S*C*≡C), 74.1 (H*C*≡C), 39.4 (S*C*H$_2$) ppm.

Diphenylmethyl Ethynyl Sulfide (2b): Compound **2b** was prepared as described for **2a**. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.61–7.30 (m, 10 H, Ph-*H*), 5.73 (s, 1 H, SC*H*), 2.89 (s, 1 H, *H*C≡C) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.3 (Ph-C_{ipso}), 128.5, 128.4, 127.7 (Ph-*C*), 84.0 (S*C*≡C), 74.2 (H*C*≡C), 57.6 (S*C*H) ppm.

Triphenylmethyl Ethynyl Sulfide (2c): Compound **2c** was prepared as described for **2a** with an 8 d reaction time. The completeness of the conversion was checked by thin layer chromatography (*n*-hexane/toluene, 5:1). Alkyne **2c** crystallizes in large light-yellow prisms from a saturated diethyl ether solution upon cooling. Yield: 76%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.39–7.26 (m, 15 H, Ph-*H*), 2.85 (s, 1 H, *H*C≡C) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.7 (Ph-C_{ipso}), 129.7, 127.8, 127.3 (Ph-*C*), 86.5 (S*C*≡C), 75.4 (H*C*≡C), 70.8 (S*C*Ph$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3279 (m, H–C$_2$), 2029 (w, C≡C) cm^{-1}. $C_{21}H_{16}S$ (300.42): calcd. C 83.96, H 5.37, S 10.67; found C 83.44, H 5.65, S 10.42.

Bis(benzylthio)acetylene (3a): A solution of **2a** (32.2 g, 0.218 mol) in diethyl ether (300 mL) cooled to –78 °C was treated with *n*-butyllithium (10 M solution in *n*-hexane, 21.8 mL). After 10 min, sulfur (6.98 g, 0.218 mol), which was first dried in vacuo, was added. After stirring at –78 °C for a further 15 min, the mixture was warmed to room temperature and stirred until total consumption of the sulfur. To the resulting clear yellow–red solution was added benzyl bromide (25.2 mL, 0.218 mol) at 0 °C, and the mixture was stirred at room temperature overnight. Product **3a** was isolated as large yellow crystals by an aqueous workup and crystallization from diethyl ether at –35 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.31–7.18 (m, 10 H, Ph-*H*), 3.79 (s, 4 H, SCH_2) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 136.4 (Ph-C_{ipso}), 129.0, 128.4, 127.6 (Ph-*C*), 87.9 (*C*≡*C*), 41.3 (S*C*H$_2$) ppm. Raman: $\tilde{\nu}$ = 2058 (s, C≡C) cm^{-1}. $C_{16}H_{14}S_2$ (270.42): calcd. C 71.06, H 5.22, S 23.71; found C 70.75, H 5.34, S 23.56.

Bis(triphenylmethylthio)acetylene (3c): A solution of **2c** (2.5 g, 8.3 mmol) in diethyl ether (300 mL) was cooled to –78 °C forming a light yellow suspension. Lithium diisopropylamide (890 mg, 8.3 mmol) dissolved in THF (15 mL) was added. After stirring for 15 min at –78 °C, sulfur (265 mg, 8.3 mmol), which was dried in vacuo for one hour, was added to the clear yellow solution, and the mixture was slowly warmed to –40 °C. After consumption of the sulfur in the course of two hours, the color of the mixture had changed from yellow to red–brown. At –60 °C, a solution of triphenylmethyl chloride (2.3 g, 8.3 mmol) in toluene (25 mL) was slowly added, and the mixture was stirred at ambient temperature overnight. Subsequently, the solvents were removed in vacuo, and the residue was extracted with toluene (150 mL) and filtered through celite. The brown clear solution was reduced in volume to approximately 30 mL. Precipitation of a white powder, finally at –30 °C, was observed in the course of two weeks. Product **3c** (1.7 g, 36%) was isolated by filtration, washing with diethyl ether (5 mL), and drying in vacuo. Crystallization was achieved by cooling a saturated benzene solution (30 mg **3c**/mL benzene). ^{13}C NMR (50 MHz, C_6D_6): δ = 144.4 (Ph-C_{ipso}), 130.4, 128.2, 127.4 (Ph-*C*), 95.0 (*C*≡*C*), 73.1 (S*C*Ph$_3$) ppm.$C_{40}H_{30}S_2$ (574.81): calcd. C 83.58, H 5.26, S 11.16; found C 83.15, H 5.38, S 10.82.

Trimethylsilylethynyl Trimethylsilylethyl Sulfide (4): Sulfide **4** was prepared as described for **1a** by using trimethylsilylacetylene (10 mL, 71 mmol), diethyl ether (100 mL), *n*-butyllithium (10 M in *n*-hexane, 7.1 mL), sulfur (2.27 g, 71 mmol), and finally 2-trimethylsilylethylbromide (11.2 mL, 12.9 g, 71 mmol) as the alkylating agent. Extraction of the crude product with *n*-hexane (80 mL and 3 × 20 mL), filtration, and removal of the solvent in vacuo yielded **4** (14.0 g, 86%) analytically pure as a light yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.98 (m, 2 H, CH_2S), 1.00 (m, 2 H, CH_2Si), 0.16 [s, 9 H, (CH_3)$_3$SiCH$_2$], 0.03 [s, 9 H, (CH_3)$_3$SiCC] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 100.9 (C≡*C*Si), 95.2 (C≡*C*S), 32.3 (*C*H$_2$S), 17.1 (*C*H$_2$Si), 0.00 [(*C*H$_3$)$_3$SiCC], –1.93 [(*C*H$_3$)$_3$SiCH$_2$] ppm. $C_{10}H_{22}SSi_2$ (230.52): calcd. C 52.10, H 9.62, S 13.91; found C 52.39, H 9.87, S 13.71.

Bis(trimethylsilylethylthio)acetylene (5): A solution of **4** (5 g, 21.7 mmol) in THF (100 mL) was cooled to –78 °C. Methyllithium·lithium chloride (1.5 M solution in *n*-hexane, 14.5 mL, 21.7 mmol) was added to the clear colorless solution, and the resulting yellow–orange mixture was stirred for half an hour at this temperature. Subsequently, the mixture was slowly warmed to 0 °C and stirred for two hours at this temperature. After again being cooled to –78 °C, sulfur (0.69 g, 21.7 mmol), which was dried in the usual manner, was added. The mixture was stirred for 30 min at –78 °C and then warmed to room temperature. To the resulting clear, dark red solution was added 2-trimethylsilylethylbromide (3.4 mL, 3.9 g, 21.7 mmol) at 0 °C. After stirring overnight at ambient temperature, the solvents were removed in vacuo. The residue was extracted into *n*-hexane (60 mL and 3 × 5 mL). The filtrate was reduced to a small volume in vacuo and purified by column chromatography (*n*-hexane). Disulfide **5** (4.3 g, 68%) was obtained as a light yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.74 (m, 4 H, CH_2S), 0.97 (m, 4 H, CH_2Si), 0.02 [s, 18 H, (CH_3)$_3$Si] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 86.8 (C≡*C*S), 33.0 (*C*H$_2$S), 17.1 (*C*H$_2$Si), –1.81 [(*C*H$_3$)$_3$SiCH$_2$] ppm. $C_{12}H_{26}S_2Si_2$ (290.64): calcd. C 49.59, H 9.02, S 22.07; found C 49.72, H 8.87, S 21.91.

Exchange of the Protection Groups: Benzyl bromide (240 μL, 2.0 mmol) was added to a solution of **5** (290 mg, 1.0 mmol) in THF (7 mL). At room temperature, tetrabutylammonium fluoride (0.5 M solution in THF, 4.1 mL) was added. The removal of the trimethylsilylethyl protecting groups evolves ethylene that ceased after about 15 min. After stirring for 12 h, the reaction mixture was dried in vacuo, and the residue was purified by column chromatography on SiO_2 (toluene). According to NMR and mass spectroscopic evidence, the eluted product was pure bis(benzylthio)acetylene (**3a**; 195 mg, 70%).

Compound 6: To a solution of **2a** (2.56 g, 17.3 mmol) in diethyl ether (100 mL), cooled to –78 °C, was added *n*-BuLi (10 M solution in *n*-hexane, 1.73 mL, 17.3 mmol) by syringe. After 10 min, sulfur (0.55 g, 17.3 mmol) was added. The mixture was then warmed to 0 °C followed by the addition of chlorotrimethylsilane (2.2 mL, 17.3 mmol). After stirring for 24 h, the solvent was removed in vacuo. The residue was dissolved in *n*-hexane, and the solution filtered. The red–brown filtrate crystallized instantly. The crystals were dried in vacuo. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.26–7.01 (m, 10 H, Ph-*H*), 3.80 (s, 2 H, SCH_2), 3.64 (s, 2 H, SCH_2), 0.26 [s, 9 H, Si(CH_3)$_3$], 0.15 [s, 9 H, Si(CH_3)$_3$] ppm. ^{13}C NMR (50 MHz, C_6D_6): δ = 140.2 (C=*C*), 137.7, 136.0 (Ph-C_{ipso}), 129.9 (C=*C*), 128.3–125.8 (6 × Ph-*C*), 107.7 (*C*=C), 40.1, 37.4 (S*C*H$_2$), –1.3

[Si(CH_3)$_3$], –2.0 [Si(CH_3)$_3$] ppm, the fourth *C*≡C resonance is obscured. MS (MALDI-TOF): *m*/*z* = 504 [M]$^+$, 431 [M – $SiMe_3$]$^+$, 413 [M – C_7H_7]$^+$.

Crystal Structure Determination: Single crystals suitable for X-ray analysis were coated in paratone oil and mounted on a glass fiber. The intensity data of the complexes were collected with a Bruker AXS Apex system equipped with a rotating anode. The data was measured by using graphite monochromated Mo-K_α radiation. Data collection, cell refinement, data reduction, and integration as well as absorption correction were performed with the Bruker AXS program packages SMART, SAINT, and SADABS. Crystal and space group symmetries were determined by using the XPREP program. All crystal structures were solved with SHELXS[21] by direct methods and were refined by full-matrix least-square techniques against F_o^2 with SHELXL.[22] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at calculated positions with fixed thermal parameters. The disorder phenomenon in the crystal of **6** applies to the whole molecule about a virtual inversion center.

Crystal Data for 2c:[23] $C_{21}H_{16}S$, M_r = 300.40 g mol^{-1}; colorless prisms, size 0.33 × 0.21 × 0.15 mm^3; monoclinic; space group *P*2(1)/*n*; *a* = 10.1146(7) *b* = 9.0173(6), 17.1278(11) Å; *β* = 95.271(1)°; *V* = 1555.56(18) Å^3; *T* = 153 K; *Z* = 4; $\rho_{calcd.}$ = 1.283 g cm^{-1}; μ(Mo-K_α) = 0.201 mm^{-1}; reflections: 14767 collected, 3561 unique, 3173 observed; $F_o \geq 2\sigma(F_o)$, $2.25 \leq \Theta \leq 27.50$; R_{int} = 0.0257, 263 parameter, 0 restrains; R_1(obs) = 0.0360, wR_2(obs) = 0.0933; R_1(all) = 0.0402, wR_2(all) = 0.0960; GOF = 1.045; largest difference peak/hole: 0.367/–0.187 e Å^3.

Crystal Data for 3c:[23] $C_{40}H_{30}S_2$, M_r = 574.76 g mol^{-1}; colorless prisms, size 0.19 × 0.14 × 0.08 mm^3; triclinic; space group $P\bar{1}$; *a* = 9.1879(5) *b* = 11.3494(6), 14.9572(9) Å; *α* = 92.356(1); *β* = 103.939(1); *γ* = 91.837(1)°; *V* = 1511.07(15) Å^3; *T* = 153 K; *Z* = 2; $\rho_{calcd.}$ = 1.263 g cm^{-1}; μ(Mo-K_α) = 0.204 mm^{-1}; reflections: 12244 collected, 5312 unique, 4645 observed; $F_o \geq 2\sigma(F_o)$, $1.40 \leq \Theta \leq 25.00$; R_{int} = 0.0228, 499 parameter, 0 restrains; R_1(obs) = 0.0338, wR_2(obs) = 0.0863; R_1(all) = 0.0387, wR_2(all) = 0.0895; GOF = 1.048; largest difference peak/hole: 0.278/–0.195 e Å^3.

Crystal Data for 6:[23] $C_{24}H_{32}S_4Si_2$, M_r = 504.92 g mol^{-1}; colorless plates, size 0.11 × 0.09 × 0.03 mm^3; monoclinic; space group *C*2/*c*; *a* = 16.631(6) *b* = 25.825(2), 28.350(10) Å; *β* = 102.209(7)°; *V* = 2684.2(16) Å^3; *T* = 153 K; *Z* = 4; $\rho_{calcd.}$ = 1.249 g cm^{-1}; μ(Mo-K_α) = 0.454 mm^{-1}; reflections: 14738 collected, 3905 unique, 2835 observed $F_o \geq 2\sigma(F_o)$, $1.47 \leq \Theta \leq 30.02$; R_{int} = 0.0466, 147 parameter, 0 restrains; R_1(obs) = 0.0441, wR_2(obs) = 0.0967; R_1(all) = 0.0683, wR_2(all) = 0.1061; GOF = 1.013; largest difference peak/hole: 0.361/–0.236 e Å^3.

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[23] CCDC-631392 (for **2c**), -631393 (for **3c**), -631394 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk.

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