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CONTRIBUTIONS TO THE CHEMISTRY OF SILICON–SULPHUR COMPOUNDS

XLII *. BIS(1-METHYLDIBENZOSILOLE)SULPHIDE: ITS SYNTHESIS, CRYSTAL STRUCTURE, AND REACTION WITH CHROMIUM HEXACARBONYL

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Summary

The reaction of 1-methyldibenzosilole with elemental sulphur gave almost quantitatively bis(1-methyldibenzosilole)sulphide (I), the structure of which was determined by X-ray diffraction. The crystals are monoclinic, space group $P2_1/n$ (No. 14) with a 1772.8(3), b 921.6(3), c 1417.5(2) pm, β 102.09(1)° and $Z = 4$. The molecule is bent, with an Si–S–Si bond angle of 108.8(1)°.

Reaction of I with chromium hexacarbonyl gave η^6 -[bis(1-methyldibenzosilacyclopentadienyl)sulphide]chromium tricarbonyl, in which the chromium tricarbonyl moiety is bonded to one of the six-membered rings.

Introduction

During studies of the reaction between triorganosilanes and elemental sulphur we have shown that this reaction provides a convenient route to various silanethiols and disilthianes [2,3]. We describe here an efficient preparation of the title compound: bis(1-methyldibenzosilole)sulphide (I), which is representative of a new class of silyl sulphides, in which the silicon atom is part of a rigid silafluorene framework.

* For part XLI see ref. 1.

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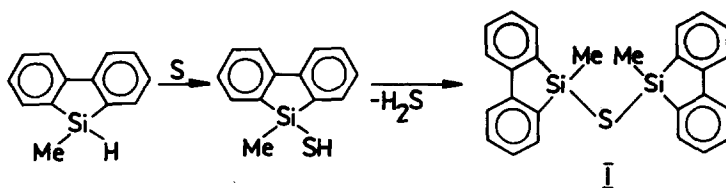
This compound was also of interest for our structural studies of crowded organosilicon molecules with bridging sulphur. We recently described the structures of $\text{Ph}_3\text{SiSSiPh}_3$ [4] and $(t\text{-BuO})_3\text{SiSSi}(\text{OBu-}t)_3$ [5], in which, because of steric effects, the Si–S–Si angle is widened up to a value of 112° from the normal value of ca. 100° [6].

A recent report of Ishikawa and Tabohashi [7] on the synthesis of the first transition metal complex containing a 9-silafluorene ligand prompted us to investigate the reaction of $\text{Cr}(\text{CO})_6$ with our sulphur-bridged bis-silafluorene system.

Synthesis

The reaction of 1-methyldibenzosilole with elemental sulphur at $180\text{--}190^\circ\text{C}$ gave bis(1-methyldibenzosilole)sulphide (I), m.p. $114.5\text{--}115^\circ\text{C}$, in 90% yield.

Compound I results from insertion of sulphur into a Si–H bond followed by condensation of the silanethiol so formed (eq. 1):



It is noteworthy that under similar conditions reaction of Ph_2MeSiH with sulphur yields both silanethiol and silyl sulphide [2].

Compound I, like $\text{Ph}_3\text{SiSSiPh}_3$ [4], is not attacked by water which rapidly cleaves the Si–S bond in Ph_3SiSH [8]. We assume that given the steric hindrance by the bulky substituents in the crowded silyl sulphides, in which rotation around the Si–S–Si bridge is suppressed, the lone pairs of sulphur also cause a steric hindrance to the formation of a transition complex involving water.

The ^{29}Si NMR shift of I was recorded at 4.76 ppm (CDCl_3); that of $(\text{Ph}_2\text{MeSi})_2\text{S}$ [2] was determined for comparison, because of the close similarity in the neighbourhood of silicon, and a value $\delta(^{29}\text{Si})$ 0.40 ppm was found. In our opinion [9] the difference between these two values is due to the deviation from tetrahedral configuration of Si in the five-membered ring of I ($\text{C–Si–C} = 92^\circ$).

In contrast to the high yield obtained in the preparation of I, the reaction of elemental sulphur with 2,5-diphenyl-1-silacyclopentadiene gave a mixture from which only a small amount of 2,5-diphenylthiophene could be isolated. However, the mass spectrum of this mixture showed the molecular ion of the desired bis(2,5-diphenyl-1-silacyclopentadienyl)sulphide (m/e 526).

Structure

The crystal structure of I was determined by a single crystal diffraction study. The crystallographic data, atomic parameters and selected bond lengths and angles are listed in Tables 1–3. Figure 1 shows a perspective drawing of I with the atom labelling and Fig. 2 is a stereoscopic projection.

Supplementary material relating to the structure determination can be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggen-

(Continued on p. 309)

TABLE 1
CRYSTAL DATA, INTENSITY COLLECTION AND REFINEMENT FOR I (T 298 K)

Compound; molecular weight	$C_{26}H_{22}Si_2S$; 422.69 amu
Crystal size	$0.3 \times 0.5 \times 0.2$ mm
Lattice constants (standard deviations)	a 1772.8(3) pm b 921.6(3) pm c 1417.5(2) pm β 102.09(1) $^\circ$
Space group (No.)	$P2_1/n$ (14)
Molecular volume; number of formula units per cell	$340.99 \text{ cm}^3 \text{ mol}^{-1}$; $Z = 4$
Calculated density	$d_x = 1.240 \text{ g cm}^{-3}$
Diffractometer; radiation	SYNTEX-P3, four circle, Mo- K_α , graphite monochromator
μ ; $F(000)$	2.5 cm^{-1} ; 888
Scan, scan range	ω ; $3.5 \leq 2\theta \leq 55.0^\circ$
Scan speed	$0.5\text{--}29.3 \text{ deg min}^{-1}$
$N(hkl)$; $N'(F > 3\sigma(F))$	2614; 2497
Structure refinement	SHELXTL [10] on Eclipse S/250 computer
R (aniso); H atoms isotropic	0.036

TABLE 2
ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($\text{pm}^2 \times 10^{-1}$)^a

Atom	x	y	z	U_{eq}
S(1)	1613(1)	4660(1)	-2261(1)	53(1)
Si(1)	432(1)	4722(1)	-2094(1)	47(1)
Si(2)	2327(1)	5659(1)	-1031(1)	43(1)
C(1)	319(2)	3777(4)	-984(2)	62(1)
C(2)	3305(2)	5634(4)	-1301(2)	59(1)
C(101)	-118(2)	3991(3)	-3262(2)	50(1)
C(102)	-110(2)	2641(4)	-3689(2)	63(1)
C(103)	-525(2)	2395(4)	-4616(3)	80(2)
C(104)	-949(2)	3505(5)	-5118(3)	86(2)
C(105)	-974(2)	4853(4)	-4712(2)	71(1)
C(106)	-559(2)	5123(4)	-3775(2)	53(1)
C(107)	-525(2)	6518(4)	-3251(2)	54(1)
C(108)	-954(2)	7747(4)	-3593(3)	71(1)
C(109)	-893(2)	8977(4)	-3031(3)	83(2)
C(110)	-413(2)	9017(4)	-2125(3)	78(2)
C(111)	11(2)	7784(4)	-1771(3)	64(1)
C(112)	-32(2)	6535(3)	-2327(2)	49(1)
C(201)	2005(2)	7479(3)	-702(2)	46(1)
C(202)	1921(2)	8786(3)	-1198(2)	61(1)
C(203)	1664(2)	10015(3)	-790(3)	75(2)
C(204)	1490(2)	9929(4)	115(3)	76(2)
C(205)	1578(2)	8652(4)	624(2)	62(1)
C(206)	1840(2)	7409(3)	228(2)	46(1)
C(207)	1969(2)	5965(3)	702(2)	45(1)
C(208)	1844(2)	5639(4)	1615(2)	60(1)
C(209)	1996(2)	4257(4)	1980(2)	75(1)
C(210)	2262(2)	3194(4)	1451(3)	75(1)
C(211)	2385(2)	3501(3)	538(2)	60(1)
C(212)	2242(2)	4887(3)	156(2)	45(1)

^a Defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 3

SELECTED BOND LENGTHS (pm) AND ANGLES ($^{\circ}$) (standard deviation in parentheses)

S–Si(1)	215.6(1)	S–Si(2)	213.7(1)
Si(1)–C(1)	184.7(3)	Si(2)–C(2)	185.2(3)
Si(1)–C(101)	186.3(3)	Si(2)–C(201)	186.2(3)
Si(1)–C(112)	186.1(3)	Si(2)–C(212)	186.1(3)
C(101)–C(106)	141.1(4)	C(201)–C(206)	141.1(4)
C(106)–C(107)	148.0(5)	C(206)–C(207)	148.6(4)
C(107)–C(112)	141.5(4)	C(207)–C(212)	140.7(4)
Si(1)–S–Si(2)	108.8(1)		
S–Si(1)–C(1)	111.2(1)	S–Si(2)–C(2)	104.2(1)
S–Si(1)–C(101)	103.4(1)	S–Si(2)–C(201)	115.6(1)
S–Si(1)–C(112)	114.1(1)	S–Si(2)–C(212)	115.2(1)
C(1)–Si(1)–C(101)	117.2(1)	C(2)–Si(2)–C(201)	114.4(1)
C(1)–Si(1)–C(112)	116.9(1)	C(2)–Si(2)–C(212)	116.0(1)
C(101)–Si(1)–C(112)	92.1(1)	C(201)–Si(2)–C(212)	91.8(1)
Si(1)–C(101)–C(106)	108.7(2)	Si(2)–C(201)–C(206)	109.1(2)
C(101)–C(106)–C(107)	115.1(2)	C(201)–C(206)–C(207)	114.9(2)
C(106)–C(107)–C(112)	115.3(3)	C(206)–C(207)–C(212)	114.9(2)
Si(1)–C(112)–C(107)	108.6(2)	Si(2)–C(212)–C(207)	109.3(2)

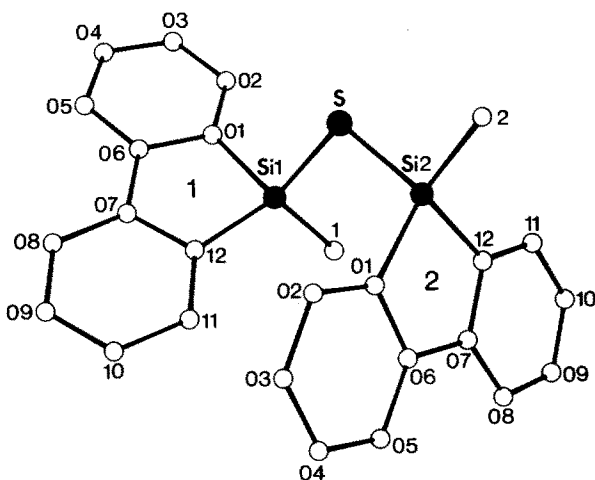


Fig. 1. Atom labeling for bis(1-methyldibenzosilole)sulphide (I).

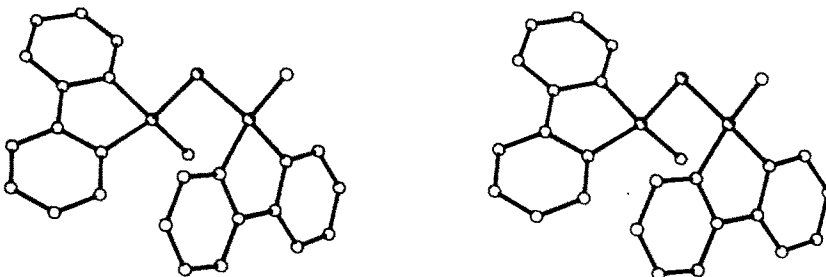


Fig. 2. A stereoscopic drawing of I.

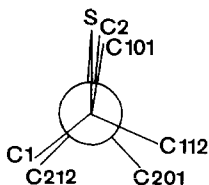


Fig. 3. Newman projection of I down Si(1)–Si(2) (angles increase clockwise). S(0°); C(1) (232.9°); C(101) (8.0°); C(112) (115.2°); C(2) (5.1°); C(201) (136.1°); C(212) (227.9°).

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From the stereoscopic and Newman projections (Fig. 2 and 3) it can be seen that the conformations of the two dibenzosilole frameworks as viewed along the Si(1)–Si(2) axis are rather eclipsed than staggered (for a possible explanation see ref. 4). Examination of non-bonding distances in molecule I (the distances between the C(1) methyl group–framework 2 (Fig. 1) and frameworks 1–2 are about 200 pm) shows that the rotation around the Si–S–Si bridge is suppressed by steric hindrance (Fig. 2). Steric hindrance also causes the Si–S–Si angle (108.8°) to be wider than in the less crowded molecules (see Table 4 in [4]).

It should be noted that the structure is favoured over that in which both frameworks would be face-to-face and almost parallel even though the shortest non-bonding distances would be much greater (about 350–300 pm) for the latter. It appears that the observed conformation of I reflects the stereochemistry of the reaction pathway and directional preferences during the condensation of two silanethiol molecules (eq. 1).

Reaction with chromium hexacarbonyl

The reaction of bis(1-methyldibenzosilole)sulphide (I) with chromium hexacarbonyl was carried out as previously described [11]. η^6 -[Bis(1-methyldibenzosilacyclopentadienyl)sulphide]chromium tricarbonyl (II) was isolated in 10% yield. The mass, IR, and ^1H NMR spectra of II confirmed that only one $\text{Cr}(\text{CO})_3$ moiety was bonded to one of the six-membered rings. The ^1H NMR spectrum also indicated that the chromium is outside the cavity of the molecule; two methyl signals were observed with 0.2 ppm separation.

We did not obtain a sandwich type complex with chromium inserted between two sulphur-bridged dibenzosilole frameworks.

Experimental

General comments

All reactions were carried out under nitrogen, a vacuum line and Schlenk tubes being used in the case of transition metal complexes. Solvents were dried and distilled before use. $\text{Cr}(\text{CO})_6$ was purchased from Aldrich Chemical. MeHSiCl_2 was kindly provided by Rhône Poulenc Spécialités Chimiques. 2,2'-Dilithiobiphenyl was prepared according to Gilman [12]. Melting points were determined with an oil circulating apparatus and are uncorrected. IR spectra were recorded with a

Perkin–Elmer 298 spectrophotometer and NMR spectra with a Varian EM 360 (^1H) or Bruker AM 250 (^{29}Si , 49.694 MHz, $\text{Cr}(\text{acac})_3$ as relaxation agent) spectrometer, with TMS as internal reference. Mass spectra were recorded on a Jeol JMS-D 100 spectrometer (electron impact, 70 eV).

Preparation of 1-methyldibenzosilole

A 1/1 mixture of 2,2'-dilithiobiphenyl and methyldichlorosilane (freshly distilled over CaH_2) in ether was refluxed for 20 h. Some LiAlH_4 was then added (to remove any excess of chlorosilane) and the mixture refluxed for a further hour. Treatment with saturated aqueous NH_4Cl followed by the usual work-up gave 60% yield of 1-methyldibenzosilole, m.p. 41–42°C.

IR(CCl_4) ν (Si–H): 2130 cm^{-1} ; ^1H NMR(CCl_4 , δ (ppm)): 7.0–7.9 (m, 8H), 4.8 (q, 1H, J 4 Hz), 0.5 (d, 3H, J 4 Hz); ^{29}Si NMR (C_6D_6): –20.1 ppm. Analysis: Found: C, 79.58; H, 6.22; Si, 14.20. $\text{C}_{13}\text{H}_{12}\text{Si}$ calcd.: C, 79.53; H, 6.16; Si, 14.31%. (IR and NMR spectra were identical with those reported by Ishikawa et al. [13].)

Preparation of bis(1-methyldibenzosilole)sulphide (I)

A mixture of 1.732 g (8.82 mmol) of 1-methyldibenzosilole and 0.283 g (8.82 mmol) of elemental sulphur in an evacuated Carius tube was heated at 180–190°C in an oil bath for 48 h. The product was washed with benzene and the solvent removed under vacuum. Addition of 10 ml of pentane gave a solution from which sulphide I crystallized easily (yield 90%). Two recrystallizations from pentane gave 1.503 g (61%) of pure I, m.p. 114.5–115°C.

^1H NMR (CCl_4 , δ (ppm)): 7.15 (m, 16 H_{ar}), 0.45 (s, 6H, Me); ^{29}Si NMR (CDCl_3): 4.76 ppm. Analysis: Found: C, 74.08; H, 5.28. $\text{C}_{26}\text{H}_{22}\text{SSi}_2$ calcd.: C, 73.88; H, 5.25%. Mass spectrum m/e (abundance): 422(54) M ; 407(62) $M - \text{Me}$; 195(100) $\text{C}_{13}\text{H}_{11}\text{Si}$, $M - \text{C}_{13}\text{H}_{11}\text{SSi}$; 165(30).

Preparation of η^6 -[bis(1-methyldibenzosilacyclopentadienyl)sulphide]chromium tricarbonyl (II)

A mixture of 0.789 g (1.5 mmol) of I and 0.330 g (1.5 mmol) of $\text{Cr}(\text{CO})_6$ in 24 ml $n\text{-Bu}_2\text{O}$ and 2 ml THF was refluxed for 2 h. Evaporation of the solvents and extraction of the residue with pentane gave a yellow-orange solution, from which a yellow solid crystallized out at –20°C, which was recrystallized from pentane to give II in 10% yield, m.p. 150–152°C (dec.).

IR (toluene) ν (CO): 1965, 1895 cm^{-1} ; ^1H NMR(CDCl_3 , δ (ppm)): 6.8–7.6 (m, 12H), 5.0–5.5 (m, 4H), 0.6 (s, 3H), 0.4 (s, 3H). Mass spectrum m/e (abundance): 558(6.5) M ; 474(90) $M - 3\text{CO}$; 459(9) $M - 3\text{CO} - \text{Me}$; 422(9) $M - \text{Cr}(\text{CO})_3$; 407(15) $M - \text{Cr}(\text{CO})_3 - \text{Me}$; 195(100) $\text{C}_{13}\text{H}_{11}\text{Si}$.

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