Synthesis, Structures,† and Reactivities of Some Pentamethylcyclopentadienyl–Sulphur Compounds

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The pentamethylcyclopentadienyl–sulphur compounds $S(C_5Me_5)_2$ (**1**) and $S_2(C_5Me_5)_2$ (**2**) have been prepared by the reaction of $Li(C_5Me_5)$ with SCl_2 and S_2Cl_2, respectively. Compounds (**1**) and (**2**) were characterised by n.m.r. and mass spectroscopy. The *X*-ray crystal structure of (**1**) has been determined. Compound (**1**) crystallises in the monoclinic space group $P2_1/c$ (no. 14), with a = 10.375(2), b = 11.274(2), c = 16.132(9) Å, β = 91.92(3)°, and Z = 4. The reaction of (**1**) with $[Fe_2(CO)_9]$ results in the known cluster compound, $[Fe_3S_2(CO)_9]$ (**3**), the identity of which was confirmed by *X*-ray crystallography. Unsuccessful attempts were made to prepare cations of the type $[S(C_5Me_5)_2]^{n+}$ by (*i*) oxidation of (**1**) and (**2**), or (*ii*) the reaction of $S(C_5Me_5)Cl$ (prepared *in situ*) with Al_2Cl_6. Cyclic voltammetric experiments on (**1**) and C_5Me_5H suggest that oxidation occurs at the carbocyclic ring rather than at the sulphur atom.

Our interest in cyclopentadienyl-substituted sulphur compounds was prompted by a more general concern with π-bonded carbocyclic complexes of the main-group elements.[1] Such main-group annulene complexes have now been recognised for fragments involving Group 1B—5B elements; however, the only instances of multihapto-bonding involving a Group 6B element are Dewar thiophene derivatives.[2] Moreover, with the exception of sulphonium ylides of the type $R_2SC_5H_5$ (R = alkyl),[3] there is very little information in the literature regarding cyclopentadienyl-substituted sulphur compounds. Indeed, our own attempts to prepare $S(C_5H_5)_2$ met with failure due to the thermal instability of this species.[4] In the hope of preparing somewhat more stable sulphur derivatives, we turned our attention to the pentamethylcyclopentadienyl ligand. In the present paper we describe the synthesis of $S(C_5Me_5)_2$ (**1**) and $S_2(C_5Me_5)_2$ (**2**). The structure of (**1**) has been determined by *X*-ray crystallography.

Results and Discussion

Preparation and Structures.—Yellow, crystalline $S(C_5Me_5)_2$ (**1**) was prepared by the reaction of SCl_2 with two equivalents of $Li(C_5Me_5)$ in Et_2O solution at 0 °C. Initial characterisation of (**1**) was effected by n.m.r. and high-resolution mass spectroscopy (h.r.m.s.). A 2:2:1 pattern was apparent in both the $^{13}C-\{^1H\}$ and ^1H n.m.r. spectra, thus suggesting η^1 attachment of two equivalent C_5Me_5 rings to the sulphur atom. This structure assignment for (**1**) was confirmed by *X*-ray crystallography. Listings of bond lengths, bond angles, and positional parameters appear in Tables 1—3, pertinent crystallographic data are collected in Table 4, and views of the structure of (**1**) are presented in Figures 1 and 2. The sulphur atom is within bonding distance of only one carbon atom on each ring, and these two carbon–sulphur distances [C(1)–S(1) 1.848(4) and C(6)–S(1) 1.864(4) Å] and the C(1)–S(1)–C(6) angle [111.7(2)°] are normal for a dialkyl sulphide.[5] A further indication of the monohapto-nature of the ring attachment is provided by the fact that both C(1) and C(6) adopt tetrahedral geometries. Moreover, for both rings it is clear that the double bonds are localised between the β- and γ-carbon atoms. Thus, the bond lengths C(2)–C(3) 1.329(5) and C(4)–C(5) 1.327(6) Å are both significantly shorter than the C(3)–C(4) bond length of 1.454(6) Å. The same is true for the other ring: C(7)–C(8) 1.315(5), C(9)–C(10) 1.329(5), C(8)–C(9) 1.475(5) Å. Taken collectively, the foregoing data are consistent with the structure shown for (**1**).

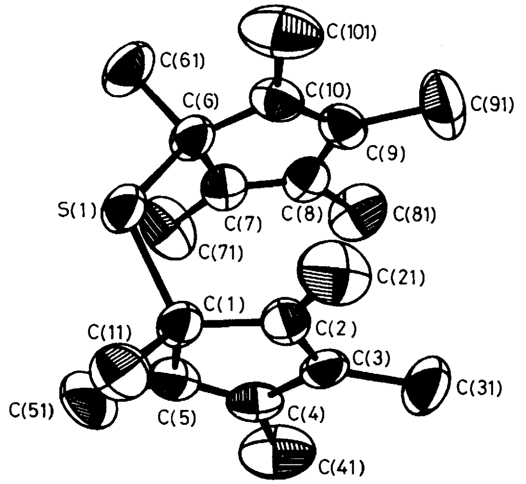
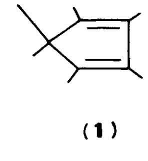


Figure 1. ORTEP view of $S(C_5Me_5)_2$ (**1**), showing the atom numbering scheme. Thermal ellipsoids are shown at the 50% probability level

Possibly the most unusual aspect of the structure of (**1**) concerns the overall geometry. It is clear from Figure 1 that the



(**1**)

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† *Supplementary data available* (No. SUP 56192, 11 pp.): H-atom co-ordinates for (**1**), thermal parameters for (**1**) and (**3**), full bond lengths and angles for (**3**). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

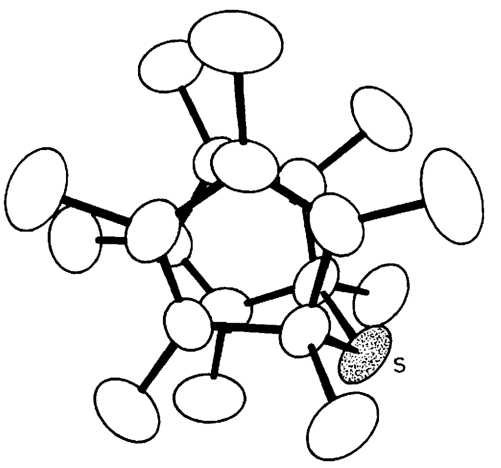


Figure 2. Alternative view of $S(C_5Me_5)_2$ (**1**)

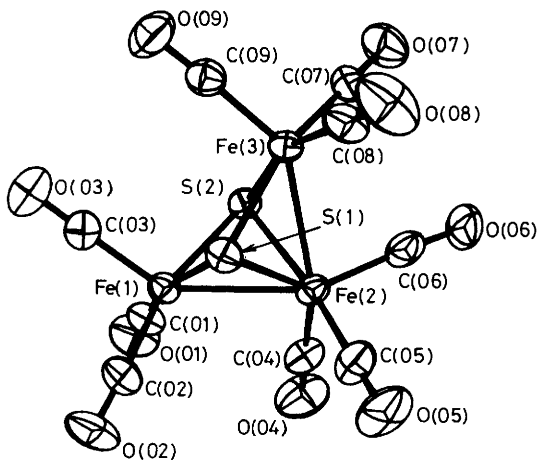
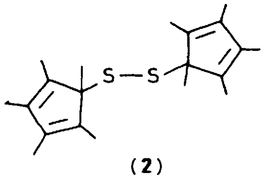


Figure 3. ORTEP view of $[Fe_3S_2(CO)_9]$ (**3**), showing the atom numbering scheme. Thermal ellipsoids are shown at the 50% probability level

two C_5Me_5 rings are almost coplanar [inter-plane angle 168.1(4)°] and, as shown in Figure 2, the rings are slightly staggered. It is tempting to view this structure as being of the metallocene type, in which the sulphur atom has 'slipped' from an η^5- to an η^1-bonding posture. However, such a view is somewhat misleading in that it implies a more extensive ring–sulphur interaction than C–S σ-bonding. Moreover, the use of models indicates that the observed conformation of (**1**) is the one that minimises steric interactions.

The ^1H n.m.r. spectrum of (**1**) in $[^2H_8]$toluene at 100 °C is identical with that at room temperature, indicating that at and below this temperature (**1**) does not exhibit the fluxionality common amongst η^1-cyclopentadienyl compounds.

The reaction of S_2Cl_2 with two equivalents of $Li(C_5Me_5)$ in Et_2O solution at 0 °C affords $S_2(C_5Me_5)_2$ (**2**) as a yellow oil.



(**2**)

Table 1. Bond distances (Å) in (**1**)*

S(1)–C(1)	1.848(4)	C(5)–C(51)	1.485(6)
S(1)–C(6)	1.864(4)	C(6)–C(7)	1.509(5)
C(1)–C(2)	1.497(5)	C(6)–C(10)	1.499(6)
C(1)–C(5)	1.517(5)	C(6)–C(61)	1.504(6)
C(1)–C(11)	1.536(5)	C(7)–C(8)	1.315(5)
C(2)–C(3)	1.329(5)	C(7)–C(71)	1.489(6)
C(2)–C(21)	1.478(6)	C(8)–C(9)	1.475(5)
C(3)–C(4)	1.454(6)	C(8)–C(81)	1.504(6)
C(3)–C(31)	1.496(6)	C(9)–C(10)	1.329(5)
C(4)–C(5)	1.327(6)	C(9)–C(91)	1.493(6)
C(4)–C(41)	1.513(6)	C(10)–C(101)	1.506(6)

* Here, and in other Tables estimated standard deviations in the least significant digit are given in parentheses.

Disulphide (**2**) was characterised by h.r.m.s. and n.m.r. spectroscopy. The $^{13}C-\{^1H\}$ and ^1H n.m.r. spectra of (**2**) are very similar to those of (**1**), hence a similar di-η^1-bonded structure can be inferred. As in the case of (**1**), there is no evidence for the migration of sulphur around the C_5Me_5 rings.

Attempts were also made to prepare $S(C_5Me_5)Cl$ by treating SCl_2 with one equivalent of $Li(C_5Me_5)$ in Et_2O at low temperatures. Although yellow solutions of the presumed product are stable below −50 °C, all attempts at isolating this compound were unsuccessful.

Reactivities of $S(C_5Me_5)_2$ (**1**) *and* $S_2(C_5Me_5)_2$ (**2**).—Given the monohapto-nature of the C_5Me_5 ring attachment, the sulphur lone pairs of (**1**) were anticipated to be chemically active. However, whilst the reaction of (**1**) with $[Fe_2(CO)_9]$ in n-hexane proceeds smoothly to afford a dark red crystalline material, (**3**), i.r. and mass spectroscopic evidence indicated the absence of C_5Me_5 groups. Positive identification of (**3**) as the iron–sulphur cluster, $[Fe_3S_2(CO)_9]$, was effected by *X*-ray crystallography (Figure 3). The structure of (**3**) in admixture with $[Fe_2S_2(CO)_6]$ was reported by Wei and Dahl[6] twenty years ago. The same authors noted that they had also determined the structure of isolated (**3**); however, to the best of our knowledge, no details have appeared. We therefore report the relevant selected bond lengths, bond angles, and atomic positional parameters in Tables 5 and 6. No comments on the structure of (**3**) are necessary in view of the adequate discussion by Wei and Dahl.[6]

Mechanistically, it is not clear how (**3**) is formed from (**1**). However, King[7] has reported that the reaction of cyclohexene sulphide (1,2-epithiocyclohexane) or 3-chloropropylene sulphide (1-chloro-2,3-epithiopropane) with $[Fe_3(CO)_{12}]$ results in the formation of (**3**). In fact, the desulphurisation of organic sulphides by iron carbonyls is a fairly common occurrence.[8]

From a theoretical standpoint, we have noted[9] that perhapto-attachment of carbocyclic rings in bent-sandwich molecules is to be anticipated when the total of ring-π plus main-group element electrons is 14. The structures of bis(cyclopentadienyl)-tin(II),[10] bis(pentamethylcyclopentadienyl)lead(II),[10] and the bis(pentamethylcyclopentadienyl)arsenic(III) cation[11] exemplify this principle. Amongst Group 6B analogues, therefore, bis-(pentahapto)-attachment of cyclopentadienyl rings is expected, for example, for the dication $[S(C_5Me_5)_2]^{2+}$. However, all attempts at generating C_5Me_5-substituted sulphur cations by oxidation of (**1**) resulted in a bright purple intractable oil. Similar observations were made when the synthesis of single-ring sulphur cations was attempted by the reaction of (**1**) or (**2**) with $HBF_4{\cdot}OEt_2$ or $[Me_3O][BF_4]$, or by the reaction of $S(C_5Me_5)Cl$ (prepared *in situ* at −78 °C) with Al_2Cl_6. To gain more insight into the purple product(s), cyclic voltammetric experiments were conducted on (**1**) and C_5Me_5H in tetra-

Table 2. Bond angles (°) in (**1**)

C(1)–S(1)–C(6)	111.7(2)	C(3)–C(4)–C(5)	110.2(4)	C(6)–C(7)–C(8)	109.4(3)
S(1)–C(1)–C(2)	115.4(3)	C(3)–C(4)–C(41)	123.5(4)	C(6)–C(7)–C(71)	122.0(4)
S(1)–C(1)–C(5)	113.7(3)	C(5)–C(4)–C(41)	126.2(4)	C(8)–C(7)–C(71)	128.1(4)
S(1)–C(1)–C(11)	102.9(3)	C(1)–C(5)–C(4)	108.3(3)	C(7)–C(8)–C(9)	109.6(4)
C(2)–C(1)–C(5)	102.8(3)	C(1)–C(5)–C(51)	121.6(4)	C(7)–C(8)–C(81)	127.9(4)
C(2)–C(1)–C(11)	111.5(3)	C(4)–C(5)–C(51)	130.1(4)	C(9)–C(8)–C(81)	122.5(4)
C(5)–C(1)–C(11)	110.8(3)	S(1)–C(6)–C(7)	113.8(3)	C(8)–C(9)–C(10)	108.8(4)
C(1)–C(2)–C(3)	109.3(3)	S(1)–C(6)–C(10)	112.7(3)	C(8)–C(9)–C(91)	122.5(4)
C(1)–C(2)–C(21)	122.3(4)	S(1)–C(6)–C(61)	102.5(3)	C(10)–C(9)–C(91)	128.7(4)
C(3)–C(2)–C(21)	128.2(4)	C(7)–C(6)–C(10)	102.5(3)	C(6)–C(10)–C(9)	109.6(4)
C(2)–C(3)–C(4)	109.4(3)	C(7)–C(6)–C(61)	113.4(4)	C(6)–C(10)–C(101)	122.0(4)
C(2)–C(3)–C(31)	127.5(4)	C(10)–C(6)–C(61)	112.4(4)	C(9)–C(10)–C(101)	128.3(4)
C(4)–C(3)–C(31)	123.1(4)				

Table 3. Final position parameters for (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
S(1)	0.785 2(2)	0.224 4(2)	0.726 52(8)	C(6)	0.857 8(6)	0.345 7(5)	0.665 0(3)
C(1)	0.682 3(5)	0.126 2(5)	0.660 8(3)	C(7)	0.764 5(5)	0.402 9(5)	0.603 3(4)
C(2)	0.739 2(5)	0.087 9(5)	0.581 0(3)	C(8)	0.811 1(6)	0.396 4(5)	0.528 6(3)
C(3)	0.659 6(5)	0.117 6(5)	0.518 2(3)	C(9)	0.935 3(5)	0.332 7(5)	0.532 5(3)
C(4)	0.546 6(5)	0.176 2(5)	0.550 0(4)	C(10)	0.962 7(5)	0.302 5(5)	0.610 8(4)
C(5)	0.555 6(5)	0.182 4(6)	0.632 1(4)	C(61)	0.907 4(7)	0.429 4(7)	0.731 2(4)
C(11)	0.658 7(7)	0.020 0(6)	0.718 0(4)	C(71)	0.648 5(7)	0.468 7(6)	0.629 9(5)
C(21)	0.859 9(7)	0.018 6(6)	0.578 5(5)	C(81)	0.752 8(7)	0.444 4(7)	0.448 9(4)
C(31)	0.676 3(7)	0.094 0(7)	0.427 9(4)	C(91)	1.011 2(7)	0.308 8(7)	0.457 3(5)
C(41)	0.435 9(7)	0.221 4(7)	0.495 3(5)	C(101)	1.081 7(7)	0.241 8(7)	0.645 9(5)
C(51)	0.462 4(7)	0.228 4(7)	0.692 2(5)				

Table 4. Crystallographic and intensity data collection parameters for (**1**) and (**3**)

	(**1**)	(**3**)
Formula	$C_{20}H_{30}S$	$C_9Fe_3O_9S_2$
M	302.21	483.75
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	10.375(2)	6.805(2)
b/Å	11.274(2)	9.116(2)
c/Å	16.132(9)	13.111(3)
α/°		93.80(2)
β/°	91.92(3)	94.27(3)
γ/°		110.90(3)
U/Å^3	1 886(2)	754(1)
Z	4	2
D_c/g cm^{-3}	1.066	2.131
μ(Mo-K_α)/cm^{-1}	1.6	31.6
λ(Mo-K_α)/Å	0.710 69	0.710 69
Crystal size (mm)	0.5 × 0.3 × 0.2	0.4 × 0.3 × 0.3
Data collection mode	ω–2θ	ω–2θ
Decay of standards	< 1.0%	< 0.5%
ω-scan angle (°)	0.8 + 0.35 tanθ	0.8 + 0.35 tanθ
2θ limits (°)	$2.0 \leqslant 2\theta \leqslant 50.0$	$2.0 \leqslant 2\theta \leqslant 50.0$
Total unique measured data	3 296	2 385
No. of data observed	1 863	2 273
Data omission factor	$I > 2.5\sigma(I)$	$I > 3.0\sigma(I)$
No. of variables	191	209
R	0.0733	0.0397
R′	0.1185	0.0537
Goodness of fit	2.24	1.58

Table 5. Selected bond lengths (Å) and bond angles (°) for (**3**)

(*i*) Bond lengths

Fe(1)–Fe(2)	2.598(1)	Fe(2)–S(1)	2.237(1)
Fe(2)–Fe(3)	2.589(1)	Fe(2)–S(2)	2.257(1)
Fe(1)–S(1)	2.223(1)	Fe(3)–S(1)	2.231(1)
Fe(1)–S(2)	2.242(1)	Fe(3)–S(2)	2.238(1)

(*ii*) Bond angles

Fe(2)–Fe(1)–S(1)	54.61(2)	Fe(3)–Fe(2)–S(1)	54.49(2)
Fe(2)–Fe(1)–S(2)	55.00(2)	Fe(3)–Fe(2)–S(2)	54.48(2)
S(1)–Fe(1)–S(2)	80.66(3)	S(1)–Fe(2)–S(2)	80.04(3)
Fe(1)–Fe(2)–Fe(3)	81.01(2)	Fe(2)–Fe(3)–S(1)	54.69(2)
Fe(1)–Fe(2)–S(1)	54.13(2)	Fe(2)–Fe(3)–S(2)	55.18(2)
Fe(1)–Fe(2)–S(2)	54.46(2)	S(1)–Fe(3)–S(2)	80.58(3)
Fe(1)–S(1)–Fe(2)	71.26(3)	Fe(1)–S(2)–Fe(2)	70.54(2)
Fe(1)–S(1)–Fe(3)	98.28(3)	Fe(1)–S(2)–Fe(3)	97.53(3)
Fe(2)–S(1)–Fe(3)	70.83(2)	Fe(2)–S(2)–Fe(3)	70.34(2)

hydrofuran solution. The oxidation of (**1**) occurs in an irreversible, two-electron process. The onset of oxidation occurs at 1.05 V *versus* Ag/Ag$^+$. Three products are formed as a result of the two-electron oxidation, although the identity of these products has not been established. Interestingly, the cyclic voltammogram of C_5Me_5H is virtually identical to that of (**1**). We conclude that the purple product(s) arise from oxidation of the C_5Me_5 ring(s), which, in turn, indicates that the highest occupied molecular orbital is associated with ring π-orbitals rather than the sulphur atom. The chance of isolating simple cyclopentadienyl–sulphur cations therefore seems remote.

Experimental

General Considerations.—All experiments were performed under an atmosphere of dry dinitrogen using standard Schlenk techniques. All solvents were freshly distilled over sodium/benzophenone prior to use.

Spectroscopic Measurements.—Hydrogen-1 n.m.r. spectra were recorded on Varian EM390 and Nicolet NT200 spectrometers operating at 90 and 200 MHz respectively. ^{13}C-{^1H}

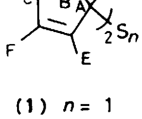
Table 6. Final position parameters for (**3**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(1)	0.132 4(2)	0.414 5(1)	0.242 02(8)	O(08)	0.317 7(9)	0.036 8(7)	0.103 6(6)
Fe(2)	2.385 3(1)	0.696 7(1)	0.338 03(8)	O(09)	0.388(1)	0.616 0(8)	0.952 1(5)
Fe(3)	0.417 6(2)	0.762 7(1)	0.160 46(8)	C(01)	0.205(1)	0.277 8(9)	0.318 6(7)
S(1)	0.084 2(3)	0.626 0(2)	0.187 1(1)	C(02)	0.144(1)	0.674 3(9)	0.735 7(7)
S(2)	0.470 8(3)	0.578 0(2)	0.250 9(1)	C(03)	0.107(1)	0.312 1(9)	0.119 8(6)
O(01)	0.249(1)	0.191 0(7)	0.364 0(5)	C(04)	0.282(1)	0.590(1)	0.447 1(6)
O(02)	−0.317 8(9)	0.267 4(8)	0.274 9(6)	C(05)	0.093(1)	0.775 7(9)	0.381 6(6)
O(03)	0.086(1)	0.249 6(7)	0.038 5(5)	C(06)	0.507(1)	0.875 6(9)	0.379 6(6)
O(04)	0.281(1)	0.526 3(8)	0.520 3(5)	C(07)	0.302(1)	0.120 2(8)	0.823 5(6)
O(05)	−0.026 6(8)	0.824 5(7)	0.409 4(5)	C(08)	0.353(1)	0.930 3(9)	0.127 3(7)
O(06)	0.355 3(9)	0.011 1(7)	0.589 0(5)	C(09)	0.405(1)	0.675 9(9)	0.033 5(6)
O(07)	0.874 2(9)	0.952 7(8)	0.185 9(6)				

N.m.r. spectra were recorded on Varian FT80A and Nicolet NT200 spectrometers operating at 20 and 50 MHz respectively. All spectra were recorded in C_6D_6 as solvent unless otherwise stated and were referenced internally to $SiMe_4$ (0.0 p.p.m.) for both ^1H and ^{13}C, positive values being to high frequency in both cases. Medium- and high-resolution mass spectra were recorded on DuPont Consolidated Model 24-491 and 21-100 instruments respectively and perfluorokerosene was used as the calibrant for h.r.m.s. I.r. spectra were recorded on a Perkin-Elmer 1330 spectrophotometer.

Starting Materials.—The chlorides SCl_2 and S_2Cl_2 were obtained commercially and used without further purification. Literature procedures were employed for the synthesis of $[Fe_2(CO)_9]$[12] and C_5Me_5H.[13]

Preparation of $S(C_5Me_5)_2$ (**1**).—A solution of $LiBu^n$ (20 cm^3 of a 1.6 mol dm^{-3} solution) was added slowly to a solution of C_5Me_5H (4.35 g, 32 mmol) in Et_2O (500 cm^3). After stirring for 2 h at room temperature, the solution containing $Li(C_5Me_5)$ was cooled to 0 °C and SCl_2 (1 cm^3, 16 mmol) in Et_2O (50 cm^3) was added. Filtration of the yellow solution followed by removal of the solvent produced a yellow solid which afforded pale yellow crystals of (**1**) after recrystallisation from hexane at −30 °C (1.63 g, 33.7% yield). ^1H N.m.r., δ 0.99 (s, 6 H, Me_D), 1.58 (s, 12 H, $Me_{E/F}$), 1.76 (s, 12 H, $Me_{E/F}$); ^{13}C-{^1H}, δ 10.3, 11.3 ($C_{E,F}$), 21.5 (C_D), 63.5 (C_A), 132.9, 137.1 ($C_{B,C}$). H.r.m.s.: calculated for $C_{20}H_{30}S$, 302.2068; found, 302.2073.



(**1**) $n = 1$

(**2**) $n = 2$

Preparation of $S_2(C_5Me_5)_2$ (**2**).—The procedure employed for the preparation of (**2**) was identical to that used for (**1**) except that S_2Cl_2 (1.28 cm^3, 16 mmol) was used instead of SCl_2. Removal of the LiCl by filtration followed by removal of the solvent afforded a yellow oil, (**2**) (1.57 g, 29.4% yield). ^1H N.m.r., δ 1.05 (s, 6 H, Me_D), 1.72 (s, 12 H, $Me_{E/F}$), 1.77 (s, 12 H, $Me_{E/F}$); ^{13}C-{^1H}, δ 10.2, 11.4 ($C_{E,F}$), 18.9 (C_D), 66.3 (C_A), 135.0, 139.1 ($C_{B,C}$). H.r.m.s. calculated for $C_{20}H_{30}S_2$, 334.1789; found, 334.1782.

Preparation of $[Fe_3S_2(CO)_9]$ (**3**).—Solid $[Fe_2(CO)_9]$ (0.12 g, 0.33 mmol) was added to a solution of (**1**) (0.1 g, 0.33 mmol) in Et_2O (20 cm^3). The mixture was allowed to stir overnight, during which time the solution assumed a dark red colour. The solvent was removed and the dark residue redissolved in a small volume of hexane. Purification by column chromatography on Fluorisil using hexane as eluant gave a single dark red solution. After reduction of the solvent volume, dark red crystals of (**3**) were formed from the saturated solution held at −30 °C (0.006 g, 7.5% yield). I.r.: ν(C≡O) (hexane solution) at 2 058s, 2 040s, 2 020s, 2 005w cm^{-1}. The mass spectrum for (**3**) showed no parent peak at m/e = 484 but did show a peak at 455 due to $[Fe_3S_2(CO)_8]$. In addition, all CO-loss peaks were seen down to Fe_3S_2 (m/e = 232). Peaks at m/e = 176 and 120 were also observed corresponding to Fe_2S_2 and FeS_2 respectively.

X-Ray Analysis of $S(C_5Me_5)_2$ (**1**).—Crystals of (**1**) were grown from a hexane solution cooled to −20 °C. A suitable single crystal was glued to a glass fibre and mounted on an Enraf-Nonius CAD-4F diffractometer. Initial lattice parameters were obtained from a least-squares fit to 25 accurately centred reflections, $10.0 \leqslant 2\theta \leqslant 20.0°$. These were subsequently refined using higher angle data and indicated a monoclinic lattice which was confirmed using axial photography. Data were collected for one independent quadrant, $+h, +k, \pm l$, using ω–2θ scans. The final scan speed was varied according to the intensity gathered in an initial pre-scan from 2 to 6° min^{-1}. Two check reflections were monitored every 30 min throughout the 43 h of data collection and showed <1% intensity variation. Inspection of systematic absences uniquely determined the space group as $P2_1/c$.

Data were corrected for Lorentz and polarisation effects but not for decay or absorption (μ = 1.6 cm^{-1}). The sulphur atom position was revealed by a Patterson map and all carbon atoms were located from a subsequent difference Fourier calculation. All non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions 0.96 Å from their respective carbon atoms and included in the structure factor calculation. In the final stages of refinement a weighting scheme was introduced to downweight intense reflections. The final full-matrix least-squares calculation converged smoothly to give the final residuals shown in Table 4. No chemically significant peaks were present in the final difference map.

All calculations were performed on a DEC PDP11/44 computer using the Enraf-Nonius SDP PLUS program package.

X-Ray Analysis of $[Fe_3S_2(CO)_9]$ (**3**).—Crystals of (**3**) suitable for *X*-ray diffraction were grown from hexane at −30 °C. The details of data collection and structure solution are essentially as described for (**1**). Pertinent data-collection parameters and crystallographic data are presented in Table 4. Selected bond lengths and bond angles are in Table 5.

Electrochemistry of $S(C_5Me_5)_2$ (**1**).—The experiments were performed in triply distilled benzonitrile with tetrabutylammonium fluoroborate as supporting electrolyte. A three-compartment cell was employed; the working electrode was a planar platinum disc, the potential of which was measured *versus* a Ag/Ag^+ quasi-reference electrode. The techniques used were cyclic voltammetry and bulk coulometry.

The oxidation of (**1**) occurs *via* an irreversible, two-electron process. It is irreversible because of follow-up chemical reactions which are very rapid. The onset of oxidation occurs at 1.05 V *versus* Ag/Ag^+. Since the process is irreversible, no information is available concerning the thermodynamics or the standard reduction potential, E°. Three products are formed as a consequence of the two-electron oxidation. However, these products have not been identified; the oxidised solution is violet-purple.

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