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SYNTHETIC AND STRUCTURAL STUDIES ON SOME 1,3-DITHIA- AND 1,3-DISELENA-[3]FERROCENOPHANES OF PHOSPHORUS AND ARSENIC. CRYSTAL AND MOLECULAR STRUCTURE OF 1,3-DITHIA-2-PHENYLARSINO-[3]FERROCENOPHANE AT 163 K

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Summary

A series of [3]ferrocenophanes of general formula $Fe(C_5H_4E)_2Y$, (E = S, Se; Y = PC_6H_5, AsC_6H_5) has been prepared by the reaction of ferrocene-1,1′-dithiol or ferrocene-1,1′-diselenol with chloride complexes of the Group V elements. The phosphorus containing compounds react with elemental sulfur and with iodomethane to form a phosphine sulfide and a methiodide salt, respectively, whereas the arsenic containing compounds do not react under analogous conditions. Spectroscopic properties of the compounds are reported. The crystal structure of 1,3-dithia-2-phenylarsino-[3]ferrocenophane has been determined at 163 K. At that temperature the crystals have space group $P2_1/c$ with a 20.286(5), b 5.730(2), c 15.526(4) Å, β 125.90(3)° and $Z = 4$. Least-squares refinement gave $R = 0.062$ for 2999 independent significant reflections whose intensities were measured by counter diffractometry. The As–S bond lengths are 2.252 and 2.255(1) Å, and the S–As–S bond angle is 98.6(1)°. The S atoms are displaced out of the ring planes away from the Fe atom by 0.06 and 0.07 Å giving a non-bonded S...S separation of 3.42 Å. The S–C bond lengths are 1.758 and 1.764(4) Å, and the As–S–C bond angles are 97.3(2) and 99.3(1)°. The cyclopentadienyl rings adopt an eclipsed conformation with a mean twist angle of 2.6° and the ring planes inclined at only 0.6°. The phenyl ring occupies the sterically less crowded *exo*-position with As–C 1.948(4) Å, As–C–C angles of 116.6 and 123.6(3)°, and S–As–C bond angles of 95.1 and 96.3(2)°.

Introduction

As part of a general study of [3]ferrocenophanes in which atoms other than carbon are involved in the bridge, we have recently described synthetic and struct-

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ural studies on [3]ferrocenophanes with symmetrical trichalcogen chains and on 1,3-diselena-[3]ferrocenophanes that incorporate an atom of a Group IV element in the 2-position in the bridge [1,2]. We have now extended this study to a series of 1,3-dithia- and 1,3-diselena-[3]ferrocenophanes that incorporate an atom of a Group V element in that position. To gain further insight into the factors influencing the structures of this class of compounds, we have determined the crystal and molecular structure of 1,3-dithia-2-phenylarsino-[3]ferrocenophane at 163 K.

Experimental

^{1}H NMR spectra were recorded at 100 MHz using a Jeol MH 100 spectrometer. ^{13}C and ^{31}P NMR spectra were recorded at 25 and 40.5 MHz, respectively, using a Jeol PS/PFT 100 spectrometer. Mass spectra were recorded on a V.G. Micromass 16F instrument. Analyses were obtained from the Exeter University departmental service or from Butterworth Laboratories, Teddington, Middlesex. All solvents were dried and degassed before use and all reactions were carried out under purified nitrogen.

Ferrocene-1,1′-dithiol [3], ferrocene-1,1′-diselenol [1], dichloro(phenyl)arsine [4], and dichloro(*cis*,*cis*-1,5-cyclooctadiene)platinum(II) [5] were prepared by literature methods.

1,3-Dithia-2-phenylphosphino-[3]ferrocenophane (I)

Dichloro(phenyl)phosphine (0.6 cm^3, 4.4 mmol) was added to a stirred solution of ferrocene-1,1′-dithiol (0.87 g, 3.5 mmol) in benzene (100 cm^3). Triethylamine (1.1 cm^3, 8.2 mmol) was then added and the reaction mixture refluxed for 2 h. The cooled mixture was filtered and the solvent removed to give the crude product which was extracted with hexane in a Soxhlet apparatus. On completion of the extraction, the solution was cooled to produce yellow needles which were filtered and dried. Yield 0.78 g (62%).

1,3-Dithia-2-phenylarsino-[3]ferrocenophane (II)

This was prepared from dichloro(phenyl)arsine (0.6 cm^3, 4.1 mmol), ferrocene-1,1′-dithiol (0.78 g, 3.1 mmol), and triethylamine (1.0 cm^3, 7.2 mmol) in a manner similar to that described for I. Yield 0.80 g (65%), yellow needles.

1,3-Dithia-2-phenylsulfidophosphino-[3]ferrocenophane (III)

Sulfur (0.23 g, 7.2 mmol) was added to a stirred solution of 1,3-dithia-2-phenylphosphino-[3]ferrocenophane (0.19 g, 0.56 mmol) in toluene (50 cm^3), and the reaction mixture was refluxed for 2 h. The cooled mixture was filtered and solvent removed from the filtrate to give the crude product which was subjected to dry column chromatography on grade II alumina. Elution with hexane produced a small amount of sulfur, and further elution with a benzene/hexane (2/1) mixture produced a pale yellow band containing the product, later crystallized from hexane as yellow platelets. Yield 0.10 g (46%).

(Ferrocene-1,1′-dithiolato)methylphenylphosphonium iodide (IV)

1,3-Dithia-2-phenylphosphino-[3]ferrocenophane (0.24 g, 0.7 mmol) was dissolved in iodomethane (10 cm^3, 160 mmol) and the mixture refluxed for 24 h. The resulting

suspension was cooled at −20°C for 2 h and then filtered to give the product as air-sensitive yellow needles. Yield 0.28 g (80%).

1,3-Diselena-2-phenylphosphino-[3]ferrocenophane (V)

This was prepared from dichloro(phenyl)phosphine (0.3 cm^3, 2.3 mmol), ferrocene-1,1′-diselenol (0.64 g, 1.9 mmol), and triethylamine (0.6 cm^3, 4.3 mmol) in the same way as described for I. Yield 0.59 g (71%), orange crystals.

1,3-Diselena-2-phenylarsino-[3]ferrocenophane (VI)

This was prepared from dichloro(phenyl)arsine (0.2 cm^3, 1.5 mmol), ferrocene-1,1′-diselenol (0.42 g, 1.2 mmol), and triethylamine (0.4 cm^3, 2.9 mmol) in a manner similar to that described for I, except that the reaction mixture was refluxed for 4 h, and the crude product was purified by dry column chromatography on grade II alumina. Elution with benzene/hexane (1/1) yielded a single band containing the product, later crystallized from hexane as orange plates. Yield 0.23 g (38%).

1,3-Diselena-2-phenylsulfidophosphino-[3]ferrocenophane (VII)

This was prepared from 1,3-diselena-2-phenylphosphino-[3]ferrocenophane (0.19 g, 0.42 mmol) and sulfur (0.42 g, 13.2 mmol) in a manner similar to that described for III, except that the reaction mixture was refluxed for 24 h. Yield 0.49 g (24%), yellow platelets.

Reaction of 1,3-dithia-2-phenylarsino-[3]ferrocenophane with sulfur

This reaction was carried out in a manner similar to that described for the synthesis of III, using 1,3-dithia-2-phenylarsino-[3]ferrocenophane (0.25 g, 0.6 mmol) and sulfur (0.22 g, 6.8 mmol), and the reaction mixture was refluxed for 20 h. Purification by column chromatography yielded only the starting material II (0.14 g) characterized by its melting point and mass spectrum.

Reaction of 1,3-dithia-2-phenylarsino-[3]ferrocenophane with iodomethane

This reaction was carried out as described for the preparation of IV, using the reactants 1,3-dithia-2-phenylarsino-[3]ferrocenophane (0.35 g, 0.9 mmol) and iodomethane (10 cm^3, 160 mmol). When cooled, the mixture yielded only II (0.19 g), characterized by its melting point, mass spectrum, and analytical data.

Dichlorobis(1,3-dithia-2-phenylphosphino-[3]ferrocenophane)platinum(II)

A solution of 1,3-dithia-2-phenylphosphino-[3]ferrocenophane (0.17 g, 0.5 mmol) in benzene (10 cm^3) was added to a stirred solution of dichloro(*cis,cis*-1,5-cyclooctadiene)platinum(II) (0.072 g, 0.19 mmol) in benzene (50 cm^3). After 1 h the resulting precipitate was filtered off, washed with chloroform, and air dried. Yield 0.14 g (74%) of a yellow powder that decomposed at temperatures above 200°C. Anal. Found: C, 39.22; H, 2.79. $C_{32}H_{26}Cl_2Fe_2P_2PtS_4$ calcd.: C, 39.28; H, 2.68%. The compound was insoluble in all common organic solvents.

X-ray crystallography

Crystal data. Crystals suitable for X-ray study, in the form of orange-yellow plates, were obtained by slow cooling of a saturated dichloromethane solution in a variable temperature bath. Crystal data for the specimen used are given in Table 1.

TABLE 1

CRYSTAL DATA

Molecular formula	$C_{16}H_{13}AsFeS_2$	
Molecular weight	400.2	
Space group	$P2_1/c$	
Temperature (K)	163	293
a (Å)	20.286(5)	20.456(4)
b (Å)	5.730(2)	5.770(2)
c (Å)	15.526(4)	15.550(3)
β (°)	125.90(2)	126.16(2)
U (Å^3)	1462(2)	1482(2)
Z	4	4
D_x (g cm^{-3})	1.819(2)	1.794(2)
$F(000)$	800	
λ (Mo-K_α) (Å)	0.71069	
μ (cm^{-1})	37	
Crystal size (mm)	$0.65 \times 0.50 \times 0.50$	
Independent reflections used	2999 (83.7% with $I > 2.5\sigma(I)$)	
2θ max. (°)	60	
Scan range (2θ°)	2.62–3.00	
Scan speed (° min^{-1})	2.93–29.3	

Crystal symmetry and space group were determined from 25° precession photographs taken at room temperature with Mo-K_α radiation. The systematic absences observed: $0k0$ with k odd and $h0l$ with l odd, uniquely define the space group. The sample was cooled to 163 K by use of the Nicolet LT-1 cooling device. No phase change was apparent on cooling the sample to that temperature. Unit cell parameters were derived for the cooled crystal by a least-squares fit to the setting angles for 15 strong general reflections measured with monochromatic Mo-K_α radiation on a Nicolet P3m automated diffractometer.

Intensity data. Intensity measurements were made for a single quadrant of reciprocal space using the ω–2θ scan method, with a scan rate dependent on reflection intensity as judged by a 2 s prescan. Background measurements were made at either end of the scan range for a total time equal to that spent on the scan. Mo-K_α radiation was used, made monochromatic by Bragg reflection from the (002) planes of a pyrolytic graphite crystal. The intensities of two reference reflections, monitored after every 50 scans, showed a random variation about their means not exceeding 2.3%. An absorption correction was applied [6] and structure amplitudes derived in the usual way *.

Structure determination and refinement. The structure was solved without difficulty using the heavy atom method, the positions of the As, Fe, and S atoms having been found from a three-dimensional sharpened Patterson map. Isotropic least-squares refinement converged at $R = 0.085$. Hydrogen atoms were introduced at

* Initial data reduction and calculations involved in the structure determination and refinement were carried out on an XDS Sigma 2 computer with locally written programs. The absorption correction was applied using a DEC PDP-11 computer and the ENRAF–NONIUS structure solving package.

calculated positions and refinement of all atomic parameters continued with anisotropic thermal parameters adopted for the non-hydrogen atoms. At convergence, R was 0.062, R(w) 0.082, with a ratio of observations to parameters of 13/1 and a maximum shift to error ratio of 0.07. The weighting factor used was $1/[\sigma^2(F) + 0.0007F^2]$. Scattering factors were taken from International Tables for X-ray Crystallography [7] and allowance was made for anomalous dispersion effects for As, Fe, and S *.

Results and discussion

Ferrocene-1,1′-dithiol and ferrocene-1,1′-diselenol in benzene, reacted in the presence of triethylamine with dichlorides of phosphorus and arsenic to give good yields of [3]ferrocenophanes (eq. 1).

$$Fe(C_5H_4EH)_2 + Cl_2Y + 2Et_3N \rightarrow Fe(C_5H_4E)_2Y + 2Et_3NHCl \quad (1)$$

(E = S, Se; Y = PC_6H_5, AsC_6H_5)

1,3-Dithia-2-phenylphosphino-[3]ferrocenophane reacted readily with iodomethane to produce the quaternary phosphonium iodide in high yield, as an air-sensitive yellow solid. Under similar conditions 1,3-dithia-2-phenylarsino-[3]ferrocenophane did not react with iodomethane. The two phosphorus containing [3]ferrocenophanes reacted smoothly with elemental sulfur to produce phosphine sulfides, whereas the arsenic containing compounds did not react with sulfur under comparable conditions. The lack of reactivity of tertiary arsines towards sulfur is borne out by studies on more conventional arsines [8].

1,3-Dithia-2-phenylphosphino-[3]ferrocenophane reacted as a ligand towards dichloro(*cis*,*cis*-1,5-cyclooctadiene)platinum(II), rapidly displacing the cyclooctadiene and giving dichlorobis(1,3-dithia-2-phenylphosphino-[3]ferrocenophane)platinum(II) in high yield as a yellow powder. Because of the low solubility of this compound in all common organic solvents, little could be determined about its structure or reactivity, and it is likely that the compound is polymeric. With the exceptions of the phosphonium iodide and the platinum(II) complex already noted, the [3]ferrocenophanes are air-stable crystalline solids, soluble in organic solvents, and give satisfactory analytical results. Reaction yields, analytical results, and some physical properties of the compounds are listed in Table 2. In the mass spectrometer the [3]ferrocenophanes show molecular ions, often as the most abundant species, with good agreement of the isotope pattern with theory.

The details of the ^{1}H NMR spectra of the [3]ferrocenophanes are listed in Table 3. At room temperature the patterns for the cyclopentadienyl groups resemble those found in the low-temperature limiting spectra of symmetrical [3]ferrocenophanes, e.g. 1,2,3-triselena-[3]ferrocenophane, and can be classified as ABCD spectra. Because of the unsymmetrical nature of the group at the 2-position in the bridge, this implies either a rapid bridge reversal process or the presence of only one isomer. Variable temperature studies on 1,3-diselena-2-phenylphosphino-[3]ferrocenophane

* A Table of observed and calculated structure amplitudes and a complete listing of anisotropic thermal parameters have been deposited with the British Library at Boston Spa, Wetherby, LS23 7BQ (Great Britain) as Supplementary Publication No. SUP 90101 (23 Pages).

TABLE 2

REACTION YIELDS, ANALYTICAL DATA, AND SOME PHYSICAL PROPERTIES OF [3]FERROCENOPHANES INVOLVING GROUP V ELEMENTS

Compound	Bridge groups [a]		Yield (%)	M.p. (°C)	Analysis (Found (Calcd.) (%))		Mass spectrum [b] Obs. (calcd.) (abundance [c])
	E	Y			C	H	
I	S	PC_6H_5	62	192–194	53.96 (53.95)	3.68 (3.68)	356 (356) (100)
II	S	AsC_6H_5	65	219–222 dec.	47.65 (48.02)	3.18 (3.27)	400 (400) (100)
III	S	$P(S)C_6H_5$	46	204–205	49.18 (49.49)	3.29 (3.37)	388 (388) (100)
IV	S	$P(C_6H_5)(CH_3)I$	80	175–180 dec.	40.16 (40.99)	3.08 (3.23)	not observed
V	Se	PC_6H_5	71	182–184	43.07 (42.70)	3.02 (2.91)	452 (452) (100)
VI	Se	AsC_6H_5	38	207–210	38.87 (38.90)	2.57 (2.65)	496 (496) (100)
VII	Se	$P(S)C_6H_5$	24	190–191	39.82 (39.85)	2.55 (2.72)	484 (484) (86)

[a] See eq. 1 for explanation of symbols. [b] Base peak of molecular ion. [c] Percentage abundance related to the most abundant ion.

from 30 to 150°C showed only changes in chemical shifts, and no change in overall pattern or evidence for a detectable concentration of another isomer. By analogy with other [3]ferrocenophanes [9,10], it is expected that the bridge is undergoing a rapid reversal at room temperature, and that the most probable conformation at phosphorus or arsenic is with the phenyl group in the sterically less hindered *exo*-position.

In the ^{13}C NMR spectra (Table 4) the [3]ferrocenophanes display five separate signals for the cyclopentadienyl carbon atoms. Four of these absorbances, in the range δ 68.9–76.5 ppm are of approximately equal intensity and correspond to the C(2,3,4,5) atoms. The fifth absorbance, of low intensity, in the range δ 80.3–84.8

TABLE 3

^1H NMR DATA FOR SOME [3]FERROCENOPHANES INVOLVING GROUP V ELEMENTS

Compound	Chemical shifts (multiplicity, relative intensity) [a,b,c]		
	Ferrocenyl signals	Phenyl signals	
		H(2,4,6)	H(3,5)
I [d]	4.11(m,2) 4.31(m,4) 4.39(m,2)	7.54(m,3)	7.93(m,2)
II [d]	4.03(m,2) 4.34(m,6)	7.51(m,3)	7.92(m,2)
III	4.12(m,2) 4.41(m,2) 4.50(m,2) 4.64(m,2)	7.62(m,3)	8.31(m,2)
IV	4.06(m,2) 4.57(m,2) 4.67(m,4)	7.85(m,3)	8.22(m,2) [e]
V	4.17(m,2) 4.32(m,6)	7.49(m,3)	7.95(m,2)
VI	4.10(m,2) 4.32(m,6)	7.47(m,3)	7.96(m,2)
VII	4.10(m,2) 4.47(m,4) 4.56(m,2)	7.62(m,3)	8.24(m,1) 8.39(m,1)

[a] δ(ppm), δ(TMS) = 0. [b] $CDCl_3$ solution unless otherwise indicated. [c] m = multiplet. [d] CD_2Cl_2 solution. [e] $\delta(CH_3)$ 3.25(d,3); $^2J(^{31}P-^1H)$ 12 Hz.

TABLE 4

^{13}C AND ^{31}P NMR DATA FOR SOME [3]FERROCENOPHANES INVOLVING GROUP V ELEMENTS

Compound	^{13}C chemical shifts [a,b]						^{31}P chemical shifts [c,d]
	Ferrocenyl signals		Phenyl signals				
	C(1)	C(2,3,4,5)	C(1)	C(2,3,5,6)		C(4)	
I	83.5(9.5)	69.0 70.4 71.1 76.1	[e]	133.0(23)	129.0(8)	131.5	119
II	84.8	68.9 70.0 71.0 76.5	136.8	132.9	131.0	129.2	
III	81.8(3.5)	70.0 71.2 74.0 75.4	[e]	128.8(12)	132.0(12)	133.2	133
V	80.3(10)	69.3(1.5) 69.9 73.1(1.5) 76.1	[e]	133.1(22)	130.0(6)	131.2	117(247)
VI	80.4	69.1 69.7 73.0 76.5	136.4	133.3	129.2	130.6	
VII	82.0(4.6)	70.2(1.5) 70.8 74.7 75.6	[e]	130.0(13)	131.4(11)	133.1(3)	84(424)

[a] δ(ppm), δ(TMS) = 0, $CDCl_3$ solution. [b] Coupling constants (Hz) for P–C in parentheses. [c] δ(ppm), $\delta(H_3PO_4$, external) = 0, $CDCl_3$ solution. [d] Coupling constants (Hz) for P–Se in parentheses. [e] Not observed.

TABLE 5

POSITIONAL PARAMETERS AND THEIR STANDARD DEVIATIONS [a]

Atom	*x/a*	*y/b*	*z/c*
As	0.27518(3)	0.09583(8)	0.50345(3)
Fe	0.14070(3)	0.05643(10)	0.21249(4)
S(1)	0.33785(7)	−0.02060(22)	0.42979(9)
S(2)	0.18076(7)	−0.18878(21)	0.43963(9)
C(1a)	0.2646(2)	0.0855(7)	0.3004(3)
C(2a)	0.2284(3)	0.3105(8)	0.2682(3)
C(3a)	0.1752(3)	0.3126(7)	0.1545(3)
C(4a)	0.1805(3)	0.0899(8)	0.1180(3)
C(5a)	0.2344(3)	−0.0515(7)	0.2066(3)
C(1b)	0.1128(2)	−0.0892(7)	0.3082(3)
C(2b)	0.0742(3)	0.1321(8)	0.2703(3)
C(3b)	0.0223(3)	0.1242(8)	0.1572(3)
C(4b)	0.0288(3)	−0.1035(8)	0.1252(3)
C(5b)	0.0840(3)	−0.2352(8)	0.2170(3)
C(1c)	0.3511(3)	−0.0519(8)	0.6411(3)
C(2c)	0.3706(3)	0.0724(8)	0.7296(4)
C(3c)	0.4236(3)	−0.0212(10)	0.8299(4)
C(4c)	0.4586(3)	−0.2356(11)	0.8438(4)
C(5c)	0.4411(3)	−0.3617(9)	0.7556(4)
C(6c)	0.3861(3)	−0.2702(8)	0.6536(4)
H(2a)	0.240(4)	0.454(12)	0.309(5)
H(3a)	0.136(4)	0.470(13)	0.114(5)
H(4a)	0.146(4)	0.036(11)	0.041(4)
H(5a)	0.257(3)	−0.192(8)	0.216(3)
H(2b)	0.086(4)	0.267(11)	0.322(5)
H(3b)	−0.010(3)	0.217(10)	0.113(4)
H(4b)	−0.003(4)	−0.159(13)	0.059(5)
H(5b)	0.098(4)	−0.435(11)	0.216(5)
H(2c)	0.345(3)	0.228(8)	0.716(3)
H(3c)	0.424(6)	0.033(20)	0.898(8)
H(4c)	0.501(5)	−0.285(17)	0.909(7)
H(5c)	0.472(4)	−0.510(13)	0.766(5)
H(6c)	0.382(5)	−0.396(15)	0.604(7)

[a] E.s.d.'s, given in parentheses, are applicable to the least significant digits.

ppm, is attributable to the C(1) atom. These spectral features are consistent with the unsymmetrical grouping at the 2-position and the rapid reversal of the bridge.

The ^{31}P NMR spectral results for the [3]ferrocenophanes with a phosphorus atom at the bridgehead are shown in Table 4. The $^{1}J(^{77}Se-^{31}P)$ coupling constants for the 1,3-diselena compounds are within the range 200–500 Hz found for formally single Se–P bonds [11], and increase, as expected, on going from phosphorus(III) to phosphorus(V). The values of $^{1}J(^{77}Se-^{31}P)$, 247 and 424 Hz, compare with 205 and 341 Hz for $(CH_3)_2PSeCH_3$ and $(CH_3)_2P(S)SeCH_3$, respectively [12].

Atomic parameters for the asymmetric unit of the crystal structure at 163 K of 1,3-dithia-2-phenylarsino-[3]ferrocenophane are given in Table 5. The asymmetric unit contains a single molecule with no molecular symmetry implied. A view of the molecule, drawn with the program ORTEP [13] and showing the numbering scheme adopted is given in Fig. 1. Because of uncertainties as to the exactness of the absorption correction applied, no attempt has been made to analyze thermal anisotropy in terms of rigid body motions. Bond distances, uncorrected for the effects of thermal motion, are given in Table 6, and bond angles are given in Table 7. Equations of mean planes through selected atomic groupings of interest are given in Table 8.

The two As–S bond distances are not significantly different from one another nor from the average of the As–S bond distances found in As_4S_8 and As_4S_6 (2.24(1) Å) [14]. The As–C bond is of expected length and the two S–C bond distances do not differ significantly. There are significant differences among the C–C bonds of the cyclopentadienyl moieties, and the pattern of difference is the same in each case with C(4)–C(5) short (1.407(6) Å) and C(1)–C(5) long (1.439(5) Å). Because of the minimal disparity between the ideal ring bite and the S...S bite of the S–As–S moiety, there are no significant differences among the 10 Fe–C bond distances, with the mean of 2.053(4) Å being identical to the thermally corrected value for this mean in 1,3-dithia-2-selena-[3]ferrocenophane (DSF) [1].

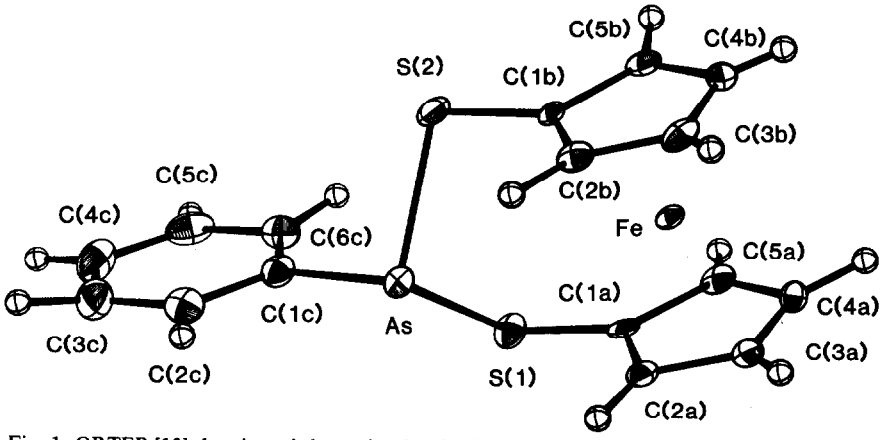

Fig. 1. ORTEP [13] drawing of the molecule of 1,3-dithia-2-phenylarsino-[3]ferrocenophane as found in the crystal at 163 K, and showing the numbering scheme adopted. Hydrogen atoms are numbered to correspond to the carbon of attachment. Thermal ellipsoids are drawn to the 50% probability boundary surface and hydrogen atoms are represented by spheres of arbitrary radius.

TABLE 6

BOND LENGTHS (Å) [a]

As–S(1)	2.252(1)	As–S(2)	2.255(1)
S(1)–C(1a)	1.764(4)	As–C(1c)	1.948(4)
S(2)–C(1b)	1.758(4)		
Mean	1.761(4)		
Fe–C(1a)	2.046(4)	Fe–C(1b)	2.052(4)
Fe–C(2a)	2.056(4)	Fe–C(2b)	2.058(4)
Fe–C(3a)	2.048(4)	Fe–C(3b)	2.059(4)
Fe–C(4a)	2.055(4)	Fe–C(4b)	2.055(4)
Fe–C(5a)	2.051(4)	Fe–C(5b)	2.053(4)
Mean	2.051(5)	Mean	2.055(3)
C(1a)–C(2a)	1.422(5)	C(1b)–C(2b)	1.424(5)
C(2a)–C(3a)	1.429(5)	C(2b)–C(3b)	1.423(6)
C(3a)–C(4a)	1.425(5)	C(3b)–C(4b)	1.430(6)
C(4a)–C(5a)	1.408(6)	C(4b)–C(5b)	1.408(6)
C(5a)–C(1a)	1.437(5)	C(5b)–C(1b)	1.441(5)
Mean	1.419(13)	Mean	1.425(12)
C(1c)–C(2c)	1.384(6)	C(2c)–C(3c)	1.380(7)
C(3c)–C(4c)	1.371(8)	C(4c)–C(5c)	1.398(7)
C(5c)–C(6c)	1.398(7)	C(6c)–C(1c)	1.395(6)
		Mean	1.388(10)

[a] E.s.d.'s, given in parentheses, are applicable to the least significant digits. Values are uncorrected for the effects of thermal motion.

Differences in the exocyclic C–C–S bond angles (means 129.2(3) vs. 122.8(3)°) reflect steric interactions between the central As atom and the C(2) atoms of the cyclopentadienyl rings, an effect common to all [3]ferrocenophanes thus far studied. A comparable asymmetry is evident in the two As–C–C angles (123.6(4) vs. 116.6(4)°), reflecting crowding of S(1) and C(6c) (S...C, 3.33 Å). The phenyl ring, however, does occupy the less crowded *exo*-site on As.

TABLE 7

SELECTED BOND ANGLES (°) [a]

As–S(1)–C(1a)	97.3(2)	As–S(2)–C(1b)	99.3(2)
As–C(1c)–C(2c)	116.6(4)	As–C(1c)–C(6c)	123.6(4)
S(1)–As–S(2)	98.6(1)		
S(1)–C(1a)–C(2a)	129.0(3)	S(2)–C(1b)–C(2b)	129.5(3)
S(1)–C(1a)–C(5a)	122.7(3)	S(2)–C(1b)–C(5b)	122.8(3)
C(5a)–C(1a)–C(2a)	108.2(4)	C(5b)–C(1b)–C(2b)	107.7(4)
C(1a)–C(2a)–C(3a)	107.6(4)	C(1b)–C(2b)–C(3b)	108.1(4)
C(2a)–C(3a)–C(4a)	107.7(4)	C(2b)–C(3b)–C(4b)	107.8(4)
C(3a)–C(4a)–C(5a)	108.9(4)	C(3b)–C(4b)–C(5b)	108.5(4)
C(4a)–C(5a)–C(1a)	107.5(4)	C(4b)–C(5b)–C(1b)	107.9(4)
C(6c)–C(1c)–C(2c)	119.9(4)	C(1c)–C(2c)–C(3c)	120.0(5)
C(2c)–C(3c)–C(4c)	121.0(5)	C(3c)–C(4c)–C(5c)	119.9(5)
C(4c)–C(5c)–C(6c)	119.4(5)	C(5c)–C(6c)–C(1c)	119.8(4)

[a] E.s.d.'s, given in parentheses, are applicable to the least significant digit.

TABLE 8

EQUATIONS OF SELECTED LEAST-SQUARES MEAN PLANES [a]

Cyclopentadienyl ring C(1a)–C(5a)					
$-0.94646X - 0.32225Y + 0.01902Z = -2.57894$					
Deviations (Å)					
C(1a)	0.000	C(1b)	3.307	As	1.576
C(2a)	−0.004	C(2b)	3.303	S(1)	−0.064
C(3a)	0.007	C(3b)	3.313	S(2)	3.350
C(4a)	−0.007	C(4b)	3.326	Fe	1.655
C(5a)	0.004	C(5b)	3.322		
Cyclopentadienyl ring C(1b)–C(5b)					
$-0.94843X - 0.31586Y + 0.02665Z = 0.75602$					
Deviations (Å)					
C(1a)	−3.308	C(1b)	−0.001	As	−1.709
C(2a)	−3.307	C(2b)	0.001	S(1)	−3.364
C(3a)	−3.306	C(3b)	−0.000	S(2)	0.051
C(4a)	−3.332	C(4b)	0.000	Fe	−1.659
C(5a)	−3.319	C(5b)	0.000		
Plane As, S(1), S(2)					
$0.19421X - 0.55656Y + 0.80779Z = 5.00362$					
Plane S(1), S(2), C(1a), C(1b)					
$-0.26102X + 0.89541Y + 0.36070Z = 1.09489$					
Deviations (Å)					
S(1)	−0.018	C(1a)	0.019	As	1.420
S(2)	0.018	C(1b)	−0.019	Fe	−0.081
Phenyl ring C(1c)–C(6c)+As					
$0.89735X + 0.43696Y + 0.06189Z = 1.52802$					
Deviations (Å)					
C(1c)	−0.004	C(2c)	0.008	C(3c)	−0.004
C(4c)	−0.006	C(5c)	0.012	C(6c)	−0.007
As	0.001				

[a] $X = x + z\cos\beta$, $Y = y$, $Z = z\sin\beta$.

The ferrocene moiety adopts an eclipsed conformation with a mean twist angle * of 2.6°, and with the ring planes inclined at only 0.6°. The two S atoms are displaced from the respective ring planes by 0.05 and 0.06 Å, displacements comparable to the 0.04 Å found for DSF.

A detailed analysis of molecular geometry in relation to steric strain in these heteroatom bridged [3]ferrocenophanes forms the topic of a later contribution [15].

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* Defined as the mean of the torsion angles C(na)–Ct(a)–Ct(b)–C(nb), $n = 1,5$ where Ct is the ring centroid.

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