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FERROCENYLTRITHIOCARBONATES

I. DIRECT ACCESS FROM α-FERROCENYLCARBINOLS BY A S_Ni MECHANISM. ABSOLUTE X-RAY STRUCTURE DETERMINATION OF (*R*)-FERROCENYLMETHYLMETHANE *S*-METHYLTRITHIOCARBONATE

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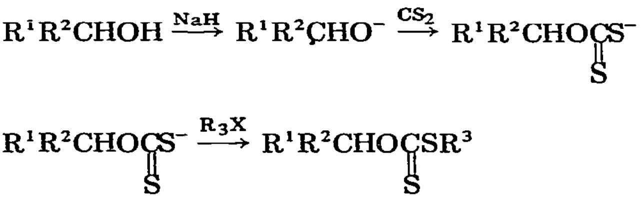
Summary

Ferrocenyltrithiocarbonates (I) are readily obtained by treating α-ferrocenylcarbinols (II) successively with sodium hydride, carbon disulfide and alkyl halide. Formation of I occurs by intramolecular nucleophilic displacement of oxygen by sulfur with retention of configuration. This is supported by the nature of the other products formed and by the X-ray structure determination of an optically active compound I, which was refined to R = 0.038. The title compound of *R* configuration was obtained from (*R*)-ferrocenylmethylmethanol.

Introduction

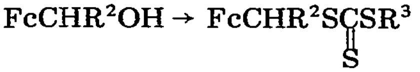
In connection with our study of the new ligand *S*-alkyldithiocarbonate (or *S*-alkyl xanthate) [1,2] we have attempted to prepare the corresponding ferrocenyl derivatives according to the general procedure [3] summarized in equation 1.



$$\mathrm{R^1R^2CHOH \xrightarrow{NaH} R^1R^2CHO^- \xrightarrow{CS_2} R^1R^2CHO\underset{\underset{S}{\|}}{C}S^-} \qquad (1)$$

$$\mathrm{R^1R^2CHO\underset{\underset{S}{\|}}{C}S^- \xrightarrow{R_3X} R^1R^2CHO\underset{\underset{S}{\|}}{C}SR^3}$$

With α-ferrocenylcarbinols (II, Fc- for $C_5H_5FeC_5H_4$) we found that the major product was the trithiocarbonate I rather than the expected xanthate (eq. 2)



$$\mathrm{FcCHR^2OH} \rightarrow \mathrm{FcCHR^2S\underset{\overset{\|}{S}}{C}SR^3} \qquad (2)$$

(II: R^2 = H, Me, Ph) (I)

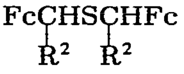
Compounds such as I are difficult to prepare but they may be obtained from thiols [4] and are also present in the mixture resulting from the rearrangement of xanthates catalysed by Lewis acids [5].

Our unexpected result led us to study in more detail the scope and limitations of this reaction. We also describe the mechanism of this transformation. An accurate X-ray structural determination provides proof of the retention of configuration, consistent with a S_Ni reaction.

Results and discussion

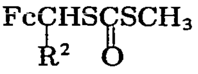
Synthesis of α-ferrocenyltrithiocarbonates

Alcohols II are treated with NaH in refluxing THF (step 1) then CS_2 is added at the same temperature (step 2) and finally the mixture is quenched with methyl iodide (step 3). After reaction under these conditions two products can be separated by chromatography. The major product is the trithiocarbonate I and the minor one has structure III.



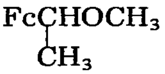
$\mathrm{Fc\underset{R^2}{C}HS\underset{R^2}{C}HFc}$

(III)



$\mathrm{Fc\underset{R^2}{C}HS\underset{\overset{\|}{O}}{C}SCH_3}$

(IV)



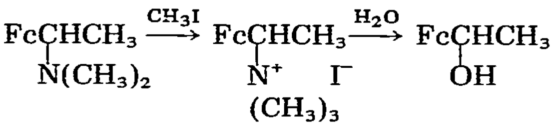
$\mathrm{Fc\underset{CH_3}{C}HOCH_3}$

(V)

When CS_2 is added at room temperature (step 2), in addition to I and III compound IV can also be isolated and characterized. Finally when CS_2 is added at 0°C the only product formed is 1-methoxyferrocenylethane (V) [6], showing that CS_2 does not react with the oxygen anion.

Synthesis of (R)-ferrocenylmethylmethane S-methyltrithiocarbonate

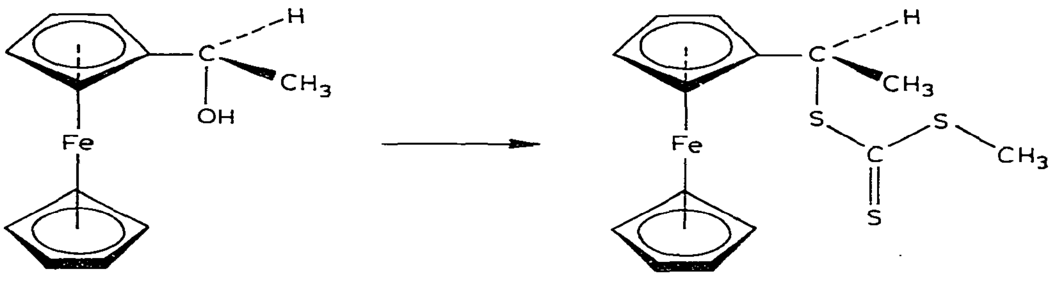
Resolution of racemic α-ferrocenylethyldimethylamine (VI) affords both enantiomers [7]. After quaternization with methyl iodide the ammonium salt VII is hydrolysed and the two enantiomers of α-ferrocenylethanol (VIII) are obtained optically pure [8].



$$\mathrm{Fc\underset{N(CH_3)_2}{C}HCH_3} \xrightarrow{CH_3I} \mathrm{Fc\underset{\underset{(CH_3)_3}{N^+\quad I^-}}{C}HCH_3} \xrightarrow{H_2O} \mathrm{Fc\underset{OH}{C}HCH_3}$$

(VI) (VII) (VIII)

Treatment of alcohol VIII ($[\alpha]_D^{22}$ −31°, *R*-configuration) [8] as described above in refluxing THF gave the optically active trithiocarbonate in 62% yield ($[\alpha]_D^{22}$ +68°, *R*-configuration by X-ray structure determination).



(VIII) (I)

Several unsuccessfull attempts have been made to correlate the configuration of optically active I with VIII or VI. For instance we have found that $LiAlH_4$ reduction of I gave the corresponding alcohol with retention of optical activity ranging from 11 to 28% depending on the reaction conditions.

In order to elucidate the nature of the reaction and to obtain information about the mechanism the structure of I ($R = CH_3$, $[\alpha]_D^{22}$ +68°) was determined by X-ray diffractometry.

Structure of I

The molecular structure of derivative I is shown in Fig. 1. The unit cell is obviously non centrosymetric and contains two identical molecules (Fig. 2) related by a two fold axis. The three dimensional packing of these molecules has only weak intermolecular contacts: the shortest distance is 3.706 Å between C(1) and the methyl group C(14).

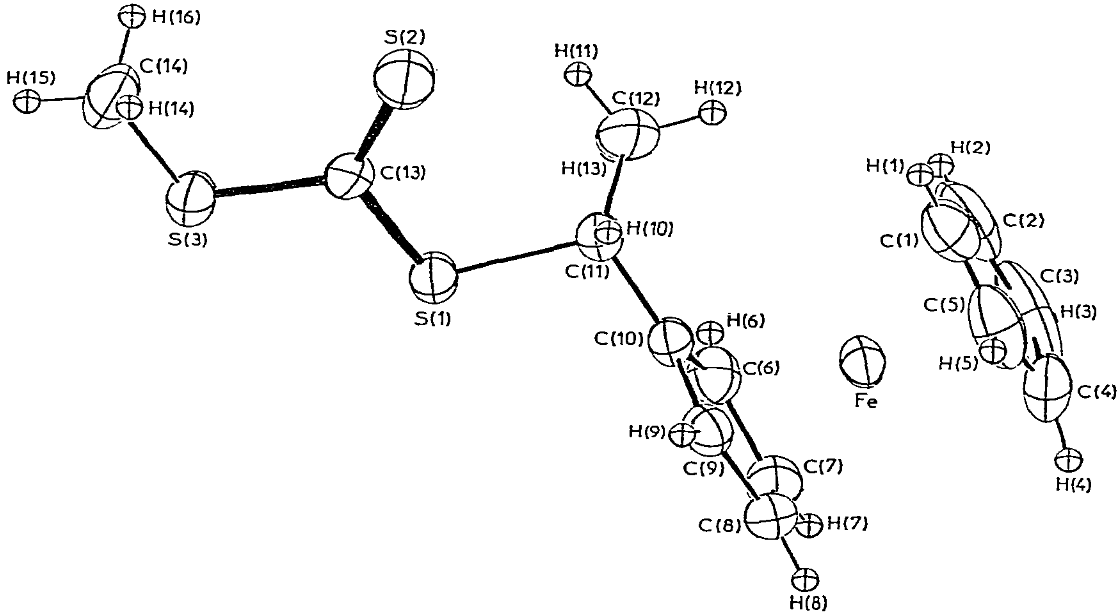


Fig. 1. Molecular structure of compound I.

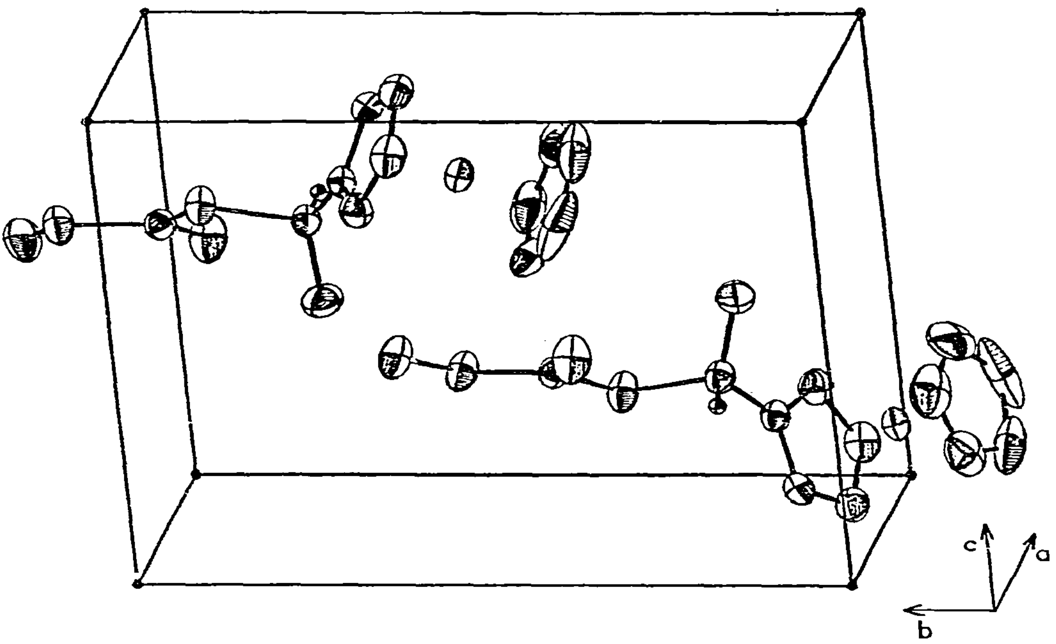


Fig. 2. Unit cell containing two molecules of I.

The ferrocenyl moiety does not show any particular features. The least-squares mean planes through the two cyclopentadienyl rings (Table 4) are nearly parallel with a dihedral angle of 1.69°, and the most important departures —0.006 Å for the atoms C(1) and C(2) establish the planarity of the two rings (χ^2 = 3.06 and 4.13). The iron atom lies at the same distance from the two rings (1.654 and 1.652 Å). The non-substituted ring has the most important thermal vibration as observed in other cyclopentadienyl compounds [18] and this gives rise to a shorter carbon—carbon mean bond length of 1.365 Å in that ring compared with 1.416 Å in the other.

The most interesting part of the molecule is the trithiocarbonate moiety because, to our knowledge, there are very few crystallographic data for this functional group [19]. The trithiocarbonate moiety is nearly planar (Table 4) with a χ-square value of 28, and presents a C_{2v} symmetry. The shortest carbon—sulfur distance is 1.634(3) Å between C(13)—S(2) and so shows a double bond character compared to the other carbon—sulfur bonds C(13)—S(1) and C(13)—S(3) respectively 1.743(2) and 1.741(2) Å. The bond angles around C(13)—126.92(11), 125.96(5) and 107.09(5)° corresponds to a sp^2 hybridization of the C(13) carbon atom. This geometry of the trithiocarbonate function is in agreement with the observed values in 2-thioxo-1,3-dithiolane (ethylene trithiocarbonate) [20]. The main difference lies in the bond angles, which are closer to 120° in the former compound; this may result from the cyclic structure which imposes a more rigid geometry. On the other hand the double bond length C=S of 1.652 Å and the single bond lengths C—S of 1.748 and 1.727 Å are very close to our results. The bond distances 1.838(2) and 1.790(4) Å between the dithiolane sulfur atoms and the sp^3 carbon atoms in our compound have the same magnitude as in the ethylene trithiocarbonate (1.821 and 1.814 Å).

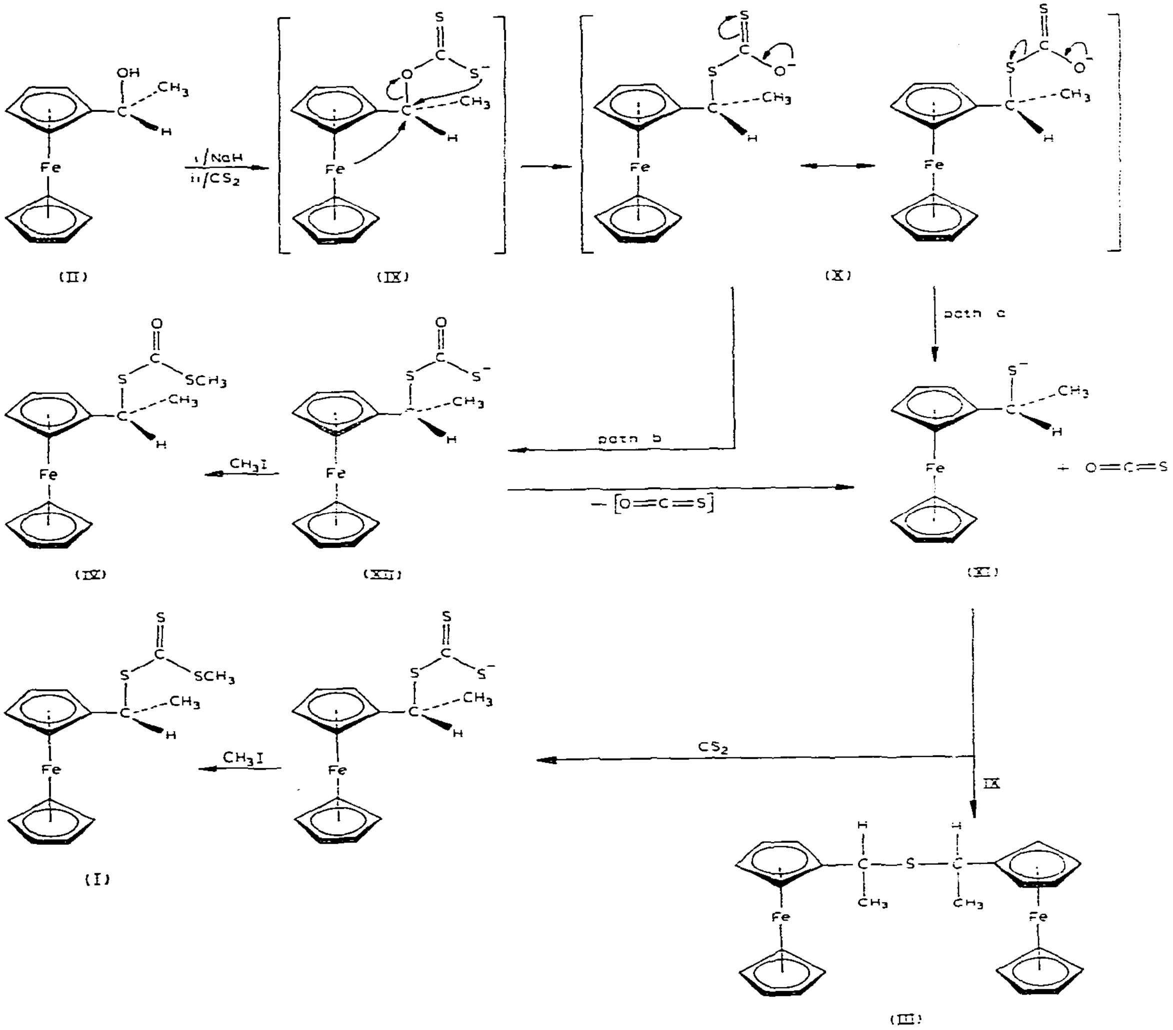
The absolute configuration of the asymetric carbon atom C(11) can be deduced from Fig. 1. The hydrogen atom points towards the viewer and C(11) has the *R*-configuration proving that the reaction described above occurs with retention of configuration.

Interpretation

The ability of ferrocene to stabilize a carbenium ion at the α-carbon is well documented [9,10] and a number of reactions have been shown to proceed via such an intermediate.

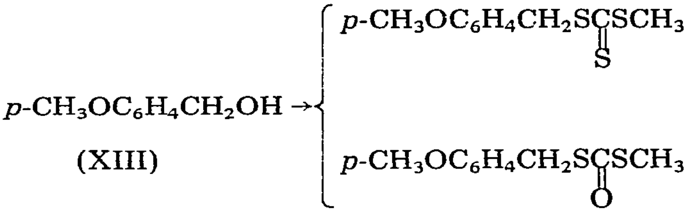
In our case anion IX formed by condensation of CS_2 on the alcoholate must be transformed into intermediate X with retention of configuration. The

SCHEME 1



sulfur anion is known to be a better nucleophile than its oxygen analogue and in addition cleavage of the C—O bond is facilitated by anchimeric assistance from the ferrocene nucleus. A few examples of nucleophilic substitutions proceeding with retention of configuration have been described: fragmentation of chlorosulfites [11], decomposition of chloroformates [12], pyrolysis of sulfonamate esters [13]. These results are commonly explained by dissociation into an intimate ion pair [14] followed by attack of the nucleophile from the same side. With ferrocene the carbenium ion is not only easily generated but can also be generated stereospecifically, and restricted rotation has been observed for the exocyclic bond of the fulvene ligand [10].

Starting from X there are two possible ways (Scheme 1, paths a or b) following elimination of COS to reach the sulfur anion XI. Although no direct evidence has been found for path a it is the most probable when the reaction is conducted in refluxing THF. At room temperature the reaction proceeding via path b is supported by the isolation of compound IV. The most important intermediate is XI, which reacts with CS_2 to afford trithiocarbonate I after methylation. But XI can also react with intermediate IX (S_N2) or with the α-ferrocenylcarbonium ion (S_N1) to produce dimer III, which is always isolated as a minor component. This direct formation of trithiocarbonates is only possible when the cationic center is stabilized. In aliphatic compounds this reaction has never been observed, but we have shown that *p*-methoxybenzyl alcohol (XIII) affords a mixture of trithiocarbonate (70%) and dithiocarbonate (30%): eq. 3.



$$p\text{-}CH_3OC_6H_4CH_2OH \rightarrow \begin{cases} p\text{-}CH_3OC_6H_4CH_2S\underset{\displaystyle\|\atop S}{C}SCH_3 \\ \\ p\text{-}CH_3OC_6H_4CH_2S\underset{\displaystyle\|\atop O}{C}SCH_3 \end{cases} \qquad (3)$$

(XIII)

Conclusion

X-ray structure determination of optically active trithiocarbonate (I, R = CH_3) proves that this novel reaction occurs with retention of configuration, in keeping with a S_Ni mechanism. Further studies are being conducted in order to generalize this direct synthesis of trithiocarbonates to other cases in which there is the possibility of stabilizing an intermediate carbenium ion.

Experimental

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. ^1H NMR spectra were recorded using a Varian A60 and ^{13}C NMR spectra using a Brucker WP 80, with TMS as an internal standard and $CDCl_3$ as solvent. Petroleum ether refers to the fraction with b.p. 40—60°C and the solvent mixtures are described in ratios of volume. TLC and PLC were carried out on Merck Kieselgel plates: TLC refers to thin layer chromatography (0.2 mm) and PLC refers to preparative layer chromatography (1 mm). Optical rotations were measured on a Perkin—Elmer 241 MC polarimeter. Organic solutions were dried over $MgSO_4$. Mass spectra were recorded using a Varian MAT 311. Satisfactory elemental analyses were obtained for all new compounds.

X-ray data collection and refinement

The crystals are monoclinic, space group $P2_1$, with 2 formulas per unit cell a 6.013(1) Å, b 12.332(1) Å, c 10.118(2) Å, β 102.11(1)°, V 733.6 Å^3, mol. wt. = 336; d_m 1.57 g cm^{-3}; $d_{calc.}$ 1.58 g cm^{-3}; μ(Mo-K_α) 14.9 cm^{-1}; rotatory power $[\alpha_D]$ +68°.

A suitable paralellepipedic crystal of 0.37 × 0.22 × 0.20 mm was mounted on an automatic four circle Nonius diffractometer. The unit cell parameters were refined from 25 accurately centered diffractometer reflections. The data collection, with an $\omega/2\theta$ scan technique with scan angles given by $s = (1.00 + 0.35 \tan\theta)°$ and an aperture width of $(2 + 0.4 \tan\theta)$ mm, was performed with a graphite monochromated Mo-K_α radiation.

The intensities and estimated standard deviations of 1995 independent Friedel pairs were collected up to $\sin\theta/\lambda$ 0.81 Å^{-1}. All measured reflections were considered in the subsequent calculations. Three standard reflections were monitored every hour of exposure and no significant variation was observed. Absorption and Lorentz-polarization corrections were applied by the programs Maxe [15] and Agnost [16].

Most of the atoms of the molecule were located by the program Multan [17] and from a three dimensional electron density difference map the positions of all suceeding non hydrogen atoms were found. After successive full matrix least-squares refinement cycles with anisotropic thermal parameters for these atoms, all the hydrogen atoms were located on a three dimensional electron density difference map and then refined with a constant isotropic thermal parameter fixed at 5.0 Å^2.

After a few cycles of refinement for both enantiomers the absolute configuration of the molecule shown in Fig. 1 was obtained: $R = 0.038$ and $R_\omega = 0.040$ versus $R = 0.051$ and $R_\omega = 0.061$ for 3990 reflexions and 212 refined parameters.

The final positional and thermal parameters with their e.s.d. are listed in Tables 1a and 1b, relevant bond distances and angles in Tables 2 and 3. Tables of observed and calculated structure factors are available from the authors on request.

Ferrocenyltrithiocarbonates

To a solution of alcohol II (10 mmol) in 50 ml of THF was added NaH (1 g, 50% suspension) and the mixture was refluxed for 1 h under N_2 with stirring. Excess CS_2 (3 ml) was added, and after 30 min the mixture was quenched by the addition of CH_3I (3 ml) followed by a further refluxing for 30 min. After cooling the mixture was poured into water and extracted with ether. The usual treatment was followed by PLC (ether/petrol 1/9) to separate I from III. Both compounds were crystallized from pentane or hexane (yields are given after crystallization).

TABLE 1a

FINAL ATOMIC FRACTIONAL COORDINATES AND THEIR e.s.d. ($\times 10^4$) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS GIVEN BY:

$$B_{eq.} = \frac{4}{3}\sum_{ij}\beta_{ij}(\vec{a}_i\vec{a}_j)\ \text{Å}^2$$

Atom	X	Y	Z	$B_{eq.}$
Fe	8689(1)	0	1431(0)	3.00
S(1)	8212(2)	3719(1)	2221(1)	3.92
S(2)	4512(1)	4025(1)	3798(1)	5.13
S(3)	7194(2)	5838(1)	2901(1)	4.31
C(1)	6770(12)	−730(3)	2585(6)	6.81
C(2)	8947(15)	−877(4)	3153(6)	8.56
C(3)	9945(9)	−1424(4)	2219(11)	9.62
C(4)	8223(14)	−1603(3)	1076(7)	7.65
C(5)	6261(7)	−1157(3)	1265(5)	6.19
C(6)	1278(2)	1691(4)	248(9)	3.73
C(7)	0974(5)	735(2)	482(4)	4.12
C(8)	8790(6)	752(3)	353(3)	4.07
C(9)	7333(5)	1322(2)	339(3)	3.38
C(10)	8600(4)	1660(2)	1612(3)	2.94
C(11)	7769(6)	2299(2)	2654(3)	3.30
C(12)	8946(10)	2079(4)	4106(4)	5.30
C(13)	6485(5)	4482(2)	3053(3)	3.18
C(14)	5215(8)	6556(3)	3677(5)	5.27
H(1)	6028(117)	−450(55)	3092(75)	5.00
H(2)	9518(87)	−623(40)	3927(54)	5.00
H(3)	1294(89)	−1551(41)	2474(50)	5.00
H(4)	8046(105)	−1799(54)	209(67)	5.00
H(5)	4959(90)	−1122(43)	815(49)	5.00
H(6)	2014(64)	1324(29)	2408(39)	5.00
H(7)	2271(92)	419(50)	258(53)	5.00
H(8)	8399(54)	442(29)	1172(37)	5.00
H(9)	5880(52)	1540(24)	14(31)	5.00
H(10)	6234(113)	2226(58)	2395(67)	5.00
H(11)	0407(97)	2204(46)	4231(53)	5.00
H(12)	8509(88)	1355(55)	4291(56)	5.00
H(13)	8416(82)	2526(44)	4694(52)	5.00
H(14)	3609(99)	6394(46)	3228(57)	5.00
H(15)	5507(108)	7283(60)	3662(64)	5.00
H(16)	5565(82)	6391(44)	4697(55)	5.00

TABLE 1b

FINAL ANISOTROPIC THERMAL PARAMETERS AND THEIR e.s.d. ($\times 10^4$) IN THE FORM: exp − $(\Sigma_{ij}\beta_{ij}h_ih_j)$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	226(1)	37(0)	94(0)	6(0)	41(0)	8(0)
S(1)	358(3)	43(0)	125(1)	−1(1)	113(1)	0(1)
S(2)	400(3)	67(0)	174(1)	−6(1)	159(1)	0(0)
S(3)	404(3)	46(1)	126(1)	−15(1)	84(2)	−10(1)
C(1)	737(25)	67(2)	195(8)	−28(6)	224(14)	24(4)
C(2)	926(38)	85(4)	151(7)	−102(10)	93(13)	64(4)
C(3)	317(14)	87(4)	493(19)	53(6)	120(14)	142(8)
C(4)	984(38)	42(2)	216(8)	10(7)	259(15)	4(3)
C(5)	397(14)	65(3)	217(7)	−51(5)	4(9)	37(4)
C(6)	249(9)	53(2)	117(4)	−14(3)	43(5)	1(2)
C(7)	297(9)	59(2)	135(4)	4(4)	103(5)	4(2)
C(8)	429(11)	53(2)	89(3)	17(4)	82(5)	3(2)
C(9)	267(9)	47(2)	88(3)	11(3)	22(4)	11(2)
C(10)	240(8)	38(2)	84(3)	−6(3)	41(4)	2(2)
C(11)	282(9)	41(1)	94(3)	−7(3)	48(4)	1(2)
C(12)	578(21)	74(3)	85(4)	34(6)	44(7)	1(3)
C(13)	247(8)	47(2)	85(3)	10(3)	36(4)	−3(2)
C(14)	469(16)	58(2)	150(5)	21(5)	60(7)	−27(3)

TABLE 2

PRINCIPAL BOND LENGTHS AND e.s.d. (Å)

Atoms	Distance	Atoms	Distance
Fe—C(1)	2.017(7)	S(3)—C(14)	1.790(4)
Fe—C(2)	2.029(6)	C(1)—C(2)	1.327(10)
Fe—C(3)	2.009(6)	C(1)—C(5)	1.317(8)
Fe—C(4)	2.018(4)	C(2)—C(3)	1.394(12)
Fe—C(5)	2.032(4)	C(3)—C(4)	1.399(11)
Fe—C(6)	2.039(3)	C(4)—C(5)	1.387(9)
Fe—C(7)	2.046(3)	C(6)—C(7)	1.405(5)
Fe—C(8)	2.042(3)	C(6)—C(10)	1.440(4)
Fe—C(9)	2.041(2)	C(7)—C(8)	1.404(4)
Fe—C(10)	2.057(2)	C(8)—C(9)	1.418(4)
S(1)—C(11)	1.838(2)	C(9)—C(10)	1.415(3)
S(1)—C(13)	1.743(2)	C(10)—C(11)	1.485(4)
S(2)—C(13)	1.634(3)	C(11)—C(12)	1.516(4)
S(3)—C(13)	1.741(2)		

$FcCH(R^2)SC(=S)SCH_3$

R^2 = H: 62%; m.p. 66—67°C. ^{1}H NMR: δ 4.42 (2 H); 4.18 (9 H); 2.74 (S—CH_3) ppm; ^{13}C NMR: δ 224.5 (C=S); 37.9 (CH_2); 20.0 (S—CH_3) ppm; mass spectrum: 322 (M^+); 246 (M^+ — CS_2); 199 (Fc—CH_2, 100%).

R^2 = CH_3: 58%; m.p. 119—120°C. ^{1}H NMR: δ 5.22 (q, 1 H); 4.20 (9 H); 2.76 (S—CH_3); 1.80 (d, 3 H) ppm; ^{13}C NMR: δ 224.4 (C=S); 46.9 (CH); 20.7 (S—CH_3); 19.9 (CH_3) ppm; mass spectrum: 336 (M^+); 260 (M^+ — CS_2); 213 (100%).

R^2 = C_6H_5: 67% (oil). ^{1}H NMR: δ 7.50 (5 H); 6.50 (1 H); 4.20 (9 H); 2.73 (S—CH_3) ppm; mass spectrum: 398 (M^+); 322 (M^+ — CS_2); 275 (100%).

TABLE 3

SELECTED NON HYDROGEN BOND ANGLES (°)

Atoms	Angle	Atoms	Angle
C(1)—Fe—C(2)	38.28(27)	C(3)—C(4)—C(5)	106.12(42)
C(1)—Fe—C(5)	37.96(28)	C(1)—C(5)—C(4)	108.36(49)
C(2)—Fe—C(3)	40.40(30)	C(7)—C(6)—C(10)	108.47(27)
C(3)—Fe—C(4)	40.65(29)	C(6)—C(7)—C(8)	108.44(28)
C(4)—Fe—C(5)	40.04(24)	C(7)—C(8)—C(9)	107.87(23)
C(6)—Fe—C(7)	40.24(13)	C(8)—C(9)—C(10)	108.98(28)
C(6)—Fe—C(10)	41.17(12)	C(6)—C(10)—C(9)	106.24(19)
C(7)—Fe—C(8)	40.19(13)	C(6)—C(10)—C(11)	126.45(20)
C(8)—Fe—C(9)	40.64(13)	C(9)—C(10)—C(11)	127.29(24)
C(9)—Fe—C(10)	40.39(12)	S(1)—C(11)—C(10)	104.46(22)
C(11)—S(1)—C(13)	105.54(13)	S(1)—C(11)—C(12)	109.89(26)
C(13)—S(3)—C(14)	103.76(17)	C(10)—C(11)—C(12)	115.77(31)
C(2)—C(1)—C(5)	111.48(54)	S(1)—C(13)—S(2)	126.92(11)
C(1)—C(2)—C(3)	107.29(44)	S(1)—C(13)—S(3)	107.09(5)
C(2)—C(3)—C(4)	106.73(41)	S(2)—C(13)—S(3)	125.96(5)

TABLE 4

LEAST-SQUARES PLANES IN THE ORTHONORMAL RIGHT HANDED REFERENCE SYSTEM DEFINED BY $\vec{a}, \vec{c}^* \wedge \vec{a}, \vec{c}^*$

(a) Equation of the C(1), C(2), C(3), C(4), C(5) plane					
$0.3029\,X + 0.8723\,Y - 0.3837\,Z + 0.7071 = 0$					
$X^2 = 3.06$					
Atom distances from the plane (Å)					
C(1)	0.006	C(2)	−0.006	C(3)	0.002
C(4)	0.003	C(5)	−0.003	Fe	1.654
(b) Equation of the C(6), C(7), C(8), C(9), C(10) plane					
$0.3161\,X + 0.8576\,Y - 0.40572\,Z - 2.6330 = 0$					
$X^2 = 4.13$					
Atom distances from the plane (Å)					
C(6)	−0.004	C(7)	0.004	C(8)	−0.002
C(9)	−0.000	C(10)	0.002	Fe	−1.652
(c) Equation of the S(1), S(2), S(3), C(13) plane					
$-0.5113\,X + 0.0727\,Y - 0.8563\,Z + 3.8339 = 0$					
$X^2 = 28.50$					
Atom distances from the plane (Å)					
S(1)	0.000	S(2)	0.001	S(3)	0.000
C(13)	−0.015	C(14)	0.0099	C(11)	−0.309
Fe	+0.105				

$FcCH(R^2)SCH(R^2)Fc$

R^2 = H: a very small amount of this product was recovered after PLC and characterized by its mass spectrum, 430 (M^+).

$R^2 = CH_3$: 17%, m.p.: 142—145°C. ^{1}H NMR: δ 5.24 (q, 1 H); 4.22 (9 H); 1.82 (d, 3 H) ppm; mass spectrum: 458 (M^+). 245, 213.

$R^2 = C_6H_5$ = 13%; m.p. 78°C. ^{1}H NMR: δ 7.50 (5 H); 6.32 (1 H); 4.18 (9 H) ppm.

Ferrocenyldithiocarbonate (IV)

As described above, the alcohol II (R = H, CH_3) 10 mmol, was refluxed with NaH in THF. After cooling to room temperature CS_2 was added and the mixture stirred at room temperature for 1 h. After addition of CH_3I and stirring at room temperature for 1 h the mixture was poured into water and the work-up was as before. For R = CH_3 the yields and R_f are respectively: I (38%; 0.7); III (8%; 0.55); IV (18%; 0.45).

$R^2 = CH_3$: m.p. 84—87°C, ν(C=O) (Nujol) 1650 cm^{-1}. ^{1}H NMR: δ 4.78 (q, 1 H); 4.20 (9 H); 2.45 (S—CH_3); 1.75 (d, 3 H) ppm; ^{13}C NMR: δ 189.7 (C=O); 41.0 (C—H); 21.9 (S—CH_3); 12.9 (CH_3) ppm; mass spectrum: 320 (M^+); 260 (M^+ — COS); 213 (100%).

R^2 = H: m.p. 58°C, ν(C=O) (Nujol) 1650 cm^{-1}. ^{1}H NMR: δ 4.21 (1 H); 4.12 (2 H); 2.50 (3 H) ppm; ^{13}C NMR: δ 189.9 (C=O); 30.9 (CH_2); 13.0 (S—CH_3) ppm; mass spectrum: 306 (M^+); 246 (M^+ — COS); 199 (100%).

(R)-Ferrocenylmethylmethane S-methyltrithiocarbonate

Racemic α-ferrocenylethyldimethylamine was prepared and the enantiomers resolved using R(+) tartaric acid [7]. The amine (6 g) $[\alpha]_D^{22}$ +13°7 (*c* 0.225; ethanol) was treated with methyl iodide in acetone at 0°C to give the ammonium salt, which was dissolved in water and allowed to hydrolyse at room temperature for 48 h. α-Ferrocenyl ethanol of *R*-configuration $[\alpha]_D^{22}$ −31°2 (*c* 0.347; benzene) was obtained in 69% yield as described [8]. The optically active alcohol was treated as described above to afford 63% of trithiocarbonate I ($R^2 = CH_3$), m.p. 119°C (acetone), $[\alpha]_D^{22}$ +68° (*c* 0.185; benzene).

Reduction of trithiocarbonate

To a solution of I (0.2 g) in diethyl ether was added at 0°C under N_2 one molar equivalent of $LiAlH_4$. After 1 h the mixture was hydrolysed either by diluted NaOH or by water at 0 or 25°C. In every cases α-ferrocenylcarbinol was recovered partially racemized instead of the expected thiol.

p-Methoxybenzyl trithiocarbonate

To 0.1 mol of *p*-methoxybenzyl alcohol in 150 ml of dry THF was added NaH (1.1 mol) and the mixture was refluxed for 3 h. Then CS_2 (16 ml) were added and the reflux continued for 24 h. After addition of CH_3I (0.11 mol) and reflux for 2 h the mixture was cooled, poured into water, extracted with ether and treated. The NMR spectrum of the crude product showed 70% of trithiocarbonate and 30% of dithiocarbonate, these were separated by PLC (3 g of the crude material).

p-$CH_3OPhCH_2SC(S)CH_3$ (oil, less polar 1.4 g). NMR: δ 7.16 (4 H); 4.66 (2 H); 3.86 (O—CH_3); 2.80 (S—CH_3); mass spectrum: 244 (M^+); 168 ($M^+ - CS_2$); 121 (CH_3OPhCH_2) 100%.

p-$CH_3OPhCH_2SC(O)CH_3$ (oil, more polar), 0.55 g ν(C=O), 1660 cm^{-1}. NMR: δ 7.16 (4 H); 4.27 (2 H); 3.86 (O—CH_3); 2.46 (S—CH_3). mass spectrum: 228 (M^+); 168 (M^+ — COS); 121 (100%).

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