Novel Trithioanhydride Complexes of Transition Metals; *X*-Ray Crystallographic Characterization of $[(\eta\text{-}C_5H_5)(CO)\overline{FeSC(Fp)SC}S(Fp)]SO_3CF_3$, [Fp = $Fe(CO)_2(\eta\text{-}C_5H_5)$]

Vincenzo G. Albano,*[a] Dario Braga,[a] Luigi Busetto,*[b] Magda Monari,[a] and Valerio Zanotti[b]

[a] *Istituto Chimico 'G. Ciamician,' Facoltà di Scienze dell'Università, Via Selmi 2, 40126 Bologna, Italy*
[b] *Facoltà di Chimica Industriale dell'Università, Viale Risorgimento 4, 40136 Bologna, Italy*

Nucleophilic addition of the thione sulphur atom in the complexes $[FpC(=S)SML_n]$ [ML_n = Fp or $Re(CO)_5$; Fp = $Fe(CO)_2(\eta\text{-}C_5H_5)$] at the thiocarbonyl carbon atom in the complexes $[FpCS]^+$ gives five-membered metallacycles $[(\eta\text{-}C_5H_5)(CO)\overline{FeSC(Fp)SC}S(ML_n)]SO_3CF_3$, ascertained by an *X*-ray crystal-structure determination of the complex with ML_n = Fp; the reactivity of the exocyclic sulphur atom has been studied.

Although bis(thioacyl)sulphides (**1**) were reported for the first time in 1976,[1] their instability has precluded extensive investigation.[2] Now that the field of stabilization of unusual organic ligands by their complexation with transition metals is developing so rapidly[3] it is realistic to consider the synthesis of complexes containing the C_2S_3 unit. The ideal candidates for achieving such a goal are the complexes (**2**) and (**3**) (Scheme 1) since they may react together *via* nucleophilic addition of the basic[4] thione sulphur atom at the electrophilic[5] thiocarbonyl carbon centre. In fact if CH_2Cl_2 solutions of these derivatives are stirred together at room temperature for *ca.* 0.5 h, the deep green stable cationic derivatives (**4a**) and (**4b**) may be almost quantitatively (94% yield) isolated. In order to assign a structure to complexes (**4**)† unambiguously, an *X*-ray crystal-structure determination was undertaken for complex (**4a**).‡

Crystal data: (**4a**) $C_{23}H_{15}F_3Fe_3O_8S_4$, M = 772.2, monoclinic, space group $P2_1/n$, a = 9.68(1), b = 18.78(1), c = 15.40(1) Å, β = 92.83(5)°, U = 2797 Å^3, Z = 4, D_c = 1.83 g cm^{-3}, Mo-K_α radiation, λ = 0.7107 Å, 1456 observed reflections with $F_o > 5\sigma F_o$ from 3411 measured at room temperature on an Enraf-Nonius CAD4 diffractometer, θ range 2—20°. The structure was solved by standard methods and refined by full-matrix least-squares (SHELX 76)[6] with anisotropic thermal parameters for the iron and sulphur atoms and isotropic for the remaining; hydrogen atoms were placed in calculated positions. Final R = 0.12 (R' = 0.10); the crystals diffracted poorly.

The structure of the cation (**4a**) is shown in Figure 1 together with relevant bond parameters. It contains a C_2S_3 skeleton acting as a tetradentate ligand. One carbon and one sulphur atom [C(1) and S(3)] are chelated to a $Fe(CO)(\eta\text{-}C_5H_5)$ fragment forming a metallocyclopentane ring to which two Fp units are bonded through C(2) and S(1). The CO ligand bonded to Fe(2) points downwards while those bonded to Fe(1) and Fe(3) point upwards. The cation as a whole is asymmetric and in addition it contains a chiral centre at Fe(2). Among the two possible diastereoisomeric pairs the one with overall longer intramolecular contacts has been obtained. The FeC_2S_2 ring deviates slightly from planarity and, although the bond lengths have not been determined very accurately, two very short distances [C(2)–Fe(3) and C(1)–S(1)] support the electronic structure shown in Scheme 1, in which the C_2S_3 unit formally acts as a 6e donor. Delocalized π-bonding stabilizes the ring. We suggest that complexes (**4**) are formed *via* open-chain intermediates formed in a sterically enforced *Z* sulphur-addition step,[7] and these intermediates undergo ring closure and then chiral induction at Fe(2) to give the five-membered rings in a stereo- and diastereo-selective reaction.

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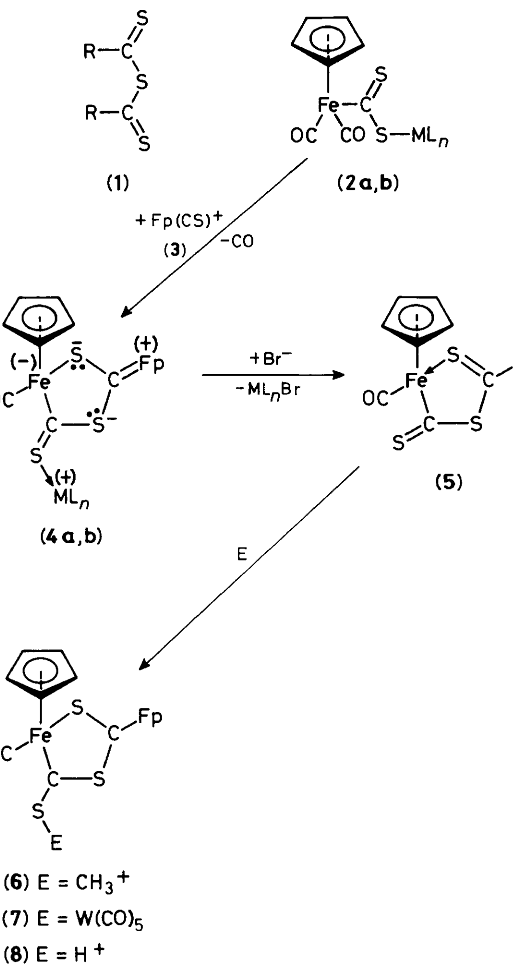
† Satisfactory microanalytical data were obtained for all the new complexes described. (**4a**): i.r. ν(CO) (CH_2Cl_2) 2045 and 2002s cm^{-1}; ν(CS) (KBr) 998ms, 934ms, 798m, and 750m cm^{-1}; ^{1}H n.m.r. (CD_3COCD_3) δ 5.58, 5.53, and 5.13 ($\eta\text{-}C_5H_5$); Λ_m(Me_2CO) 137 Ω^{-1} cm^2 mol^{-1}; (**4b**): i.r. ν(CO) (CH_2Cl_2) 2143m, 2044s, and 2003s cm^{-1}; ν(CS) (KBr) 997ms, 925ms, 802m, and 755m cm^{-1}; ^{1}H n.m.r. (CD_3COCD_3) δ 5.50 and 5.21 ($\eta\text{-}C_5H_5$); Λ_m(Me_2CO) 148 Ω^{-1} cm^2 mol^{-1}.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



Scheme 1. **a**; $ML_n = Fe(CO)_2(\eta\text{-}C_5H_5)(Fp)$
b; $ML_n = Re(CO)_5$

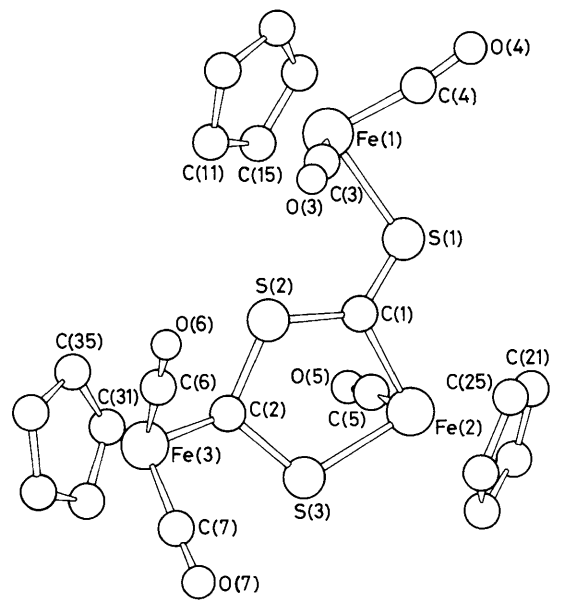


Figure 1. Perspective drawing of the cation (**4a**) showing the atom labelling; hydrogen atoms are omitted. Relevant bond distances (Å) and angles (°) with e.s.d.s in parentheses: Fe(1)–S(1), 2.35(1); C(1)–S(1), 1.50(3); C(1)–S(2), 1.65(3); C(2)–S(2), 1.73(4); Fe(3)–C(2), 1.67(3); C(2)–S(3), 1.88(4); Fe(2)–S(3), 2.32(1); Fe(2)–C(1), 2.08(3); average Fe–C–O distances, 1.77, 1.14; average Fe–C(Cp) distance 2.10; C(1)–S(2)–C(2), 122(2); S(2)–C(2)–S(3), 102(2); C(2)–S(3)–Fe(2), 112(1); S(3)–Fe(2)–C(1), 87(1); Fe(2)–C(1)–S(2), 116(2); Fe(3)–C(2)–S(2), 136(2); Fe(1)–S(1)–C(1), 107(1); S(1)–C(1)–S(2), 131(2).

The cationic derivatives (**4**) react with NEt_4Br in refluxing CH_2Cl_2 with preferential cleavage of the exocyclic metal–sulphur bond producing ML_nBr and (**5**)§ in 46% yield after 24 h.

This reaction is in agreement both with the dipolar nature of the $=S \rightarrow ML_n$ bond suggested above and with the reactivity of the metallodithiocarbene–metal complexes $[FpC(SR)SML_n]^+$ which are known to react with halide ions to form [FpC(S)SR] and ML_nX.[8] The nature of the trithioanhydride derivative (**5**) was confirmed further by its reactivity towards Lewis acids (E). In particular we have found that $CH_3OSO_2CF_3$ and $[W(CO)_5(thf)]$ (thf = tetrahydrofuran) easily react at the free sulphur atom of (**5**) to give the cationic alkylated (**6**)§ and the neutral metallated (**7**)§ complexes, respectively. The presence of the FeC_2S_3 group in these derivatives is shown by comparison of their i.r. spectra with spectra of the strictly analogous derivatives (**4**) which invariably show four ν(CS) absorptions that seem to be characteristic of these types of compounds. Finally complex (**5**) is immediately protonated in Et_2O with $HOSO_2CF_3$ to form (**8**) which has been characterized by its i.r. spectrum.§

The newly synthesized complexes contain the MS_2C_2 ring which has previously been observed in the few cases in which metal-promoted head-to-tail condensation of two CS_2 molecules has been studied.[9] Notwithstanding this the examples reported here represent the first derivatives in which the FeC_2S_2 ring is generated by a trithioanhydride C_2S_3 unit.

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§ (**5**), green crystals, m.p. 145 °C; i.r. ν(CO) (CH_2Cl_2) 2040s, 1994s, and 1958s cm^{-1}; ν(CS) (KBr) 998ms, 968m, 840m, and 700w cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 5.13 and 4.75 (η-C_5H_5); (**6**): i.r. ν(CO) (CH_2Cl_2) 2046 and 2004s cm^{-1}; ν(CS) (KBr) 1000ms, 932m, 802m, and 756m cm^{-1}; ^1H n.m.r. δ 5.32 and 5.17 (η-C_5H_5); 3.15 (CH_3); (**7**), brown crystals, m.p. 155 °C; i.r. ν(CO) (CH_2Cl_2) 2058ms, *2041*s, *1999*s, *1971*s, 1920vs, and 1887sh cm^{-1}; the bands due to the precursor (**5**) are italicised; ν(CS) (KBr) 998m, 942m, 806m, and 750w cm^{-1}; ^1H n.m.r. δ 8.43 and 5.15 (η-C_5H_5); (**8**): i.r. ν(CO) (CH_2Cl_2) 2050s and 2003s cm^{-1}.