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HYDROCARBON METAL SULPHIDE COMPLEXES

II*. CYCLOPENTADIENYLCARBONYLIRON TRITHIOCARBONATE COMPLEXES

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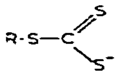
As a direct consequence of experimental observations which will be described, in detail, elsewhere, we were led to examine the preparation and properties of alkyl and aryl trithiocarbonate complexes of transition metals. In particular we were interested in those complexes which could also have a carbonyl and/or hydrocarbon ligand, but had not been previously reported. Several preparations of salts of the monoalkyl esters of trithiocarbonic acid have been recorded throughout the early literature[2], but examples of the corresponding transition metal complexes are scarce and poorly characterised[3]. These have been variously stated to be less stable than the corresponding alkali metal derivatives, to decompose into the metal mercaptide and carbon disulphide, and, for copper at least, prepared from copper alkylmercaptide and carbon disulphide[4]. It is generally accepted, however, that metal derivatives of monoalkyl esters of trithiocarbonic acid are fairly unstable (see *e.g.* ref. 5). Nevertheless it seemed possible that this type of complex could be stabilised by the incorporation of a good π-bonding ligand into the molecule.

The trithiocarbonate group has three sulphur atoms, each in a formally different environment, and each potentially able to bond to a suitable metal, either independently or in conjunction with at least one of the other two; in addition more than one metal atom could be involved in complex formation. Consequently a wide variety of different complexes can be envisaged incorporating the different modes of bonding. This first paper describes the preparation and properties of two different types of trithiocarbonate complex, and provides additional information on the currently topical μ-mercaptido compounds[6].



Iron forms the widest range of sulphur complexes, where the metal is in a low valency state, and also bonded to such ligands as carbon monoxide, nitric oxide, phosphines, or a cyclopentadienyl group. Several examples are described in the preceding paper of two types of compounds (III) and (V), which could conceivably undergo carbon disulphide insertion to yield trithiocarbonates. However, several trial experiments failed to reveal the expected reaction. By contrast cyclopentadienyldicar-

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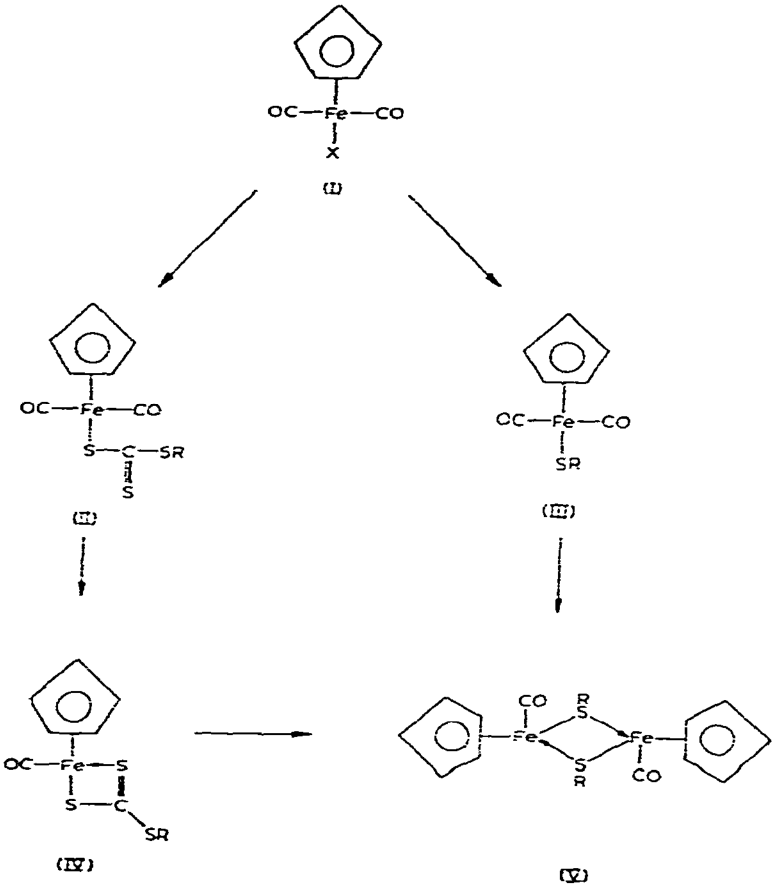
* Part I, Ref. 1.

bonyliron halide[7] reacted very readily at, or below, room temperature, with sodium alkyl or aryl trithiocarbonates. The experiment was best carried out in THF solution by reacting excess mercaptan with the calculated quantity of sodium hydride, at 0° or below, and then adding carbon disulphide to produce a yellow solution of the salt of the desired acid. Dropwise addition of a THF solution of cyclopentadienyldicarbonyliron halide resulted in an immediate colour change and precipitation of sodium halide. Chromatography revealed a number of products; for the methyl and ethyl derivatives the major component of each mixture was [(II), R = CH_3; C_2H_5] in approx. 75 % yield. However, sodium phenyl trithiocarbonate appears to be unstable, even in the presence of a gross excess of carbon disulphide. Consequently the principal product from such reactions was the terminal mercaptide[1] (III, R = C_6H_5) (56–85 %) and only 35 % of the trithiocarbonate complex (II, R = C_6H_5). These derivatives (II) are highly crystalline, orange red solids, with melting points near to 100°, and are stable to air in the solid state. In solution decomposition occurs slowly at ambient temperature, producing the same organometallic compound (IV) found as a by-product during the preparation of (II).



When decomposition of the dicarbonyls (II) was deliberately induced by irradiating benzene solutions with UV light, one CO per molecule was eliminated very smoothly and mononuclear monocarbonyl complexes (IV) were obtained in high yield. This photolytic displacement of CO parallels the conversion of σ-allyl to π-allyl complexes, described by Green and co-workers[8]. This similarity is further emphasized since the chelated trithiocarbonate group and the π-allyl group are isosteric, and thus the complexes (IV) and the less stable π-allyl-π-cyclopentadienyliron carbonyl are analogous. The monocarbonyl derivatives (IV, R = CH_3, C_2H_5, C_6H_5) are deep red air stable crystalline solids, having lower melting points (below 100°) but greater solubilities than their precursors. They are sublimable at room temperature, but not without some decomposition involving loss of carbon disulphide.

The bridged mercaptide complexes (V)[1] are produced when the dicarbonyl compounds are refluxed in toluene. These are the thermodynamically favoured isomers when R = CH_3 and C_2H_5, but both known isomers when R = C_6H_5. This conversion may be followed spectroscopically; under the reaction conditions (III) are not stable but it is probable that the preferred sequence is

$$(\mathrm{II}) \longrightarrow (\mathrm{IV}) \longrightarrow (\mathrm{V})$$

Unlike the stable isomers of (V), both (II) and (IV) can be chromatographed without difficulty, and do not appear to be unusually sensitive to acid.

INFRARED SPECTRA

The structures of compounds (II) and (IV) follow from their analyses and infrared spectra.

(*a*) *Carbonyl region*

The dicarbonyltrithiocarbonate complexes (II) show two fundamental stretching frequencies in the terminal carbonyl region (Table 1) as expected, and both values lie between those for (I) and (III). The monocarbonyl complexes (IV) each show a single terminal carbonyl frequency, and the position of this peak is almost insensitive

TABLE 1

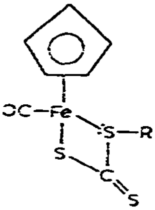
INFRA-RED SPECTRA IN THE METAL CARBONYL REGION

Values (cm^{-1}) obtained as CCl_4 solutions.

Compound	*Cl*	*I*	CH_3	C_2H_5	C_6H_5
(I)	2050 2010	2062[a] 2020			
(II)			2044 2002	2040 1998	2048 2001
(III)			2029 1981	2028[a] 1983	2030 1987
(IV)			1964	1966	1964

[a] As $CHCl_3$ solution.

to the nature of the group R [*cf.* value for (IV) in Table 1 with values for (V) given in Table 1 in Ref. 1]. This suggests that the S of the SR group is not bonded to an iron atom, and taken with other evidence supports structure (IV) but not structure (VI). A comparison of the position of this carbonyl frequency [(IV); R = CH_3), 1964 cm^{-1} in CCl_4; 1956 cm^{-1} in CH_2Cl_2] with that given for the recently reported analogous dimethyldithiocarbamate complex[9] (1940 cm^{-1} in CH_2Cl_2) reveals a shift in the expected direction; the larger electron releasing power of $(CH_3)_2N$ over CH_3S promotes a higher iron–carbon bond order, reflected in a shift to lower frequency for the carbonyl group in the carbamate complex.



(VI)

(*b*) *Other regions*

The compounds discussed in this paper do not show the pronounced "9–10" bands common to ferrocene chemistry[10]; even the C=S stretching frequency of (II) expected to occur close to this region[11,13], cannot be assigned with certainty, although it is observed that medium intensity bands in the region 1040–1053 cm^{-1} in (II) are not present in (IV). However, carbonyl region apart, the most striking difference between the spectra of (II) and (IV) is the appearance of a strong band near 950–970 cm^{-1} in the latter series. This band position appears to be sensitive to the nature of R, and is always accompanied by one, or two, other bands of lesser intensity, now known to be also characteristic of R. Thus the ethyl derivatives (IV), $C_2H_5SCS_2Mn(CO)_4$[14] and $(C_2H_5SCS_2)_2Ni_2(SC_2H_5)_2$[14] each show one other medium intensity band on the high frequency side, whilst the methyl derivative (IV) shows two other

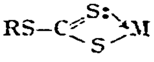
TABLE 2

OTHER CHARACTERISTIC INFRA-RED BANDS

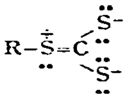
Values (cm^{-1}) obtained as CCl_4 solutions; m = medium; s = strong; sh = shoulder.

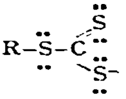
Compound	CH_3	C_2H_5	C_6H_5
(II)	1040 m	1052 m	1053 m
	605 m	603 m	611 m
	570 s	568 s	576 s
	542 m	540 m	548 m
(IV)	969 s	960 s (971 sh)	948 s
	560 m	561 m	560 m
	522 m	523 m	523 m

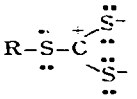
medium to weak bands, one either side of the predominant band. This principal band is probably associated with a C–S stretching mode of the chelated



system, since both the location and intensity of the band can be reconciled with such a grouping; to what extent this band can be attributed to a major contribution by any of the canonical forms







cannot be judged. One other easily recognisable and characteristic (but unassigned) difference between the spectra of the dicarbonyl (II) and monocarbonyl (IV) trithiocarbonates occurs in the 500–600 cm^{-1} region (Table 2). The dicarbonyls each exhibit three bands of medium to weak intensity, the centre band being the strongest, in the region 540–610 cm^{-1}. This pattern changes for the chelated monocarbonyls (IV) which show only two bands (m → w) in the 520–560 cm^{-1} region. Although outside the region usually assigned to a metal–sulphur stretching mode (400–440 cm^{-1})[12] it is noted that similar bands occur in the relevant regions for (III), (V) and $(C_2H_5SCS_2)_2Ni_2(SC_2H_5)_2$, but not for $[Ni(SC_2H_5)_2]_n$.

PMR SPECTRA

Several features of the PMR spectra of these sulphur complexes are worth noting. Referring to the values given in the table (Table 3) it is seen that the cyclopentadienyl resonance is virtually unchanged by variations of R within a group [(II), ~ 4.9 τ; (IV), ~ 5.4 τ]. This suggests that any inductive effect due to a change in R, operating through the system, is minimal. Also the shift in this cyclopentadienyl ring τ value from (II) to (IV) follows the same direction as found with (III) to (V), when both systems increase the coordination of sulphur to metal. Such increased

TABLE 3

NMR VALUES

τ-Values referred to TMS as internal standard in CS_2 solutions.

Compound	C_5H_5	CH_3	C_2H_5		C_6H_5
(II, R = CH_3)	4.92	7.40			
(II, R = C_2H_5)	4.92		6.80[a]	8.75[b,c]	
(II, R = C_6H_5)	4.96				2.61[d]
(IV, R = CH_3)	5.40	7.45			
(IV, R = C_2H_5)	5.40		6.85[a]	8.63[b,c]	
(IV, R = C_6H_5)	5.43				2.57[e]

[a] CH_2 quadruplet. [b] CH_3 triplet. [c] J = 7.5 cps. [d] Sharp; width at half-peak height 1.3 cps. [e] Very sharp; width at half-peak height < 1 cps.

shielding of ring protons is expected when carbonyl groups attached to the metal are replaced by other ligands of greater donor and/or poorer acceptor capacity. Finally, additional evidence against structure (VI) may be found from an inspection of the τ values for the group R of RS. These are usually rather strongly shielded when attached directly to an iron atom, and consequently in (VI) would be expected to occur closer to those in (III) or (V) than (II).

EXPERIMENTAL

For general experimental procedure and reagents see Part I[1]. The infrared spectra were obtained using a Perkin-Elmer model 125 grating spectrophotometer, and the PMR spectra recorded with a Perkin-Elmer 40 m/c instrument operating at 32.5°. Photochemical experiments were conducted using the equipment previously described. Microanalyses were by Dr. A. BERNHARDT (Max-Planck Institute) and osmometric molecular weight determinations by Mrs. M. KILPATRICK of this department.

Cyclopentadienyldicarbonyliron methyl trithiocarbonate (II, R = CH_3)

Methanethiol (2 ml, excess) was added from a syringe to a suspension of sodium hydride (1.94 g, 50% dispersion in mineral oil, 0.04 mole) in THF (20 ml) at −70°, using a CO_2 condenser. The mixture was stirred magnetically for 2 h when gas evolution had ceased and the internal temperature had fallen below 0°. Carbon disulphide (10 ml) in THF (10 ml) was added dropwise, causing the white suspension to completely dissolve, and leaving a yellow solution. Cyclopentadienyldicarbonyliron bromide (6.9 g, 0.027 mole) in THF (50 ml) was added to the cold solution over 10 min, the mixture allowed to warm to room temperature over 14 h, evaporated, and extracted with benzene (400 ml). The extract was chromatographed on active alumina using petrol as eluant.

The first band yielded a metal and carbonyl free, foul smelling yellow oil (800 mg) which was rejected. The second, red, band was (IV, R = CH_3) (400 mg, 20%), identified by m.p. and IR comparison with a sample obtained photochemically (see below). This was well separated from a major, orange-red band which was eluted, evaporated, and crystallised from methylene chloride/petrol yielding orange-red crystals of (II, R = CH_3) (5.9 g, 77%), m.p. 104.5°. (Found: C, 35.89; H, 2.78; O, 10.82; S, 31.97. $C_9H_8FeO_2S_3$ calcd.: C, 36.01; H, 2.69; O, 10.66; S, 32.05%.)

Cyclopentadienyldicarbonyliron ethyl trithiocarbonate (II, R = C_2H_5)

Sodium hydride (1.66 g, 50% dispersion, 0.034 mole) in THF (20 ml) was treated at 0° with ethanethiol (2.12 g, 0.034 mole) in THF (20 ml). Carbon disulphide (3 ml, excess) in THF (20 ml) was added after gas evolution had ceased (15 min), and the mixture stirred at 0° until a clear yellow solution had been formed. Cyclopentadienyldicarbonyliron iodide (8.1 g, 0.027 mole) in THF (50 ml) was added dropwise, the mixture stirred for 6 h at room temperature, evaporated, and the residue extracted with benzene (200 ml). The extract was filtered through kieselguhr, and chromatographed on neutral, 4 h alumina. Ether/petrol (1:1) eluted two bands; ether eluted a red gum (210 mg) which rapidly decomposed, and a black solid (40 mg) devoid of carbonyl absorption in the IR, and only slightly soluble in chloroform. These bands were not investigated further. The two bands eluted first were rechromatographed; petrol successively removed a trace of an organo-sulphur compound and (IV, R = C_2H_5) (25 mg, 1 %), identified by its IR spectrum. A main orange-red band yielded the complex (II, R = C_2H_5) which was isolated as orange red platelets (6.31 g, 74 %) from ether/petrol, m.p. 82.5°. (Found: C, 37.95; H, 3.13; O, 10.31; S, 30.33. $C_{10}H_{10}FeO_2S_3$ calcd.: C, 38.22; H, 3.21; O, 10.18; S, 30.59 %.)

Cyclopentadienyldicarbonyliron phenyl trithiocarbonate (II, R = C_6H_5)

Thiophenol (4.4 g, 0.04 mole) in carbon disulphide (10 ml) was added dropwise to a stirred suspension of sodium hydride (1.94 g, 50 % dispersion, 0.04 mole) in carbon disulphide (20 ml) maintained at 0°. A very slight reaction occurred to give a pale yellow colour. After 15 min THF (20 ml) was added dropwise, causing immediate gas evolution and an exothermic reaction. The resulting yellow solution was stirred for 10 min and a solution of cyclopentadienyldicarbonyliron bromide (7.7 g, 0.03 mole) in carbon disulphide (100 ml) and THF (50 ml) was added slowly. The mixture was stirred for 14 h, evaporated, extracted with benzene (250 ml), filtered through Kieselguhr and re-evaporated to small volume. Chromatography on active alumina using petrol eluted diphenyl disulphide (570 mg), a red gum (250 mg) containing mostly diphenyl disulphide but showing a single terminal metal carbonyl band in the IR, and a red solid (130 mg) grossly contaminated with diphenyl disulphide, but showing two bands in the terminal metal carbonyl region of the IR. Ether/petrol (1:1) eluted cyclopentadienyldicarbonyliron phenylmercaptide (3.915 g, 56 %)[1] (III, R = C_6H_5) and orange-red cyclopentadienyldicarbonyliron phenyl trithiocarbonate (II, R = C_6H_5) (2.085 g, 35 %), m.p. 106.5° from ether/petrol. (Found: C, 46.56; H, 2.85; O, 9.03; S, 26.48. $C_{14}H_{10}FeO_2S_3$ calcd.: C, 46.41; H, 2.78; O, 8.84; S, 26.55 %.)

When the above reaction was carried out using only a slight excess of carbon disulphide (3.2 g, 0.042 mole), diphenyl disulphide (800 mg) and (III, R = C_6H_5) (7.3 g, 85 %) were the only products at room temperature. When this reaction was repeated and the mixture refluxed, a yellow crystalline product was obtained before the addition of the bromide at room temperature; diphenyl disulphide (540 mg) and (III, R = C_6H_5) (2.785 g, 65 %) were the only products detected by chromatography.

The photochemical conversion of (II) to (IV)

(*a*) *R = CH_3*. The dicarbonyl complex (3.0 g, 0.01 mole) dissolved in benzene (250 ml) was irradiated for 6 h at room temperature. As in the subsequent experiments [(*b*) and (*c*)] very little decomposition occurred. The irradiated solution was evaporated and chromatographed on active alumina; petrol eluted an organo-sulphur compound (50 mg) which was rejected. *(Methyltrithiocarbonato)cyclopentadienyliron carbonyl* (IV, R = CH_3) (1.98 g, 78 %) was eluted with 20 % ether/petrol. An analytical sample, m.p. 55°, was obtained as ruby-red prisms from ether/petrol; it was volatile at room temperature/10^{-3} mm (Found: C, 35.16; H, 3.06; O, 6.07; S, 35.26; mol. wt., 277. $C_8H_8FeOS_3$ calcd.: C, 35.29; H, 2.98; O, 5.87; S, 35.34 %; mol. wt., 272.) Pure ether eluted (II, R = CH_3) (200 mg) (7 % recovery).

(*b*) *R = C_2H_5*. The above experiment was repeated using the ethyl derivative (II, R = C_2H_5) (3.0 g, 0.095 mole). Chromatography separated an organo-sulphur compound (band 1) (500 mg) (rejected) and (II, R = C_2H_5) (470 mg, 17 % recovery) (band 3) from *(ethyltrithiocarbonato)cyclopentadienyliron carbonyl* (IV, R = C_2H_5)

(1.68 g, 64 %) (band 2) ruby-red crystals (ether), m.p. 60°. (Found: C, 37.68; H, 3.71; O, 5.72; S, 33.37. $C_9H_{10}FeOS_3$ calcd.: C, 37.76; H, 3.53; O, 5.59; S, 33.62 %.)

(*c*) $R = C_6H_5$. *(Phenyltrithiocarbonato)cyclopentadienyliron carbonyl* (IV, $R = C_6H_5$) (490 mg, 62 %) was obtained as deep red crystals, m.p. 92° (ether/petrol) from the dicarbonyl complex (II, $R = C_6H_5$) (860 mg, 0.0028 mole) after 6 h irradiation. (Found: C, 46.50; H, 3.30; O, 5.14; S, 28.58. $C_{13}H_{10}FeOS_3$ calcd.: C, 46.72; H, 3.02; O, 4.79; S, 28.78 %.)

The conversion of (II) to (V) in refluxing toluene

(*a*) $R = CH_3$. A solution of cyclopentadienyldicarbonyliron methyl trithiocarbonate (2 g) in toluene (30 ml) was refluxed for 1 h, causing the colour of the solution to darken until it became brown-black. The metal carbonyl region of the infrared spectrum of this solution was recorded every 15 min; initially the intensity of the 2044 cm^{-1} and 2002 cm^{-1} peaks decreased as a new peak [due to (IV)] at 1964 cm^{-1} developed, but towards the end of the reaction this peak also decreased and was replaced by a single peak at approx. 1950 cm^{-1} (V). The toluene was evaporated at room temperature/10^{-3} mm and the residual brown gum chromatographed in ether/petrol (1:1) on neutral, 4 h alumina. A single olive-brown band was eluted (ν_{CO} 1950 cm^{-1} which yielded (V, $R = CH_3$) (700 mg, 54 %), m.p. and mixed m.p. 106–108°, after evaporation and subimation (100°/10^{-3} mm). The position of the metal carbonyl peak in the IR spectrum indicated that the product was the stable isomer[1] of (V, $R = CH_3$).

(*b*) $R = C_2H_5$. The decomposition of (II, $R = C_2H_5$) (1 g) in toluene (80 ml) at reflux was followed spectroscopically during 1 h. Following the work-up procedure described in (*a*), (V, $R = C_2H_5$) (490 mg, 73 %) was isolated and identified as the thermodynamically stable isomer by m.p. and IR (ν_{CO} 1952 cm^{-1}).

(*c*) $R = C_6H_5$. Cyclopentadienyldicarbonyliron phenyl trithiocarbonate (II, $R = C_6H_5$) (150 mg) was converted after 1 h in boiling toluene (30 ml) into both known isomers of (V, $R = C_6H_5$)[1]. Chromatography (neutral, 10 h alumina) using ether/petrol (1:4) separated the stable isomer (14 mg, 13 %) (ν_{CO} approx. 1940 cm^{-1}) from the less stable isomer (69 mg, 64 %) (ν_{CO} 1980 cm^{-1}) and showed that (II) had been completely consumed.

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SUMMARY

Sodium alkyl or aryl trithiocarbonates react with cyclopentadienyldicarbonyliron halide, producing cyclopentadienyldicarbonyliron alkyl or aryl trithiocarbonates [$C_5H_5Fe(CO)_2CS_3R$] which readily lose carbon monoxide. UV irradiation converts these dicarbonyls ($R = CH_3$, C_2H_5, C_6H_5) into chelated monocarbonyls, (alkyl- or aryltrithiocarbonato)cyclopentadienyliron carbonyl [$C_5H_5Fe(CO)CS_3R$], which suffer carbon disulphide elimination in refluxing toluene yielding the known di-μ-mercaptido-

is(cyclopentadienylcarbonyliron) $[C_5H_5Fe(CO)SR]_2$. The IR and PMR spectra of hese complexes are discussed.

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