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HYDROCARBON METAL SULPHIDE COMPLEXES

I. CYCLOPENTADIENYLCARBONYLIRON MERCAPTIDES

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Considering the fairly extensive range of transition metal sulphide complexes which also contain a π-bonded ligand, it was considered somewhat surprising that mononuclear derivatives, where a mercaptide group (–SR) is attached to a single metal atom, had not been reported. By contrast, a variety of binuclear and polynuclear compounds are known, where the metal atoms are linked by mercaptide bridges. The latter have been investigated quite extensively by Hieber* and his co-workers, and more recently by King[2], Schropp[3], and by Stone and co-workers[4], and the complete crystal structures of some derivatives are known (see *e.g.* ref. 5).

An empirical description of the bonding in these binuclear compounds can be obtained if it is assumed that each sulphur atom of the bridging groups effectively donates three electrons. Since these three electrons are shared between two metal atoms, it seems reasonable to suppose that such complex formation *could* take place in *at least* two distinct stages, involving bonding of one electron (as a radical) and then a pair of electrons, or *vice-versa*. An examination of the published experimental procedure for the preparation of many of the known compounds indicates that the mechanism of their formation could be accommodated by this simple hypothesis. In particular, complex formation resulting from those reactions where the rather weak disulphide bond suffers homolytic cleavage by a metal carbonyl, can be easily explained. Also, if the resulting bridging mercaptide product from the metal carbonyl does not possess a metal–metal bond, then a mononuclear derivative with a terminal sulphide group could be an intermediate. As a preliminary to a detailed investigation of possible mechanisms, an examination of the preparation and properties of terminal mercaptide complexes was undertaken. This paper describes the syntheses and subsequent reactions of some mononuclear iron carbonyl mercaptides, and employs the same method that we have previously found to be successful for other systems[6]. Since the completion of our work, King and Bisnette[7] have given a description of an entirely different route leading to (III, R = CH_3), but do not appear to have observed the spontaneous decay of this compound giving isomers of (V). Very recently Osborne and Stone[8] have given a preliminary description of another mononuclear mercaptide $C_6F_5SRe(CO)_5$.

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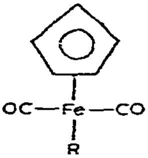
* Much of this work has been summarised in ref. 1.

DISCUSSION

It is quite clear from available information that should mononuclear mercaptide complexes be at all sensitive, they would probably not survive the experimental conditions that have always led to the isolation of the corresponding binuclear bridged species. However, an attractive method, which had not been exploited was the nucleophilic displacement of halogens by mercaptide anions[9], under non-hydroxylic conditions. The sodium salts of methyl, ethyl, and phenyl mercaptan obtained by addition of the thiols to sodium hydride in tetrahydrofuran, reacted readily with cyclopentadienyldicarbonyliron bromide. The major product from each reaction was the respective cyclopentadienyldicarbonyliron mercaptide (III). These compounds were produced in 60–85 % yield, and isolated as low-melting orange-brown to vermillion crystalline solids. They possess good air stability in the solid state, but are sensitive in solution. The phenyl derivative (III, R = C_6H_5) is very much more stable than the ethyl derivative (III, R = C_2H_5), which is only slightly more stable than its methyl analogue (III, R = CH_3). Nevertheless there is a pronounced increase in stability over the corresponding aryl- and alkyliron compounds[10] (II), resulting from the insertion of a sulphur atom. This is undoubtedly due in part to the availability of vacant orbitals in the sulphur, suitable for back-donation of electrons from the iron atom (see discussion of IR spectra).



(II)

It was of considerable interest, in view of the points discussed in the introduction, to effect the controlled dimerisation of these terminal mercaptide complexes. The two most reasonable routes for such a dimerisation would lead to (I) and (V).

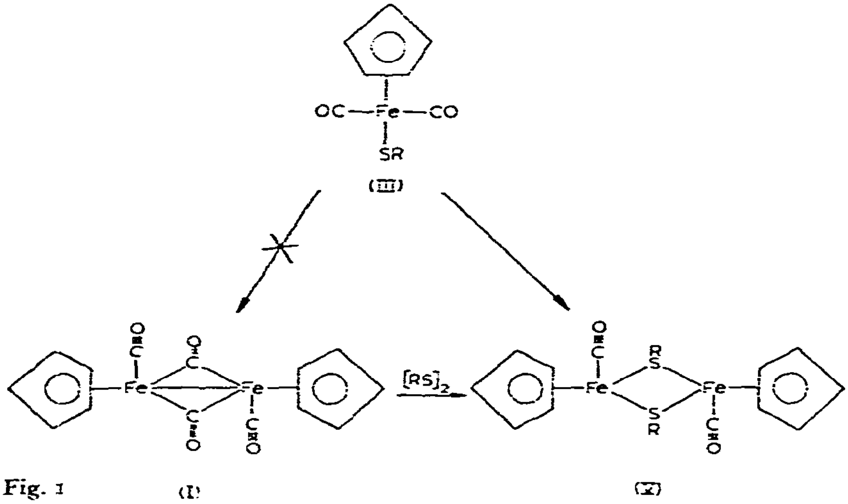
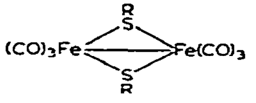


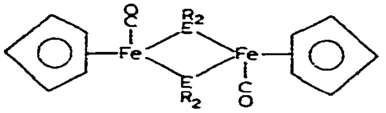
Fig. 1 (I) (V)

Only a single derivative of formula (V, $R = CH_3$) has been described[11], but examination shows that in fact a minimum of five geometrical isomers of this structure could exist, depending on the geometry of the iron–sulphur cycle* (Fig. 2). This assumption follows principally from the work of King[12], and Hayter[13]. The former has separated the *cis* and *trans* forms of sulphide (IV), whilst Hayter has isolated compounds arising from the two different stable arrangements of carbonyl and cyclopentadienyl groups, about the iron atoms in (VI). Furthermore complexes (V) and (VI) are isosteric.



(IV)

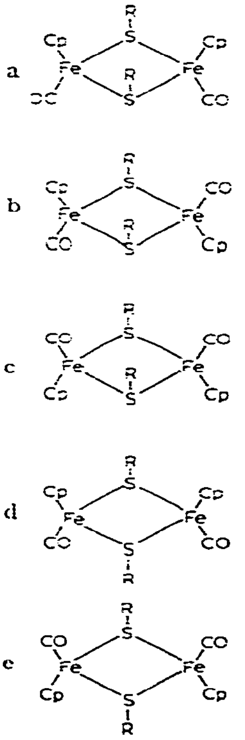
$R = CH_3$



(VI)

$E = As, P$

$R = CH_3, C_6H_5$



	Multiplicity	
	Cp	R
a	1	1
b	2	1
c	1	1
d	1	2
e	1	1

Fig. 2

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* The reported[4] $[C_5H_5Mo(CO)_2SCH_3]_2$ was isolated as a probable mixture of two isomers.

Controlled decompositions of (III, R = CH_3, C_2H_5, C_6H_5) were carried out (*a*) in solution at room temperature, (*b*) in refluxing benzene, and (*c*) by UV irradiation. The reactions occurred quite cleanly in the absence of air and in each instance only isomers of (V) were obtained; in no case was the tetracarbonyl (I) detected. At room temperature the reactions (*a*) proceeded rather slowly in either diethyl ether or THF solution. After 12 h the methyl derivative (III, R = CH_3) had suffered approximately 55 % conversion to (V, R = CH_3), (48 % yield). This isomer, m.p. 82°, was different from the known isomer[11], m.p. 109°, which was also produced in small yield after 14 h in THF. The low melting isomer was the exclusive product (68 %) when an ether solution of (III, R = CH_3) was irradiated with UV light for 6 h, but only the higher melting derivative was obtained after 6 h in refluxing benzene. The thermal instability of the m.p. 82° compound was demonstrated by its complete isomerisation under these conditions, and also less rapidly at room temperature in the solid state. Consequently obtaining the physical data on a pure sample of this isomer was a somewhat tedious process.

Parallel reactions involving the ethyl derivative (III, R = C_2H_5) gave very similar results, and allowed the isolation of two isomeric forms of (V, R = C_2H_5). The stability of this series appears to be only marginally greater than that of the equivalent methyl compounds.

A very pronounced difference was observed between the behaviour of the alkyl and phenyl compounds (III) and (V). Thus over 50 % of the terminal cyclopentadienyl dicarbonyliron phenylmercaptide was recovered after 18 h at room temperature in ether, and a detectable quantity (2 %) after 6 h in refluxing benzene. From both these experiments, as well as the UV irradiation of (III, R = C_6H_5), two isomers of (V, R = C_6H_5) were always obtained. This indication that the stabilities of the two isomers were more nearly equivalent was confirmed when only 50 % isomerisation occurred after the less stable compound was heated in refluxing benzene for 6 h.

It appears then that the less stable isomers are the products of kinetic control for (R = CH_3, C_2H_5) and that these easily revert to the thermodynamically favoured isomers. However, the qualitative observations on the stabilities of the phenyl isomers, together with the isolation of both isomers from all reactions suggests that while one isomer (m.p. 170°) is thermodynamically more stable than the other (m.p. 166°), both isomers can result by independent paths from kinetic control of the decomposition of (III, R = C_6H_5). There was no evidence of an equilibrium between these two isomers. Attempts are being made to obtain accurate kinetic data on these transformations.

In order to obtain samples for comparison, the method first used to obtain the stable complex (V, R = CH_3) in 9 % yield[11] from dimethyl disulphide and (I) was modified, so that the yield increased to 88 % (together with a trace of the unstable isomer). Applied to diethyl disulphide, only a 67 % yield of a stable isomer (V, R = C_2H_5) was obtained from (I). Diphenyl disulphide was much less reactive and 61 % (I) was recovered; two isomers of (V, R = C_6H_5) were isolated from this reaction, the stable one (21 % conversion) preponderating over the less stable (0.3 % conversion). Chromatography proved to be a much more advantageous method of isolating all these complexes than the sublimation process first used, but the stable isomers (V, R = CH_3, C_2H_5, C_6H_5) were sensitive and could not be rechromatographed without considerable decomposition. Notwithstanding partial isomerisation, the unstable isomers were chromatographed more easily; for (V, R = C_6H_5) this was eluted before the thermodynamically stable isomer, but for (R = CH_3, C_2H_5) these eluted after the stable isomers and could be hidden by decomposition products. The nature of these rather curious decomposition products has not been elucidated (see EXPERIMENTAL).

IR and PMR spectra: stereochemistry of complexes

From the location of the fundamental metal–carbonyl absorption bands the relatively poor acceptor properties of a sulphur atom for π-bonding to a metal have been noted previously[14,15]; the data obtained in this work support this suggestion. Furthermore a direct estimate of the effect of a sulphur atom is obtained by comparison between the alkyl(aryl)iron and alkyl(aryl)thio iron complexes (Table 1).

TABLE 1

INFRA-RED SPECTRA IN THE METAL CARBONYL REGION

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

Compound	*CH_3*	*C_2H_5*	*C_6H_5*
(II)^a	2010 1955	2010 1950	2020 1960
(III)	2029 1981	2028^b 1983	2030 1987
(V) stable	1951	1952	1978
unstable	1929	1929	1938

^{a} Ref. 10. ^{b} As $CHCl_3$ solution.

TABLE 2

τ-VALUE FOR C_5H_5 PROTON RESONANCE

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

Compound	*CH_3*	*C_2H_5*	*C_6H_5*
(III)	5.13	5.16	5.17
(V) stable	5.74	5.75	5.51^a
unstable	5.78	5.80	5.97

^{a} 5.42 τ in $CDCl_3$.

Comparison between the positions of the respective terminal metal carbonyl bands for the pairs of isomers (V) (Table 1) reveals a substantial (30–40 cm^{-1}) difference which is of value in identifying the unstable isomer. This always has the lowest frequency. Likewise the PMR spectra show that this isomer has a lower τ value for

TABLE 3

τ-VALUES FOR R GROUP PROTON RESONANCE

τ-Values referred to TMS in CS_2 solution.

R	*CH_3*	*C_2H_5*		*C_6H_5*
		Quadruplet	*Triplet*	
(III)	8.42	8.03^a	8.9^d	2.95
(V) stable	8.69	8.39^b	9.28	2.96^e
unstable	8.42	8.11^c	9.12	2.8^d

^{a} J = 7.2 cps. ^{b} J = 6.4 cps. ^{c} J = 7.2 cps. ^{d} Approximate centre of signal. ^{e} 2.89 τ in $CDCl_3$ solution.

the R group (Table 3) but a higher τ value for the C_5H_5 ring protons (Table 2) than the stable isomer. Studies of other systems[6] indicate that this pattern is of wider significance.

Referring to Fig. 2 it is seen that in principle the PMR spectra should be of value in identifying the stereochemistry of the ring system of (V) according to (a) through (c), except in the case of each set of protons for (b) and (d) being magnetically equivalent. For the six compounds (V) studied, the C_5H_5 resonance was very sharp and no compelling evidence for multiplicity of the R signal was found; structures (b) and (d) may be eliminated. For $R = CH_3$ the alkyl signals were sharp singlets for both isomers; for $R = C_6H_5$ the stable isomer gave a fairly narrow (width at half height = 2 cycles) phenyl signal but the unstable isomer gave a diffuse band which did not appear to be an overlapping doublet pattern. *Both* ethyl isomers showed further slight splitting ($\sim$ 2 cps maximum) in the methylene quartet, but since similar behaviour occurs with (III, $R = C_2H_5$) and $C_2H_5CS_3Mn(CO)_4$[16] this need not be taken in favour of structure (d). Further differentiation between possibilities (a), (c) and (e) by *e.g.* dipole moment measurements was not attempted.

EXPERIMENTAL

Melting points were measured in sealed, evacuated capillaries and corrected by graphical interpolation using known standards.

Infra-red spectra were obtained using a Perkin-Elmer model 125 grating spectrophotometer and calibrated against references at 1601, 1944 and 2000 cm^{-1}; PMR spectra were run on a Perkin-Elmer 40 m/c instrument operating at 32.5°.

Reagents

Purely for the sake of convenience the fraction of petroleum ether of b.p. 40–60° is referred to as petrol and the fraction b.p. 60–80° is called ligroin. All reactions were carried out under an atmosphere of oxygen-free nitrogen using rigorously dried solvents. Active alumina was Spence's "Activated Alumina Ungraded"; "x h", alumina is conveniently defined as that alumina which has been exposed to air for "x" hours. Neutral active alumina was prepared by storing alumina in ethyl acetate for several days, filtering, washing copiously with methanol and then water, and reactivating at 160° for at least 4 h.

For this series of experiments alkali washed glassware was used throughout.

Analyses were by Dr. A. BERNHARDT, Max-Planck Institute.

Cyclopentadienyldicarbonyliron mercaptide complexes (III)

$R = CH_3$. Excess methanethiol was added to sodium hydride (1.25 g, 50% dispersion, 0.025 mole) in ether (20 ml) at room temperature, in a flask equipped with a CO_2 condenser. The suspension was stirred magnetically until effervescence ceased and cyclopentadienyl dicarbonyliron bromide (5 g, 0.0194 mole) in ether added dropwise. After 12 h the mixture was filtered, evaporated, and the residue chromatographed on 12 h neutral alumina in pentane/ether (4:1). The unstable isomer of (V, $R = CH_3$), (30 mg, 0.08%) was eluted first, followed by (I) (50 mg, 0.15%) and (III, $R = CH_3$) (3.2 g, 75%). An analytical sample of the latter was obtained as light reddish-brown leaflets, m.p. 72°, from ether/pentane. It was readily soluble in all

common solvents except petroleum ether and the solutions were light sensitive. The solid sublimed at room temperature/10^{-2} mm.

In a similar experiment performed in THF over 16 h the yield of (V, R = CH_3) increased to approximately 0.25 % and (III, R = CH_3) decreased to 53 %.

R = *C_2H_5*. Ethanethiol (1.8 cc, 1.55 g, 0.025 mole), sodium hydride dispersion (1.29 g) and cyclopentadienyldicarbonyliron bromide (5.0 g) were reacted over 12 h in ether solution in a similar manner to the experiment described above. Chromatography separated an unstable isomer of (V, R = C_2H_5) (540 mg, 13 %), (I) (280 mg, 8 %), and (III, R = C_2H_5) (2.9 g, 57.5 %) which was eluted with ether. An analytical sample, m.p. 77.5–80°, was obtained as dark brown leaflets from ether/pentane. Its properties were similar to the methyl analogue.

R = *C_6H_5*. Thiophenol (4.4 g, 0.04 mole) was converted into its sodium salt in THF (40 ml) using 50 % sodium hydride dispersion (1.94 g, 0.04 mole). Cyclopentadienyldicarbonyliron bromide (7.7 g, 0.03 mole) in THF (50 ml) was added dropwise and the mixture stirred for 13 h at room temperature. After evaporation the residue was extracted with a minimum of cold benzene and chromatographed on active alumina. Elution with ether/petrol (1:1) gave diphenyl disulphide (800 mg), followed by a trace of (I), and (III, R = C_6H_5) (7.3 g, 85 %) m.p. 80.5° as vermillion crystals from ether/pentane. A similar experiment in ether gave a 72 % yield of (III, R = C_6H_5).

Decomposition of terminal mercaptide complexes (III)

A. At room temperature

(*1*) (*III*, *R* = *CH_3*). The methyl compound (500 mg) was stirred at room temperature in ether under nitrogen for 12 h. After evaporation of the solvent the products were isolated by chromatography on neutral 12 h alumina, eluting with ether/30–40° petroleum (1:4). The first olive-green-brown band gave the known isomer (V, R = CH_3) (30 mg, 8 %) which gave black crystals m.p. 109° from ether/pentane. The second yellow-brown band gave an isomer of (V, R = CH_3) (120 mg, 32 %) which crystallised from ether/pentane at −70° as dark brown crystals, m.p. 82°. Ether eluted unchanged starting material (200 mg, 40 %). In a second experiment (III, R = CH_3) (750 mg) in THF was converted during 12 h at room temperature into the second isomer of (V, R = CH_3) (320 mg, 48 %) m.p. 82°, and 340 mg (45 %) of the starting material was recovered.

(*2*) *R* = *C_2H_5*. Cyclopentadienyldicarbonyliron ethylmercaptide (500 mg) was stirred in ether for 12 h. The products were separated by chromatography on neutral 12 h alumina. The first yellow brown band eluted with ether/30–40° petrol (1:4) had an olive green leading edge but gave a single substance (V, R = C_2H_5) (120 mg, 25 %) m.p. 114.5° as dark brown crystals from petrol/ether; ether eluted starting material (200 mg, 40 %). The m.p. of this isomer of (V, R = C_2H_5) was found to be very variable, according to the rate of heating of the m.p. apparatus and the temperature at which the sample was inserted.

(*3*) *R* = *C_6H_5*. The phenyl derivative (III, R = C_6H_5) (500 mg) was stirred for 18 h in ether. Chromatography was effected on 1 h neutral alumina using ether/30–40° petroleum (1:9) as eluant. The first red-brown band gave dark brown crystals of (V, R = C_6H_5) (30 mg, 11 %) m.p. 166° after several recrystallisations from methylene chloride/ligroin. The second isomer of (V, R = C_6H_5) (120 mg, 43 %) was obtained from the yellow-brown band as black crystals, m.p. 170°, after recrystallisation from methylene chloride/ligroin. The third light purple band gave (260 mg, 52 % recovery) starting material.

B. In refluxing benzene

(1) $R = CH_3$. (III, R = CH_3) (1.5 g) was heated in refluxing benzene for 6 h. Chromatography separated (V, R = CH_3) (500 mg, 46 %) m.p. 109° from unchanged starting material (600 mg, 40 % recovery).

(2) $R = C_2H_5$. The ethyl derivative (4.0 g) was decomposed as in B(1) and gave the stable isomer of (V, R = C_2H_5) (3.1 g, 90 %) as dark brown crystals, m.p. 118°, after crystallisation from ether/petrol.

(3) $R = C_6H_5$. Both isomers (V, R = C_6H_5) were obtained from a similar experiment with (III, R = C_6H_5) (2.0 g). The first band on chromatography gave material (130 mg, 8 %) m.p. 166°; and the second band gave 1.5 g (90 %) of crystals, m.p. 170°; unchanged starting material amounted to 30 mg (1.5 %).

Repeated chromatography of each of the stable isomers (V) caused extensive decomposition. On active acid or neutral alumina they chromatographed as olive-green or brown bands in ether, but in petrol became turquoise and left some blue decomposition products on the column, although addition of ether once more partly reconverted the blue band into brown material. Brown acetone solutions of the stable complexes became turquoise blue on addition of water without causing precipitation; only traces of material could be re-extracted from these aqueous solutions.

C. By UV light

The irradiation experiments were performed under nitrogen at room temperature using interchangeable 3-necked cylindrical pyrex vessels (approximately 600 ml, 1500 ml, or 3000 ml capacity) constructed to hold in the centre neck the 500 watt lamp and water-cooled quartz jacket from a Hanovia 10 l photochemical reactor. The solution was stirred magnetically and the complete assembly placed in a large aluminium foil-lined box to afford visual protection and maximum irradiation.

(1) $R = CH_3$. (III, R = CH_3) (500 mg) in ether (300 ml) was irradiated for 6 h.

TABLE 4

ANALYTICAL DATA

Compound		ν_{CO}	*Percentage composition*							
	R	*(cm⁻¹)*	*Calculated*				*Found*			
			C	*H*	*O*	*S*	*C*	*H*	*O*	*S*
(III)	CH_3		42.89	3.60	14.29	14.32	42.81	3.75	14.42	14.15
	C_2H_5		45.42	4.24	13.45	13.47	45.26	4.22	13.62	13.34
	C_6H_5		54.57	3.53	11.19	11.21	54.50	3.53	11.43	11.11
(V)	CH_3	1951	42.88	4.11	8.16	16.36	43.06	4.00	8.28	16.25
	CH_3	1929	42.88	4.11	8.16	16.36	42.75	4.12	8.36	16.18
	C_2H_5	1952	45.74	4.80	7.60	15.26	46.05	4.92	7.83	15.13
	C_2H_5	1929	45.74	4.80	7.60	15.26	45.87	4.87	7.87	15.01
	C_6H_5	1938	55.82	3.91	6.20	12.43	55.74	3.90	6.42	12.39[a]
	C_6H_5	1978	55.82	3.91	6.20	12.43	55.73	3.87	6.41	12.28[a]

[a] Mass spectrometric molecular weights found 516; calculated molecular weight 516. (The mass-spectrometric behaviour of these and related compounds will be reported later[17].)

The less stable isomer (V, R = CH_3) m.p. 82°, (250 mg, 67 %) was the only product.

(2) $R = C_2H_5$. (III, R = C_2H_5) (500 mg) produced the less stable isomer (V, R = C_2H_5) (250 mg, 57 %) under similar conditions to *C(1)*.

(3) $R = C_6H_5$. The phenylmercaptide complex (3 g) was dissolved in benzene (250 ml) and irradiated for 6 h. Using neutral 10 h alumina, ether/petrol (1:4) eluted 0.44 g (46 %) (V, R = C_6H_5) m.p. 166°, and ether/petrol (1 : 1) eluted the isomer m.p. 170°, 0.41 g (42 %). A 49 % (1.46 g) recovery of starting material was obtained.

Isomerisation of the μ-mercaptido complexes (V)

The procedure for each of these experiments was similar; (V, R = CH_3; ν_{CO} 1929 cm^{-1}) and (V, R = C_2H_5; ν_{CO} 1929 cm^{-1}) were heated separately in refluxing benzene for 6 h, causing 100 % conversion to (V, R = CH_3; ν_{CO} 1951 cm^{-1}) and (V, R = C_2H_5; ν_{CO} 1952 cm^{-1}) respectively. Under identical conditions the conversion of (V, R = C_6H_5; ν_{CO} 1938 cm^{-1}) occurred only to the extent of 50 ± 5 %; the other isomer (V, R = C_6H_5; ν_{CO} 1978 cm^{-1}) was not affected, even after 24 h under these conditions.

Reaction of dicyclopentadienyltetracarbonyldiiron (I) with dimethyl disulphide

This reaction was carried out in an identical manner to that described by Stone *et al.*[11] using (I) (3.55 g, 0.01 mole) and dimethyl disulphide (5 ml, 0.056 mole) but the isolation procedure was more efficient. After the reaction had occurred, the reaction solution was filtered through kieselguhr and evaporated to dryness at room temperature/10^{-1} mm Hg. The resulting dark green solid was dissolved in a minimum volume of ether and chromatographed on neutral 10 h alumina. Petrol eluted two products: (*a*) (V, R = CH_3) (3.25 g, 88 %) as dark brown crystals, m.p. 108° dec. after several recrystallisations from ether/ligroin, lit.[11] m.p. 104–105° dec., ν_{CO} 1951 cm^{-1}; and (*b*) (V, R = CH_3) (20 mg), a brown solid, m.p. 82.5°, ν_{CO} 1929 cm^{-1}.

Reaction of dicyclopentadienyltetracarbonyldiiron (I) with diethyl disulphide

Dicyclopentadienyl tetracarbonyldiiron (I) (3 g, 0.0084 mole) and diethyl disulphide (1.5 ml, 0.012 mole) were heated in refluxing benzene (approx. 150 ml) for 7 h. The cooled solution was filtered, evaporated, and chromatographed on 12 h neutral alumina. Elution with ether/30–40° petrol (1 :4) separated (V, R = C_2H_5) (2.37 g, 67 %) which was obtained as dark brown crystals, m.p. 118° after recrystallisation from ether/petrol, ν_{CO} 1952 cm^{-1}. Starting material (I) (100 mg, 0.3 %) was recovered with ether elution.

Reaction between dicyclopentadienyltetracarbonyldiiron (I) and diphenyl disulphide

Dicyclopentadienyl tetracarbonyldiiron (I) (4 g, 0.011 mole) and diphenyl disulphide (3.1 g, 0.014 mole) were heated in refluxing benzene (approximately 200 ml) for 7 h, the mixture cooled, evaporated, and chromatographed on neutral 1 h alumina. Ether/30–40° petrol (1 :9) eluted successively, diphenyl disulphide and (*a*) (V, R = C_6H_5) (160 mg, 0.3 %), ν_{CO} 1938 cm^{-1}, m.p. 166° after recrystallisation; (*b*) (V, R = C_6H_5) (1.75 g, 21 %), ν_{CO} 1978 cm^{-1}, m.p. 170° after recrystallisation; and (*c*) starting material (I) (2.45 g, 61 % recovery).

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SUMMARY

Stable monomeric cyclopentadienyl dicarbonyliron alkyl(aryl)mercaptide complexes have been isolated and the controlled decompositions of these into pairs of isomeric binuclear di-μ-mercaptido-bis(carbonylcyclopentadienyliron) complexes studied. Specific methods are described for the kinetic or thermodynamic control of these decompositions. Improved procedures for the preparation of di-μ-mercaptido-bis(carbonylcyclopentadienyliron) are described. The stereochemistry of these complexes are discussed in relation to IR and PMR spectra.

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