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HYDROCARBON METAL SULPHIDE COMPLEXES
V*. COMPARISONS BETWEEN THE REACTIVITY OF CYCLOPENTA-, -HEXA-, AND -HEPTADIENYLIRON COMPLEXES

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SUMMARY

Stabilisation of iron carbonyl sulphide complexes by homocyclic dienyl ligands increases in the order cyclopentadienyl > cycloheptadienyl ≫ cyclohexadienyl. Nucleophilic attack of sulphide ion occurs at the cycloalkadienyl ligand in the corresponding cationic tricarbonyliron derivatives.

Considerable attention has been devoted to the various sulphide complexes with a carbonylcyclopentadienyliron skeleton[2,3,4]. Reactivity[5] and stereochemical[1,6] factors have been investigated in detail, using various techniques, and in particular the extent to which the organic residue attached to sulphur dictates bonding effects is understood quite well. This paper describes the behaviour of several homocyclic dienyl analogues of these iron carbonyl sulphide derivatives.

Previous investigations have suggested the possible relationship between π-cyclopentadienyliron compounds and the iso-π-electronic cyclohexadienyl and cycloheptadienyl systems[7]. The covalent iododicarbonyliron derivatives of each cyclic ligand have become available and these were chosen for comparative studies. It had already been demonstrated[2] that the iodide ligand of the cyclopentadienyl series could be displaced by sulphide anions to give the compounds $RSFe(CO)_2C_5H_5$. The stability of such compounds varied enormously with the nature of R. For simple alkyl derivatives spontaneous intermolecular displacement of CO occurred, yielding binuclear derivatives with bridging RS groups. For aryl derivatives similar behaviour was dictated by the nature of the substituents on the aromatic nucleus[8]. Extreme lack of reactivity occurred with the C_6F_5S group; $C_6F_5SFe(CO)_2C_5H_5$ was unaffected by UV irradiation[9] after 10 h in benzene solution, and 62% was recovered unchanged after pyrolysis at 200° for 1 h. From the latter reaction a small yield (~10%) of $C_6F_5Fe(CO)_2C_5H_5$ was obtained as a product of sulphur extrusion from the sulphide complex[9]. Very recently[10] it has been demonstrated that this sulphide complex is susceptible to photochemical substitution by phosphite. If similar trends in stability were displayed by the cyclo-C_6 and cyclo-C_7 complexes, then the (pentafluorophenyl)thio derivatives, (I, $R = SC_6F_5$), would be expected to be the most stable.

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* For Part IV see ref. 1.

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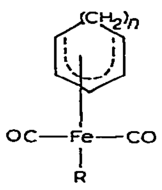
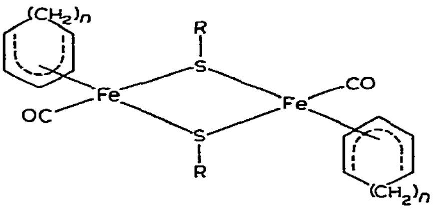


(I)



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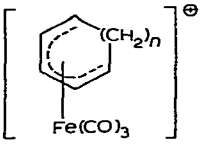
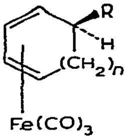


(III)



(IV)

Pentafluorothiophenoxide anion reacted smoothly with iododicarbonylcycloheptadienyliron to give the expected product (I, $n=2$, $R=SC_6F_5$). This compound suffered slow decomposition on irradiation with UV light, without forming the binuclear species (II, $n=2$, $R=C_6F_5$). A similar displacement reaction of the iodide was attempted with the anions of thiophenol and methanethiol respectively. In each case the reactions which were followed spectrometrically, were very sluggish at ambient temperature, and at elevated temperature extensive decomposition occurred. From thiophenoxide ion a brown product was obtained in low yield which was an inseparable mixture of (I, $n=2$, $R=SC_6H_5$) and (II, $n=2$, $R=C_6H_5$) according to IR evidence. Using the anion of methanethiol, the principal product was a green, carbonyl-free, polymeric substance of undetermined composition. The minor product was a brown substance which analysed approximately for the mononuclear species (I,

TABLE 1

INFRARED CARBONYL STRETCHING FREQUENCIES ASSIGNED TO COMPOUNDS (I), (II), AND (IV), IN CCl_4 SOLUTION UNLESS OTHERWISE INDICATED

Compound	R	$n=0^a$	$n=1$	$n=2$
(I)	I^b	2062	2049	2035
		2020	2003	2002
	C_6F_5S	2042^c	2040	2031
		1990	1975	1992
	C_6H_5S	2030		2066^f
		1987		1994
	CH_3S	2029		2016
		1981		2001
(II)	C_6H_5	1978^d		1973^f
	CH_3	1951^d		1968
(IV)	C_6F_5S		2045^e	2044^g
			1965	1972

[a] Ref. 2. [b] Ref. 7. [c] Ref. 9. [d] Stable isomer. [e] Liquid film. [f] Nujol. [g] KBr.

$n=2$, $R=SCH_3$), but IR evidence again indicated it to be a mixture with (II, $n=2$, $R=CH_3$). This material decomposed extensively during attempted purification by conventional methods, and the green polymeric substance was always obtained.

Iododicarbonylcyclohexadienyliron reacted rapidly with C_6F_5SNa to give the expected mononuclear mercaptide (I, $n=1$, $R=SC_6F_5$) according to IR evidence. However concomitant reactions occurred such that (I) decomposed, apparently to (II), and polymeric material. Thus the mononuclear material did not survive the reaction conditions. The instability of this material, (I, $n=1$, $R=SC_6F_5$), is somewhat surprising in view of the remarkable stability exhibited by the analogous cyclopentadienyl and cycloheptadienyl derivatives. However it has been noted previously[7] that for the corresponding cyanodicarbonyl iron complexes (I, $R=CN$) the C_5 and C_7 systems were stable whereas the cyclohexadienyl compound was not. It thus appears that dicarbonyl dienyl derivatives have the reversed order of stability associated with the tricarbonyl diene complexes.

The IR data for the derivatives (I) and (II) are collected in Table 1.

It has been shown that the 6- and 7-membered ring cations (III, $n=1$ and 2) can react with nucleophiles in three ways. When the attacking nucleophile is iodide, the product (I, $R=I$) is formed by displacement of carbon monoxide[7]. Most other nucleophiles (R) add to the hydrocarbon ligand (presumably by *exo*-attack[7,11]) to give (IV), whilst the third possibility is dimerisation[12] via C–C bond formation. It was therefore of interest to determine the nucleophilic character of the pentafluorothiophenoxide ion in such reactions. The fluoroborate complex (III, $n=2$) reacted with pentafluorothiophenoxide anion under various conditions to give an unstable yellow crystalline substance (IV, $n=2$, $R=SC_6F_5$); the analogous product from (III, $n=1$) was a much less stable yellow oil. Both products were adequately characterised by IR and mass spectrometry. In neither example was displacement [to give (I)] or dimerisation encountered. This behaviour parallels that of cyanide ion.

EXPERIMENTAL

For general procedures see Part I (ref. 2). In every case the progress of the reactions was followed by IR methods using a Perkin–Elmer model 237 spectrophotometer. Mass spectra were obtained by Dr. S. Aftalion on an A.E.I. MS-9 instrument. Pentafluorothiophenol was obtained from the Imperial Smelting Corporation.

Reactions of dicarbonylcycloheptadienyliodoiron with thiols

(*a*). *Pentafluorothiophenol.* This thiol (2.0 g, 0.01 mole) was added to sodium hydride (0.7 g, 50% dispersion, 0.015 mole) in ether (50 ml) and stirred until effervescence had ceased. Dicarbonylcycloheptadienyliodoiron (3.32 g, 0.01 mole) was added, and after 4 h at room temperature the mixture was filtered, evaporated, and the residue chromatographed on neutral alumina (3 h). The product (I, $n=2$, $R=C_6F_5S$) was isolated from a red-brown band eluted with dichloromethane, and gave red crystals, m.p. 84° (dec.) from petrol/dichloromethane. Yield 0.51 g (10%). (Found: C, 44.44; H, 2.38; F, 23.64; S, 7.73; $C_{15}H_9F_5FeO_2S$ calcd.: C, 44.58, H. 2.24; F, 23.50; S, 7.94%.)

(*b*). *Thiophenol.* The anion of this thiol (1.10 g, 0.01 mole) was prepared from sodium hydride dispersion (0.7 g, 0.015 mole) in either (50 ml)/and THF (50 ml), and the iodo complex (I, $n=2$, $R=I$) (3.32 g, 0.01 mole) added. The reaction mixture was stirred at ambient temperature for up to 20 h, filtered and evaporated. The residue was dissolved in dichloromethane, filtered rapidly, diluted with ligroin and cooled to −70°. The resulting brown precipitate was apparently a mixture of (I, $n=2$, $R=C_6H_5S$) and (II, $n=2$, $R=C_6H_5$) according to IR evidence [ν(CO) 2060, 1994, 1973 cm^{-1}]. Chromatography was not an effective method of separating this mixture.

When triethylamine was used as a base in place of sodium hydride, a mixed product was again obtained.

(*c*). *Methanethiol.* The anion of this thiol, obtained at −30° using sodium hydride (0.015 mole) in THF (50 ml) was stirred with the iodide (I, $n=2$, R=I) (2.98 g, 0.009 mole) at room temperature for 22 h. The mixture was filtered, evaporated, and the green-black solid residue dissolved in warm chloroform, leaving a dark green solid undissolved. The chloroform solution was rapidly cooled to −70° and diluted with ligroin yielding a brown precipitate. Repeated purification in this manner always gave some green polymeric substance. Analysis and IR spectroscopy (Table 1) indicated that the brown material was a mixture of (I, $n=2$, $R=SCH_3$) and (II, $n=2$, $R=CH_3$). Found: C, 38.95; H, 5.52; O, 14.53; S, 11.27. $C_{10}H_{12}FeO_2S$ calcd.: C, 47.66; H, 4.80; O, 12.70; S, 12.72%.)

Reaction of dicarbonylcyclohexadienyliodoiron with pentafluorothiophenol

Pentafluorothiophenol (0.04 g, 0.002 mole) was converted to its sodium salt in THF (50 ml) using sodium hydride (0.14 g, 50%, 0.003 mole) and treated with the iodo complex (I, $n=1$, R=I) (0.636 g, 0.002 mole) at ambient temperature. During 2 h the intense metal carbonyl peaks at approximately 2050 and 2000 cm^{-1} were replaced initially by two peaks of similar intensity at 2040 and 1975 cm^{-1} which also became less intense as the peak at 1958 cm^{-1} developed. A black solid which precipitated out of the mixture showed IR peaks at 2040, 1975 and 1958 cm^{-1} and is considered to be mixture of $C_6H_7Fe(CO)_2SC_6F_5$ and $[C_6H_7Fe(CO)SC_6F_5]_2$ with polymeric material. It could not be separated by crystallisation or chromatography.

Reactions of pentafluorothiophenoxide

(*a*). *With tricarbonylcycloheptadienyliron fluoroborate.* Pentafluorothiophenol (1 g, 0.005 mole) was added to sodium hydroxide (0.2 g, 0.005 mole) in water (50 ml) and a suspension of the fluoroborate salt (1.60 g, 0.005 mole) in water (50 ml) added, together with benzene (50 ml). After 24 h the yellow organic phase was separated, washed, dried, evaporated and the residue repeatedly crystallised from petrol at 0°. A crystalline yellow solid, (IV, $n=2$, $R=SC_6F_5$), m.p. approx. 5°, was obtained. Mass spectrometry showed this to have the formula $C_{16}H_9F_5FeO_3S$, mol.wt. 432. The $[P-3\ CO]^+$ ion was the base peak of the spectrum.

(*b*). *With tricarbonylcyclohexadienyliron fluoroborate.* The sodium salt of pentafluorothiophenol (4.77 g, 0.024 mole) in THF (50 ml) was obtained sodium hydride in the usual manner. The fluoroborate salt (6.06 g, 0.02 mole) was added and had completely reacted after 18 h at room temperature. The product did not crystallise, and decomposed when subjected to distillation at 0.002 mm Hg. A portion was successfully chromatographed in 30–40° petrol on a short column of "Florisil", the yellow eluate yielding a clear yellow liquid (IV, $n=1$, $R=SC_6F_5$) on evaporation. (Found: C, 43.83; H, 2.03; S, 7.97; mol.wt. mass spectrometrically, 418. $C_{15}H_7F_5FeO_3S$ calcd.: C, 43.19; H, 1.46; S, 7.69%; mol.wt., 418.)

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