Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

HYDROCARBON METAL SULPHIDE COMPLEXES IV*. SOME OBSERVATIONS ON THE ISOMERISATION OF BIS-μ-(ARYLTHIO)BIS(CARBONYLCYCLOPENTADIENYLIRON)

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(Received March 31st, 1969)

SUMMARY

Some observations on the stereochemistry of bis-μ-(arylthio)bis(carbonylcyclopentadienyliron) complexes are correlated with the NMR spectra of these materials. The kinetics and mechanism of isomerisation of an unstable phenylthio derivative to a stable form have been investigated in CS_2 and in THF solutions.

There is a large variety of di- and polynuclear metal carbonyl derivatives which have ligands bridging the metal atoms. Many of these complexes do not have metal–metal bonds and in these cases the bridging ligand is usually derived from a compound of oxygen, sulphur, nitrogen, phosphorus, etc., or the halogens. The majority of these complexes exhibit stereoisomerism, either at the metal atoms, or at the bridging groups, or at both locations. It has frequently been possible to prepare and separate these various stereoisomeric forms, which can then be either reconverted to an equilibrium mixture or transformed to the thermodynamically favoured configuration[2]. Typical of these latter species are the iron complexes $[CpFe(CO)SR]_2$ (I). These have been obtained in two isomeric forms[3] for various R groups and it was found that the "unstable" isomer could be converted to the thermodynamically favoured modification under reasonable conditions. It was of considerable interest to obtain an insight into the mechanism of this transformation, and a kinetic approach was therefore adopted.

At the time the work described in this paper was completed, the structures of the two isomeric materials (I) were not known. However, an X-ray crystallographic analysis[4] of the "stable" isomer (I, $R = C_6H_5$) has recently shown that this possesses structure (IIa) with a folded Fe–S ring system. Unfortunately it has not been possible to obtain suitable crystals of the unstable isomer for $R = C_6H_5$, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-FC_6H_4 or p-ClC_6H_4, so the exact structure of this modification of the compound is not known. Nevertheless this is believed to possess the structure (IIIa) for the previously described[3] and following additional reasons. The aryl groups are in the same relative environment according to ^1H NMR evidence. In addition to the appearance of the aromatic protons signal, the methyl and methoxy groups in

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* For Part III see ref. 1.
** Abstracted in part from the B.Sc. thesis of C.G.R., April, 1966.

p-tolyl and *p*-anisyl isomers respectively each only exhibit one type of CH_3 resonance. An even more sensitive probe into the environment of an aromatic group is the ^{19}F shielding parameter of a *p*-fluoro substituent. For the unstable isomer $[p\text{-}FC_6H_4SFe(CO)C_5H_5]_2$ a single, sharp, signal is exhibited at +117.5 ppm (relative to $CFCl_3$). This is 1.5 ppm downfield from the singlet of the stable isomer. These findings strongly suggest that of the 5 possible isomeric forms based on a planar ring system (*i.e.* for which there could be 10 conformers caused by folding of the ring) only the two *cis* isomers* need to be considered. One of these forms, (II), has a conformation (IIa) which is that of the stable isomer in the solid state. For structure (III) the sterically most likely is probably (IIIa)**. We therefore believe that the results described herein may relate to the isomerisation (IIIa)→(IIa).

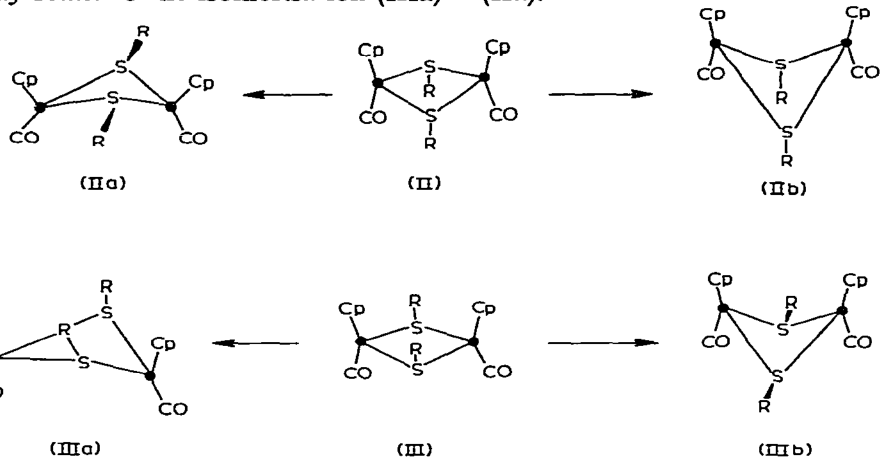

Fig. 1. Possible structures of $[RSFe(CO)C_5H_5]_2$. For simplicity iron atoms represented thus •.

KINETIC RESULTS

Practical difficulties associated with solubility and stability factors prevented the use of ^1H NMR techniques for studying the kinetics of the isomerisation. Nevertheless an IR method following the decay in intensity of the metal carbonyl peak of the unstable isomer in both CS_2 and THF solutions proved satisfactory. Only the

TABLE 1

VALUES (CM^{-1}) FOR METAL CARBONYL STRETCHING FREQUENCIES FOR $[C_6H_5SFe(CO)C_5H_5]_2$ ISOMERS

Solvent	Isomer (III)	Isomer (II)
CS_2	1932[a]	1972
THF	1933	1964

[a] An additional medium intensity peak at 1946 cm^{-1} was observed in this solvent; in CCl_4 solution the peaks at 1937 cm^{-1} and 1950 cm^{-1} were less well resolved.

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* In this context *cis* is used to describe the environment of ligands of the same type, *e.g.* the two RS groups, the two CO groups etc.

** We have no evidence relating to the possibility of the conformational interchanges (IIa) ⇄ (IIb), (IIIa) ⇄ (IIIb), etc.

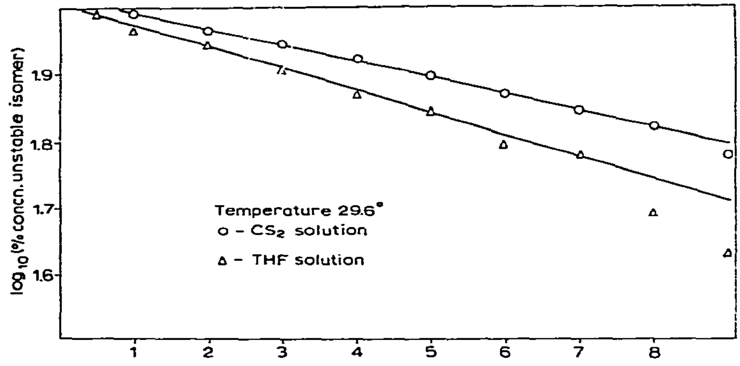


Fig. 2. Isomerisation rate of $[PhSFe(CO)C_5H_5]_2$.

parent system ($R = C_6H_5$) was investigated in detail. The values of the CO fundamental stretching frequencies for each isomer in these solvents are given in Table 1.

Using rigorously purified solvents the isomerisations were found to be first-order reactions in the absence of air. The first-order plots were linear to approximately 70% isomerisation, but the presence of decomposition products caused tailing off, and consequently the reactions could not be followed to completion (Fig. 2). Rate constants evaluated for each solvent at different temperatures are shown in Table 2. The

TABLE 2

RATE CONSTANTS, FOR CONVERSION (III, $R=C_6H_5$) TO (II, $R=C_6H_5$) IN SOLUTION, OBTAINED BY GRAPHICAL INTERPOLATION

Temp. (°C)	$k_1 \times 10^5$ (sec^{-1})	
	THF	CS_2
29.6	2.277	1.592
41.3	16.65	11.42
54.2	114.4	

values of k_1 increase with temperature as expected, but it is also interesting to note that the isomerisation is a faster process in the more polar solvent THF (D_{20} 7.58) than in CS_2 (D_{20} 2.65). This trend had been observed qualitatively in diethyl ether (D_{20} 4.34) and benzene (D_{20} 2.28). It is possible that participation of the oxygen lone pairs somehow assists the reaction, but a discrete long-lived THF-containing intermediate is not envisaged for several reasons. ^1H NMR measurements in THF-d_8 and

TABLE 3

CHANGES IN ENTROPY FOR CONVERSION (III, $R=C_6H_5$) TO (II, $R=C_6H_5$)

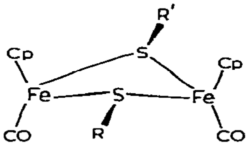
Temp. (°C)	ΔS (e.u.)	
	THF	CS_2
29.6	21.55±0.2	24.67±0.3
41.3	21.66±0.2	24.67±0.3
54.2	21.70±0.4	

C_6D_6/THF-d_8 mixtures revealed no "new" resonance signals. Secondly a 50% increase in rate is probably insufficient to justify anything other than casual involvement of solvent. This is supported by the values of changes in entropy ΔS (Table 3). These are only marginally lower in THF than in CS_2. From the values of k_1 the activation energy was calculated to be 30.68±0.60 kcal/mole in THF (from an Arrhenius plot) and 31.84±0.54 kcal/mole in CS_2.

Solubility factors limited the range of concentrations which could be investigated. However within experimental error the rate of isomerisation in THF at 41.3° was unchanged over the concentration range 0.00270 to 0.0223 *M*.

MECHANISM OF ISOMERISATION

Since it was not possible to determine from the kinetic results whether isomerisation was an intramolecular or an intermolecular process, a "mixing" experiment was performed. It was shown that the unstable *p*-totyl isomer was transformed into the more stable configuration at a very similar rate to the transformation of the unstable phenyl isomer. Approximately equimolar amounts of the unstable isomers (phenyl and *p*-tolyl) were therefore mixed and isomerised in refluxing benzene. Analysis of the products by ^1H NMR spectrometry in the C_5H_5 region* (τ 5.0–6.5 ppm) revealed that as well as the stable phenyl isomer (44%) and stable *p*-tolyl isomer (40%) an additional complex (16%) was produced. Although the latter could not be separated, mass spectrometry showed it to be the unsymmetrical material (IV) ($R=C_6H_5$; $R'=p\text{-}CH_3C_6H_4$). When a similar experiment was performed in THF at the dilution used for the kinetic measurements, the percentage of (IV) dropped to around 8%.



(IV)

The simplest mechanism which can be conceived for (III) changing to (II) involves inversion at both sulphur atoms. This is probably the limiting case at high dilution. A competing total dissociative-recombination mechanism becomes apparent at higher concentration of reactants, but is not predominant since the yield of (IV) does not approach the statistically expected value of 50%.

Inversion at sulphur has been observed previously for various palladium[5] and platinum[5,6] complexes. For some chelate compounds an energy barrier to their

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* In saturated CS_2 solution the phenyl complex showed a C_5H_5 singlet at τ 5.53 ppm (lit.[3] 5.51), the *p*-tolyl complex a C_5H_5 *doublet* at τ 5.55 ppm (separation 0.3 Hz), and the unsymmetrical complex (IV), a C_5H_5 doublet at τ 5.57 ppm (separation 0.3 Hz). Corresponding CH_3 signals occurred as singlets at τ 7.79 (ditolyl) and 7.68 ppm (complex IV). The origins of the doublet nature of the C_5H_5 signals for two of the above is obscure. However X-ray crystallography has demonstrated that in (II, $R = C_6H_5$) whilst the two C_5H_5 groups occupy similar relative positions in the molecule, one appears to possess a greater freedom for rotation than the other. The reasons for this difference are not clear. If this ease of rotation is the manifestation of different metal–C_5H_5 bond strength, then slight differences in the chemical shift for the protons of each ring would be expected.

TABLE 4

ANALYTICAL DATA

Compound		Analyses, found (calcd.) (%)			
No.	R	C	H	O	S
(II)	p-$CH_3C_6H_4$	57.59	4.33	5.99	12.13
		(57.38)	(4.40)	(5.88)	(11.80)
	p-$CH_3OC_6H_4$	54.20	4.32	11.28	10.98
		(54.18)	(4.20)	(11.10)	(11.15)
	p-FC_6H_4	52.30	3.42		11.73
		(52.20)	(3.29)		(11.62)
(III)	p-$CH_3C_6H_4$	57.59	4.02	6.41	12.26
		(57.38)	(4.40)	(5.88)	(11.80)
	p-$CH_3OC_6H_4$	54.06	4.23	11.25	11.08
		(54.18)	(4.20)	(11.10)	(11.15)
	p-FC_6H_4	52.29	3.31		11.67
		(52.20)	(3.29)		(11.62)

interconversion of about 5 kcal has been estimated. For other platinum complexes E_a is around 18 kcal/mole. However for each of these compounds an equilibrium state exists which differentiates them from the iron compounds described in this paper. Nevertheless the mechanism for the inversion of each of the systems is probably similar. This could involve the displacement of one sulphur lone pair by the other lone pair on the same tetrahedral sulphur atom, with concomitant rotation around the formally single Fe–S bond (Fig. 3). The conversion (III)⟶(II) is achieved by the same process occurring at both sulphur atoms. It is not known whether steric effects alone present sufficient motivation for the irreversible change (III)⟶(II), but the relative importance of electronic effects is being investigated.

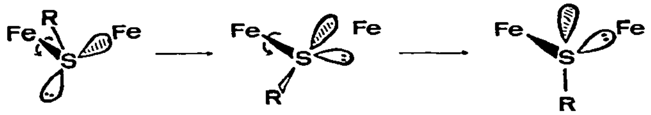

Fig. 3. Mechanism of isomerisation.

EXPERIMENTAL

For general comments see Part I (ref. 3).

Preparation of bis-μ-(arylthio)bis(carbonylcyclopentadienyliron) complexes, (II) and (III)

(*a*). $R = C_6H_5$. These were prepared by the methods in ref. 3.

(*b*). $R = p\text{-}CH_3C_6H_4$. The sodium salt of toluene-*p*-thiol was reacted with bromodicarbonylcyclopentadienyliron to yield (*p*-tolylthio)dicarbonylcyclopentadienyliron (92%), m.p. 84–85° as dark green-black crystals; IR (CCl_4): ν(CO) 2026, 1987 cm^{-1}; ^1H NMR (CS_2): τ 2.98 (C_6H_4), 5.21 (C_5H_5) 7.79 (CH_3) ppm. (Found: C, 56.11; H, 4.06; O, 11.04; S, 10.74. $C_{14}H_{12}FeO_2S$ calcd.: C, 56.01; H, 4.00; O, 10.67; S, 10.69%.) This terminal mercaptide was decomposed by UV light, using the preparative and isolation techniques described in Part I. The unstable isomer (III, R=p-$CH_3C_6H_4$), m.p. 196°, was obtained as a black solid in 50% yield. The light brown stable isomer (II, R=p-$CH_3C_6H_4$), m.p. 190°, was obtained in 35% yield.

When di-p-totyl disulphide and dicyclopentadienyldiiron tetracarbonyl were heated together in refluxing benzene, the unstable isomer (III) (1%) was produced together with the stable isomer (II) (82%).

(*c*). *R*=*p*-$CH_3OC_6H_4$. [(p-Methoxyphenyl)thio]dicarbonylcyclopentadienyliron [m.p. 61°, (lit.[7] m.p. 55°)] was irradiated in benzene solution with UV light for 6 h. The progress of the reaction was monitored by IR and TLC techniques. Chromatography on neutral alumina allowed the separation of (III, R=p-$CH_3OC_6H_4$) softening at 126°, m.p. 185°, from (II, R=p-$CH_3OC_6H_4$), m.p. 183°.

(*d*). *R*=*p*-FC_6H_4. [(p-Fluorophenyl)thio]dicarbonylcyclopentadienyliron was obtained in approximately 25% yield as dark maroon crystals, m.p. 63°, from the sodium salt of p-fluorothiophenol and $C_5H_5Fe(CO)_2I$. IR (CS_2): ν(CO) 2028, 1982 cm^{-1}; ^1H NMR: τ 2.67 (q), 3.35 (t) (C_6H_4), 5.19 (C_5H_5) ppm. (Found: C, 51.45; H, 3.04; S, 10.43. $C_{13}H_9FFeO_2S$ calcd.: C, 51.34; H, 3.01; S, 10.54%.)

Irradiation of this material in benzene with UV light gave the two desired compounds; the unstable isomer (III, R=p-FC_6H_4), m.p. 192°, was separated by chromatography from the stable isomer (II, R=p-FC_6H_4), m.p. 187°.

TABLE 5

SPECTROSCOPIC DATA

Compound		IR[a] ν(CO)	^1H NMR[a], τ (ppm)		
No.	R		C_6H_4[b]	C_5H_5	CH_3
(II)	p-$CH_3C_6H_4$	1973(b)	2.94(c)	5.42(c)	7.76(c)
			~2.9(d)	5.60(d)	7.81(d)
	p-$CH_3OC_6H_4$	1969(d)	~3.0(d)	5.62(d)	6.31(d)
	p-FC_6H_4	1968(b)		5.41(c)	
				5.58(d)	
(III)	p-$CH_3C_6H_4$	1938(a)	2.76(c)	5.87(c)	7.70(c)
		1931, 1944(d)	2.86(d)	6.02(d)	7.73(d)
	p-$CH_3OC_6H_4$	1929(d)	2.98(d)	6.01(d)	6.26(d)
	p-FC_6H_4	1932(d)		5.83(c)	
		1936(b)			

[a] Solution in (a) CCl_4, (b) $CHCl_3$, (c) $CDCl_3$, (d) CS_2. [b] Centre of A_2B_2 multiplet.

Kinetic studies

Accurately known weights of the stable and unstable phenyl isomers were weighed into a tube and diluted with solvent such that the solution had an overall concentration of 4 mg/cc (0.00775 *M*) in THF and 3 mg/cc in CS_2. The spectra of these solutions were recorded in the region 2000–1900 cm^{-1} for 8 different concentration ratios in the range 7% stable isomer to 93% stable isomer. The positions of the maxima in each solvent are recorded in Table 1. Graphs of % isomer concentration *vs.* relative intensity of carbonyl absorption were linear to 80% (stable isomer) in THF and approximately 60% (stable isomer) in CS_2. A Perkin–Elmer 237 grating model spectrophotometer was used throughout the kinetic measurements.

Experimental procedure. In a typical run the unstable isomer (32 mg) was dissolved in THF (2 cc) and filtered through a kieselguhr/charcoal pad into a small flask. The pad was washed with up to 6 cc of THF to give a solution of the required concentration. The flask was purged with nitrogen, sealed with a rubber "Suba-Seal", and immersed in the constant temperature bath. Aliquots were withdrawn thereafter at specific time intervals, using a syringe, and quenched in a CO_2 bath. Spectra were recorded immediately and the isomer compositions estimated by comparison of the ratios of the two MC–O peaks using the empirical graph obtained for known mixtures. Using this monitoring process the data gave good linear plots of $\log_{10}[\%$ composition$]$ *vs.* time (Fig. 2). Estimated rate constants from the slopes of the graphs were reproducible to better than 5% for up to 3 runs.

In this manner rate constants were determined at this concentration for temperatures of 29.6, 41.3 and 54.2°. The procedure was repeated for concentrations of 0.0223, 0.00775 and 0.00270 *M* at 41.3°.

Using CS_2 as solvent, reactions were carried out at 29.6 and 41.3° in a manner similar to that described above.

In all cases solvents were redistilled under N_2 immediately before use. THF was purified by distillation from $LiAlH_4$.

ACKNOWLEDGEMENTS

The authors thank International Nickel Ltd. for generous supplies of iron carbonyl. The ^{19}F NMR spectra were obtained through the courtesy of M. Green of Perkin–Elmer Ltd. using a 60 Mc instrument equipped with a CAT.

REFERENCES

1 E. S. Bolton, R. Havlin and G. R. Knox, *J. Organometal. Chem.*, 18 (1969) 153.
2 M. Ahmad, R. Bruce and G. R. Knox, *Z. Naturforsh.*, *B*, 21 (1966) 289.
3 M. Ahmad, R. Bruce and G. R. Knox, *J. Organometal. Chem.*, 6 (1966) 1.
4 G. Ferguson, C. Hannaway and K. M. S. Islam, *Chem. Commun.*, (1968) 1165.
5 E. W. Abel, R. P. Bush, F. J. Hopton and C. R. Jenkins, *Chem. Commun.*, (1966) 58.
6 P. Haake and P. C. Turley, *J. Amer. Chem. Soc.*, 89 (1967) 4611.
7 E. S. Bolton, R. Havlin, G. R. Knox, J. Lyon, R. Greatrex and N. N. Greenwood, Part VI, to be published.