Journal of Organometallic Chemistry, 85 (1975) 89—99

REACTIONS OF METAL CARBONYL DERIVATIVES

XVII*. TRI- AS WELL AS DI-NUCLEAR PRODUCTS FROM THE REACTIONS OF BIS(DICARBONYL-η-CYCLOPENTADIENYLIRON) WITH VARIOUS DIALKYL DISULPHIDES**.

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(Received August 12th, 1974)

Summary

The reaction of $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ with the dialkyl and diaryl disulphides R_2S_2 ($R = CH_3$, C_2H_5, i-C_3H_7, t-C_4H_9, $CH_2C_6H_5$ and C_6H_5) produces a trinuclear product characterised as $[Fe_3(\eta\text{-}C_5H_5)_3(CO)_2(S)SR]$, as well as the dinuclear derivatives $[Fe(\eta\text{-}C_5H_5)(CO)SR]_2$. The spectroscopic properties, including Mössbauer, and the electrochemical behaviour of the trinuclear species are discussed. Whereas the alkyl sulphido complexes $[Fe(\eta\text{-}C_5H_5)(CO)SR]_2$ ($R = CH_3$, C_2H_5, i-C_3H_7 and n-C_4H_9) can be isolated in two isomeric forms, corresponding derivatives of the bulkier disulphides R_2S_2 (R = t-C_4H_9 and $CH_2C_6H_5$) are obtained as single isomers only. On the other hand three isomers of the phenyl sulphido derivative $[Fe(\eta\text{-}C_5H_5)(CO)SC_6H_5]_2$ can be isolated. The nature of the isomerism is discussed.

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[*] For Part XVI see ref. 1.

[**] A preliminary communication of some of this work has appeared [2].

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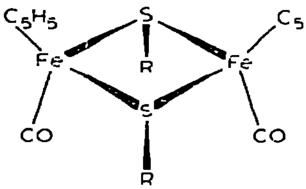
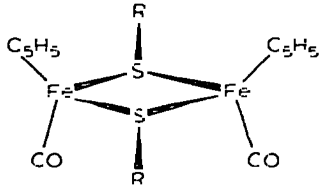
Introduction

The first compound of the type [Fe(η-C_5H_5)(CO)SR]$_2$ to be reported [3] was the methyl derivative synthesised by reaction of [Fe(η-C_5H_5)$(CO)_2$]$_2$ with $(CH_3)_2S_2$ in 2,2,4-trimethylpentane under reflux. Subsequent studies [4, 5] have shown that the ethyl, tertiary butyl and phenyl derivatives may be obtained similarly or by the thermal or photochemical degradation of [Fe(η-C_5H_5)$(CO)_2$SR].

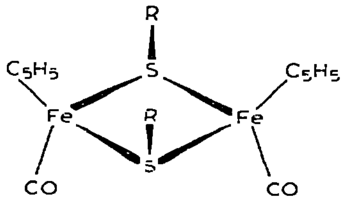
Five stereoisomers or [Fe(η-C_5H_5)(CO)SR]$_2$ are possible and these are illustrated below:



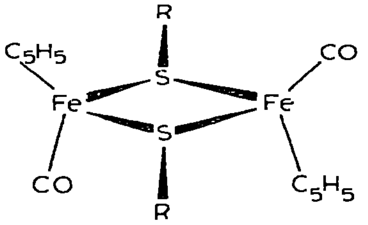
cis-(I)



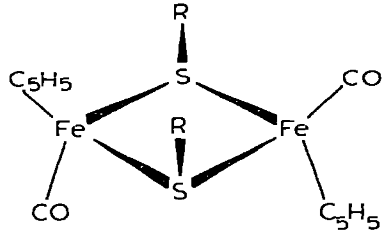
cis-(II)



cis-(III)



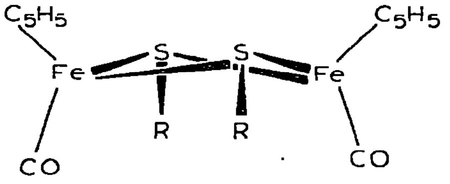
trans-(I)



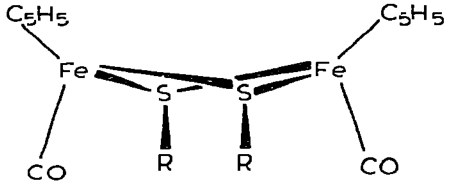
trans-(II)

The methyl, ethyl and phenyl derivatives, [Fe(η-C_5H_5)(CO)SR]$_2$ (R = CH_3, C_2H_5 or C_6H_5), have been isolated in two isomeric forms, one of which is thermally unstable with respect to the other [5]. The NMR spectra of all six compounds were shown to contain only single cyclopentadienyl and methyl or phenyl resonances, thereby eliminating structures *cis*-(II) and *trans*-(II) as possibilities, and the C—O stretching frequency for the stable isomer was found to be ca. 20-40 cm^{-1} higher than that for the unstable isomer. Two isomeric forms have also been isolated for the analogous phosphino and arsino derivatives [Fe(η-C_5H_5)(CO)E$(CH_3)_2$]$_2$ (E = P or As). For each of these compounds one isomer was shown to give NMR spectra containing just a single methyl resonance; this is split into a triplet in the case of the phosphino compound as a result of coupling with the two phosphorus atoms [6]. In contrast the NMR spectra of the second isomer were shown to contain two methyl resonances and this was taken to indicate non-equivalence of the two methyl groups bonded to each phosphorus or arsenic atom. On the basis of these results it was proposed that the former isomer contains the two cyclopentadienyl rings *trans*-disposed with respect to the Fe_2E_2 ring and that the latter contains them *cis*-disposed [6]. A planar Fe_2E_2 ring was assumed. Significantly the C—O stretching frequency for the *cis* isomer was found to be 37 cm^{-1} higher than that for the *trans* isomer.

For a non-planar Fe_2S_2 ring each of the five isomers represented above can exist in two conformational forms as shown below for isomer *cis*-(I):

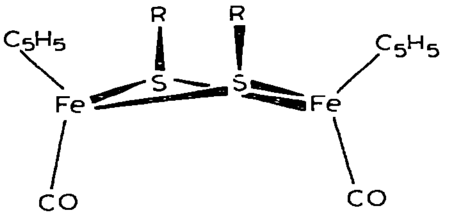


(a)



(b)

The crystal structure of the stable isomer of $[Fe(\eta\text{-}C_5H_5)(CO)SC_6H_5]_2$ has been determined and a slight puckering of the Fe_2S_2 ring established [7]. The structure of the compound is that represented by *cis*-(I) (a). Primarily on the basis of NMR data for $[Fe(\eta\text{-}C_5H_5)(CO)SR]_2$ (R = C_6H_5, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-FC_6H_4 or *p*-ClC_6H_4), the unstable isomer described above has been proposed [8] to have the structure shown below:



The kinetics of isomerisation of the unstable isomer to the stable isomer has been reported [8] for $[Fe(\eta\text{-}C_5H_5)(CO)SR]_2$ (R = aryl group).

As part of a general study of the oxidative behaviour of bridged dinuclear derivatives of iron, in which it was necessary to synthesise compounds of the type $[Fe(\eta\text{-}C_5H_5)(CO)SR]_2$, it was found that the reactions of $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ with dialkyl disulphides afford tri- as well as di-nuclear products. These compounds as well as the isomerism of $[Fe(\eta\text{-}C_5H_5)(CO)SR]_2$ are now discussed.

Results and discussion

Treatment of $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ with the dialkyl disulphides R_2S_2 (R = CH_3, C_2H_5, i-C_3H_7 or $CH_2C_6H_5$) in benzene under reflux gave the dinuclear derivatives $[Fe(\eta\text{-}C_5H_5)(CO)SR]_2$ in high yield, and a similar reaction in xylene yielded $[Fe(\eta\text{-}C_5H_5)(CO)S\text{—t-}C_4H_9]_2$. The dimer $[Fe(\eta\text{-}C_5H_5)(CO)SC_6H_5]_2$ on the other hand was best obtained by ultraviolet irradiation of a refluxing solution of $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ and $(C_6H_5)_2S_2$ in benzene. These reactions also afforded the mononuclear species $[Fe(\eta\text{-}C_5H_5)(CO)_2SR]$ and a third type of product in very low yield which, in the case of the reactions involving dimethyl, diethyl, di-tert-butyl and dibenzyl disulphide, could be separated from the major

TABLE 1

MELTING POINTS AND ANALYTICAL AND MOLECULAR WEIGHT DATA

Compound[a]	M.p. (°C)	Analyses found (calcd.) (%) C	H	S	Others	Mol. wt. Found (calcd.)
cis-[FeCp(CO)SMe]$_2$	102	43.3 (42.9)	4.0 (4.1)			
trans-[FeCp(CO)SMe]$_2$	93	42.8 (42.9)	3.9 (4.1)			
cis-[FeCp(CO)SEt]$_2$	110	45.9 (45.7)	4.8 (4.8)			
cis-[FeCp(CO)S-i-Pr]$_2$	158	48.2 (48.2)	5.5 (5.4)	14.3 (14.3)		
cis-[FeCp(CO)S-t-Bu]$_2$	136	50.5 (50.4)	5.8 (5.9)	13.5 (13.5)		
cis-[FeCp(CO)SBz]$_2$	129	56.9 (57.4)	4.3 (4.4)	12.0 (11.8)		
cis-[FeCp(CO)SPh]$_2$ (A)	164	55.8 (55.8)	3.9 (3.9)			
cis-[FeCp(CO)SPh]$_2$ · ½PhH (C)	127	58.5 (58.4)	4.0 (4.2)			
trans-[FeCp(CO)SPh]$_2$ (B)	165	54.5 (55.8)	3.8 (3.9)			
[Fe$_3$Cp$_3$(CO)$_2$(S)SMe]	197[b]	44.3 (45.0)	3.8 (3.8)	12.3 (13.4)	32.4 (34.9) (Fe) 6.7 (6.7) (O)	503 (480)[c]
[Fe$_3$Cp$_3$(CO)$_2$(S)SEt]	178[b]	44.6 (44.6)	3.9 (3.9)		32.0 (32.7) (Fe)	
[Fe$_3$Cp$_3$(CO)$_2$(S)S-t-Bu]	151[b]	46.5 (46.7)	4.5 (4.5)	11.7 (11.9)	29.8 (31.0) (Fe) 5.7 (5.9) (O)	586 (540)[c]
[Fe$_3$Cp$_3$(CO)$_2$(S)SBz]	188[b]	50.2 (50.2)	3.9 (3.9)	11.1 (11.2)	29.3 (29.2) (Fe) 5.7 (5.6) (O)	580 (574)[d]

[a] Abbreviations: Me, CH$_3$; Et, C$_2$H$_5$; i-Pr, i-C$_3$H$_7$; t-Bu, t-C$_4$H$_9$; Bz, CH$_2$C$_6$H$_5$; Ph, C$_6$H$_5$; Cp, (η-C$_5$H$_5$). [b] Decomposition point. [c] Measured in CHCl$_3$. [d] Measured in benzene.

products by means of column chromatography. The resulting black crystalline compounds were characterised by means of elemental analysis and molecular weight measurements as $[Fe_3(\eta\text{-}C_5H_5)_3(CO)_2(S)SR]$. Trinuclear products of this type could not be isolated from the reactions of di-isopropyl and diphenyl disulphide with $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ but their formation was indicated by means of infrared spectroscopy.

The melting points and analytical data for all compounds studied are given in Table 1.

Spectroscopic properties and electrochemical behaviour of the trinuclear species

The formulation of the trinuclear species as $[Fe_3(\eta\text{-}C_5H_5)_3(CO)_2(S)SR]$ was confirmed for R = CH_3 and C_2H_5 by the observation of the appropriate parent molecular ion in the mass spectra. Peaks corresponding to the loss of two carbonyl groups and to the ion $[Fe_3(C_5H_5)_3S_2]^+$ were also detected, the latter being the most abundant. In the infrared spectra of these compounds (see Table 2) there are no bands in the terminal carbonyl stretching region, but bands corresponding to bridging carbonyl groups are present. Table 2 also lists the proton NMR data for these derivatives and it can be seen that there are two cyclopentadienyl resonances of relative intensity 2/1, indicating non-equivalence of one of the cyclopentadienyl groups with respect to the other two. On the basis of the foregoing spectroscopic evidence and bearing in mind the 18-electron

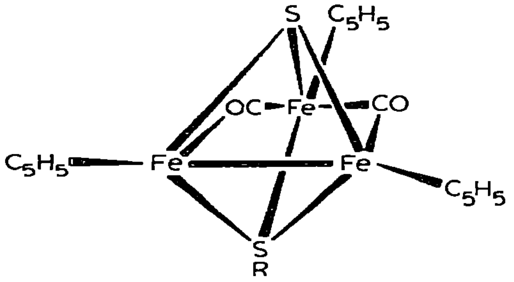
TABLE 2

INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC DATA

Compound[a]	C—O Stretching frequencies[b, c] (cm^{-1})	Proton resonances[d, e]	
		C_5H_5	Others
cis-[FeCp(CO)SMe]$_2$	1957 s, 1926 w	5.66	8.57s(CH_3)[f]
trans-[FeCp(CO)SMe]$_2$	1946 ms, 1932 s	5.66	8.34s(CH_3)[f]
cis [FeCp(CO)SEt]$_2$	1955 s, 1926 w	5.84	9.20t[J(HH)7.5Hz](CH_3)[g]
trans-[FeCp(CO)SEt]$_2$	1944 ms, 1931 s		
cis-[FeCp(CO)S-i-Pr]$_2$	1953 s, 1925 w	5.86	9.17d[J(HH)6.0Hz](CH_3)[g]
trans-[FeCp(CO)S-i-Pr]$_2$	1946 ms, 1931 s		
cis-[FeCp(CO)SBu]$_2$	1954 s, 1926 w	5.83[f]	
trans [FeCp(CO)SBu]$_2$	1943 ms, 1930 s	5.66[f]	
cis-[FeCp(CO)S-t-Bu]$_2$	1952 s, 1924 w	5.78	8.91s(CH_3)[g]
cis-[FeCp(CO)SBz]$_2$	1954 s, 1921 w	6.14	6.98(CH_2); 2.8[k](C_6H_5)[g]
cis-[FeCp(CO)SPh]$_2$ (A)	1983 s, 1974 (sh)[i]	5.41	2.88(C_6H_5)[f]
cis [FeCp(CO)SPh]$_2$ (C)	1983 (sh), 1974 s[j]	5 38	2.80[k](C_6H_5)[f]
trans-[FeCp(CO)SPh]$_2$ (B)	1953 ms, 1938 s	5.86	2.42; 2.82(C_6H_5)[f]
[$Fe_3Cp_3(CO)_2$(S)SMe]	1801 s, 1763 w	5.48 s, 6.01 s	9.40s(CH_3)[g]
[$Fe_3Cp_3(CO)_2$(S)SEt]	1800 s, 1762 w		
[$Fe_3Cp_3(CO)_2$(S)S-t-Bu]	1801 s, 1764 w	5.26 s, 5.64 s	9.27s(CH_3)[f]
[$Fe_3Cp_3(CO)_2$(S)SBz]	1802 s, 1766 w	5.20 s, 5.88 s	8.15(CH_2); 2.86(C_6H_5)[f]

[a] Abbreviations. Me, CH_3; Et, C_2H_5, i-Pr, i-C_3H_7; Bu, n-C_4H_9; t-Bu, t-C_4H_9; Bz, $CH_2C_6H_5$, Ph, C_6H_5; Cp, (η-C_5H_5). [b] Abbreviations: s, strong; m, medium; w, weak, sh, shoulder. [c] Measured in cyclohexane. [d] τ scale (TMS reference); measured at 38°. [e] Abbreviations: s, singlet; d, doublet; t, triplet. [f] Measured in $CDCl_3$. [g] Measured in C_6D_6. [i] The shoulder at 1974 cm^{-1} could be due to isomer C as impurity. [j] The shoulder at 1983 cm^{-1} could be due to isomer A as impurity. [k] Centre of multiplet.

rule, the structure represented below is proposed for these trinuclear compounds.



The iron-57 Mössbauer spectra of $[Fe_3(\eta\text{-}C_5H_5)_3(CO)_2(S)SR]$ (R = t-C_4H_9 and $CH_2C_6H_5$) contain only two resonance lines, with the peak at lower velocity being slightly broader and less intense than the other component. Inequivalence of the iron environments is therefore indicated but the individual components which contribute to the quadrupole doublet do not differ sufficiently in their chemical isomer shifts and quadrupole splittings to allow the intensity ratio of ca. 2/1, required by the structure proposed above, to be visually confirmed. The benzyl derivative was studied at 4.2, 77, and 295 K, whereas the butyl derivative was studied at 77 K only. All of the spectra gave acceptable chi-squared values when fitted with only two Lorentzian lines and the Mössbauer parameters derived on this basis are given in Table 3. The spectrum of the benzyl derivative at 295 K did show a slightly more pronounced asymmetry than did the other spectra, and attempts were therefore made to curve fit this room-temperature data with four peaks. The most realistic fit was that given in Table 3 and shown in Fig. 1. In this attempt the halfwidths of all four peaks were held equal but their intensities were totally unconstrained. The chi-squared value (266 on 240 degrees of freedom) is slightly smaller than that for the two-line fit (281 on 243 degrees of freedom) but there is clearly little to chose between the two models on this criterion. However the most encouraging aspect of the four-line fit is that the intensities emerge in the ratio 1.6/1.1/1.0/2.0: The outer two lines can therefore be tentatively assigned to the two equivalent iron atoms in the proposed structure and the inner pair of lines to the unique iron atom. Attempts to fit the 77 and 4.2 K spectra with four peaks proved less successful. Realistic line intensities could only be obtained by imposing quite severe constraints, and in such cases the chi-squared values were much higher than those for the simple two-line fits. This was also found to be the case for the related trinuclear species $[Fe_3(CO)_9S_2]$, which has been shown by X-ray crystallography to contain one iron atom in different environment from the other two [9]. This compound also gives only a sharp Mössbauer doublet over a wide range of temperature. The parameters at 85 K (see Table 3) are in good agreement with data of Crow and Cullen who recorded the spectrum at 80 K only [10]. The much lower value of δ for this compound compared with the values for the cyclopentadienyl derivatives reflects the superior π-accepting capacity of the terminal carbonyl groups over that of the $\eta\text{-}C_5H_5$ group.

Cyclic voltammograms of $[Fe_3(\eta\text{-}C_5H_5)_3(CO)_2(S)SR]$ (R = t-C_4H_9 or $CH_2C_6H_5$) in 1,2-dimethoxyethane were measured and shown to exhibit waves

TABLE 3

MÖSSBAUER SPECTROSCOPIC DATA

Compound[a]	Temperature (K)	Chemical[b] isomer shift δ (mm s^{-1})	Quadrupole splitting Δ (mm s^{-1})	Width at half-height Γ (mm s^{-1})	Relative intensity	Chi-squared/ Degrees of freedom
[$Fe_3Cp_3(CO)_2(S)S$-t-Bu]	77	0.27 ± 0.01	1.70 ± 0.01	0.34, 0.31	0.98/1.00	368/193
[$Fe_3Cp_3(CO)_2(S)SBz$]	4.2	0.25 ± 0.01	1.69 ± 0.01	0.29, 0.29	0.95/1.00	308/243
	77	0.27 ± 0.01	1.67 ± 0.01	0.28, 0.27	0.90/1.00	250/243
	295	0.29 ± 0.02	1.65 ± 0.01	0.27, 0.26	0.86/1.00	281/243
	295[c]	(A)0.29	1.71	0.25, 0.25	1.59/2.00	266/240
		(B)0.30	1.59	0.25, 0.25	1.07/1.02	
[$Fe_3(CO)_9S_2$]	85	0.04 ± 0.01[d]	0.56 ± 0.01	0.27, 0.27	0.99/1.00	383/379
	295	−0.04 ± 0.01	0.55 ± 0.01	0.22, 0.24	0.97/1.00	372/379

[a] Abbreviations: t-Bu, t-C_4H_9; Bz, $CH_2C_6H_5$. Cp, (η-C_5H_5). [b] Relative to metallic iron at 295 K. The spectra were obtained using a $^{57}Co/Rh$ source at the same temperature as the absorber; to compare the shifts with data obtained using a source at room temperature, a correction factor of + 0.12 mm s^{-1} must be added to the 77 K data, and 0.16 mm s^{-1} to the 4.2 K data [c] Results obtained by fitting four peaks to the data; (A) refers to the outer doublet, lines 1 and 4, and (B) refers to the inner doublet, lines 2 and 3. [d] In this run only, the source temperature (295 K) differed from that of the absorber and the correction factors discussed in b do not therefore apply.

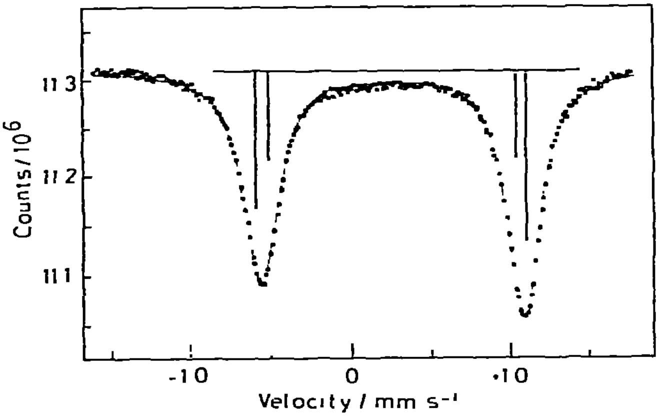


Fig. 1. Mossbauer spectrum of $[\mathrm{Fe_3(\eta\text{-}C_5H_5)_3(CO)_2(S)SCH_2C_6H_5}]$ at 295 K, showing a possible four-line fit. The velocity scale is relative to metallic iron.

corresponding to two reversible processes. These are assigned to:

$[\mathrm{Fe_3(\eta\text{-}C_5H_5)_3(CO)_2(S)SR}] - e \rightleftharpoons [\mathrm{Fe_3(\eta\text{-}C_5H_5)_3(CO)_2(S)SR}]^+$ and

$[\mathrm{Fe_3(\eta\text{-}C_5H_5)_3(CO)_2(S)SR}]^+ - e \rightleftharpoons [\mathrm{Fe_3(\eta\text{-}C_5H_5)_3(CO)_2(S)SR}]^{2+}$

on the basis of the potentials involved. These species could not be obtained chemically however. Treatment of $[\mathrm{Fe_3(\eta\text{-}C_5H_5)_3(CO)_2(S)SR}]$ (R = t-C_4H_9 or $CH_2C_6H_5$) with iodine gave a product with a C—O stretching frequency at ca. 1835 cm^{-1} and which is assumed to be $[\mathrm{Fe_3(\eta\text{-}C_5H_5)_3(CO)_2(S)SR}]^+$ but it decomposed fairly rapidly to a dinuclear cation of the type $[\mathrm{Fe(\eta\text{-}C_5H_5)(CO)SR}]_2^+$. The cyclic voltammogram of $[\mathrm{Fe_3(CO)_9S_2}]$ was also measured and found to exhibit a wave corresponding to a single redox process. The potentials of this wave are considerably more cathodic than the potentials associated with the oxidation of $[\mathrm{Fe_3(\eta\text{-}C_5H_5)_3(CO)_2(S)SR}]$ and a one- or two- electron reduction is thus presumably involved. The oxidative behaviour of the dinuclear compounds $[\mathrm{Fe(\eta\text{-}C_5H_5)(CO)SR}]_2$ has been reported previously [14].

Isomerism of the dinuclear species

The major products viz. $[\mathrm{Fe(\eta\text{-}C_5H_5)(CO)SR}]_2$, of the reaction of $[\mathrm{Fe(\eta\text{-}C_5H_5)(CO)_2}]_2$ with the dialkyl disulphides R_2S_2 (R = CH_3, C_2H_5 or i-C_3H_7) were separated by column chromatography into two isomers (A and B). The yield of isomer (B) in the reactions described above was very low but it could be produced in substantial yield by irradiation of isomer A with ultraviolet light at room temperature; heating of solutions of isomer B readily reconverted it to isomer A. Two isomers of $[\mathrm{Fe(\eta\text{-}C_5H_5)(CO)S\text{—}n\text{-}C_4H_9}]_2$ were also isolated but in this case the dinuclear product was obtained by treatment of $[\mathrm{Fe(\eta\text{-}C_5H_5)(CO)_2Br}]$ with $\mathrm{NaSC_4H_9}$ followed by irradiation of the resultant solution at either 70° or room temperature as appropriate. They were identified by means of infrared spectroscopy only. In contrast $[\mathrm{Fe(\eta\text{-}C_5H_5)(CO)S\text{—}t\text{-}C_4H_9}]_2$ and $[\mathrm{Fe(\eta\text{-}C_5H_5)(CO)SCH_2C_6H_5}]_2$ were obtained in one isomeric form only (A), and all attempts to convert this isomer to isomer B proved unsuccessful.

The frequencies of the C—O stretching modes for isomers A and B of $[Fe(\eta\text{-}C_5H_5)(CO)SR]_2$ ($R = CH_3$, C_2H_5, i-C_3H_7, n-C_4H_9, t-C_4H_9 and $CH_2C_6H_5$) are recorded in Table 2. It is apparent that the isomers labelled A and B in this text correspond respectively with the isomers labelled stable and unstable by Knox et al. for which structures *cis*-(I) (a) and *cis*-(III) (a) have been proposed [5, 8]. The difference in the frequency of these modes between isomers A and B is of the same order as that found between the two isomers of $[Fe(\eta\text{-}C_5H_5)(CO)ER'_2]_2$ (E = P or As; $R' = CH_3$ or C_6H_5) [6]. The NMR data for the isomer of $[Fe(\eta\text{-}C_5H_5)(CO)E(CH_3)_2]_2$ with the lower C—O stretching frequency has been interpreted in terms of *trans*-disposition of the cyclopentadienyl groups with respect to the Fe_2E_2 ring* while that for the higher frequency isomer has been explained in terms of *cis*-disposition of these groups as described previously in the text [6]. By analogy it is now suggested that isomer A of the sulphido derivatives $[Fe(\eta\text{-}C_5H_5)(CO)SR]_2$ contains *cis*-disposed cyclopentadienyl groups while isomer B contains them *trans*-disposed with respect to the Fe_2S_2 ring**. The NMR spectra of the A isomers of $[Fe(\eta\text{-}C_5H_5)(CO)SR]_2$ ($R = CH_3$, C_2H_5, i-C_3H_7 or t-C_4H_9) contain single methyl resonances, thereby eliminating *cis*-(II) as a possible structure. The infrared and NMR data cannot differentiate between isomers *cis*-(I) and *cis*-(III) although as mentioned previously the structure of the stable isomer of $[Fe(\eta\text{-}C_5H_5)(CO)SC_6H_5]_2$ has been established to be *cis*-(I) [7]. The cation in $[Fe(\eta\text{-}C_5H_5)(CO)SCH_3]_2BF_4$ has also been shown to adopt this structure [13]. A single cyclopentadienyl resonance in the NMR spectrum of *trans*-$[Fe(\eta\text{-}C_5H_5)(CO)SCH_3]_2$ is indicative of structure *trans*-(I).

The phenylsulphido derivative $[Fe(\eta\text{-}C_5H_5)(CO)SC_6H_5]_2$, obtained by irradiating a refluxing solution of $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ and $(C_6H_5)_2S_2$ in benzene with ultraviolet light for ca. 12 h followed by irradiation at 5°, was separated into three isomers (A, B, and C). From their infrared spectra isomers A and C are thought to correspond to two of the *cis*-isomers represented by *cis*-(I), *cis*-(II), and *cis*-(III), whereas the infrared and NMR data suggest that isomer B adopts structure *trans*-(I). These compounds occlude solvent very readily (as revealed by NMR), and are therefore difficult to isolate solvent-free.

Experimental

The infrared and NMR spectra were recorded on a Perkin—Elmer model 621 grating spectrophotometer and on the Varian A60A and HA100 instruments respectively. The Mössbauer spectrometer comprised an MVT3 transducer, an MD3 drive amplifier, and an MFG3 waveform generator from Elscint Ltd., Israel. These units were coupled with a Northern Scientific Inc. NS630 multi-

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* In this discussion puckering of the Fe_2E_2 or Fe_2S_2 ring is not taken into consideration. In any case the exchange between the possible conformations of the Fe_2E_2 or Fe_2S_2 ring is likely to be very rapid in solution as found for instance for $[Fe(CO)_3P(CH_3)_2]_2^{2-}$ [11]. Although equivalent exchange for $[Fe(CO)_3P(CH_3)_2]_2$ is much slower [11] this can be attributed to the presence of a metal—metal bond. Further the presence of a single methyl resonance in the NMR spectra of *trans*-$[Fe(\eta\text{-}C_5H_5)(CO)E(CH_3)_2]_2$ can only be explained in terms of a planar or fluxional Fe_2E_2 ring.

** The possibility of isomers A and B differing only in the relative orientations of the alkyl groups attached to the sulphur atoms as previously suggested is also considered to be highly unlikely on the basis that the C—O stretching frequencies for *syn*- and *anti*-$[Fe(CO)_3SR]_2$ are almost identical [12].

channel analyser. The radioactive source was a nominal 25 mCi of ^{57}Co diffused into a rhodium matrix, as supplied by the Radiochemical Centre, Amersham. The source and powdered absorbers were maintained at the same temperature (295, 77, or 4.2 K) in a cryostat manufactured by Elscint.

All experiments were performed under nitrogen. The photochemical reactions employed a Hanovia medium pressure arc photochemical reactor. Chromatographic separations were carried out on an alumina column (50 × 1.5 cm; Merck basic alumina, activity III). The elemental analyses and molecular weight determinations were performed by Alfred Bernhardt Microanalytical Laboratory, Elbach-uber-Engelskirchen, West Germany.

Synthesis of cis-$[Fe(\eta\text{-}C_5H_5)(CO)SR]_2$ *(R =* CH_3, C_2H_5, $i\text{-}C_3H_7$, $t\text{-}C_4H_9$ *and* $CH_2C_6H_5$*) and* $[Fe_3(\eta\text{-}C_5H_5)_3(CO)_2(S)SR]$ *(R =* CH_3, C_2H_5, $t\text{-}C_4H_9$ *and* $CH_2C_6H_5$*)*

A solution of $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ and excess R_2S_2 (R = CH_3, C_2H_5, $i\text{-}C_3H_7$, $t\text{-}C_4H_9$ or $CH_2C_6H_5$) in benzene was refluxed for 10-30 h. The solvent was removed under reduced pressure to afford a brown residue which was dissolved in a minimum of benzene/petroleum ether (1/3) and transferred to a basic alumina column. The column was first eluted with petroleum ether and then with benzene/petroleum ether (1/5) to remove excess ligand and side-products. Elution with benzene/petroleum ether (1/3) afforded a strong brown band which was collected. The solvent was removed and the brown residue, *cis*-$[Fe(\eta\text{-}C_5H_5)(CO)SR]_2$, crystallised from petroleum ether. Yield of *cis*-$[Fe(\eta\text{-}C_5H_5)(CO)SR]_2$: > 80%.

The column was eluted with benzene/petroleum ether (1/1) and then with benzene/dichloromethane (1/1) to afford a black band which was collected. The solvent was removed to afford a black crystalline residue which was rechromatographed as above. The crystalline compound so obtained was recrystallised a number of times from benzene/petroleum ether to afford pure $[Fe_3(\eta\text{-}C_5H_5)_3(CO)_2(S)SR]$. Yield of $[Fe_3(\eta\text{-}C_5H_5)_3(CO)_2(S)SR]$: ca. 6%.

cis-$[Fe(\eta\text{-}C_5H_5)(CO)S\text{—}t\text{-}C_4H_9]_2$ was obtained best however by performing the above reaction in xylene under reflux conditions for 10 h.

Synthesis of cis-$[Fe(\eta\text{-}C_5H_5)(CO)S\text{—}n\text{-}C_4H_9]_2$

A solution of $[Fe(\eta\text{-}C_5H_5)(CO)_2S\text{—}n\text{-}C_4H_9]$, prepared by a previously reported method [5], in benzene under reflux was irradiated with ultraviolet light for 20 h. The solvent was removed under reduced pressure to afford a red-brown oil. This was purified chromatographically as described above and the product finally isolated as an oil. Yield: ca. 40%.

Synthesis of trans-$[Fe(\eta\text{-}C_5H_5)(CO)SR]_2$ *(R =* CH_3, C_2H_5, $i\text{-}C_3H_7$ *and* $n\text{-}C_4H_9$*)*

A solution of *cis*-$[Fe(\eta\text{-}C_5H_5)(CO)SR]_2$ (R = CH_3, C_2H_5, $i\text{-}C_3H_7$ or $n\text{-}C_4H_9$) in benzene at 4° was irradiated with ultraviolet light until conversion to the *trans* isomer ceased, as determined by monitoring the reaction with infrared. The solvent was removed under reduced pressure and the residue separated chromatographically into the *cis* and *trans* isomers by the method used for the purification of the *cis* isomers described above. Both isomers were eluted with benzene/petroleum ether mixtures but the *cis* isomer was always eluted first. Crystallisation of the *trans* isomer was from benzene/petroleum ether or petroleum ether depending on the compound. Yield ca. 10-20%.

Synthesis of cis- and trans-$[Fe(\eta\text{-}C_5H_5)(CO)SC_6H_5]_2$

A solution of $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ and excess $(C_6H_5)_2S_2$ in benzene under reflux was irradiated with ultraviolet light for 14 h. The solution was then irradiated at ± 5° for a further 36 h. The solvent was removed under reduced pressure and the residue dissolved in a minimum of benzene and transferred to an alumina column. The column was eluted with petroleum ether to remove excess $(C_6H_5)_2S_2$. Elution with benzene/petroleum ether (1/3) produced a brown band which was collected. The residue isolated from this solution was crystallised from dichloromethane/petroleum ether to afford the *trans* isomer in pure form. Yield ca. 35%.

Elution of the column with benzene/petroleum ether (1/2) produced a second brown band. This was collected, the solvent removed under reduced pressure and the residue crystallised from dichloromethane/petroleum ether. The product was established to be the A isomer of *cis*-$[Fe(\eta\text{-}C_5H_5)(CO)SC_6H_5]_2$. Yield ca. 25%.

Elution with benzene/petroleum ether (1/1) gave a dark red band which was collected. The product isolated from this solution was dissolved in benzene and the solution re-irradiated with ultraviolet light at ± 5° for 20 h. The solvent was removed under reduced pressure. Careful chromatographic separation of the reaction mixture produced three bands. The third band was collected and the product isolated from solution was crystallised from benzene/petroleum ether. This product was established to be isomer C of *cis*-$[Fe(\eta\text{-}C_5H_5)(CO)SC_6H_5]_2$. Yield ca. 10%.

Acknowledgements

The authors thank Professor N.N. Greenwood of the University of Leeds for Mössbauer facilities and Dr. K.G.R. Pachler of the National Chemical Research Laboratory, C.S.I.R., Pretoria and Mr. M. van Wijk of the University of Pretoria for the measurement of the NMR spectra.

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