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A STUDY OF THE COMPLEXES $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (WHERE $n = 3$–12) BY MASS SPECTROMETRY AND DIFFERENTIAL SCANNING CALORIMETRY

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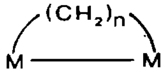
Summary

The new $\mu(1,n)$-alkanediyl binuclear iron complexes $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (where $n = 7$–12; $Cp = \eta^5\text{-}C_5H_5$) have been prepared and fully characterized. The mass spectra of the complexes of this type where $n = 3$–12 are reported and discussed. Differential Scanning Calorimetry (DSC) has been used to study the effect of heat on this series of complexes. The organic products formed on decomposition of some of the compounds in the solid state are reported.

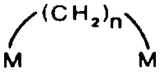
Introduction

There is considerable current interest in methylene and alkanediyl bridged binuclear complexes. These complexes may serve as useful models for intermediates in important catalytic reactions which involve the growth of methylene chains on a catalyst surface; for example in the Fischer-Tropsch synthesis [1]. Although many complexes with a methylene bridge have been reported in the last few years [2], there are still relatively few complexes known where an alkanediyl group bridges two metal atoms [3].

(1,n)-Alkanediyl bridged compounds are known, either with a metal–metal bond (I) or without a metal–metal bond (II).



I



II

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Few compounds of type I are known at present and none with $n > 4$ have been reported so far. Recent examples of compounds of this type include $[Cp(CO)Co\{\mu\text{-}(CH_2)_n\}Co(CO)Cp]$ ($n = 2$–4) [4] and $[(CO)_4Os\{\mu\text{-}(CH_2)_n\}Os(CO)_4]$ ($n = 1$–3) [5]. The first type II alkanediyl bridged compounds prepared were the binuclear iron compounds $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ ($n = 3$–6) [6]. Recently reported compounds of this type include $[CpRu(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ ($n = 1$–4) [7] and $[(phen)I(Me)_2Pt]_2\{\mu\text{-}(CH_2)_n\}$ (phen = 1,10-phenanthroline; $n = 2$–5) [8].

We became interested in the di-iron compounds $[CpFe(CO)_2]_2\text{-}\{\mu\text{-}(CH_2)_n\}$ some years ago and carried out a structural study of the compounds with $n = 3$ and 4 [9]. This study confirmed that the two iron atoms are bridged by an alkanediyl chain $-(CH_2)_n-$ and no unusual bond lengths or angles were observed. Recently there has been renewed interest in alkanediyl bridged compounds, particularly in the decomposition of this type of compound, as a result of their catalytic significance [10–13]. We now report on the synthesis of new members of the series of alkanediyl bridged binuclear iron compounds and present results of our studies of this series of compounds ($n = 3$–12) by mass spectrometry and Differential Scanning Calorimetry.

Results and discussion

Synthesis of the complexes

The new complexes $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (where $n = 7$–12) were prepared by essentially the same method as that reported for the earlier members of the series [6].

$$2Na[CpFe(CO)_2] \xrightarrow[\text{THF, 70°C}]{Br(CH_2)_nBr} \underset{\text{(III–XII)}}{[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}} \quad \text{where } n = 3\text{–}12$$

The new complexes VII–XII were all isolated as stable yellow crystalline solids and fully characterized by microanalysis (Table 1), infrared and ^1H NMR data (Table 2)

TABLE 1

YIELD AND ELEMENTAL ANALYSES FOR THE NEW COMPLEXES $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ ($n = 7$–12)

Compound (n) [a]	Yield (%)	Analyses (Found (calcd.) (%)) C	H
VII	37	55.7 (55.8)	5.4 (5.4)
VIII	53	56.9 (56.7)	5.6 (5.6)
IX	38	57.3 (57.5)	5.9 (5.8)
X	47	58.3 (58.3)	6.2 (6.1)
XI	64	59.2 (59.1)	6.4 (6.3)
XII	53	59.9 (59.8)	6.7 (6.5)

[a] Compound number is the same as the number of methylene groups in the polymethylene chain.

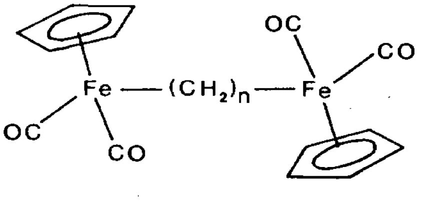
TABLE 2

IR AND NMR DATA FOR THE NEW COMPLEXES $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$

Compound (n) [a]	ν(CO) (cm^{-1}) [b]	^{1}H NMR [c] (ppm)	
		δ(Cp)	δ(CH_2)
VII	2009s, 1955vs	4.71 (10H)	1.46,1.31 (14H)
VIII	2007s, 1995sh 1981w, 1952vs	4.68 (10H)	1.49,1.32 (16H)
IX	2010s, 1956vs	4.90 (10H)	1.57,1.40 (18H)
X	2008s, 1954vs	4.85 (10H)	1.55,1.35 (20H)
XI	2008s, 1954vs	4.78 (10H)	1.48,1.29 (22H)
XII	2008s, 1994w 1954vs, 1923w	4.84 (10H)	1,54,1.32 (24H)

[a] Compound number is the same as the number of methylene groups in the polymethylene chain. [b] Hexane solution; s = strong, w = weak, sh = shoulder. [c] $CDCl_3$ solution; Cp resonances appear as sharp singlets, CH_2 resonances appear as broad singlets.

and mass spectrometry (see later). The homologous series of the complexes III–XII now make up the most extensive series of alkanediyl bridged transition metal complexes so far prepared.



(III) – (XII) n = 3 – 12

Mass spectra for the compounds III–XII

A comprehensive study of the mass spectra of the compounds III–XII has been made. Extensive fragmentation pathways are established on the basis of information from metastable peaks. High resolution mass spectrometry was used to resolve the complex fragmentation patterns of the longer chain compounds.

Molecular ion peaks are observed in the mass spectra of all the compounds but are of low intensity. All spectra exhibit several peaks characteristic of compounds containing the $(C_5H_5)Fe(CO)_2$ group [14–16], which can be assigned to the ions $[(C_5H_5)Fe(CO)_2]^+$ (m/e 177), $[(C_5H_5)Fe(CO)]^+$ (m/e 149), $[(C_5H_5)Fe]^+$ (m/e 121), $[(C_3H_3)Fe]^+$ (m/e 95), $[C_5H_5]^+$ (m/e 65) and $[Fe]^+$ (m/e 56).

An intense peak at m/e 186 from the ion $[(C_5H_5)_2Fe]^+$ is observed in the spectra of all the compounds. This ion is also significant in the mass spectra of mononuclear cyclopentadienyl iron dicarbonyl compounds and is thought [14] to arise from the ionisation of ferrocene formed by thermal decomposition of the sample compound in the ion source. In this study, as the ion source temperatures used (90–140°C) are considerably lower than the decomposition temperatures of the compounds in the series, the contribution of pyrolysis products will be small. The formation of this ion may thus be attributed to a fragmentation and rearrangement of the sample.

The intensities and probable assignments for the other major high mass peaks in the mass spectra of compounds III–XII are given in Tables 3 and 4. Fragmentation

TABLE 3

PEAK INTENSITIES AND ASSIGNMENTS FOR COMPOUNDS III–VII

Ion[a]	Relative peak intensity[b]				
	III	IV	V	VI	VII
$[M]^+$	3	0.5	2	1	2
$[M-CO]^+$	1	0.5	1	1	5
$[M-2CO]^+, [M-CO-C_2H_4]^+$	1	1	3	2	5
$[M-3CO]^+, [M-2CO-C_2H_4]^+$	0.5	1	2	3	7
$[M-4CO]^+, [M-3CO-C_2H_4]^+$	1	2	2	2	4
$[M-4CO-H_2]^+$	1	1	2	3	7
$[M-C_nH_{2n}]^+$	3	–	0.5	–	–
$[M-CO-C_nH_{2n}]^+$	7	1	1	–	2
$[M-2CO-C_nH_{2n}]^+$	8	2	3	3	5
$[M-3CO-C_nH_{2n}]^+$	7	5	8	6	3
$[M-4CO-C_nH_{2n}]^+$	22	13	19	13	11
$[M-CO-(C_5H_5)Fe(CO)_2]^+$	21	64	44	48	34
$[M-2CO-(C_5H_5)Fe(CO)_2]^+$	29	62	18	16	14
$[M-CO-C_5H_6]^+$	–	–	2	2	5
$[M-2CO-C_5H_6]^+$	–	2	17	31	100
$[M-3CO-C_5H_6]^+$	4	7	18	30	17
$[M-4CO-C_5H_6]^+$	12	29	50	23	31
$[M-4CO-C_5H_6-H_2]^+$	3	–	10	–	14

[a] $M = (C_5H_5)_2Fe_2(CO)_4(C_nH_{2n})$. [b] Percentage of base peak m/e 121 in low resolution mass spectrum.

TABLE 4

PEAK INTENSITIES AND ASSIGNMENTS FOR COMPOUNDS VIII–XII

Ion[a]	Relative peak intensity[b]				
	VIII[c]	IX[c]	X[d]	XI[d]	XII[d]
$[M]^+$	2	0.5	0.5	0.5	> 0.2[e]
$[M-CO]^+$	3	1	2	0.8	0.7
$[M-2CO]^+$	3	1	3	0.3	2
$[M-3CO]^+$	5	3	10	4	4
$[M-4CO]^+$	3	2	8	3	3
$[M-4CO-H_2]^+$	4	2	10	3	3
$[M-CO-C_nH_{2n}]^+$	3	2	5	11	2
$[M-2CO-C_nH_{2n}]^+$	8	14	19	13	11
$[M-3CO-C_nH_{2n}]^+$	16	14	30	20	17
$[M-4CO-C_nH_{2n}]^+$	21	14	45	12	11
$[M-CO-(C_5H_5)Fe(CO)_2]^+$	49	28	13	20	15
$[M-2CO-(C_5H_5)Fe(CO)_2]^+$	14	8	8	5	4
$[M-CO-C_5H_6]^+$	4	2	3	0.5	2
$[M-2CO-C_5H_6]^+$	55	22	33	10	7
$[M-3CO-C_5H_6]^+$	22	9	8	5	4
$[M-4CO-C_5H_6]^+$	39	11	11	4	3
$[M-4CO-C_5H_6-H_2]^+$	21	10	–	8	7

[a] $M = (C_5H_5)_2Fe_2(CO)_4(C_nH_{2n})$. [b] Percentage of base peak in low resolution mass spectrum. [c] Base peak m/e 121. [d] Base peak m/e 194, 208 and 222 for compounds V, XI and XII respectively (for the $[Fe(C_nH_{2n-2})]^+$ ion). [e] Intensity below detection limit of instrument when low mass peaks on scale.

schemes for compounds III and VIII are shown in Schemes 1 and 2 respectively. Solid arrows indicate the fragmentations confirmed by a metastable peak.

Four decomposition pathways of varying significance have been established for compounds VII–XII on the basis of the high resolution mass determinations. The major pathway involves stepwise CO loss from the molecular ion to give $[(C_5H_5)_2Fe_2(C_nH_{2n})]^+$, or $[(C_5H_5)_2Fe_2(C_nH_{2n-2})]^+$ if the fourth CO is eliminated as COH_2. These ions then generally decompose by elimination of the whole hydrocarbon chain, to $[(C_5H_5)_2Fe_2]^+$ (m/e 242) but for some compounds, intermediate species such as $[(C_5H_5)_2Fe_2(C_2H_4)]^+$ are observed. The ion $[(C_5H_5)_2Fe_2]^+$ fragments by loss of Fe or (C_5H_5) to give $[(C_5H_5)_2Fe]^+$ (m/e 186) or $[(C_5H_5)Fe_2]^+$ (m/e 177).

Only one decomposition of the molecular ions i.e. via CO loss, can be established on the basis of observed metastable peaks, so it appears that the three other decomposition pathways also commence with a CO loss from the molecular ion. The three routes involve the elimination of different fragments from the ion $[(C_5H_5)_2Fe_2(CO)_3(C_nH_{2n})]^+$ in competition with further CO loss.

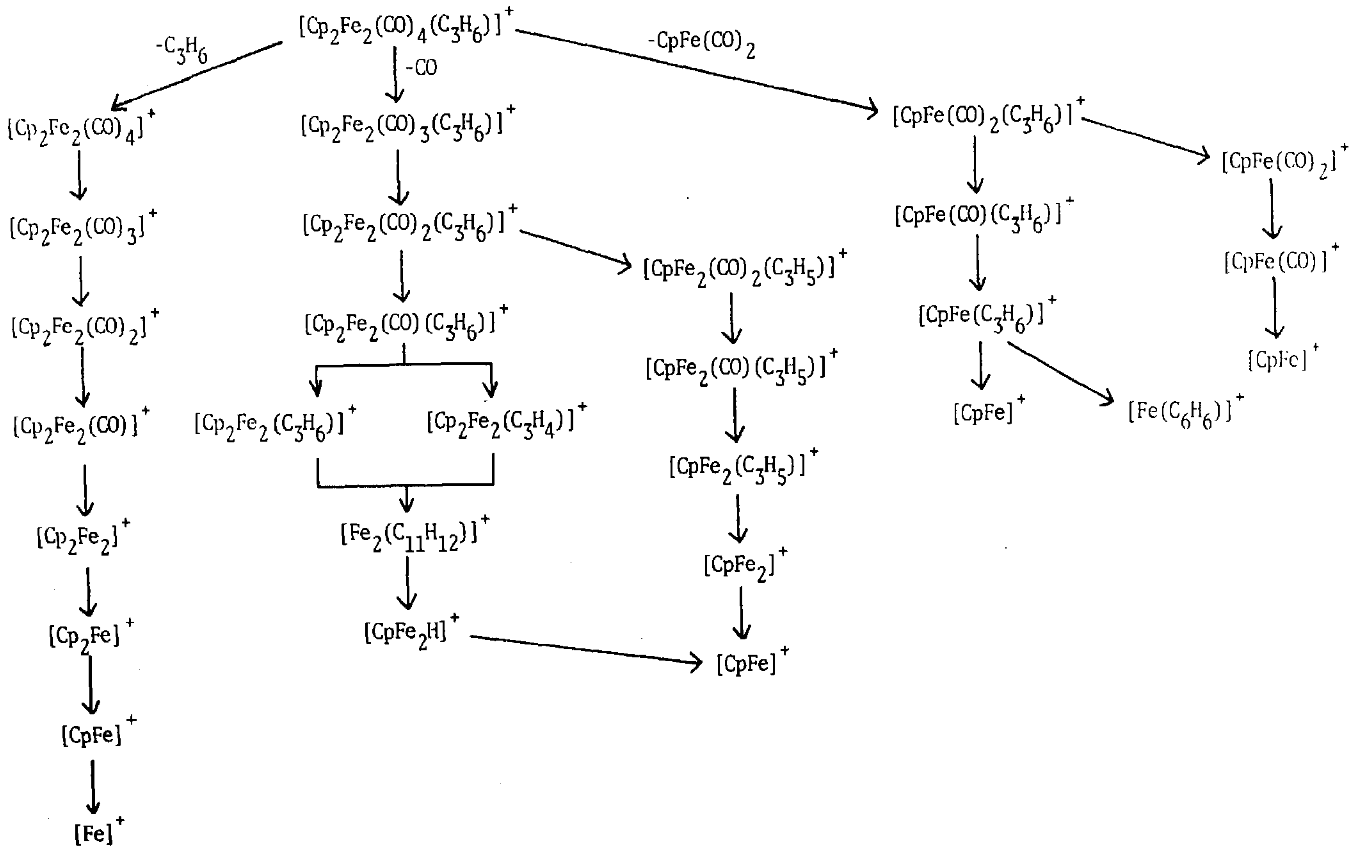
One pathway involves elimination of the entire C_nH_{2n} bridge to give $[(C_5H_5)_2Fe(CO)_3]^+$ (m/e 326). The intensity of the peak for this ion is generally low and this route is the least significant of the four competing pathways (see Table 4). $[(C_5H_5)_2Fe_2(CO)_3]^+$ decomposes, by stepwise elimination of CO, to $[(C_5H_5)_2Fe_2]^+$ (m/e 242). In a second decomposition route, $[(C_5H_5)_2Fe_2(CO)_3(C_nH_{2n})]^+$ loses a $(C_5H_5)Fe(CO)_2$ fragment in a single step. The resulting ion $[(C_5H_5)Fe(CO)(C_nH_{2n})]^+$ eliminates CO to give $[(C_5H_5)Fe(C_nH_{2n})]^+$ which then decomposes by elimination of H_2, C_2H_4 and C_3H_6 fragments, probably from the alkyl chain, to $[(C_5H_5)Fe]^+$ (m/e 121).

The third decomposition route for the $[(C_5H_5)_2Fe_2(CO)_3(C_nH_{2n})]^+$ ion, competing with further CO loss, is the most significant. This involves the elimination of a C_5H_6 fragment to give an ion of formula $[Fe_2O_3(C_{n+8}H_{2n+4})]^+$ which is most likely the alkenyl species $[(C_5H_5)Fe_2(CO)_3(C_nH_{2n-1})]^+$. This would be formed by loss of one cyclopentadienyl group and a hydrogen atom from the alkanediyl bridge. Such an elimination of a cyclopentadienyl group from a metal carbonyl species is unprecedented. In all previous studies of cyclopentadienyl carbonyl complexes, preferential loss of CO over C_5H_5 was observed [9–11]. The alkenyl ion $[(C_5H_5)Fe_2(CO)_3(C_nH_{2n-1})]^+$ fragments by stepwise CO loss to $[(C_5H_5)Fe_2(C_nH_{2n-1})]^+$. This ion decomposes by elimination of H_2 and hydrocarbon fragments, generally in a stepwise fashion to $[(C_5H_5)Fe_2H]^+$ (m/e 178) and $[(C_5H_5)Fe_2]$ (m/e 177) which fragment further to $[(C_5H_5)Fe]^+$ (m/e 121) and $[Fe_2]^+$ (m/e 112). (For example, see the fragmentation pattern for the ion $[(C_5H_5)Fe_2(C_8H_{15})]^+$ in Scheme 2).

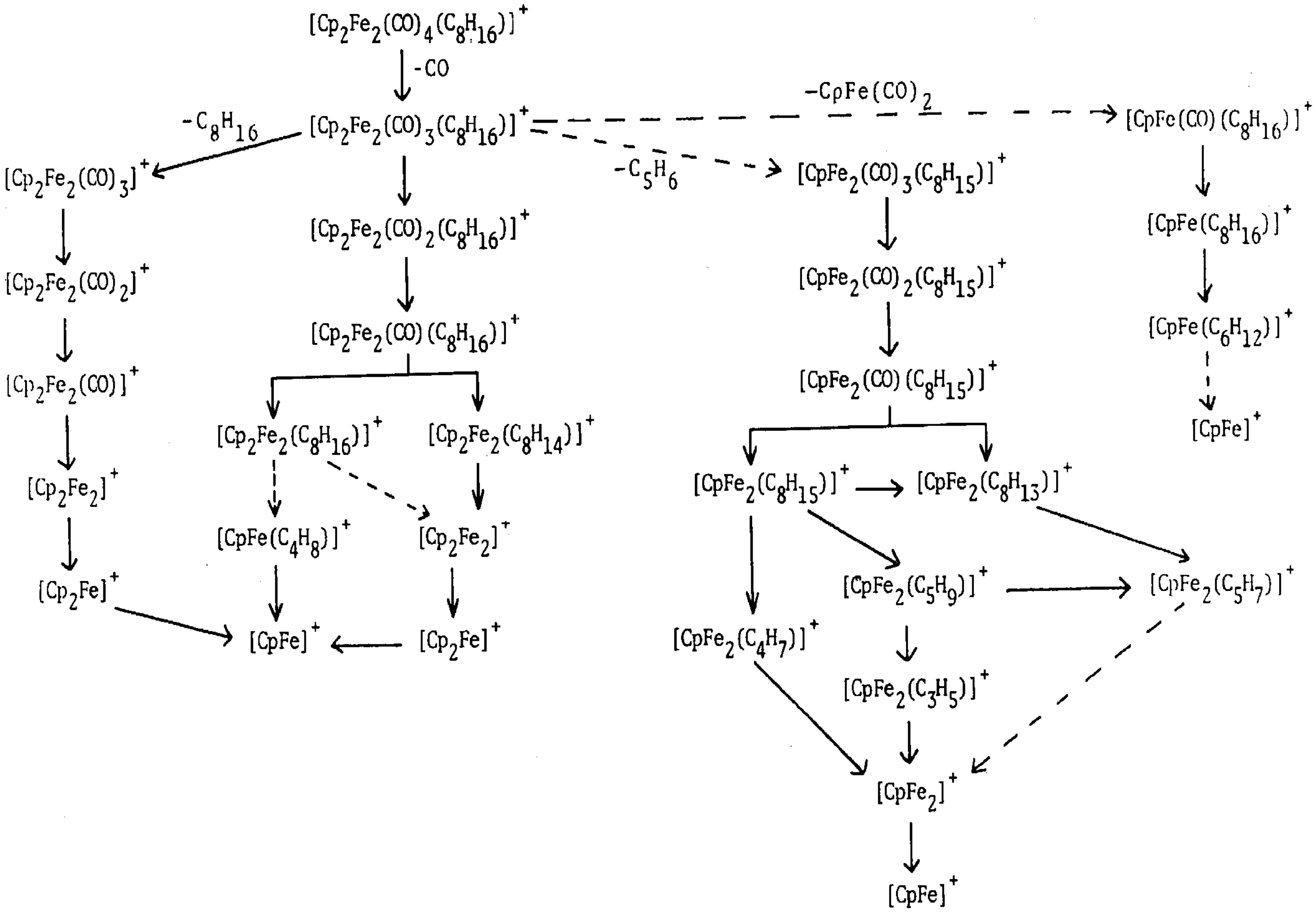
The same four decomposition pathways are observed for the shorter chain compounds III–VII however the significance of the various routes is different. For compound III, the major decomposition route involves loss of the C_3H_6 bridge from the molecular ion followed by stepwise loss of CO (Scheme 1). Competing elimination of CO and $(C_5H_5)Fe(CO)_2$ from the molecular ion is also observed. For compounds IV–VIII the molecular ion decomposes by stepwise CO loss but there is competing elimination of C_2H_4 fragments, presumably from the C_nH_{2n} bridge, from the $[M - xCO]^+$ ions ($x = 1$–3) (see Tables 3 and 4). Decomposition via loss of a C_5H_6 fragment is insignificant for III but this route becomes increasingly significant with increasing length of the hydrocarbon bridge.

(Continued on p. 262)

SCHEME 1. Fragmentation scheme for $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_3\}$.



SCHEME 2. Fragmentation scheme for $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_8\}$.



Differential Scanning Calorimetry (DSC) for the compounds III–XII

The DSC traces of compounds III–XII recorded over the range 35–225°C under nitrogen, are shown in Fig. 1. All the traces show a sharp endothermic peak and an exothermic peak at higher temperature. For compounds IV and VIII an additional endothermic peak is observed next to the first. The onset and peak temperatures of the endotherms and exotherms for compounds III–XII are given in Table 5. The endothermic peaks in the DSC traces of III, V–VII and IX–XII correspond to melting of the crystalline samples. The temperature ranges for these endotherms agree well with the melting ranges determined by conventional methods (Table 5). For compounds IV and VIII, the appearance of two endotherms suggests that these compounds are polymorphic and can exist in two different crystalline forms at ordinary temperatures and pressures. The lower temperature endotherm corresponds to the phase transition from one form to another and the second is the melting endotherm. The two crystalline forms of compounds IV and VIII are probably conformational polymorphs differing only in the degree of rotation about the Fe–C and C–C bonds in the alkanediyl bridge. The crystallographic study of IV [9] has shown that one form has a structure with a distorted centrosymmetric molecular conformation.

The higher temperature polymorph of IV and VIII is apparently the more stable form since the endothermic phase transition is not reversible. If a sample is heated to beyond the phase transition and cooled, only the melting endotherm appears on reheating. However both forms crystallize from the melt in the same proportions obtained on crystallisation from solution.

The plot of melting point against *n*, the number of carbons in the alkanediyl bridge (Fig. 2) shows the trends in melting point for the series III–XII. The melting points of compounds III–X fall on two straight lines, one for the compounds with *n* even and the other for those with *n* odd. Two such smooth melting point curves are also observed for various homologous series of aliphatic compounds [17]. The

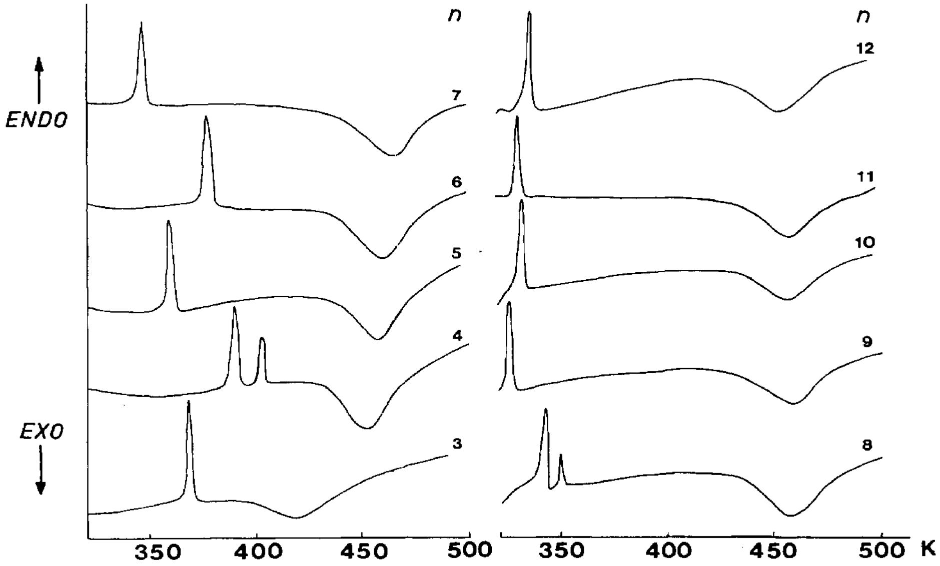


Fig. 1. DSC traces for compounds $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$.

TABLE 5

MELTING RANGES AND DSC RESULTS FOR COMPOUNDS III–XII

Compound	Melting range [a] (°C)	$T_{(endo)}$ (°C)		ΔH_m (kJ mol^{-1})	$T_{(exo)}$ (°C)		$\Delta H_{dec.}$ (kJ mol^{-1})
		T_{onset} [b]	T_{max} [c]		T_{onset} [b]	T_{max} [c]	
III	104–105	104	107	33±2	127	158	−53±2
IV	112–115 (A)	114	117		159	178	−130±2
	125–126 (B)	125	128	12±1			−134±2
V	83–85	83	88	38±1	161	182	
VI	100–103	103	105	54±2	163	187	−137±2
VII	66–68	67	70	38±2	163	186	−136±2
VIII	63–65 (A)	65	68		161	183	−153±1
	73–75 (B)	74	78	10±2			
IX	45–48	46	51	41±2	159	182	−159±1
X	56–58	57	59	46±1	163	185	−149±1
XI	52–54	53	55	45	162	187	−140±2
XII	59–62	61	63	39	158	185	−146±3

[a] Determined on a Kofler Hot Stage microscope. [b] Temperature corresponding to onset of peak. [c] Temperature at peak maximum.

smooth variation in m.p. in the two series, n even and n odd, suggests that the compounds in each series are of the same structural type. The deviation of the melting points of compounds XI and XII from the smooth curves could reflect a sudden change in structural type. A similar sudden increase in melting point is observed in the series of dibromoalkanes $Br(CH_2)_nBr$ with n odd above $n = 9$.

In the plot of melting point against n, the one for the n odd compounds lies below that for the compounds with n even. This indicates that the compounds with n odd have a structure with lower packing density in the crystal than the compounds with n even.

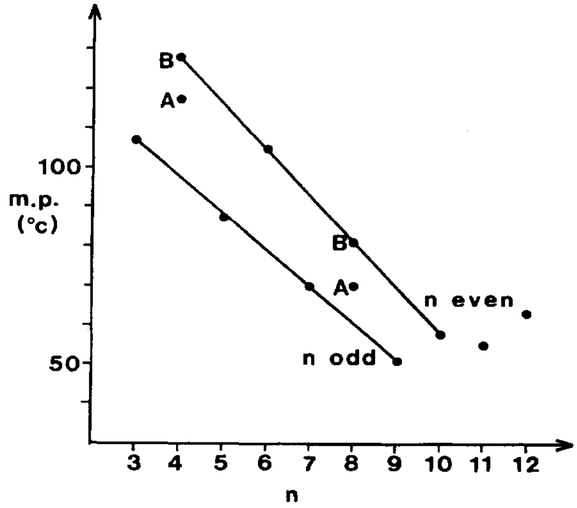


Fig. 2. Plot of melting point versus n for compounds $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$. For compounds IV and VIII, **A** corresponds to a phase transition and **B** to melting.

The values of ΔH_m, the enthalpy of melting, for the compounds III–XII are given in Table 5. Error in these values is based on an estimated error of ±2–3 units in the peak areas. Enthalpies for the phase transition of IV and VIII cannot be determined accurately since the proportion of the lower temperature form in the sample is not known. However the relative peak areas of endotherms **A** and **B** in the DSC traces of these compounds indicate that the enthalpy of the phase transition is considerably greater than the enthalpy of melting as is generally observed for compounds displaying conformational polymorphism [18].

The exotherms in the DSC traces of compounds III–XII correspond to decomposition of the samples. The decomposition temperatures vary little in the series IV–XII but III decomposes at a significantly lower temperature. Steric factors could contribute to the lower stability of the propanediyl bridged species. The decomposition enthalpies, $\Delta H_{dec.}$, are given in Table 5. These values are averages of values determined from several scans.

Studies of the thermolyses of compounds III–V [10–13] have shown that the decomposition reaction is elimination of the alkanediyl bridge to form $[CpFe(CO)_2]_2$ and that the reaction mechanism may vary with the length of the alkanediyl bridge. The production of propene and cyclopropane on decomposition of III has been rationalised on the basis of formation of a dimetallocyclic intermediate which decomposes by β-elimination and reductive elimination [11–14]. This mechanism has also been suggested to account for the formation of butenes on decomposition of IV [11–13]. Knox et al. [11,12] found that the major product of the decomposition of V was pentane and postulated a radical decomposition mechanism for this compound. These results indicate a change in the decomposition mechanism from IV to

TABLE 6

ORGANIC PRODUCTS OF SOLID STATE THERMOLYSES OF COMPOUNDS III–VIII

Compound	T^a (°C)	Hydrocarbon product (mol%) [b]	Alkene/Alkane ratio [b]
III	105–198	propene (24 ± 1.5)	1/3.1 ± 0.2
		cyclopropane (75 ± 1)	
		propane (0.9 ± 0.1)	
IV	128–220	but-1-ene (56 ± 8)	24 ± 1/1
		t-but-2-ene (25 ± 3)	
		c-but-2-ene (13 ± 4)	
		n-butane (6 ± 2)	
V	130–220	pent-1-ene (62 ± 1.5)	28 ± 1/1
		t-pent-2-ene (23 ± 1)	
		c-pent-2-ene (11.5 ± 0.5)	
		n-pentane (3.5 ± 0.1)	
VI	130–228	hex-1-ene (30 ± 7)	1.5 ± 0.4/1
		t-hex-2-ene (23 ± 6)	
		c-hex-2-ene (7 ± 2)	
		n-hexane (40 ± 8)	
VII	165–220	heptenes (30)	1/2.3
		n-heptane (70)	
VIII	165–220	octenes (25)	1/3.3
		n-octane (75)	

[a] Heating range for thermolysis. [b] Average of 2–4 experiments.

V and compounds VI–VII may be expected to decompose by the same mechanism as V.

To test this, we have investigated the solid state thermolyses of compounds III–VIII using gas chromatography to analyse the organic products. The results are shown in Table 6. Although our results agree fairly well with those of Knox et al. [12] for compounds III and IV, we observed pent-1-ene as the major decomposition product of V. This suggests that V decomposes mainly by a similar mechanism to IV, i.e. via a dimetallocyclic intermediate. Wegner and Sterling [10] have reported that pent-1-ene is also the major product of the decomposition of V in solution. Compound VI produces significant amounts of hexane and hexenes on decomposition while the longer chain compounds VII and VIII produce mainly alkane. Our results thus suggest that a change in the predominant decomposition mechanism occurs at VI and that a radical mechanism may be dominant for the longer chain compounds.

Experimental

^{1}H NMR spectra were recorded on a Varian EM 360 instrument using tetramethylsilane as internal reference standard. IR spectra were recorded on a Perkin–Elmer 983 spectrophotometer. The low resolution electron impact mass spectra were measured on a VG Micromass 16 F spectrometer at 70 eV using an accelerating voltage of 4 kV; the solid samples were introduced into the spectrometer on a probe at room temperature and the source temperature increased from 90°C until the sample vaporized and ions could be detected; this occurred in the range 90–140°C.

High resolution mass spectra of compounds VIII–XII were recorded on a Varian 311 A spectrometer coupled to a Varian 71 data system. An operating voltage of 70 eV and source temperature of 138°C were used. Samples were introduced as solids on a heated probe (50–120°C).

Differential Scanning Calorimetry was carried out using a Perkin–Elmer DSC 2 instrument. The solid crystalline samples (of typical sample size 2–5 mg) were contained in crimped aluminium pans. The samples were heated over the range 320–500 K at a rate of 20 K min^{-1} under an atmosphere of nitrogen. Peak areas were measured with a planimeter and compared to the melting endotherm of pure indium metal (ΔH_m 28.5 J g^{-1}).

Thermolyses were performed on solid samples of ca. 150 mg under vacuum using the apparatus of Hall et al. [19]. Gas chromatographic analyses of the organic decomposition products were carried out on a Varian 3700 instrument. For compounds III–VI, a 2 m n-octane/poracil column was used and for compounds VII and VIII a 2 m column of 3% OV 101 on Chromosorb 100/120 mesh WIP. Peak integration was performed on a Varian CDS 401 terminal.

Melting points were determined on a Kofler hot-stage microscope and are uncorrected. Microanalyses were performed in the microanalytical laboratory at the University of Cape Town. All reactions were carried out under an atmosphere of nitrogen using Schlenk tube techniques. $[CpFe(CO)_2]_2$, purchased from Strem Chemicals, U.S.A. and the dibromoalkanes, from Aldrich Chemical Company, were used without further purification. Tetrahydrofuran was distilled from $LiAlH_4$.

Samples of the known compounds of type $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ ($n = 3$–6) (i.e. compounds III–VI) were prepared by a slight modification to the reported route of King [6]. The new members of the homologous series of binuclear iron complexes were prepared by the general method given below.

General method for the synthesis of the compounds $[CpFe(CO)_2]_2\{\mu\text{-}CH_2)_n\}$ (where $n = 7\text{–}12$) i.e. compounds VII–XII

A solution of $[CpFe(CO)_2]_2$ (2.0 g, 5.7 mmol) in tetrahydrofuran (40 cm^3) was stirred with a sodium amalgam (0.5 g Na in 6 cm^3 Hg) for 2 h under an atmosphere of nitrogen. The resulting solution of $Na[CpFe(CO)_2]$ (11.4 mmol) was transferred by syringe to a Schlenk tube and the dibromoalkane $Br(CH_2)_nBr$ ($n = 7\text{–}12$) (5.70 mmol) was added dropwise with stirring. The reaction mixture was stirred for 15 h at room temperature then heated under reflux for 6–8 h. The solvent was removed under reduced pressure. The residue was extracted with dichloromethane (50 cm^3), the resulting solution filtered and the solvent again removed under reduced pressure to leave a brown oil. Addition of hexane (20 cm^3) and cooling caused the rapid formation of yellow crystals. Recrystallisation of these crystals from hexane gave the required products as yellow plates. Yields, melting points and elemental analysis are given in Table 1; IR and ^1H NMR data in Table 2.

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