Halogenoalkyl complexes of the transition metals

VII *. The synthesis and properties of the ω-halogenoalkyl complexes [(η-C5R5)(CO)2Fe(CH2)nX] (R = H, n = 3–10, X = Br, I; R = CH3, n = 3–5, X = Br, I)

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Abstract

The new complexes $[Cp(CO)_2Fe(CH_2)_nBr]$ (Cp = η-C_5H_5, n = 6–10) and $[Cp^{\star}(CO)_2Fe(CH_2)_nBr]$ (Cp* = η-$C_5(CH_3)_5$, n = 3–5) have been synthesized, the complexes $[(\eta$-$C_5R_5)(CO)_2Fe(CH_2)_nBr]$ (R = H, n = 3–6, 8–10; R = CH$_3$, n = 3–5) were treated with NaI to give the new complexes $[(\eta$-$C_5R_5)(CO)_2Fe(CH_2)_nI]$. The properties of these compounds, including their ^{13}C NMR and mass spectra, are discussed.

Introduction

Complexes of the type L_yMCH_2X (L_yM = transition metal and its associated ligands, X = halogen) are fairly well known and some have recently been extensively studied [1–4]. Complexes with longer alkyl chains $[L_yM(CH_2)_nX]$ (n > 1) are far less well known, though some, notably those of Pt [5,6], Mo and W [7,8], have been studied. Of the iron haloalkyl complexes of the type $[Cp(CO)_2Fe(CH_2)_nX]$, where n > 1, only $[Cp(CO)_2Fe(CH_2)_nBr]$ (n = 3–5) [9] and $[Cp(CO)_2Fe(CH_2)_3I]$ [10] have been reported, although the latter complex was not fully characterised. Very little work has been reported on the reactions of these ω-haloalkyl complexes. $[Cp(CO)_2Fe(CH_2)_3Br]$ was, however, shown to react with $Na[Cp(CO)_3Mo]$ to give

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⋆ For part VI see ref. 4.

[Cp(CO)$_2$Fe(CH$_2$)$_3$Mo(CO)$_3$Cp] in low yield [9]. [Cp(CO)$_2$Fe(CH$_2$)$_3$I] was shown to react with Na[CpRu(CO)$_2$] to give [Cp(CO)$_2$Fe(CH$_2$)$_3$Ru(CO)$_2$Cp] in high yield [10], suggesting that [Cp(CO)$_2$Fe(CH$_2$)$_n$I] complexes might be good precursors to heterobimetallic complexes of type [Cp(CO)$_2$Fe(CH$_2$)$_n$ML$_y$] (ML$_y$ = a transition metal and its associated ligands). Heterobimetallic complexes are of interest since they may be model compounds for catalytic processes [11,12], and much work has been devoted to their study in recent years [13]. Haloalkyl transition metal complexes are also precursors for cyclic carbene complexes [7-9], whilst [Cp(CO)$_2$Fe(CH$_2$)$_3$Br] has recently been shown to have good organic synthetic utility as a cyclopropane precursor [14]. We now report on the syntheses of [Cp(CO)$_2$Fe(CH$_2$)$_n$Br] and [Cp*(CO)$_2$Fe(CH$_2$)$_n$Br] and their conversion into [Cp(CO)$_2$Fe(CH$_2$)$_n$I] and [Cp*(CO)$_2$Fe(CH$_2$)$_n$I], respectively, and discuss the properties of these haloalkyl complexes. We will report later on the usefulness of these complexes as precursors for a wide range of heterobimetallic complexes [15].

Results and discussion

The new complexes [Cp(CO)$_2$Fe(CH$_2$)$_n$Br] (n = 6–10) were prepared by the general method shown in eq. 1:

$$Na[Cp(CO)_2Fe] + Br(CH_2)_nBr \rightarrow [Cp(CO)_2Fe(CH_2)_nBr] + NaBr \tag{1}$$

(n = 6–10).
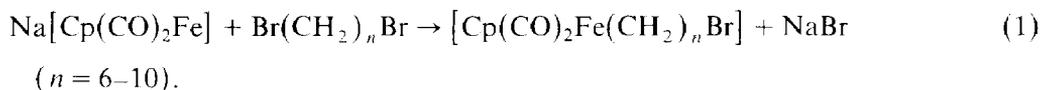
The reaction gives a high yield of the ω-bromoalkyl compounds, but difficulty was experienced in separating the product from unreacted Br(CH$_2$)$_n$Br. This difficulty increases with the length of the alkyl chain; however separation was effected by chromatography. All these compounds are yellow oils or low melting solids, and are stable in air at room temperature for short periods. [Cp*(CO)$_2$Fe(CH$_2$)$_n$Br] (n = 3–5) were prepared by a method analogous to that depicted in eq. 1, i.e.:

$$Na[Cp^\star(CO)_2Fe] + Br(CH_2)_nBr \rightarrow [Cp^\star(CO)_2Fe(CH_2)_nBr] + NaBr \tag{2}$$

(n = 3–5).
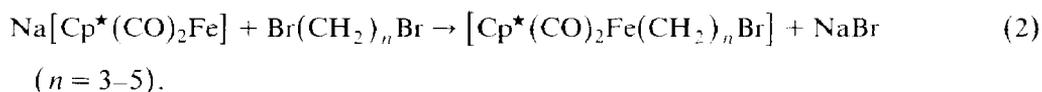
The Cp* complexes are yellow crystalline solids and are much more stable in air than their cyclopentadienyl analogues, both in solution and in the pure state. [Cp(CO)$_2$Fe(CH$_2$)$_n$Br] (n = 3–6, 8–10) were reacted with NaI to give [Cp(CO)$_2$Fe(CH$_2$)$_n$I] in high yield eq. 3:

$$[Cp(CO)_2Fe(CH_2)_nBr] + NaI \rightarrow [Cp(CO)_2Fe(CH_2)_nI] + NaBr \tag{3}$$

(n = 3–6, 8–10).
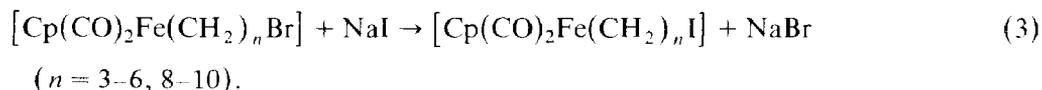
[Cp(CO)$_2$Fe(CH$_2$)$_n$I] was also synthesized by the method reported by Knox et al. [10] for the synthesis of [Cp(CO)$_2$Fe(CH$_2$)$_3$I], eq. 4:

$$Na[Cp(CO)_2Fe] + I(CH_2)_nI \rightarrow [Cp(CO)_2Fe(CH_2)_nI] + NaI \tag{4}$$
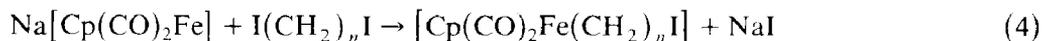
This was found not to be a good method, since, except for the complex with n = 3, the product could not be separated from unchanged I(CH$_2$)$_n$I, and also the yield of pure product was low for n = 3. [Cp*(CO)$_2$Fe(CH$_2$)$_n$Br] (n = 3–5) was

Table 1

Data for $[Cp(CO)_2Fe(CH_2)_nX]$

n	X	yield (%)	m.p. (°C)	IR (νCO) [a] (cm^{-1})	Elemental analysis		Molecular ion $[M^{\cdot+}]$
					C: found (calcd.)	H: found (calcd.)	
3	Br	[b]	22–24	2013, 1963	[b]	[b]	298/300
	I	78	42–43	2013, 1961	34.90 (34.72)	3.25 (3.21)	346
4	Br	[b]	oil	2011, 1957	[b]	[b]	312/314
	I	86	oil	2011, 1957	36.85 (36.68)	3.70 (3.61)	360
5	Br	[b]	oil	2009, 1956	[b]	[b]	326/328
	I	41	77–81	2009, 1956	38.70 (38.51)	3.85 (4.01)	374
6	Br	57	28–32	2009, 1955	45.90 (45.76)	5.05 (4.98)	340/342
	I	78	30	2009, 1956	40.30 (40.22)	4.35 (4.38)	388
7	Br	90	oil	2009, 1955	46.50 (47.34)	5.10 (5.35)	354/356
8	Br	70	oil	2009, 1955	[c]	[c]	368/370
	I	60	oil	2009, 1955	[c]	[c]	[c]
9	Br	60	oil	2009, 1955	49.85 (50.15)	6.15 (6.01)	382/384
	I	46	oil	2008, 1954	44.40 (44.67)	5.10 (5.35)	430
10	Br	81	oil	2009, 1955	51.60 (51.40)	6.20 (6.30)	396/398
	I	35	oil	2009, 1955	46.20 (45.95)	5.90 (5.63)	444

[a] Measured in hexane. [b] Data in ref. 9. [c] Not obtained.

found to react with NaI to give $[Cp^*(CO)_2Fe(CH_2)_nI]$ in fairly high yield (ca. 65%), eq. 5:

$$[Cp^*(CO)_2Fe(CH_2)_nBr] + NaI \rightarrow [Cp^*(CO)_2Fe(CH_2)_nI] + NaBr \qquad (5)$$

$(n = 3-5)$.
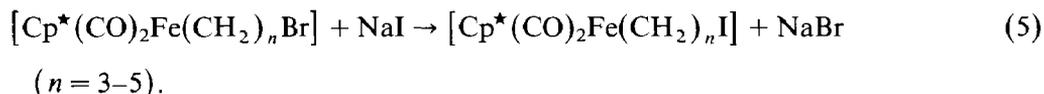
As was the case with the ω-bromoalkyl complexes, the new Cp^* iodoalkyl complexes show greater thermal stability than their cyclopentadienyl analogues. They are also more stable in solution. For both the cyclopentadienyl and penta-methylcyclopentadienyl complexes, the bromides are more stable in air than the corresponding iodides. In general the Cp iodo complexes have higher melting points than the corresponding bromides. In contrast, the melting points of the Cp^* bromo and corresponding iodo complexes are very similar for $n = 3$ and 5, and the bromide has a higher melting point than the iodide for $n = 4$. The melting points of the Cp^* complexes decrease as n increases for each series. The characterization data for $[Cp(CO)_2Fe(CH_2)_nX]$ (X = Br, I) are reported in Tables 1–3. The data for the Cp^* complexes are presented in Tables 4–6.

From Tables 1 and 4 it can be seen that there is no significant change in the positions of the carbonyl bands in the IR spectra between the bromo and corresponding iodo complexes, and that there is only a very slight trend towards lower wave numbers as the carbon chain lengthens from $n = 3$ to 5. No change is seen in the position of the carbonyl bands beyond $n = 5$ for the Cp complexes. As is generally found, the $\nu(CO)$ frequency for the Cp^* complexes is lower than that for the analogous Cp complexes by about 20 cm^{-1}.

The ^1H NMR data for the Cp complexes are shown in Table 2. The CH_2Br and CH_2CH_2Br proton peaks show no further shift with increasing chain length after $n = 5$, suggesting that the inductive or steric efect of the iron group is no longer felt by the terminal protons at chain lengths exceeding five carbons. The upfield shift of

Table 2

^{1}H NMR data for [Cp(CO)$_2$Fe(CH$_2$)$_n$X] [a]

n	X	Cp	CH$_2$X	CH_2CH$_2$X	α-CH$_2$	β-CH$_2$	γ-CH$_2$	δ-CH$_2$
3	Br	4.76s (5H)	3.34t (2H, ^3J 7.2)	1.95qn (2H, J 7.8)	1.33m (2H)			
	I	4.76s (5H)	3.10t (2H, ^3J 7.6)	1.97qn (2H, J J 8.0)	1.26m (2H)			
4	Br	4.77s (5H)	3.45s (2H, ^3J 6.6)	1.84m (2H)	1.41m (2H)	1.56m (2H)		
	I	4.72s (5H)	3.18t (2H, ^3J 7.0)	1.85qn (2H, J 6.7)	1.40m (2H)	1.56m (2H)		
5	Br	4.76s (5H)	3.42t (2H, ^3J 6.6)	1.81m (2H)	1.41 (4H)		1.48s (2H)	
	I	4.72s (5H)	3.18t (2H, ^3J 7.0)	1.80qn (2H, J 6.5)	1.40s (4H)		1.50s (2H)	
6	Br	4.71s (5H)	3.40t (2H, ^3J 6.9)	1.84qn (2H, J 6.7)	1.41sh (2H)	1.58s (2H)	1.37s (2H)	1.43sh (2H)
	I	4.72s (5H)	3.19t (2H, ^3J 7.0)	1.81qn (2H, J 6.7)	1.44s (4H)		1.37s (2H)	1.38s (2H) [b]
7	Br	4.74s (5H)	3.40t (2H, ^3J 6.9)	1.85qn (2H, J 6.4)	1.34s (4H)	1.49s (6H)		
8	Br	4.75s (5H)	3.40t (2H, ^3J 6.8)	1.85qn (2H, J 6.3)	1.25s (6H)	1.41s (6H)		
	I	4.72s (5H)	3.17t (2H, ^3J 7.1)	1.82qn (2H, J 6.4)	1.24s (6H)	1.40s (6H)		
9	Br	4.72s (5H)	3.40t (2H, ^3J 6.4)	1.84qn (2H, J 6.8)	1.28s (8H)	1.42s (6H)		
	I	4.68s (5H)	3.13t (2H, ^3J 6.1)	1.78qn (2H, J 6.3)	1.20s (10H)	1.49s (4H)		
10	Br	4.71s (5H)	3.40t (2H, ^3J 6.8)	1.84qn (2H, J 6.8)	1.26s (10H)	1.43s (6H)	1.57s (2H)	
	I	4.76s (5H)	3.19t (2H, ^3J 7.0)	1.82qn (2H, J 6.7)	1.27s (10H)	1.44s (4H)		

[a] Measured in CDCl$_3$ relative to TMS (δ 0.00 ppm, coupling constants in Hz), α-CH$_2$ refers to the protons on the CH$_2$ α to iron etc. [b] Peaks below this line could not be assigned.

Table 3

^{13}C NMR data for [Cp(CO)$_2$Fe(CH$_2$)$_n$X] ^{a}

n	X	CO	Cp	α-CH$_2$	CH$_2$X	CH$_2$CH$_2$X	β-CH$_2$	γ-CH$_2$	δ-CH$_2$	ε-CH$_2$
3	Br	216.49	84.97	−0.82	35.58	40.90				
	I	216.51	84.86	1.90	9.32	41.85				
4	Br	216.73	84.97	1.34	33.56	35.90	37.03			
	I	216.89	85.01	1.14	7.28	37.96	38.63			
5	Br	217.59	85.29	2.88	32.54	34.25	37.21	33.15		
	I	216.96	84.92	2.59	7.41	33.00	36.67	35.20		
6	Br	217.10	85.01	3.04	34.18	32.92	38.00 ^{b}	33.87 ^{b}	27.90	
	I	217.02	84.79	2.89	7.24	33.68	37.98	30.25	33.64	
7	Br	217.62	85.02	3.41	34.01	32.81	34.50 ^{b}	28.16 ^{b}	28.30	38.05
9	Br	217.09	84.98	3.52	33.93	32.61	38.04, 34.57,	29.25, 29.02,	28.51, 29.02,	27.94 ^{b} (6×CH$_2$)
	I	217.70	85.28	3.69	7.42	33.55	38.26, 34.79,	30.47, 29.45,	29.25, 29.45,	28.52 ^{b} (6×CH$_2$)
10	Br	217.98	85.81	3.37	33.77	32.47	37.93, 34.48,	29.22, 29.06,	28.97, 29.06,	28.37, 27.81 ^{b} (7×CH$_2$)
	I	217.45	85.45	3.89	7.56	33.64	38.44, 34.94,	30.60, 29.69,	29.51, 29.69,	29.44, 28.62 ^{b} (7×CH$_2$)

^{a} Measured in CDCl$_3$, peaks are externally referenced to TMS (δ 0.00 ppm), α-CH$_2$ refers to the CH$_2$ carbon α to iron. ^{b} Peak assignments uncertain.

Table 4

Data for $[Cp^*(CO)_2Fe(CH_2)_nX]$

n	X	yield (%)	m.p. (°C)	IR (νCO) [a] (cm^{-1})	Elemental analysis		Molecular ion $[M^{\cdot+}]$
					C: found (calcd.)	H: found (calcd.)	
3	Br	51	98–101	1991, 1938	49.05 (48.78)	5.60 (5.69)	368/370
	I	73	100–103	1991, 1939	43.80 (43.27)	5.00 (5.05)	416
4	Br	69	52–54	1989, 1935	50.40 (50.13)	5.80 (6.00)	382/384
	I	66	35–36	1989, 1935	44.90 (44.68)	5.10 (5.35)	430
5	Br	66	37–39	1988, 1934	51.30 (51.42)	5.90 (6.30)	396/398
	I	68	37–40	1988, 1934	45.70 (45.98)	5.60 (5.63)	444

[a] Measured in hexane.

0.2 to 0.4 ppm of the CH_2X peaks as X is changed from Br to I is as expected owing to the difference in their electronegativities. The effect of the halogen rapidly diminishes along the carbon chain.

Assignments of the ^{13}C NMR data were made as far as possible by using COSY and HETCOR experiments, as well as by comparisons with the ^{13}C NMR data for alkyl halides [16]. The chain length or the nature of the halogen do not appear to affect the position of the CO peaks. Similarly, the chain length has no effect on the δ values of the Cp peaks; however, the Cp peaks for the bromide complexes tend to be at marginally higher field values than those for the corresponding iodides. The effect of the halogen on the δ value of the CH_2 carbon α to iron for the compounds where $n = 3$ and 4 is very apparent. At higher values of n the effect of the halogen on the α-carbon diminishes with increasing n. The peak due to the α-carbon is shifted upfield for complexes with smaller values of n. This is contrary to what one would expect from consideration of the inductive effects of the halogens. Of particular interest are the compounds with $n = 3$, for which the peak for the CH_2 carbon α to iron is at a higher field for X = Br than for X = I. These observations could possibly be explained in terms of a weak bonding interaction between the halogen and the iron. This is also indicated by the mass spectral data. The interaction between iron and X is also shown by the ca. 2 ppm downfield shift of the peaks of the carbons α to X for $n = 3$, relative to the corresponding peaks for compounds with $n = 4$–10. Thus as n increases the distance between X and Fe increases, and the effect of their interaction would decrease. The proposed interaction between iron and bromine is supported by the observation that iron must participate in the cleavage of the γ-carbon–halogen bond of $[Cp(CO)_2Fe(CH_2)_3Br]$ upon formation of cyclopropane [14]. Also apparent from the ^{13}C NMR data is the large chemical shift difference (ca. 27 ppm) between the carbons α to Br and I, reflecting the different electron withdrawing abilities of the halogens.

The ^1H NMR of the Cp^* complexes (Table 5) shows that the protons α to Fe are much more shielded than are those of the Cp analogues. Whilst changing the halogen has no effect on the signals from these protons, the chemical shift values move down-field as n increases. The protons α to the halide show the expected upfield shift as X changes from Br to I, but the effect is not apparent for the protons β to the halogens. The β peaks move slightly upfield as n increases.

From the ^{13}C NMR data for the Cp^* complexes (Table 6) it can be seen that the halogen has no significant effect on the positions of the corresponding CO or

Table 5

^{1}H NMR data and assignments for $[Cp^*(CO)_2Fe(CH_2)_nX]$ ^{a}

n	X	$C_5(CH_3)_5$	α-CH$_2$	β-CH$_2$	γ-CH$_2$	δ-CH$_2$	ϵ-CH$_2$
3	Br	1.73s (15H)	0.78m (2H)	1.93m (2H)	3.32t (2H, ^3J 7.5)		
	I	1.73s (15H)	0.78m (2H)	1.92m (2H)	3.12t (2H, ^3J 7.6)		
4	Br	1.70s (15H)	0.86m (2H)	1.53m (2H)	1.88m (2H)	3.40t (2H, ^3J 7.1)	
	I	1.68s (15H)	0.84m (2H)	1.47m (2H)	1.85qn (2H, ^3J 7.2)	3.16t (2H, ^3J 7.3)	
5	Br	1.68s (15H)	0.89m (2H)	1.43m (4H)		1.84m (2H, ^3J 6.7)	3.36t (2H, ^3J 6.9)
	I	1.71s (15H)	0.90m (2H)	1.41m (4H)		1.84qn (2H, ^3J 6.6)	3.17t (2H, ^3J 7.3)

^{a} Measured in CDCl$_3$, relative to TMS (δ 0.00 ppm, coupling constants in Hz). α-CH$_2$ refers to the protons on the CH$_2$ α to Fe.

Table 6

^{13}C NMR data for [Cp*(CO)$_2$Fe(CH$_2$)$_n$X] ^{a}

n	X	CO	C$_5$(CH$_3$)$_5$	C$_5$(CH$_3$)$_5$	α-CH$_2$	β-CH$_2$	γ-CH$_2$	δ-CH$_2$	ε-CH$_2$
3	Br	218.97	94.98	9.30	9.54	40.80	36.75		
	I	218.97	94.96	9.32	12.66	41.45	10.97		
4	Br	219.33	94.86	9.30	12.01	36.05	38.70	33.93	
	I	219.27	94.81	9.30	11.72	38.40	39.42	7.30	
5	Br	219.48	94.77	9.27	13.30	36.80 ^{b}	34.51 ^{b}	32.80	34.51
	I	219.46	94.78	9.30	13.28	36.51 ^{b}	36.60 ^{b}	33.59	7.93

^{a} Measured in CDCl$_3$ relative to TMS ($\delta = 0.0$ ppm). α-CH$_2$ refers to the CH$_2$ carbon α to iron.
^{b} Assignment ambiguous. i.e. the assignments could be interchanged.

pentamethylcyclopentadienyl peaks. However, as n increases the CO peaks move slightly downfield, whilst the C$_5$(CH$_3$)$_5$ peaks move slightly upfield. These observations are consistent with a weak bonding interaction between Fe and X, with this interaction decreasing as n increases. The methyl peaks of the Cp* are not affected by either n or X. The effect of Fe on the carbon α to X, and the effect of X on the CH$_2$ carbon α to Fe can be seen to rapidly diminish as n increases. Thus the peak for the carbon α to Fe moves downfield and the peak for the carbon α to X moves upfield. The fact that the peak for the carbon α to Fe is at a higher field for X = Br than for X = I when $n = 3$, again implies a degree of Fe/X interaction, as does the ca. 2 ppm downfield shift of the peaks of the carbon α to X for $n = 3$ relative to the corresponding peaks α to X for $n = 4$ and 5. The carbons α to Fe in the Cp* complexes are significantly (6–10 ppm) more deshielded than those in the corresponding Cp complexes. So too are the carbonyl carbon peaks, though to a lesser degree. This deshielding effect is no longer apparent for the β carbons of the carbons of the methylene chain.

The low resolution electron impact mass spectra were obtained for all the compounds under discussion, excluding [Cp(CO)$_2$Fe(CH$_2$)$_8$I]. The intensities of the major organometallic peaks of [Cp(CO)$_3$Fe(CH$_2$)$_n$X] ($n = 3$–10. X = Br; $n = 3$–6, 9, 10; X = I) are reported in Table 7 with probable assignments, while those of [Cp*(CO)$_2$Fe(CH$_2$)$_n$X] ($n = 3$–5; X = Br, I) are reported in Table 8. The fragmentation of [Cp(CO)$_2$Fe(CH$_2$)$_4$Br], which has a potentially very ambiguous fragmentation pattern, was studied in detail. Its fragmentation pathways, established by use of information obtained from high resolution mass spectrometry, metastable peaks and linked scans, are shown in Scheme 1. High resolution mass spectra were also obtained for [Cp(CO)$_2$Fe(CH$_2$)$_4$I] and [Cp(CO)$_2$Fe(CH$_2$)$_5$Br].

Molecular ion peaks are observed in the mass spectra of all the Cp compounds but are of low intensity. All spectra exhibit peaks which are characteristic of compounds containing the [Cp(CO)$_2$Fe] group [17–19], which gives rise to the ions [Cp(CO)$_2$Fe]$^+$ (m/z 177), [Cp(CO)Fe]$^+$ (m/z 149), [CpFe]$^+$ (m/z 121), [(C$_3$H$_3$)Fe]$^+$ (m/z 95), [Cp]$^+$ (m/z 65) and [Fe]$^+$ (m/z 56). A peak at m/z 186, assigned to [Cp$_2$Fe]$^+$, is observed in all the spectra. This ion is a characteristic of the spectra of compounds containing [Cp(CO)$_2$Fe] and is believed to be due to either the ionisation of ferrocene, formed by thermal decomposition of these compounds in the ion source or the fragmentation and rearrangement of the sample compounds in the mass spectrometer [17]. The most abundant peak observed corresponds to [CpFe]$^+$

Table 7

Some mass spectral data for [Cp(CO)$_2$Fe(CH$_2$)$_n$X]

Ion [a]	$n=$ 3		4		5		6		7	8	9		10	
$X=$	Br	I	Br[c]	I[c]	Br[c]	I	Br	I	Br	Br	Br	I	Br	I
M	4	3	4	3	4	3	4	10	4	3	4	3	4	1
$M-\text{CO}$	10	10	10	8	10	12	8	18	10	8	8	7	8	3
$M-2\text{CO}$	10	20	15	18	18	30	17	60	18	22	16	23	28	12
$M-2\text{CO}-\text{CpH}$	15	18	36	24	24	28	36	45	26	56	38	35	34	16
$M-2\text{CO}-\text{CpH}-\text{C}_2\text{H}_4$			2	2	45	56	30	50	20	21	6	4	6	1
$M-2\text{CO}-\text{CpH}-\text{C}_3\text{H}_6$ [d]			6	1	2	1	18	58	16	15	7	5	8	2
$M-2\text{CO}-\text{HX}$ [e]	8	8	19	17	19	16	13	17	18	8	7	7	7	7
$M-2\text{CO}-\text{HX}-\text{CpH}$	5	5	36	34	18	8	35	21	44	85	100	100	100	100
$M-2\text{CO}-\text{HX}-\text{CpH}-\text{C}_2\text{H}_4$					8	7	15	11	6	18	11	8	10	8
$M-2\text{CO}-\text{HX}-\text{CpH}-\text{C}_3\text{H}_6$ [f]							12	9	36	34	38	38	26	26
$M-(\text{CH}_2)_n$	5	23	–	–	–	2	–	2	–	–	2	5	3	1
$M-(\text{CH}_2)_n-\text{CO}$	8	17	–	2	2	3	–	4	7	8	2	2	2	3
$M-2\text{CO}-(\text{CH}_2)_n$	61	55	49	37	53	45	35	51	30	19	13	14	7	7
$M-(\text{CH}_2)_n\text{X}$	17	8	8	8	10	8	10	10	11	13	13	11	9	7
$M-(\text{CH}_2)_n\text{X}-\text{CO}$	17	16	19	18	21	18	19	22	24	26	22	17	15	17
$M-(\text{CH}_2)_n\text{X}-2\text{CO}$	100	100	100	100	100	100	100	100	100	100	80	81	62	60
Cp$_2$Fe	8	18	3	2	13	8	4	5	3	4	4	3	8	3
FeX	14	20	9	8	8	11	8	11	4	5	5	6	3	6

[a] $M = [\text{Cp(CO)}_2\text{Fe(CH}_2)_n\text{X}]$; all ions have a single positive charge; ion refers to probable assignment. [b] Peak intensities are relative to the base peak at m/z 121 ($n = 3$–8), m/z 180 ($n = 9$) and m/z 194 ($n = 10$). [c] Assignments confirmed by high resolution mass spectrometry. [d] Ions corresponding to $M - 2\text{CO} - \text{CpH} - \text{C}_m\text{H}_{2m}$ ($4 \leq m < n$) are also seen (intensity $\leq 12\%$). [e] Ions corresponding to $M - 2\text{CO} - \text{HX} - \text{C}_m\text{H}_{2m}$ ($m \geq 2$) usually observed, (intensity $\leq 10\%$). [f] Ions corresponding to $M - 2\text{CO} - \text{HX} - \text{CpH} - \text{C}_m\text{H}_{2m}$ ($m \geq 4$) also observed, (intensity $\leq 19\%$).

$[Cp(CO)_2Fe(CH_2)_4Br]^+$

$[Cp(CO)_2Fe]^+$

$[Cp(CO)Fe]^+$

$[Cp(CO)Fe(CH_2)_4Br]^+$

$[CpFe(CH_2)_4Br]^+$

$[FeC_4H_7Br]^+$

$[FeC_2H_3Br]^+$

$[FeC_4H_6]^+$

$[CpFeBr]^+$

$[CpFeC_4H_7]^+$

$[CpFeBrH]^+$

$[FeBr]^+$

$[CpFe]^+$

$[Fe]^+$

$[FeC_3H_3]^+$
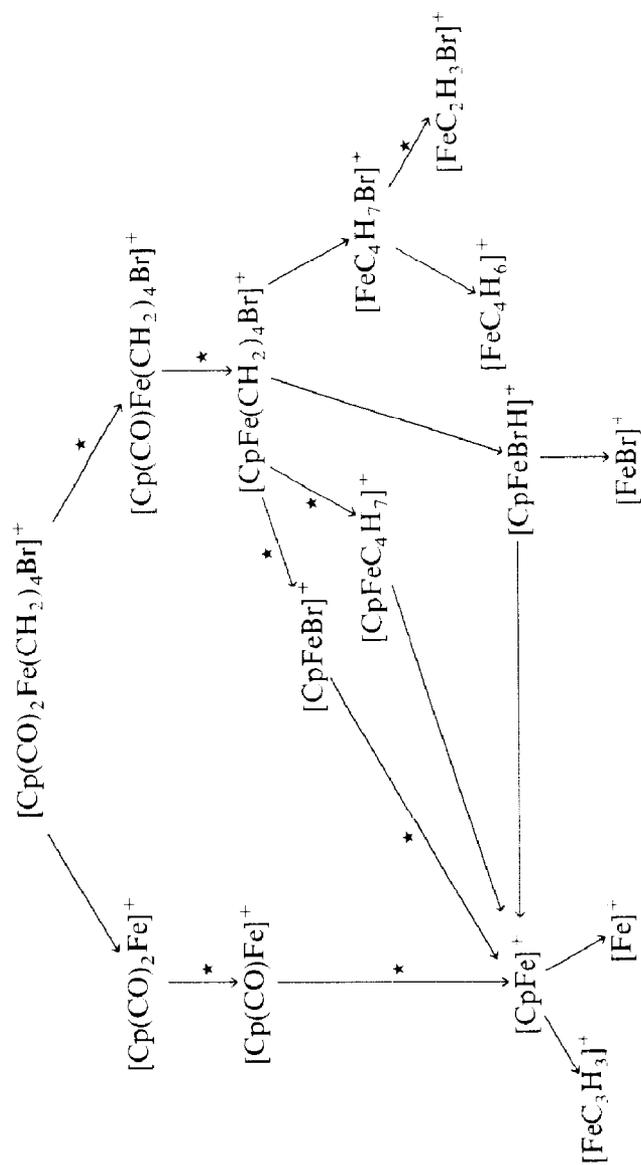
Scheme 1. Mass spectral fragmentation scheme for $[Cp(CO)_2Fe(CH_2)_4Br]$ Fragmentations confirmed by metastable data are denoted with ★.

Table 8

Some mass spectra data for $[Cp^*(CO)_2Fe(CH_2)_nX]$

Ion[a]	Relative peak intensities (%) [b]					
	$n =$ 3		4		4	5
	X = Br	I	Br	I	Br	I
M	3	3	7	5	8	5
$M - CO$	7	5	6	7	8	5
$M - 2CO$	2	2	6	4	2	2
$M - 2CO - HX$	3	3	7	5	2	3
$M - (CH_2)_n$	6	17	6 [c]	4 [c]	2	1
$M - (CH_2)_n - CO$	6	15	4	12	8	10
$M - (CH_2)_n - 2CO$	100	100	100	100	100	100
$M - (CH_2)_nX$	17	9	10	7	8	6
$M - (CH_2)_nX - CO$	22	16	23	17	26	18
$M - (CH_2)_nX - 2CO$	42	35	39	30	38	22
Cp^*_2Fe	–	2	2 [d]	–	2 [d]	–
$C_9H_{13}FeX$	14	16	18	17	18	17
FeX	2	6	2	10	14	2

[a] $M = [Cp^*(CO)_2Fe(CH_2)_nX]$; all ions have a single positive charge; ion refers to probable assignments. [b] Peak intensities are relative to the base peak at m/z 270/272 for X = Br and m/z 318 for X = I. [c] Same peak as $M - 2CO$ in low resolution mass spectrum. [d] Same peak as $M - (CH_2)_n$ in low resolution mass spectrum.

(m/z 121) for $n = 3-8$, X = Br and $n = 3-6$, X = I. For $n = 9$ and 10 (X = Br and I), the most abundant peak corresponds to $[FeC_nH_{2n-2}]^+$ (m/z 180, $n = 9$; m/z 194, $n = 10$). This species and daughter ions, formed through losses of C_mH_{2m} fragments from it, are observed in all the Cp spectra of the Cp compounds. All the $[Cp(CO)_2Fe(CH_2)_nX]$ compounds studied fragment according to two main pathways illustrated in Scheme 1, while some follow a third route as well. The first pathway involves the sequential loss of CO from the molecular ion to give $[Cp(CO)Fe(CH_2)_nX]^+$ and then $[CpFe(CH_2)_nX]^+$, which can fragment in four ways; (a) by losing C_nH_{2n} (either as a unit or in increments) to give $[CpFeX]^+$ (m/z 200/202 X = Br, m/z 248 X = I); (b) by losing HX to give $[CpFe(C_nH_{2n-1})]^+$; (c) by losing CpH to give $[Fe(C_nH_{2n-1})X]^+$; or (d) by losing C_nH_{2n-1} to give $[CpFeXH]$. The second fragmentation pathway, common to all the compounds, involves the formation of $[Cp(CO)_2Fe]^+$ (m/z 177) probably by the loss of $(CH_2)_nX$ from the molecular ion. The further fragmentation of $[Cp(CO)_2Fe]^+$ is discussed above. A third fragmentation of the molecular ion involves the loss of the hydrocarbon chain from the molecular ion and migration of X to Fe to give $[Cp(CO)_2FeX]^+$ (m/z 256/258 X = Br, m/z 304 X = I) followed by the loss of CO to give $[Cp(CO)FeX]^+$ (m/z 228/230 X = Br, m/z 276 X = I) and possibly also $[CpFeX]^+$. The fragments $[Cp(CO)_2FeX]^+$ and $[Cp(CO)FeX]^+$ are observed in most of the spectra at low relative intensities but have significant relative intensity in the cases where $n = 3$. This indicates that the Fe–X bond is formed much more easily for the complexes where $n = 3$. The relative intensities also suggest that the Fe–I bond is more readily formed than the Fe–Br bond lending further support to the explanation of the deshielding effect seen in the ^{13}C NMR discussed earlier.

Molecular ions are observed in the mass spectra of all the Cp^* compounds. The relative intensities of the ions $[Cp^*(CO)_2Fe]^+$ (m/z 247) and $[Cp^*(CO)Fe]^+$ (m/z

219) are similar to those of their Cp analogues, whilst the intensity of the ion [Cp*Fe] (m/z 191) is also fairly high. This indicates that the successive losses of CO from $[M - (CH_2)_n X]^+$ is an important fragmentation route for both the Cp and Cp* compounds. As for the Cp complexes, the ion corresponding to $[M - (CH_2)_n]^+$ for the Cp* complex where $n = 3$ and X = I is the most intense. This indicates a high degree of Fe/I interaction in $[Cp^*(CO)_2 Fe(CH_2)_3 I]$, as observed in the ^{13}C NMR spectra and for the analogous Cp compound.

Some significant differences are observed, however, between the mass spectra of the Cp* complexes and those of their Cp analogues. Unlike the Cp complexes, where CpH is lost from $[M - 2CO]^+$, no loss of Cp*H from $[M - 2CO]^+$ is observed for the Cp* complexes. Furthermore, the loss of HX from $[M - 2CO]^+$ yields only low intensity ions in the spectra of the Cp* complexes, indicating that this route is not as favoured for these complexes. For the Cp* compounds, the ions corresponding to successive losses of CO from $[M - (CH_2)_n]^+$ are quite significant. The peak corresponding to $[Cp^*FeX]^+$, which would be formed by this fragmentation pathway, is the base peak for the Cp* complexes. A peak corresponding to $[Cp^*_2 Fe]$ (m/z 326) is not observed in many of the spectra of the Cp* complexes, and in cases where such a peak is seen its assignment is ambiguous.

Experimental

All reactions were carried out under nitrogen by standard Schlenk tube techniques. Tetrahydrofuran (THF) was distilled from sodium and acetone from $CaCl_2$. NaI was dried before use. The dihalogenoalkanes (Aldrich) were used without further purification. Alumina (BDH, active neutral, Brockmann grade 1) was deactivated before use. Melting points were recorded on a Kofler hot-stage microscope (Reichert Thermovar) and are uncorrected. Microanalyses were performed by the University of Cape Town Microanalytical Laboratory. Infrared spectra were recorded on a Perkin Elmer 983 spectrophotometer. ^1H NMR spectra were recorded either on a Bruker WH90 or a Varian XR 200 spectrometer. ^{13}C NMR spectra were recorded on a Varian XR 200 spectrometer which was also used for the COSY and HETCOR experiments. Low resolution mass spectra and metastable traces were recorded with a VG Micromass 16F spectrometer, operated at 70 eV ionising voltage. The source temperature was initially 50–60°C and was raised to ca. 150°C during data collection. High resolution mass spectra and linked scans were recorded on a Kratos MS 80 RFA spectrometer, operating at a source temperature of 200°C and solid probe temperature of ca. 140°C The m/z values quoted refer to the ions containing the isotopes of highest natural abundance.

Preparation of [Cp(CO)$_2$Fe(CH$_2$)$_n$Br], n = 3–10

$Na[Cp(CO)_2 Fe]$ (10 mmol) in THF (20 ml) was added during 20 min. to a stirred solution of $Br(CH_2)_n Br$ (12 mmol) in THF (20 ml) at -20 to $-25°C$. The solution was stirred at -20 to $-25°C$ for 15 min then allowed to attain room temperature (ca. 75 min). The solvent was removed under reduced pressure, leaving a yellow/brown oily residue. This was extracted with hexane, and the solution was filtered, concentrated under reduced pressure, and transferred to an alumina column. Upon elution with hexane, a broad yellow band was collected, and this was concentrated then cooled to $-78°C$ under N_2. The yellow product separated from

this solution. The mother liquor was syringed off and the product dried under reduced pressure. Yields and physical properties are listed in Table 1. Elution of the column with ether gave two red bands containing small quantities of [Cp(CO)$_2$FeBr] and [Cp(CO)$_2$Fe]$_2$ respectively, as identified by IR and ^{1}H NMR spectroscopy.

Preparation of [Cp*(CO)$_2$Fe(CH$_2$)$_n$Br], n = 3–5

Na[Cp*(CO)$_2$Fe] (3 mmol) in THF (12 ml) was added during 15 min to a stirred solution of Br(CH$_2$)$_n$Br (3.3 mmol) in THF (25 ml) at between -60 and $-40\,^\circ$C. The temperature of the solution was allowed to rise to $-25\,^\circ$C and kept there for 20 min. The solution was then allowed to attain room temperature (ca. 75 min). The work-up was identical to that for the [Cp(CO)$_2$Fe(CH$_2$)$_n$Br] compounds. Yields and physical properties are listed in Table 4. Minor quantities of [Cp*(CO)$_2$FeBr] and [Cp*(CO)$_2$Fe]$_2$ were isolated as by-products.

Preparation of [(η-C$_5$R$_5$)(CO)$_2$Fe(CH$_2$)$_n$I], (R = H, n = 3–6, 8–10; R = CH$_3$, n = 3–5)

NaI (12 mmol) was added to a solution of [(η-C$_5$R$_5$)(CO)$_2$Fe(CH$_2$)$_n$Br] (6 mmol) in acetone (8 ml). The solution was stirred at room temperature for 24 hours, after which the ^{1}H NMR spectrum of a sample isolated from the reaction solution no longer showed the triplet due to the CH_2Br. The solvent was removed under reduced pressure and the product extracted with hexane, concentrated, and transferred to an alumina column. Elution with hexane gave a yellow band, which was concentrated and cooled to $-78\,^\circ$C under N$_2$. The [(η-C$_5$R$_5$)(CO)$_2$Fe(CH$_2$)$_n$I] complex separated out, the mother liquor was syringed off, and the product dried under reduced pressure. Yields and physical properties are listed in Tables 1 and 4. Elution of the column with ether gave a red band, from which a small quantity of [(η-C$_5$R$_5$)(CO)$_2$FeI] was isolated.

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