



Synthesis, characterization and reactions of the transition metal halogenoalkyl carbocation complexes $[\text{Cp}(\text{CO})_2\text{M}\{\eta^2\text{-CH}_2\text{CH}(\text{CH}_2)_n\text{X}\}]\text{PF}_6$ ($n = 1\text{--}8, 10$, $\text{M} = \text{Fe}$; $n = 3, 4$ $\text{M} = \text{Ru}$; $\text{X} = \text{Br}, \text{I}$)

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ABSTRACT

The halogenoalkyl complexes $[\text{Cp}(\text{CO})_2\text{M}\{(\text{CH}_2)_n\text{X}\}]$ ($n = 3\text{--}10, 12$, $\text{M} = \text{Fe}$; $n = 5, 6$, $\text{M} = \text{Ru}$, $\text{X} = \text{Br}, \text{I}$) react with Ph_3CPF_6 in dry CH_2Cl_2 to give the corresponding carbocation complexes $[\text{Cp}(\text{CO})_2\text{M}\{\eta^2\text{-}(\text{CH}_2\text{CH}(\text{CH}_2)_{n-2}\text{X})\}]\text{PF}_6$ in high yields. NMR evidence indicates that the metals form metallacyclopropane type structures with the carbocation ligand. The reactions of some of the cationic complexes with NaI , PPh_3 , $\text{Na}[\text{Cp}(\text{CO})_2\text{Fe}]$ and Et_3N are discussed. NaI and $\text{Na}[\text{Cp}(\text{CO})_2\text{Fe}]$ displace the halogeno-olefin, while PPh_3 adds at the $\beta\text{-CH}^{\delta+}$ giving the unstable phosphonium adducts $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{CH}_2\text{CH}(\text{PPh}_3)(\text{CH}_2)_{n-2}\text{X}\}]\text{PF}_6$ which decompose to the halogeno-olefins and the cationic PPh_3 complex $[\text{Cp}(\text{CO})_2\text{Fe}(\text{PPh}_3)]^+$. Et_3N causes allylic deprotonation forming internal olefin complexes of the type $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_{n-3}\text{X}\}]\text{PF}_6$.

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1. Introduction

Transition metal alkyl complexes of the type $[\text{L}_x\text{MR}]$ are conveniently converted to the cationic complexes $[\text{L}_y\text{M}\{\eta^2\text{-}(\text{CH}_2\text{CHR})\}]\text{X}$ ($\text{X} = \text{PF}_6, \text{BF}_4$ etc.) through hydride abstraction by triphenylcarbenium salts [1–3]. Similarly, transition metal η^1 -alkenyl complexes of the type $[\text{Cp}(\text{CO})_2\text{Fe}\{\eta^1\text{-}(\text{alkenyl})\}]$ undergo β -hydride abstraction to give cationic diene complexes in which the metal is bonded to only one of the double bonds [4]. We were surprised to note that the hydride abstraction reaction has not been studied for transition metal halogenoalkyl complexes, although they have been known [5–8] and used as precursors for certain bimetallic complexes for more than two decades [5,9–12]. To our knowledge the only references to cationic transition metal complexes involving halogenated olefins in the literature appear to be the bromopropenyl complex $[\text{Cp}(\text{CO})_2\text{Fe}\{\eta^2\text{-}(\text{CH}_2=\text{CHCH}_2\text{Br})\}]\text{PF}_6$ [13] and the bromocyclopentenyl complex



[14]. These were synthesized by the bromination of the corresponding acyclic and cyclic η^1 -allyl complexes, $[\text{Cp}(\text{CO})_2\text{Fe}(\eta^1\text{-allyl})]$, respectively.

Halogenoalkyl complexes may react with the hydride abstractors and undergo either α - or β -hydride abstraction. We were interested in determining which of the two possible pathways (a, or b shown in Scheme 1) would dominate, especially in the shorter chain complexes where the $\beta\text{-CH}_2$ group is close to the electron-withdrawing halogen. Consequently, we studied the reactions of a series of halogenoalkyl complexes with trityl salt and our findings are reported here. The reactions of some of the products with selected nucleophiles are also discussed.

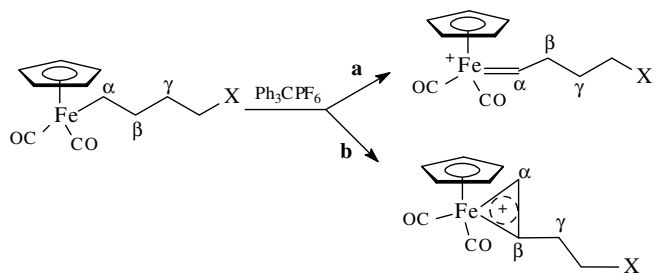
2. Results and discussion

2.1. Synthesis

The reaction of the halogenoalkyl complexes $[\text{Cp}(\text{CO})_2\text{M}\{(\text{CH}_2)_n\text{X}\}]$ ($n = 3\text{--}10$, $\text{M} = \text{Fe}$; $n = 5, 6$ $\text{M} = \text{Ru}$) with Ph_3CPF_6 in dry CH_2Cl_2 at room temperature followed pathway b (Scheme 1). Only the metallacyclopropane complexes $[\text{Cp}(\text{CO})_2\text{M}\{\eta^2\text{-CH}_2\text{-CH}(\text{CH}_2)_{n-2}\text{X}\}]\text{PF}_6$ were isolated. The halogenopropyl complexes $[\text{Cp}(\text{CO})_2\text{M}\{(\text{CH}_2)_3\text{X}\}]$ underwent significant decomposition, resulting in only 18% yield of impure product after 12 h. Although the rates of hydride abstraction reaction were not measured, it was noted that the time required for the reactions to go to completion was dependent on the chain length of the halogenoalkyl ligand as well as the halide at the end of the chain. The longer the chain the shorter the time required for the reactions to go to completion. Hence, for the complexes where $n > 5$ the reactions were complete in less than 1 h, whilst for the shorter chain complexes the reac-

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Scheme 1. Hydride abstraction reaction from the halogenobutyl complex.

tions took more than 3 h to go to completion. For example, in the reaction of the C_3 complex $[\text{Cp}(\text{CO})_2\text{Fe}[(\text{CH}_2)_3\text{I}]]$ with Ph_3CPF_6 about half of the starting material was still unreacted even after more than 14 h of reaction. In the complexes where $n = 4$ and 5, the reactions of the iodoalkyl complexes reached completion faster than their bromoalkyl analogues. For example, whereas the reaction of $[\text{Cp}(\text{CO})_2\text{Fe}[(\text{CH}_2)_4\text{I}]]$ with Ph_3CPF_6 was complete within 4 h, the reaction of $[\text{Cp}(\text{CO})_2\text{Fe}[(\text{CH}_2)_5\text{Br}]]$ required more than 4 h to go to completion.

The complexes where $n = 4$ precipitated out of solution as yellow solids, while the rest were obtained by precipitation with diethyl ether. All the complexes were characterized by IR, NMR

Table 1
Data for the complexes $[\text{Cp}(\text{CO})_x\text{M}(\text{CH}_2\text{CH}(\text{CH}_2)_n\text{X})]\text{PF}_6$ ($X = \text{Br}, \text{I}$)

n	X	ML_y	Yield (%)	M.p. ($^\circ\text{C}$)	$\text{IR}\nu(\text{CO})$ (cm^{-1}) ^a	Elemental analysis	
						C: found (calc)	H: found (calc)
2	Br	$\text{Cp}(\text{CO})_2\text{Fe}$	68	Dec > 128	2072, 2042		
2	I	$\text{Cp}(\text{CO})_2\text{Fe}$	66	Dec > 127	2075, 2041	26.9 (26.2)	2.13 (2.40)
3	Br	$\text{Cp}(\text{CO})_2\text{Fe}$	57	124–126	2076, 2040	31.4 (30.6)	2.57 (3.00)
3	I	$\text{Cp}(\text{CO})_2\text{Fe}$	58	Dec > 120	2076, 2040	28.8 (27.8)	2.39 (2.72)
4	Br	$\text{Cp}(\text{CO})_2\text{Fe}$	64	114–116	2075, 2039	33.1 (32.2)	2.91 (3.33)
4	I	$\text{Cp}(\text{CO})_2\text{Fe}$	69	110–111	2075, 2039	31.6 (29.4)	2.74 (3.03)
6	Br	$\text{Cp}(\text{CO})_2\text{Fe}$	71	103–105	2075, 2038	36.3 (35.1)	3.82 (3.93)
6	I	$\text{Cp}(\text{CO})_2\text{Fe}$	68	117–119	2075, 2038	33.5 (32.2)	3.30 (3.60)
7	Br	$\text{Cp}(\text{CO})_2\text{Fe}$	72	90–92	2075, 2037	35.7 (36.5)	3.75 (4.21)
7	I	$\text{Cp}(\text{CO})_2\text{Fe}$	75	96–97	2075, 2038	34.3 (33.5)	3.44 (3.86)
8	Br	$\text{Cp}(\text{CO})_2\text{Fe}$	73	110–112	2075, 2038	38.5 (37.7)	4.35 (4.47)
10	Br	$\text{Cp}(\text{CO})_2\text{Fe}$	82	113–115	2075, 2038	40.6 (40.1)	4.36 (4.96)
3	Br	$\text{Cp}(\text{CO})_2\text{Ru}$	60	125–127	2084, 2043	27.9 (29.2)	2.57 (2.73)
4	I	$\text{Cp}(\text{CO})_2\text{Ru}$	64	100–103	2085, 2042		

^a Recorded in CH_2Cl_2 .

Table 2
¹H NMR data for the complexes $[\text{Cp}(\text{CO})_x\text{M}\{\eta^2\text{-CH}_2\text{CH}(\text{CH}_2)_n\text{Br}\}]\text{PF}_6$ ^a

n	ML_y	CpM	<i>cis</i> -MCH ₂	<i>trans</i> -MCH ₂	MCH ₂ CH	MCH ₂ CHCH ₂	CH ₂ Br	Others
1	$\text{Cp}(\text{CO})_2\text{Fe}$	6.06 (s, 5H)	4.20 (d, 1H, 7.9) ^b	3.90 (d, 1H, 13.9)	5.50 (m, 1H)		4.58 (dd, 1H, 3.71 (t, 1H)	
2	$\text{Cp}(\text{CO})_2\text{Fe}$	5.95 (s, 5H)	4.22 (d, 1H, 8.2)	3.72 (d, 1H, 14.3)	5.17 (m, 1H)	3.11 (m, 1H), 2.04 (m, 1H)	3.72 (m, 1H) 3.56 (m, 1H)	
3	$\text{Cp}(\text{CO})_2\text{Fe}$	5.93 (s, 5H)	4.13 (d, 1H, 8.2)	3.72 (d, 1H, 14.4)	5.31 (m, 1H)	2.66 (m, 1H), 1.74 (m, 1H)	3.56 (m, 2H)	2.21 (m, 1H) 2.05 (m, 1H)
4	$\text{Cp}(\text{CO})_2\text{Fe}$	5.91 (s, 5H)	4.08 (d, 1H, 8.2)	3.68 (d, 1H, 14.6)	5.30 (m, 1H)	2.58 (m, 1H), 1.64 (m, 1H)	3.50 (t, 2H, 6.5)	1.93 (m, 2H), 1.83 (m, 1H), 1.64 (m, 1H)
6	$\text{Cp}(\text{CO})_2\text{Fe}$	5.92 (s, 5H)	4.08 (d, 1H, 8.2)	3.67 (d, 1H, 13.6)	5.32 (m, 1H)	2.56 (m, 1H), 1.36 (m, 1H)	3.50 (t, 2H, 6.5)	1.87 (q, 2H), 1.56 (m, 6H)
7	$\text{Cp}(\text{CO})_2\text{Fe}$	5.92 (s, 5H)	4.08 (d, 1H, 8.2)	3.65 (d, 1H, 14.6)	5.31 (m, 1H)	2.60 (m, 1H), 1.65 (m, 1H)	3.55 (t, 2H, 6.5)	1.88–1.65 br m
8	$\text{Cp}(\text{CO})_2\text{Fe}$	5.91 (s, 5H)	4.06 (d, 1H, 8.2)	3.64 (d, 1H, 14.6)	5.35 (m, 1H)	2.56 (m, 1H), 1.42 (m, 1H)	3.48 (t, 2H, 6.8)	1.60 (br m, 12H)
10	$\text{Cp}(\text{CO})_2\text{Fe}$	5.93 (s, 5H)	4.08 (d, 1H, 8.2)	3.67 (d, 1H, 14.6)	5.33 (m, 1H)	2.53 (m, 1H), 1.33 (m, 1H)	3.51 (t, 2H, 6.7)	1.87 (q, 2H), 1.61 (m, 14H)
3	$\text{Cp}(\text{CO})_2\text{Ru}$	6.22 (s, 5H)	4.11 (d, 1H, 8.3)	4.08 (d, 1H, 14.0)	5.45 (m, 1H)	2.60 (m, 1H),	3.61 (m, 2H)	2.10 (br m, 3H)

^a Spectra recorded in acetone- d_6 .

^b J values are given in Hz.

spectroscopy and elemental analysis. The iron complexes are yellow solids that melt or decompose without melting above 90°C , while those of ruthenium are white solids which melt at temperatures above 100°C .

2.2. IR spectroscopy

IR spectra of the compounds in CH_2Cl_2 show two strong $\nu(\text{CO})$ bands in the region of $2085\text{--}2038\text{ cm}^{-1}$ as expected for cationic $\text{Cp}(\text{CO})_2\text{M}$ carbonyls ($\text{M} = \text{Fe}$ or Ru). The IR, melting/decomposition points, elemental analysis data and yields (%) are summarized in Table 1.

2.3. ¹H NMR spectroscopy

These data are summarized in Tables 2 and 3. The ¹H NMR spectra show signals characteristic of half sandwich metallacyclopropanes [1,9,15]. For example, they show a sharp singlet due to the five Cp protons at about 5.9 ppm, a multiplet due to the β -CH proton at about 5.3 ppm and two doublets due to the diastereotopic γ -CH₂ protons at about 3.7 ppm ($J = 14.6\text{ Hz}$) and 4.1 ppm ($J = 8.2\text{ Hz}$) among others. In these complexes the γ -CH₂ protons are also diastereotopic, showing distinct multiplets at about 2.6 ppm and 1.6 ppm.

All the ¹H NMR spectra, except those of the C_3 – C_5 complexes, show a distinct triplet at about 3.50 ppm due to the CH₂X protons. In the C_3 and C_4 complexes the CH₂X protons are diastereotopic, showing distinct multiplets at about 3.1 ppm and 2.04 ppm (partially obscured by solvent peak) in the spectra. In the C_5 complex the signal due to the CH₂X protons is complicated by the neighbouring diastereotopic protons and appears as a complex multiplet. The CH₂Br protons are more deshielded than those of the CH₂I, as would be expected, due to the higher electronegativity of the bromide.

2.4. ¹³C NMR spectroscopy

All the Fe complexes show two carbonyl peaks in their ¹³C NMR spectra at about 210 ppm and 208 ppm corresponding to the non-equivalent carbons of the CO groups (Tables 4 and 5). The Ru complexes show two more strongly shielded CO signals at about 196 and 193 ppm. These data agree well with those reported for related mono- and bimetallic complexes. The signals of the γ - and β -carbon atoms (see Scheme 1 for labeling) appear in the same regions as those reported for related monometallic and bimetallic cationic

Table 3¹H NMR data for the complexes [Cp(CO)_xM(η²-CH₂CH(CH₂)_nI)]PF₆^a

<i>n</i>	M _{L_y}	CpM	<i>cis</i> -MCH ₂	<i>trans</i> -MCH ₂	MCH ₂ CH	MCH ₂ CHCH ₂	CH ₂ I	Others
2	Cp(CO) ₂ Fe	5.96 (s, 5H)	4.19 (d, 1H, 8.2) ^b	3.77 (d, 1H, 14.5)	5.13 (m, 1H)	3.07 (m, 1H), 2.04 (m, 1H)	3.54 (m, 1H), 3.35 (m, 1H)	
3	Cp(CO) ₂ Fe	5.93 (s, 5H)	4.12 (d, 1H, 8.1)	3.72 (d, 1H, 14.4)	5.30 (m, 1H)	2.63 (m, 1H); 1.69 (m, 1H)	3.33 (m, 2H)	2.17 (m, 1H), 2.04 (m, 1H)
4	Cp(CO) ₂ Fe	5.95 (s, 5H)	4.11 (d, 1H, 8.2)	3.72 (d, 1H, 14.5)	5.32 (m, 1H)	2.63 (m, 1H); 1.63 (m, 1H)	3.32 (t, 2H, 6.81)	1.68–1.98 (m, 4H)
6	Cp(CO) ₂ Fe	5.92 (s, 5H)	4.07 (d, 1H, 8.2)	3.67 (d, 1H, 14.8)	5.32 (m, 1H)	2.53 (m, 1H); 1.64 (m, 1H)	3.25 (t, 2H, 6.9)	1.42–1.80 (m, 8H)
7	Cp(CO) ₂ Fe	5.90 (s, 5H)	4.05 (d, 1H, 7.8)	3.63 (d, 1H, 14.8)	5.29 (m, 1H)	2.54 (m, 1H); 1.38 (m, 1H)	3.27 (t, 2H, 6.7)	1.38–1.80 (m, 10H)
4	Cp(CO) ₂ Ru	6.21 (s, 5H)	4.08 (d, 1H, 8.1)	4.05 (d, 1H, 14.0)	5.41 (m, 1H)	2.54 (m, 1H), 1.67 (m, 1H)	3.32 (t, 2H, 6.84)	1.88 (m, 4H)

^a Spectra recorded in acetone-*d*₆.^b *J* values are given in Hz.**Table 4**¹³C NMR data of the complexes [Cp(CO)_xM(CH(η²-CH₂CH(CH₂)_nBr))]PF₆^a

<i>n</i>	M _{L_y}	CO	Cp	MCH ₂	MCH ₂ CH	MCH ₂ CHCH ₂	CH ₂ Br	Others
1	Cp(CO) ₂ Fe	213.0, 209.6	86.4	86.1	90.0			
2	Cp(CO) ₂ Fe	210.1, 207.7	89.4	55.4	83.2			
3	Cp(CO) ₂ Fe	211.2, 209.0	90.2	55.6	86.5	39.3	4.7	
4	Cp(CO) ₂ Fe	211.0, 209.2	90.3	55.3	88.3	36.2	31.8	34.2, 32.7,
6	Cp(CO) ₂ Fe	210.4, 208.2	89.1	53.9	87.9	35.9	27.3	27.7, 32.1, 32.2, 33.6
7	Cp(CO) ₂ Fe	211.0, 209.2	89.1	53.9	88.2	36.1		32.3 ^b
8	Cp(CO) ₂ Fe	211.0, 209.2	90.1	54.9	89.1	37.0	28.5	33.2, 33.3, 34.6
10	Cp(CO) ₂ Fe	210.5, 208.2	89.1	53.9	88.2	36.1	27.6	28.3, 28.6, 32.3, 32.4, 33.7
3	Cp(CO) ₂ Ru	195.6, 193.9	91.3	51.4	83.0	35.1	32.1	35.1

^a Spectra recorded in acetone-*d*₆.^b Partially obscured by solvent peak.**Table 5**¹³C NMR data of the complexes [Cp(CO)_xM(η²-CH₂CH(CH₂)_nI)]PF₆^a

<i>n</i>	M _{L_y}	CO	Cp	MCH ₂	MCH ₂ CH	MCH ₂ CHCH ₂	CH ₂ I	Others
2	Cp(CO) ₂ Fe	210.8, 209.0	90.7	56.7	84.6	40.6	5.9	
3	Cp(CO) ₂ Fe	210.4, 208.3	90.2	55.6	86.2	37.7	5.2	36.7
4	Cp(CO) ₂ Fe	210.4, 208.1	89.2	54.2	87.1	34.9	5.8	33.0, 32.4
6	Cp(CO) ₂ Fe	211.5, 209.2	90.1	55.0	88.9	36.9	7.5	28.4, 30.6, 32.4, 33.1
7	Cp(CO) ₂ Fe	210.4, 208.2	89.1	53.4	88.1	36.0	6.8	27.7, 28.4, 29.8, 32.2, 33.1,
4	Cp(CO) ₂ Ru	196.8, 195.0	92.2	52.0	85.6	36.5	6.8	34.2, 33.4

^a Spectra recorded in acetone-*d*₆.

complexes. This implies that the carbocationic ligands in these complexes are coordinated to the metal in the same metallacyclic fashion as those of the reported complexes [1,13,15,9].

2.5. Reactions with Et₃N

The complexes rapidly undergo allylic deprotonation when reacted with Et₃N in dry CH₂Cl₂ to give amber oils consisting mainly of the neutral internal olefin complexes [Cp(CO)₂Fe(CH₂CH=CHR)] (R = CH₂X, CH₂CH₂X etc.; X = Br, I). That these reactions go to completion within a short time, giving quantitative yields, shows that metal complexation significantly influences the acidity of the allylic protons. In the cases examined, the products are obtained as mixtures of the *cis* and *trans* isomers in almost equal amounts as judged from the intensities of the NMR peaks. For example, the deprotonation of [Cp(CO)₂Fe(η²-CH₂CHCH₂CH₂Br)]PF₆ gave the *cis* and *trans* isomers of [Cp(CO)₂Fe(η²-CH₂CH=CHCH₂Br)]PF₆, which were identified by their distinct Cp proton signals: 5.27 (s, *cis* isomer Cp), and 4.80 (s, *trans* isomer Cp), respectively. The assignment is in agreement with reported data of related compounds [13]. Thus, Cutler et al. reported that the deprotonation of [Cp(CO)₂Fe(η²-CH₂CHCH₂CH₃)]PF₆ with Et₃N gave *cis* and *trans* isomers identified by their distinct Cp signals because the rest of the signals of the *cis* isomer appeared at the same positions as those of the *trans* isomer. The Cp proton assignment was confirmed

by the separate synthesis and NMR spectral analysis of the *trans* isomer [13].

2.6. Reactions with NaI

The bromo cationic complexes reacted rapidly with NaI resulting in olefin displacement and some halide exchange as assayed by ¹H NMR spectroscopy. This was not totally expected given that conversion of bromoalkyl complexes of the type [L_yM{(CH₂)_n-CH₂Br}] to their iodoalkyl derivatives is readily achieved by simply stirring them with NaI at ambient temperature in acetone [6,7,11]. The olefin displacement in this study suggests that the metal centre is more electrophilic than the CH₂ attached to the bromide and thus attack takes place at the metal in spite of the metal being sterically hindered. There was no evidence of addition products seen in the proton spectra, suggesting that neither the α-CH₂ nor the β-CH carbon is sufficiently electrophilic to yield addition products. It was noticed, however, that if the reaction mixtures were left standing for more than 3 h, there were two types of olefins in solution. For example, when the reaction mixture of [Cp(CO)₂Fe(η²-CH₂CH(CH₂)₄Br)]PF₆ with NaI was left standing in an NMR tube for 5 h, the ¹H NMR spectrum showed that all the starting material was completely consumed and in its place were the bromo- and iodo-olefins, and the iodide complex [Cp(CO)₂FeI]. The olefins were identified by the =CH and CH₂ olefinic proton signals at 5.81 ppm

and 4.96 ppm, respectively, and distinguished by the two triplets at 3.49 and 3.27 ppm which are assignable to the CH_2Br and CH_2I protons, respectively. All the other proton signals of the bromo olefin are equivalent to those in the iodo analogue. It appears that halide exchange occurs after olefin displacement. This can also be inferred from the fact that some bromo olefin is seen in solution after all the starting material has been completely consumed. Thus, halide exchange stops once all the excess iodide is consumed.

2.7. Reactions with PPh_3

The reaction of the cationic complexes with triphenyl phosphine was followed by NMR spectroscopy and found to give the phosphonium ion adducts e.g. $[\text{Cp}(\text{CO})_2\text{Fe}\{\eta^2\text{-CH}_2\text{CH}(\text{PPh}_3)(\text{CH}_2)_3\text{X}\}]^+$, which decompose with time to the olefins and $[\text{Cp}(\text{CO})_2\text{Fe}(\text{PPh}_3)]^+$. Thus, in the reaction of $[\text{Cp}(\text{CO})_2\text{Fe}\{\eta^2\text{-CH}_2\text{CH}(\text{CH}_2)_3\text{I}\}]\text{PF}_6$ with PPh_3 , there was no evidence of olefin displacement initially, but after about 10 min a new PPh_3 phenyl proton signal, assignable to $[\text{Cp}(\text{CO})_2\text{Fe}(\text{PPh}_3)]^+$, appeared between those of the PPh_3 of the phosphonium adduct complex and the free ligand. These suggested formation of the phosphonium adduct prior to olefin displacement, although the expected multiplets at about 5.8 and 5.0 ppm due to the $=\text{CH}$ and $=\text{CH}_2$ olefinic protons, respectively, were, initially, too weak to be observed. After about 1 h the dominant peaks were still those assignable to the phosphonium adduct and the unreacted starting material. The phosphonium salt was identified by the characteristic one proton multiplet at about 4.22 ppm due to the CH-PPh_3 proton (see Section 4).

When the reaction was allowed to continue overnight at 5°C , the ^1H NMR spectrum recorded showed that the amount of the phosphonium adduct had decreased, while that of the olefin and $[\text{Cp}(\text{CO})_2\text{Fe}(\text{PPh}_3)]^+$ had increased. Peaks due to the unreacted carbocationic complex $[\text{Cp}(\text{CO})_2\text{Fe}\{\eta^2\text{-CH}_2\text{CH}(\text{CH}_2)_3\text{I}\}]\text{PF}_6$ were still visible. The spectrum showed three distinct Cp signals due to the Cp protons of the starting material, the $[\text{Cp}(\text{CO})_2\text{Fe}(\text{PPh}_3)]^+$, and the phosphonium adduct $[\text{Cp}(\text{CO})_2\text{Fe}\{\eta^2\text{-CH}_2\text{CH}(\text{PPh}_3)(\text{CH}_2)_3\text{I}\}]\text{PF}_6$, respectively. At this time the multiplets at 5.8 and 5.0 ppm due to the $=\text{CH}$ and $=\text{CH}_2$ olefinic protons were clearly visible, confirming the presence of the olefin. The fact that the intensities of the Cp signals due to the phosphonium adduct and the starting material decreased while that of the phosphine complex $[\text{Cp}(\text{CO})_2\text{Fe}(\text{PPh}_3)]^+$ increased, indicated that some of the adduct salt was decomposing to give the olefin and the phosphine complex.

The initial formation of the phosphonium adduct salt may be attributed to steric and electronic factors. The ligand, PPh_3 , being a bulky nucleophile cannot approach the sterically hindered metal centre directly. Hence, due to its high nucleophilicity, it adds to the carbocationic CH^+ carbon giving the phosphonium salt. However, it was found that the phosphonium salts are unstable, decomposing to the halogenoalkene and the phosphine complex $[\text{Cp}(\text{CO})_2\text{Fe}(\text{PPh}_3)]^+$ (see Scheme 2). Similar observations were made by Len-

non et al. in reactions between cationic organoiron complexes and PPh_3 [16].

2.8. Reaction of $[\text{Cp}(\text{CO})_2\text{Fe}(\eta^2\text{-CH}_2\text{CH}(\text{CH}_2)_6\text{I})]\text{PF}_6$ with $\text{Na}[\text{Cp}(\text{CO})_2\text{Fe}]$

Halide displacement from complexes of the type $[\text{Cp}(\text{CO})_n\text{M}(\text{CH}_2)_m\text{X}]$ is one method of synthesizing alkyl-bridged homo and heterobimetallic complexes [12]. It was therefore thought that the reaction of the salt $\text{Na}[\text{Cp}(\text{CO})_2\text{Fe}]$ with $[\text{Cp}(\text{CO})_2\text{Fe}\{\eta^2\text{-CH}_2\text{CH}(\text{CH}_2)_6\text{I}\}]\text{PF}_6$ may lead to the bimetallic cationic complex $[\text{Cp}(\text{CO})_2\text{Fe}\{\eta^2\text{-CH}_2\text{CH}(\text{CH}_2)_6\}\text{Fe}(\text{CO})_2\text{Cp}]\text{PF}_6$. The reaction of the anion with this long chain complex, where the CH_2I is far from the carbocationic centre and thus free of unfavourable steric and electronic factors, however, resulted in instant olefin displacement leading to the formation of the very stable iron dimer $[\text{Cp}(\text{CO})_2\text{Fe}]_2$, judging by the instant colour change of the solution. This displacement was further confirmed by ^1H NMR spectroscopy and there was no evidence of halide substitution by the metal complex anion. The complexes $[\text{Cp}(\text{CO})_2\text{Fe}\{\eta^2\text{-CH}_2\text{CH}(\text{CH}_2)_n\}\text{Fe}(\text{CO})_2\text{Cp}]\text{PF}_6$, made by a different route, are stable and have characteristic spectra which were not observed for this reaction [15,17].

3. Conclusions

The halogenoalkyl complexes have been shown to undergo β -hydride abstraction to give the stable cationic complexes $[\text{Cp}(\text{CO})_2\text{M}\{\eta^2\text{-CH}_2\text{CH}(\text{CH}_2)_n\text{X}\}]\text{PF}_6$ in moderate to high yields. It has been demonstrated by specific examples that the cationic complexes undergo facile allylic deprotonation in the presence of Et_3N to give complexes of functionalized internal olefins. It has also been shown that they react with PPh_3 to give the phosphonium adduct $[\text{Cp}(\text{CO})_2\text{Fe}\{\eta^2\text{-CH}_2\text{CH}(\text{PPh}_3)(\text{CH}_2)_3\text{I}\}]\text{PF}_6$ which decomposes with time to the halogeno-olefin and the salt $[\text{Cp}(\text{CO})_2\text{Fe}(\text{PPh}_3)]\text{PF}_6$. Reactions with NaI and $\text{Na}[\text{Cp}(\text{CO})_2\text{Fe}]$ lead to olefin displacement and formation of $[\text{Cp}(\text{CO})_2\text{FeI}]$ and $[\text{Cp}(\text{CO})_2\text{Fe}]_2$, respectively. The latter reaction implies that these halogenoalkyl carbocationic compounds cannot be used as starting materials for bimetallic cationic complexes.

4. Experimental

4.1. General

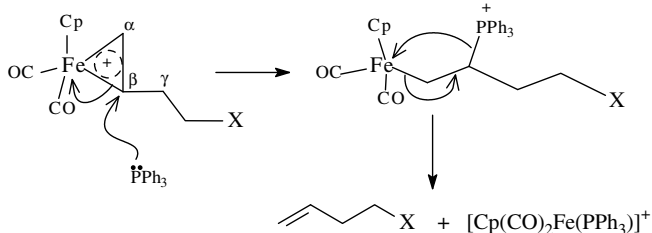
All reactions were carried out under inert atmosphere (UHP or HP nitrogen) using standard Schlenk tube techniques. Solvents were dried using standard procedures, freshly distilled and degassed before use.

Melting points were recorded on an Ernst Leitz Wetzlar hot-stage microscope and are uncorrected. Elemental analyses were performed on a LECO CHNS-932 elemental analyzer. Infrared spectra were recorded on a Nicolet Impact 400D 5DXFT spectrophotometer between 4000 and 400 cm^{-1} , in solution using liquid cell NaCl windows (Aldrich 99.99%). NMR spectra were recorded on Varian Gemini 300 MHz and Varian Inova 400 MHz spectrometers.

The halogenoalkyl complexes $[\text{Cp}(\text{CO})_2\text{Fe}\{(\text{CH}_2)_n\text{X}\}]$ ($\text{X} = \text{Br}, \text{I}$; $n = 3\text{--}10, 12$) [7] and $[\text{Cp}(\text{CO})_2\text{Ru}\{(\text{CH}_2)_n\text{X}\}]$ ($\text{X} = \text{Br}, \text{I}$, $n = 5, 6$) [6] were prepared by literature methods.

4.2. Reaction of the complexes $[\text{Cp}(\text{CO})_2\text{M}\{(\text{CH}_2)_n\text{X}\}]$ with Ph_3CPF_6 ($n = 3\text{--}10, 12$, $\text{M} = \text{Fe}$; $n = 5, 6$ $\text{M} = \text{Ru}$; $\text{X} = \text{Br}, \text{I}$)

The reaction of $[\text{Cp}(\text{CO})_2\text{Fe}\{(\text{CH}_2)_4\text{I}\}]$ is described as an illustration of the procedure followed in reacting the halogenoalkyl complexes with the hydride abstractor. A filtered solution of Ph_3CPF_6 (0.65 g, 1.67 mmol) in CH_2Cl_2 (10 mL) was added to a solution of



Scheme 2. Formation and decomposition of the phosphonium adduct $[\text{Cp}(\text{CO})_2\text{Fe}\{\eta^2\text{-CH}_2\text{CH}(\text{PPh}_3)(\text{CH}_2)_2\text{X}\}]^+$.

[Cp(CO)₂Fe{(CH₂)₄I}] (0.60 g, 1.67 mmol) in CH₂Cl₂ (5 mL) in a Schlenk tube and the mixture allowed to stand for 4 h under nitrogen at room temperature. After 2 h, a solid started precipitating in the Schlenk tube, but the reaction mixture was allowed to stand until IR monitoring showed the reaction to be complete (the starting materials shows two strong IR bands at around 1956 and 1941 cm⁻¹, while the cationic products show two strong bands at around 2075 and 2039 cm⁻¹). In the complex, where *n* = 4, the mother liquor was removed through a cannula and the solid washed with two 3 ml portions of CH₂Cl₂ and dried under reduced pressure. The cationic products did not initially precipitate from solution where *n* > 4. Thus, when the reaction was deemed complete, the reaction mixture was filtered by cannula into a clean, pre-weighed, Schlenk tube and diethyl ether added to precipitate the product, usually as a yellow solid. The mother liquor was then removed through a cannula and the solid dried under reduced pressure. The reactions of the bromoalkyl complexes required ca. 1 h longer to go to completion than the iodoalkyl analogues. The yields, melting/decomposition temperatures, IR and elemental analysis data are given in Table 1. ¹H NMR and ¹³C NMR spectroscopic data are given in Tables 2–5.

4.3. Reactions of the complexes [Cp(CO)₂Fe{CH₂CH(CH₂)_nBr}]PF₆ (*n* = 2, 6, 7) with NaI

About 10 mg of a given complex was dissolved in nitrogen saturated acetone-*d*₆ in an NMR tube and the ¹H NMR spectrum was recorded. About 10 mg of NaI was added to the tube and the reaction followed by recording spectra at intervals of 5 min until there was no further change in the spectra. It was noticed that the iodide ion displaced the α-bromoalkene and formed the complex [Cp(CO)₂FeI]. Some halide exchange was also noticed because a growing triplet at around 3.30 ppm due to the CH₂I protons was observed. The intensity of the CH₂Br triplet of the starting material decreased as the triplet due to the CH₂Br of the displaced olefin grew.

The reaction of [Cp(CO)₂Fe{CH₂CH(CH₂)₆Br}]PF₆ gave the alkene CH₂=CH(CH₂)₆Br. ¹H NMR (δ, acetone-*d*₆): 5.80 (m, CH₂=CH), 4.98 (d, *J* = 17.3 Hz, CH₂=CH), 4.89 (d, *J* = 9.3 Hz, CH₂=CH), 3.50 (t, CH₂Br), 2.08 (m, =CHCH₂), 1.83 (m, CH₂CH₂Br), 1.32–1.45 (brm, -(CH₂)₃). The iodo alkene also present was recognized by the distinct triplet due to the CH₂I protons at 3.26 ppm. The reaction of [Cp(CO)₂Fe{CH₂CH(CH₂)₇Br}]PF₆ gave CH₂=CH(CH₂)₇Br. ¹H NMR (δ, acetone-*d*₆): 5.80 (m, CH₂=CH), 4.98 (d, *J* = 17.3 Hz, CH₂=CH), 4.89 (d, *J* = 9.3 Hz, CH₂=CH), 3.52 (t, CH₂Br), 2.08 (m, =CHCH₂), 1.88 (m, CH₂CH₂Br), 1.45–1.51 (brm, (CH₂)₄). The iodo analogue also present was identified by the distinct triplet at 3.25 ppm. The reaction of [Cp(CO)₂Fe{CH₂CH(CH₂)₂Br}]PF₆ with NaI and subsequent standing for 5 h gave a mixture of CH₂=CH(CH₂)₄Br and CH₂=CH(CH₂)₄I; ¹H NMR (δ, acetone-*d*₆): 5.81 (m, CH₂=CH), 5.00 (d, *J* = 17.0 Hz, CH₂=CH), 4.93 (d, *J* = 10.2 Hz, CH₂=CH), 3.48 (t, CH₂Br), 2.09 (m, =CHCH₂, very close to solvent peak), 1.83 (m, CH₂CH₂Br) and 1.50 (m, =CHCH₂CH₂), 3.27 (m, CH₂I). ¹³C NMR (δ, acetone-*d*₆): 214.6 (CO of [Cp(CO)₂FeI]), 85.6 (Cp of [Cp(CO)₂FeI]); 138.8 (CH₂=CH), 114.9 ((CH₂=CH), 33.5 (CH₂Br), 33.1 (=CHCH₂), 32.7 (CH₂CH₂Br), 28.9 (CHCH₂CH₂Br).

4.4. Reaction of [Cp(CO)₂Fe{CH₂CH(CH₂)₂Br}]PF₆ with PPh₃

About 10 mg of the complex was dissolved in nitrogen saturated acetone-*d*₆ or nitromethane-*d*₃ in an NMR tube and the ¹H NMR spectrum was recorded. The spectrum showed characteristic peaks at 5.95 (s, Cp), 4.22 (d, *cis* FeCH₂), 3.72 (d, *trans* FeCH₂), and 5.17 (m, FeCH₂CH), whose disappearance was followed during the course of the reaction of the complex with PPh₃. About 10 mg of PPh₃ was added to the tube and the reaction followed by recording

spectra at intervals of 5 min until there was no further change in the spectra. Free PPh₃ showed a double multiplet at 7.30 ppm. After 5 min of reaction the ¹H NMR spectrum showed a new double multiplet at 7.88 ppm due to the phosphonium ion phenyl protons and a new singlet at 5.08 ppm due to Cp of the phosphonium adduct complex. These continued increasing in intensity with time. As these were growing, the originally observed starting material signals decreased. This procedure was repeated with [Cp(CO)₂Fe{CH₂CH(CH₂)₂I}]PF₆ and [Cp(CO)₂Fe{CH₂CH(CH₂)₃I}]PF₆.

The reaction of [Cp(CO)₂Fe{CH₂CH(CH₂)₃I}]PF₆ with PPh₃ was followed for a longer period. After about 1 h of reaction a third PPh₃ signal started growing at 7.60 ppm along with another singlet at 5.62 ppm. These were due to the PPh₃ and Cp group, respectively, of the complex [Cp(CO)₂Fe(PPh₃)]⁺ formed by the decomposition of the phosphonium adduct [Cp(CO)₂Fe{CH₂CH(PPh₃)-(CH₂)₃I}]PF₆. At the same time signals characteristic of the displaced iodo-olefin started growing in the olefinic proton regions. The reaction mixture was left standing overnight in the NMR tube at 5 °C. The ¹H NMR spectrum recorded after this showed peaks attributable to the starting material, the phosphonium adduct salt and [Cp(CO)₂Fe(PPh₃)]⁺.

[Cp(CO)₂Fe{CH₂CH(PPh₃)(CH₂)₂Br}]PF₆ ¹H NMR (δ, acetone-*d*₆): 7.8 (dm, P-phenyl), 5.21 (s, C₅H₅), 3.85, 2.60 (m, CH(PPh₃)CH₂, diastereotopic), 4.21 (m, CH-P), 3.55 (t, CH₂Br), 3.16, 1.84 (m, CH₂CH₂Br, diastereotopic). [Cp(CO)₂Fe{CH₂CH(PPh₃)(CH₂)₂I}]PF₆ ¹H NMR (δ, nitromethane-*d*₃): 7.80 (dm, P-phenyl) 5.05 (s, C₅H₅), 3.81 (m CH-P), 3.61, 2.50 (m, CH(PPh₃)CH₂, diastereotopic), 3.28 (m, CH₂I), 2.82, 1.86 (m, CH₂CH₂I, diastereotopic). [Cp(CO)₂Fe{CH₂CH(PPh₃)(CH₂)₃I}]PF₆ ¹H NMR (δ, acetone-*d*₆): 7.90 (dm, P-phenyl), 5.18 (s, Cp), 4.20 (m, CH-P), 3.80, 2.40 (m, CH(PPh₃)CH₂, diastereotopic), 3.54 (m, CH₂I), 2.32, 1.86 (m, CH₂CH₂I, diastereotopic), 2.40, 1.58 (m, FeCH₂, diastereotopic). [Cp(CO)₂Fe(PPh₃)], 7.60 (dm, phenyl protons), 5.6 (s, Cp of [Cp(CO)₂Fe(PPh₃)]). The unreacted cationic complex [Cp(CO)₂Fe{CH₂CH(PPh₃)(CH₂)₃I}]PF₆ was also observed (see Table 2 for spectral data).

4.5. Reaction of [Cp(CO)₂Fe{CH₂CH(CH₂)₆I}]PF₆ with Na[Cp(CO)₂Fe]

The complex [Cp(CO)₂Fe{CH₂CH(CH₂)₆I}]PF₆ (0.1 g, 0.18 mmol) was dissolved in 10 cm³ CH₂Cl₂ and cooled in a dry ice-acetone bath to -78 °C. A solution of Na[Cp(CO)₂Fe] (0.1 g 0.18 mmol) in THF was added dropwise to the solution while stirring, upon which the solution turned maroon in colour. The mixture was maintained at -78 °C for 20 min and then allowed to warm up to room temperature (1 h). The solvent mixture was removed under reduced pressure and a maroon paste obtained. ¹H NMR of the crude product showed that it consisted of only the iron dimer [Cp(CO)₂Fe]₂ and the iodo-octene CH₂=CH(CH₂)₆I identified as follows: ¹H NMR (δ, acetone-*d*₆): 4.94 (s, Cp of [Cp(CO)₂Fe]₂); CH₂=CH(CH₂)₆I ¹H NMR (δ, acetone-*d*₆): 5.80 (m, CH₂=CH), 4.98 (d, *J* = 17.3 Hz, CH₂=CH), 4.89 (d, *J* = 9.3 Hz, CH₂=CH), 3.15 (t, CH₂I), 2.16 (m, =CHCH₂), 1.80 (m, CH₂CH₂I) and 1.34 (m br, -(CH₂)₃-).

4.6. Reaction of the complexes [Cp(CO)₂Fe{CH₂CH(CH₂)_nBr}]PF₆ (*n* = 2, 10) with Et₃N

This reaction was carried out by following the procedure of Cutler et al. [13]. Thus, a solution of [Cp(CO)₂Fe{CH₂CH(CH₂)₂Br}]PF₆ (0.31 g, 0.68 mmol) in CH₂Cl₂ was cooled to -50 °C, and triethylamine (0.1 g, 0.99 mmol) was added with stirring. The solution was allowed to warm up to room temperature and the reaction was followed with IR until it was complete (about 20 min). The solvent was then removed under reduced pressure, and the residue extracted thrice with 20 ml portions of diethyl ether. The extracts were concentrated and chromatographed on activity III neutral alumina with methylene chloride-ether (1:1) to give the product,

[Cp(CO)₂Fe{CH₂CH=CHCH₂Br}]PF₆ as an amber oil (0.29 g, 93%). IR (νCO, CH₂Cl₂): 2007, 1951 cm⁻¹. ¹H NMR (δ, CDCl₃): 6.25 (m, 1H, =CHCH₂I), 5.13 (m, 1H, FpCH₂CH=), 5.27 (s, *cis* isomer Cp), 4.80 (s, *trans* isomer Cp), 3.66 (d, 2H, *J* = 7.7 Hz, CH₂Br), 2.04 (d, 2H, *J* = 8.6 Hz, FeCH₂CH). This procedure was also followed in the reaction of Et₃N (0.042 g, 0.42 mmol) with [Cp(CO)₂Fe{CH₂CH-(CH₂)₁₀Br}]PF₆ (0.2 g, 0.41 mmol). The reaction was complete after 15 min with the formation of two products, the *cis* and *trans* isomers of [Cp(CO)₂Fe{CH₂CH=CH(CH₂)₉Br}]PF₆. IR (νCO, CH₂Cl₂): 2000, 1946 cm⁻¹. ¹H NMR (δ, CDCl₃): 5.62 (m, CH=CHCH₂), 5.30 (m, *cis* isomer FeCH₂CH=CH), 5.00 (m, *trans* isomer, FeCH₂CH=CH), 4.70 (s, *cis* isomer Cp), 4.65 (s, *trans* isomer Cp), 3.40 (t, CH₂Br), 2.16 (m, *cis* and *trans* isomer FeCH₂CH), 1.82 (m, CH₂CH₂Br), 2.00, 1.44–1.15 (m, (CH₂)₆). ¹³C NMR (δ, CDCl₃): 217.0, 217.2 (CO), 140.0, 139.0 (=CHCH₂), 123.0, 124.0 (FeCH₂CH), 85.8 (*cis* isomer Cp), 85.4 (*trans* isomer Cp), 34.2 (CH₂Br), 32.9 (=CHCH₂), 30.2 (CH₂CH₂Br), 29.8, 29.4, 29.2, 28.8, 28.2, 27.2 (-(CH₂)₆-), 4.0, -2.0 (FeCH₂).

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