

# A study of $\beta$ -hydride abstraction from alkanediyl homobimetallic complexes $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(C}_n\text{H}_{2n})\}]$ ( $n = 4\text{--}10$ , $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ )

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## Abstract

The alkyl-bridged iron(II) complexes  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(C}_n\text{H}_{2n})\}]$  ( $n = 6\text{--}10$ ,  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) undergo both single and double hydride abstraction when reacted with one equivalent of  $\text{Ph}_3\text{CPF}_6$  to give both the monocationic complexes,  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(C}_n\text{H}_{2n-1})\}]\text{PF}_6$ , and the dicationic complexes,  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(C}_n\text{H}_{2n-2})\}](\text{PF}_6)_2$ . The ratios of monocationic to dicationic complexes decrease with the increase in the value of  $n$ . The complexes where  $n = 4$  and 5 undergo only single hydride abstraction under similar conditions. When reacted with two equivalents of  $\text{Ph}_3\text{CPF}_6$ , the complexes where  $n = 6\text{--}10$  undergo double hydride abstraction to give dicationic complexes only. In contrast, the complex where  $n = 5$  gives equal amounts of the monocationic and the dicationic complexes, while the complex where  $n = 4$  only gives the monocationic complex.  $^1\text{H}$  and  $^{13}\text{C}$  NMR data show that in the monocationic complexes one metal is  $\sigma$ -bonded to the carbenium ion moiety while the other is bonded in a  $\eta^2$ -fashion forming a chiral metallacyclopropane type structure. In the dicationic complexes both metals are bonded in the  $\eta^2$ -fashion. The monocationic complexes where  $n = 4\text{--}6$ , react with methanol to give  $\eta^1$ -alkenyl complexes  $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_n\text{CH}=\text{CH}_2]$  ( $n = 2\text{--}4$ ) as the major products and  $\sigma$ -bonded ether products  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(CH}_2)_n\text{CH}(\text{OCH}_3)\text{CH}_2\}]$  as the minor products. The complex where  $n = 8$  reacted with iso-propanol to give the  $\eta^1$ -alkenyl complex  $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_6\text{CH}=\text{CH}_2]$ . The dicationic complexes where  $n = 5, 8$  and 9 were reacted with  $\text{NaI}$  to give the respective  $\alpha, \omega$ -dienes and  $[\text{Cp}(\text{CO})_2\text{FeI}]$ .

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## 1. Introduction

Since King and Bisnette reported the first hydride abstraction from the alkyl-bridged complex  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(CH}_2)_3\}]$  in 1967 [1], there have been few reports involving other homodinuclear [2,3] and heterodinuclear [4–6] complexes. However, there have been no reports of hydride abstraction reactions involving alkanediyl complexes where the metal centres are separated by more than six methylene groups, even though these complexes have

been reported [7,8]. These long chain alkanediyl complexes are of interest because they may have two effectively independent  $\beta\text{-CH}_2$  groups, each of which is capable of undergoing hydride abstraction (Fig. 1). No reports on double hydride abstraction from the same alkanediyl complex have appeared in the literature. Archer et al. [9] concluded from IR and NMR data that in heterobimetallic alkanediyl complexes, where the metals are separated by more than three  $\text{CH}_2$  groups, the metals do not influence each other. This implied that, if the metals were separated by a sufficiently long alkyl bridge, it may be possible to activate both  $\beta\text{-CH}_2$  groups in these dinuclear complexes.

Friedrich and Moss [6] showed that the reactions of  $[\{\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_n\text{Ru}(\text{CO})_2\text{Cp}\}]$  ( $n = 4$  or 6) with  $\text{Ph}_3\text{CPF}_6$

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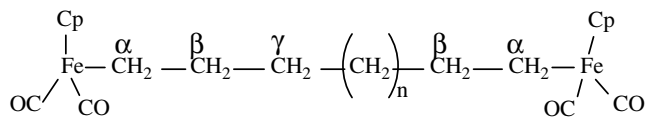


Fig. 1. Structural formula of an alkanediyl complex showing labeling of  $\text{CH}_2$  positions.

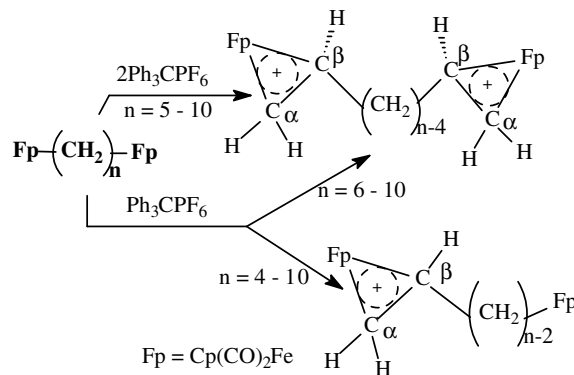
gave a mixture of equal amounts of the compounds  $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{CH}_2\text{CH}(\text{CH}_2)_n\text{Ru}(\text{CO})_2\text{Cp}\}]\text{PF}_6$  and  $[\text{Cp}(\text{CO})_2\text{Fe}\{(\text{CH}_2)_n\text{CHCH}_2\}\text{Ru}(\text{CO})_2\text{Cp}]\text{PF}_6$  ( $n = 2$  or  $4$ ). There was no evidence of hydride abstraction from both  $\beta$  carbon atoms. More importantly, Lennon et al. [10,11] reported the synthesis of stable long chain dicationic iron(II) complexes by a ligand exchange reaction involving  $[\text{Cp}(\text{CO})_2\text{Fe}(\text{isobutylene})]^+$  and  $\alpha,\omega$ -dienes or by treatment of the corresponding diepoxide  $\text{CH}_2(\text{O})\text{CH}(\text{CH}_2)_n\text{CH}(\text{O})\text{CH}_2$  ( $n = 3-5$ ) with two equivalents of  $\text{Na}[\text{Cp}(\text{CO})_2\text{Fe}]$ , followed by dehydration with  $\text{HBF}_4$ .

Although valuable information on the nature of metal-ligand bonding may be obtained from a systematic study of  $^{13}\text{C}$  chemical shifts of a series of compounds [12], most of the reported mono and dicationic complexes of the types  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_n\text{H}_{2n-1})\}]\text{X}$ , and  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_n\text{H}_{2n-2})\}]\text{X}_2$  ( $\text{X} = \text{PF}_6^-$ ,  $\text{BF}_4^-$  or  $\text{BPh}_4^-$ ) have not been studied by  $^{13}\text{C}$  NMR spectroscopy. We were, therefore, interested in the possibility of abstracting two hydrides from long chain alkyl-bridged complexes to give dicationic complexes and to systematically study their  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and now report our findings.

## 2. Results and discussion

### 2.1. Reactions of $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{CH}_2)_n\}]$ ( $n = 4-10$ ) with one equivalent of $\text{Ph}_3\text{CPF}_6$

The alkanediyl complexes  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{CH}_2)_n\}]$  ( $n = 6-10$ ) react with one equivalent of the hydride abstractor  $\text{Ph}_3\text{CPF}_6$  at room temperature to give both monocationic  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_n\text{H}_{2n-1})\}]\text{PF}_6$  and



Scheme 1. Reaction of alkanediyl complexes with one and two equivalents of  $\text{Ph}_3\text{CPF}_6$ .

dicationic complexes  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_n\text{H}_{2n-2})\}](\text{PF}_6)_2$  (see Scheme 1). The dicationic complexes are formed as yellow precipitates after about 2 h of reaction and are easily separated by filtration under nitrogen. The monocationic complexes remain in solution and are precipitated as yellow microcrystalline solids by addition of diethyl ether to the filtrates obtained after the separation of the dicationic products. It can be seen from Table 1 that the ratio of monocationic to dicationic products decreases with increase in chain length of the bridging alkyl group. Thus it is easier to remove hydrides from both  $\beta$ -positions in the same molecule when these are further apart.

The complexes where  $n = 4$  and  $5$  react with one equivalent of the hydride abstractor to give only the known monocationic products  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_n\text{H}_{2n-1})\}]\text{PF}_6$  [3]. There was no evidence of dicationic complexes in the reaction mixtures even after standing under nitrogen overnight. This shows that once one hydride is abstracted it becomes difficult to abstract a second hydride from a  $\text{CH}_2$  group near a charged  $\text{CH}^{\delta+}$  moiety, because this would be strongly held to the carbon atom due to the inductive effect caused by the  $\text{CH}^{\delta+}$  group. The influence of the positive charge is seen in the resonances of the protons and carbon atoms in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, in

Table 1  
Data for monocationic and dicationic iron (II) complexes

Compound	M.p. ( $^{\circ}\text{C}$ )	%Yield <sup>a</sup>	Elemental analysis		IR $\nu(\text{CO})/\text{KBr}$
			%C Found (Calc)	%H Found (Calc)	
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_5\text{H}_9)]\text{PF}_6$	Dec > 120	(40)	40.2 (41.3)	3.4 (3.4)	2075, 2032, 1998, 1934
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_5\text{H}_8)](\text{PF}_6)_2$	Dec > 125	(48)	32.0 (32.1)	2.4 (2.6)	2079, 2039
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_6\text{H}_{11})]\text{PF}_6$	Dec > 119	55	40.9 (41.2)	3.7 (3.6)	2076, 2038, 2003, 1941
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_6\text{H}_{10})](\text{PF}_6)_2$	Dec > 130	4 (73)	32.8 (33.1)	2.6 (2.8)	2073, 2036
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_7\text{H}_{13})]\text{PF}_6$	Dec > 110	65	43.4 (42.3)	4.1 (3.8)	2075, 2043, 1989, 1942
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_7\text{H}_{12})](\text{PF}_6)_2$	Dec > 130	6 (73)	33.7 (34.1)	3.0 (3.0)	2079, 2037
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_8\text{H}_{15})]\text{PF}_6$	Dec > 85	18	43.6 (43.3)	4.0 (4.1)	2075, 2035, 1994, 1932
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_8\text{H}_{14})](\text{PF}_6)_2$	Dec > 135	57 (90)	35.2 (35.1)	3.2 (3.2)	2069, 2015
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_9\text{H}_{17})]\text{PF}_6$	Dec > 90	15	44.2 (44.3)	4.0 (4.4)	2076, 2044, 1987, 1929
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_9\text{H}_{16})](\text{PF}_6)_2$	Dec > 95	32 (87)	35.8 (36.0)	3.2 (3.4)	2076, 2032
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_{10}\text{H}_{19})]\text{PF}_6$	Dec > 98	5	46.6 (45.2)	4.5 (3.6)	2076, 2034, 1998, 1937
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_{10}\text{H}_{18})](\text{PF}_6)_2$	Dec > 135	27 (88)	36.7 (36.8)	3.7 (3.6)	2080, 2035

<sup>a</sup> Values in brackets are yields obtained by reacting starting materials with 2 equiv. of  $\text{Ph}_3\text{CPF}_6$ .

which the signals are significantly shifted downfield with respect to the corresponding peaks in the starting materials (Sections 2.4–2.7).

## 2.2. Reactions of $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{CH}_2)_n\}]$ ( $n = 4-10$ ) with two equivalents of $\text{Ph}_3\text{CPF}_6$

The reactions of the alkanediyl complexes  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{CH}_2)_n\}]$  ( $n = 6-10$ ) with two equivalents of  $\text{Ph}_3\text{CPF}_6$  result in immediate formation of the dicationic complexes  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_n\text{H}_{2n-2})\}](\text{PF}_6)_2$  in >70% yields. These precipitate as soon as the solutions of the reactants are mixed and are easily separated by filtration under nitrogen. A minute amount of the monocationic complex was detected (IR  $\nu(\text{CO})$ ) in the filtrate of the reaction of the complex where  $n = 6$  only, but there was too little to isolate. The dications are air stable yellow powders, which thermally decompose without melting in the range 120–135 °C. They are insoluble in most common organic solvents (e.g.  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and hexane) and were characterised by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, IR and elemental analysis.

The complex where  $n = 4$  gave only the monocationic complex, even after standing for 16 h. Sanders and Giering reported the synthesis of the dicationic complex  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_4\text{H}_6)\}](\text{HCl})_2$  by the reaction of the butadiene complex  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_4\text{H}_6)\}]$  with anhydrous  $\text{HCl}$  gas [13]. However, they did not isolate the compound but inferred its structure by IR and by its thermal decomposition to  $\text{Cp}(\text{CO})_2\text{FeCl}$ . These authors did not report detection of butadiene or any other  $\text{C}_4$  alkene.

The complex where  $n = 5$  gave almost equal amounts of the monocationic and dicationic complexes after overnight reaction with two equivalents of  $\text{Ph}_3\text{CPF}_6$ . Attempts to force the reaction to go to completion by reaction with 4 mol of  $\text{Ph}_3\text{CPF}_6$  only increased the amount of the dicationic product relative to the monocationic product, but the reaction did not go to completion. The dicationic complex  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_5\text{H}_8)\}](\text{PF}_6)_2$  was found to be unstable in solution due to the lability of the  $\text{Cp}(\text{CO})_2\text{Fe}$  groups. For example, it was noted that when alkanediyl complex was reacted with 4 mol of  $\text{Ph}_3\text{CPF}_6$  and the mixture allowed to stand overnight without stirring, the products obtained were the dicationic complex  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_5\text{H}_8)\}](\text{PF}_6)_2$  and the monometallic cationic product  $[\text{Cp}(\text{CO})_2\text{FeCH}_2=\text{CHC}_3\text{H}_7](\text{PF}_6)$ .

## 2.3. IR spectroscopy

The monocationic complexes,  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_n\text{H}_{2n-1})\}]\text{PF}_6$  ( $n = 4-10$ ), show four carbonyl absorption peaks that characterise the separate cationic and neutral Fp centres (Fp=Cp(CO)<sub>2</sub>Fe; cationic Fp:  $\nu_{\text{CO}}$  above 2030 and 2070  $\text{cm}^{-1}$ ; neutral Fp:  $\nu_{\text{CO}}$  around 1940 and 2012  $\text{cm}^{-1}$ ). The dications on the other hand show only the two peaks characteristic of the cationic Fp centres. There is no significant shift in the  $\nu_{\text{CO}}$  peak positions upon changing the

length of the polymethylene chain. The data are summarized in Table 1. These complexes show a single medium intensity band in the olefinic C–H stretching region at 3125–3129  $\text{cm}^{-1}$  and a weak band in the C=C stretching region at 1515–1527  $\text{cm}^{-1}$ . The C=C bands are shifted to smaller wavenumbers by >115  $\text{cm}^{-1}$  relative to free alkenes as expected for coordinated alkenes [14].

## 2.4. $^1\text{H}$ NMR spectroscopy of the monocationic complexes $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_n\text{H}_{2n-1})\}]\text{PF}_6$ ( $n = 7-10$ )

The  $^1\text{H}$  NMR data for the monocationic complexes are summarized in Table 2. The complexes show two characteristic singlet peaks at 4.9 ppm and 5.9 ppm for the five equivalent Cp protons of the neutral and cationic Fp groups, respectively. This is in good agreement with the data reported for similar complexes [3]. These positions are not altered with change in alkenyl chain length. The spectra also show two characteristic doublets (each integrating for 1H) at 4.06 ppm (average  $J_{\text{HH}} = 8.3$  Hz) and 3.64 ppm (average  $J_{\text{HH}} = 14.6$  Hz) assigned to the diastereotopic protons of the  $\text{CH}_2$   $\alpha$  to the cationic Fp<sup>+</sup> group. These two protons are *cis* and *trans* to the  $\beta$ -CH proton, respectively, as determined from the coupling constants, and they show no geminal coupling. The protons of the  $\text{CH}_2$  group alpha to the  $\text{CH}^{\delta+}$  (i.e.  $\gamma$  to the cationic Fp<sup>+</sup>, see Scheme 1) show separate resonances, a distinct multiplet at around 2.50 ppm and a multiplet at about 1.60 ppm. Similarly, the protons of the  $\delta$ - $\text{CH}_2$  show separate resonances, distinct multiplets at 1.69 ppm and at about 1.40 ppm, respectively. The spectra of the complexes where  $n = 7-10$  also show unresolved proton resonances between 1.10 and 1.68 ppm.

The presence of the two well resolved doublets assignable to the  $\alpha$ - $\text{CH}_2$  protons, and the observation that both the  $\gamma$ - $\text{CH}_2$  (the peaks are  $\approx 0.9$  ppm apart) and  $\delta$ - $\text{CH}_2$  (the peaks are  $\approx 0.2$  ppm apart) protons are diastereotopic in the  $^1\text{H}$  NMR spectra of these complexes is convincing evidence that the complexes are chiral. The  $\beta$ -CH carbon is the chiral centre and it is therefore expected that the methylene protons in its neighbourhood should be non-equivalent [15]. The influence of an asymmetric centre is often observed in protons that are more than two bonds away from the asymmetric centre. The pattern of signals in the spectra, especially the signals assignable to the  $\alpha$ - $\text{CH}_2$  protons, resemble those observed in the reported complexes  $[\{\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2=\text{CHOEt})\}]\text{PF}_6$  [16] and  $[\{\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2=\text{CHOMe})\}]\text{PF}_6$  [17] in which the metals have been shown to be  $\eta^2$ -bonded to the carbenium ion moieties. Evidently, therefore, the same bonding prevails in these bimetallic complexes.

## 2.5. $^{13}\text{C}$ NMR spectroscopy of the monocationic complexes $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_n\text{H}_{2n-1})\}]\text{PF}_6$

The  $^{13}\text{C}$  NMR data for the monocationic complexes are summarized in Table 3. These complexes show two peaks

Table 2

<sup>1</sup>H NMR data for the monocationic complexes  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(C}_n\text{H}_{2n-1})\}]\text{PF}_6$  in acetone-*d*<sub>6</sub>

<i>n</i>	σ-CpFe	π-CpFe	<i>cis</i> -FeCH <sub>2</sub> , <sup>3</sup> <i>J</i> (HH) <sup>b</sup>	<i>trans</i> -FeCH <sub>2</sub> , <sup>3</sup> <i>J</i> (HH) <sup>b</sup>	β-CH	γ-CH <sub>2</sub>	δ-CH <sub>2</sub>	Others (not resolved)	BPh <sub>4</sub>
4 <sup>a</sup>	5.0 (5H, s)	5.8 (5H, s)	3.9 (1H, d, 6.7)	3.5 (1H, d, 14.7)	5.3 (1H, m)	2.5 (1H, m); 1.3 (1H, m)	1.6 (2H, m)		7.4s, 7.0t, 6.8t
5 <sup>a</sup>	4.9 (5H, s)	5.8 (5H, s)	4.0 (1H, d, 7.9)	3.6 (1H, d, 13.7)	5.3 (1H, m)	2.6 (1H, m); 1.5 (1H, m)	1.8 (1H, m); 1.6 (1H, m)	1.8 (2H, m)	7.4s, 7.0t, 6.8t
7	4.9 (5H, s)	5.9 (5H, s)	4.1 (1H, d, 8.2)	3.6 (1H, d, 14.7)	5.3 (1H, m)	2.5 (1H, m); 1.4 (1H, m)	1.7 (1H, m); 1.5 (1H, m)	1.4–1.6m	
8	4.9 (5H, s)	5.9 (5H, s)	4.1 (1H, d, 8.4)	3.7 (1H, d, 14.5)	5.3 (1H, m)	2.5 (1H, m)		1.3–1.7m	
9	4.9 (5H, s)	5.9 (5H, s)	4.1 (1H, d, 8.2)	3.7 (1H, d, 14.6)	5.3 (1H, m)	2.5 (1H, m); 1.3 (1H, m)		1.3–1.6m	
10	4.9 (5H, s)	5.9 (5H, s)	4.1 (1H, d, 8.2)	3.7 (1H, d, 14.3)	5.3 (1H, m)	2.5 (1H, m);		1.1–1.7m, 15H	

<sup>a</sup> Counter ion is BPh<sub>4</sub><sup>-</sup>.<sup>b</sup> Coupling constants are given in Hz.

Table 3

<sup>13</sup>C NMR data for the complexes  $[\text{Cp}(\text{CO})_2\text{Fe}(\text{C}_n\text{H}_{2n-1})\text{Fe}(\text{CO})_2]\text{PF}_6$ 

<i>n</i>	σ-CpFeCO	π-CpFeCO	σ-CpFe	π-CpFe	π-FeCH <sub>2</sub>	CH	CHCH <sub>2</sub>	CHCH <sub>2</sub> CH <sub>2</sub>	CHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	α-CH <sub>2</sub> <sup>a</sup>	β-CH <sub>2</sub>	γ-CH <sub>2</sub>	δ-CH <sub>2</sub>	BPh <sub>4</sub>
4 <sup>b</sup>	217.3, 217.2	210.7, 208.5	85.7	88.8	51.5	89.2	44.3			5.2				135.9, 124.9d, 121.1
5 <sup>b</sup>	217.8	210.6, 208.4	85.6	89.0	53.6	87.9	41.3	41.1		1.4				135.9, 124.8d, 121.1
7	218.0	210.4, 208.2	85.5	89.1	53.8	88.8	33.8	32.1	37.5	2.3	36.2			
8	218.1	210.5, 208.2	85.5	89.1	53.9	88.3	34.2	32.5	37.7	2.6	28.4	36.1		
9	218.1	210.4, 208.2	85.5	89.1	53.9	88.3	34.4	32.4	37.8	2.7	27.8	28.0	36.1	
10	218.3	210.5, 208.2	85.3	89.3	53.7	88.0	34.4	34.3	37.6	2.4	28.6	32.2	36.3	

<sup>a</sup> CH<sub>2</sub> α to the σ-bonded Fe etc.<sup>b</sup> counter ion is BPh<sub>4</sub><sup>-</sup>.

at about 86 ppm and 89 ppm assignable to the Cp carbons of the neutral and cationic Fp groups, respectively. These positions are in good agreement with the data reported for mononuclear cationic complexes [18] and dinuclear neutral complexes [19]. The neutral Fp carbonyls show one peak at around 217 ppm, while the cationic Fp carbonyls show separate peaks at 210 ppm and 208 ppm, respectively, indicating that the carbonyls are non-equivalent, as expected for these structures in which the  $\beta$  carbon is chiral. Furthermore, molecular structures of the complexes  $[\text{Cp}^*(\text{CO})_2\text{Fe}\{\mu-(\text{C}_3\text{H}_5)\}\text{Fe}(\text{CO})_2\text{Cp}]\text{PF}_6$  [4],  $[\text{Cp}^*(\text{CO})_2\text{Fe}\{\mu-(\text{C}_3\text{H}_5)\}\text{Ru}(\text{CO})_2\text{Cp}]\text{PF}_6$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) [5],  $[\{\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2=\text{CHOEt})\}\text{PF}_6$  [16] and  $[\{\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2=\text{CHOMe})\}\text{PF}_6$  [17] show that one of the carbonyls is *cis* to the  $\alpha\text{-CH}_2$ , while the second is *cis* to  $\beta\text{CH}^{\delta+}$ , which form the metallacyclopropane structure with the Fe atom. Therefore, they are effectively in different magnetic environments and hence they show different signals in the  $^{13}\text{C}$  NMR. They are shielded by more than 7 ppm relative to the starting materials. This may be due to reduced back donation from the metal to the CO because the electrons are directed to the  $\beta\text{-CH}^{\delta+}$  group. The reduced back donation causes the oxygen atom to donate more electrons to the C atom thus causing shielding. This is corroborated by the IR spectra in which the cationic Fp carbonyls occur at higher wavenumbers, indicating strengthened C–O bonds as compared to the neutral Fp carbonyls.

All the complexes show a weak resonance at about 88 ppm assignable to the carbon of the  $\beta\text{CH}^{\delta+}$  group in the carbenium ion moiety. This is significantly less deshielded than the  $\beta\text{CH}$  moiety of  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_3\text{H}_5)\}]\text{PF}_6$ , which resonates at 128 ppm, but sufficiently significantly deshielded to imply a considerable degree of carbenium ion character. The carbon of the  $\text{CH}_2$   $\alpha$  to the  $\text{Fp}^+$  group shows a resonance at about 54 ppm which is more deshielded than the  $\alpha$  carbon atom of the complex  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_3\text{H}_5)\}]\text{PF}_6$  which resonates at 24 ppm. In all the complexes the carbon atom of the  $\text{CH}_2$  group  $\alpha$  to the  $\beta\text{CH}^{\delta+}$  group ( $\gamma$  to the  $\text{Fp}^+$  group) is significantly less deshielded than would be expected for a  $\text{CH}_2$  group next to a positively charged CH group. For example, in the neutral complex  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{CH}_2)_4\}]$ , the  $\beta\text{-CH}_2$  carbon atoms resonate at 43.6 ppm in the  $^{13}\text{C}$  NMR (acetone- $d_6$ ) spectrum. On the other hand, in the corresponding carbenium ion complex  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_4\text{H}_7)\}]\text{PF}_6$ , the  $\gamma\text{-CH}_2$  ( $\alpha$  to  $\text{CH}^{\delta+}$  group and  $\beta$  to the neutral Fp group) resonates at 44.3 ppm in the  $^{13}\text{C}$  NMR spectrum. Thus the  $\gamma\text{-CH}_2$  is shifted downfield by only 0.7 ppm relative to the neutral complex. Similar observations have been made in the  $^{13}\text{C}$  NMR spectra of the shorter chain complexes  $[\text{Cp}^*(\text{CO})_2\text{Fe}\{\mu-(\text{C}_3\text{H}_5)\}\text{Fe}(\text{CO})_2\text{Cp}]\text{PF}_6$  and  $[\text{Cp}^*(\text{CO})_2\text{Fe}\{\mu-(\text{C}_3\text{H}_5)\}\text{Ru}(\text{CO})_2\text{Cp}]\text{PF}_6$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ). X-ray crystallographic data of these complexes show that the metal attached to the  $\text{Cp}^*$  ligand is coordinated to the carbenium ion in a  $\eta^2$ -fashion leading to a metallacyclopropane type structure [4,5]. This suggests that similar coordination is present in these long

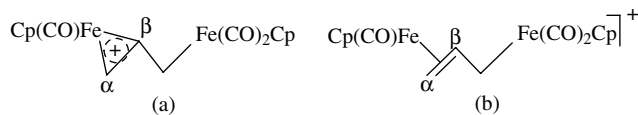


Fig. 2. (a) Metallacyclopropane structure, (b)  $\pi$ -bonded structure.

chain carbenium ion complexes. It therefore seems more accurate to represent the bonding between the carbenium ion and the transition metal as a metallacyclopropane type structure as shown in Fig. 2a rather than the traditional side-on bonding structure [14,20] in Fig. 2b.

It has been reported that  $\pi$ -complexation with an  $\text{Fp}^+$  group shifts an unsubstituted alkene carbon upfield by 60 ppm in the  $^{13}\text{C}$  NMR spectra [12]. Given that the chemical shifts of the  $\alpha$  and  $\beta$  olefinic carbons of terminal olefins normally appear at about 114 and 140 ppm, respectively [15],  $\pi$ -complexation with an  $\text{Fp}^+$  group would shift the  $\alpha$  carbon resonances upfield to about 54 ppm and the  $\beta$  carbon to about 80 ppm. This is in close agreement with the data given in column 6 of Table 3, but the  $\beta=\text{CH}$  resonances are shifted much further upfield than expected for this bonding mode (see column 7 in Table 3). Furthermore, considering the increased chemical shift differences between the olefinic carbon atoms of the carbenium ion complexes (Table 4), it is clear that there is a much greater contribution from back-donation to the overall bonding between the metals and the “carbenium ions” [12]. Increased back-donation from the metal to the carbenium ion can also be deduced from the deshielding of the carbon atoms of the cyclopentadienyl ring of the  $\text{Fp}^+$  group ( $\delta$  89.1 ppm) relative to those of the neutral Fp group ( $\delta$  85.5 ppm) (Table 3).

#### 2.6. $^1\text{H}$ NMR spectroscopy of the dicationic complexes $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_n\text{H}_{2n-2})\}](\text{PF}_6)_2$ ( $n = 5\text{--}10$ )

The  $^1\text{H}$  NMR data for these complexes are summarized in Table 5. The spectra show that hydrides were abstracted from both of the  $\beta\text{-CH}_2$  groups. For example, they show only one singlet peak at about 5.90 ppm assignable to the 10 equiv. Cp protons of the cationic Fp groups. This position does not significantly change with increase in the carbocation chain length and is deshielded relative to that of the Cp group in the starting material (4.7 ppm). These complexes have two chiral centres (one at each  $\beta\text{-CH}$

Table 4  
Chemical shifts of olefinic carbon atoms of some compounds and the differences between them

Compound	$=\text{CH}_2(\text{C}_1)$	$=\text{CH}(\text{C}_2)$	$\delta(\text{C}_2 - \text{C}_1)$
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_4\text{H}_7)\text{BPh}_4]$	51.5	89.2	36.7
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_5\text{H}_9)\text{BPh}_4]$	53.6	87.9	34.3
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_7\text{H}_{12})](\text{PF}_6)_2$	53.8	88.8	35.0
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_8\text{H}_{14})](\text{PF}_6)_2$	53.9	88.3	34.4
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_9\text{H}_{16})](\text{PF}_6)_2$	53.9	88.3	34.4
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_{10}\text{H}_{18})](\text{PF}_6)_2$	53.7	88.0	34.3

Table 5  
 $^1\text{H}$  NMR data for  $[\text{Cp}(\text{CO})_2\text{Fe}(\text{C}_n\text{H}_{2n-2})\text{Fe}(\text{CO})_2](\text{PF}_6)_2$  in acetone- $d_6$

$n$	Cp	$cis\text{-FeCH}_2$ , $^3J(\text{HH})^c$	$trans\text{-FeCH}_2$ , $^3J(\text{HH})^c$	$\beta\text{-CH}$	$\gamma\text{-CH}_2$	$\delta\text{-CH}_2$	$\omega\text{-CH}_2$	BPh <sub>4</sub>
5 <sup>a</sup>	5.8 (10H, s)	4.2 (2H, d, 8.2), 4.1 (2H, d, 7.6)	3.8 (2H, d, 14.7), 3.7 (2H, d, 13.7)	5.3 (2H, m), 5.1 (2H, m)	2.9 (2H, m); 2.7 (2H, m)			
6 <sup>b</sup>	5.8 (10H, s)	3.9 (2H, m)	3.4 (2H, m)	4.9 (2H, m)	2.8 (1H, m); 1.5 (1H, m)	2.5 (1H, m); 1.6 (1H, m)		
7	5.9 (10H, s)	4.1 (2H, d, 4.8)	3.7 (2H, d, 13.6)	5.3 (2H, m)	2.6 (2H, m)	1.6–1.9 (4H, m)		
8	6.0 (10H, s)	4.1 (2H, d, 6.0)	3.7 (2H, d, 13.8)	5.9 (2H, m)	2.6 (2H, m)	1.6–1.9 (6H, m)		
8 <sup>a</sup>	5.7 (10H, s)	3.9 (2H, d, 7.0)	3.6 (2H, d, 14.2)	5.1 (2H, m)	2.5 (2H, m)	1.5–1.8 (6H, m)		7.4, 7.0t, 6.8t
9	5.9 (10H, s)	4.0 (2H, d, 5.9)	3.6 (2H, d, 14.1)	5.3 (2H, m)	2.6 (2H, m); 1.5 (2H, m)	1.7 (2H, m); 1.5 (2H, m)	1.5 (2H, m)	
9 <sup>a</sup>	5.7 (10H, s)	3.9 (2H, d, 8.2)	3.5 (2H, d, 14.6)	5.1 (2H, m)	2.5 (2H, m); 1.5 (2H, m)	1.7 (2H, m); 1.5 (1H, m)	1.5 (2H, m)	7.4m, 7.0t, 6.8t
10	5.9 (10H, s)	4.1 (2H, d, 7.7)	3.6 (2H, d, 14.3)	5.3 (2H, m)	2.5 (2H, m); 1.4 (2H, m)	1.7 (2H, m); 1.6 (2H, m)	1.4 (4H, m)	

<sup>a</sup> Counter ion is BPh<sub>4</sub>.

<sup>b</sup> Recorded in CD<sub>3</sub>CN.

<sup>c</sup> Coupling constants are given in Hz.

group) and thus there are two diastereomeric possibilities: RR(SS) and RS(SR) which may be present in equal amounts in solution. However, the spectra of the complexes where  $n = 7\text{--}10$  do not show any evidence to support the existence of more than one diastereomer in solution. This is not surprising given the fact that in these complexes the chiral centres are separated by more than three CH<sub>2</sub> groups, in which case they are too far apart to induce a diastereomeric effect. Thus, the spectra observed for the diastereomers are indistinguishable by NMR spectroscopy. This is confirmed by the <sup>13</sup>C NMR spectra (Section 2.7).

The spectrum of the complex where  $n = 6$  suggests that the chiral centres are sufficiently close and there appear to be two pairs of diastereomers in equal amounts in solution. For example, the expected doublets assignable to the  $\alpha\text{-CH}_2$  protons overlap partially to resemble triplets, but the signals of the other methylene protons overlap completely so that they are indistinguishable. The spectrum of the complex where  $n = 5$  clearly shows the presence of two pairs of diastereomers in solution. Four signals are observed as expected for each pair of diastereomers as follows: a multiplet for the  $\beta\text{-CH}$  protons, two doublets for the diastereotopic  $\alpha\text{-CH}_2$  protons and a multiplet assignable to the two  $\gamma\text{-CH}_2$  protons, which may be equivalent because their environments are mirror images. The chemical shifts of the signals are significantly different so that all eight signals are seen separately in the spectrum.

### 2.7. <sup>13</sup>C NMR spectroscopy of the dicationic complexes $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-}(\text{C}_n\text{H}_{2n-2})\}](\text{PF}_6)_2$

The <sup>13</sup>C NMR data are summarized in Table 6. The number of peaks assignable to the carbon atoms of the carbene ion moiety in the spectra of the complexes where  $n = 6\text{--}10$  support the conclusion that the two pairs of diastereomers are not distinguishable by NMR. For example, in the complexes where  $n$  is even the number of peaks observed is  $1/2n$ , while  $1/2n + 1$  peaks were observed in spectra of the complexes where  $n$  is odd. Thus, the chiral centres are sufficiently far apart that they do not interact and the possible diastereomers are not distinguishable by <sup>13</sup>C NMR spectroscopy. All the spectra show one peak around 89 ppm assigned to the Cp carbons of the cationic Fp group. This is in good agreement with the data reported for mononuclear monocationic complexes [18]. The spectra show two resonances at about 210.6 ppm and 208.2 ppm assignable to the cationic Fp carbonyls. The number of peaks observed in the spectrum of the complex where  $n = 5$  supports the suggestion that there are two pairs of diastereomers in solution. For example, it shows four resonances at 210.7, 210.5, 208.7 and 208.6 ppm assignable to the cationic Fp carbonyl carbon atoms. Moreover, the spectrum also shows that the signals of the carbon atoms closest to the chiral centres (i.e.  $\alpha\text{-CH}_2$  and  $\gamma\text{-CH}_2$ ) are split. This is convincing evidence that diastereomers are present in solution [21]. There are no <sup>13</sup>C NMR data for

Table 6  
 $^{13}\text{C}$  NMR data for  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(C}_n\text{H}_{2n-2})\}](\text{PF}_6)_2$  in acetone- $d_6$

$n$	CO	Cp	FeCH <sub>2</sub>	$\beta$ -CH	$\gamma$ -CH <sub>2</sub>	$\delta$ -CH <sub>2</sub>	$\omega$ -CH <sub>2</sub>	BPh <sub>4</sub>
5 <sup>a</sup>	210.7, 210.5, 208.7, 208.6	90.6	56.3, 55.3	87.9	42.8, 42.7			136.9, 125.8, 122.2
6 <sup>b</sup>	211.3, 209.1	90.2	56.0	85.6	39.5			
7	210.2, 208.0	89.2	54.3	86.5	35.4	29.3		
8	210.3, 208.1	89.2	54.1	87.4	35.7	31.7		
8 <sup>a</sup>	211.5, 209.5	90.4	55.5	88.3	37.2	33.1		137.1, 126.1d, 122.4
9	210.4, 208.2	89.2	54.1	87.8	35.9	32.0	28.5	
9 <sup>a</sup>	210.3, 208.3	89.0	53.9	87.4	36.0	32.2	28.3	135.9, 124.9, 121.2
10	211.5, 209.3	90.3	55.1	89.1	37.2	33.4	29.4	

<sup>a</sup> Counter ion is BPh<sub>4</sub><sup>-</sup>.

<sup>b</sup> Recorded in CD<sub>3</sub>CN.

long chain dicationic complexes of this type in the literature to compare.

### 2.8. Reaction with sodium tetraphenylborate

When reacted with sodium tetraphenylborate in acetone, the complexes  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_4\text{H}_7)]\text{PF}_6$ ,  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_5\text{H}_9)]\text{PF}_6$ ,  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_5\text{H}_8)](\text{PF}_6)_2$  and  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_9\text{H}_{16})](\text{PF}_6)_2$  readily underwent counter ion exchange. The displacement of the PF<sub>6</sub><sup>-</sup> by BPh<sub>4</sub><sup>-</sup> was confirmed by <sup>1</sup>H- and <sup>13</sup>C NMR spectroscopy and elemental analysis. The counter ion BPh<sub>4</sub><sup>-</sup> confers more stability to the dicationic complexes and makes them more soluble in deuterated acetone. Thus, whereas the PF<sub>6</sub><sup>-</sup> complexes give broad signals in the <sup>1</sup>H NMR spectra, the BPh<sub>4</sub><sup>-</sup> complexes give spectra with sharp and well resolved resonances in solution. However, even when this counter ion was present, the dicationic complex where  $n = 5$  still decomposed in acetone- $d_6$  with the loss of Fp<sup>+</sup> groups to give the FpBPh<sub>4</sub> salt and 1,4-pentadiene. It had been anticipated that the change of the counter ion would make the compounds more crys-

talline, but only when  $n = 4$  and 5 was a change observed from microcrystals in the PF<sub>6</sub> salts to bright yellow plates in the BPh<sub>4</sub> salts. The other complexes still formed powders (see Table 7).

### 2.9. Reactions with NaI, CF<sub>3</sub>COOH, CH<sub>3</sub>OH and (CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>OH

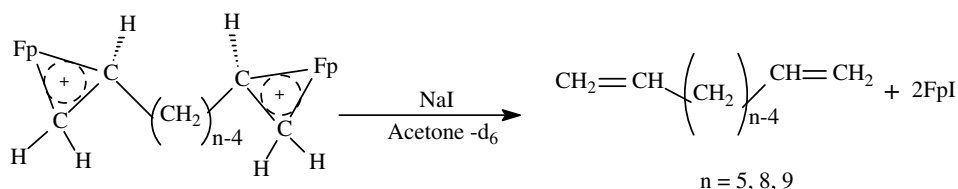
When the dicationic complexes where  $n = 5, 8$  and 9 reacted with NaI in deuterated acetone in NMR tubes they liberated the respective  $\alpha, \omega$ -dienes which were detected by proton NMR spectroscopy (see Scheme 2). This is further evidence that the long chain alkanediyl complexes underwent double hydride abstraction. The monometallic complex  $[\text{Cp}(\text{CO})_2\text{Fe}(\text{C}_5\text{H}_{10})]\text{BPh}_4$  gave pentene on reaction with NaI. The fact that the complexes react with a nucleophile (I<sup>-</sup>) to give alkenes indicates that there is more positive charge on the metal centre than on the olefinic carbon atoms, making the alkene group less reactive towards nucleophiles. This behaviour is similar to *umpolung*, a phenomenon observed in transition metal olefin complexes

Table 7  
 Data for  $[\text{Cp}(\text{CO})_2\text{Fe}(\text{C}_n\text{H}_{2n-1})\text{Fe}(\text{CO})_2]\text{BPh}_4$

$n$	%Yield	M.p. (°C)	IR $\nu(\text{CO})$ (cm <sup>-1</sup> ) in CH <sub>2</sub> Cl <sub>2</sub>	Elemental analysis	
				C Found (Calc)	H Found (Calc)
4	57	Dec > 120	2071, 2034, 2008, 1950	69.4 (69.2)	5.1 (5.1)
5	72	Dec > 128	2073, 2036, 2004, 1945	68.7 (69.6)	5.3 (5.5)
5 <sup>a</sup>	70	Dec > 115	2079 <sup>b</sup> , 2041	74.5 (75.9)	5.8 (5.6)
8 <sup>a</sup>	74	Dec > 110	2072 <sup>b</sup> , 2034	76.4 (76.3)	5.8 (5.9)
9 <sup>a</sup>	79	Dec > 125	2071 <sup>b</sup> , 2033	76.7 (76.4)	5.9 (6.0)

<sup>a</sup> Dicationic complex.

<sup>b</sup> KBr pellet.



Scheme 2. Reactions with sodium iodide.

[22]. This reaction also supports the conclusion that the bonding between the metal and the carbenium ion moiety tends more towards the metallacyclopropane model than the  $\pi$ -bonded model.

The most significant difference (chemically) between metallacyclopropanes and those olefins coordinated according to the Dewar–Duncason–Chatt model is that the latter tend to have a residual positive charge on the vinylic carbon while the former have it on the metal. The latter are subject to nucleophilic attack on the vinylic carbon [22] leading to nucleophilic addition products rather than olefin liberation.

The complex  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2(\text{C}_4\text{H}_7)]\text{PF}_6$  reacted with  $\text{CF}_3\text{COOH}$  in THF to give the previously reported cationic monometallic complex  $[\text{Cp}(\text{CO})_2\text{FeCH}_2=\text{CHCH}_2\text{CH}_3]\text{PF}_6$  [23] and the acetate complex  $[\text{Cp}(\text{CO})_2\text{FeOOC}\text{CF}_3]$  as detected by NMR and IR spectroscopy. The NMR spectra indicate that the metal in the complex  $[\text{Cp}(\text{CO})_2\text{FeCH}_2=\text{CHCH}_2\text{CH}_3]\text{PF}_6$  forms a metallacyclopropane type structure with the carbenium ion moiety. For example, the protons of both the  $\alpha$ - and  $\gamma$ - $\text{CH}_2$  groups are diastereotopic, and the  $^{13}\text{C}$  NMR spectrum shows two carbonyl peaks.

The monocationic complexes  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_n\text{H}_{2n-1})\}]\text{PF}_6$ , ( $n = 4-6$ ) react with methanol to form the previously reported [24]  $\eta^1$ -alkenyl complexes,  $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_{n-2}\text{CH}=\text{CH}_2]$ , as the main products and the new  $\sigma$ -bonded ether complexes,  $[\text{Cp}(\text{CO})_2\text{FeCH}_2\text{CH}(\text{OCH}_3)(\text{CH}_2)_{n-2}\text{Fe}(\text{CO})_2\text{Cp}]$  as the minor products (see Scheme 3). The  $\sigma$ -bonded ether complexes were very unstable and were only detected by  $^1\text{H}$  NMR spectroscopy.

The monometallic olefin complex  $[\text{Cp}(\text{CO})_2\text{FeCH}_2=\text{CHCH}_2\text{CH}_3]\text{PF}_6$  reacted with methanol in an NMR tube giving 1-butene as the major product and the  $\sigma$ -bonded ether complex,  $[\text{Cp}(\text{CO})_2\text{FeCH}_2\text{CH}(\text{OCD}_3)\text{CH}_2\text{CH}_3]$ , as the minor product. Monometallic ether complexes have been reported in high yields (>70%) [25] when Fp ethene and propene complexes were reacted with methanol, while a lower yield of 18% was achieved with a styrene complex.

The complex  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_8\text{H}_{15})\}]\text{PF}_6$  reacted with iso-propanol to give the  $\eta^1$ -alkenyl complex  $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_6\text{CH}=\text{CH}_2]$  as the major product (95% yield) and the  $\sigma$ -bonded ether complex  $[\text{Cp}(\text{CO})_2\text{FeCH}_2-$

$\text{CH}(\text{OCH}_3)(\text{CH}_2)_6\text{Fe}(\text{CO})_2\text{Cp}]$  as the minor product. Sublimation at  $80^\circ\text{C}$  under reduced pressure gave the  $\eta^1$ -alkenyl complex as the sublimate but the ether complex decomposed in the process. Thus, the low yields of the  $\sigma$ -bonded ether complexes  $[\text{Cp}(\text{CO})_2\text{FeCH}_2\text{CH}\{\text{OCH}(\text{CH}_3)_2\}\text{R}]$  ( $\text{R}=\text{CH}_3$ ,  $n\text{-C}_4\text{H}_9$  and  $n\text{-C}_{13}\text{H}_{27}$ ) reported by Clayton et al. [23] in the reactions of the monometallic olefin complexes  $[\text{Cp}(\text{CO})_2\text{Fe}(\eta^2\text{-CH}_2=\text{CHR})]^+$  with iso-propanol may be due to the fact that the free olefin, which they may not have detected, is the major product.

These reactions indicate that the metal centre is more electrophilic than both olefinic carbons. The formation of the  $\sigma$ -bonded ether complexes does, however, indicate that there is some degree of the positive charge on the  $\beta\text{-CH}^{\delta+}$  group.

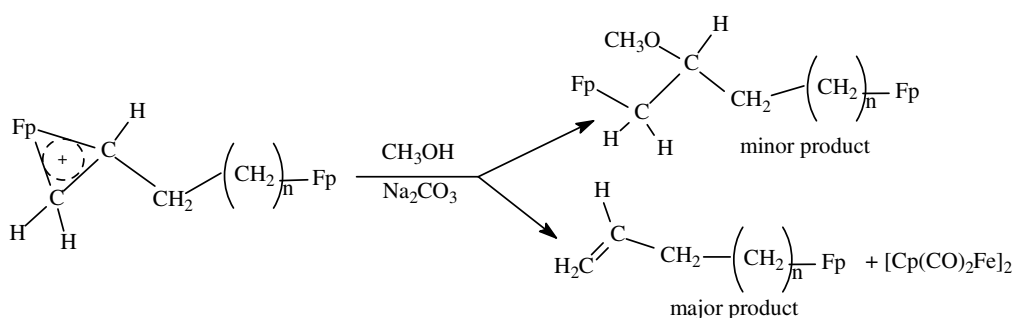
## 2.10. Conclusions

The reactions of the complexes  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_n\text{H}_{2n})\}]$ , where  $n = 4-10$ , with one and two equivalents of  $\text{Ph}_3\text{CPF}_6$  have shown that the  $\text{CH}_2$  groups  $\beta$  to the metal centres can be activated independently in complexes where  $n \geq 5$ . The NMR data have shown that in the monocationic complexes, one metal centre is  $\sigma$ -bonded to one end of the carbenium ion moiety, while the other is bonded to the olefinic end in a fashion leading to chiral metallacyclopropane type structures. In the dicationic complexes, both metals form chiral metallacyclopropane type structures with the carbenium ion moieties. The complex where  $n = 4$  did not give the dicationic complex under any of the conditions used and thus  $n = 5$  appears to be the lower limit for double hydride abstraction.

## 3. Experimental

### 3.1. General procedures

All manipulations of the organometallic compounds were carried out under nitrogen using standard Schlenk line techniques. The complexes  $[\text{Cp}(\text{CO})_2\text{Fe}]_2$  [26],  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{CH}_2)_n\}]$  ( $n = 4-10$ ) [27] were synthesised by published methods. Triphenylcarbenium hexafluorophosphate (Aldrich) was used as purchased without



Scheme 3. Reaction of the carbenium ion complexes with methanol.



further purification. Tetrahydrofuran and hexane were distilled from sodium/benzophenone ketyl under nitrogen. Diethyl ether was dried and distilled from sodium wire. Dichloromethane was dried and distilled from phosphorous pentoxide under nitrogen. Acetone was dried by refluxing over anhydrous calcium chloride and distilling under nitrogen. Hexane, THF and diethyl ether were kept over sodium wire; the other solvents were kept over molecular sieves and nitrogen saturated before use.

### 3.2. Reaction of $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_4\text{H}_8)\}]$ with one equivalent of $\text{Ph}_3\text{CPF}_6$

A filtered solution of  $\text{Ph}_3\text{CPF}_6$  (0.30 g, 0.50 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) was added to a solution of the complex  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{CH}_2)_4\}]$  (0.19 g, 0.50 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 ml) in a Schlenk tube and the mixture allowed to stand for 16 h under nitrogen at room temperature. The orange red solution was then filtered through a cannula into a clean pre-weighed Schlenk tube. Dry nitrogen-saturated diethyl ether was added to the mother liquor until the yellow solid precipitated out. This was allowed to settle and the mother liquor syringed off. The solid was dried under reduced pressure and found to be the reported monocationic complex  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_4\text{H}_7)\}]\text{PF}_6$  [3].

### 3.3. Reaction of $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_5\text{H}_{10})\}]$ with one equivalent of $\text{Ph}_3\text{CPF}_6$

The same procedure as described in Section 3.2 was used and only the reported [3] monocationic  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_5\text{H}_9)\}]\text{PF}_6$  complex was obtained.

### 3.4. Reactions of $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_n\text{H}_{2n})\}]$ ( $n = 6-10$ ) with one equivalent of $\text{Ph}_3\text{CPF}_6$

The procedure for the complex where  $n = 6$  will be described to illustrate the general procedure followed. A filtered solution of  $\text{Ph}_3\text{CPF}_6$  (0.42 g, 1.07 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) was added to a solution of the complex  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{CH}_2)_6\}]$  (0.47 g, 1.07 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 ml) in a Schlenk tube and the mixture allowed to stand under nitrogen at room temperature. After 2 h a yellow precipitate had settled at the bottom of the Schlenk tube. The mother liquor was then filtered through a cannula into a pre-weighed Schlenk tube and treated as explained below. The precipitate was washed twice with 2 ml portions of  $\text{CH}_2\text{Cl}_2$  and dried under reduced pressure and found to be the dicationic compound  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_6\text{H}_{10})\}](\text{PF}_6)_2$ . Diethyl ether was added to the mother liquor until the yellow solid precipitated out. This was allowed to settle and the mother liquor syringed off. The solid was dried under reduced pressure and found to be the monocationic complex  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_6\text{H}_{11})\}]\text{PF}_6$  [3]. The complexes where  $n = 7-10$  were treated similarly and gave the new monocationic and dicationic complexes.

### 3.5. Reaction of $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{CH}_2)_4\}]$ with two equivalents of $\text{Ph}_3\text{CPF}_6$

A filtered solution of  $\text{Ph}_3\text{CPF}_6$  (0.33 g, 0.84 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) was added to a solution of  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{CH}_2)_4\}]$  (0.17 g, 0.42 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 ml) in a Schlenk tube and the mixture allowed to stand for 10 h at room temperature under nitrogen. No precipitate was observed. The IR  $\nu(\text{CO})$  spectrum showed that only the monocationic complex had formed. Work-up was done as in Section 3.2. The elemental analysis data and IR spectrum matched that of the reported compound  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_4\text{H}_7)\}]\text{PF}_6$  [3].

### 3.6. Reaction of $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{CH}_2)_5\}]$ with two equivalents of $\text{Ph}_3\text{CPF}_6$

A filtered solution of  $\text{Ph}_3\text{CPF}_6$  (0.68 g, 1.76 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) was added to a solution of  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{CH}_2)_5\}]$  (0.37 g, 0.88 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 ml) in a Schlenk tube and the mixture was allowed to stand overnight under nitrogen at room temperature. At the end of the reaction period a yellow precipitate had settled at the bottom of the Schlenk tube. The mother liquor was filtered through a cannula into a pre-weighed Schlenk tube, the precipitate washed twice with 2 ml portions of  $\text{CH}_2\text{Cl}_2$  and dried under reduced pressure. This was found to be the new dicationic compound  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_5\text{H}_8)\}](\text{PF}_6)_2$ . Diethyl ether was added to the mother liquor and a yellow solid precipitated out. The mother liquor was syringed off and the solid dried under reduced pressure. The elemental analysis data and IR spectrum matched that of the reported compound  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_5\text{H}_9)\}]\text{PF}_6$  [3].

### 3.7. Reaction of $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{CH}_2)_5\}]$ with four equivalents of $\text{Ph}_3\text{CPF}_6$

A solution of  $\text{Ph}_3\text{CPF}_6$  (1.83 g, 4.72 mmol) in 10 ml  $\text{CH}_2\text{Cl}_2$  was added to a solution of  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{CH}_2)_5\}]$  (0.5 g, 1.2 mmol) in 2 ml  $\text{CH}_2\text{Cl}_2$  and the mixture allowed to stand under nitrogen for 4 h. The solution turned yellow green and a yellow precipitate was observed at the bottom of the reaction vessel. Work-up proceeded as reported in Section 3.2 above to give the dicationic complex  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_5\text{H}_8)\}](\text{PF}_6)_2$  and the monocationic complex  $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_5\text{H}_9)\}]\text{PF}_6$ .

In another experiment, the reaction above was allowed to continue overnight instead of 4 h. Again the dicationic product was obtained but in place of the bimetallic monocationic complex, the previously reported [23] monometallic cationic product complex  $[\text{Cp}(\text{CO})_2\text{FeCH}_2=\text{CHC}_3\text{H}_7]\text{PF}_6$  was isolated after work-up. M.p. = 110–114 °C (partial decomposition). IR  $\nu(\text{CO})$  ( $\text{cm}^{-1}$ ) 2075, 2038;  $^1\text{H}$  NMR (acetone- $d_6$ ) in ppm, 5.95 (Cp, singlet, 5H), 5.28m ( $\text{CH}_2=\text{CH}$ , 1H); 4.08d (*cis*- $\text{CH}_2=\text{CH}$ , 1H,  $J_{\text{HH}} = 5.0$  Hz), 3.67d (*trans*- $\text{CH}_2=\text{H}$ , 1H,  $J_{\text{HH}} = 14.2$  Hz), 2.52m, 1.71m

(CHCH<sub>2</sub>, 2H), 1.53m (CHCH<sub>2</sub>CH<sub>2</sub>, 2H), 0.97t (CH<sub>3</sub>, 3H,  $J_{\text{HH}} = 6.3$  Hz); <sup>13</sup>C NMR in ppm, 90.4 (Cp), 89.0 (CH<sub>2</sub>=CH), 55.3 (CH<sub>2</sub>=CH), 39.1 (CHCH<sub>2</sub>), 26.5 (CHCH<sub>2</sub>CH<sub>2</sub>), 13.7 (CH<sub>3</sub>); elemental analysis, Found (Calc) %, C, 36.9 (36.7); H, 3.7 (4.1).

### 3.8. Reactions of the [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{CH}_2)_n\}$ ] ( $n = 6-10$ ) with two equivalents of Ph<sub>3</sub>CPF<sub>6</sub>

The procedure for the complex where  $n = 6$  is described as an example of the general procedure used in these reactions. A filtered solution of Ph<sub>3</sub>CPF<sub>6</sub> (0.61 g, 1.76 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) was added to a solution of [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{CH}_2)_6\}$ ] (0.35 g, 0.79 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 ml) in a Schlenk tube. A yellow precipitate appeared upon mixing of the solutions. However, the mixture was allowed to stand for 2 h under nitrogen at room temperature to ensure complete reaction. The mother liquor was filtered through a cannula into a pre-weighed Schlenk tube, the precipitate washed twice with 2 ml portions of CH<sub>2</sub>Cl<sub>2</sub> and dried under reduced pressure. This was found to be the dicationic compound [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_6\text{H}_{10})\}$ ](PF<sub>6</sub>)<sub>2</sub>. A very small amount of the monocationic product was detected by IR in the mother liquor, but there was too little to isolate. The complexes where  $n = 7-10$  were treated in the same way as the complex where  $n = 6$  and only dicationic complexes were obtained. No monocationic complexes were detected in the respective mother liquors.

### 3.9. Reaction of [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_4\text{H}_7)\}$ ]PF<sub>6</sub> with NaBPh<sub>4</sub>

The compound [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_4\text{H}_7)\}$ ]PF<sub>6</sub> (0.12 g, 0.22 mmol) and NaBPh<sub>4</sub> (0.17 g, 0.48 mmol) were weighed into a Schlenk tube and 10 ml acetone added. The mixture was stirred for 1 h. The solvent was then removed under reduced pressure. The residue was extracted thrice with 20 ml CH<sub>2</sub>Cl<sub>2</sub> and filtered through a cannula into a pre-weighed Schlenk tube. Diethyl ether was added to the solution to precipitate the product. A bright yellow-orange solid precipitated as thin plates. The mother liquor was syringed off and the solid dried under reduced pressure.

### 3.10. Reaction of [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_5\text{H}_9)\}$ ]PF<sub>6</sub> with NaBPh<sub>4</sub>

This was carried out in the same manner as reported in Section 3.9 above, except that the reaction time was only 10 min.

### 3.11. Reaction of [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_5\text{H}_8)\}$ ](PF<sub>6</sub>)<sub>2</sub> with NaBPh<sub>4</sub>

The complex [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_5\text{H}_8)\}$ ](PF<sub>6</sub>)<sub>2</sub> (0.40 g, 0.53 mmol) and NaBPh<sub>4</sub> (0.40 g, 1.1 mmol) were weighed into a Schlenk tube and 10 ml acetone added. The mixture was stirred for 4 h. The mixture was filtered through a can-

nula into a pre-weighed Schlenk tube. Diethyl ether was added to the solution to precipitate the product. A yellow powder precipitated. The mother liquor was syringed off and the solid [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_5\text{H}_8)\}$ ](BPh<sub>4</sub>)<sub>2</sub> dried under reduced pressure.

In a separate experiment, the reaction above was allowed to continue overnight. After work up, the monometallic complex [ $\{\text{Cp}(\text{CO})_2\text{FeCH}_2=\text{CHC}_3\text{H}_7\}$ ]BPh<sub>4</sub> was isolated and not the expected dicationic complex. The compound decomposed above 115 °C; IR  $\nu(\text{CO})$  (CH<sub>2</sub>Cl<sub>2</sub>) (cm<sup>-1</sup>) 2071, 2035; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) in ppm, 7.36s, 6.95t, 6.80t (BPh<sub>4</sub>), 5.85 (Cp, singlet, 5H), 5.28m (CH<sub>2</sub>=CH, 1H); 4.04d (*cis*-CH<sub>2</sub>=CH, 1H,  $J_{\text{HH}} = 10.5$  Hz), 3.65d (*trans*-CH<sub>2</sub>=CH, 1H,  $J_{\text{HH}} = 14.8$  Hz), 2.51m, 1.70m (CHCH<sub>2</sub>, 2H), 1.53m (CHCH<sub>2</sub>CH<sub>2</sub>, 2H), 0.99t (CH<sub>3</sub>, 3H,  $J_{\text{HH}} = 7.1$  Hz); <sup>13</sup>C NMR in ppm, 135.9, 124.9d (B-C,  $J_{\text{BC}} = 5.9$  Hz), 121.1 (BPh<sub>4</sub>), 89.1 (Cp), 87.8 (CH<sub>2</sub>=CH), 54.0 (CH<sub>2</sub>=CH), 38.0 (CHCH<sub>2</sub>), 25.4 (CHCH<sub>2</sub>CH<sub>2</sub>), 12.6 (CH<sub>3</sub>); elemental analysis, Found (Calc)%, C, 74.5 (76.5); H, 5.9 (6.1).

### 3.12. Reaction of [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_9\text{H}_{16})\}$ ](PF<sub>6</sub>)<sub>2</sub> with NaBPh<sub>4</sub>

The complex [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_9\text{H}_{16})\}$ ](PF<sub>6</sub>)<sub>2</sub> (0.20 g, 0.26 mmol) and NaBPh<sub>4</sub> (0.21 g, 0.63 mmol) were weighed into a Schlenk tube and 10 ml acetone added. The mixture was stirred for 3 h (the dicationic complex is sparingly soluble in acetone). The mixture was filtered through a cannula into a pre-weighed Schlenk tube. Diethyl ether was added to the solution to precipitate the product as a yellow powder. The mother liquor was syringed off and the solid dried under reduced pressure.

### 3.13. Reactions of some of the cationic complexes with sodium iodide

Approximately 10 mg of a given complex was dissolved in N<sub>2</sub>-saturated deuterated acetone in an NMR tube and its <sup>1</sup>H NMR spectrum recorded. About 10 mg of NaI was added to the solution in the NMR tube and the reaction followed by recording spectra at 5 min intervals until there was no more change observed in the spectra. The complexes [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_n\text{H}_{2n-2})\}$ ](BPh<sub>4</sub>)<sub>2</sub> ( $n = 5, 8, 9$ ) gave the corresponding  $\alpha, \omega$ -dienes, while the monometallic cationic complex [ $\{\text{Cp}(\text{CO})_2\text{FeCH}_2=\text{CHC}_3\text{H}_7\}$ ]BPh<sub>4</sub> gave 1-pentene as detailed below.

- [ $\{\text{Cp}(\text{CO})_2\text{FeCH}_2=\text{CHC}_3\text{H}_7\}$ ]BPh<sub>4</sub> showed the following peaks: 5.72m (=CH), 4.94m (=CH<sub>2</sub>), 1.92m (=CHCH<sub>2</sub>), 1.36m (CH<sub>2</sub>CH<sub>3</sub>), 0.84t (CH<sub>3</sub>).
- [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_5\text{H}_8)\}$ ](BPh<sub>4</sub>)<sub>2</sub> showed the following peaks: 6.10 (=CH), 5.04m (=CH<sub>2</sub>), 3.14m (=CHCH<sub>2</sub>), 5.35s (C<sub>5</sub>H<sub>5</sub>(CO)<sub>2</sub>FeI).
- [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu-(\text{C}_8\text{H}_{14})\}$ ](BPh<sub>4</sub>)<sub>2</sub> showed the following peaks: 5.84m (=CH), 4.94m (=CH<sub>2</sub>), 2.04m (=CHCH<sub>2</sub>), 1.43m (=CHCH<sub>2</sub>CH<sub>2</sub>).

(d) [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(C}_9\text{H}_{16})\}\text{](BPh}_4)_2$  showed the following peaks: 5.84m ( $=\text{CH}$ ), 4.91 ( $=\text{CH}_2$ ), 2.05m ( $=\text{CHCH}_2$ ), 1.43m ( $=\text{CHCH}_2\text{CH}_2$ ).

### 3.14. Reaction of [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(C}_4\text{H}_7)\}\text{]PF}_6$ with $\text{CF}_3\text{COOH}$

One milliliter of  $\text{CF}_3\text{COOH}$  was added to a solution of [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(C}_4\text{H}_7)\}\text{]PF}_6$  (0.2 g, 0.36 mmol) in THF (10 ml). The mixture was stirred at room temperature overnight. A yellow solid was seen in the reaction mixture. It was allowed to settle and the mother liquor removed through a cannula into a pre-weighed Schlenk tube. The solid was washed with 3 ml diethyl ether, dried under reduced pressure and found to be the reported butenyl complex [ $\text{Cp}(\text{CO})_2\text{Fe}(\text{C}_4\text{H}_8)\text{]PF}_6$  [23]. Dry diethyl ether was added to the mother liquor to precipitate a yellow micro-crystalline solid. The mother liquor was removed through a cannula into a pre-weighed Schlenk tube, the solid dried under reduced pressure and found to also be butenyl complex [ $\text{Cp}(\text{CO})_2\text{Fe}(\text{C}_4\text{H}_8)\text{]PF}_6$ . The mother liquor was evaporated to dryness under reduced pressure to give a maroon gum which was found to consist mainly of the acetyl complex [ $\text{Cp}(\text{CO})_2\text{FeOCCF}_3$ ] with small quantities of the iron dimer [ $\text{Cp}(\text{CO})_2\text{Fe}\}_2$ . [ $\text{Cp}(\text{CO})_2\text{FeOCCF}_3$ ] IR ( $\text{CH}_2\text{Cl}_2$ )  $\text{cm}^{-1}$  2062, 2016 (Fp CO), 1689 (acetyl CO);  $^1\text{H}$  NMR (acetone- $d_6$ ) ppm, 5.43s (Cp); [ $\text{Cp}(\text{CO})_2\text{Fe}\}_2$   $\nu_{\text{CO}}$  ( $\text{CH}_2\text{Cl}_2$ ) 2057, 1956, 1772  $\text{cm}^{-1}$ .

### 3.15. Reactions of the complexes [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(C}_n\text{H}_{2n-1})\}\text{]PF}_6$ with methanol

The procedure for the reaction of the complex [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(C}_6\text{H}_{11})\}\text{]PF}_6$  is described as an illustration of the general procedure followed in these reactions. The compound [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(C}_6\text{H}_{11})\}\text{]PF}_6$  (0.26 g, 0.44 mmol) and  $\text{Na}_2\text{CO}_3$  (0.06 g, 0.55 mmol) were weighed into a Schlenk tube and 25 ml methanol added. The yellow complex dissolved completely after 10 min and the solution became maroon in colour. The mixture was stirred for 1 h during which time all the carbonate dissolved. The solvent was removed under reduced pressure to give a maroon residue. The residue was extracted twice with 20 ml hexane and filtered through a cannula. The solvent was evaporated under reduced pressure, leaving a maroon oily material.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra showed this oily solid to contain [ $\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_4\text{CH}=\text{CH}_2$ ] as the major product, [ $\text{Cp}(\text{CO})_2\text{Fe}\}_2$  and [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-CH}_2\text{CH}(\text{OCH}_3)\text{-(CH}_2)_4\}$ ] as the minor product. The oily material was dissolved in minimum of hexane and transferred to an alumina column prepared in hexane and eluted with hexane. A yellow band was collected and the solvent removed under reduced pressure leaving amber oil. IR and NMR data showed this to be the previously reported complex [ $\text{Cp}(\text{CO})_2\text{FeCH}_2(\text{CH}_2)_3\text{CH}=\text{CH}_2$ ] [24]. The maroon layer was eluted with  $\text{CH}_2\text{Cl}_2$  and found to contain only the iron

dimer [ $\text{Cp}(\text{CO})_2\text{Fe}\}_2$ . The complexes [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(C}_n\text{H}_{2n-1})\}\text{]PF}_6$  (where  $n = 4, 5$ ) were treated in the same way and gave the same results. However, the amounts of the  $\sigma$ -ether complexes observed were very small for these two complexes. [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-CH}_2\text{CH}(\text{OCH}_3)\text{-(CH}_2)_4\}$ ]  $^1\text{H}$  NMR ( $\text{CD}_3\text{Cl}$ ), 4.73s, 4.70s (Cp), 1.50m [ $\text{CH}_2\text{CH}(\text{OCH}_3)\text{CH}_2$ ], 3.27s ( $\text{OCH}_3$ ), 2.98m ( $\text{CH}_2\text{CH}$ ), 2.03m [ $\text{CH}(\text{OCH}_3)\text{CH}_2$ ], 1.42m ( $\text{CH}_2$ );  $^{13}\text{C}$  NMR, 85.3, 85.6 (Cp), 6.0 (Fp $\text{CH}_2\text{CH}$ ), 67.9 (Fp $\text{CH}_2\text{CH}$ ), 55.9 ( $\text{OCH}_3$ ), 38.6 [ $\text{CH}(\text{OCH}_3)\text{CH}_2$ ], 36.0 [ $\text{CH}(\text{OCH}_3)\text{-CH}_2\text{CH}_2$ ], 30.8 ( $\text{CH}_2\text{CH}_2\text{Fe}$ ), 3.7 ( $\text{CH}_2\text{Fe}$ ).

The above reaction was carried out with the complexes [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(C}_6\text{H}_{11})\}\text{]PF}_6$  and [ $\text{Cp}(\text{CO})_2\text{Fe}(\text{C}_4\text{H}_8)\text{]PF}_6$  in NMR tubes in  $\text{CD}_3\text{OD}$  and the reactions followed by recording  $^1\text{H}$  NMR spectra at intervals of 5 min until there was no further change observed in the spectra. After 20 min all the [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(C}_6\text{H}_{11})\}\text{]PF}_6$  had reacted and the spectrum showed the presence of two products in solution as follows:

[ $\text{Cp}(\text{CO})_2\text{Fe}_2\{\mu\text{-CH}\}_2\text{CH}(\text{OCD}_3)(\text{CH}_2)_4$ ] in  $\text{CD}_3\text{OD}/\text{ppm}$ , 5.32s (CpFe $\text{CH}_2\text{CH}$ ) 4.94s (CpFe $\text{CH}_2\text{CH}_2$ ), 2.93m [ $\text{CH}(\text{OCD}_3)$ ], 2.16m [ $\text{CH}(\text{OCH}_3)\text{CH}_2$ ], 1.53m ( $\text{CH}_2$ ) and  $\text{CH}_2\text{Fe}$ ;

[ $\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_4\text{CH}=\text{CH}_2$ ] in  $\text{CD}_3\text{OD}/\text{ppm}$ , 5.84m ( $\text{CH}_2=\text{CH}$ ), 5.14m ( $\text{CH}_2=\text{CH}$ ), 4.93s (Cp), 2.12m ( $\text{CHCH}_2$ ), 1.54m ( $=\text{CH}_2$ ) and  $\text{CH}_2\text{Fe}$ . The  $\eta^1$ -olefin complex, [ $\{\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_4\text{CH}=\text{CH}_2$ ], was the major product.

The reaction of [ $\text{Cp}(\text{CO})_2\text{Fe}(\text{C}_4\text{H}_8)\text{]PF}_6$  with  $\text{CD}_3\text{OD}$  did not go to completion even after 40 min. The spectrum showed the presence of four compounds which were identified as the unreacted starting complex [ $\text{Cp}(\text{CO})_2\text{Fe}(\text{C}_4\text{H}_8)\text{]PF}_6$ , free 1-butene, the iron dimer and the  $\sigma$ -ether complex [ $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{CH}(\text{OCD}_3)\text{CH}_2\text{CH}_3$ ]. 1-Butene was the major product as judged from the intensity of the peaks. The peaks appeared as follows: 1-butene ( $\text{CD}_3\text{OD}/\text{ppm}$ , 5.93m ( $=\text{CH}$ ), 5.04m ( $=\text{CH}_2$ ), 1.63m ( $=\text{CHCH}_2$ ), 0.91t ( $\text{CH}_3$ ); [ $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{CH}(\text{OCD}_3)\text{-CH}_2\text{CH}_3$ ], 5.53s (Cp), 3.14m ( $\text{CH}_2\text{CH}$ ), 1.45m ( $\text{FeCH}_2$ ), 1.16t ( $\text{CH}_3$ ); [ $\text{Cp}(\text{CO})_2\text{Fe}(\text{C}_4\text{H}_8)\text{]PF}_6$ , 5.77s (Cp), 5.15m ( $\text{CH}$ ), 3.93d ( $J = 8.2$  Hz, *cis*- $\text{CH}_2$ ), 3.53d ( $J = 14.7$  Hz, *trans*- $\text{CH}_2$ ), 2.42m, 1.63m ( $=\text{CHCH}_2$ ), 1.28t ( $\text{CH}_3$ ).

### 3.16. Reaction of [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(C}_8\text{H}_{15})\}\text{]PF}_6$ with iso-propanol

The complex [ $\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{\mu\text{-(C}_8\text{H}_{15})\}\text{]PF}_6$  (0.03 g, 0.05 mmol) was weighed into a Schlenk tube and 10 ml acetone was added, followed by 6 ml iso-propanol and  $\text{Na}_2\text{CO}_3$  (0.005 g, 0.05 mmol). The mixture was stirred for 3 h at room temperature. The solids dissolved after 1 h but the mixture was stirred for two more hours. The solvent was removed under reduced pressure leaving an amber oily residue. Sublimation under reduced pressure at 80 °C gave amber oil on the cold finger. IR and NMR spectroscopy showed that this was the reported complex [ $\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_6\text{CH}=\text{CH}_2$ ] [24]. The maroon residue left

behind consisted mainly of the iron dimer and some of the unsublimed complex  $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_6\text{CH}=\text{CH}_2]$ .

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