THE SYNTHESIS AND REACTIVITY OF FUNCTIONALISED ALKYL TRANSITION METAL COMPLEXES

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by

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ABSTRACT

The complexes $[CpFe(CO)_2CH_2X]$ and $[CpW(CO)_3CH_2X]$ ($Cp = \eta^5\text{-}C_5H_5$; X = Cl, Br, I) have been prepared and their reactivity with a series of tertiary phosphines, amines, SMe_2 and $AsPh_3$ in THF, CH_3CN and MeOH has been investigated. Two types of cationic products, namely the ylide complexes $[CpM(CO)_nCH_2L]^+$ or the disubstituted complexes $[CpML_2(CO)_{n-1}]^+$ (M = Fe, n = 2; M = W, n = 3) were obtained, depending on the halide (X), the ligand (L), the metal (M) and the solvent used. The variables X, L, M and the solvent used were also all found to influence the rates of the reactions. Thus the relative reaction rates of the complexes $[CpFe(CO)_2CH_2Br]$ and $[CpW(CO)_3CH_2Br]$ with L were determined by ^1H NMR spectroscopy and found to increase with increasing pK_a and decreasing cone angle of L. In general, the rate of reaction of $[CpFe(CO)_2CH_2X]$ and $[CpW(CO)_3CH_2X]$ with L increases in the sequence Cl < Br < I and the reactions of $[CpFe(CO)_2CH_2X]$ with L are significantly faster than the corresponding reactions of $[CpW(CO)_3CH_2X]$. The reactions of $[CpFe(CO)_2CH_2Br]$ and $[CpW(CO)_3CH_2Br]$ with dppe {dppe = bis(diphenylphosphino)ethane} yield the bridged dicationic ylide complexes $[\{Cp(CO)_2FeCH_2\}_2\{PPh_2(CH_2)_2PPh_2\}]$ and $[\{Cp(CO)_3WCH_2\}_2\{PPh_2(CH_2)_2PPh_2\}]$ respectively.

The new complexes $[CpFe(CO)_2\{(CH_2)_nBr\}]$ (n = 6 - 10) and $[Cp^*Fe(CO)_2\{(CH_2)_nBr\}]$ ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$; n = 3 - 5) have been synthesized. The complexes $[(\eta^5\text{-}C_5R_5)Fe(CO)_2\{(CH_2)_nBr\}]$ (R = H, n = 3 - 6, 8 - 10; R = CH_3 , n = 3 - 5) were treated with NaI to give the new complexes $[(\eta^5\text{-}C_5R_5)Fe(CO)_2\{(CH_2)_nI\}]$. The properties of these complexes, including their ^{13}C NMR and mass spectra, are discussed.

The iodoalkyl complexes $[(\eta^5\text{-}C_5R_5)Fe(CO)_2\{(CH_2)_nI\}]$ were reacted with $Na[ML_y]$ to give the new heterodinuclear compounds $[(\eta^5\text{-}C_5R_5)(CO)_2Fe(CH_2)_nML_y]$ $\{R = H,\ n = 3 - 6,\ ML_y = Ru(CO)_2Cp,\ Mo(CO)_3Cp,\ W(CO)_3Cp,\ Re(CO)_5;\ R = CH_3,\ n = 3 - 5,\ ML_y = Ru(CO)_2Cp,\ n = 4,\ ML_y = Re(CO)_5\}$. The related mixed ligand complex $[Cp(CO)_2Fe(CH_2)_3Fe(CO)_2Cp^*]$ has also been prepared.

The reactivity of some of the above heterobimetallic alkanediyl complexes with some tertiary phosphines, trityl salt and halides was investigated. The reactions of PPh_3 with $[Cp(CO)_2Fe(CH_2)_3ML_y]$ $\{ML_y = Ru(CO)_2Cp,\ Mo(CO)_3Cp,\ W(CO)_3Cp,\ Re(CO)_5\}$ were found to be totally metalloselective, with the phosphine always attacking the expected metal site predicted by the reactivities of the corresponding monometallic or homodinuclear alkyl species. Chain length was found to not influence the site of the nucleophilic attack. The reaction of $[Cp(CO)_2Fe(CH_2)_3ML_y]$ $\{ML_y = Ru(CO)_2Cp,\ Mo(CO)_3Cp,\ W(CO)_3Cp\}$ with trityl salt (Ph_3CPF_6) gave the complexes $[Cp(CO)_2Fe(C_3H_5)ML_y]PF_6$ where the β-CH unit is weakly bonded to both metal centres. The reaction of $[Cp(CO)_2Fe(CH_2)_nRu(CO)_2Cp]$ (n = 4, 6) with trityl salt was found to not be metalloselective, giving equal quantities of $[Cp(CO)_2FeCH_2CH(CH_2)_{n-2}Ru(CO)_2Cp]PF_6$ and $[Cp(CO)_2Fe(CH_2)_{n-2}CHCH_2Ru(CO)_2Cp]PF_6$. In contrast, the reactions of $[Cp(CO)_2Fe(CH_2)_4W(CO)_3Cp]$ with trityl salt gave only $[Cp(CO)_2FeCH_2CH(CH_2)_2W(CO)_3Cp]PF_6$ *i.e.* a complex with a Fe-C π-bond and a W-C σ-bond. Complete metalloselectivity was observed for the reaction of $[Cp(CO)_2Fe(CH_2)_6W(CO)_3Cp]$ with HCl, with the W-C bond being cleaved.

ABBREVIATIONS

acac = acetyl acetone

APT = attached proton test

Bu^n = n-butyl

Bu^t = t-butyl group

COD = cycloocta 1,5-diene

Cp = η^5-C_5H_5

Cp* = η^5-$C_5(CH_3)_5$

CI = chemical ionisation

COSY = correlated spectroscopy

Cy = cyclohexyl group

dec = decomposed

DH = monoanion of dimethylglyoxime

dppe = diphenylphosphinoethane

dppm = diphenylphosphinomethane

DSC = differential scanning calorimetry

ei = electron impact

eqn. = equation

Et = ethyl group

ether = diethyl ether

h = hour(s)

HETCOR = heteronuclear correlation

IR = infrared {vs = very strong, s = strong, m = medium, w = weak, (sh) = shoulder, br = broad}

L, L_x, L_y = ligand(s)

M = transition metal

M^+ = molecular ion

Me = methyl group

men = menthyl group

m.p. = melting point

ms = mass spectrometry

m/z = mass to charge ratio

NMR = nuclear magnetic resonance (m = multiplet, qn = quintet, q = quartet, t = triplet, d = doublet, s = singlet, dd = doublet of doublets, tt = triplet of triplets)

Ph = phenyl group

ppm = parts per million

Pr^i = i-propyl group

Pr^n = n-propyl group

PR_3 = tertiary phosphine

py = pyridine

pzH = pyrazole

R = alkyl group

RT = room temperature

THF = tetrahydrofuran

TMS = tetramethylsilane

NOTE: COMPOUND AND FIGURE NUMBERS ARE VALID WITHIN EACH INDIVIDUAL CHAPTER ONLY

PUBLICATIONS

The following work from this thesis has already been presented.

PAPERS:

1. "Haloalkyl complexes of the transition metals VI. A study of the reactions of halomethyldicarbonylcyclopentadienyliron complexes with some tertiary phosphine, amine and sulphur ligands", G.C.A. Bellinger, H.B. Friedrich and J.R. Moss, J. Organomet. Chem., 366 (1989) 175.

2. "Halogenoalkyl complexes of the transition metals VII. The synthesis and properties of the ω-halogenoalkyl complexes $[(\eta\text{-}C_5R_5)(CO)_2Fe(CH_2)_nX]$ (R = H, n = 3-10, X = Br, I; R = CH_3, n = 3-5, X = Br, I)", H.B. Friedrich, P.A. Makhesha, J.R. Moss and B.K. Williamson, J. Organomet. Chem., 384 (1990) 325.

3. "The synthesis and properties of heterodinuclear alkanediyl complexes of iron(II) containing molybdenum(II), tungsten(II), rhenium(I) and ruthenium(II)", H.B. Friedrich, J.R. Moss and B.K. Williamson, J. Organomet. Chem., *in press*.

4. "Halogenoalkyl complexes of the transition metals", H.B. Friedrich and J.R. Moss, Adv. Organomet. Chem., accepted for publication.

CONFERENCE CONTRIBUTIONS:

1. Poster titled "The synthesis and reactivity of $[(\eta\text{-}C_5R_5)Fe(CO)_2(CH_2)_nX]$ (n = 3 - 10; R = H, CH_3; X = Br, Cl)", H.B. Friedrich, P.A. Makhesha and J.R. Moss, presented at "Inorganic 88" in Gordons Bay, RSA (1988).

2. Short talk and poster titled "Heterobimetallic alkanediyl complexes: their preparation, properties and reactivity", H.B. Friedrich and J.R. Moss, presented at the 30th Convention of the South African Chemical Institute, Johannesburg, RSA (1989).

3. Poster titled "Reactivity patterns in binuclear alkyl complexes", S.J. Archer, M.A. Bothma, H.B. Friedrich, S.F. Mapolie and J.R. Moss, presented at the XXVII International Conference of Coordination Chemistry, Gold Coast, Australia (1989).

4. Lecture titled "Heterobimetallic transition metal complexes", presented by H.B. Friedrich at the 4th International Chemistry Conference in Africa, Zomba, Malawi (1989).

5. Poster titled "Heterobimetallic transition metal complexes", H.B. Friedrich and J.R. Moss, presented at "Inorganic 90", Golden Gate, RSA (1990).

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CHAPTER 1

A REVIEW OF MONO FUNCTIONALISED (Cl, Br, I, OCH_3) ALKYL TRANSITION METAL COMPLEXES - THEIR SYNTHESIS AND REACTIVITY

1.1 INTRODUCTION

Haloalkyl complexes of the main group metals have been extensively studied and shown to be important reagents in synthetic chemistry [1-3]. Methoxymethyl and haloalkyl transition metal complexes of type $[L_yM\{(CH_2)_nX\}]$ (L_y = ligands, M = transition metal, X = Cl, Br, I or OCH_3, $n \geq 1$) are less well known. Such complexes are precursors for a variety of compounds. Complexes in which n = 1, including carbene complexes, $[L_yM{=}CH_2]^+$, and hydroxymethyl complexes, $[L_yMCH_2OH]$, have been proposed as intermediates in many catalytic processes [4-6]. Methoxymethyl complexes of the later transition metals have been found to be convenient precursors to methylene complexes [7]. These transition metal carbenes have been proposed as promising reagents for electrophilic cyclopropanations [8,9] and alkene metathesis [10], whilst transition metal bound hydroxymethyl complexes have been implicated as key intermediates in the homogeneous catalysed reduction of carbon monoxide [11]. Successive formation of formyl, formaldehyde, hydroxymethyl, carbene and alkyl surface intermediates have been proposed for the Fischer-Tropsch reaction and related processes [4,12-

14]. Indeed metal-C_1 complexes in general are believed to be important as models for catalytic intermediates [15].

Complexes of type $[L_yM\{(CH_2)_nX\}]$, where n>1, have been shown to be effective precursors for hetero- and homobimetallic $\mu(\alpha,\omega)$ alkanediyl complexes, $[L_xM(CH_2)_nM'L_y]$ (where ML_x is not necessarily the same as $M'L_y$). Such compounds have been proposed as models for intermediates in the Fischer-Tropsch reaction [16,17] and other catalytic processes [18-21]. Some $[L_yM\{(CH_2)_nX\}]$ complexes are also precursors to cyclic carbene complexes (see for example section 1.3), whilst others have been shown to have organic synthetic utility [22]. Since the subject of transition metal haloalkyl compounds has not previously been reviewed, we now cover this subject including the most important references in this field.

1.2 MONOHALOMETHYL AND METHOXYMETHYL TRANSITION METAL COMPLEXES

1.2.1 Iron, Ruthenium and Osmium

The first syntheses of methoxymethyl and halomethyl transition metal complexes were reported by Jolly and Pettit [23] in 1966 and Green *et al.* in 1967 [24]. Both papers reported the synthesis of $[CpFe(CO)_2CH_2OCH_3]$ (1) and $[CpFe(CO)_2CH_2Cl]$ (2). Green further reported the bromomethyl analogue of (2), [$CpFe(CO)_2CH_2Br$] (3). Similar synthetic routes were used by both groups. The methoxymethyl complex was synthesized by the reaction of chloromethyl methyl ether with the iron anion (equation 1).

$$Na^+[M]^- + ClCH_2OCH_3 \longrightarrow [MCH_2OCH_3] + NaCl \qquad (\underline{1})$$
$$\{M = CpFe(CO)_2\}$$

The reaction of [$CpFe(CO)_3$]$^+$ with $NaBH_3CN$ in methanol also gives, *via* the intermediacy of [$CpFe(CO)_2CH_2OH$], the methoxymethyl complex (1) [25,26].

The chloro- and bromomethyl complexes were synthesized by reacting the appropriate methoxymethyl complex from equation 1 with HX gas (equation 2):

$$[MCH_2OCH_3] + HX \longrightarrow [MCH_2X] + CH_3OH \qquad (\underline{2})$$
$$(M = CpFe(CO)_2;\ X = Cl, Br)$$

Similarly, the acetoxymethyl iron complex, [$CpFe(CO)_2\{CH_2OC(O)Me\}$], reacts with HCl gas to give [$CpFe(CO)_2CH_2Cl$] [27]. Complex (2) was also obtained by reacting [$CpFe(CO)_2CH_2NMe_2$] with CH_3COCl [28].

The iodomethyl complex [$CpFe(CO)_2CH_2I$] (4) has been prepared by two routes [29, chapter 2]. The first route involves the reaction of complex (1) with HI gas, as shown in equation 2. The second route involves the reaction of complex (3) with NaI.

The methoxymethyl complex (1) was isolated as an air-sensitive oil, while the haloalkyl complexes were isolated as air- and light-sensitive solids. The bromomethyl complex (3) was found to be less stable than the chloromethyl complex (2) in all respects. The iodomethyl complex (4) was found to be the least stable of these complexes.

King and Braitsch prepared a number of halomethyl complexes of transition metals by reacting the appropriate transition metal anion with dihalomethanes according to equation 3 [30].

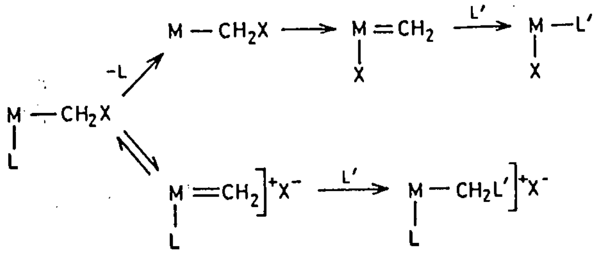
$$\mathrm{Na[M]} + \mathrm{XCH_2X'} \longrightarrow \mathrm{[MCH_2X]} + \mathrm{NaX'} \qquad (\underline{3})$$

{M = $\mathrm{CpMo(CO)_3^-}$, $\mathrm{CpW(CO)_3^-}$, $\mathrm{CpFe(CO)_2^-}$, $\mathrm{Mn(CO)_5^-}$;
$\mathrm{XCH_2X'}$ is a dihaloalkane *e.g.* $\mathrm{CH_2ClI}$}.

$\mathrm{CH_2ClI}$ was used to prepare the chloromethyl derivatives of $\mathrm{[MCH_2X]}$ directly. Since the C-I bond is weaker than the C-Cl bond, the C-I bond is preferentially cleaved in most cases. This method is a good synthetic route to the chloromethyl complexes of Mo and W, but not for those of Mn or Fe.

Facile conversion of (2) to (1) was achieved by reaction with NaOMe [24]. The Cl in $\mathrm{[CpFe(CO)_2CH_2Cl]}$ (2) proved to be highly susceptible to nucleophilic attack, and a number of complexes of type $\mathrm{[CpFe(CO)_2CH_2Z]}$ {Z = OEt, SEt, $\mathrm{O(CH_2)_2NMe_2H}$, $\mathrm{OCR_2CH{=}CH_2}$ (R=Me,H)} were synthesized [24]. The complexes $\mathrm{[CpFe(CO)_2CH_2X]}$ have since been shown to react with neutral nucleophiles, L (L= tertiary phosphines, amines, sulphides and

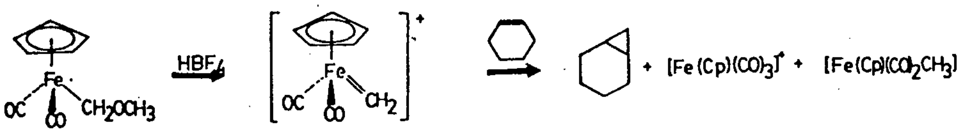
$AsPh_3$), to form complexes of the type $[CpFe(CO)_2CH_2L]^+$ or $[CpFe(L)_2(CO)]^+$, depending on the size and pKa of the ligand, the halide and on the solvent used [29,31,32, chapter 2]. A proposed pathway for the reactions of $[M(L_y)(CH_2X)]$ complexes with ligands L is shown in SCHEME 1.



SCHEME 1

Whilst the complex (**2**) did not react with $P(OMe)_3$ or NEt_3 under normal conditions, it reacted with the above ligands and with all other neutral nucleophiles tried, in the presence of the halide abstractor $TlBF_4$, to give $[CpFe(CO)_2CH_2L]BF_4$ [33].

Jolly and Pettit found that the addition of HBF_4 to $[CpFe(CO)_2CH_2OCH_3]$ (**1**) gave a species which could convert cyclohexene to norcarane [23]. The intermediacy of $[CpFe(CO)_2(=CH_2)]^+$ (**5**) was proposed (equation 4):



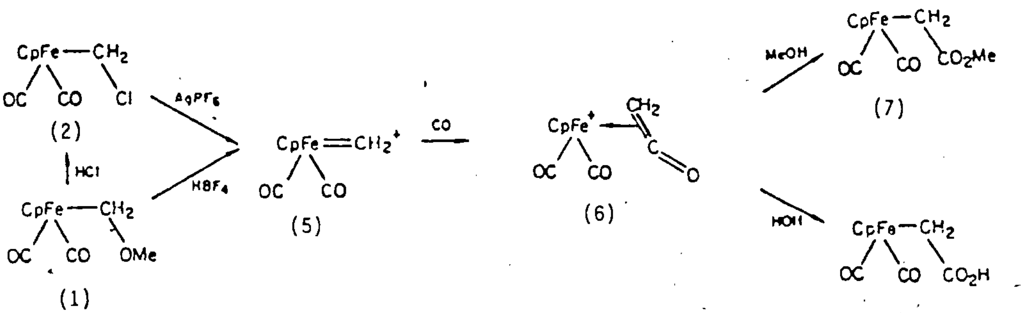
(4)

Workup of the reaction mixture (in the absence of cyclohexene), however, gave mainly the ethylene complex $[CpFe(CO)_2(H_2C=CH_2)]^+$. Brookhart has

Workup of the reaction mixture (in the absence of cyclohexene), however, gave mainly the ethylene complex $[CpFe(CO)_2(H_2C{=}CH_2)]^+$. Brookhart has since reported that (5) is too unstable for observation by ^{1}H-NMR at -80°C [34]. The methylene transfer reaction appears to be general and specific. Thus, the reaction shown in equation 4 carried out in the presence of cis- or trans-2-butene gave cis- or trans-1,2-dimethylcyclopropane respectively. Similarly to (1), (2) reacts with $AgBF_4$ to yield $[CpFe(CO)_2CH_3]$, $[CpFe(CO)_2C_2H_4]^+$ and $[CpFe(CO)_3]^+$. Heating (2) with cyclohexene at 50°C yields $[CpFe(CO)_2Cl]$ and norcarane (80%). $[CpMo(CO)_3CH_2OCH_3]$ also reacts with HBF_4 in the presence of cyclohexene to produce norcarane, suggesting that other methoxymethyl complexes may behave in an analogous manner.

The existence of (**5**) as an intermediate was also proposed by Green *et al.* [24], whilst Steven and Beauchamp have shown that (**5**) occurs in the electron impact mass spectrum of $[CpFe(CO)_2CH_2OCH_3]$ (1) if protonation agents are present [35]. Complex (**5**) was also obtained from the reaction of (2) with $AgPF_6$, where it was successfully used as an alkylating agent towards coordinated ligands [36].

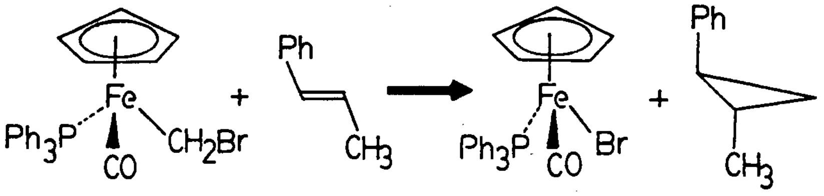
Bodnar and Cutler reported that (1), after reaction with HBF_4, can react with exogenous CO to give a stable (η^2-C,C) ketene complex (6), which transforms into its carbomethoxymethyl group (7) in the presence of methanol (**SCHEME 2**) [37].



SCHEME 2

Refluxing complex (1) in acetonitrile with an excess of PPh_3 or $P(OMe)_3$ for 4 and 10 days respectively, gave the alkoxyacetyl complexes $[CpFe(PR_3)(CO)\{C(O)CH_2OCH_3\}]$ (PR_3 = PPh_3, $P(OMe)_3$). These vigorous reaction conditions exemplify the difficulty with which methoxymethyl complexes undergo alkyl-acyl migrating insertion. The comparable reaction of PR_3 with $[CpFe(CO)_2CH_3]$ is complete after less than one day of refluxing. The above alkoxyacetyl complexes serve as precursors to free methyl- or ethylacetate, ethylene and acetaldehyde [25].

The triphenyl phosphine containing complexes $[CpFe(PPh_3)(CO)CH_2OCH_3]$ (8) and $[CpFe(PPh_3)(CO)CH_2Cl]$ (9) as well as $[CpFe(PPh_3)(CO)CH_2I]$ (11) were briefly reported by Davidson *et al*. [38]. Flood *et al*. later reported the full characterisation of (8) and (9) [39]. Complex (8) was synthesized by the irradiation of $[CpFe(CO)_2CH_2OCH_3]$ (1) in the presence of PPh_3. This product, (8), was then reacted with HCl gas to yield (9) as shown in equation 2 [39]. Optically pure (-)$[CpFe(PPh_3)(CO)CH_2Cl]$ (9) was prepared by reacting (-)$[CpFe(PPh_3)(CO)CH_2OMen]$ (Men = menthyl) with HCl at 0°C. Flood also prepared the bromo- (10) and iodomethyl (11) analogues of (9) by reacting [CpFe(PPh_3)(CO)CH_2OMen] with HBr or HI gas as shown in equation 2. Only (10) was reported to be sufficiently stable to characterise. Again, the chloride of the chloromethyl complex (9) was reported to be susceptible to nucleophilic attack by nucleophiles such as OMe^-, H^- and CN^-. Complex (9) could also be converted into the alkyl compounds, [CpFe(PPh_3)(CO)R], using Grignard reagents, or RLi (R = CH_3, CH_2CH_3, $CH(CH_3)_2$, C_6H_5, γ-C_3H_5). Complex (9) also reacts with $NaOC_{10}H_{19}$ to give [CpFe$(CO)_2CH_2$OMen] [38]. As with [CpFe$(CO)_2CH_2Cl$] [23], (9), (10) and (11) were also found to be sources of [CH_2] [39]. Hence, for example, [CpFe(PPh_3)(CO)CH_2Br] reacted with [PhCH=$CHCH_3$] to yield a substituted cyclopropane (equation 5).

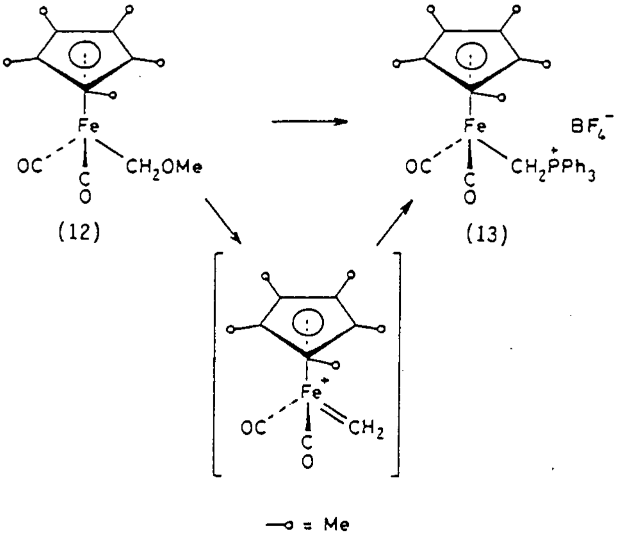


(5)

Complex (9) and [CpFe(o-BP)(CO)CH_2Cl] {o-BP = tri(o-biphenyl)phosphite}, were also prepared by the reaction of HCl with [CpFe(L)(CO)CH_2OEt] (L = PPh_3, o-BP) [40]. Alkylation of these two complexes with sodium t-butyl acetoacetate and pyrroline cyclohexanone enamine yielded six of the eight possible alkylation products. The two products where L was o-BP and the nucleophile was t-butyl acetoacetate did not form, presumably due to excessive steric hindrance. The excess of one diastereomer over the other ranged from 10-64 %.

All attempts to carbonylate complex (8) or [InFe(PPh_3)(CO)CH_2OCH_3] (In = η^5-indenyl ligand) were unsuccessful. The latter complex, on reaction with CO under severe conditions, gave [InFe$(CO)_2CH_2OCH_3$], thus again showing the difficulty with which some methoxymethyl complexes undergo "CO insertion" [41].

Recently the methoxymethyl complex [Cp*Fe(CO)$_2$(CH$_2$OCH$_3$)] (Cp* = η-C$_5$Me$_5$) (12) has been synthesized [42,43]. Acid treatment of (12) in the presence of PPh$_3$ gave the cationic ylide complex [Cp*Fe(CO)$_2$(CH$_2$PPh$_3$)]BF$_4$ (13). The authors propose that (13) is formed according to **SCHEME 3**. *ie. via* the intermediacy of [Cp*Fe(CO)$_2$(CH$_2$)]$^+$.

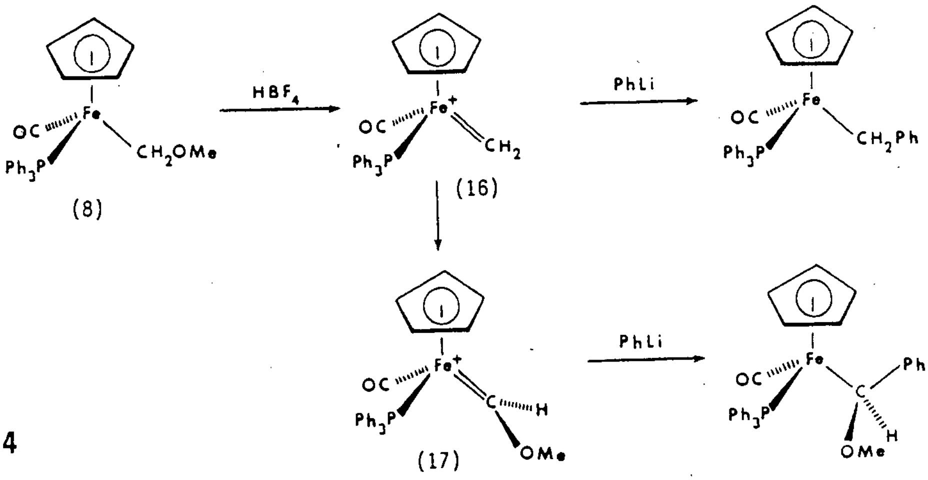


SCHEME 3

The formation of (13) proves the electrophilic nature of the methylene ligand. Protonation of (12) in ether generates the methyl complex [Cp*Fe(CO)$_2$CH$_3$], as well as [Cp*Fe(CO)$_2$(Z)]$^+$ (Z = CO, OEt$_2$). No evidence for [Cp*Fe(CO)$_2$C$_2$H$_4$] or C$_2$H$_4$ was found, unlike for the analogous [CpFe(CO)$_2$CH$_2$OCH$_3$] complex, where both [CpFe(CO)$_2$CH$_3$] and [CpFe(CO)$_2$C$_2$H$_4$]$^+$ were identified [23]. Complex (12) undergoes an α-hydride abstraction with Ph$_3$CPF$_6$ at -80°C to give the cis-isomer of [Cp*Fe(CO)$_2$(=CHOCH$_3$)]PF$_6$ which isomerises to the trans form on warming [44,45]. Photolysis of (12) in the presence of PPh$_3$ gave

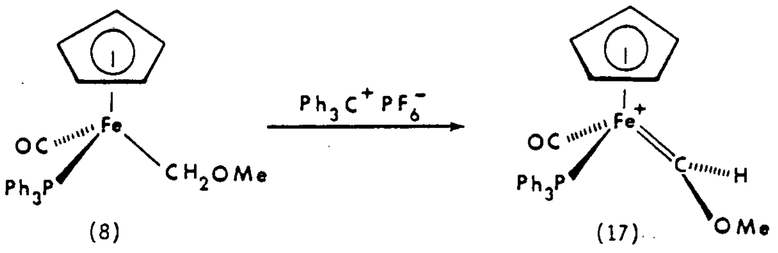
[Cp*Fe(PPh$_3$)(CO)CH$_2$OCH$_3$] **(14)** as a red, air-sensitive compound, in 50% yield. Reacting **(14)** with either CF_3CO_2H, $Me_3SiOSO_2SF_3$ or HBF_4-Et_2O at -90°C gave the cationic methylene complex [Cp*Fe(PPh$_3$)(CO)(=CH$_2$)]$^+$ **(15)** [42,43].

The cyclopentadienyl compound analogous to **(15)**, [CpFe(PPh$_3$)(CO)(=CH$_2$)]BF$_4$ **(16)**, has since been reported by Davies and Maberly, who proposed it as an intermediate in the reaction of [CpFe(PPh$_3$)(CO)CH$_2$OCH$_3$] **(8)** with HBF_4 and PhLi (**SCHEME 4**) [46].



SCHEME 4

To explain the formation of **(17)** in **SCHEME 4**, the authors propose that **(16)** acts as a hydride abstractor capable of removing a hydride ion from **(8)** with concomitant formation of the methylene complex [CpFe(PPh$_3$)(CO)CH$_3$], which would not be expected to survive the reaction conditions. Complex **(8)** also reacts with trityl salt to give the substituted carbene species **(17)** (equation 6) [46].



(6)

The complex [CpFe(dppe)CH_2OCH_3] (dppe = $PPh_2CH_2CH_2PPh_2$) **(18)** was synthesized by irradiation of [CpFe$(CO)_2CH_2OCH_3$] in the presence of bis(diphenylphosphino)ethane [47]. Acid treatment of **(18)** was again carried out to give a carbene species $[CpFe(dppe)(=CH_2)]^+$ **(19)**, which has since been spectroscopically characterised [48].

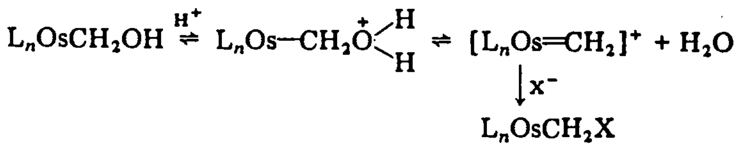
The complex [Cp*Fe(dppe)CH_2OCH_3] **(20)** has since been reported. This complex reacts with Ph_3CPF_6 to give the methoxymethyl cation $[Cp^*Fe(dppe)(CH_2OCH_3)]^+PF_6^-$ in very high yield [49]. The cation in turn reacts with Bu^tOK at -80°C to give the methoxycarbene $[Cp^*Fe(dppe)(=CHOCH_3)]PF_6$ and an equivalent amount of **(20)** and Bu^tOH [49].

The iodomethyl complex $[Fe\{P(OCHMe_2)_3\}_2(CO)_2(I)CH_2I]$ was prepared by the addition of HX to the formaldehyde complex $[Fe\{P(OCHMe_2)_3\}_2(CO)_2(\eta^2\text{-}CH_2O)]$ [50]. This reaction proceeds via the intermediacy of $[Fe\{P(OCHMe_2)_3\}_2(CO)_2(I)CH_2OH]$. Methylation of the very similar formaldehyde complex $[Fe\{P(OMe)_3\}_2(CO)_2(CH_2O)]$ by CH_3OSO_2F and subsequent addition of NBu_4I gave the methoxymethyl complex $[Fe\{P(OMe)_3\}_2(CO)_2CH_2OCH_3]$ **(21)**. Complex **(21)** reacts with CO in ether to give the methoxyacetyl complex $[Fe\{P(OMe)_3\}_2(CO)_2\{C(O)CH_2OCH_3\}]$ [51]. This "CO insertion" reaction is interesting since, according to both theoretical [52] and kinetic considerations [53], the migration of a methoxymethyl group onto a coordinated CO group is much less likely to occur compared to a methyl group.

The ruthenium complexes [$CpRu(CO)_2CH_2OCH_3$] (**22**) and [$CpRu(CO)_2CH_2Cl$] were reported by Moss *et al.* [31,54]. Complex (**22**) also forms when [$CpRu(CO)_2CH_2OH$], prepared from [$CpRu(CO)_3$]PF_6 and $NaBH_3CN$, reacts with methanol [55]. Unlike [$CpFe(CO)_2CH_2Cl$], [$CpRu(CO)_2CH_2Cl$] did not react with PPh_3 in methanol.

The pentamethylcyclopentadienyl ruthenium complex [$Cp^*Ru(CO)_2CH_2OCH_3$] (**23**) has been prepared by Malish *et al.* by reacting K[$Cp^*Ru(CO)_2$] with $MeOCH_2Cl$ [56]. Complex (**23**), like complex (**22**), was obtained as one of the products of the reaction of [$Cp^*Ru(CO)_3$]PF_6 with $NaBH_3CN$ in methanol [57]. Other products of this reaction were [$Cp^*Ru(CO)_2H$] and [$Cp^*Ru(CO)_2CH_2OH$]. The reaction of (**23**) with HCl gives [$Cp^*Ru(CO)_2CH_2Cl$]. Complex (**23**) undergoes an α-hydride abstraction with Ph_3CPF_6 to give the cis-isomer of [$Cp^*Ru(CO)_2(=CHOCH_3)$]PF_6 which isomerises to the trans form on warming [44,45].

Roper *et al.* reported that [$Os(PPh_3)_2(CO)_2(\eta^2-CH_2O)$] proved to be a useful synthetic precursor for stable hydroxymethyl, methoxymethyl and halomethyl complexes [58,59]. [$Os(PPh_3)_2(CO)_2(\eta^2-CH_2O)$] reacts with excess HX (X = Cl, Br, I) to yield the halomethyl complexes [$Os(PPh_3)_2(CO)_2(X)CH_2X$]. The reaction proceeds with the hydroxymethyl complex [$Os(PPh_3)_2(CO)_2(X)CH_2OH$] acting as an intermediate. The proposed mechanism is shown in equation 7.



$$\begin{array}{l} L_nOsCH_2OH \overset{H^+}{\rightleftharpoons} L_nOs{-}CH_2\overset{+}{O}{<}^{H}_{H} \rightleftharpoons [L_nOs{=}CH_2]^+ + H_2O \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow X^- \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad L_nOsCH_2X \end{array}$$

(7)

The reactivity order observed for the hydrogen halides was HI > HBr >

HCl. The postulated intermediate methylene complex could not be isolated.

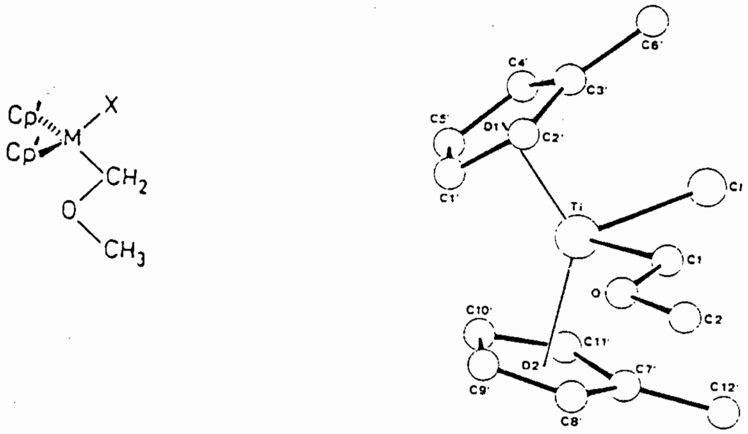
$[Os(PPh_3)_2(CO)_2(I)CH_2I]$ [58] reacts with SeH^- to initially form $[Os(PPh_3)_2(CO)_2I(CH_2SeH)]$ [60]. On recrystallisation, HI is rapidly lost and $[Os(PPh_3)_2(CO)_2(\eta^2\text{-}CH_2Se)]$ is obtained.

$[Os(PPh_3)_2(CO)_2(\eta^2\text{-}CH_2O)]$ reacts with methyl triflate in benzene to give the methoxymethyl cation $[Os(PPh_3)_2(CO)_2(H_2O)CH_2OCH_3]^+$ which readily reacts with lithium chloride in ethanol to give the neutral complex $[Os(PPh_3)_2(CO)_2(Cl)CH_2OCH_3]$ **(24)** [61]. This complex, **(24)**, is also formed by the reaction of $[Os(PPh_3)_2(CO)_2(Cl)CH_2Cl]$ with methanol.

The chloromethyl complex $[Os(PPh_3)_2(NO)(Cl)_2CH_2Cl]$ **(25)** was prepared by the reaction of $[Os(PPh_3)_2(NO)Cl(=CH_2)]$ and Cl_2 [62]. Complex **(25)** undergoes a rearrangement reaction to give $[Os(PPh_3)(NO)(Cl)_3CH_2PPh_3]$. This rearrangement is thought to proceed via the cationic methylene complex $[Os(PPh_3)_2(NO)Cl_2(=CH_2)]^+$.

1.2.2. Titanium and Zirconium

The complex $[(\eta\text{-}C_5H_4CH_3)_2TiCl_2]$ reacts with excess CH_3OCH_2MgCl at -30°C to give $[(\eta\text{-}C_5H_4CH_3)_2Ti(Cl)CH_2OCH_3]$ in 73% yield - **figure 1** [63].



X = Cl

Cp' = (η^5-$C_5H_4CH_3$)

Figure 1: Molecular formula and structure of
[(η^5-$C_5H_4CH_3$)$_2$Ti(Cl)CH_2OCH_3] [63]

In contrast, the reaction of [(Cp)$_2$ZrCl$_2$] with CH_3OCH_2MgCl gives [(Cp)$_2$Zr(Cl)CH_2OCH_3] as a η^2-donor inside complex (figure 2) [63,64].

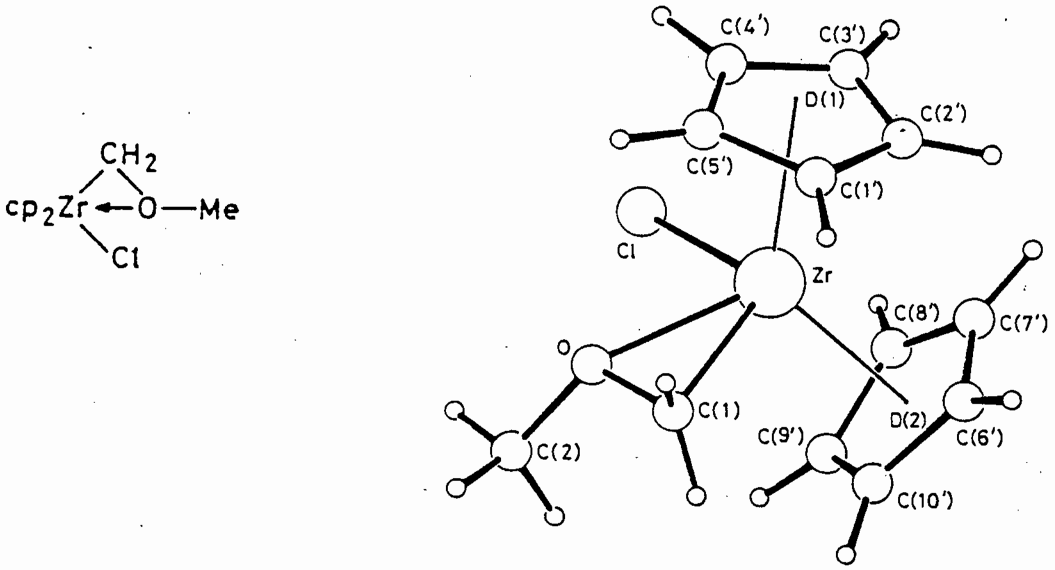
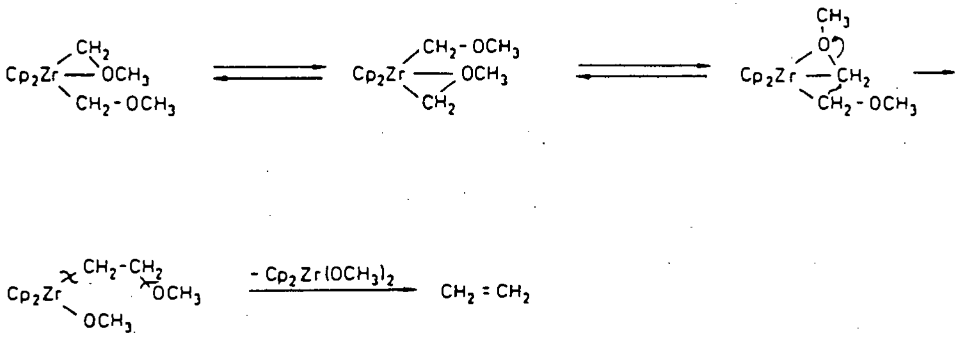


Figure 2: Molecular formula and structure of [(Cp)$_2$Zr(Cl)CH_2OCH_3] [64].

The di-methoxymethyl complex [(RCp)$_2$Zr(CH_2OCH_3)$_2$] (26) (R = H, Me), obtained by reacting [(RCp)$_2$Zr(OCH_3)Cl] with 2 molar equivalents of

$ClMgCH_2OCH_3$, has two chemically different methoxymethyl ligands. Low temperature dynamic NMR spectra of this complex indicate the presence of a η^2-CH_2OCH_3 ligand as well as a "normal" η^1-bonded CH_2OCH_3 group. Thermolysis of complex (26) at 70°C gives ethylene and $[(RCp)_2Zr(OCH_3)_2]$. The proposed mechanism for this thermolysis is shown in **SCHEME 5**.



SCHEME 5

The methylene insertion from the three membered $ZrCH_2OR$ ring system into the adjacent metal-carbon σ-bond makes these complexes good models for Fischer-Tropsch type chemistry [65].

1.2.3. Chromium, Molybdenum and Tungsten

The reaction of CH_2N_2 with $[CpCr(NO)_2Cl]$ gives the stable green complex $[CpCr(NO)_2CH_2Cl]$ (27) in high yield [66]. The complexes $[CpCr(NO)_2CH_2Br]$ (28), $[(\eta^5\text{-}C_5H_4CH_3)Cr(NO)_2CH_2X]$ (29) and $[Cp^*Cr(NO)_2CH_2X]$ (30) (X = Cl, Br), were prepared in a similar fashion. The reaction of $[CpCr(NO)_2CH_2Cl]$ with $AgBF_4$ results in migration of the methylene moiety into a C-H bond of the Cp ring to give the cation $[(\eta^5\text{-}C_5H_4CH_3)Cr(NO)_2]^+$. Unlike the analogous iron complex $[CpFe(CO)_2CH_2Cl]$ [23], none of (27), (28) or (29) transfer methylene to cyclohexene. The cause of the intramolecular reactivity is believed to be due to the extremely strong π-withdrawing power of the two nitrosyl ligands working together [66]. Complexes (27) and (28) react with AgOTs to give $[CpCr(NO)_2CH_2OTs]$ in high yield.

Dodd and Johnson prepared the halomethyl complexes $[Cr(H_2O)_5CH_2X]^{2+}$ (X = Cl, Br, I) via the reaction shown in equation 8 [67].

$$2\ Cr^{2+}(aq) + CH_2X_2 \longrightarrow [Cr(H_2O)_5X]^{2+} + [Cr(H_2O)_5CH_2X]^{2+} \qquad (\underline{8})$$

X = Cl, Br, I

These authors noted that the $[Cr(H_2O)_5CH_2X]^{2+}$ complexes are also obtained by the reaction of a large excess of Cr^{2+} with CHX_3 (X = Cl, Br, I). This they attributed to the conversion of $[Cr(H_2O)_5CHX_2]^{2+}$ - which forms initially - by reaction with excess Cr^{2+} - equation 9.

$$[Cr(H_2O)_5CHCl_2]^{2+} + 2\ Cr^{2+}(aq) + H^+ \longrightarrow [Cr(H_2O)_5CH_2Cl]^{2+} + [Cr(H_2O)_6]^{3+} + [Cr(H_2O)_5Cl]^{2+} \qquad (\underline{9})$$

The presence of these $[Cr(H_2O)_5CH_2X]^{2+}$ complexes, as intermediates, was earlier proposed in the stepwise reduction of haloforms and methylene halides by $CrSO_4$ in DMF-H_2O [68]. A kinetic and mechanistic study on the formation of $[Cr(H_2O)_5CH_2Cl]^{2+}$ has been reported [69]. This study implied that the rate determining step is a bimolecular halogen atom abstraction reaction of $CrCHCl_2^{2+}$ and Cr^{2+} to form $CrCl^{2+}$ and $CrCHCl^{2+}$. This latter intermediate rapidly exchanges with Cr^{2+} to form the intermediate Cr_2CHCl^{4+}, which in turn gives Cr^{3+} and $CrCH_2Cl^{2+}$ in a protonolysis step.

The complex $[Cr(H_2O)_5CH_2Cl]^{2+}$ was found to react with IBr with electrophilic cleavage of the Cr-C bond to give CH_2ClI as the only volatile product - equation <u>10</u> [70].

$$[Cr(H_2O)_5CH_2Cl]^{2+} + IBr + H_2O \longrightarrow CH_2ClI + [Cr(H_2O)_6]^{3+} + Br^- \qquad (\underline{10})$$

Similarly $[Cr(H_2O)_5CH_2X]^{2+}$ (X = Cl, Br, I) reacted with Y_2 (Y = Br, I) to afford CH_2XY, $[Cr(H_2O)_6]^{3+}$ and Y^- [71,72]. The rate of the reaction was found to follow the order $k(IBr) \simeq k(Br_2) >> k(I_2)$. Physical and kinetic evidence suggests that the reactions proceed via a S_E2 mechanism with an "open" transition state.

The complexes $[Cr(H_2O)_5CH_2X]^{2+}$ (X = Cl, Br, OCH_3) were found to react with mercuric nitrate - equation 11 [67,73].

$$[Cr(H_2O)_5CH_2X]^{2+} + Hg^{2+} \longrightarrow HgCH_2X^+ + Cr^{3+} \qquad (11)$$

This reaction is believed to involve a binuclear displacement of Cr by attack of Hg on the carbon atom. In contrast the reaction of $[Cr(H_2O)_5CH_2I]^{2+}$ with Hg^{2+} involves an attack of Hg on the iodide - equation 12.

$$[Cr(H_2O)_5CH_2I]^{2+} + Hg^{2+} \longrightarrow HgI^+ + CH_2 + Cr^{3+} \qquad (12)$$

The reaction of $[Cr(H_2O)_5CH_2I]^{2+}$ with Cr^{2+} as shown in equation 13 has also been reported [74].

$$[Cr(H_2O)_5CH_2I]^{2+} + 2\ Cr^{2+}(aq) + 2\ H^+ \longrightarrow 2\ [Cr(H_2O)_6]^{3+} + [Cr(H_2O)_5I]^{2+} + CH_4 \qquad (13)$$

This reaction is believed to proceed via a carbon-bridged dinuclear chromium intermediate.

The chromium-carbon bond of $CrCH_2OCH_3{}^{2+}$ is also cleaved by reaction with Cu^{2+} and Fe^{3+} [75].

The positions trans to the CH_2X (X = Cl, CH_2OCH_3) group have been found to be several orders of magnitude kinetically more labile than the same position in the corresponding inorganic complexes of Cr^{3+} (*i.e.* $[Cr(H_2O)_5X]^{2+}$) - equation 14 [76,77].

$$[Cr(H_2O)_5CH_2X]^{2+} + SCN^- \longrightarrow \textit{trans}\text{-}[Cr(H_2O)_4(NCS)CH_2X]^+ + H_2O \qquad (\underline{14})$$

Both Jolly and Pettit [23], and Green *et al.* [24] reported the preparation of $[CpMo(CO)_3CH_2OCH_3]$ (31). Green further reported the synthesis of $[CpMo(CO)_3CH_2X]$ {X = Cl(32), Br(33)}. Compounds (31)-(33) were prepared according to the method shown in equations 1 and 2. Complex (32) was also prepared in very high yield by the reaction of $[CpMo(CO)_3\{CH_2OC(O)Me\}]$ with HCl [27]. Complex (32) was also prepared by King and Braitsch by reacting the molybdenum anion with $ClCH_2I$ (equation 3) [30]. Reaction of $Na[CpMo(CO)_3]$ with CH_2I_2 was reported to give $[CpMo(CO)_3CH_2I]$ (34) in low yield [30]. Complex (34) has only been partially characterised and is reported as being unstable in air. Complex (31) was isolated an air-sensitive oil; complexes (32) and (33) as air- and light sensitive solids.

Facile conversion of (32) to (31) was achieved by reaction with NaOMe [24]. Like its iron analogue, $[CpMo(CO)_3CH_2OCH_3]$ reacts with HBF_4 in the presence of cyclohexene to produce norcarane [23]. The carbene complex $[CpMo(CO)_3(CH_2)]^+$ was also generated by the reaction of (28) with $AgPF_6$ [36]. The reactivity of $[CpMo(CO)_3CH_2Cl]$ (32) with PPh_3 differs from that of its tungsten analogue $[CpW(CO)_3CH_2Cl]$. Thus, (32) reacts with PPh_3 in methanol to give $[CpMo(PPh_3)(CO)_2\{C(O)CH_2OCH_3\}]$, $[CpMo(PPh_3)(CO)_2Cl]$ and $[CpMo(PPh_3)_2(CO)Cl]$ depending on reaction time [32]. In contrast, unlike $[CpMo(CO)_3CH_3]$ which underwent "CO insertion", complex (32) did not react with $C_6H_{11}CN$ [78]. A proposed pathway for the reactions of the $[M(L)CH_2X]$ complex with ligands, L, is shown in **SCHEME 1** [32].

As for its iron analogue (**2**), complex (**32**) reacts with L (L = py, SMe_2, SMePh), using $TlBF_4$ as an electrophilic substitution promoter, to give ylide type complexes $[CpMo(CO)_3CH_2L]BF_4$ [33].

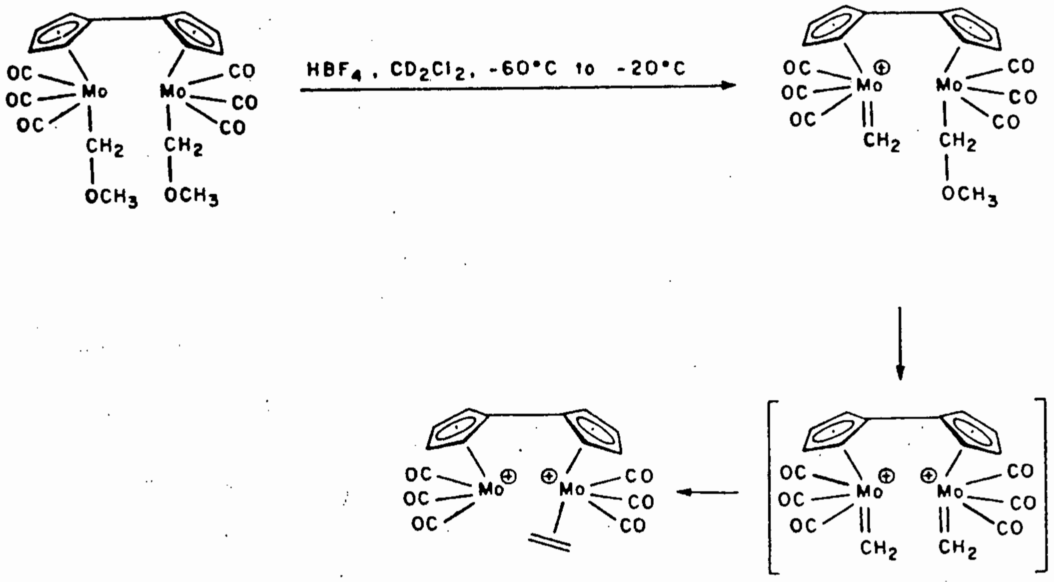
The pentamethylcyclopentadienyl analogues of compounds (**31**)-(**34**), $[Cp^*Mo(CO)_3CH_2X]$ (X = OCH_3, Cl, Br, I) were recently reported [79]. In contrast to $[Cp^*W(CO)_3CH_2Cl]$, $[Cp^*Mo(CO)_3CH_2Cl]$ reacts with PPh_3 to give $[Cp^*Mo(PPh_3)(CO)_2Cl]$ and not the ylide type product obtained from $[Cp^*W(CO)_3CH_2Cl]$ (see later). As with the Cp complexes, the Cp* molybdenum complex $[Cp^*Mo(CO)_3CH_2Cl]$ is reported to be less stable than its tungsten analogue $[Cp^*W(CO)_3CH_2Cl]$.

The triphenylphosphine methoxymethyl complex $[CpMo(PPh_3)(CO)_2CH_2OCH_3]$ (**35**) has been reported to react with $(CH_3)_3SiOSO_2CF_3$ at -90°C to form the carbene complex $[CpMo(PPh_3)(CO)_2(=CH_2)]^+$ (**36**) [80].

Similarly, $[CpMo(PPh_3)(CO)_2CH_2OCH_3]$ reacts with Ph_3CAsF_6 to give a mixture of $[CpMo(PPh_3)(CO)_2(=CHOCH_3)]^+$ and $[CpMo(PPh_3)(CO)_2(CH_3)]$. These latter two complexes are believed to form due to hydride transfer from (**35**) to the carbene (**36**).

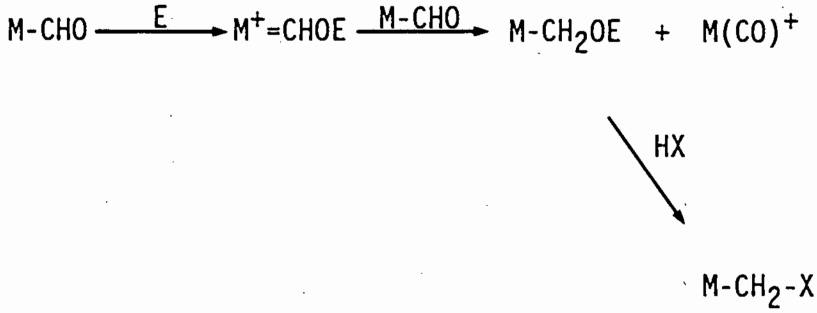
The unusual di-methoxymethyl complex $[FvMo_2(CO)_2(CH_2OCH_3)_2]$ (**37**) (Fv = fulvalene) was prepared by reacting $[FvMo_2(CO)_6]^{2-}$ (obtained from the Na-Hg reduction of $[FvMo_2(CO)_6]$) with $ClCH_2OCH_3$ [81]. Treatment of (**37**) with $HBF_4{\cdot}(Et_2O)$ at -20°C in CD_2Cl_2 produced

$[FvMo_2(CO)_6(CH_2OCH_3)(=CH_2)]^+$ (38) (as detected by ^1H-NMR spectroscopy). Warming the solution to 0°C gave the carbene-coupled product $[FvMo_2(CO)_6(C_2H_4)]^{2+}$ (39). The proposed reaction sequence is shown in **SCHEME 6**.



SCHEME 6

The complexes *trans*-$[CpMo\{P(OPh)_3\}(CO)_2CH_2X]$ (X = Cl, Br, I) were prepared by the novel route of utilising the ability of the formyl complex $[CpMo\{P(OPh)_3\}(CO)_2CHO]$ to transfer hydride in the presence of electrophilic reagents [15] as shown in the following scheme (**SCHEME 7**).



E = H or CH_3; X = Cl,Br,I

SCHEME 7

The direct conversion of the formyl complex to the halomethyl complex occurs by the action of HX. The stereochemistry of the initial formyl complex was preserved in the halomethyl products.

The complexes $[CpW(CO)_3CH_2X]$ {X = OCH_3(**40**), Cl(**41**), Br(**42**)} were first reported by Green *et al*. [24]. They were prepared according to the scheme shown in equations 1 and 2. Facile conversion of (**41**) to (**40**) was achieved by reaction with NaOMe, though the yield was low.

King and Braitsch prepared (**41**) by the alternative route of reacting the tungsten anion with $ClCH_2I$ (see equation 3) [30]. The reaction of the tungsten anion with CH_2I_2 gave the new (but only partially characterised) compound $[CpW(CO)_3CH_2I]$ (**43**), in poor yield. This iodomethyl complex was reported to be highly unstable. Recent evidence suggests that compound (**43**) is more stable than previously reported and it can be prepared in high yield [chapter 3].

The pentamethylcyclopentadienyl analogues of compounds **(40)**-**(43)**, [$Cp^*W(CO)_3CH_2X$] (X = OCH_3, Cl, Br, I) were recently reported [79]. [$Cp^*W(CO)_3CH_2X$] reacted with PPh_3 to form the ylide complex [$Cp^*W(CO)_3CH_2PPh_3$]X (X = Cl, I) [79]. Similarly, [$CpW(CO)_3CH_2Cl$] reacts with PPh_3 in acetonitrile or methanol to give [$CpW(CO)_3CH_2PPh_3$]Cl [32,54]. The Cp* tungsten haloalkyl complexes are reported to be more stable than their Cp analogues and have a stability order of CH_2Cl > CH_2Br > CH_2I.

1.2.4 Manganese and Rhenium

King and Braitsch found [$Mn_2(CO)_{10}$] to be the only product of the reaction between Na[$Mn(CO)_5$] and $ClCH_2I$ at room temperature [30]. Moss and Pelling, however, found that the same reaction at -20°C gave [$Mn(CO)_5CH_2Cl$] **(44)** in 50% yield [31]. Compound **(44)** had previously been referred to by Jolly and Pettit [23]. Moss *et al.* also reported the synthesis of, and full characterisation data for, cis-[$Mn(PPh_3)(CO)_4CH_2Cl$] [31,54].

Complex **(44)** reacts with PPh_3 in CH_3CN at room temperature to give [$Mn(PPh_3)_2(CO)_3Cl$] [32]. The methoxymethylpentacarbonyl manganese complex [$Mn(CO)_5CH_2OCH_3$] **(45)** has been reported [53] from the reaction of Na[$Mn(CO)_5$] with $ClCH_2OCH_3$ analogous to equation <u>1</u>. Complex **(45)**, which had previously been reported by Jolly and Pettit [23], reacted with PPh_3 in CH_3CN to give *cis*-$[Mn(PPh_3)(CO)_4\{C(O)CH_2OCH_3\}]$ [32]. In methanol **(45)** reacted with excess PPh_3 to give *cis*-$[Mn(PPh_3)(CO)_4CH_2OCH_3]$, initially, and trans-$[Mn(PPh_3)_2(CO)_3CH_2OCH_3]$ after prolonged reaction times [32]. $[Mn(CO)_5CH_2I]$ **(46)** has been prepared by Gladysz *et al*. by the reaction of **(45)** with $(CH_3)_3SiI$ [82].

A novel method for the synthesis of the complexes $[Mn(CO)_5CH_2X]$ (X = Cl, Br , I) involves the facile electrophilic halogen exchange between BX_3 (X = Cl, Br, I) with $[Mn(CO)_5CH_2F]$ as shown in equation <u>15</u>.

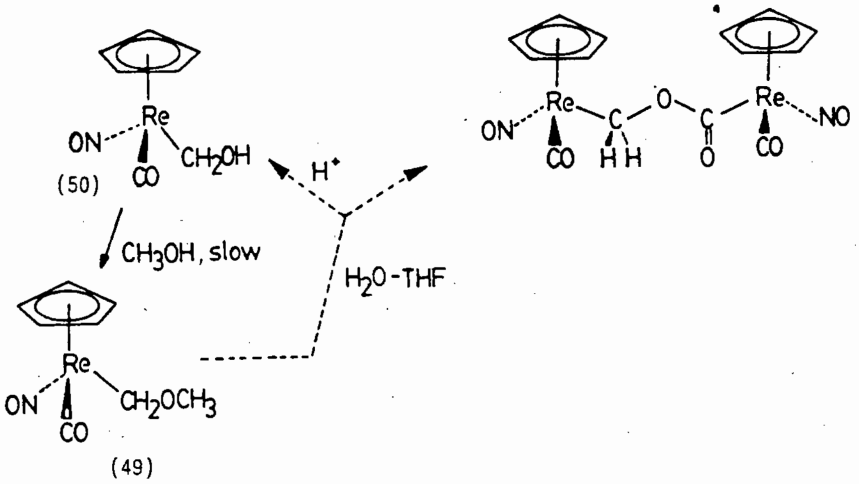
$$[Mn(CO)_5CH_2F] + BX_3 \longrightarrow [Mn(CO)_5CH_2X] + BX_2F \qquad (\underline{15})$$

The formation of the strong B-F bond is believed to be the driving force for the overall reaction [83,84].

Complex **(46)** does not appear to react with PPh_3 in CD_3CN and decomposes to form $[Mn(CO)_5I]$. As expected, complex **(46)** was observed to act as a methylene transfer reagent, reacting with cyclohexene to form norcarane [85].

The complexes $[Re(CO)_5CH_2OCH_3]$ **(47)** and $[Re(CO)_5CH_2Cl]$ **(48)** were first mentioned by Jolly and Pettit [23]. Moss *et al*. later reported their synthesis and full characterisation data [31,54]. Unlike their Mn analogues, neither **(47)** nor **(48)** react with PPh_3.

The complex $[CpRe(CO)(NO)CH_2OCH_3]$ **(49)** was obtained from the methanolysis of [CpRe(CO)(NO)(CH_2OH)] **(50)**. An attempt to hydrolyse **(49)** by dissolution in water-THF in the presence of CF_3CO_2H gave the dimeric metalloester [{CpRe(CO)(NO)}$_2$(μ-CH_2OCH_2)]. The hydroxymethyl complex **(50)** was obtained when the above acid catalysed hydrolysis of **(49)** was quenched with 0.15 equivalents of $N(C_2H_5)_3$ prior to work-up - **SCHEME 8** [5,86].



SCHEME 8

The triphenylphosphine analogue of **(49)**, [CpRe(PPh_3)(NO)CH_2OCH_3] **(51)** has been synthesized from the carbene species [CpRe(PPh_3)(NO)(=CH_2)]PF_6 by Gladys *et al*. [87]. Treatment of **(51)** with CH_3SO_3F at -60°C gave [CpRe(PPh_3)(NO)(CH_3)], $(CH_3)_2O$ and [CpRe(PPh_3)(NO)($CHOCH_3$)]$^+SO_3F^-$. Adding **(51)** to [CpRe(PPh_3)(NO)(=CH_2)] gave [CpRe(PPh_3)(NO)(=$CHOCH_3$)]PF_6 and [CpRe(PPh_3)(NO)(CH_3)]. Both the above reactions were carried out in order to verify that **(51)** is an intermediate in the formation of [CpRe(PPh_3)(NO)(CH_3)] from [CpRe(PPh_3)(NO)(CHO)] and CH_3SO_3F.

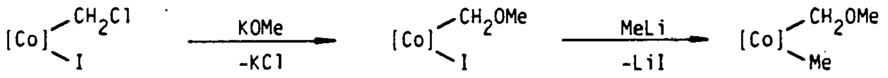
The Cp* complex [Cp*Re(PPh_3)(NO)(Cl)CH_2Cl]BF_4 was obtained in the decomposition of the dichloromethane complex [Cp*Re(PPh_3)(NO)($ClCH_2Cl$)]BF_4 [88].

As was observed for $[CpMo\{P(OPh)_3\}(CO)_2CHO]$, the formyl complexes mer,trans $[Re\{P(OPh)_3\}_2(CO)_3CHO]$ and cis-$[Mn(PPh_3)(CO)_4CHO]$ react with HX, utilising the ability of some formyls to transfer hydride in the presence of electrophilic reagents, to give mer, trans $[Re\{P(OPh)_3\}_2(CO)_3CH_2X]$ and cis-$[Mn(PPh_3)(CO)_4CH_2X]$ (X = Cl, Br, I) respectively, with retention of stereochemistry (as shown in **SCHEME 7**). The complexes mer,trans-$[Mn(PPh_3)_2(CO)_3(CHO)]$ and mer,trans-$[Mn\{P(OPh)_3\}_2(CO)_3(CHO)]$ react with methyl triflate as the initial electrophile to give the corresponding methoxymethyl species (**SCHEME 7**), which then react with HX to give the halomethyl complexes mer,trans-$[Mn(PPh_3)_2(CO)_3CH_2X]$ and mer,trans-$[Mn\{P(OPh)_3\}_2(CO)_3CH_2X]$ (X = Cl, Br, I) [15].

The complex $[LRe(CO)(NO)CH_2I]BF_4$ (L = 1,4,7-triazacyclononane) was prepared by oxidation of $[LRe(CO)(NO)(CH_3)]BF_4$ with I_2. The complex $[LRe(CO)(NO)CH_2I]BF_4$ reacts in aqueous solution to give the complex $[\{LRe(CO)(NO)\}_2(\mu\text{-}CH_2OCH_2)]I_2$, a complex with a previously unknown 2-oxapropane-1,3-diide bridge. This reaction is believed to be due to the hydrolysis of Re-CH_2I with H_2O, followed by dimerisation to give the -CH_2-O-CH_2- bridged product [89].

1.2.5 Cobalt, Rhodium and Iridium

Several halo- and methoxymethyl cobalt complexes are known. [CpCo(PMe$_3$)(CO)] or [CpCo(PMe$_3$)(C$_2$H$_4$)] reacted with CH$_2$ClI at low temperature (-50°C) to give a mixture of [CpCo(PMe$_3$)(I)CH$_2$Cl] (52) and [CpCo(PMe$_3$)(Cl)I] (53) [90,91]. Complex (52) is stable in the solid state, though in solution at temperatures exceeding -30°C it eliminates CH$_2$ to form (53). The reaction of (52) with KOMe gives the methoxymethyl cobalt(III) complex [CpCo(PMe$_3$)(I)CH$_2$OCH$_3$] (54). This methoxymethyl complex can also be prepared in a "one pot" synthesis with [CpCo(PMe$_3$)(CO)], CH$_2$ClI and methanolate. The complex (54) reacts with MeLi, with substitution of the metal bonded iodide, to give the complex [CpCo(PMe$_3$)(Me)CH$_2$OCH$_3$] (55) - equation (16).



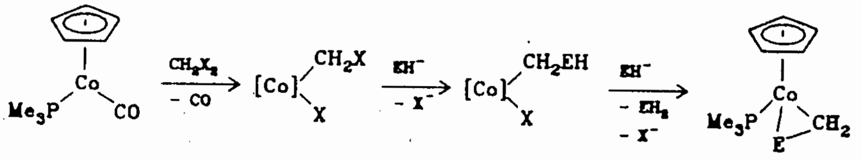
(52) (54) (55)

[Co] = CpCo(PMe$_3$)

(16)

The reaction of (55) with HBF$_4$ does not yield the expected [CpCo(PMe$_3$)(C$_2$H$_4$)H]BF$_4$, but the complex [CpCo(PMe$_3$)$_2$H]BF$_4$ [90]. Addition of an equimolar quantity of a two-electron donor, L {where L= PMe$_3$, P(OMe)$_3$, CNMe} to (52) produces the corresponding [CpCo(PMe$_3$)(L)CH$_2$Cl]$^+$ cations. These cations can also be prepared by the reaction of [CpCo(PMe$_3$)(CO)] with CH$_2$ClI in the presence of L. The cations react at room temperature with PMe$_3$ to produce the ylidic [CpCo(PMe$_3$)(L)CH$_2$PMe$_3$]$^{2+}$ dications. Similarly, Klein and Hammer obtained cobalt coordinated ylidic alkylidene-trimethylphosphorane ligands by the oxidative additions of 1,1-dichloroalkanes with $Co(PMe_3)_4$ [92]. They proposed that the formation of these complexes involved chloroalkane cobalt intermediates.

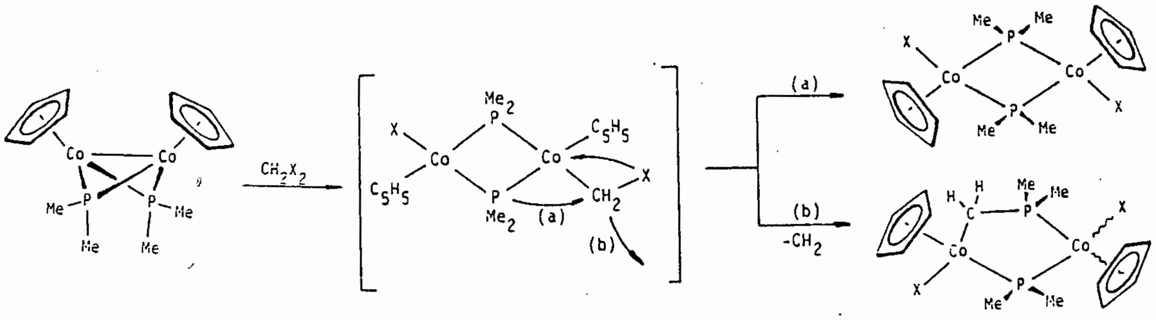
The chloromethyl complex $[CpCo(PMe_3)(X)CH_2X]$ (X = Br, I) has been proposed as a labile intermediate in the formation of $[CpCo(PMe_3)(\eta\text{-}CH_2E)]$ (E = S, Se) from $[CpCo(PMe_3)(CO)]$ according to equation 17.



(17)

$[Co] = CpCo(PMe_3)$; E = S, Se

In contrast $[CpCo(PMe_3)(I)CH_2Cl]$, reacting with NaSH or NaSeH, gave only $[CpCo(PMe_3)(Cl)I]$ [93]. Similarly, halomethyl intermediates are proposed in the reactions of $[CpCo(\mu\text{-}PMe_2)]_2$ with CH_2X_2 (X = Br, I) to give $[\{CpCoX\}_2(\mu\text{-}PMe_2)_2]$ and $[\{CpCoX\}_2(\mu\text{-}PMe_2)(\mu\text{-}CH_2PMe_2)]$ - equation 18 [94].



(18)

The cobalt halomethyl compound $[Cp^*Co(CO)(Cl)CH_2Cl]$ (56) was recently prepared by Dahl *et al.*[95]. This complex was synthesized by the photolytic reaction of $[Cp^*Co(CO)_2]$ with CH_2Cl_2 and represents the first example of an oxidative addition product from a non-porphyrin cobalt(I) species. Compound **(56)** is reported to be relatively air-stable and is stable at room temperature in non-coordinating solvents. In a room temperature photolytic reaction, **(56)** reacts with PMe_3 to give two products, $[Cp^*Co(PMe_3)(Cl)CH_2Cl]$ and $[Cp^*Co(PMe_3)Cl_2]$.

The remarkable chloromethyl complex $[Co(CO)_4CH_2Cl]$ was prepared by the decarbonylation of the chloroacetyl complex $[Co(CO)_4\{C(O)CH_2Cl\}]$. This reaction is reversible and thus represents the first example of a carbonylation/decarbonylation reaction couple of a MCH_2X *vs.* $MC(O)CH_2X$ pair. A mixture of the decarbonylated and carbonylated species reacted with PPh_3 to give $[Co(PPh_3)(CO)_3\{C(O)CH_2Cl\}]$ **(57)**. This represents the first example where a chloromethyl transition metal complex reacts with PPh_3 to yield a CO substitution product, and it is also the first example of a ligand-induced migratory insertion reaction in this class of compounds. The chloroacetyl complex **(57)** could be decarbonylated at 40°C to give the corresponding chloromethyl derivative $[Co(PPh_3)(CO)_3CH_2Cl]$ **(58)**. This latter complex, **(58)**, can in turn be carbonylated to give **(57)** again. An alternative route to complex **(58)** involves the reaction of $Na[CoPPh_3(CO)_3]$ and $ClCH_2I$ [96].

The complexes $[Co([14]aneN_4)(H_2O)CH_2X]^{2+}$ (X = Cl, Br, I; $[14]aneN_4$ = the tetraazacyclotetradecatraene ligand) were prepared by Bakac and Espenson [97]. Irradiation of these complexes with visible light led to the homolysis of the Co-C bond.

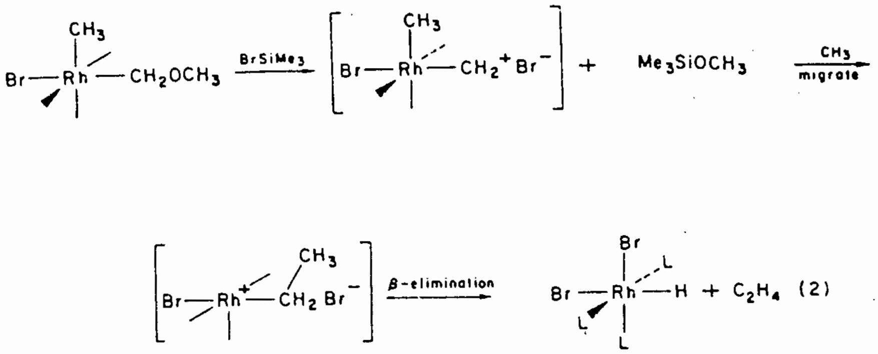
The unusual bromomethyl complex, $[$*(Co)*$CH_2Br]$, where *(Co)* represents vitamin B_{12s}, was prepared by Smith *et al.* according to equation 19 [98].

$$[(Co)] + BrCH_2Br \longrightarrow [(Co)CH_2Br] \qquad (\underline{19})$$
$$(Co) = \text{vitamin } B_{12s}$$

The halomethyl cobaloxime complexes $[Co(DH)_2\{P(OCH_3)_3\}CH_2X]$ (59) (X = Cl, Br, I; DH = dimethylglyoximato ligand) have also been reported [99,100]. The rate of dissociation of $P(OCH_3)_3$ from complexes (59) follows the order $CH_2Cl > CH_2Br$ [99]. The very similar complex $[Co(bae)CH_2Cl]$ {bae = N,N$'$-bis(acetylacetonato)ethylenediimine} has also been reported [101].

Treatment of the cobalt porphyrins [Co(TPP)X] (X = Cl, Br, I) and [Co(OEP)Br] (TPP = meso-tetraphenylporphine and OEP = octaethylporphine) with diazomethane gives the corresponding halomethyl cobalt(II) porphyrins $[Co(TPP)CH_2X]$ (X = Cl, Br, I) and $[Co(OEP)CH_2Br]$ respectively. These reactions are proposed to proceed via the insertion of the carbene moity into a Co-N bond, and only subsequent nucleophilic attack by the halide results in the formation of the CH_2X group [102].

D.L.Thorn prepared $[Rh(PMe_3)_3(CH_3)(Br)CH_2OCH_3]$ (60) by reacting $[Rh(PMe_3)_4(CH_3)]$ with bromomethyl methyl ether. Complex (60) is reported as being stable indefinitely in solution at room temperature under an inert atmosphere. It reacts with $BrSiMe_3$ with C-O bond cleavage, to yield $[Rh(PMe_3)_3(Br)_2(H)]$ and C_2H_4, as shown in equation 20.



(20)

None of the intermediates postulated in equation 20 were observed, but the mechanism is supported by analogy to the chemistry of the related iridium complex, $[IrBr(PMe_3)_3(CH_3)CH_2OCH_3]$ (61) [103]. Reacting (60) with $AgSbF_6$ or $TlBF_4$ (bromide abstractors) gave the solvated cation $[Rh(PMe_3)_3(CH_3)(S)CH_2OCH_3]^+$ (60a) (S = acetonitrile). The cation (60a) decomposes in dichloromethane solution to form methyl vinyl ether, methyl ethyl ether and $[Rh(PMe_3)_4H_2]^+$ [104].

Rhodium complexes of the general formula $[CpRh(L)(L')CH_2I]PF_6$ and $[CpRh(L)_2CH_2I]PF_6$ were prepared according to the method shown in equations (21), (22) and (23) [90,105-107].

$$[CpRhLL'] + CH_2I_2 \longrightarrow [CpRhLL'CH_2I]I \xrightarrow[-I^-]{PF_6^-} [CpRhLL'CH_2I]PF_6 \qquad (21)$$

L	L'	L	L'
PMe_3	PMe_2Ph	PMe_3	PPr^i_3
PMe_3	$PMePh_2$	PMe_3	CNMe
PMe_3	$P(OMe)_3$	PEt_3	$P(OMe)_3$
PMe_3	$P(OEt)_3$	PMe_2Ph	$P(OMe)_3$
		$PMePh_2$	$P(OMe)_3$

$$[CpRhL_2] + CH_2I_2 \longrightarrow [CpRhL_2CH_2I]I \xrightarrow[-I^-]{PF_6^-} [CpRhL_2CH_2I]PF_6 \quad . \qquad (22)$$

$$L = CNMe,\ Bu^tCN,\ P(OEt)_3$$

$$\underset{(62)}{[CpRh(PMe_3)_2]} + CH_2I_2 \rightarrow [CpRh(PMe_3)_2CH_2I]I \xrightarrow{BF_4^-} [CpRh(PMe_3)_2CH_2I]BF_4 \qquad (23)$$

$[CpRh(PMe_3)\{P(OMe)_3\}CH_2I]PF_6$ and $[CpRh\{P(OEt)_3\}_2CH_2I]PF_6$ react with NaI to give the neutral dialkylphosphonate complexes $[CpRh(PMe_3)\{P(O)(OMe)_2\}CH_2I]$ and $[CpRh\{P(OEt)_3\}\{P(O)(OEt)_2\}CH_2I]$ in a Michaelis - Arbuzov type reaction [105]. The complexes $[CpRh(PMe_3)_2CH_2I]^+$ (63) and $[CpRh(PR_3)(L)CH_2I]PF_6$ {L = $P(OMe)_3$, PR_3 = PMe_3, PMe_2Ph, $PMePh_2$; L = $P(OEt)_3$, PR_3 = PMe_3} isomerise thermally, or on addition of NEt_3 (as catalyst), to form ylide rhodium(III) complexes $[CpRh(PMe_3)(I)CH_2PMe_3]PF_6$ and $[CpRh(L)(I)CH_2PR_3]PF_6$, respectively [90,105-107]. In all cases the ligand with the strongest donor properties migrates from the metal to the carbon. The reaction of $[CpRh(PMe_3)_2CH_2I]^+$ with the softer base SMe^- gives a mixture of $[CpRh(PMe_3)(SMe)CH_2PMe_3]I$ (64) and $[CpRh(PMe_3)_2CH_2SMe]I$. Complex (64) has been shown to form rapidly via the intermediate

$[CpRhI(PMe_3)CH_2PMe_3]I$ [106]. In none of the observed interactions of the rhodium haloalkyl complexes has the breaking of a $Rh-PMe_3$ bond been observed. It has therefore been proposed that the isomerism proceeds via an intramolecular mechanism involving a four-centre transition state formed with the aid of the catalyst (figure 3).

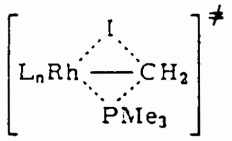


Figure 3

Substitution of the carbon-bonded iodide in $[CpRh(PMe_3)_2CH_2I]I$ with PMe_3 and $[CpRh(PMe_3)\{P(O)(OMe)_2\}CH_2I]$ with L (L = PMe_3, PMe_2Ph, $PMePh_2$, PMeEtPh, $P(OMe)_3$, SMe_2) leads to the formation of the ylide complexes $[CpRh(PMe_3)_2CH_2PMe_3]I_2$ and $[CpRh(PMe_3)\{P(O)(OMe)_2\}CH_2L]I$.

The chloromethyl rhodium complexes $[CpRh(PMe_3)_2CH_2Cl]PF_6$ were prepared according to equation (<u>24</u>), whilst $[CpRh(PMe_3)\{P(OMe)_3\}CH_2Br]^+$ and $[CpRh(PMe_3)\{P(OMe)_3\}CH_2Cl]^+$ were prepared by the reaction of $[CpRh(PMe_3)\{P(OMe)_3\}]$ with CH_2Br_2 and CH_2ClI respectively [105].

$$[CpRh(PMe_3)_2] + CH_2ClX \rightarrow [CpRh(PMe_3)_2CH_2Cl]X \xrightarrow[-X^-]{PF_6^-} [CpRh(PMe_3)_2CH_2Cl]PF_6$$

X = Cl, I (24)

The reaction of complex **(62)** with CH_2Br_2 gave $[CpRh(PMe_3)_2CH_2Br]Br$, but not in pure form [105].

Similarly $[CpRh(R_2PCH_2CH_2PR_2)]$ (R = Me, Ph) reacted with CH_2I_2 in the presence of NH_4PF_6 to give $[CpRh(R_2PCH_2CH_2PR_2)CH_2I]PF_6$. The latter complex (where R = Me) isomerized in the presence of NEt_3 to form the cation $[Cp(I)RhCH_2PMe_2CH_2CH_2PMe_2]^+$, which contains an α-C, ω-P bonded cyclic ylide ligand [107].

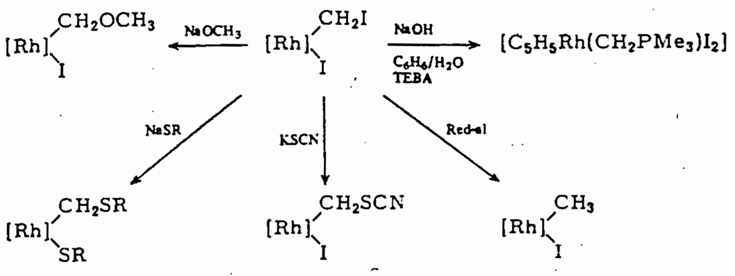
The neutral complex $[CpRh\{P(OMe)_3\}(I)CH_2I]$ can be synthesised by the reaction of $[CpRh\{P(OMe)_3\}(C_2H_4)]$ or $[CpRh\{P(OMe)_3\}_2]$ with CH_2I_2 [105].

The ethylene complex $[CpRh(PMe_3)(C_2H_4)]$ undergoes an oxidative substitution reaction with CH_2I_2, CH_2Br_2 and CH_2ICl to give $[CpRh(PMe_3)(X')CH_2X]$ [108-110] - see equation <u>25</u>.

$$[CpRh(PMe_3)(C_2H_4)] + CH_2XX' \longrightarrow [CpRh(PMe_3)(X')CH_2X] + C_2H_4 \qquad (\underline{25})$$

	X	X'
(65)	I	I
	Br	Br
	Cl	I

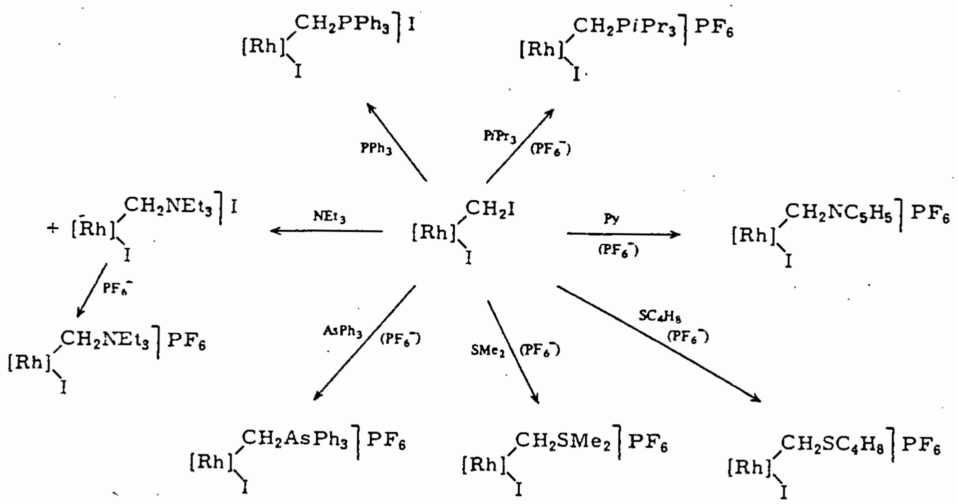
Thus displacement of the ethylene group and the formation of a Rh-C and a Rh-X bond causes the oxidation of Rh(I) to Rh(III). Complex (65) can also be prepared by the reaction of $[CpRh(L)(L')]$ {L = PMe_3, L' = CO, PPh_3, $P(OPh)_3$} [109]. The carbon bonded iodide in (65) is very labile. Thus complex (65) reacts with a whole range of anionic nucleophiles, as shown in **SCHEME 9** [110,111]



[Rh] = CpRh(PMe$_3$); R = CH$_3$, C$_6$H$_5$

SCHEME 9

Notable is the isomerisation of (65) in the presence of [NEt$_3$(CH$_2$Ph)]Cl (TEBA) to [CpRh(I)$_2$CH$_2$PMe$_3$] (66). Complex (66) is also formed when (65) was reacted with NEt$_3$ [109]. Further more complex (65) reacts with neutral nucleophiles with substitution of the carbon bonded iodide as shown in SCHEME 10

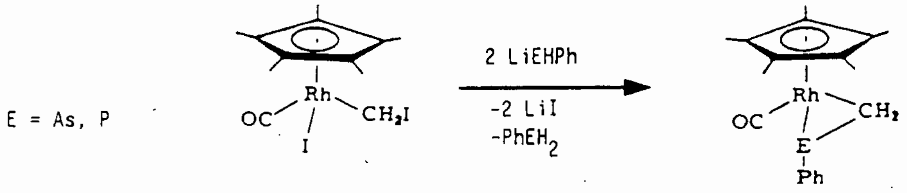


[Rh] = CpRh(PMe$_3$)

SCHEME 10

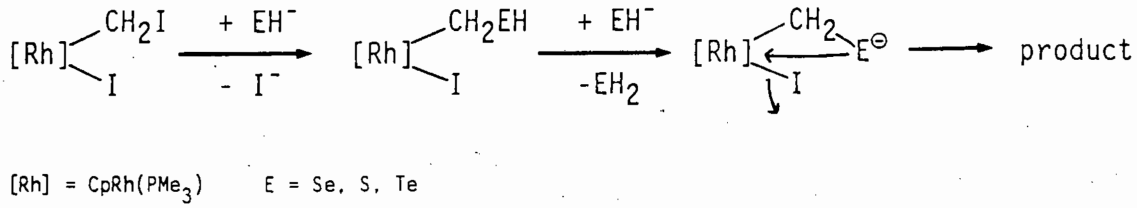
The reactions of (65) with py, $AsPh_3$, SMe_2, and SC_4H_8 are considerably slower than those of PPh_3 and PPr^i_3. It is notable is that the ylides CH_2AsPh_3 and CH_2SMe_2 are stabilised when coordinated to the metal.

Werner and Paul reported that the highly unstable molecule CH_2Se can be fixed by the reaction of $[CpRh(PMe_3)(I)CH_2I]$ with NaSeH, to give $[CpRh(PMe_3)(\eta^2\text{-}CH_2Se)]$ [112]. A similar reaction was carried out by Headford and Roper, using $[Os(PPh_3)_2(CO)_2(I)CH_2I]$, to obtain $[Os(PPh_3)_2(CO)_2(\eta^2\text{-}CH_2Se)]$ [60]. $[Cp^*Rh(CO)(I)CH_2I]$ has been shown to react similarly [113]. The complex $[Cp^*Rh(CO)(I)CH_2I]$ also reacts with LiEHPh (E = As or P) to give $[Cp^*Rh(CO)CH_2EPh]$ (equation <u>26</u>). Ph-As=CH_2 is not known in its "free" (uncoordinated) form [114].



(<u>26</u>)

Similar complexes to those above are obtained in fairly good yield by reacting $[CpRh(PMe_3)(I)CH_2I]$ with NaSH and NaTeH. The reaction has been proposed to proceed as shown in **SCHEME 11** [115].



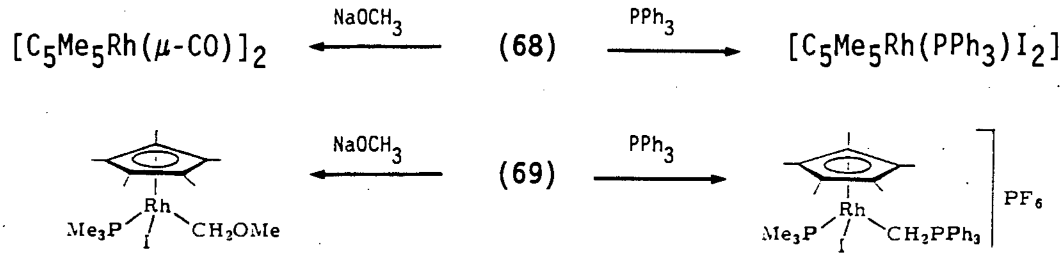
SCHEME 11

Whilst $[CpRh(CO)_2]$ (67) does not react with CH_2I_2, the reaction of $[Cp^*Rh(CO)_2]$ with CH_2I_2 gives $[Cp^*Rh(CO)(I)CH_2I]$ (68) [116], presumably due to the increased electron density on the rhodium caused by the Cp* group. In general, the reaction of $[Cp^*Rh(CO)L]$ $\{L = PMe_3, PMe_2Ph, P(OMe)_3$ and CO$\}$ with CH_2IX (X = I, Cl) gives complexes of the type $[Cp^*Rh(L)(I)CH_2X]$ - equation 27.

$$[Cp^*RhL(CO)] \xrightarrow[-CO]{CH_2IX} [Cp^*RhL(I)CH_2X] \qquad (27)$$

	L	X
(69)	PMe_3	I
	PMe_3	Cl
	PMe_2Ph	I
	$P(OMe)_3$	I

Complex (67) does not react with CH_2Br_2. Complex (69) can also be prepared by reacting $[Cp^*Rh(PMe_3)C_2H_4]$ with CH_2I_2. Complexes (68) and (69) show a surprisingly different reactivity. Whilst (69) reacts with $NaOCH_3$ like its analogous Cp complex (65) to form $[C_5Me_5Rh(PMe_3)(I)CH_2OCH_3]$ (70), complex (68) reacts to form the dimer $[Cp^*Rh(\mu\text{-}CO)]_2$ (SCHEME 12).



SCHEME 12

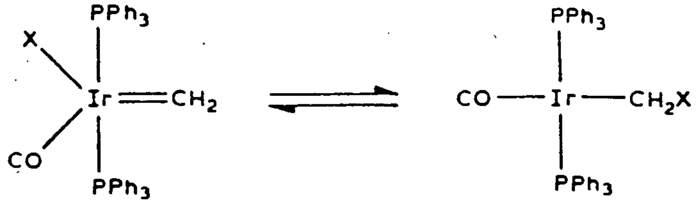
The reaction of (68) with PMe_3 leads to a ligand rearrangement and formation of (69). The reaction of (68) with PPh_3 results in the formation of $[Cp^*Rh(PPh_3)I_2]$ (71), whilst the reaction of (69) with PPh_3 gives the expected ylide complex $[Cp^*Rh(PMe_3)(I)CH_2PPh_3]I$ (72). Complex

(**68**) reacts with dppm, with displacement of a CO group *and* substitution of the carbon bonded iodide, to form the complex $[Cp^*Rh(I)CH_2PPh_2CH_2PPh_2]I$ (**73**). This complex is similar to the complex $[CpRh(I)CH_2PMe_2(CH_2)_2PMe_2]PF_6$, discussed earlier [107].

The halomethyl porphyrin complexes $[(TPP)RhCH_2X]$ (X = Cl, Br, I; TPP = the dianion of tetraphenylporphyrin) were prepared by the reaction of electrochemically generated [(TPP)Rh] and CH_2X_2 [117]. The complexes where X = Cl [118] and X = I [119] have been reported before, the latter by the reaction of [(TPP)RhI] with CH_2N_2.

Marder *et al.* showed that the square-planar cationic complexes $[M(dmpe)_2]Cl$ (M = Rh, Ir) react with CH_2Cl_2 to give trans-$[M(dmpe)_2(Cl)CH_2Cl]Cl\cdot CH_2Cl_2$ in high yields [120]. Similarly, the neutral complex $[Rh(PMe_3)_3Cl]$ reacts with CH_2Cl_2 to give two products, namely mer,cis-$[Rh(PMe_3)_3(Cl)_2CH_2Cl]$ (**74**) and what is believed to be $[Rh(PMe_3)_2(Cl)_3CH_2PMe_3]$. Preliminary results indicate that the complex (**74**) reacts slowly with PMe_3 *via* Cl^- displacement from Rh, rather than $RhCH_2Cl$, to give trans-$[Rh(PMe_3)_4(Cl)CH_2Cl]Cl$.

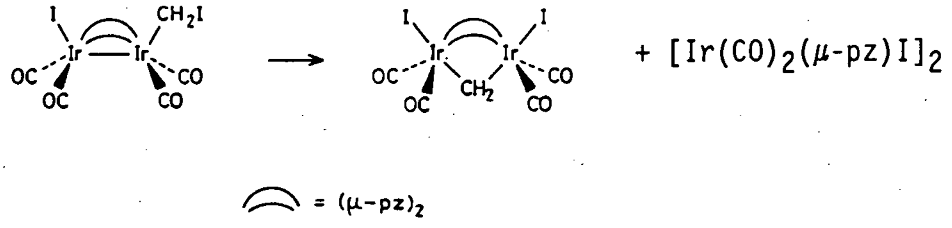
The reaction of $[Ir(PPh_3)_2(CO)Cl]$ with CH_2N_2 was investigated by Mango and Dvoretzky and gave what was assumed from its infra-red spectrum and reactivity to be the chloromethyl compound [121]. It appeared that a CH_2 group had been inserted into a metal-chloride bond. The authors proposed that this reaction proceeded via a carbene intermediate (equation <u>28</u>).



(28)

Assuming the equilibrium in equation 28 to be valid, (*i.e.* left to right being a "migratory insertion" and right to left an "α-elimination"), Roper *et al.* concluded that the position of the equilibrium would depend on X (the halogen), and a weak C-I bond would therefore favour the methylene form [122]. Reaction of [Ir(PPh$_3$)$_2$(CO)I] with CH$_2$N$_2$ in THF at -50°C proved this to be correct, yielding [Ir(PPh$_3$)$_2$(CO)I(=CH$_2$)] in 93% yield.

Harrison and Stobart reported that the reaction of [Ir(CO)$_2$(μ-pz)]$_2$ (pzH = pyrazole) with CH$_2$I$_2$ gave a mixture (70:20:10 ratio) of [Ir$_2$(CO)$_4$(μ-pz)$_2$(I)CH$_2$I] (75), [Ir$_2$(CO)$_4$(μ-pz)$_2$I$_2$(μ-CH$_2$)] (76) and [Ir(CO)$_2$(μ-pz)I]$_2$ (77) [123]. Heating the mixture in benzene resulted in compounds (76) and (77) in a 70:30 ratio (equation 29).



(29)

The rearrangement of the iodomethyldi-iridium species to form the isomeric methylene complex (equation 29) is the first authenticated example of this type of transformation. The reaction of [Ir(cod)(μ-pz)]$_2$ (cod = 1,5-cyclooctadiene) (78) and [Ir$_2$(PPh$_3$)(CO)(μ-

pz)$_2$] with CH_2I_2 afforded stable binuclear iodomethyl derivatives, *i.e.* [$Ir_2(cod)_2(\mu$-$pz)_2(I)CH_2I$] **(79)** and [$Ir_2(PPh_3)_2(CO)_2(\mu$-$pz)_2(I)CH_2I$] **(80)** respectively [123]. Whilst **(79)** does not undergo "oxidative isomerisation" to the di-iridium(III) methylene complex, complex **(80)** does - thus forming [$Ir_2(PPh_3)_2(CO)_2(\mu$-$pz)_2(I)_2(\mu$-$CH_2)$] [124]. Mass spectral analysis indicates that the isomerisation process is intramolecular. The chloromethyl analogue of **(79)** was formed by a photochemically induced net two-electron reduction of [$Ir(cod)(\mu$-$pz)]_2$ **(78)** in CH_2Cl_2, leading to the two-centre oxidative addition product [$Ir_2(cod)_2(\mu$-$pz)_2(Cl)CH_2Cl$] [125]. This reaction does not take place in the dark.

The dinuclear complex [$Ir_2(CO)_4(\mu$-$C_5H_4NS)_2$] reacts with CH_2I_2 to give the dinuclear iodomethyl complex [$Ir_2(CO)_4(\mu$-$C_5H_4NS)_2(I)CH_2I$] [126]. Unlike previous observations [equation <u>29</u>,119,120] the complex [$Ir_2(CO)_4(\mu$-$C_5H_4NS)_2(I)CH_2I$] does not form [$\{Ir(CO)_2(\mu$-$C_5H_4NS)I\}_2(\mu$-$CH_2)$] on heating.

The complexes [$Ir(PMe_3)_2(CO)(Cl)_2CH_2Cl$], [$Ir(PMe_3)_2(CO)(Cl)(Br)CH_2Br$], [$Ir(PMe_3)_2(CO)(Cl)(I)CH_2I$] and [$Ir(PMe_3)_2(CO)(Cl)_2CH_2OCH_3$] were prepared by the oxidative addition of CH_2Cl_2, CH_2Br_2, CH_2I_2 and $ClCH_2OCH_3$, respectively, to trans-[$Ir(PMe_3)_2(CO)Cl$] [127]. Similarly, [$Ir(PMePh_2)_2(CO)(Cl)_2CH_2OCH_3$] was prepared by the oxidative addition of $ClCH_2OCH_3$ to [$Ir(PMePh_2)_2(CO)Cl$]. Evidence suggests that the chloromethyl methyl ether reacts *via* a S_N2-type reaction pathway, whilst the dihalomethanes appear to react via a radical pathway [127].

Very similar complexes to those above were prepared by the addition of CH_2IX (X = Cl, I) to $[IrL_2(CO)Cl]$ (L = PMe_3, PMe_2Ph, $PMePh_2$) [128]. The trans-phosphine complexes $[IrL_2(CO)(Cl)(I)CH_2X]$ were obtained when L = PMe_3 or $PMePh_2$, whilst a mixture of both cis- and trans- phosphine isomers were obtained when L = PMe_2Ph. Addition of methanol to a solution of these isomers resulted in the isomerisation of the cis complex to the trans complex. In contrast, heating of $[Ir(PMe_3)_2(CO)(Cl)(I)CH_2I]$ in methanol gave the methoxymethyl derivative $[Ir(PMe_3)_2(CO)(Cl)(I)CH_2OCH_3]$.

Thorn prepared the stable complex $[Ir(PMe_3)_3(C_2H_4)CH_2OCH_3]$ according to the route shown in **SCHEME 13** [7].

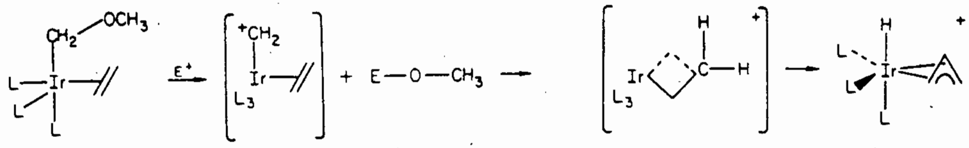
$$[IrL_4]Cl \xrightarrow{H_2} [IrH_2L_4]Cl \xrightarrow{Bu^tKO} \underset{(I)}{IrHL_4} + Bu^tHO + KCl$$

$$(I) \xrightarrow{BrCH_2OCH_3} \underset{(II)}{[Ir(H)L_4(CH_2OCH_3)][Br]} \xrightarrow{Bu^tKO} \underset{(III)}{IrL_4(CH_2OCH_3)} + Bu^tHO$$

$$(III) \xrightarrow{C_2H_4} \underset{(81),\ L\ =\ PMe_3}{Ir(C_2H_4)L_3(CH_2OCH_3)}$$

SCHEME 13

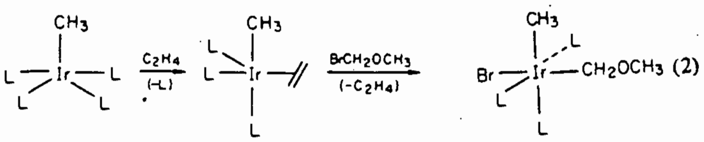
Complex $[Ir(PMe_3)_3(C_2H_4)CH_2OCH_3]$ (81) is reactive towards a number of electrophilic reagents, yielding the cationic hydrido alkyl complex $[Ir(PMe_3)_3H(C_3H_5)]^+$ (82). The proposed mechanism for this reaction is shown in **SCHEME 14**.



SCHEME 14

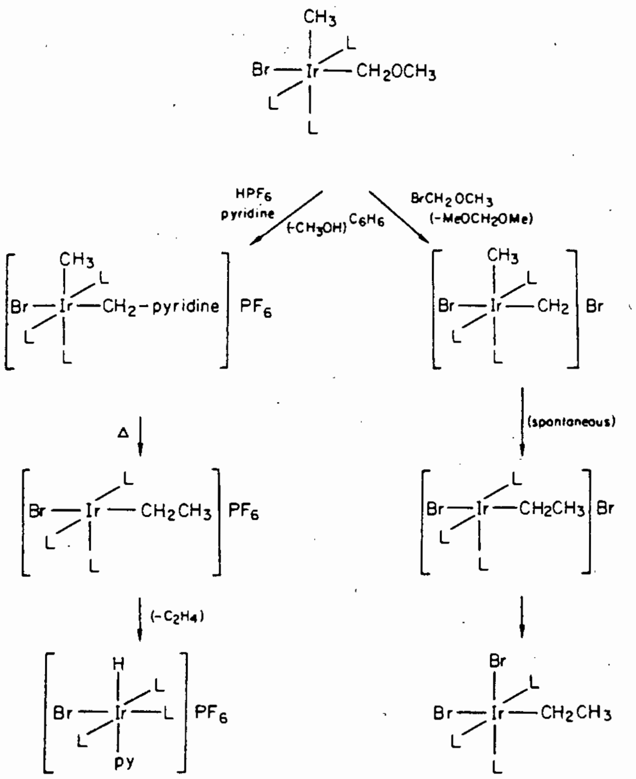
Attempted preparations of the rhodium analogues of (81) have failed, presumably due to the immediate decomposition of the hydrido alkyl analogues of (83).

The methoxymethyl methyl complex $[Ir(PMe_3)_3(CH_3)(Br)CH_2OCH_3]$ (61) has been prepared (equation 30) [102].

 (30)

L = PMe_3

Complex (61), when pure, is stable at room temperature in the absence of air. It reacts rapidly with electrophilic reagents resulting in cleavage of a C-O bond of the $-CH_2OCH_3$ group to form a transient cationic methylene complex, two examples of which are shown in **SCHEME 15**.

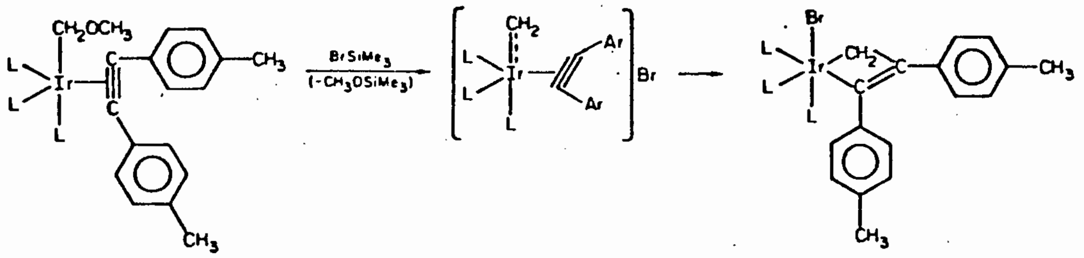


L = PMe_3

SCHEME 15

The methylene complex then undergoes methyl migration to the methylene group. The "pyridine trapped" intermediate (**84**) requires heating to 60°C for this second step to occur.

The (methoxymethyl)iridium(I) acetylene complex $[Ir(PMe_3)_3(p\text{-}tol\text{-}C{\equiv}C\text{-}p\text{-}tol)CH_2OCH_3]$ (tol = tolyl = $CH_3C_6H_4^-$) reacts with bromotrimethylsilane to form the iridium(III) metallocyclobutene fac-$[Ir\{CH_2C(p\text{-}tol)=C\}Br(PMe_3)_3]$ [6]. A methylene species is again postulated as an intermediate (**SCHEME 16**).



SCHEME 16

Another chloromethyl complex of Ir, $[Ir(PPh_3)_2(Cl)_2CH_2Cl]$, was obtained from the spontaneous rearrangement of the coordinatively unsaturated acyl complex $[Ir(PPh_3)_2Cl_2\{C(O)CH_2Cl\}]$ [129].

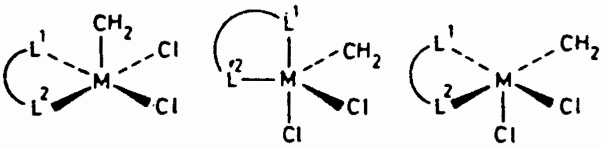
1.2.6 Palladium and Platinum

The first halomethylpalladium(II) complex, cis-$[Pd(PPh_3)_2(I)CH_2I]$ **(85)** was obtained from $[Pd(PPh_3)_4]$ and CH_2I_2 [130]. Complex **(85)** failed to react with PPh_3, although it reacted with the more basic PEt_3 to yield cis-$[Pd(PPh_3)_2(I)CH_2PEt_3]I$.

Reaction of dichloro(2,2,N,N-tetramethyl-3-buten-1-amine)palladium(II) with CH_2N_2 gives the carbene insertion product, a-chloro-b-(chloromethyl)-d,c-(2,2,N,N-tetramethyl-3-buten-1-amine)palladium(II) **(86)**, together with analogous ethoxymethyl and methyl complexes [131]. Similarly, **(86)** reacts with sodium methoxide to give small quantities of the methoxymethyl analogue of (86). In the same way, treatment of dichloro(2,2-di-methyl-3-buten-1-yl methyl sulphide)palladium(II) with CH_2N_2 gives the expected chloromethyl complex and a cyclopropanation product.

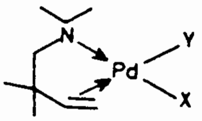
In general, reaction of CH_2N_2 with a whole range of palladium dichloride and dibromide complexes containing bidentate chelating ligands has been found to lead to the formation of mono(halomethyl) products [132] (figure 4). Methylpalladium derivatives are obtained as biproducts in these reactions if the chelating ligand is an olefin. Performing the reaction at -65°C reduces the proportion of the methyl product. The insertion of CH_2 into a Pd-Br bond occurs less readily than CH_2 insertion into the corresponding Pd-Cl bond. This is rationalised to be due to the greater leaving ability of Cl over Br in nucleophilic substitution reactions. The insertion process has been proposed to proceed *via* a series of steps:

[complex + CH_2N_2 → square-pyramidal adduct (87a) → trigonal-bipyramidal species (87b) → square-pyramidal adduct (87c)] (SCHEME 17).

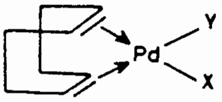


(87a) (87b) (87c)

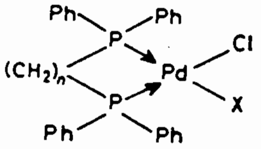
SCHEME 17



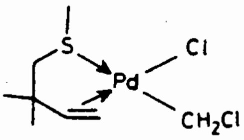
$X=CH_2Cl$, $Y=Cl$
$X=CH_2Br$, $Y=Br$

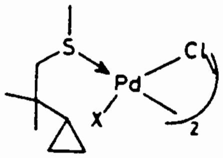


$X=CH_2Cl$, $Y=Cl$
$X=CH_2Br$, $Y=Br$

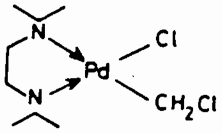


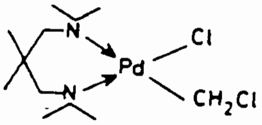
n=2,3

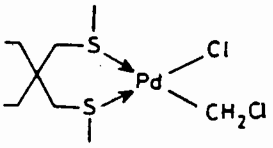


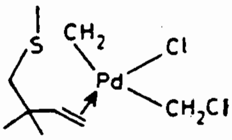


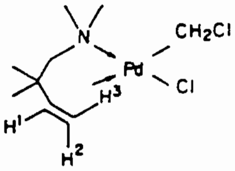
$X=CH_2Cl$











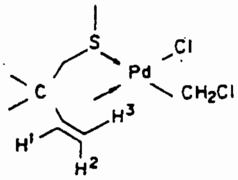


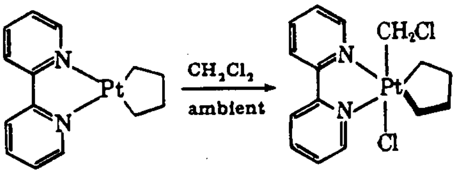
Figure 4

The bromomethyl derivatives are less stable than their chloromethyl analogues. All the chloromethyl complexes showed some tendency to revert to the starting dichloro complexes.

Chloromethyl palladium compounds were also formed by the reaction of dichloropalladium complexes with bis(dichloro)mercury, as well as with a preformed chloromethyl complex by ligand exchange. Whilst reaction times are longer, yields are higher for the transmetallation reactions.

The strongly nucleophilic complexes [Pd(np$_3$)] and [Pt(PPh$_3$)np$_3$] {np$_3$ = tris(2-diphenylphosphinoethyl)amine} react with CH_2Cl_2 at room temperature to give the five coordinate chloromethyl complexes [M(np$_3$)CH$_2$Cl]$^+$ in very high yield. These complexes were isolated as their BPh$_4^-$ salts [133].

During the investigation of the thermal decomposition of 1,4-tetramethylene-bis(tri-n-butylphosphine)platinum(II) in CH_2Cl_2, Young and Whitesides postulated the formation of the complex [Pt(L$_2$)(Cl)CH$_2$Cl] on the basis of its ^{31}P and ^{1}H NMR spectra, as well as its chemical behaviour [134]. Young and Whitesides also synthesized [Pt(bipy)(CH$_2$)$_4$(Cl)CH$_2$Cl] (equation 31).



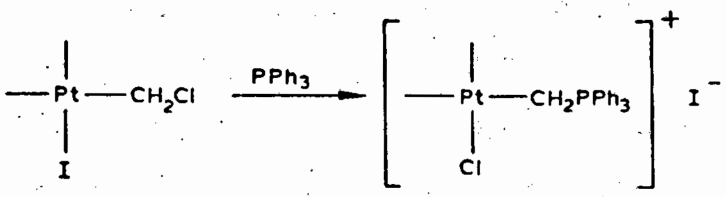
(31)

The choromethyl complexes, cis- and trans-[Pt(PPh$_3$)$_2$(Cl)CH$_2$Cl] were synthesized by the photo-induced oxidative addition of CH_2Cl_2 to

$[Pt(PPh_3)_2(C_2H_4)]$ [135]. The reaction appears to involve free-radicals and is inhibited by duroquinone. No reaction occurs in the dark. When exposed to light, cis-/trans-$[Pt(PPh_3)_2(Cl)CH_2Cl]$ decomposes in solution with loss of CH_2, to give $[Pt(PPh_3)_2(Cl)_2]$.

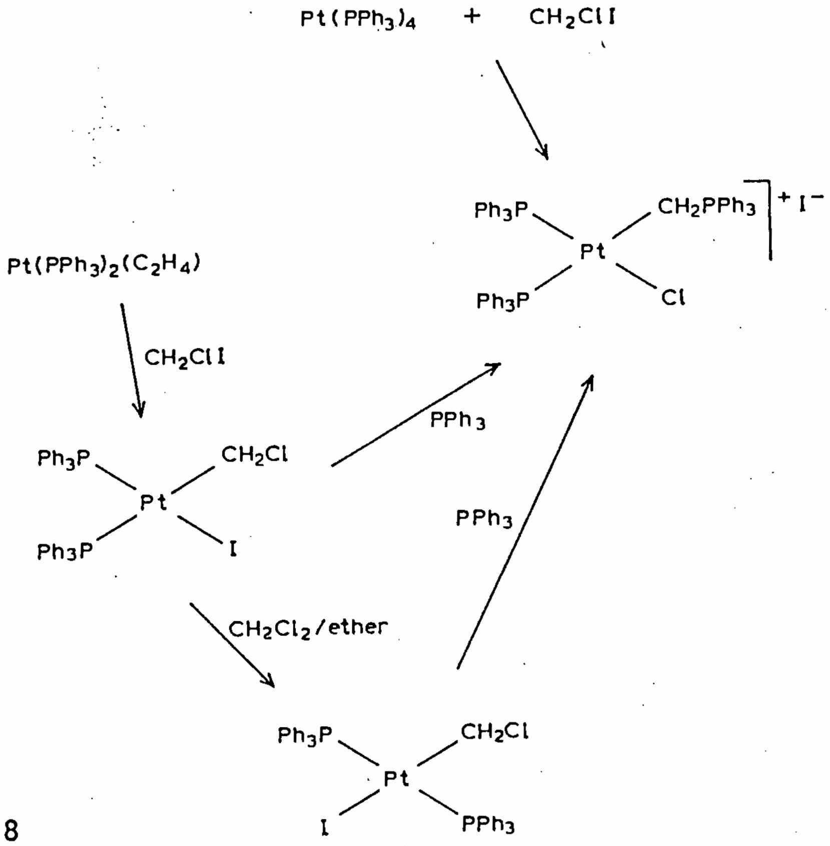
The reaction of $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ with CH_2XY (CH_2I_2, CH_2Br_2, CH_2ClBr, CH_2BrI or CH_2ClI) gave trans- (and usually cis-) $[Pt(PPh_3)_2(Y)CH_2X]$ [138]. The production of the complexes where X = Cl, Y = Br and where X = Cl, Y = I also gave halogen-redistributed products in smaller yields. Thus complexes where X = Br, Y = Cl; X = Y = Br and X = Y = Cl were also obtained from these reactions [136-138]. Heating a mixture of isomers in CH_2Cl_2 caused complete conversion to the trans-isomers. For CH_2Br_2 or CH_2Cl_2 additions there was a preponderance of the trans-products at 25°C (Cl > Br > I).

Both the cis and trans forms of $[Pt(PPh_3)_2(I)CH_2Cl]$ (88) react with PPh_3 to give the ylide complex, cis-$[Pt(PPh_3)_2(Cl)CH_2PPh_3]^+$ (89) (equation <u>32</u> [137,139].



$$-\underset{\displaystyle I}{\overset{|}{Pt}}-CH_2Cl \xrightarrow{PPh_3} \left[-\underset{\displaystyle Cl}{\overset{|}{Pt}}-CH_2PPh_3\right]^+ I^- \qquad (\underline{32})$$

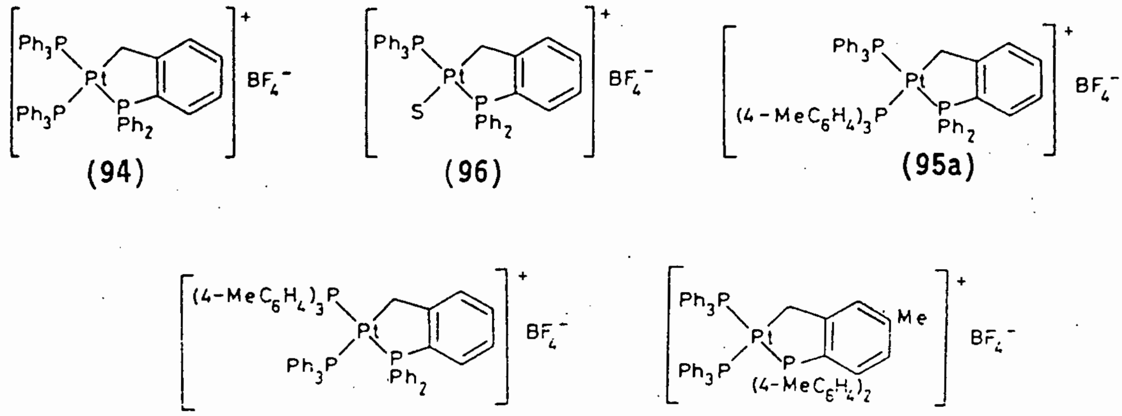
The novelty of the reaction in equation <u>32</u> is the specific formation of (89) which involves the migration of Cl from C to Pt with loss of I^- from the coordination sphere of the metal. This result implies that the complex (88) is an intermediate in the reaction of $[Pt(PPh_3)_4]$ with CH_2ClI to give $[Pt(PPh_3)_2(Cl)CH_2PPh_3]^+$ **(SCHEME 18)** [139].



SCHEME 18

Lappert *et al.* reported that the reaction of $[Pt(PEt_3)_3]$ with CH_2I_2 gave trans-$[Pt(PEt_3)_2(I)CH_2PEt_3]$ (90), which they believed formed *via* the α-functionalised alkyl, cis-$[Pt(PEt_3)_2(I)CH_2I]$ [130], and which has since been isolated [140]. Similar ylides were obtained by reacting cis- or trans-$[Pt(PPh_3)_2(X)CH_2X]$ (X = Cl, Br or I) with PEt_3, $PBu^n{}_3$, $PMePh_2$, $PEtPh_2$ or PPh_3.

The trans isomers of $[Pt(PPh_3)_2(Y)CH_2X]$ {X = Y = I (91); X = Cl, Y = Br (92) or X = Cl, Y = I (93)} were treated with 2 equivalents of $AgBF_4$ in the presence of 1 equivalent of L to give the cationic metallocycle $[Pt\{PPh_2(2\text{-}C_6H_4CH_2)\}(PPh_3)L]BF_4$ {L = PPh_3, $P(C_6H_4Me\text{-}4)_3$} (94 and 95) [138]. The formation of the metallocycle (94) involves attack by the carbon centre of the halomethyl substituent on the ortho position of a phosphine phenyl group. This is in stark contrast to previous reports of attack on phophorus atoms. The reaction of *trans*-(91), (92) and (93) with only two equivalents of $AgBF_4$ gave $[Pt\{PPh_2(2\text{-}C_6H_4CH_2)\}(PPh_3)(S)]BF_4$ (96) (S = solvent molecule) as the sole product (figure 5).

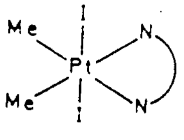


(94) (96) (95a)

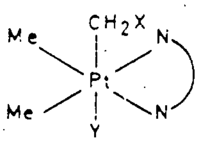
Figure 5 (95b) (95c)

The cyclic products were obtained irrespective of variations in X or Y [138].

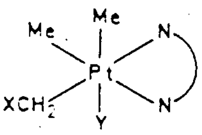
The iodoalkanes, CH_2I_2 and CH_2ClI, oxidatively add to $[Pt(phen)Me_2]$ (phen = 1,10-phenanthroline), *via* a free radical mechanism, to give a mixture of complexes (97,98a and 99a) and (97, 98b, 99b, 98c and 99c) respectively, with the cis-adducts (99) slowly isomerising to the trans-adducts (98) [141,142] (figure 6).



(97)



(98a-f)



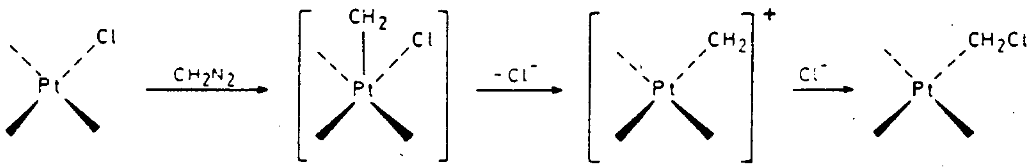
(99a-f)

a: X = Y = I; b : X = Cl, Y = I; c: X = Y = Cl; d: X = Y = Br; e: X = Cl, Y = Br; f: X = Y = Cl

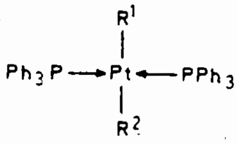
Figure 6

In a similar way, CH_2Br_2, CH_2BrCl and CH_2Cl_2 add to $[Pt(phen)Me_2]$ to form the complexes (**98d**, **99d**, **98e**, **99e**, **98f** and **99f**). The reactions of CH_2I_2 and CH_2ClI were very fast, while those of CH_2ClBr, CH_2Br_2 and CH_2Cl_2 were slow. In all cases a mixture of cis and trans isomers was obtained [143].

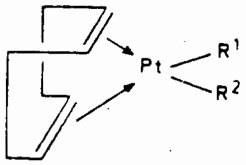
McCrindle *et al.* have prepared a whole range of both mono and bis platinum halomethyl and methoxy methyl complexes (**figure 7**) [144,145]. The halomethyl complexes were prepared by treating a range of platinum(II) halide complexes with CH_2N_2. Methoxy methyl complexes are obtained when the reaction is carried out in the presence of methanol. With only one exception, the methylene insertion appears to occur only when the metal-halogen bond is trans to a group of high trans influence (olefin, phosphine, alkyl or hydride). A proposed mechanism for the insertion of the methylene moiety into the Pt-Cl bond is shown in **SCHEME 19**.



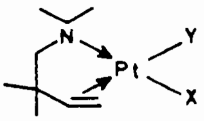
SCHEME 19



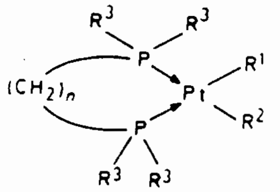
(100) R^1=Cl, R^2=CH_2Cl
(101) R^1=CH_2Cl, R^2=H
(102) R^1=Cl, R^2=Me
R^1=CH_2Cl, R^2=Me
R^1=CH_2I, R^2=CF_3



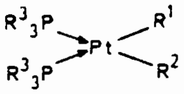
(103) R^1=Cl, R^2=CH_2Cl
(104) R^1=R^2=CH_2Cl
R^1=R^2=CH_2I
R^1=CH_2Cl, R^2=CH_2OMe
R^1=R^2=CH_2OMe
R^1=Cl, R^2=CH_2OMe



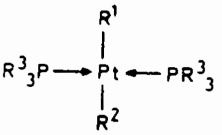
X=Cl, Y=Cl
X=Cl, Y=CH_2Cl
X=CH_2Cl, Y=Cl



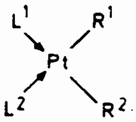
(105) R^1=Cl, R^2=CH_2Cl, R^3=Ph; n=3
(106) R^1=R^2=CH_2Cl, R^3=Ph; n=3
R^1=R^2=CH_2Cl, R^3=C_6H_{11}; n=2



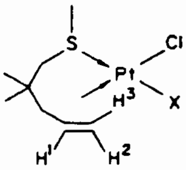
(107) R^1=R^2=CH_2Cl, R^3=Ph
R^1=R^2=CH_2Cl, R^3=Et
R^1=Cl, R^2=CH_2Cl, R^3=Ph
R^1=Cl, R^2=CH_2Cl, R^3=Et



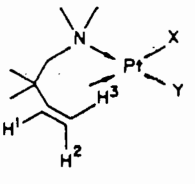
R^1=Cl, R^2=CH_2Cl, R^3=C_6H_{11}
R^1=H, R^2=CH_2Cl, R^3=Et
R^1=Me, R^2=CH_2Cl, R^3=Et



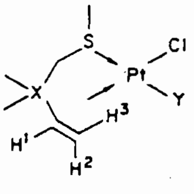
R^1=R^2=CH_2Cl, L^1=PEt_3, L^2=Bu^tNC
R^1=Cl, R^2=CH_2Cl, L=PEt_3, L^2=Bu^tNC



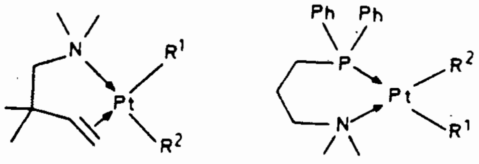
X=CH_2Cl



X=CH_2Cl, Y=Cl
X=Cl, Y=CH_2Cl



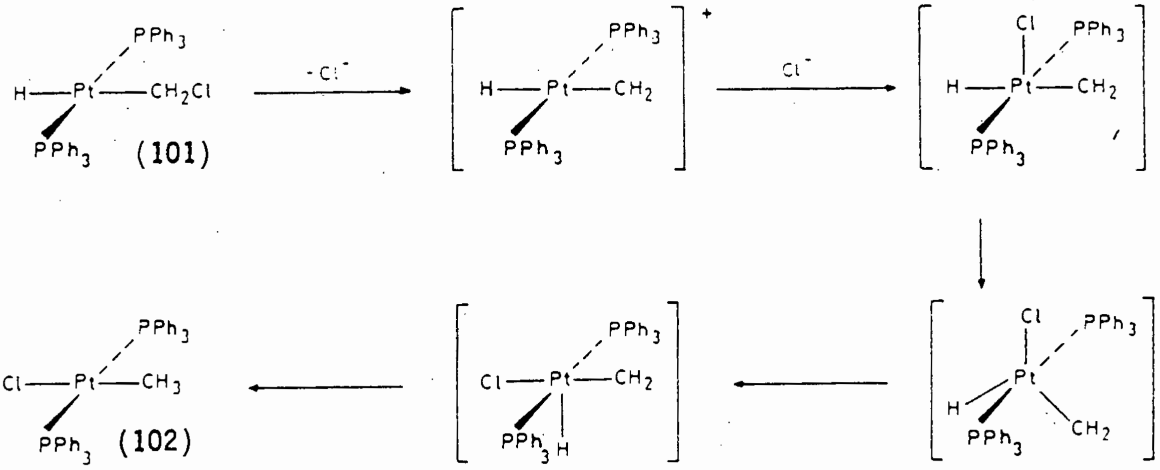
X=C, Y=CH_2Cl
X=Si, Y=CH_2Cl



R^1=CH_2Cl, R^2=Cl
R^1=Cl, R^2=CH_2Cl

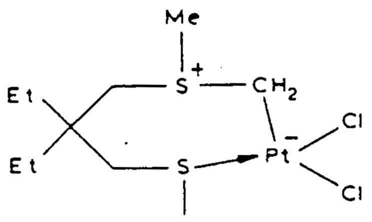
Figure 7

The one exception is the formation of trans-[Pt(PPh_3)$_2$(Cl)CH_2Cl] (100) from trans-[Pt(PPh_3)$_2Cl_2$], which appears to be the only case where direct insertion into a Pt-Cl bond trans to a ligand (Cl) of low trans effect may have taken place. The complex, trans-[Pt(PPh_3)$_2$(H)CH_2Cl] (101), was observed to rearrange to the trans-chloro(methyl) complex (102). The proposed mechanism for this rearrangement is shown in SCHEME 20 [144].



SCHEME 20

Displacement of cod from the complexes (103) and (104) occurs by treatment with 1,3-bis(diphenyl-phosphino)propane to give the complexes (105) and (106). Similarly (104) reacts with two molar equivalents of PPh_3 to give (107). In neither example is the Cl of the CH_2Cl group attacked by the nucleophile. Complex (104) reacts with 2,2-diethyl-1,3-bis(methylthio)-propane to give a product which is postulated to be (108) (figure 8) [146].



(108)

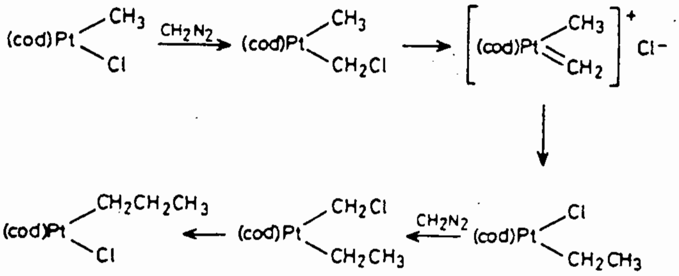
Figure 8

Treatment of [Pt(cod)(CH_2I)$_2$] with three or more equivalents of PPh_3 surprisingly gave the zwitterionic bis(phosphonium ylide) complex [Pt(PPh_3)I(CH_2PPh_3)$_2$]I (109). Complex (109) was also obtained by treatment of [Pt(PPh_3)$_2$(CH_2Cl)$_2$] (110) with one equivalent of PPh_3 and an excess of NaI. The failure to isolate the expected [Pt(PPh_3)$_2$(CH_2I)$_2$] from the ligand displacement reaction is rationalised by assuming that the nucleophilic displacement of iodide becomes competitive with cyclo-octadiene replacement in the bis(iodomethyl) complex. The complex [Pt(PPh_3)$_2$(CH_2I)$_2$] can, however, be prepared by the reaction of a large excess of NaI with (110). The reaction of excess PMe_3 with [Pt(cod)(CH_2I)$_2$] gave a high yield of the bis(ylide) complex, [Pt(PMe_3)$_2$(CH_2PMe_3)$_2$]I_2 [147].

Insertion of CH_2 into the platinum halogen bond of [Pt(dppm)(X)$_2$] (X = Cl, Br, I) to give the complexes [Pt(dppm)(CH_2X)$_2$] has also been reported [148]. The stability of these complexes in solution follows the order Cl > Br > I. The complex [Pt(dppm)(CH_2Cl)$_2$] (111) was found to react with HCl to give [Pt(dppm)(Cl)CH_2Cl]. Ethylene was obtained as a major product on decomposition of [Pt(dppm)(CH_2I)$_2$] on irradiation. Treatment of (111) with neutral nucleophiles, L, resulted in a ring expansion to give [Pt($CH_2PPh_2CH_2PPh_2$)(L)CH_2Cl]Cl (L = NC_5H_5, PPh_3,

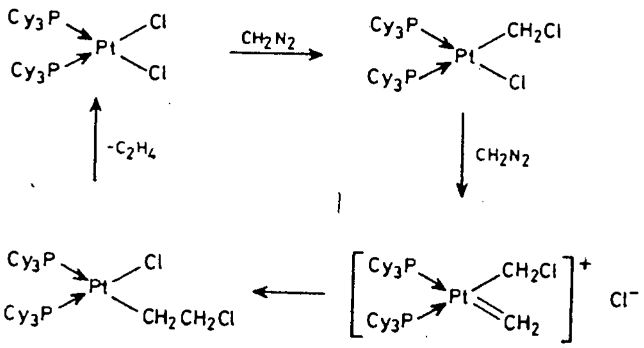
PPh_2H). This ring expansion is unique to dppm chelates [144].

McCrindle *et al.* reported that [Pt(cod)(CH_3)Cl] reacted with CH_2N_2 to give [Pt(cod)(CH_3)CH_2Cl] (**112**), which was stable under ambient conditions, in good yield [149]. Complex (**112**) can also be prepared from [Pt(cod)(Cl)CH_2Cl] and MeLi [149]. The carbene insertion reaction is again proposed to proceed *via* a platinum carbene intermediate. Complex (**112**) rapidly transforms into [Pt(cod)Cl(CH_2CH_3)] (**113**) when dissolved in $CDCl_3$ containing $(CF_3)_2CHOH$. Reacting (**113**) with CH_2N_2 gave largely [Pt(cod)(CH_2CH_3)CH_2Cl] (**114**), as well as small quantities of [Pt(cod)(CH_3)CH_2Cl] and [Pt(cod)(CH_2Cl)$_2$]. Complex (**114**), when dissolved in $CDCl_3/(CF_3)_2CHOH$ (9:1) gave [Pt(cod)Cl($CH_2CH_2CH_3$)]. Since the insertion of a methylene group into a metal-alkyl bond has been proposed as a key step in the polymerisation of CH_2N_2 by transition metal complexes [121,150,151], these authors propose **SCHEME 21** as a model for chain growth.



SCHEME 21

The reaction of cis-bis(tricyclohexylphosphino)platinum(II)dichloride (113) with a large excess of CH_2N_2 gave immediate evolution of ethylene gas. Once all the CH_2N_2 had been consumed, the starting complex (**113**) was recovered in essentially quantitative yield. The proposed mechanism involves chloromethyl complexes (SCHEME 22).



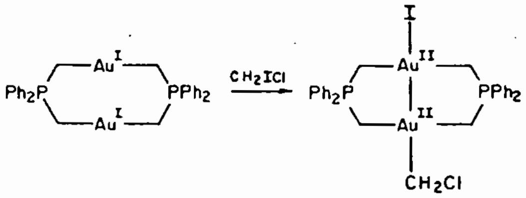
SCHEME 22

1.2.7 Gold

The complexes [Au(L)CH_2Cl] (**114**) {L = PPh_3, PEt_3 and $P(OPh)_3$} were first prepared by Nesmeyanov *et al.* from [Au(PPh_3)Cl] and CH_2N_2 [152]. They reacted *via* a trans oxidative addition reaction with [Pt(bipy)Me_2] to give the complexes [Cl$(Me)_2$(bipy)PtCH_2AuL] (bipy = bipyridine) [153]. Kinetic evidence showed that the C-Cl bond of complex (**114**) is strongly activated by the metal (by a factor of $\geq 10^3$) to oxidative addition relative to CH_3Cl. Complex (**114**) decomposed back to [Au(PPh_3)Cl] with loss of CH_2. Complex (**114**) was shown to act as a methylene transfer reagent, reacting with 3-cyclohexenol to give bicyclo[4.1.0]heptan-2-ol. The reaction of (**114**) with KI afforded [Au(PPh_3)I], the latter complex is believed to be the decomposition product of [Au(PPh_3)CH_2I], which is very unstable. Complex (**114**) reacts with aqueous NaCN to give $[CH_3PPh_3]^+[Au(CN)_2]^-$ [152].

$[CH_3PPh_3]^+[Au(CN)_2]^-$ [152].

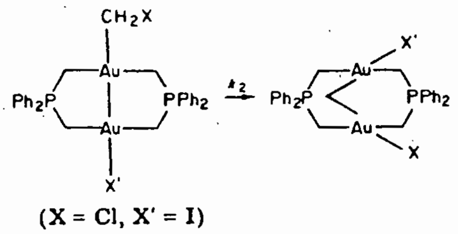
Fackler *et al.* reported that the reaction of $[Au(CH_2)_2PPh_2]_2$ in undiluted CH_2XX' (X = Cl, X′ = Br,I) initially gave the dinuclear Au(II) alkyl halides $[\{Au(CH_2)_2PPh_2\}_2(X')CH_2X]$ (**115**) (equation 33a) [154].



(33a)

The crystal structure of $[\{Au(CH_2)_2PPh_2\}_2(Br)CH_2Cl]$ (**116**) shows evidence of a close contact between one Au centre and the Cl of the coordinated CH_2Cl. Allowing the reaction solution to stand for 45 minutes results in the formation of $[\{Au(CH_2)_2PPh_2\}_2(\eta\text{-}CH_2)BrCl]$. This rearrangement is postulated to involve the formation of a gold(I)-gold(III) Fischer type carbene species, along with the Au-Cl bond at the Au(III) centre, prior to the rearrangement to the final A-frame product [155].

Allowing the $[\{Au(CH_2)_2PPh_2\}_2(I)CH_2Cl]$ reaction solution to stand also gives the bridging (methylene)gold(III) ylide dimer $[(\eta\text{-}CH_2)\{Au(CH_2)_2PPh_2\}_2ICl]$ (equation 33b).



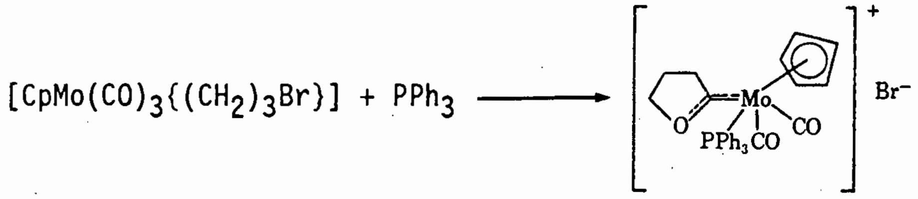
(33b)

1.3 ω-HALOALKYL TRANSITION METAL COMPLEXES

In 1967, King and Bisnette reported that the reaction of Na[CpM(CO)$_3$] (M = Mo or W) with 1,3-dibromopropane and 1,4-dibromobutane yielded [CpM(CO)$_3${(CH$_2$)$_n$Br}] (n = 3, 4; M = Mo, W) [156]. The physical properties of these compounds resemble those of other [CpM(CO)$_3$R] (R = alkyl) complexes. The tungsten complexes were observed to be more stable than their molybdenum analogues. Attempts to synthesize compounds of the type [L$_x$M-(CH$_2$)$_n$-M′L$_y$] containing two different metal atoms by the reactions of [CpM(CO)$_3${(CH$_2$)$_n$Br}] (n = 3, 4) with Na[CpFe(CO)$_2$] and Na[Mn(CO)$_5$], yielded only [{CpFe(CO)$_2$}$_2$(μ-CH$_2$)$_n$] (n = 3, 4) and what was later shown to be a dimanganese cyclic carbene complex [(CO)$_5$MnMn(CO)$_4${CO(CH$_2$)$_2$CH$_2$}] [157,158]. This was presumably due to the very high nucleophilicity of the iron and manganese anions.

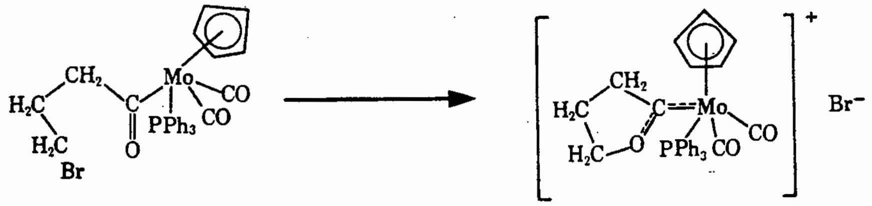
The ω-haloalkyl manganese compounds [Mn(CO)$_5${(CH$_2$)$_n$Cl}] were prepared by the reaction of the [Mn(CO)$_5$]$^-$ anion with Cl(CO)(CH$_2$)$_n$Cl, to give [Mn(CO)$_5${C(O)(CH$_2$)$_n$Cl}] (n = 3, 4), and the subsequent decarbonylation of this acyl product. The reaction of the anion [Mn(CO)$_5$]$^-$ with [Mn(CO)$_5${(CH$_2$)$_3$Cl}] (**117**) gave the carbene complex [(CO)$_5$MnMn(CO)$_4${CO(CH$_2$)$_2$CH$_2$}]. The complexes [Mn(CO)$_5${(CH$_2$)$_n$Cl}] readily reacted with phosphines, L, to give the carbonyl inserted products [MnL(CO)$_4${C(O)(CH$_2$)$_n$Cl}]. These products could in turn be decarbonylated to give [MnL(CO)$_4${(CH$_2$)$_n$Cl}] (n = 3, 4). The complexes [MnL(CO)$_4${(CH$_2$)$_n$Cl}] reacted with I$^-$ to give the cyclic carbene complexes [MnL(I)(CO)$_3${CO(CH$_2$)$_{n-1}$CH$_2$}] (L = CO, n = 3, 4; L = P(OCH$_2$)$_3$CCH$_3$; n = 3) [159].

[CpMo(CO)$_3${(CH$_2$)$_3$Br}] (118) reacted with PPh$_3$ in acetonitrile to give [CpMo(PPh$_3$)(CO)$_2${CO(CH$_2$)$_2$CH$_2$}]Br (119) (equation 34) [160].



(34)

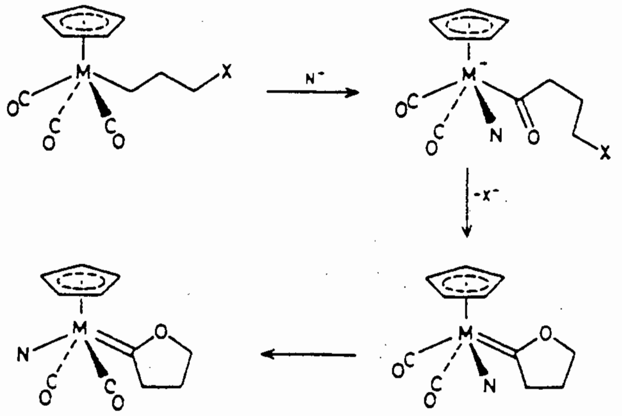
This cyclic carbene species is presumably formed by initial attack of PPh$_3$ on the Mo resulting in CO insertion to form the acyl derivative [CpMo(PPh$_3$)(CO)$_2${C(CO)(CH$_2$)$_3$Br}]. This latter species spontaneously undergoes internal nucleophilic attack of the acyl oxygen atom on the γ-carbon atom to displace Br$^-$ and form the cyclic carbene cation (119) (equation 35) [160].



(35)

The reaction of [CpMo(CO)$_3$]$^-$ with I(CH$_2$)$_3$I in THF led to [CpMo(CO)$_3${(CH$_2$)$_3$I}] (120), which reacted further under reflux to give [CpMo(CO)$_2$I{CO(CH$_2$)$_2$CH$_2$}] (121), a complex very similar to (119) [161]. Complex (121) can also be obtained by the reaction of (118) with LiI. However, the analogous bromide complex is not obtained from a similar reaction with LiBr. It is proposed that the formation of (121) involves the attack of the nucleophile I^- on $[CpMo(CO)_3\{(CH_2)_3X\}]$ (X = Br, I) to generate the intermediate acyl species $[CpMo(CO)_2I\{C(O)(CH_2)_3X\}]^-$, which undergoes rapid spontaneous cyclisation to form (121) [161]. Interestingly, $[CpMo(CO)_3\{(CH_2)_4I\}]$ reacts with LiI to form only $[CpMo(CO)_3I]$ and not the 2-oxacyclohexylidene complex expected [161]. As in the reactions shown in equations <u>34</u> and <u>35</u>, (118) reacts with other nucleophiles, such as SPh^- and CN^-, to give $[CpMo(CO)_2X\{CO(CH_2)_2CH_2\}]$ (122) (X = SPh or CN) [162]. The cyclisation was shown to be independent of the Cp ring and substitution of a proton of the ring by Me, C(O)Me or $SiMe_3$ yielded products similar to (122).

The tungsten analogue of (118), $[CpW(CO)_3\{(CH_2)_3Br\}]$ (123) undergoes carbene formation with I^- and CN^- to form $[CpW(CO)_2X\{CO(CH_2)_2CH_2\}]$ (X = I or CN), though the reaction proceeds more slowly than that for Mo. The proposed mechanism for the carbene formation is depicted in **SCHEME 23**.



N^- = nucleophile

SCHEME 23

The key step in **SCHEME 23** is the migration of the alkyl chain to an adjacent carbonyl group and coordination of the nucleophile to the metal atom.

However, the formation of cyclic carbenes appears to be dependent on the halide of the haloalkyl group involved [163]. Hence, $[CpMo(CO)_3\{(CH_2)_3Cl\}]$ **(124)** reacts with PPh_3 to give trans-$[CpMo(PPh_3)(CO)_2\{C(O)(CH_2)_3Cl\}]$ *i.e.* a haloacyl complex. A similar reaction with $[CpMo(CO)_3\{(CH_2)_4I\}]$ and PPh_3 gave the acyl complex $[CpMo(PPh_3)(CO)_2\{C(O)(CH_2)_4I\}]$. Acyl complexes were also obtained in the reaction of $[CpMo(CO)_3\{(CH_2)_nBr\}]$ (n = 4,5) with PPh_3 (equation 36) [163].

$$[CpMo(CO)_3\{(CH_2)_nBr\}] + PPh_3 \longrightarrow \text{trans-}[CpMo(PPh_3)(CO)_2\{(CH_2)_nBr\}] \qquad (\underline{36})$$

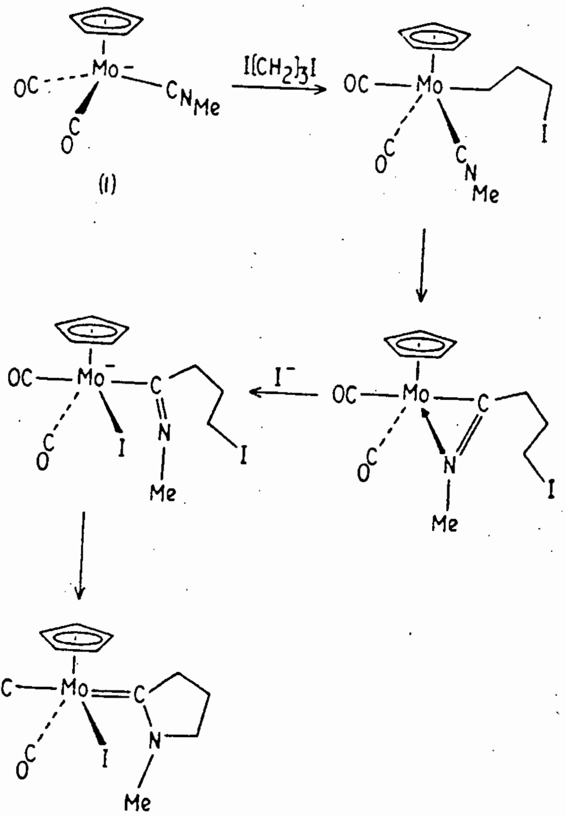
These results are thought to be due to competition between two possible reaction pathways after nucleophilic attack by PPh_3; either rapid intramolecular cyclisation by the cis isomer formed initially, or intramolecular geometrical isomerisation to form the trans-haloacyl complex. Hence, **(124)** forms the haloacyl complex because Cl is a poorer leaving group than Br (slowing the attack of the acyl oxygen), and consequently decreasing the rate of cyclisation relative to isomerisation. Similarly, when the halogen is further removed from the metal atom, formation of the trans haloacyl becomes favoured due to the retardation in the rate of ring closure for rings containing more than five members [163].

The complexes trans-[CpMoL(CO)$_2${(CH$_2$)$_3$Br}] (L = PPh$_3$ or P(OMe)$_3$) were prepared from Na[CpMoL(CO)$_2$] and Br(CH$_2$)$_3$Br [162]. Neither complex reacts with I$^-$ to produce carbene complexes.

The iodide analogues of **(118)**, [CpMo(CO)$_3${(CH$_2$)$_3$I}] {M = Mo **(125)**, W **(126)**} were originally prepared by Winter *et al.* [164]. Both **(125)** and **(126)** react with excess iodide to form [CpM(CO)$_2$I{CO(CH$_2$)$_3$CH$_2$}]. Winter *et al.* found that transition metal anions may induce similar cyclisation reactions. Hence, reaction of excess Na[CpMo(CO)$_3$] with Br(CH$_2$)$_3$Br yields **(118)**, which reacts with further Na[CpMo(CO)$_3$] to form an intermediate anionic acyl complex, which in turn undergoes elimination of Br$^-$ to form the carbene ligand in a manner similar to that depicted in **SCHEME 23**. Na[CpW(CO)$_3$] reacts with **(118)** to give [Cp(CO)$_3$MoW(CO)$_2${C-O-(CH$_2$)$_2$CH$_2$}Cp]. However, the reaction of **(118)** with [Mn(CO)$_5$]$^-$ leads exclusively to the dimanganese species [(CO)$_5$MnMn{C-O-(CH$_2$)$_2$CH$_2$}(CO)$_4$], while reaction with [CpFe(CO)$_2$]$^-$ produces [{CpFe(CO)$_2$}$_2${μ-(CH$_2$)$_3$}]. Both reactions eliminate [CpMo(CO)$_3$]$^-$. [CpW(CO)$_3$]$^-$ does not react with [CpW(CO)$_3${(CH$_2$)$_3$Br}] at the tungsten centre; instead the bromide is displaced to give the dimetallopropane [{CpW(CO)$_3$}$_2${μ-(CH$_2$)$_3$}] in moderate yield. Similarly, [CpW(CO)$_3$]$^-$ reacts with I(CH$_2$)$_4$I to yield [{CpW(CO)$_3$}$_2${μ-(CH$_2$)$_4$}] *via* the intermediate [CpW(CO)$_3${(CH$_2$)$_4$I}]. The complex [{CpMo(CO)$_3$}$_2${μ-(CH$_2$)$_4$}] is prepared similarly, by the reaction of [CpMo(CO)$_3$]$^-$ with I(CH$_2$)$_4$I, involving [CpMo(CO)$_3${(CH$_2$)$_4$I}] as an intermediate [164].

The reaction of [CpMo(CO)$_2$(CNMe)]$^-$ with I(CH$_2$)$_3$I in THF gives cis-

$[CpMo(CO)_2I\{C(NMe)(CH_2)_2CH_2\}]$ **(127)**. It is proposed that complex **(127)** forms *via* the intermediate $[CpMo(CO)_2(CNMe)\{(CH_2)_3I\}]$ **(SCHEME 24)** [165].



SCHEME 24

In similar reactions to that above, $[CpM(CO)_2(CNMe)]^-$ reacts with $I(CH_2)_nI$ to give the cyclic carbene species, cis-$[CpM(CO)_2\{CN(Me)(CH_2)_{n-1}CH_2\}]$ (M = Mo, n = 2, 3; M = W, n = 2) [166]. Again, haloalkyl intermediates are implicated.

The reactions of $[Cp^*M(CO)_3]^-$ (M = Mo, W) with $Br(CH_2)_3Br$ give the halopropane complexes $[Cp^*M(CO)_3\{CH_2)_3Br\}]$ **(128)**. These reactions are reported as being cleaner than those of their Cp analogues, presumably due to the greater nucleophilicity of the $[Cp^*M(CO)_3]^-$ anions, imparted by the Cp* group, relative to the $[CpM(CO)_3]^-$ anions. The reaction of the complex (**128**) (M = Mo) with LiI gives the cis- and trans-carbenes, $[Cp*MoI(CO)_2\{=C(CH_2)_3O\}]$. Similarly, as for $[CpMo(CO)_3\{(CH_2)_3Br\}]$, (**128**) (M = Mo) reacts with CN^- to give trans-$[Cp*Mo(CO)_2(CN)\{=C(CH_2)_3O\}]$. Whilst $[CpMo(CO)_3\{(CH_2)_3Br\}]$ does not react with Br^- or SCN^- to form a bromocarbene complex, the $[Cp*Mo(CO)_3\{(CH_2)_3Br\}]$ complex does react with Br^- and SCN^-, to form the respective cyclic carbene complexes, $[Cp*Mo(CO)_2Z\{=C(CH_2)_3O\}]$ (Z=Br, SCN) [167].

A further difference in the reactivity of the Cp*Mo complex (**128**) relative to its Cp analogue (**118**) is illustrated by its reaction with $[CpFe(CO)_2]^-$. Whilst $[CpMo(CO)_3\{(CH_2)_3Br\}]$ reacts with $[CpFe(CO)_2]^-$ with elimination of both Br^- and $[CpMo(CO)_3]^-$ to form $[\{CpFe(CO)_2\}_2\{\mu-(CH_2)_3\}]$, the MoCp* complex (**128**) reacts with $[CpFe(CO)_2]^-$ to form $[Cp^*Mo(CO)_3(CH_2)_3Fe(CO)_2Cp]$ [167].

As with its Cp analogue, $[Cp^*W(CO)_3\{(CH_2)_3Br\}]$ reacts with I^- to give $[Cp*WI(CO)_2\{=C(CH_2)_3O\}]$.

Moss synthesized $[CpFe(CO)_2\{(CH_2)_nX\}]$ (n = 3 - 5, X = Br; n = 3, X = Cl) by reacting $Na[CpFe(CO)_2]$ with an excess of the α,ω-dihaloalkanes at -20°C (equation <u>37</u>) [17].

$$\mathrm{Na[CpFe(CO)_2] + X(CH_2)_nX \xrightarrow{-20^\circ C,\ THF} [CpFe(CO)_2\{(CH_2)_nX\}] + NaX} \quad (\underline{37})$$

$(n = 3 - 5, X = Br;\ n = 3, X = Cl)$

The reaction of $Na[CpFe(CO)_2]$ with $Br(CH_2)_2Br$ was found to yield only $[CpFe(CO)_2]_2$ and ethylene [168].

The complexes $[CpFe(CO)_2\{(CH_2)_3X\}]$ (X = Cl, Br) and $[CpFe(CO)_2\{CH_2CH_2CH(CH_3)Br\}]$ have recently been shown to have good organic synthetic utility as cyclopropane precursors when reacted with $AgBF_4$ [22]. In contrast, the formation of cyclobutane and cyclopentane, from the corresponding $[CpFe(CO)_2\{(CH_2)_nBr\}]$ (n = 4, 5) was slow and inefficient. The reaction of the γ-haloalkyl iron complexes to produce cyclopropanes is rationalised as being due to participation of iron in the cleavage of the γ-carbon-halogen bond [22].

$[CpFe(CO)_2\{(CH_2)_3Br\}]$ was shown to react with $Na[CpFe(CO)_2]$ to yield $[\{CpFe(CO)_2\}_2\{\mu\text{-}(CH_2)_n\}]$ (n = 3, 4, 5). The synthesis of $[CpFe(CO)_2\{\mu\text{-}(CH_2)_3\}Mo(CO)_3Cp]$, attempted unsuccessfully by King and Bisnette using $[CpMo(CO)_3\{(CH_2)_3Br\}]$ and $Na[CpFe(CO)_2]$ [156], was achieved by Moss by reacting $[CpFe(CO)_2\{(CH_2)_3Br\}]$ **(129)** with $Na[CpMo(CO)_3]$ [17] (equation <u>38</u>).

$$\mathrm{[CpFe(CO)_2\{(CH_2)_3Br\}] + Na[CpMo(CO)_3] \longrightarrow [CpFe(CO)_2(CH_2)_3Mo(CO)_3Cp] + NaBr} \quad (\underline{38})$$

The reaction of **(129)** with PPh_3 resulted in the formation of two complexes: **(130)** and an acyl complex **(131)** as shown in equation 39 [17].

$$[CpFe(CO)_2\{(CH_2)_3Br\}] + PPh_3$$

$$\text{reflux}\ \Big\downarrow\ CH_3CN$$

$$[CpFe(PPh_3)(CO)COCH_2CH_2CH_2]Br \quad \textbf{(130)}$$

$$\text{reflux, } CH_3CN\ \Big\downarrow\ PPh_3$$

$$[CpFe(PPh_3)(CO)\{C(O)(CH_2)_3PPh_3\}]Br \quad \textbf{(131)} \qquad (\underline{39})$$

Knox *et al.* synthesized the iodo analogue of **(129)**, $[CpFe(CO)_2\{(CH_2)_3I\}]$ **(132)** (in low yield and not fully characterized) by reacting $Na[CpFe(CO)_2]$ with excess $I(CH_2)_3I$ [169]. Complex **(132)** was then reacted with $Na[CpRu(CO)_2]$ to give the mixed metal polymethylene bridged complex $[CpFe(CO)_2\{\mu\text{-}(CH_2)_3\}Ru(CO)_2Cp]$.

The complexes $[CpFe(CO)_2\{(CH_2)_nX\}]$ (X = Br, n = 6 - 10; X = I, n = 3 - 10) and $[Cp^*Fe(CO)_2\{(CH_2)_nX\}]$ (X = Br, I; n = 3 - 5) have since been prepared and fully characterised [170, chapter 4]. The iodoalkyl complexes have been shown to be good precursors to heterobimetallic alkanediyl complexes of the type $[(\eta^5\text{-}C_5R_5)(CO)_2Fe(CH_2)_nML_y]$ (R = H, ML_y = $Ru(CO)_2Cp$, $Mo(CO)_3Cp$, $W(CO)_3Cp$, $Re(CO)_5$, n = 3 - 6; R = CH_3, ML_y = $Ru(CO)_2Cp$, n = 3 - 5, ML_y = $Re(CO)_5$, n = 4) [171, chapter 5].

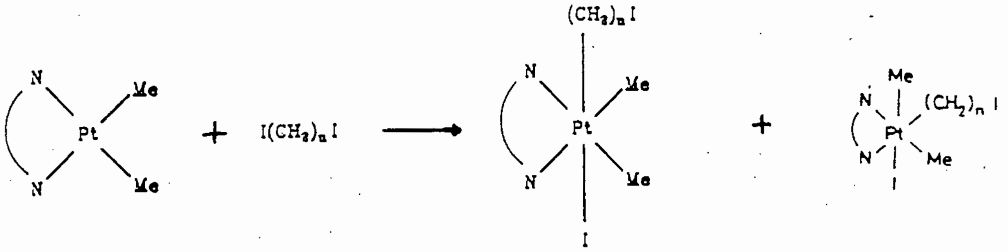
Both $[CpFe(CO)_2\{(CH_2)_3Br\}]$ and $[Cp^*Fe(CO)_2\{(CH_2)_3Br\}]$ react with LiI to form the carbene complexes [CpFe(CO)I{=C(CH$_2$)$_3$O}] and [Cp*Fe(CO)I{=C(CH$_2$)$_3$O}], respectively [172].

The ruthenium haloalkyl complexes [CpRu(CO)$_2${(CH$_2$)$_n$X}] (X = Cl, n = 3 [173]; X = Br,I, n = 3 - 5 [chapter 4]) have also been prepared, by routes similar to that shown in equation 37.

A very rare haloethyl complex, [Ir(PMe$_2$Ph)$_2$(CO)(Br)$_2$(CH$_2$CH$_2$Br)] (**133**), was prepared by Deeming and Shaw by reacting [Ir(PMe$_2$Ph)$_2$(CO)(C$_2$H$_4$)]BPh$_4$ with Br$_2$ [174]. The above haloethyl complex was found to react with MeOH to form [Ir(PMe$_2$Ph)$_2$(CO)(Br)$_2$(CH$_2$CH$_2$OCH$_3$)]. Pyrolysis of complex (**133**) gave mainly ethylene and [Ir(PMe$_2$Ph)$_2$(CO)(Br)$_3$]. The reaction of (**133**) with PMe$_2$Ph gave what is believed to be [Ir(PMe$_2$Ph)$_2$(CO)(Br)$_2$(CH$_2$CH$_2$PMe$_2$Ph)].

Harrison and Stobart reported that the reaction of [Ir(CO)$_2$(μ-pz)]$_2$ (**134**) (pzH = pyrazole) with 1,3-di-iodopropane led to the formation of the stable μ-iodoalkyl complex [Ir$_2$(CO)$_4$(μ-pz)$_2$I{(CH$_2$)$_3$I}] [175]. Reaction of (**134**) with I(CH$_2$)$_2$I yielded only [Ir(CO)$_2$(μ-pz)I]$_2$.

Monaghan and Puddephatt investigated the oxidative addition of I(CH$_2$)$_n$I (n = 1 - 5) to (dimethyl-1,10-phenanthroline)platinum(II) (**135**), to give both M(CH$_2$)$_n$X and M-(CH$_2$)$_n$-M (M = transition metal, X = halogen, n ≥ 1) complexes [141] as represented in equations 40 and 41.

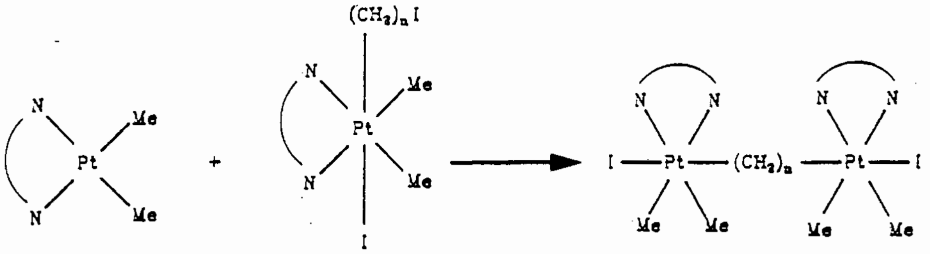


(40)

(135)

(136)
a: n = 0, b: n = 1,
c: n = 2, d: n = 3,
e: n = 4, f: n = 5

(137)
n = 1

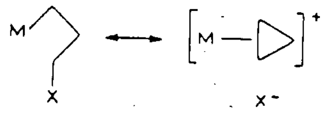


(41)

(135)

(136)

(138)
a: n = 2, b: n = 3, c: n = 4, d: n = 5

For n = 3 - 5, the reaction of (135) with $I(CH_2)_nI$ gave a mixture of complexes (136) and (138) which were easily separated. With a large excess of $I(CH_2)_nI$, only (136) was formed, by a S_N2 mechanism [142]. Complexes (138) could be prepared by reacting pure (136) with (135) (equation 41). Where n = 2, the products were (138a) and ethylene rather than (136c). Similarly, no haloalkyl products were found in the reactions of $Br(CH_2)_2Br$ with (135). Overall rates of reaction for both reactions 40 and 41 follow the sequence $n = 2 >> 3 > 4 \simeq 5 >> 1$. The low reactivity of (137) is thought to be due to steric hindrance to attack by (135). In general though, there is good evidence for metal activation of the C-I bond [141]. Monaghan and Puddephatt propose that the commonly observed activation of C-X bonds in complexes of the form MCH_2X and MCH_2CH_2X may be due to the lowering of energy in the transition state by contributions from the resonance forms $[M{=}CH_2]^+X^-$ or $[MC_2H_4]^+[X]^-$, respectively [141]. The smaller effect for $[M(CH_2)_3X]$ may then be due to the resonance forms  ,

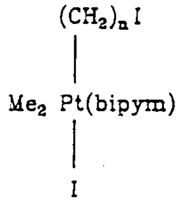
thus making displacement of the halide easier.

Further haloalkyl platinum complexes were synthesized by reacting $[PtMe_2(bipym)]$ **(139)** (bipym = 2,2′-bipyrimidine) with excess α,ω-diiodoalkanes to give the adducts **(140a-d)** (**figure 9**) [176].

a: n = 3, b: n = 4,

c: n = 5, d: n = 6

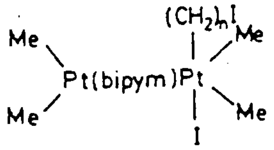
(140)



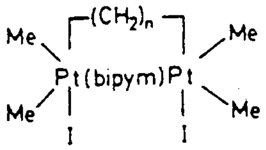
$\underset{I}{\overset{(CH_2)_nI}{Me_2\,Pt(bipym)}}$

Figure 9

(140a-d) react with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ to give **(141a-d)** respectively and not **(142)** as might be expected (**figure 10**).



(141) a: n = 3, b: n = 4
c: n = 5, d: n = 6



(142)

Figure 10

The lack of reactivity of the Pt(II) centre to intramolecular oxidative addition is believed to be due to steric hindrance and/or ring strain effects in the transition state [176].

Intermolecular oxidative addition between **(140)** and complex **(139)** gave the (μ-hydrocarbyl)diplatinum(IV) complex **(143)** (**figure 11**) [176].

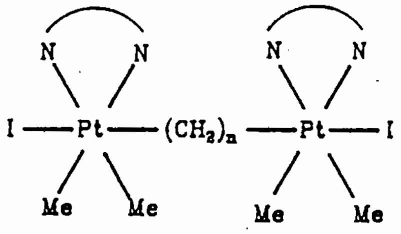


Figure 11

The oxidative addition of $I(CH_2)_nI$ (n = 3 - 6) to $[Pt_2Me_4(\mu\text{-pyen})]$ (144) {pyen = bis(2-pyridyl)ethylenediimine} gave the iodoalkyl complexes $[Pt_2Me_4(\mu\text{-pyen})(I_2)\{(CH_2)_nI\}_2]$ (145) [177]. Monitoring the reaction of (144) with $I(CH_2)_5I$ showed that the complex $[Pt_2Me_4(\mu\text{-pyen})(I_2)I\{(CH_2)_nI\}]$ (146) formed at an intermediate stage and reacted further to give a complex of type (145). The failure of (146) to undergo intramolecular oxidative addition to form a μ-polymethylene complex is believed to be due to unfavourable conformational effects.

The vitamin-B_{12s} haloalkyl complexes $[(Co)\{(CH_2)_nX\}]$ were prepared according to equation 42 [98].

$$(Co) + Br(CH_2)_nBr \longrightarrow [(Co)\{(CH_2)_nX\}] \qquad (42)$$

$\{(Co)$ = vitamin-B_{12s}; n = 3; X = Br, Cl$\}$

When n = 4, the above reaction gives $[(Co)(CH_2)_4(Co)]$ as the major, and $[(Co)\{(CH_2)_4Br\}]$ as the minor product. The complex $[(Co)\{(CH_2)_4Br\}]$ reacts with (Co) to give $[(Co)(CH_2)_4(Co)]$ [178].

The related complexes $[Co(DH)_2py\{(CH_2)_nX\}]$ (X = Br, n = 3 - 7; X = I, n = 3; DH = monoanion of dimethylglyoxime) were prepared according to equation 43 [178].

$$[Co(DH)_2pyCl] + X(CH_2)_nX \xrightarrow{MeOH,\ NaBH_4} [Co(DH)_2py\{(CH_2)_nX\}] \qquad (\underline{43})$$

(X = Br, n = 3 - 7; X = I, n = 3)

These haloalkyl complexes, where n = 4 - 6, reacted with $[Co(DH)_2pyCl]$ in the presence of sodium borohydride to give the dinuclear polymethylene-bridged cobaloximes $[py(DH)_2Co(CH_2)_nCo(DH)_2py]$, as shown in equation 44.

$$[Co(DH)_2py\{(CH_2)_3X\}] + [Co(DH)_2pyCl] \longrightarrow [py(DH)_2Co(CH_2)_nCo(DH)_2py] \qquad (\underline{44})$$

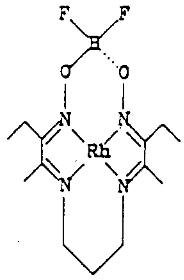
Neither the vitamin-B_{12s} complex $[(Co)\{(CH_2)_3X\}]$ (X = Br, Cl) nor the cobaloxime complex $[Co(DH)_2py\{(CH_2)_3X\}]$ (X = Br, I) reacted to form a 1,3-propanediyl compound, presumably due to steric factors [98,178]. The bromopropylcobaloxime complex gave cyclopropane and the cobaloxime-bromide on thermolysis [179].

Complexes of the type [Rh(TPP)(RX)], {RX = $C_nH_{2n}X$ (n = 3 - 5, X = Cl, Br; n = 3 - 6, X = I); TPP = dianion of tetraphenylporphyrin}, were prepared by Anderson *et al.* [180]. The nature of RX was found to determine the overall electrochemical behaviour for the reduction of [Rh(TTP)(RX)]. For some complexes, specifically those where X = Br and I, the bound alkyl halide could be reduced without cleavage of the metal-C bond. This resulted in the electrochemically initiated conversion of [Rh(TPP)(RX)] to a [Rh(TPP)(R)] complex. The E_{pc} for this reduction was dependent on the chain length and halide of the RX group and followed the trend predicted for alkyl halides. The reduction of the bound RX occured at $E_{\frac{1}{2}}$ values significantly less negative that those for reduction of free RX under the same solution conditions.

Collman *et al*. prepared halopropyl rhodium complexes by the reaction of dihalopropanes to a macrocyclic rhodium(I) complex - equation 45 [181].

$$2\ [Rh] + X(CH_2)_nX \longrightarrow X[Rh](CH_2)_nX \qquad (\underline{45})$$

[*Rh*] =



The ratio of mononuclear to binuclear product was found to be solvent dependant, with the variations in product ratios in different solvents being related to the solubility of the Rh(I) macrocycle.

1.4 CONCLUSIONS

It has been shown that a wide variety of transition metal haloalkyl complexes have been prepared by a variety of routes. The most common routes to halomethyl complexes involve (a): the reaction of a methoxymethyl transition metal complex with HX (X = Cl, Br) gas, (b): the reaction of a transition metal anion with CH_2XY (X, Y = a halogen), (c): the insertion of CH_2 into a metal-halogen bond. The most common route to ω-haloalkyl complexes involves the reaction of a transition metal anion with $X(CH_2)_nX$ (n > 1). These haloalkyl transition metal complexes are generally sufficiently stable to isolate and characterise, with the stability of homologous series of these complexes usually following the order Cl > Br > I.

These haloalkyl complexes show interesting and novel chemistry (*e.g.* some act as sources for CH_2) and can be used as precursors for many types of compounds *e.g.* transition metal ylide complexes, cyclic carbene complexes and heterobimetallic compounds.

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CHAPTER 2

THE SYNTHESIS AND PROPERTIES OF [CpFe(CO)$_2$CH$_2$X] (X = OCH$_3$, Cl, Br, I) AND THEIR REACTIVITY WITH SOME NEUTRAL DONOR LIGANDS

2.1 INTRODUCTION

As was shown in chapter 1, complexes of the type [L$_n$M-CH$_2$X] (L$_n$M = transition metal and its associated ligands, X = halogen) have been known for many years. Also evident is the susceptibility of the halomethyl carbon atom to nucleophilic attack. Previous work in these laboratories has shown that the products of reactions of certain cyclopentadienyl (Cp) or pentamethylcyclopentadienyl (Cp*) halomethyl complexes with neutral nucleophiles depend on a number of factors, including the metal and its associated ligands, the nucleophile and the solvent used [1-3]. Hence, for example, [CpFe(CO)$_2$CH$_2$Cl] reacts with PPh$_3$ in methanol to give [CpFe(CO)$_2$CH$_2$PPh$_3$]Cl, whilst [CpRu(CO)$_2$CH$_2$Cl] does not react with PPh$_3$ under identical conditions. Similarly, [CpW(CO)$_3$CH$_2$Cl] will react with PPh$_3$ in acetonitrile to give [CpW(CO)$_3$CH$_2$PPh$_3$]Cl, whilst [CpMo(CO)$_3$CH$_2$Cl], reacting under identical conditions, gives [CpMo(PPh$_3$)(CO)$_2$Cl] [1]. Previously reported work from our laboratories has shown that the reaction of [CpFe(CO)$_2$CH$_2$Cl] (1a) with tertiary phosphines can give two types of product, namely [CpFe(CO)$_2$CH$_2$L]$^+$ (2) (where L is a tertiary phosphine) or [CpFeL$_2$(CO)]$^+$ (3) depending on the solvent used and the size and pKa of the ligand involved in the reaction [1,2]. Thus the reaction of (1a) with PPh$_3$

gave $[CpFe(CO)_2CH_2PPh_3]^+$ (**2g**) in both acetonitrile and methanol, whereas the corresponding reactions of (**1a**) with PMe_2Ph yielded $[CpFe(CO)_2CH_2PMe_2Ph]^+$ (**2b**) in methanol and $[CpFe(PMe_2Ph)_2(CO)]^+$ (**3b**) in acetonitrile. In light of the above, it was decided to carry out a more detailed study of these reactions using a wider range of ligands L, to determine what effect changing the halogen in $[CpFe(CO)_2CH_2X]$ has on the reactivity of the system and the effect the solvent has on the type of product formed [4]. It was hoped that this would give further information on the mechanism of these reactions.

2.2 SYNTHESIS AND PROPERTIES OF $[CpFe(CO)_2CH_2X]$ ($X = OCH_3$, Cl, Br, I)

Both $[CpFe(CO)_2CH_2Cl]$ (**1a**) and $[CpFe(CO)_2CH_2Br]$ (**1b**) are well-known and were synthesized by published literature methods [5]. Their melting points, ^{13}C NMR and mass spectral data have, however, never been reported. In contrast, $[CpFe(CO)_2CH_2I]$ (**1c**) has not been reported before, though a report in the literature indicated that it would be too unstable to isolate and characterise [6]. We have succeeded in synthesizing the compound by two routes. The first route is similar to the method of Green *et al.* [5], *i.e.* by reacting $[CpFe(CO)_2CH_2OCH_3]$ with dry HI gas and then purifying the product by chromatography, to separate it from $[CpFe(CO)_2I]$ (which forms as a minor by-product) (eqns. 1 and 2).

$$Na[CpFe(CO)_2] + ClCH_2OCH_3 \xrightarrow{THF} [CpFe(CO)_2CH_2OCH_3] + NaCl \qquad (1)$$

$$[CpFe(CO)_2CH_2OCH_3] + HI \xrightarrow{\text{hexane}} [CpFe(CO)_2CH_2I] + CH_3OH \qquad (\underline{2})$$

The second, and more convenient, method involves treating $[CpFe(CO)_2CH_2Br]$ with NaI, a route commonly used for converting alkyl bromides into alkyl iodides [7] (eqn. 3).

$$[CpFe(CO)_2CH_2Br] \xrightarrow[\text{acetone,RT}]{\text{excess NaI}} [CpFe(CO)_2CH_2I] + NaBr \qquad (\underline{3})$$

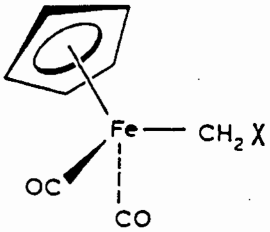
An attempt to prepare **(1c)** by a third route, shown in equation 4, was less successful.

$$Na[CpFe(CO)_2] + CH_2I_2 \longrightarrow [CpFe(CO)_2CH_2I] + NaI \qquad (\underline{4})$$

Complex **(1c)**, prepared by this route, could only be isolated in a low yield and could not be completely purified. This route of reacting a transition metal anion with a dihalomethane has however been used successfully for other transition metals eg. the reaction of $Na[CpMo(CO)_3]$ with CH_2ClI to give $[CpMo(CO)_3CH_2Cl]$ in 60 - 70 % yields [6].

We have isolated $[CpFe(CO)_2CH_2I]$ (from the routes shown in eqn.s 1 - 3) as lustrous yellow crystals, melting at 28°C, and have fully characterised the compound by IR, ^1H and ^{13}C NMR, micro-analysis and mass spectrometry (see Experimental section and Tables 2.1 and 2.2).

Pure (**1c**) was found to be stable to air and light at room temperature for short periods of time. A sample has been kept under nitrogen at -15°C for two years with only very minor degradation. Compound (**1c**), like (1a) and (**1b**), loses a methylene group to form $[CpFe(CO)_2X]$ on decomposition at room temperature both in solution and as the solid. The complexes (1a) - (**1c**) are represented in **Figure 1**.



compound	X
1a	Cl
1b	Br
1c	I

Figure 1 : Molecular formulae for complexes (1a) - (**1c**)

The IR spectra of complexes (1a) - (**1c**) (unlike the IR spectrum of $[CpFe(CO)_2CH_2OCH_3]$ which shows four bands in the carbonyl region due to rotational isomerism [8]) show only two bands in the ν(CO) region. Comparing the IR spectra of complexes (1a), (**1b**) and (**1c**), it can be seen that the peaks shift only very slightly to higher wave numbers as X changes from Cl to I.

The ^1H NMR signal for the $-CH_2X$ group shows the large expected shift due to the varying electron withdrawing effect of the halogens, whilst the Cp resonance shows only a very minor upfield shift as X varies from Cl to I (see Table 2.1). Comparing the resonances of these CH_2 protons with those of uncoordinated CH_3X { $\delta = 3.05$ (CH_3Cl), $\delta = 2.68$ (CH_3Br), $\delta = 2.16$ (CH_3I) ppm [9] }, it can be observed that the resonances of the

Table 2.1 : Spectral data and melting points of $[CpFe(CO)_2CH_2X]$

Compound	X	m.p.	$\nu(CO)^a$ (cm^{-1})	^{13}C NMR ^{b,c} (δ)	^1H NMR^b (δ)	molecular ion^d
(1a)	Cl	65-68°C	2026 1974	214.40(CO) 86.24(Cp) 33.70(CH_2)	4.90s(5H) 4.24s(2H)	226^e
(1b)	Br	54-58°C	2027 1975	214.43(CO) 86.81(Cp) 25.67(CH_2)	4.89s(5H) 3.94s(2H)	270/272^e
(1c)	I	28°C	2027 1977	214.99 (CO) 87.75 (Cp) - 6.51 (CH_2)	4.86s(5H) 3.02s(2H)	318^e

a: in hexane solution, all bands strong
b: in $CDCl_3$ relative to TMS
c: in presence of $Cr(acac)_3$ - 0.08 M [22]
d: mass of the most abundant isotope combination
e: the isotope patterns were in close agreement with a computer simulated isotope pattern of the molecular formula

iron halomethyl protons are shifted downfield (deshielded) by between *ca*. 1 and 1.2 ppm by the influence of the iron atom relative to the CH_3X protons. The ^{13}C NMR data for the carbon atom of the CH_2X group shows the following chemical shifts : X = Cl, $\delta = 33.7$; X = Br, $\delta = 25.7$; X = I, $\delta = -6.5$ ppm. The shift of the signals between X = Cl and X = Br of 8 ppm and X = Br and X = I of 19 ppm reflects the different electronegativities of the halogens. Also of interest is that the ^{13}C resonances of the Cp rings shift marginally downfield as X varies from Cl to Br to I (see Table 2.1), a trend directly opposite to that observed for the $[CpFe(CO)_2X]$ complexes; whilst the CO resonances of both complex types move downfield as X varies from Cl to I [10]. The effect on the Cp resonances of $[CpFe(CO)_2CH_2X]$ observed with changes in X is likely to be due to electronic effects, probably relating to the varying electronegativities and π-donor abilities of the halides. Possibly a canonical form of type $^{\delta+}Fe = CH_2 \cdots X^{\delta-}$ exists in solution. Such a species would withdraw electrons from the cyclopentadienyl group, reducing the ring current and hence cause an upfield shift of the Cp resonance. This effect would be greatest for X = Cl, as is observed.

Complexes **(1a)** - **(1c)** all show molecular ions of low intensity (2 - 5 %) in their low resolution mass spectra. All spectra show ions which are considered to be characteristic for $CpFe(CO)_2$ containing compounds [11-13]. Thus peaks corresponding to $[CpFe(CO)_2]^+$ (m/z 177), $[CpFe(CO)]^+$ (m/z 149), $[CpFe]^+$ (m/z 121), $[Cp]^+$ (m/z 65), $[Fe]^+$ (m/z 56) and $[C_3H_3]^+$ (m/z 39) are observed. A low intensity peak at 186 Dalton is assigned to $[Cp_2Fe]^+$, the ferrocene ion. The formation of this ion is discussed in chapter 4. The most abundant peak observed in the spectra of complexes (**1a**) and (**1b**) corresponds to $[Fe]^+$ (m/z 56). For complex (**1c**) the most abundant peak corresponds to $[CpFe(CO)CH_2I]^+$ (m/z 290). The intensities of the major peaks observed in the mass spectra of the $[CpFe(CO)_2CH_2X]$ (X = Cl, Br, I) complexes are reported in Table 2.2.

Complexes (**1a**) - (**1c**) appear to fragment according to three common pathways. The first involves sequential losses of CO from the molecular ion to give $[CpFe(CO)CH_2X]^+$ and then $[CpFeCH_2X]^+$, which fragments further with loss of HX to give a peak corresponding to $[CpFeCH]^+$ (m/z 134). This latter ion then loses Cp to leave $[FeCH]^+$ (m/z 69). The second fragmentation pathway common to (**1a**) - (**1c**), involves the loss of "CH_2X" to give $[CpFe(CO)_2]^+$. This ion then loses CO sequentially to give $[CpFe(CO)]^+$, followed by $[CpFe]^+$. The latter ion can then fragment by either losing C_2H_2 to give $[C_3H_3Fe]^+$ (m/z 95) or by losing Cp to give $[Fe]^+$. The third common fragmentation pathway is probably the most interesting. This pathway appears to involve the loss of X from the molecular ion to give an ion corresponding to the carbene species $[CpFe(CO)_2(CH_2)]^+$ (m/z 191). This carbene species then fragments by sequential losses of CO to give ions corresponding to $[CpFe(CO)(CH_2)]^+$ (m/z 163) and then $[CpFe(CH_2)]^+$ (m/z 135). The latter ion can then lose Cp to form an ion corresponding to $[Fe(CH_2)]^+$ (m/z 70). Although the peak corresponding to $[CpFe(CO)_2(CH_2)]^+$ is not observed in the mass spectrum of (**1a**), all its subsequent fragmentation peaks are observed. The peak at m/z 191, assigned to $[CpFe(CO)_2(CH_2)]^+$, is most intense in the mass spectrum of complex (**1c**) (intensity = 72 %), much less intense for complex (**1b**) (*ca.* 4 %) and too small to be observed in the mass spectrum of complex (**1a**). This implies that the carbene species is much

Table 2.2 : Some mass spectral data for $[CpFe(CO)_2CH_2X]$

Ion[a]	Relative peak intensities (%)[b]		
	X = Cl	X = Br	X = I
M	7	2	15
M - CO	56	32	100
M - 2CO	54	36	48
M - 2CO - HX	94	84	74
M - 2CO - HX - Cp	4	5	6
M - CH_2X {= $CpFe(CO)_2$}	5	2	2
M - CH_2X - CO {= CpFe(CO)}	13	6	4
M - CH_2X - 2CO {= CpFe}	69	43	40
M - X		4	72
M - CO - X	6	5	16
M - 2CO - X	7	16	5
M - 2CO - X - Cp	3	5	18
FeX			50
C_3H_3Fe	10	7	6
C_3H_2Fe		6	6
Fe	100	100	88
X			3
CpH	4	2	
Cp	6	6	10
C_3H_3	18	21	42
Cp_2Fe	8	6	6

a : Ion refers to probable assignment; *M* = $[CpFe(CO)_2CH_2X]$; all ions have a single positive charge

b : Peak intensities are relative to the base peak at m/z 56 (X = Cl, Br) and m/z 290 (X = I) more readily formed from complex **(1c)** under mass spectral conditions. In fact, the relative abundance of the proposed carbene species appears to depend on the relative abilities of the halogens as leaving groups (I >> Br > Cl). The formation of the carbene species $[CpFe(CO)_2(CH_2)]^+$ has been previously observed in the electron impact mass spectrum of $[CpFe(CO)_2CH_2OCH_3]$, although the presence of protonation agents was required [14]. The intermediacy of this carbene species has also been proposed for several organometallic reactions [5,15,16].

2.3 REACTIVITY OF $[CpFe(CO)_2CH_2X]$ (X = Cl, Br, I)

The reactions of **(1a)**, **(1b)** and **(1c)** with L in acetonitrile and THF are summarised in equations 5 and 6.

$$\underset{(1)}{[CpFe(CO)_2CH_2X]} + L \longrightarrow \underset{(2)}{[CpFe(CO)_2CH_2L]^+X^-} \qquad (5)$$

Reaction 5 in acetonitrile was successfully used in the following cases:

X = Cl; L = PEt_2Ph **(2d)**, $PEtPh_2$ **(2e)**, PPh_3 **(2g)**, $AsPh_3$ **(2k)**
X = Br; L = PMe_2Ph **(2b)**, $PMePh_2$ **(2c)**, PBu^t_3 **(2f)**, PPh_3 **(2g)**,
PMe_3 **(2h)**, NC_5H_5 **(2i)** and SMe_2 **(2j)**
X = I; L = PPh_3 **(2g)**.

Reaction 5 in THF was successfully used in the following cases:

X = Cl; L = PMe_2Ph (**2b**)
X = Br; L = PMe_3 (**2a**), PMe_2Ph (**2b**), $PMePh_2$(**2c**), PBu^t_3 (**2f**),
NMe_3 (**2h**), NC_5H_5 (**2i**) and SMe_2 (**2j**).

$$\underset{(1)}{[CpFe(CO)_2CH_2X]} + 2L \longrightarrow \underset{(3)}{[CpFe(L)_2(CO)]^+X^-} + \ldots \qquad (6)$$

Reaction 6 in acetonitrile was successfully used in the following cases:

X = Cl; L = PMe_3 (**3a**), PMe_2Ph (**3b**), PEt_2Ph (**3d**) and $PEtPh_2$ (**3e**)

Reaction 6 in THF was successfully used in the following cases:

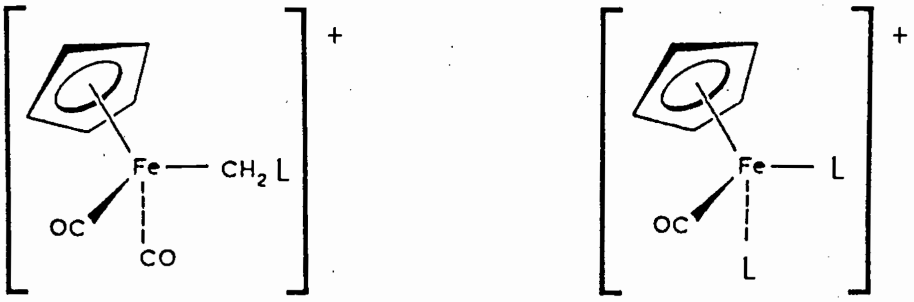
X = Cl; L = PMe_3 (**3a**)
X = Br; L = PMe_2Ph (**3b**)

All products (**Figure 2**) were isolated as their halide, BPh_4^- or PF_6^- salts and were obtained as yellow crystalline solids. Characterisation data for compounds (**2a**, **b**, **f**, **h** - **j**) are reported in Table 2.3.

Table 2.3: Products of the reaction of (1b) with L in THF

No.	Compound	React. time(d)	Yield (%)	m.p. (°C)	ν(CO)[a] (cm^{-1})	^1H NMR(δppm)[b]	Elemental Analysis[c]
2a	$[CpFe(CO)_2CH_2PMe_3]Br$	4	83	185(dec)	2021s 1964s	1.27[d,2H,^2J(PH)=13.0 Hz] 2.03[d,9H,^2J(PH)=13.0 Hz] 5.70[s,5H]	C:38.05(37.93) H: 4.60(4.60)
2b	$[CpFe(CO)_2CH_2PMe_2Ph]Br$	10	82	165(dec)	2023s 1968s	1.32[d,2H,^2J(PH)=13.0 Hz] 2.11[d,6H,^2J(PH)=13.0 Hz] 5.11[s,5H];7.43-8.13[m,5H]	C: 47.05(46.94) H: 4.40(4.50)
2f	$[CpFe(CO)_2CH_2PBu^t{}_3]BPh_4$	30	17	160- 182(dec)	2027s 1976s	1.40[d,2H,^2J(PH)=13.0 Hz] 1.38[d,27H,^2J(PH)=12.6 Hz] 4.55[s,5H],7.00-7.42[m,20H]	C: 74.10(74.14) H: 7.75(7.58)
4	$[\{CpFe(CO)_2CH_2\}_2dppe]Br_2$	11	33	200- 210(dec)	2027s 1973s	1.83[tp,4H,^2J(PH)+^2J(PH)=13.0 Hz] 2.90[d,4H,^2J(PH)=5.0Hz] 5.10[s,10H];7.57-8.40[m,20H]	C: 53.30(53.50) H: 4.03(4.20)
2h	$[CpFe(CO)_2CH_2NMe_3]Br$	5	76	193- 200(dec)	2023s 1964s	[e]3.10[s,9H];4.03[s,2H] 5.30[s,5H]	C: 39.95(39.88) H: 4.90(4.83) N: 4.20(4.23)
2i	$[CpFe(CO)_2CH_2NC_5H_5]Br$	10	14	162- 174(dec)	2022s 1967s	2.33[s,2H];5.30[s,5H] 5.43[s,2H];7.77-8.73[m,3H]; 9.50[d,2H,^2J(α-H)=6.0 Hz]	[f]C: 42.60(44.44) H: 2.85(3.42) N: 3.85(4.00)
2j	$[CpFe(CO)_2CH_2SMe_2]Br$	9	35	147-148	2030s 1975s	2.87[s,2H];3.15[s,6H]; 5.30[s,5H]	C: 35.80(36.04) H: 3.95(3.90)

a : measured in CH_2Cl_2 b : in $CDCl_3$ unless otherwise stated; s = singlet, d = doublet, tp = pseudo triplet,
m = multiplet c : calculated values in parenthesis
d : CD_3CN e : CD_3OD f : the monohydrate requires C: 42.28 H: 3.79 N: 3.79



2	L
2a	PMe_3
2b	PMe_2Ph
2c	$PMePh_2$
2d	PEt_2Ph
2e	$PEtPh_2$
2f	$PBu^t{}_3$
2g	PPh_3
2h	NMe_3
2i	py
2j	SMe_2
2k	$AsPh_3$

3	L
3a	PMe_3
3b	PMe_2Ph
3d	PEt_2Ph
3e	$PEtPh_2$

Figure 2 : Molecular formulae for complexes (2) and (3)

The products of reaction 5 are analogous to those obtained on the quaternisation of tertiary phosphines, amines and sulphides with an alkyl halide by an S_N2 mechanism [17]. Complex (2g) contains the CH_2PPh_3 ligand, which was first prepared by Wittig [18]. All these ylide type products (**2a**) - (**2k**) show a high thermal stability and are stable in air for several months. This is in contrast to the uncoordinated ylides CH_2AsPh_3 [19,20] and CH_2SMe_2 [21] which are reported to be very unstable and are thus stabilised by coordination to the transition metal. The ylide $CH_2NC_5H_5$ (CH_2py) has not yet been prepared in uncoordinated form [22].

In contrast to the reactions of tertiary phosphines with (**1b**), the reaction of tertiary amines with (**1b**) is not a general reaction and only NMe_3 and pyridine gave isolable products. In the case of the reaction of NEt_3 with (**1b**) in THF, only the amine salt $[Et_3NH]Br$ could be isolated [23]. In methanol, however, $[CpFe(CO)_2CH_2OCH_3]$ was also isolated and identified by its spectral data. A similar reaction has been observed previously by heating (**1a**) in methanol to give $[CpFe(CO)_2CH_2OCH_3]$ [1]. The isolation of the amine salt indicates that MeOH is a better nucleophile than NEt_3. The isolation of the amine salt from the THF reaction is difficult to rationalise unless the carbene $[CpFe(CO)_2(CH_2)]^+$ is generated *in situ*.

The nature of the phosphine clearly influences the product type formed. Hence the reaction of (**1b**) with PMe_3, a ligand with a high pK_a and small cone angle, gave a product of type (**3**) in CH_3CN. In contrast, the reaction of (**1b**) with PPh_3, a ligand with a low pK_a and large cone angle, gave a product of type (**2**) in the same solvent. The formation of (**2g**) from the reaction of (**1b**) with PBu^t_3, a ligand with a high pK_a and large cone angle, therefore implies that the steric size of the phosphine rather than its pK_a determines the product type formed. The

pK_a's and cone angles of the ligands under discussion are shown in Table 2.4.

The reactivity of complex (**1a**) contrasts with that of (**1b**). Thus PBu^t_3 does not react with (**1a**) in either THF, CH_3CN or methanol at either room temperature or reflux. But in a similar way to (**1b**), (**1a**) reacts with PMe_2Ph in THF to yield the ylide type product $[CpFe(CO)_2CH_2PMe_2Ph]Cl$ (**2b**) which was isolated as the BPh_4^- salt. Unlike (**1b**) though, (**1a**) reacts with PMe_3, which has a larger pK_a and smaller cone angle than PMe_2Ph, to form the disubstituted cationic product $[CpFe(PMe_3)_2(CO)]Cl$ (**3a**). These results indicate that the halogen has a considerable effect on the reactivity of the complex $[CpFe(CO)_2CH_2X]$.

The effect that the solvent has on the course of the reaction is demonstrated by the fact that neither (**1a**) nor (**1b**) react with PPh_3 in THF, though (**1a**) - (**1c**) all readily react with PPh_3 in CH_3CN or CH_3OH to form the ylide type product (**2g**). The solvent effect is further demonstrated by the fact that $[CpFe(CO)_2CH_2Cl]$ (**1a**) reacts with PMe_2Ph in CH_3CN to form a product of type (3), whereas in THF the identical reactants yield a product of type (2). A third example is the reaction of (**1b**) with PBu^t_3; the reaction in THF yielded a product of type (**2**) in 17% yield after 30 days at room temperature whereas the reaction in CH_3CN yielded (**2f**) in 65% yield after 11 days at room temperature.

The reactions of (**1b**) with PMe_2Ph, $PMePh_2$, PPh_3, pyridine, NMe_3 and SMe_2 in a 1:2 molar ratio in CH_3CN were followed by ^1H NMR, monitoring the intensities of the Cp peaks of starting material and product at room

Table 2.4 : pK_a's and cone angles for some of the ligands used in chapters 2 and 3.

Ligand L	cone angle[a] θ(°)	pK_a
PMe_3	118	8.65[b]
PMe_2Ph	122	6.49[b]
dppe	125	
PEt_3	132	8.69[c]
$PMePh_2$	136	4.59[c]
PEt_2Ph	136	6.25[b,c]
$PEtPh_2$	140	4.90[c]
PPh_3	145	2.73[b,d]
PCy_3	170	9.65[d]
PBu^t_3	182[e]	11.4[d]
py		5.20[f]
NMe_3		9.80[f]
$AsPh_3$	127[g]	

a : Data from ref.[24] unless otherwise stated

b : Ref. [25] c : Ref.[26] d : Ref.[27]

e : Ref.[28] f : Ref.[29] g : Ref.[30]

temperature. The rates of the reactions followed the order PMe_2Ph > $PMePh_2$ > PPh_3 > SMe_2 > pyridine, with $t_{\frac{1}{2}}$ values estimated as < 4 min, 4 min, 23 min, 30 min and 35 min respectively (±1 min) ($t_{\frac{1}{2}}$ is defined as the time taken for the reaction to be half completed). For the phosphines, cone angles increase and pKa's decrease in the following order PMe_2Ph < $PMePh_2$ < PPh_3 [24-29]. (The cone angles are 122, 136 and 145°, and the pKa values are 6.49, 4.59 and 2.73 respectively.) Hence the ligands with smaller cone angles and larger pKa values react more quickly. This is probably due to their greater nucleophilicity and less steric hindrance during the course of the reaction.

Similarly, monitoring the intensities in the ^1H NMR spectra of the Cp peaks of starting material and product at room temperature showed that the rate of the reaction of (1a) - **(1c)** with PPh_3 under identical conditions follows the order (Cl < Br < I), with a relative reactivity of Cl : Br of 1 : 640, the $t_{\frac{1}{2}}$ value for X=I being too fast to be observed at room temperature by the techniques used. The reaction of CH_3X with neutral nucleophiles shows a similar trend in rate *i.e.* Cl < Br < I (1 : *ca*.40 : *ca*.80) [31]. Thus the metal has a significant effect on the rate of reaction of the halomethyl complexe relative to that of the corresponding methyl halide.

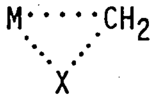
The proposed mechanism for the reaction of (1a) with L to give complexes of type (2) [2] could be generalised for all reactions of (1) with L to give **(2)** as shown in **SCHEME 2.1.**

$$\underset{(1)}{\text{M-CH}_2\text{X}} \longrightarrow \underset{(\text{Z})}{\text{M=CH}_2]^+\text{X}^-} \xrightarrow{\text{L}} \underset{(2)}{\text{M-CH}_2\text{L}]^+\text{X}^-}$$

M = CpFe(CO)_2

SCHEME 2.1

Thus the halide is proposed to migrate outside the coordination sphere of the metal to form a carbene complex (Z). This is followed by the nucleophilic attack of L at the carbon of the cationic carbene complex to give complex (2). In the absence of a ligand L, nucleophilic attack of the halide at the metal could occur with displacement of a CH_2 group as has been found in some reactions of (1a) [16] and $[\text{CpFe(PPh}_3\text{)(CO)CH}_2\text{X}]$ (X = Cl, Br, I) [32]. Indeed the organometallic products of this 1,2 halide shift, $[\text{CpFe(CO)}_2\text{X}]$, are observed on the decomposition of complexes (1a) - (1c) in solution (section 2.2). Other examples of 1,2 shifts of halogen from carbon to metal have been reported [33-36]. This 1,2 halide shift may go *via* the three-centre transition state shown below.



Such a transition state has been proposed before for complex (1a) [2] and for other 1,2 shifts from carbon to metals [37-39].

The ^{13}C NMR data of the halomethyl complexes also indicated the possible presence of the carbene intermediate (Z) in solution (section 2.2), as did the isolation of $[\text{Et}_3\text{NH}]\text{Br}$ from the reaction of (1b) with NEt_3 in

THF (see previously in this chapter). Other workers have shown that reactions of some $[M{=}CHR']^+$ (R′ = H, Me) complexes with PR_3 ligands give complexes of the type $[MCHR'PR_3]$ [38,40,41], lending further support to the mechanism shown in **SCHEME 2.1**.

The reaction of (**2b**) with excess PMe_2Ph in CH_3CN gave, on work up with $NaBPh_4$, $[CpFe(PMe_2Ph)_2(CO)]BPh_4$ in 55% yield along with $[PMe_3Ph]Br$ (as identified by IR and ^1H and ^{13}C NMR spetroscopy) in 30% yield (eqn.s <u>7</u> and <u>8</u>).

$$[CpFe(CO)_2CH_2PMe_2Ph]Br + xs\ PMe_2Ph \longrightarrow [CpFe(PMe_2Ph)_2(CO)]^+ + [PMe_3Ph]Br + \ldots \qquad (\underline{7})$$

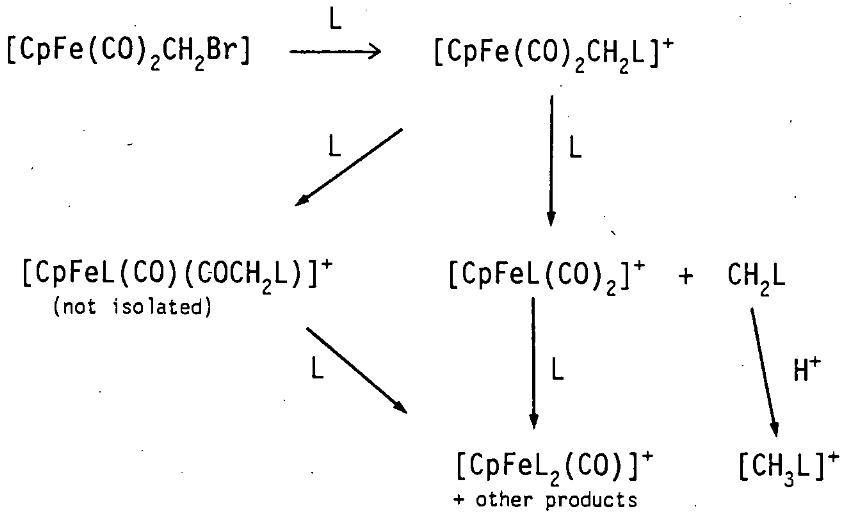
$$[CpFe(PMe_2Ph)_2(CO)]Br + NaBPh_4 \longrightarrow [CpFe(PMe_2Ph)_2(CO)]BPh_4 + NaBr \qquad (\underline{8})$$

Similarly (**2a**) reacts with excess PMe_3 to give, on work-up with $NaBPh_4$, $[CpFe(PMe_3)_2(CO)]BPh_4$ in 35% yield; ^1H NMR evidence indicates that $[PMe_4]BPh_4$ is also formed in this reaction [23]. The phosphonium salt $[PMeEt_2Ph]BPh_4$ was isolated from the reaction of (**1a**) with PEt_2Ph in CH_3CN, together with (**3d**) [2]. No evidence for a species of the type $[CpFeL(CO)CH_2L]^+$ was obtained from any of these reactions.

These results imply that in the reactions of $[CpFe(CO)_2CH_2X]$ with excess tertiary phosphines with sufficiently small cone angles and large pK_a's, $[CpFe(CO)_2CH_2L]^+X^-$ is an intermediate and that further reaction displaces CO and "CH_2-L" to give $[CpFeL_2(CO)]X$. Since

$[CpFe(CO)_2CH_2NMe_3]Br$ does not react with PMe_3 [23], it appears that the nature of the CH_2-L bond is a determining factor in whether or not CH_2=L is eliminated. Other workers have shown that $[CpFe(PMe_3)(CO)_2]I$ readily reacts with PMe_3 under reflux in CH_3CN to give $[CpFe(PMe_3)_2(CO)]I$ [42]. Similarly, we have shown that $[CpFe(PMe_2Ph)(CO)_2]I$ reacts with PMe_2Ph to give $[CpFe(PMe_2Ph)_2(CO)]I$ (for characterisation data see chapter 7). Of two proposed mechanisms for the reaction described in equation 7 [1, chapter 1], the formation of $[PMe_3Ph]Br$, $[PMe_4]Br$ and $[PMeEt_2Ph]Cl$ is consistent with the elimination of the ylide CH_2=PR_3 and its subsequent protonation to give $[PR_3CH_3]^+$. Monitoring the reaction of (**1b**) with PMe_2Ph by IR and ^1H NMR showed that at least three intermediate species could be seen during formation of (**3b**). Two of these intermediates were identified as $[CpFe(CO)_2CH_2PMe_2Ph]Br$ (**2b**) and $[CpFe(PMe_2Ph)(CO)_2]Br$. A third intermediate, with ν(CO) at 1996 and 1771 cm^{-1} and a Cp peak in the ^1H NMR at $\delta = 4.96$, could be $[CpFe(PMe_2Ph)(CO)(COCH_2PMe_2Ph)]^+$ formed by alkyl migration in (**2b**) and subsequent reaction with PMe_2Ph. Alkyl migration has been observed for transition metal ylide complexes [43]. $[PMe_3Ph]Br$ was also obtained from the above reaction in 38% yield.

The spectroscopic evidence suggests that the ylide species (**2**) form rapidly on reaction of (1) with L and this is followed by a slower reaction to give (3); the rate of this latter reaction depends greatly on the phosphine concentration. A suggested scheme for these reactions is shown in **SCHEME 2.2**.



SCHEME 2.2

The reaction of (**1b**) with dppe {bis(diphenylphosphino)ethane} gave the bridged dinuclear dicationic ylide complex $[\{Cp(CO)_2FeCH_2P(Ph)_2(CH_2)_2P(Ph)_2CH_2Fe(CO)_2Cp]^{2+}$ (**4**) as the only product; no evidence for $[CpFe(CO)(CH_2dppe)]^+$ was obtained. This reaction is in contrast to the reaction of $[Cp*Rh(CO)I(CH_2I)]$ with dppm {bis(diphenylphosphino)methane} which yields the complex $[Cp*RhCH_2PPh_2CH_2PPh_2(I)]I$ [44]. The data for complex (**4**) is reported in Table 2.3.

Analogous products to (**2h**) and (**2j**),namely $[CpFe(CO)_2CH_2NMe_3]I$ (**5**) and $[CpFe(CO)_2CH_2SMe_2]BH_4$(**6**) have been prepared previously [45,46], though by different routes. The sulphonium salt (**6**) has been shown to have organic synthetic utility as a cyclopropanation reagent [46]. Ylide complexes are indeed beginning to be exploited in stoicheometric organometallic chemistry as versatile substrates for further synthetic manipulation [47-50]. This is the same reason why phosphonium ylides are used extensively in organic synthesis [51]. Attempts were made in this laboratory to see if the phosphonium salts **(2a)** and **(2g)** would display synthetic potential in Wittig type reactions [23]. However, the ylides [$CpFe(CO)_2CH{=}PR_3$] did not lend themselves to facile synthesis by simple deprotonation of the parent quarternary salts {**(2a)** and **(2g)**} using NaOMe/MeOH in the presence of benzophenone or butyllithium in THF as base. Phosphonium ylide complexes [$LM\text{-}CH{=}PR_3$] are known, however, with other metal systems *e.g.* [$(CO)_5RePPh_2CH{=}PPh_3$] or [$(CO)_4FePPh_2CH{=}PPh_3$] [43], but these have not been synthesized by direct deprotonation of the parent complex.

2.4 CONCLUSION

The halomethyl iron complexes [$CpFe(CO)_2CH_2X$] are easily prepared by reactions of the methoxymethyl complex [$CpFe(CO)_2CH_2OCH_3$] with dry HX gas. A more convenient route to [$CpFe(CO)_2CH_2I$] involves the reaction of [$CpFe(CO)_2CH_2Br$] with NaI. These haloalkyl complexes have been shown to be more stable than previously believed. Like [$CpFe(CO)_2CH_2OCH_3$], the complexes [$CpFe(CO)_2CH_2X$] (X = Cl, Br, I) appear to form the carbene complex [$CpFe(CO)_2(CH_2)$]$^+$ under electron impact mass spectral conditions. The relative abundance of this carbene species depends on the relative strengths of the halogens as leaving groups (I >> Br > Cl).

The complexes $[CpFe(CO)_2CH_2X]$ (**1**) (X = Cl, Br, I) react with neutral nucleophiles, L, to give two types of cationic complexes; namely the ylide type complexes $[CpFe(CO)_2CH_2L]^+$ (**2**) or the disubstituted complexes $[CpFeL_2(CO)]^+$ (**3**). The halide (X), the cone angle of the ligand (L) and the solvent used have been shown to influence the product type formed, whilst X and the cone angle and pK_a of L also influence the rate of reaction.

The mechanism of the reaction of (**1**) with L to give (**2**) appears to involve a carbene intermediate. Evidence obtained strongly suggests that complexes of type (**2**) are intermediates in the formation of (**3**) from (**1**) on reaction with L.

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CHAPTER 3

THE SYNTHESIS AND PROPERTIES OF [CpW(CO)$_3$CH$_2$X] (X = OCH$_3$, Cl, Br, I) AND THEIR REACTIVITY WITH NEUTRAL DONOR LIGANDS

3.1 INTRODUCTION

As was described in the previous chapter, the reactions of halomethyl transition metal complexes depend on a number of factors. Thus the solvent used, the cone angle and pK_a of the reacting ligand (L), the ligand concentration (the ratio of ligand to metal) and the nature of the carbon bonded halogen of the halomethyl complex determine both the rate of the reaction and the products formed. Another factor determining the reactivity of [CpM(CO)$_2$CH$_2$X] systems is the nature of the metal, M. Thus [CpFe(CO)$_2$CH$_2$Cl] reacts with PPh$_3$ in methanol to give the cationic ylide complex [CpFe(CO)$_2$CH$_2$PPh$_3$]$^+$, whereas [CpRu(CO)$_2$CH$_2$Cl] gives no ligand product under similar conditions [1,2]. The metal also affects the reactivity of the related [CpM(CO)$_3$CH$_2$Cl] (M = Mo, W) system. Hence [CpW(CO)$_3$CH$_2$Cl] reacts with PPh$_3$ in acetonitrile to give [CpW(CO)$_3$CH$_2$PPh$_3$]Cl, but [CpMo(CO)$_3$CH$_2$Cl] reacting under identical conditions gives [CpMo(PPh$_3$)(CO)$_2$Cl] [1,2]. These results indicate that the reaction of [CpW(CO)$_3$CH$_2$X] (X = Cl, Br, I) with ligands, L, may give similar products to those obtained from the reaction of [CpFe(CO)$_2$CH$_2$X] with L. We were thus interested to see how the reactivity of the [CpW(CO)$_3$CH$_2$X] system would compare to that of the

$[CpFe(CO)_2CH_2X]$ system, specifically to study the effect of a change of metal (from iron to tungsten) on these halomethyl systems.

3.2 PREPARATION AND PROPERTIES OF $[CpW(CO)_3CH_2X]$

The complexes $[CpW(CO)_3CH_2X]$ {X = OCH_3 (**1**), Cl (**2a**), Br (**2b**)} were prepared in good yield according to the method of Green *et al.* [4], as shown in equations 1 and 2.

$$Na[CpW(CO)_3] + ClCH_2OCH_3 \longrightarrow [CpW(CO)_3CH_2OCH_3] + NaCl \qquad (1)$$

$$[CpW(CO)_3CH_2OCH_3] + HX\ (gas) \longrightarrow \underset{X = Cl,\ Br}{[CpW(CO)_3CH_2X]} + CH_3OH \qquad (2)$$

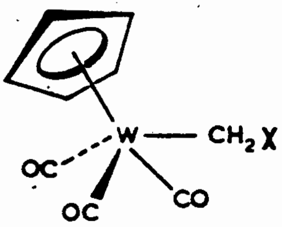
The complex $[CpW(CO)_3CH_2I]$ (**2c**) was prepared by reacting $[CpW(CO)_3CH_2Br]$ with NaI, a route commonly used for converting alkyl bromides into alkyl iodides [4] (equation 3).

$$[CpW(CO)_3CH_2Br] + NaI \longrightarrow [CpW(CO)_3CH_2I] + NaBr \qquad (3)$$

Complex (**2c**) has been previously reported, when it was obtained as a product of the reaction of $Na[CpW(CO)_3]$ with CH_2I_2 [5] in very low yield [6] - equation 4.

$$Na[CpW(CO)_3] + CH_2I_2 \longrightarrow [CpW(CO)_3CH_2I] + NaI \qquad (\underline{4})$$

Complex (**2c**) was however only partially characterised, and was reported as being too unstable to permit full characterisation [5]. The complex $[CpW(CO)_3CH_2I]$ was obtained as yellow crystals in good yield according to the method shown in equation $\underline{3}$, and was found to be stable to air and light for short periods of time (contrary to the previous report). A sample of (**2c**) has been kept under nitrogen at -15°C for over three years with only minor degradation. Complexes (**2a**) and (**2b**) were found to be more stable than complex (**2c**) under any conditions, with a stability order of $CH_2Cl \gg CH_2Br > CH_2I$. Complexes (1) - (**2c**) were also found to be less stable than their Cp* analogues, $[Cp^*W(CO)_3CH_2X]$ ($X = OCH_3$, Cl, Br, I) [7], in all respects. Compounds (**2a**), (**2b**) and (**2c**) lose a methylene group ("CH_2") on decomposition to form $[CpW(CO)_3X]$ at room temperature in both solution and in the solid state. The data for complexes (1) - (**2c**) is reported in Tables 3.1 and 3.2. Neither the melting points, ^{13}C NMR nor mass spectra of these functionalised methyl complexes have been reported previously. The complexes (**2a**) - (**2c**) are represented in **figure** 1.



X	compound no.
OCH_3	**1**
Cl	**2a**
Br	**2b**
I	**2c**

Figure 1: Molecular formula for complexes (1), (**2a**) - (**2c**)

Table 3.1 :

Data for [CpW(CO)$_3$CH$_2$X]

Compound	X	m.p. (°C)	IR (νCO)[a] (cm^{-1})	^{1}H NMR[b] (δ)	^{13}C NMR[b] (δ)	molecular[c] ion
1	OCH$_3$	44-45	2025 1940 1926	5.45[s, 5H] 4.60[s, 2H] 3.27[s, 3H]	228.5(*cis*-CO) 216.3(*trans*-CO) 91.5(Cp), 63.6(CH$_3$) 47.8(CH$_2$)	
2a	Cl	>78 (dec)	2031 1950 1934	5.57[s, 5H] 4.30[s, 2H]	227.1(*cis*-CO) 215.5(*trans*-CO) 92.6(Cp), 9.9(CH$_2$)	382
2b	Br	80-85	2031 1950 1935	5.59[s, 5H] 3.98[s, 2H]	226.9(*cis*-CO) 215.5(*trans*-CO) 93.0(Cp), -2.03(CH$_2$)	426/428
2c	I	99-102	2031 1951 1938	5.56[s, 5H] 3.16[s, 2H]	227.2(*cis*-CO) 216.0(*trans*-CO) 93.8(Cp), -36.9(CH$_2$)	474

a: measured in hexane, all bands strong.
b: measured in CDCl$_3$ relative to TMS (δ = 0.00 ppm), s = singlet
c: mass of most abundant isotope combination

The data for the [$CpW(CO)_3CH_2X$] system shows some striking differences to those of the [$CpFe(CO)_2CH_2X$] system. For example, the methoxymethyl iron complex [$CpFe(CO)_2CH_2OCH_3$] is a yellow oil, whilst (1) is a yellow solid which melts at 44-45°C. Also, whereas the [$CpFe(CO)_2CH_2X$] (X = Cl, Br, I) complexes show a decrease in their melting points as X changes from Cl to Br to I (*ca*. 65, *ca*. 54, 28 °C), the melting points of the [$CpW(CO)_3CH_2X$] complexes increase as X changes from Cl to Br to I. The tungsten halomethyl complexes also have higher melting points than their iron analogues and appear to be more stable in air, in the absence of light.

The carbonyl stretching frequencies for the W complexes show a very slight shift to higher wave numbers as X changes from Cl to Br to I and are at higher wave numbers than those of their [$CpMo(CO)_3CH_2X$] analogues [3]. Also, the carbonyl stretching frequencies were found to be 12 - 15 cm^{-1} higher than those observed for their Cp^* analogues [3,5]. This effect can be attributed to the lower electron donating ability of the Cp ligand as compared to the Cp^* ligand [8].

The ^1H NMR spectra show the expected trend for the chemical shifts (δ ppm) for the CH_2-X protons - *i.e.* $CH_2OCH_3 > CH_2Cl > CH_2Br > CH_2I$ - whilst the Cp resonance shows little or no variation with changing X. The change in the ^{13}C NMR shifts on going from X = Cl to X = Br of 11.9 ppm, and on going from X = Br to X = I of 34.9 ppm reflect the electronegativity difference between the halogens. The difference between the values of X = Br and X = I is however significantly greater for the W complex than for the Fe complex (34.9 *vs*. 19 ppm). The ^{13}C resonances of the Cp rings shift marginally downfield as X varies from Cl to Br to I. This is as observed for the iron complexes and is probably also due to electronic effects, relating to the varying electronegativities and π-donor abilities of the halides. As for the iron complexes, the observed chemical shifts can be rationalised by the existence in solution of the canonical form $^{\delta+}W\overset{\cdots}{=\!=}CH_2\cdots X^{\delta-}$. This would result in the withdrawal of electrons from the cyclopentadienyl group, reducing the ring current and hence causing an upfield shift of the Cp resonance. Such an effect would be greatest for X = Cl, as is observed.

The ^{13}C NMR assignments of complex **(1)** were made with the aid of an APT NMR experiment. The assignments for the CH_2 and CH_3 carbons agree well with those of $[CpFe(CO)_2CH_2OCH_3]$ [see chapter 7] and with other ^{13}C NMR data obtained for methoxymethyl complexes [9,10].

Low resolution electron impact mass spectra were obtained for complexes **(2a)** - **(2c)**. The intensities of the major peaks of these complexes are reported in Table 3.2 with probable assignments. The mass spectra of complexes **(2a)**, **(2b)** and **(2c)** show molecular ions of low intensity (3-5%). All spectra show peaks corresponding to $[C_3H_3]^+$ (m/z 39), which is probably due to the fragmentation of the Cp group. Complexes **(2b)** and **(2c)** also show peaks due to $[C_2H_2]^+$ (m/z 26). Peaks due to the ions $[W]^+$ (m/z 184), $[C_3H_3W]^+$ (m/z 223), $[CpW]^+$ (m/z 249), $[CpW(CO)]^+$ (m/z 277), $[CpW(CO)_2]^+$ (m/z 305) and $[CpW(CO)_3]^+$ (m/z 333) are observed in

Table 3.2: Some Mass Spectral Data for $[CpW(CO)_3CH_2X]$

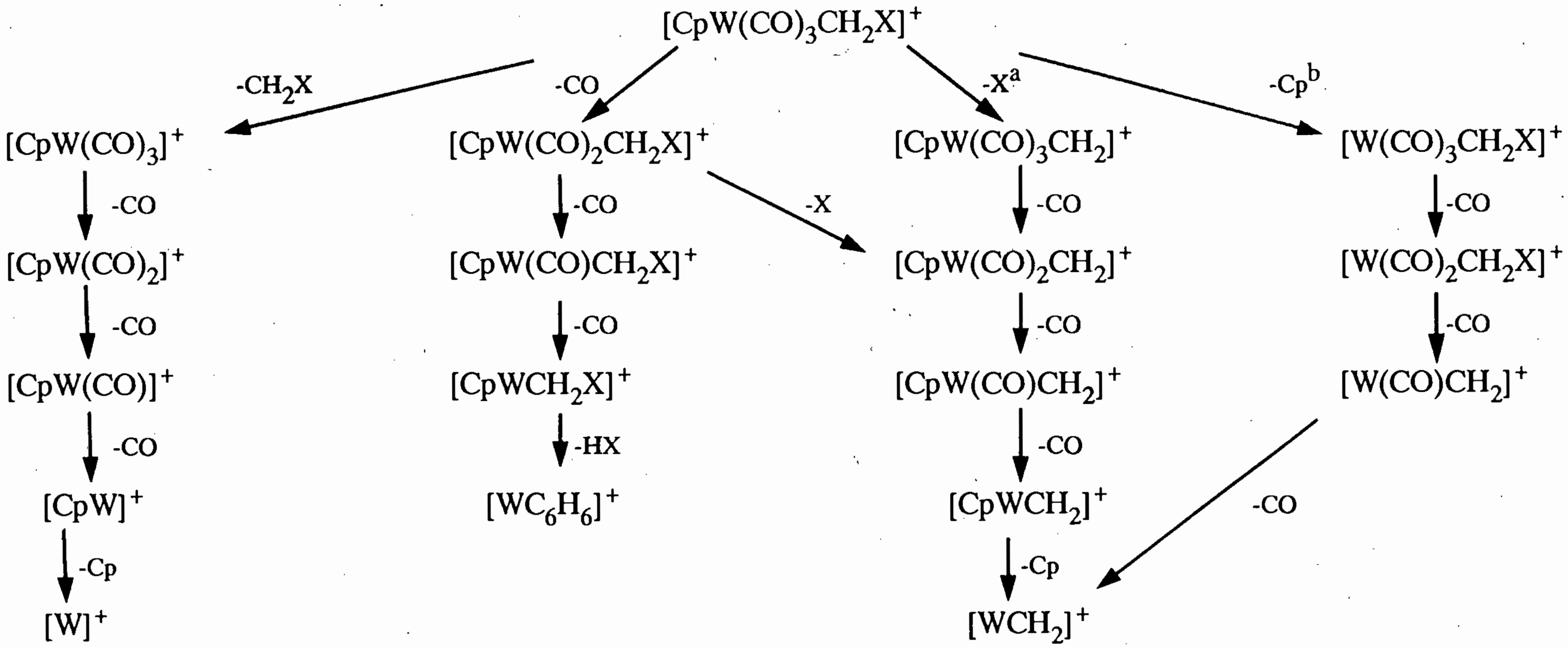
Ion[a]	Relative peak intensities (%)[b]		
	X = Cl	X = Br	X = I
M	5	3	3
M - CO	6	18	61
M - 2CO	11	36	48
M - 3CO	100	100	100
M - 3CO - HX	11	37	17
M - 2CO - HX - Cp	0	3	2
M - CH_2X {= $CpW(CO)_3$}	4	7	4
M - CH_2X - CO {= $CpW(CO)_2$}	10	13	11
M - CH_2X - 2CO {= CpW(CO)}	12	13	10
M - CH_2X - 3CO {= CpW}	24	22	20
M - X	0	6	6
M - CO - X	6	18	25
M - 2CO - X	8	21	43
M - 3CO - X	16	35	79
M - 3CO - X - Cp	3	0	0
M - Cp	5	0	0
M - Cp - CO	7	2	0
M - Cp - 2CO	10	13	0
M - Cp - 3CO	14	18	0
M - CH_2X - Cp	20	0	3
M - CH_2X - Cp - CO	0	0	6
M - CH_2X - Cp - 2CO	3	6	11
WX	24	20	0
C_3H_3W	20	12	3
C_3H_2W	10	10	1
W	4	5	4
HX	1	0	21
X	0	0	9
C_3H_3	6	12	5
C_3H_2	3	3	2
CH_2X	4	0	0
C_2H_2	0	5	5
Cp_2W	0	15	2

a: M = $[CpW(CO)_3CH_2X]$; all ions have a single positive charge; ion refers to probable assignment

b: Peak intensities are relative to the base peak at m/z 298 (X = Cl); m/z 342/344 (X = Br); m/z 390 (X = I) all the spectra. The base peak for all the spectra corresponds to $[CpWCH_2X]^+$.

The $[CpW(CO)_3CH_2X]$ (X = Cl, Br, I) complexes appear to fragment according to two main pathways, illustrated in **Scheme 3.1**. The first possible fragmentation of the molecular ion involves the loss of "CH_2X", resulting in the formation of $[CpW(CO)_3]^+$, which then loses CO sequentially to form $[CpW(CO)_2]^+$, $[CpW(CO)]^+$ and $[CpW]^+$, all of which ions are observed. The second pathway involves the loss of CO from the molecular ion to give $[CpW(CO)_2CH_2X]^+$, which in turn can fragment in two ways: (a) further sequential losses of CO to give $[CpW(CO)CH_2X]^+$ and $[CpWCH_2X]^+$; or (b) loss of X to give $[CpW(CO)_2CH_2]^+$ - the carbene species - which then loses CO sequentially to form $[CpW(CO)CH_2]^+$ and $[CpWCH_2]^+$. An ion corresponding to $[WCH_2]^+$ is observed in the mass spectrum of complex **(2a)**, whilst an ion assignable to $[CpW(CO)_3CH_2]^+$ is observed in the spectra of **(2b)** and **(2c)**. As observed for $[CpFe(CO)_2CH_2X]$, the relative abundance of the proposed carbene species appears to depend on the relative abilities of the halogens as leaving groups (I >> Br > Cl).

Steven and Beauchamp have shown that $[CpFe(CO)_2CH_2]^+$ is observed in the electron impact mass spectrum of $[CpFe(CO)_2CH_2OCH_3]$ if protonation agents are present [11]. The probable formation of carbene species in the electron impact mass spectra of complexes **(2a)** - **(2c)** in the absence of protonation agents thus suggests that the $W{=}CH_2$ carbene species are formed more easily from $[CpW(CO)_3CH_2X]$ under electron impact mass



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a: This pathway is only observed for X = Br and I (compounds **(2b)** and **(2c)**)

b: This pathway is only observed for X = Cl and Br (compounds **(2a)** and **(2b)**)

SCHEME 3.1: An illustration of possible mass spectral fragmentations giving rise to the major ions observed for complexes **(2)**

spectral conditions. Similarly, the $[CpFe(CO)_2CH_2X]$ (X = Cl, Br, I) complexes appear to readily form $Fe=CH_2$ carbene species under electron impact mass spectral conditions (see chapter 2).

A third minor fragmentation pathway appears to apply to compounds (**2a**) and (**2b**) only. This involves the loss of Cp from the molecular ion to form $[W(CO)_3CH_2X]^+$ (X = Cl, Br), followed by the sequential loss of CO to finally yield $[WCH_2X]^+$.

3.3 REACTIVITY OF $[CpW(CO)_3CH_2X]$ (X = Cl, Br, I) WITH NEUTRAL NUCLEOPHILES.

(i) IN THF

$[CpW(CO)_3CH_2Cl]$ reacts with PPh_3 in THF to give an ylide type product $[CpW(CO)_3CH_2PPh_3]^+$, which was isolated as its BPh_4^- salt. This product has been reported before [2]. In contrast, $[CpW(CO)_3CH_2Cl]$ reacted with PMe_2Ph in refluxing THF to give the disubstituted product $[CpW(PMe_2Ph)_2(CO)_2]^+$, which was isolated as its PF_6^- salt.

$[CpW(CO)_3CH_2Br]$ was reacted with excess L (L = PMe_3, $PEtPh_2$) to give the ylide type products $[CpW(CO)_3CH_2L]^+$ isolated as their BPh_4^- salts (Tables 3.3 and 3.4). The reaction of $[CpW(CO)_3CH_2Br]$ with bis(diphenylphosphino)ethane (dppe) gave the bridged dicationic ylide complex $[CpW(CO)_3CH_2P(Ph)_2(CH_2)_2P(Ph)_2CH_2W(CO)_3Cp]^{2+}$. This latter complex is unstable in solution and was characterised by IR spectroscopy, elemental analysis and partially by ^1H NMR spectroscopy (Table 3.5).

(ii) IN METHANOL

Complex (**2a**) reacted with L (L = PPh_3, $PMePh_2$, PMe_2Ph, $PEtPh_2$, $AsPh_3$) in refluxing methanol to give the ylide type complexes $[CpW(CO)_3CH_2L]^+$ in good yield. Similarly, complex (**2b**) reacted with $AsPh_3$ to give the cationic ylide complex $[CpW(CO)_3CH_2AsPh_3]^+Br^-$, which was further reacted with $[NBu^n{}_4]PF_6$ to give $[CpW(CO)_3CH_2AsPh_3]PF_6$.

To gain a greater insight into the reactions of the halomethyl tungsten complexes with ligands, L, the reaction of complex (**2a**) with $AsPh_3$ in methanol was studied in detail. The reaction of $[CpW(CO)_3CH_2Cl]$ with $AsPh_3$ in refluxing methanol gave a mixture of two products. Extraction of the crude reaction product with hexane and cooling this extract to -78°C gave a fine yellow precipitate of $[CpW(CO)_3H]$, as identified by ^1H NMR, IR and mass spectroscopy [12], in *ca*.49% yield. The other product of this reaction was the ylide complex $[CpW(CO)_3CH_2AsPh_3]Cl$, which was isolated as its PF_6^- salt in 22% (recrystallized) yield. Similarly, the reaction of $[CpW(CO)_3CH_2Br]$ with $AsPh_3$ in refluxing methanol gave $[CpW(CO)_3H]$ and $[CpW(CO)_3CH_2AsPh_3]^+$ in 57 and 32 % yields respectively.

Dissolving $[CpW(CO)_3CH_2Cl]$ (**2a**) in methanol and monitoring this solution, at room temperature, by IR spectroscopy showed that complex

(2a) is totally converted into [CpW(CO)$_3$CH$_2$OCH$_3$] (1) after *ca*. 3 hours. Removal of the solvent from this reaction mixture and work-up of the yellow residue gave a yellow solid which was shown to be a mixture of complexes (1) and (**2a**), with the former predominating slightly. A possible explanation for this partial reversal of the above reaction is that HCl forms in solution and that this reacts with (1), on evaporation of the methanol, to form complex (**2a**).

Dissolving complex (**2a**) in methanol, allowing it to react to completion to form complex (1), then adding AsPh$_3$ and refluxing the solution causes no difference in the types or ratios of products formed. However, when freshly prepared [CpW(CO)$_3$CH$_2$OCH$_3$] - according to the method shown in equation 1 - is dissolved in methanol and refluxed in the presence of AsPh$_3$, no reaction takes place; *i.e.* no ylide type product or hydride is formed (as determined by IR monitoring of the ν(CO) region). It thus seems clear that in the reaction of [CpW(CO)$_3$CH$_2$Cl] with AsPh$_3$ in methanol, although all of complex (**2a**) appears to react with methanol to form complex (1), it is a small equilibrium concentration of the chloromethyl complex (**2a**) which reacts with AsPh$_3$ to form the ylide complex.

In an attempt to determine how the hydride complex formed and what its precursor was, a pure, freshly prepared sample of [CpW(CO)$_3$CH$_2$OCH$_3$] (1) was refluxed in methanol. Even after 11 hours of reflux, no reaction was observed to have taken place (by IR monitoring of the ν(CO) region) *i.e.* no [CpW(CO)$_3$H] was observed to have formed. Similarly, no reaction occurred on reflux of complex (**1**) in acetonitrile. Reflux of

$[CpW(CO)_3CH_2Cl]$ in methanol, however, led to the quantitative formation of the hydride complex $[CpW(CO)_3H]$ after 3 hours, as determined by IR and ^1H NMR spectroscopy.

Reacting $[CpW(CO)_3CH_2Cl]$ with $AsPh_3$ in refluxing monodeuteromethanol (CH_3OD) gave a mixture of the ylide type product (3h) as well as a yellow, hexane soluble product. The ^1H NMR of this yellow product showed the expected Cp peak of $[CpW(CO)_3H]$ and a peak at $\delta = -7.21$ ppm. This high field peak integrated for 0.5 H relative to the Cp peak. It thus appeared that an equimolar mixture of $[CpW(CO)_3H]$ and $[CpW(CO)_3D]$ was present. The mass spectrum of this mixture also showed the presence of both $[CpW(CO)_3H]$ and $[CpW(CO)_3D]$.

It may therefore be that the hydroxyl proton of the solvent is at least a partial source of the hydride. It also seems clear that only $[CpW(CO)_3CH_2Cl]$ interacts with the methanol to form the hydride complex, with no reaction occurring between the methoxymethyl complex (1) and methanol. It is indeed possible that the methanol is the only source of the hydride. The presence of the $[CpW(CO)_3H]$ complex in the reaction carried out in CH_3OD may be due to two reasons. Firstly, $[CpW(CO)_3D]$ may react with other proton sources (solvent impurities, decomposition products) to form $[CpW(CO)_3H]$, and secondly, CH_3OH may form in the interaction between CH_3OD and the methoxymethyl complex (1).

Alternatively, the hydride may form from an α-migration of hydrogen from the CH_2 carbon atom to the metal. Such an α-migration (1, 2 shift) of a hydride has been observed previously for a cyclopentadienyl tungsten methyl complex [13] and 1, 2 shifts are also known for other haloalkyl metal systems [14]. The deuteride could then form by H/D exchange in refluxing CH_3OD.

(iii) IN ACETONITRILE

Like the iron $[CpFe(CO)_2CH_2X]$ system [chapter 2, 15], the reactions of $[CpW(CO)_3CH_2X]$ (X = Cl, Br) with ligands, L, in acetonitrile can give two types of ligand product - namely an ylide type product $[CpW(CO)_3CH_2L]X$ (**3**) and a disubstituted product $[CpWL_2(CO)_2]X$ (**4**). The reactions of complexes (**2a**), (**2b**) and (**2c**) with neutral nucleophiles, L, in acetonitrile are summarised in equations 5 to 8.

$$[CpW(CO)_3CH_2X] + L \longrightarrow [CpW(CO)_3CH_2L]X \qquad (\underline{5a})$$

$$[CpW(CO)_3CH_2L]X + NaBPh_4 \longrightarrow [CpW(CO)_3CH_2L]BPh_4 + NaX \qquad (\underline{5b})$$

X = Cl: L = PMe_3 (**3a**), $PMePh_2$ (**3c**) , $PEtPh_2$ (**3e**) , PPh_3 (**3f**), $AsPh_3$ (**3h**) and NMe_3 (**3i**);
no reaction for PBu^t_3, SMe_2;

X = Br: L = PMe_3 (**3a**), PMe_2Ph (**3b**), $PMePh_2$ (**3c**), $PEtPh_2$ (**3e**), PPh_3 (**3f**), PCy_3 (**3g**), $AsPh_3$ (**3h**), NMe_3 (**3i**), py (**3j**) and SMe_2 (**3k**);
no reaction for PBu^t_3, $P(OMe)_3$, NEt_3;

X = I: L = PEt_3 (**3d**), PPh_3 (**3f**).

$$[CpW(CO)_3CH_2X] + L \longrightarrow \tfrac{1}{2}[CpW(L)_2(CO)_2]X + \ldots \qquad (\underline{6a})$$

$$[CpW(L)_2(CO)_2]X + [NBu^n{}_4]PF_6 \longrightarrow [CpW(L)_2(CO)_2]PF_6 + [NBu^n{}_4]X \qquad (\underline{6b})$$

X = Cl, L = PMe_2Ph (**4b**).

$$[CpW(CO)_3CH_2X] + 2L \longrightarrow [CpW(L)_2(CO)_2]X \qquad (\underline{7a})$$

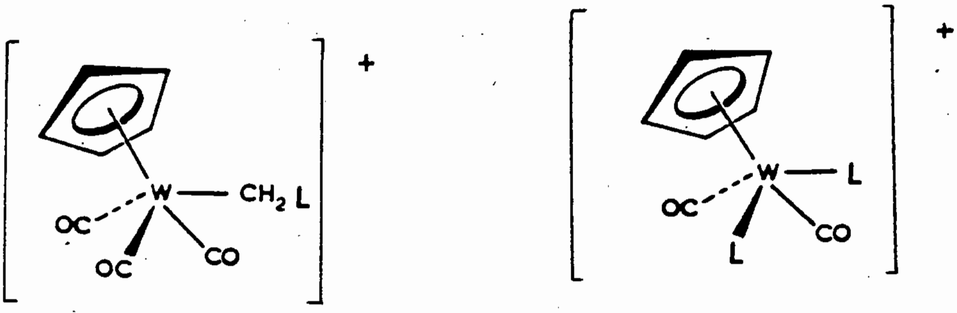
$$[CpW(L)_2(CO)_2]X + NaBPh_4 \longrightarrow [CpW(L)_2(CO)_2]BPh_4 + NaX \qquad (\underline{7b})$$

X = Cl, L = PMe_3 (**4a**), PMe_2Ph (**4b**).

$$2\ [CpW(CO)_3CH_2Br] + dppe \longrightarrow [\{CpW(CO)_3CH_2\}_2(\mu\text{-dppe})]Br_2 \qquad (\underline{8a})$$

$$[\{CpW(CO)_3CH_2\}_2(\mu\text{-dppe})]Br_2 + 2\ NaBPh_4 \longrightarrow [\{CpW(CO)_3CH_2\}_2(\mu\text{-dppe})](BPh_4)_2 + NaX \qquad (\underline{8b})$$

As can be seen from equations <u>5</u> to <u>7</u>, the ylide product is formed in nearly all cases in the reaction of complex (**2a**) with neutral nucleophiles, L. The ligand PMe_2Ph, however, reacts with (**2a**) to form only the disubstituted product {even if used in a 1:1 ratio with complex (**2a**)} (eqn. <u>6a</u>), whilst a 1 : 1 ratio of PMe_3 to (**2a**) reacts to give a mixture of $[CpW(CO)_3CH_2PMe_3]^+$ and $[CpW(PMe_3)_2(CO)_2]^+$. This result is interesting since PMe_3 has a higher pK_a and smaller cone angle than PMe_2Ph and thus might have been expected to form only the disubstituted product for both electronic and steric reasons. The IR data indicates that the carbonyl groups are trans to each other in complex (**4b**) [16]. The complexes (**3**) and (**4**) are represented in **figure 2**.



compound	L
3a	PMe_3
3b	PMe_2Ph
3c	$PMePh_2$
3d	PEt_3
3e	$PEtPh_2$
3f	PPh_3
3g	PCy_3
3h	$AsPh_3$
3i	NMe_3
3j	py
3k	SMe_2

compound	L
4a	PMe_3
4b	PMe_2Ph

Figure 2 : Molecular formulae for complexes (3) and (4)

(iv) DISCUSSION

Whilst 2 moles of $PMePh_2$ react with 1 mole of $[CpFe(CO)_2CH_2Cl]$ to give a disubstituted ligand product, the identical reaction of $PMePh_2$ with **(2a)** only forms an ylide type product. This difference may be due to a greater degree of steric crowding existing at the tungsten centre. A further difference between the iron and tungsten systems is that, whereas the iron bromomethyl complex reacts with $PBu^t{}_3$ to give an ylide type product, its tungsten analogue **(2b)** does not react with $PBu^t{}_3$. In contrast, $[CpFe(CO)_2CH_2Cl]$ does not react with PPh_3 in THF, whilst $[CpW(CO)_3CH_2Cl]$ does react to form the ylide complex. Like the iron system, however, neither complex **(2a)** nor **(2b)** react with NEt_3 or $P(OMe)_3$.

The reactivity of complex **(2b)** shows differences to that of complex **(2a)**. Thus, **(2a)** does not react with SMe_2 in CH_3CN or THF, whilst **(2b)** does react in CH_3CN to form complex **(3k)**. Also, unlike complex **(2b)**, complex **(2a)** reacts with PMe_2Ph to form the disubstituted product **(4b)**. In contrast, complex **(2b)** reacts with PMe_2Ph to form the ylide type product **(3b)**. These results clearly demonstrate the effect that the halogen has on the reactivity of $[CpW(CO)_3CH_2X]$.

The solvent can clearly affect the course of the reaction. Thus, complex **(2a)** reacts with PMe_2Ph in CH_3CN to form the disubstituted product **(4b)**, whereas in methanol the reaction of complex **(2a)** with PMe_2Ph gives the ylide type product **(3b)**. The solvent effect is further illustrated by the fact that complex **(2a)** reacts with $PMePh_2$ in CH_3CN or

CH_3OH to give the ylide product (**3c**), whereas no reaction takes place between these reagents in THF.

The data for the new ylide complexes reported in equation 5 and complex (**4b**) are reported in Tables 3.3 - 3.5. As can be seen, the ylide complexes, excluding $[CpW(CO)_3CH_2PMe_3]BPh_4$ and $[CpW(CO)_3CH_2PMe_2Ph]BPh_4$, melt or decompose between 150 and 200°C. The PMe_3 complex decomposes at a much higher temperature, namely above 272°C, whilst the PMe_2Ph complex melts at the unusually low temperature range of 82-84 °C. All the ylide complexes have very similar infrared stretching frequencies in the carbonyl region. These frequencies are at a *ca.* 3-5 cm^{-1} higher frequency than those of complexes (**2**). This is as expected from the "synergic" effect *i.e.* as the charge on the metal decreases, the extent of the back donation from metal to ligand decreases, the M-C bond becomes weaker and the C≡O bond becomes stronger [17,18].

Of interest are the ^1H NMR resonances of the $C\underline{H}_2L$ protons which correlate linearly with the pK_a of the bonded ligand, L (**Figure 3**).

Table 3.3:

Data for complexes (**3a**) - (**3k**)

Compound	no.	m.p. (°C)	IR (νCO)^a (cm^{-1})	Elemental^b Analysis
$[CpW(CO)_3CH_2PMe_3]BPh_4$	**3a**	>272(dec)	2033s, 1953(sh), 1925s	C: 58.20 (58.21) H: 4.85 (4.85)
$[CpW(CO)_3CH_2PMe_2Ph]BPh_4$	**3b**	176-180	3034s, 1951(sh), 1928s	C: 61.15 (61.17) H: 4.85 (4.72)
$[CpW(CO)_3CH_2PMePh_2]BPh_4$	**3c**	82-84	2035s, 1950(sh), 1931s	C: 63.70 (63.71) H: 4.60 (4.62)
$[CpW(CO)_3CH_2PEt_3]BPh_4$	**3d**	154-158	2027s, 1940(sh) 1916s	C: 60.20 (59.67) H: 5.20 (5.35)
$[CpW(CO)_3CH_2PEtPh_2]BPh_4$	**3e**	180-190	2035s, 1953(sh), 1929s	C: 63.55 (64.06) H: 5.00 (4.77)
$[CpW(CO)_3CH_2PPh_3]BPh_4$	**3f**	192-198^c	2035s, 1953(sh), 1933s	d d
$[CpW(CO)_3CH_2PCy_3]BPh_4$	**3g**	e	2031s, 1950m, 1921vs	e e
$[CpW(CO)_3CH_2NC_5H_5]BPh_4$	**3h**	161-163	2033s, 1953m, 1927s	C: 61.20 (61.19) H: 4.40 (4.29) N: 1.95 (1.88)
$[CpW(CO)_3CH_2NMe_3]BPh_4$	**3i**	182-184	2034s, 1957m, 1923s	C: 59.10 (59.57) H: 4.95 (4.96) N: 1.95 (1.93)
$[CpW(CO)_3CH_2SMe_2]BPh_4$	**3j**	168-176 (dec)	2037s, 1954(sh), 1935s	C: 57.25 (57.57) H: 4.60 (4.53)
$[CpW(CO)_3CH_2AsPh_3]BPh_4$	**3k**	175-177	2036s, 1955(sh), 1933s	C: 62.90 (62.90) H: 4.60 (4.31)

a: in CH_2Cl_2 solution b: calculated values in parentheses c: data from ref.[2] d: data in ref.[2]
e: not obtained

Table 3.4:

^{1}H NMR data for complexes **(3a)** - **(3k)** [a]

Compound	$C\underline{H}_2L$	Cp	Ph	Alkyl
$[CpW(CO)_3CH_2PMe_3]BPh_4$	1.38 d (^{2}J = 16.0)	5.78 s	7.82, 7.04 m (20H)	1.76 d (9H,^{2}J = 14.0)
$[CpW(CO)_3CH_2PMe_2Ph]BPh_4$	1.66 d (^{2}J = 17.0)	5.70 s	7.72, 7.29, 6.94 m (25H)	2.07 d (6H,^{2}J = 13.8)
$[CpW(CO)_3CH_2PMePh_2]BPh_4$	2.00 d (^{2}J = 16.4)	5.73 s	7.68, 7.30 m (30H)	2.38 d (6H,^{2}J = 13.2)
$[CpW(CO)_3CH_2PEt_3]BPh_4$	1.26 d (^{2}J = 15.9)	5.79s	7.33, 7.00, 6.84 m (20H)	2.08 dq (6H, ^{3}J(HH) = 7.6, ^{2}J(PH) = 12.2); 1.22dt(9H, ^{3}J(HH) = 7.6, ^{3}J(PH) = 17.5)
$[CpW(CO)_3CH_2PEtPh_2]BPh_4$	1.92 d (^{2}J = 16.0)	5.66 s	7.66, 7.30, 6.89 m (30H)	3.42 m (1H); 2.70 m (1H); 1.23 m (3H)
$[CpW(CO)_3CH_2PPh_3]BPh_4$	2.28 d (^{2}J = 16.5)	5.68 s	7.64, 7.27, 6.91 m (35H)	
$[CpW(CO)_3CH_2PCy_3]BPh_4$	1.21 d (^{2}J = 16.6)	5.83s	7.33, 6.99, 6.72 m (20H)	1.10 m (33H)
$[CpW(CO)_3CH_2NC_5H_5]BPh_4$	4.58 s	5.38 s	7.33, 7.00, 6.92 m (20H)	7.93, 7.59 m (5H)
$[CpW(CO)_3CH_2NMe_3]BPh_4$	3.08 s	5.77 s	7.33, 6.95 m (20H)	3.08 s (9H)
$[CpW(CO)_3CH_2SMe_2]BPh_4$	3.02 s	5.92 s	7.34, 6.87 m (20H)	2.94 s (6H)
$[CpW(CO)_3CH_2AsPh_3]BPh_4$	2.30 s	5.69 s	7.70, 7.30, 7.00 m (35H)	

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a: in CD_3NO_2 relative to TMS (δ = 0.00 ppm); J values in Hz, ^{2}J represents PH coupling unless otherwise stated, s = singlet, d = doublet, m = multiplet, dq = doublet of quartets, dt = doublet of triplets

Table 3.5:

Data for further products obtained from the reactions of complexes (**2**) with ligands L

Compound	m.pt. (°C)	IR(νCO)[a] (cm^{-1})	^{1}H NMR[b] (δ)	Elemental analysis[c]
$[CpW(CO)_3CH_2NMe_3]Br$	d	2030s, 1955m, 1915s	5.86s (Cp), 4.17s (CH_2), 3.16s (Me_3)	C: 59.10 (59.57) H: 4.95 (4.96) N: 1.95 (1.93)
$[CpW(CO)_3CH_2AsPh_3]PF_6$	193-195	2031s, 1944(sh) 1928s	5.68s (Cp), 2.60s (CH_2), 7.68s (Ph_3)	C: 40.58 (40.60) H: 2.76 (2.80)
$[CpW(PMe_2Ph)_2(CO)_2]PF_6$	218-220	1955m 1872vs	5.32t (Cp, $^3J(PH)$ = 2.4), 7.54m (2Ph) 2.18d ($2Me_2$, $^2J(PH)$ = 9.7)	C: 37.75 (38.01) H: 3.70 (3.72)
$[CpW(PMe_3)_2(CO)_2]BPh_4$	e	1956m 1875vs	5.78t (Cp, $^3J(PH)$ = 1.5), 7.34, 6.84m (Ph_4)[f]	e
$[\{CpW(CO)_3CH_2\}_2\{\mu\text{-dppe}\}]$ BPh_4	d	2034s 1955m 1926s	5.59s (Cp), 7.60, 7.30, 6.90m (Ph_6)[g]	C: 63.60 (63.79) H: 4.80 (4.51)

a: in CH_2Cl_2 b: in CD_3NO_2 unless otherwise stated, relative to TMS (δ = 0.00 ppm), J values in Hz
c: calculated values in parentheses d: not obtained e: compound impure f: in acetone-d_6, PMe_3 peak obscured by solvent
g: compound unstable in polar solutions

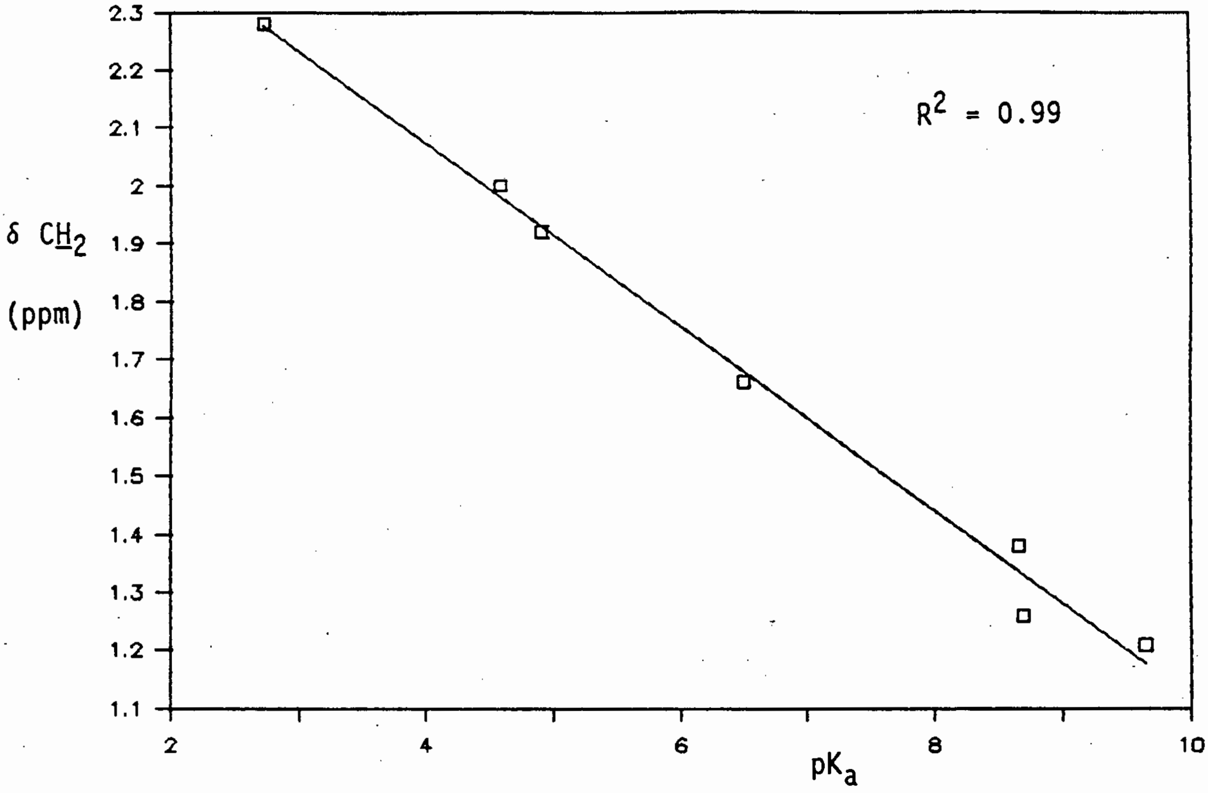

Figure 3: A plot of the pK_a of tertiary phosphines *vs.* $\delta C\underline{H}_2$ of complexes (3a) - (3g)

As can be seen from **Figure 3** , the chemical shift of the $C\underline{H}_2$ protons is directly affected by the pK_a of the attached ligand, with the least squares correlation graph having a very close fit to the experimentally obtained points. The coefficient of determination (R^2) of the least squares plot is 0.99. It may thus be possible to obtain an accurate estimate of the pK_a value of a tertiary phosphine with unknown pK_a using this graph, provided an ylide type product can be made with this ligand. As would be expected, the δ values of the $C\underline{H}_2$ peaks move downfield as the pK_a of the ligand decreases.

The reactions of (**2b**) with PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, py, NMe_3 and SMe_2 in a 1:2 molar ratio in CH_3CN were monitored by ^1H NMR spectroscopy, by determination of the relative intensities of the Cp peaks of starting material and product at room temperature. The rate of the reactions followed the sequence: $NMe_3 \approx PMe_2Ph > PMe_3 > PMePh_2 > SMe_2 > PPh_3 >$ py, with half-life values of 26 min.*, 36 min., 47 min., 85 min., 203 min., 300 min. and 445 min. respectively (± 1 min.) (where $t_{\frac{1}{2}}$ is the time taken for half-completion of the reaction). For the phosphines, the cone angles increase and the pK_a's decrease in the following order: $PMe_3 < PMe_2Ph < PMePh_2 < PPh_3$ (for values, see Table 2.4 in chapter 2). Thus, as with the $[CpFe(CO)_2CH_2X]$ complexes, the ligands with smaller cone angles and larger pK_a values react more quickly, probably because of their greater nucleophilicity and lower steric hindrance. The exception to this sequence is PMe_2Ph, which reacts more quickly than PMe_3, in spite of its greater steric bulk and lower nucleophilicity. The difference (in pK_a and bulk) between these ligands is however very small and the $[CpW(CO)_3CH_2X]$ complexes seem to be particularly reactive towards PMe_2Ph. This was already observed previously when complex (**2a**) reacted with PMe_2Ph to form complex (**4b**), whereas the reaction of (**2a**) with PMe_3 gave a mixture of complexes (**3a**) and (**4a**). Since the ylide type product is believed to be an intermediate [15] in the formation of $[CpW(PMe_2Ph)_2(CO)_2]^+$, the reaction of (**2a**) with PMe_2Ph must also be very fast. Since $PBu^t{}_3$, a ligand with a large pK_a and a large cone angle, does not react with complex (**2b**), the cone angle (steric bulk) of the ligands must be the most important factor in these reactions.

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*The ratio of ligand to metal was 1:2.2

Comparing the rates of the reaction of the ligands PMe_2Ph, $PMePh_2$, PPh_3, SMe_2 and py with $[CpFe(CO)_2CH_2Br]$ (chapter 2) and $[CpW(CO)_3CH_2Br]$, it can be seen that the reactions of the iron bromomethyl complex are between 7 and 21 times faster than those of its tungsten analogue.

Monitoring the intensities of the ^1H NMR spectrum of the Cp peaks of starting material and product at room temperature showed that the rate of the reactions of **(2a)** - **(2c)** with 2 mol PPh_3 under identical conditions follows the order Cl << Br < I, with a reactivity ratio for Br:I of 1:13. The rate for X = Cl is extremely slow, with $t_{\frac{1}{2}}$ not attained after 3 months at room temperature.

The reactions of **(2b)** with various concentrations of PMe_2Ph in CH_3CN were also monitored by ^1H NMR spectroscopy by determining the relative Cp peak intensities of starting material and product at room temperature. The rate of reaction was found to increase significantly with ligand concentrations. In fact, excluding the reaction involving a 1:1 ratio of **(2b)** : PMe_2Ph, the $t_{\frac{1}{2}}$ values correlate linearly (R^2 = 1.00) with the PMe_2Ph concentration for ratios of **(2b)** : PMe_2Ph of 1:2, 1:3 and 1:4 **(Figure 4)**.

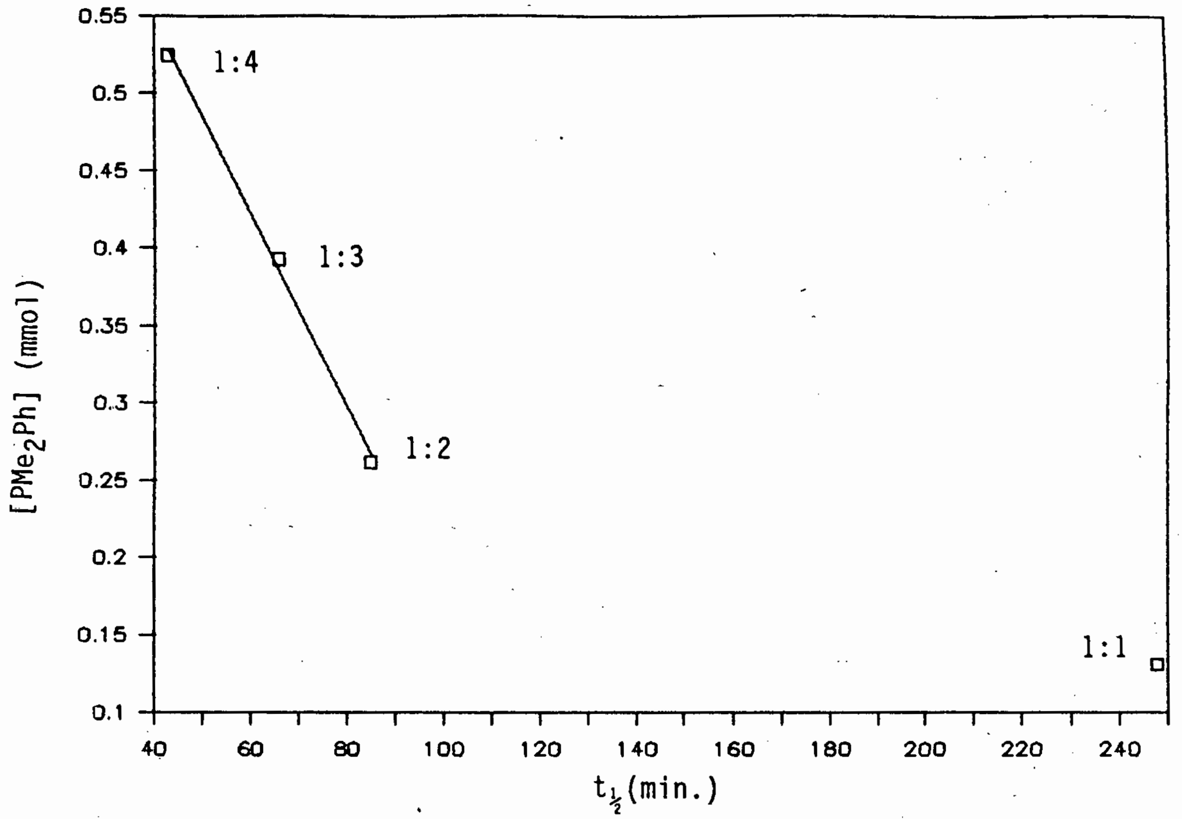
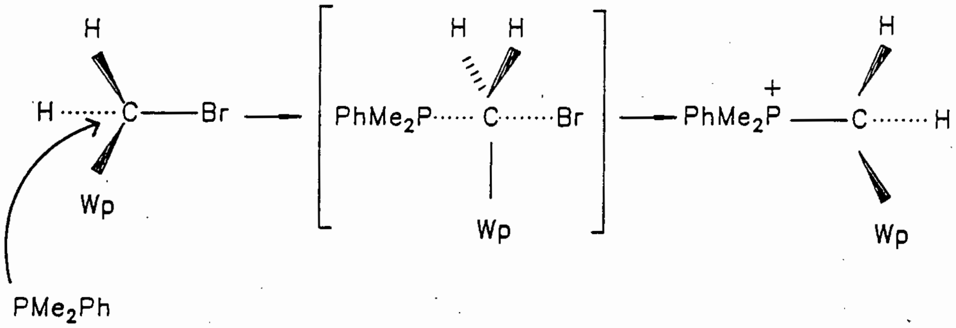


Figure 4: A plot of $t_{\frac{1}{2}}$ *vs*. concentration of PMe_2Ph in the reaction of (**2b**) with PMe_2Ph.

Qualitative kinetic data obtained indicates that, contrary to the mechanism proposed for the reactions of $[CpFe(CO)_2CH_2X]$ with L [2, chapter 2), the reaction of (**2b**) with PMe_2Ph appears to go via a concerted (S_N2) mechanism (**Scheme 3.2**).



SCHEME 3.2: A possible reaction mechanism for the reaction of (**2b**) with PMe_2Ph to form the ylide (**3b**).

The rate equation : Rate = k$[CpW(CO)_3CH_2Br][PMe_2Ph]$ appears to hold for 70 - 75 % of the course of the reaction, with k = 0.59 (±0.02) s^{-1}. No comparative data for the reactions of other halomethyl transition metal complexes with PR_3 are known.

Complexes (**3a**) - (**3g**) can be regarded as quartenary phosphonium salts. A general synthesis of phosphonium salts is in fact the reaction of a tertiary phosphine with an alkyl halide [19]. The mechanism proposed to explain the kinetic data (**Scheme 3.2**) is also supported by the observation that complex (**2b**) can be considered to be a primary alkyl halide and that primary alkyl halides usually react with tertiary phosphines via a S_N2 reaction [20].

3.4 CONCLUSION

Like their iron analogues, the tungsten halomethyl complexes $[CpW(CO)_3CH_2X]$ (X = Cl, Br) are prepared by the reaction of the methoxymethyl complex $[CpW(CO)_3CH_2OCH_3]$ with HX gas. This shows that the W-CH_2X bond is robust since it is not cleaved by HX under these conditions. The complex $[CpW(CO)_3CH_2Br]$ reacts with NaI to form $[CpW(CO)_3CH_2I]$. This iodomethyl complex was found to be more stable than previously believed. Like their iron analogues, the complexes $[CpW(CO)_3CH_2X]$ (X = Cl, Br, I) appear to form the carbene complex $[CpW(CO)_3(CH_2)]^+$ under electron impact mass spectral conditions. The relative abundance of this carbene species reflects the relative strengths of the halogens as leaving groups (I >> Br > Cl).

Like their iron analogues, $[CpW(CO)_3CH_2X]$ react with neutral nucleophiles, L, to give two types of cationic complexes, namely the ylide type complexes $[CpW(CO)_3CH_2L]^+$ (**3**) or the disubstituted complexes $[CpWL_2(CO)_2]^+$ (**4**). The reactions of the tungsten halomethyl complexes are however significantly slower than those of their iron counterparts. In contrast to the iron system, only PMe_2Ph and PMe_3 form complexes of type (**4**). No evidence of complexes of the type $[CpWL(CO)_2\{C(O)CH_2X\}]$ was obtained in any of the reactions. Although complexes of the type $[CpW(CO)_3\{C(O)CH_2X\}]$ are known, they were obtained by a different route [21]. As for the iron complexes, the halide (X), the cone angle of the ligand (L) and the solvent used influence the product type formed, whilst X and the cone angle, pK_a and concentration of L influence the rate of the reaction of $[CpW(CO)_3CH_2X]$ with L.

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CHAPTER 4

THE SYNTHESIS AND PROPERTIES OF THE ω - HALOALKYL COMPLEXES $[(\eta\text{-}C_5R_5)Fe(CO)_2\{(CH_2)_nX\}]$ (R = H, n = 3 - 10, X = Br, I; R = CH_3, n = 3 - 5, X = Br, I) AND $[CpRu(CO)_2\{(CH_2)_nX\}]$ (n = 3, 4; X = Br, I)

4.1 INTRODUCTION

Complexes of the type $[L_yMCH_2X]$ (L_yM = a transition metal and its associated ligands, X = a halogen) are well known (as shown in chapter 1), and some have recently been extensively studied [1-4]. Complexes with longer alkyl chains $[L_yM\{(CH_2)_nX\}]$ (n > 1) are less well known, though some - notably those of Pt [5,6], Mo and W [7,8] - have been studied. The known $[L_yM\{(CH_2)_nX\}]$ complexes have been reviewed in chapter 1. Of the iron haloalkyl complexes of the type $[CpFe(CO)_2\{(CH_2)_nX\}]$, where n > 1, only $[CpFe(CO)_2\{(CH_2)_nBr\}]$ (n = 3-5) [9] and $[CpFe(CO)_2\{(CH_2)_3I\}]$[10] have been reported, although the latter complex was not fully characterised. Very little work has been reported on the reactivity of these ω-haloalkyl complexes, although $[CpFe(CO)_2\{(CH_2)_3Br\}]$ was shown to react with $Na[CpMo(CO)_3]$ to give $[Cp(CO)_2Fe(CH_2)_3Mo(CO)_3Cp]$ in low yield [9]. $[CpFe(CO)_2\{(CH_2)_3I\}]$ was shown to react with $Na[CpRu(CO)_2]$ to give $[Cp(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$ in high yield [10], suggesting that $[CpFe(CO)_2\{(CH_2)_nI\}]$ complexes could be good precursors to heterobimetallic complexes of type $[Cp(CO)_2Fe(CH_2)_nML_y]$ (ML_y = a transition metal and its associated ligands). Heterobimetallic complexes are of interest since they may be model compounds for catalytic processes [11,12] and much work has been devoted to their study in recent years [13]. Haloalkyl transition metal complexes are also precursors for cyclic carbene complexes [7-9], whilst $[CpFe(CO)_2(CH_2)_3Br]$ has recently been shown to have good organic synthetic utility as a cyclopropane precursor [14]. We now report on the syntheses of $[CpFe(CO)_2(CH_2)_nBr]$ (n = 3-10) and $[Cp^*Fe(CO)_2(CH_2)_nBr]$ (n = 3-5), their conversion to $[CpFe(CO)_2(CH_2)_nI]$ and $[Cp^*Fe(CO)_2(CH_2)_nI]$ respectively, and discuss the properties of these haloalkyl complexes.

4.2 PREPARATION OF $[CpFe(CO)_2\{(CH_2)_nX\}]$ (n = 3 - 10, X = Br, I) AND $[Cp^*Fe(CO)_2\{(CH_2)_nX\}]$ (n = 3 - 5, X = Br, I)

The new complexes $[CpFe(CO)_2\{(CH_2)_nBr\}]$ (n = 6-10) were prepared by the general method shown in equation 1 :

$$Na[CpFe(CO)_2] + Br(CH_2)_nBr \longrightarrow [CpFe(CO)_2\{(CH_2)_nBr\}] + NaBr \qquad (\underline{1})$$

(where n = 6 - 10)

The route shown in equation 1 has been used previously to prepare $[CpFe(CO)_2\{(CH_2)_nBr\}]$ (n = 3 - 5) [9]. The above reaction must be carried out at -20°C to prevent the formation of the alkanediyl complexes $[\{CpFe(CO)_2\}_2(CH_2)_n]$. The latter complexes start forming at higher temperatures, presumably by the reaction of $[CpFe(CO)_2\{(CH_2)_nBr\}]$ with unreacted $[CpFe(CO)_2]^-$ [9]. The reaction shown in equation 1 gives a high yield of the ω-bromoalkyl compounds, but difficulty was experienced in separating the product from unreacted $Br(CH_2)_nBr$. This difficulty increased with the length of the alkyl chain, however separation was effected by chromatography.

The complexes $[Cp^*Fe(CO)_2\{(CH_2)_nBr\}]$ (n = 3 - 5) were prepared by a method analogous to that depicted in equation 1, *i.e.*

$$Na[Cp^*Fe(CO)_2] + Br(CH_2)_nBr \longrightarrow [Cp^*Fe(CO)_2\{(CH_2)_nBr\}] + NaBr$$

(2)

(where n = 3 - 5)

It was found that carrying out the above reaction at *ca.* -60°C, instead of -20°C, greatly increased the yield of the desired product by reducing decomposition. The Cp* bromide complexes (where n = 3 - 5) were more easily purified than their Cp analogues. The complex $[Cp^*Fe(CO)_2\{(CH_2)_6Br\}]$ could not, however, be separated from unreacted $Br(CH_2)_6Br$.

$[CpFe(CO)_2\{(CH_2)_nBr\}]$ (n = 3 - 6, 8 - 10) were reacted with NaI to give $[CpFe(CO)_2\{(CH_2)_nI\}]$ in high yield - equation 3:

$$[CpFe(CO)_2\{(CH_2)_nBr\}] + NaI \longrightarrow [CpFe(CO)_2\{(CH_2)_nI\}] + NaBr \qquad (3)$$

(where n = 3 - 6, 8 - 10)

This method had been used previously, with much success, to convert $[CpFe(CO)_2CH_2Br]$ to $[CpFe(CO)_2CH_2I]$ (see chapter 2).

$[CpFe(CO)_2\{(CH_2)_nI\}]$ was also synthesized by the method reported by Knox *et al.* [10] for the synthesis of $[CpFe(CO)_2\{(CH_2)_3I\}]$ - equation 4:

$$Na[CpFe(CO)_2] + I(CH_2)_nI \longrightarrow [CpFe(CO)_2\{(CH_2)_nI\}] + NaI \qquad (\underline{4})$$

This was not found to be a good method, since, except for the complex where n = 3, the product could not be separated from unreacted $I(CH_2)_nI$, and furthermore, the yield of pure product for the complex where n = 3 was low. It is thus critical that the starting material, $[CpFe(CO)_2\{(CH_2)_nBr\}]$, be free from any unreacted $Br(CH_2)_nBr$ in reaction 3.

The complexes $[Cp^*Fe(CO)_2\{(CH_2)_nBr\}]$ (n = 3 - 5) reacted with NaI to give $[Cp^*Fe(CO)_2\{(CH_2)_nI\}]$ in fairly high yield (ca. 65%) - equation 5:

$$[Cp^*Fe(CO)_2\{(CH_2)_nBr\}] + NaI \longrightarrow [Cp^*Fe(CO)_2\{(CH_2)_nI\}] + NaBr \qquad (\underline{5})$$

(where n = 3 - 5)

As for equation 3, it is important that the $[Cp^*Fe(CO)_2\{(CH_2)_nBr\}]$ be free from unreacted $Br(CH_2)_nBr$ for the reaction shown in equation 5 to yield a pure product.

4.3 PROPERTIES OF $[CpFe(CO)_2\{(CH_2)_nX\}]$ (n = 3 - 10, X = Br, I) AND $[Cp^*Fe(CO)_2\{(CH_2)_nX\}]$ (n = 3 - 5, X = Br, I)

All the Cp bromoalkyl compounds are yellow oils or low melting solids, and are stable to air at room temperature for short periods. The Cp* bromoalkyl complexes are yellow crystalline solids and show a much greater stability in air than their cyclopentadienyl analogues, both in solution and in the pure state. Similarly to their bromoalkyl analogues, the Cp iodoalkyl complexes were isolated either as yellow oils or yellow solids, whilst the Cp* iodoalkyl complexes were obtained as lustrous crystalline yellow solids. As was the case with the ω-bromoalkyl complexes, the new Cp* iodoalkyl complexes show greater thermal stability than their cyclopentadienyl analogues. They also show a greater stability in solution. The greater stability of complexes in which the hydrogens of the Cp ring have been substituted with methyl groups has been observed previously. This substitution can also result in a different reactivity of the complexes. These effects are believed to be due to a combination of steric and electronic factors, since the substitution of the hydrogens on the Cp ring with methyl groups can be expected to lead to an increase in the bonding between the η-C_5R_5 ring and the metal, as well as an increase in the steric bulk of the complex [15 - 19].

For both the cyclopentadienyl and pentamethylcyclopentadienyl complexes, the bromides show greater stability in air than the corresponding iodides. In general the Cp iodo complexes have higher melting points than the corresponding bromides. In contrast the melting points of the Cp* bromo and corresponding iodo complexes are very similar for n = 3 and 5, and the bromide has a higher melting point than the iodide for n = 4. The melting points of the Cp* complexes decrease as n increases for each series. The characterization data for $[CpFe(CO)_2\{(CH_2)_nX\}]$ (X = Br, I) is reported in Tables 4.1 - 4.3. The data for the Cp* complexes is reported in Tables 4.4 - 4.6.

IR

From Tables 4.1 and 4.4 it can be seen that there is no significant change in the positions of the carbonyl bands in the IR spectra between the bromo and corresponding iodo complexes, and that there is only a very slight trend towards lower wave numbers as the carbon chain lengthens from n = 3 to n = 5. No change is seen in the position of the carbonyl bands beyond n = 5 for the Cp complexes. As is generally found, the $\nu(CO)$ for the Cp* complexes is lower than the $\nu(CO)$ for the analogous Cp complexes by about 20 cm^{-1}. This is believed to be due to the increase in electron density on the metal (caused by the Cp* group) which results in increased back-bonding to the carbonyl groups, and hence, a lower $\nu(CO)$ [20].

TABLE 4.1

Data for [CpFe(CO)$_2${(CH$_2$)$_n$X}]

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

a: measured in hexane, all bands are strong. b: data in ref.[9]. c: not obtained.

TABLE 4.2

^{1}H NMR data for $[\mathrm{CpFe(CO)_2\{(CH_2)_nX\}}]^a$

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

a: measured in CDCl$_3$ relative to TMS (δ = 0.00 ppm), α-CH$_2$ refers to the protons on the CH$_2$ α to iron etc.

b: peaks reported below this line could not be assigned

TABLE 4.3

^{13}C NMR data for $[Cp(CO)_2Fe\{(CH_2)_nX\}]^a$

n	X	CO	Cp	α-$\underline{C}H_2$	-$\underline{C}H_2X$	-$\underline{C}H_2CH_2X$	β-$\underline{C}H_2$	γ-$\underline{C}H_2$	δ-$\underline{C}H_2$	ϵ-$\underline{C}H_2$
3	Br	216.49	84.97	-0.82	35.58	40.90				
	I	216.51	84.86	1.90	9.32	41.85				
4	Br	216.73	84.97	1.34	33.56	35.90	37.03			
	I	216.89	85.01	1.14	7.28	37.96	38.63			
5	Br	217.59	85.29	2.88	32.54	34.25	37.21	33.15		
	I	216.96	84.92	2.59	7.41	33.00	36.67	35.20		
6	Br	217.10	85.01	3.04	34.18	32.92	38.00^b	33.87^b	27.90	
	I	217.02	84.79	2.89	7.24	33.68	37.98	30.25	33.64	
7	Br	217.62	85.02	3.41	34.01	32.81	38.05	34.50	28.16^b	28.30^b
									———	———^{c}
9	Br	217.09	84.98	3.52	33.93	32.61	38.04	34.57	(29.25, 29.02, 28.51, 27.94)^b(4 x $\underline{C}H_2$)	
	I	217.70	85.28	3.69	7.42	33.55	38.26	34.79	(30.47, 29.45, 29.25, 28.52)^b(4 x $\underline{C}H_2$)	
10	Br	217.98	85.81	3.37	33.77	32.47	37.93	34.48	(29.22, 29.06, 28.97, 28.37, 27.81)^b(5 x $\underline{C}H_2$)	
	I	217.45	85.45	3.89	7.56	33.64	38.44	34.94	(30.60, 29.69, 29.51, 29.44, 28.62)^b(5 x $\underline{C}H_2$)	

a: measured in $CDCl_3$, peaks are externally referenced to TMS (δ = 0.00 ppm), α-CH_2 refers to the CH_2 carbon α to iron.
b: peak assignments uncertain. c: values below this line could not be assigned

TABLE 4.4

Data for $[\mathrm{Cp^*Fe(CO)_2\{(CH_2)_nX\}}]$

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

a: measured in hexane, all bands are strong.

TABLE 4.5

^{1}H NMR data and assignments for $[Cp^*Fe(CO)_2\{(CH_2)_nX\}]^a$

n	X	$C_5(C\underline{H}_3)_5$	α-$C\underline{H}_2$	β-$C\underline{H}_2$	γ-$C\underline{H}_2$	δ-$C\underline{H}_2$	ϵ-$C\underline{H}_2$
3	Br	1.73s (15H)	0.78m (2H)	1.93m (2H)	3.32t (2H, ^3J = 7.5)		
	I	1.73s (15H)	0.78m (2H)	1.92m (2H)	3.12t (2H, ^3J = 7.6)		
4	Br	1.70s (15H)	0.86m (2H)	1.53m (2H)	1.88m (2H)	3.40t (2H, ^3J = 7.1)	
	I	1.68s (15H)	0.84m (2H)	1.47m (2H)	1.85qn (2H, ^3J = 7.2)	3.16t (2H, ^3J = 7.3)	
5	Br	1.68s (15H)	0.89m (2H)	1.43m (4H)		1.84m (2H, ^3J = 6.7)	3.36t (2H, ^3J = 6.9)
	I	1.71s (15H)	0.90m (2H)	1.41m (4H)		1.84qn (2H, ^3J = 6.6)	3.17t (2H, ^3J = 7.3)

a: measured in $CDCl_3$ relative to TMS (δ = 0.00 ppm), α-CH_2 refers to the protons on the CH_2 α to Fe.

TABLE 4.6

^{13}C NMR data for $[Cp^*Fe(CO)_2\{(CH_2)_nX\}]$[a]

n	X	$\underline{C}O$	$\underline{C}_5(CH_3)_5$	$C_5(\underline{C}H_3)_5$	α-$\underline{C}H_2$	β-$\underline{C}H_2$	γ-$\underline{C}H_2$	δ-$\underline{C}H_2$	ϵ-$\underline{C}H_2$
3	Br	218.97	94.98	9.30	9.54	40.80	36.75		
	I	218.97	94.96	9.32	12.66	41.45	10.97		
4	Br	219.33	94.86	9.30	12.01	36.05	38.70	33.93	
	I	219.27	94.81	9.30	11.72	38.40	39.42	7.30	
5	Br	219.48	94.77	9.27	13.30	36.80[b]	34.51[b]	32.80	34.51
	I	219.46	94.78	9.30	13.28	36.51[b]	36.60[b]	33.59	7.93

a: measured in $CDCl_3$ relative to TMS (δ = 0.00 ppm), α-CH_2 refers to the CH_2 carbon α to iron.

b: assignment ambiguous *i.e.* the assignments could be interchanged.

^{1}H and ^{13}C NMR

The ^{1}H NMR data for the Cp complexes are shown in Table 4.2. Assignments for this data were made as far as possible using COSY and HETCOR experiments. The -C$\underline{H}_2$Br and -C$\underline{H}_2$CH$_2$Br proton peaks show no further shift on increasing chain length after n = 5, suggesting that the inductive or steric efect of the iron group is no longer felt by the terminal protons at chain lengths exceeding five carbons. The up-field shift of 0.2 to 0.4 ppm of the C$\underline{H}_2$X peaks as X changes from Br to I is as expected owing to the difference in their electronegativities. The effect of the halogen rapidly diminishes along the carbon chain. **Figure 1** shows the ^{1}H NMR spectrum and **Figure 2** shows the COSY of [CpFe(CO)$_2${(CH$_2$)$_3$Br}].

Assignments of the ^{13}C NMR data were done as far as possible by using COSY and HETCOR experiments, as well as comparisons with the ^{13}C NMR of alkyl halides [21] and [CpFe(CO)$_2$R] (R = alkyl group) complexes [22]. The chain length or halogen do not appear to affect the position of the $\underline{C}$O peaks. Similarly, the chain length has no effect on the δ values of the Cp peaks; however, the Cp peaks of the bromide complexes tend to be at marginally higher field values than those of the corresponding iodides. The effect of the halogen on the δ value of the CH$_2$ carbon α to iron for the compounds where n = 3 and 4 is very apparent. At greater values of n the effect of the halogen on the α carbon diminishes with increasing n. The peak due to the α carbon is shifted up-field for those complexes with smaller values of n. This is contrary to what one would expect considering the inductive effect of the halogens. Of

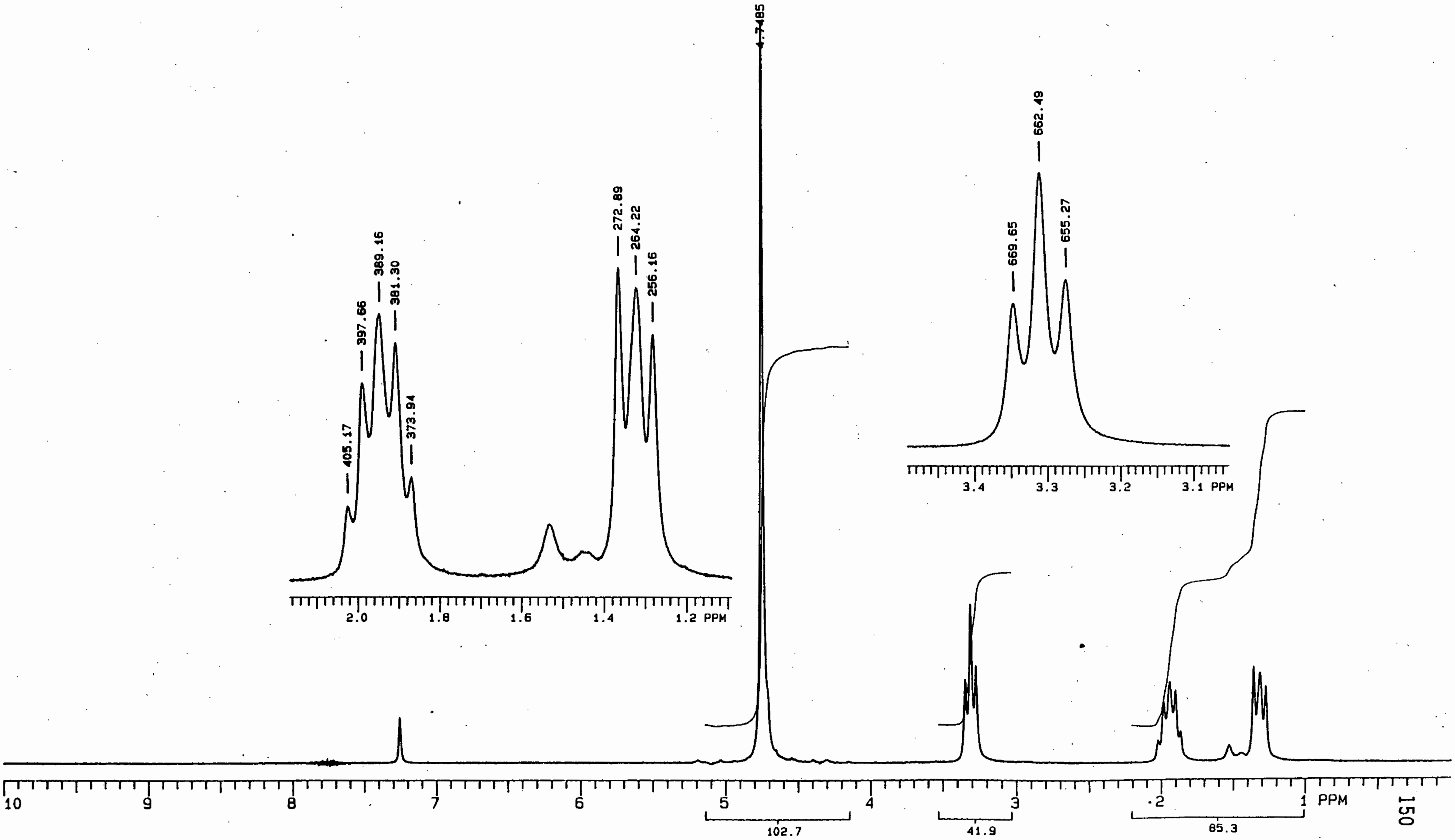


Figure 1: ^{1}H NMR spectrum of [CpFe(CO)$_2${(CH$_2$)$_3$Br}].

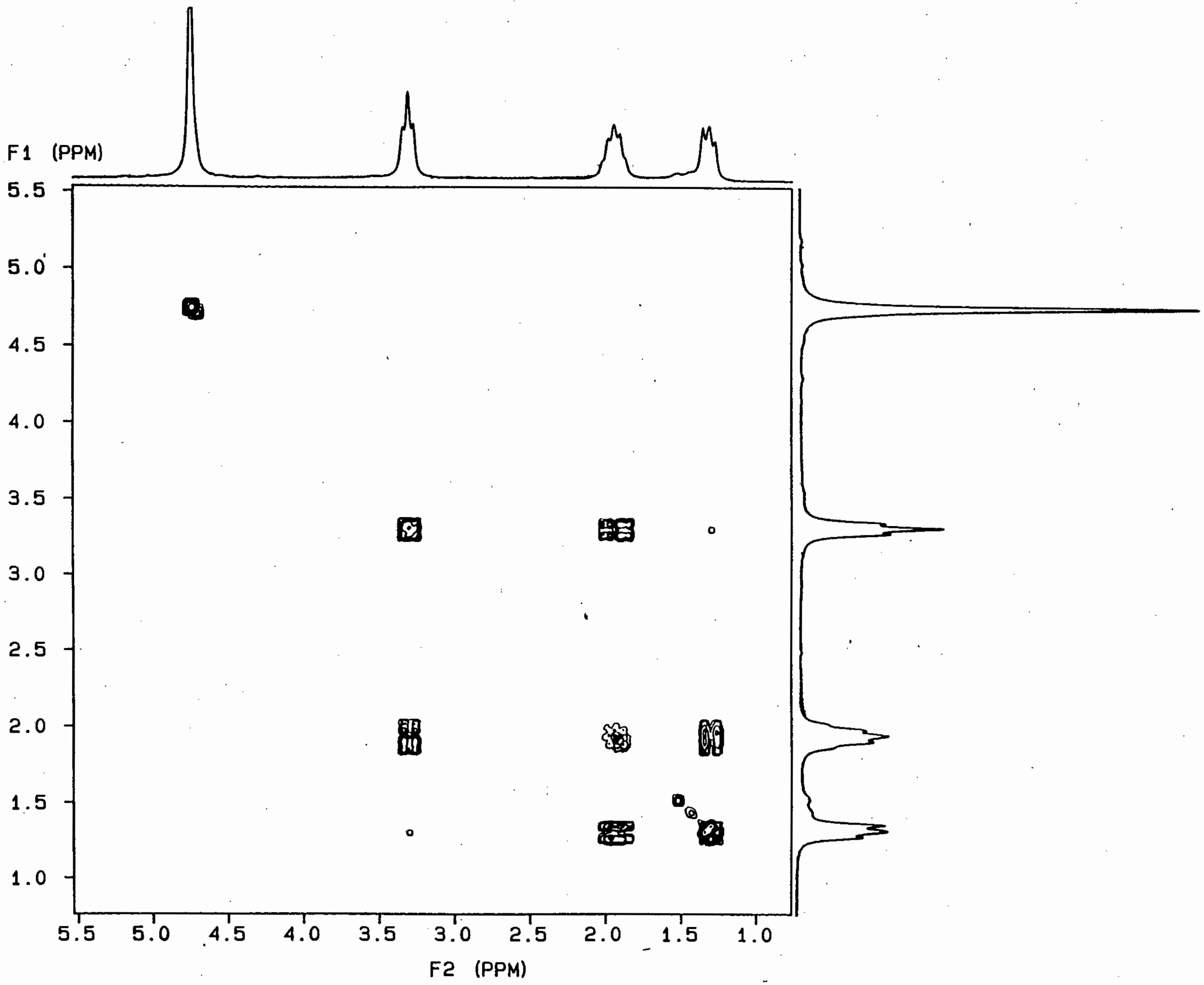


Figure 2: COSY of $[CpFe(CO)_2\{(CH_2)_3Br\}]$.

particular interest are the compounds where n = 3. Here the peak for the CH_2 carbon α to iron is at a higher field for X = Br than for X = I. These observations could possibly be explained by a weak bonding interaction between the halogen and the iron. This is also indicated by the mass spectral data. The interaction between iron and X is also shown by the *ca.* 2 ppm down-field shift of the peaks of the carbons α to X for n = 3, relative to the corresponding peaks for n = 4 - 10. Thus as n increases, the distance between X and Fe increases and the effect of their interaction would decrease. The proposed interaction between iron and bromine is supported by the observation that iron must participate in the cleavage of the γ-carbon-halogen bond of $[CpFe(CO)_2\{(CH_2)_3Br\}]$ on formation of cyclopropane [14]. Kinetic studies by Monaghan and Puddephatt have also shown that the metal atom in $[Pt(phen)(Me)_2I\{(CH_2)_3I\}]$ (phen = 1,10-phenanthroline) activates the γ-C-X bond. They propose that this may be due to the resonance form shown in **Figure 3** [5].

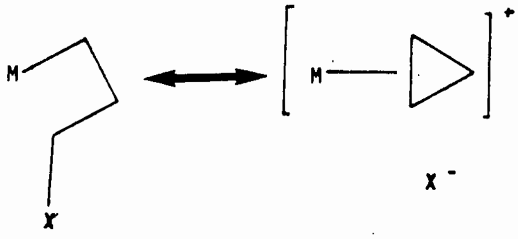


Figure 3

Also apparent from the ^{13}C NMR data is the large chemical shift difference (*ca.* 27 ppm) between the carbon α to Br and I respectively, reflecting the different electron withdrawing strengths of the halogens. **Figure 4** shows the ^{13}C NMR spectrum and **Figure 5** shows the HETCOR of $[CpFe(CO)_2\{(CH_2)_3Br\}]$.

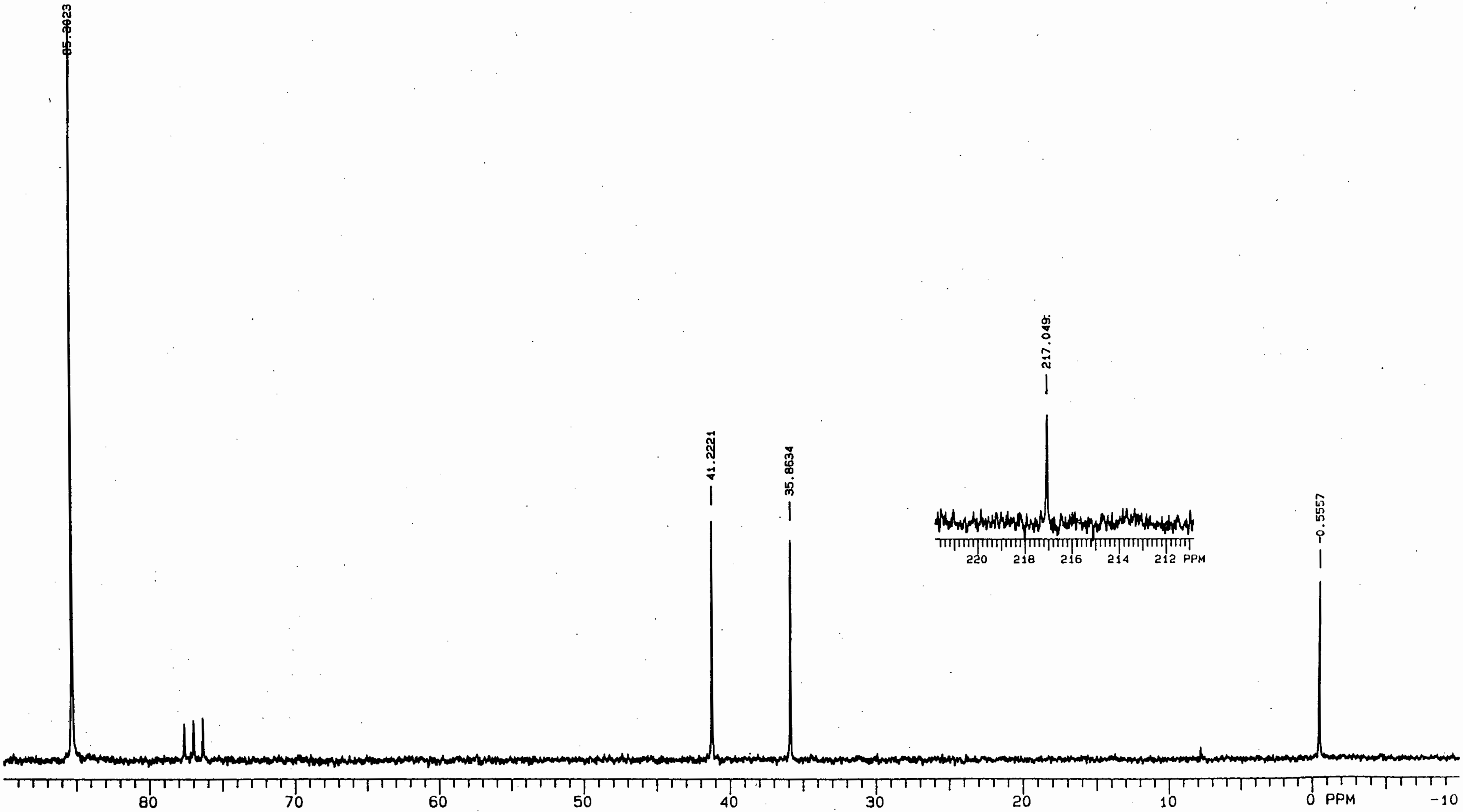


Figure 4: ^{13}C NMR spectrum of [CpFe(CO)$_2${(CH$_2$)$_3$Br}].

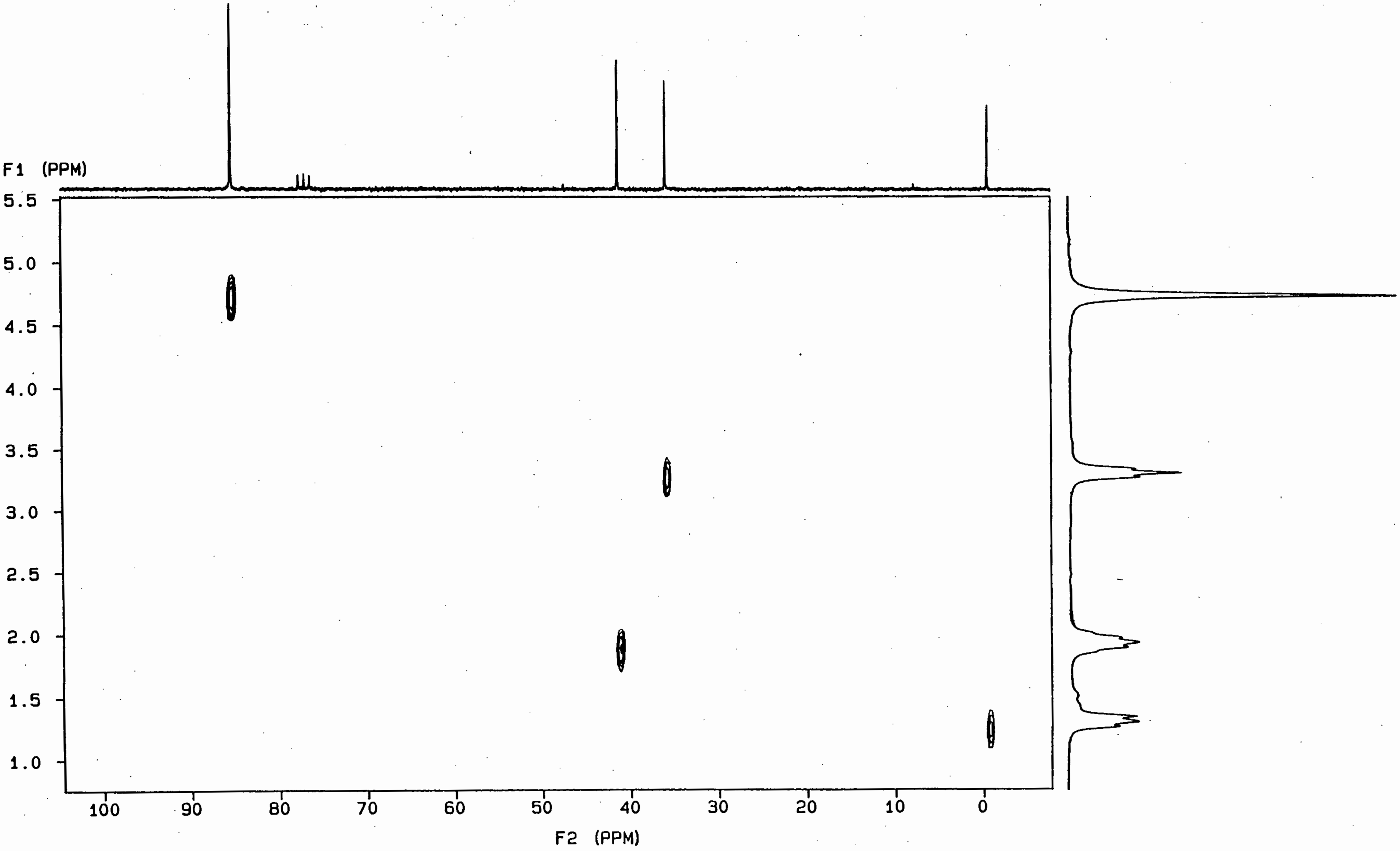


Figure 5: HETCOR of [CpFe(CO)$_2$((CH$_2$)$_3$Br)].

The ^1H NMR of the Cp* complexes (Table 4.5) shows that the protons *α* to Fe are much more shielded than are those of the Cp analogues. This is probably due to the increased electron density on the iron. Whilst changing the halogen has no effect on these *α* protons, the chemical shift values move down-field as n increases. The protons *α* to the halide show the expected up-field shift as X changes from Br to I, but the effect is not apparent on the protons *β* to the halogens. The *β* peaks only move slightly up-field as n increases. The ^1H NMR spectrum and COSY of $[Cp^*Fe(CO)_2\{(CH_2)_3Br\}]$ are shown in **Figures 6** and **7**.

In the ^{13}C NMR of the Cp* complexes (Table 4.6) it can be seen that the halogen has no significant effect on the positions of the corresponding $\underline{C}O$ or pentamethylcyclopentadienyl peaks. However, as n increases the $\underline{C}O$ peaks move slightly down-field, whilst the $\underline{C}_5(CH_3)_5$ peaks move slightly up-field. These observations are consistent with a weak bonding interaction existing between Fe and X, and with this interaction decreasing as n increases. The methyl peaks of the Cp* are not affected by either n or X. The effect Fe has on the carbon *α* to X, and the effect X has on the CH_2 carbon *α* to Fe can be seen to rapidly diminish as n increases. Thus the peak of the carbon *α* to Fe moves down-field and the peak of the carbon *α* to X moves up-field. The fact that the peak of the carbon *α* to Fe is at a higher field for X = Br than for X = I when n = 3, again implies a degree of Fe/X interaction, as does the *ca*. 2 ppm down-field shift of the peaks of the carbon *α* to X for n = 3 relative to the corresponding peaks *α* to X for n = 4 and 5. The carbons *α* to Fe in the Cp* complexes are significantly (6-10 ppm)

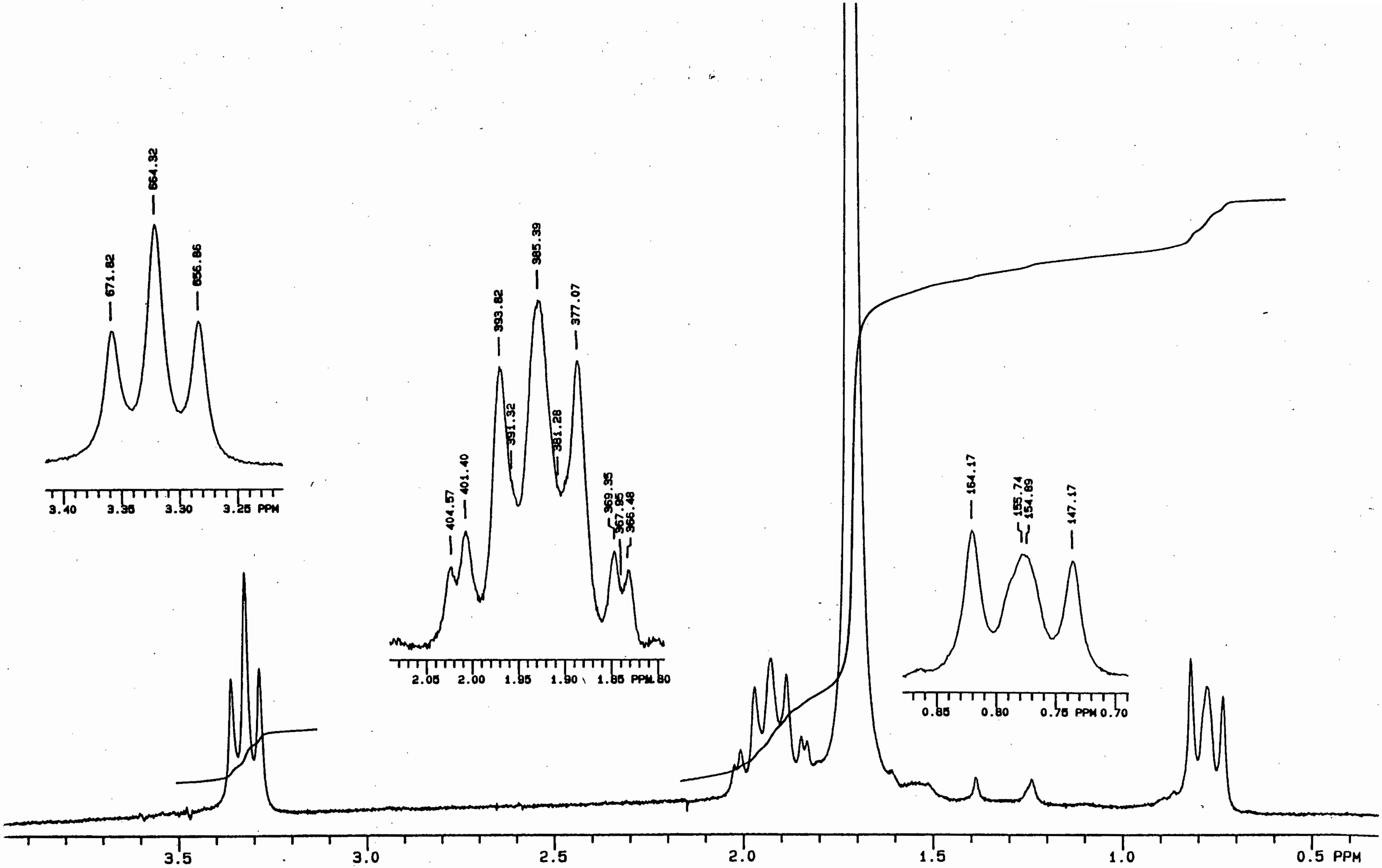


Figure 6: ^{1}H NMR spectrum of [Cp*Fe(CO)$_2${(CH$_2$)$_3$Br}].

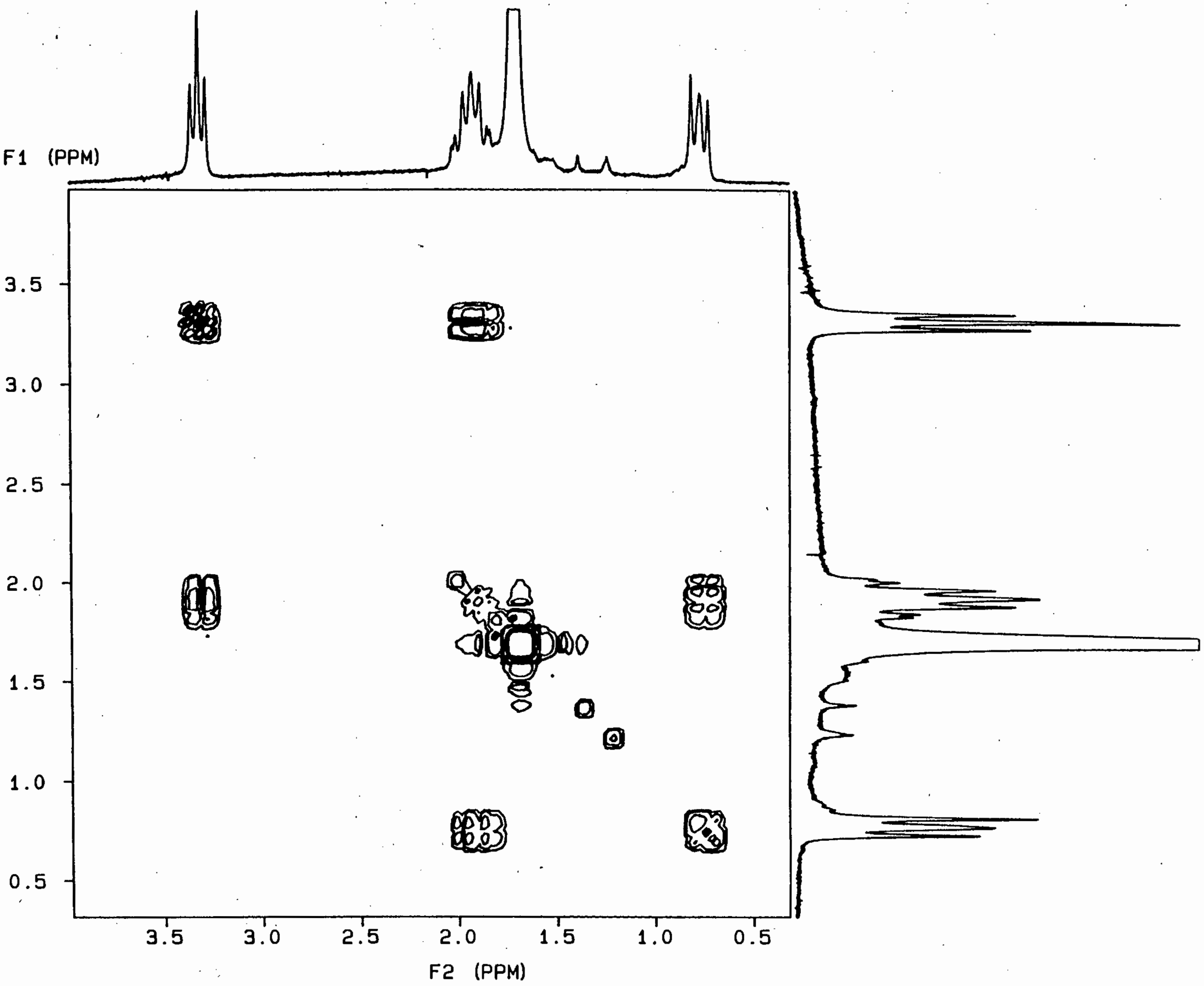


Figure 7: COSY of [Cp*Fe(CO)$_2${(CH$_2$)$_3$Br}].

more deshielded than those of the corresponding Cp complexes. So too are the carbonyl carbon peaks, though to a lesser degree. This deshielding effect is no longer apparent for the β carbons of the methylene chain. The ^{13}C NMR spectrum of $[Cp^*Fe(CO)_2\{(CH_2)_3Br\}]$ is shown in **Figure 8**.

Mass Spectra

Low resolution electron impact mass spectra were obtained for all the compounds under discussion, excluding $[CpFe(CO)_2\{(CH_2)_8I\}]$. The intensities of the major organometallic peaks of $[CpFe(CO)_2\{(CH_2)_nX\}]$ ($n = 3 - 10$, $X = Br$; $n = 3 - 6, 9, 10$; $X = I$) are reported in Table 4.7 with probable assignments, while those of $[Cp^*Fe(CO)_2\{(CH_2)_nX\}]$ ($n = 3 - 5$; $X = Br, I$) are reported in Table 4.8. The fragmentation of $[CpFe(CO)_2\{(CH_2)_4Br\}]$, which has a potentially very ambiguous fragmentation pattern, was studied in detail. Its fragmentation pathways, established using information obtained from high resolution mass spectrometry, metastable peaks and linked scans, are shown in **SCHEME 4.1**. High resolution mass spectra were also obtained for $[CpFe(CO)_2\{(CH_2)_4I\}]$ and $[CpFe(CO)_2\{(CH_2)_5Br\}]$.

Molecular ion peaks are observed in the mass spectra of all the Cp compounds but are of low intensity. All spectra exhibit peaks which are characteristic of compounds containing the $[CpFe(CO)_2]$ group [23 - 25], which gives rise to the ions $[CpFe(CO)_2]^+$ (m/z 177), $[CpFe(CO)]^+$ (m/z 149), $[CpFe]^+$ (m/z 121), $[(C_3H_3)Fe]^+$ (m/z 95), $[Cp]^+$ (m/z 65) and $[Fe]^+$ (m/z 56). A peak at m/z 186, assigned to $[Cp_2Fe]^+$,

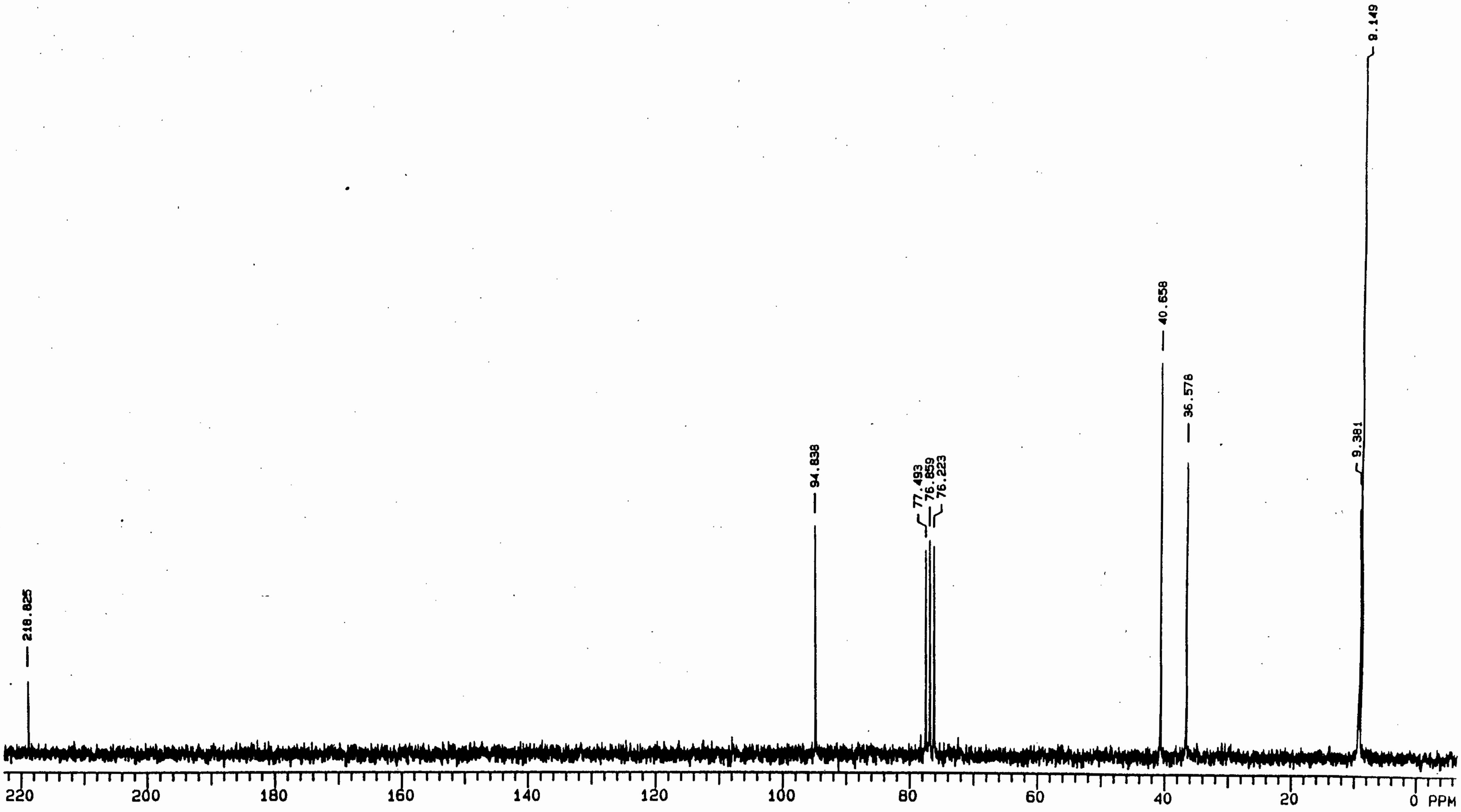


Figure 8: ^{13}C NMR spectrum of $[\mathrm{Cp^*Fe(CO)_2\{(CH_2)_3Br\}}]$.

TABLE 4.7

Some mass spectral data for [CpFe(CO)$_2${(CH$_2$)$_n$X}]

Ion[a]	Relative Peak Intensities%[b]													
	n = 3		4		5		6		7	8	9		10	
	X = Br	I	Br[c]	I[c]	Br[c]	I	Br	I	Br	Br	Br	I	Br	I
M	4	3	4	3	4	3	4	10	4	3	4	3	4	1
M-CO	10	10	10	8	10	12	8	18	10	8	8	7	8	3
M-2CO	10	20	15	18	18	30	17	60	18	22	16	23	28	12
M-2CO-CpH	15	18	36	24	24	28	36	45	26	56	38	35	34	16
M-2CO-CpH-C_2H_4			2	2	45	56	30	50	20	21	6	4	6	1
M-2CO-CpH-C_3H_6[d]			6	1	2	1	18	58	16	15	7	5	8	2
M-2CO-HX[e]	8	8	19	17	19	16	13	17	18	8	7	7	7	7
M-2CO-HX-CpH	5	5	36	34	18	8	35	21	44	85	100	100	100	100
M-2CO-HX-CpH-C_2H_4					8	7	15	11	6	18	11	8	10	8
M-2CO-HX-CpH-C_3H_6[f]							12	9	36	34	38	38	26	26
M-$(CH_2)_n$	5	23	-	-	-	2	-	2	-	-	2	5	3	1
M-$(CH_2)_n$-CO	8	17	-	2	2	3	-	4	7	8	2	2	2	3
M-2CO-$(CH_2)_n$	61	55	49	37	53	45	35	51	30	19	13	14	7	7
M-$(CH_2)_n$X	17	8	8	8	10	8	10	10	11	13	13	11	9	7
M-$(CH_2)_n$X-CO	17	16	19	18	21	18	19	22	24	26	22	17	15	17
M-$(CH_2)_n$X-2CO	100	100	100	100	100	100	100	100	100	100	80	81	62	60
Cp_2Fe	8	18	3	2	13	8	4	5	3	4	4	3	8	3
FeX	14	20	9	8	8	11	8	11	4	5	5	6	3	6

a: M = [CpFe(CO)$_2${(CH$_2$)$_n$X}]; all ions have a single positive charge; ion refers to probable assignment.

b: Peak intensities are relative to the base peak at m/z 121 (n = 3-8), m/z 180 (n = 9) and m/z 194 (n = 10)

c: assignments confirmed by high resolution mass spectrometry

d: ions corresponding to M-2CO-CpH-C_mH_{2m} ($4 \leq m < n$) are also seen (intensity $\leq$ 12%)

e: ions corresponding to M-2CO-HX-C_mH_{2m} ($m \geq 2$) usually observed. (intensity $\leq$ 10%)

f: ions corresponding to M-2CO-HX-CpH-C_mH_{2m} ($m \geq 4$) also observed. (intensity $\leq$ 19%)

-: not observed

TABLE 4.8

Some mass spectral data for $[Cp^*Fe(CO)_2\{(CH_2)_nX\}]$

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

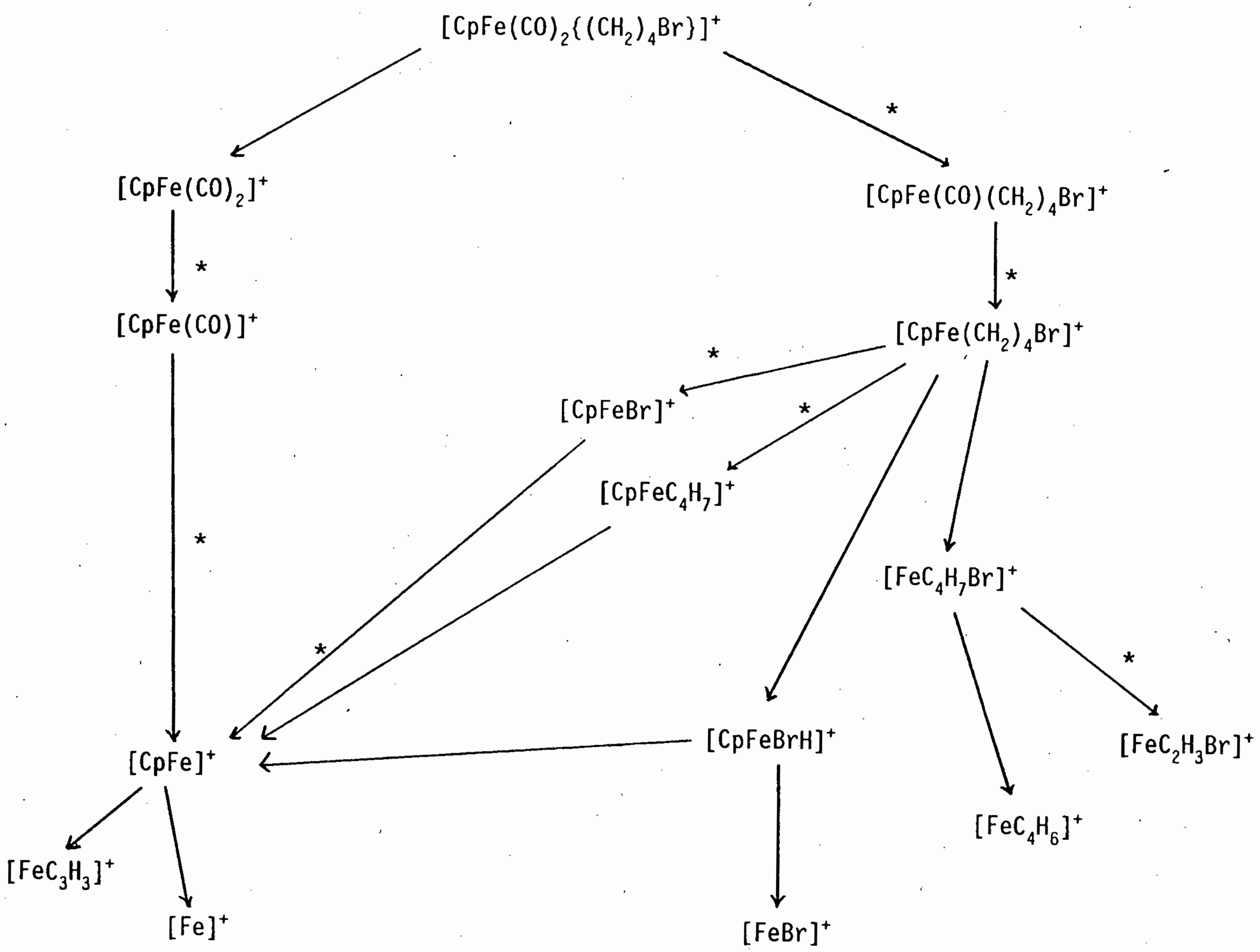
a: $M = [Cp^*Fe(CO)_2\{(CH_2)_nX\}]$; all ions have a single positive charge; ion refers to probable assignments.

b: Peak intensities are relative to the base peak at m/z 270/272 for X = Br and m/z 318 for X = I.

c: Same peak as $M-(CH_2)_n$ in low resolution mass spectrum.

d: Same peak as M-2CO in low resolution mass spectrum.

SCHEME 4.1: Mass spectral fragmentation scheme for $[CpFe(CO)_2\{(CH_2)_4Br\}]$



* : Fragmentation confirmed by metastable data.

is observed in all the spectra. This ion is a characteristic of the spectra of compounds containing [CpFe(CO)$_2$] and is believed to be due to either the ionisation of ferrocene, formed by thermal decomposition of these compounds in the ion source or, the fragmentation and rearrangement of the sample compounds in the mass spectrometer [23]. The most abundant peak observed corresponds to [CpFe]$^+$ (m/z 121) for n = 3 - 8, X = Br and n = 3 - 6, X = I. For n = 9 and 10 (X = Br and I), the most abundant peak corresponds to [FeC$_n$H$_{2n-2}$]$^+$ (m/z 180, n = 9; m/z 194, n = 10). This species and daughter ions, formed through losses of C$_m$H$_{2m}$ (m ≥ 2) fragments from it, are observed in all the spectra of the Cp compounds.

All the [CpFe(CO)$_2${(CH$_2$)$_n$X}] compounds studied fragment according to two main pathways illustrated in **SCHEME 4.1**, while some follow a third route as well. The first pathway involves the sequential loss of CO from the molecular ion to give [CpFe(CO){(CH$_2$)$_n$X}]$^+$ and then [CpFe{(CH$_2$)$_n$X}]$^+$, which can fragment in four ways; (a) by losing C$_n$H$_{2n}$ (either as a unit or in increments) to give [CpFeX]$^+$ (m/z 200/202 X = Br, m/x 248 X = I); (b) by losing HX to give [CpFe(C$_n$H$_{2n-1}$)]$^+$; (c) by losing CpH to give [Fe(C$_n$H$_{2n-1}$)X]$^+$; or (d) by losing C$_n$H$_{2n-1}$ to give [CpFeXH]$^+$. The second fragmentation pathway, common to all the compounds, involves the formation of [CpFe(CO)$_2$]$^+$ (m/z 177) probably by the loss of (CH$_2$)$_n$X from the molecular ion. The further fragmentation of [CpFe(CO)$_2$]$^+$ is discussed above. A third fragmentation of the molecular ion involves the loss of the hydrocarbon chain from the molecular ion and migration of X to Fe to give [CpFe(CO)$_2$X]$^+$ (m/z 256/258 X = Br, m/z 304 X = I) followed by the loss of CO to give [CpFe(CO)X]$^+$ (m/z 228/230 X = Br, m/z

276 X = I) and possibly also $[CpFeX]^+$. The fragments $[CpFe(CO)_2X]^+$ and $[CpFe(CO)X]^+$ are observed in most of the spectra at low relative intensities but have significant relative intensity in the cases where n = 3. This indicates that the Fe-X bond is formed much more easily for the complexes where n = 3. The relative intensities also suggest that the Fe-I bond is more readily formed than the Fe-Br bond lending further support to the explanation of the deshielding effect seen in the ^{13}C NMR spectra discussed earlier.

Molecular ions are observed in the mass spectra of all the Cp* compounds. The relative intensities of the ions $[Cp^*Fe(CO)_2]^+$ (m/z 247) and $[Cp^*(CO)Fe]^+$ (m/z 219) are similar to those of their Cp analogues, whilst the relative intensity of the ion [Cp*Fe] (m/z 191) is also fairly high. This indicates that the successive losses of CO from $[M-(CH_2)_nX]^+$ is an important fragmentation route for both the Cp and Cp* compounds. As for the Cp complexes, the ion corresponding to $[M-(CH_2)_n]^+$ for the Cp* complex where n = 3 and X = I is the most intense. This indicates a high degree of Fe/I interaction in $[Cp^*Fe(CO)_2(CH_2)_3I]$, as observed in the ^{13}C NMR and the analogous Cp compound.

Some significant differences are observed, however, between the mass spectra of the Cp* complexes and those of their Cp analogues. Unlike the Cp complexes, where CpH is lost from $[M-2CO]^+$, no loss of Cp*H from $[M-2CO]^+$ is observed for the Cp* complexes. Furthermore, the loss of HX from $[M-2CO]^+$ yields only low intensity ions in the spectra of the Cp* complexes, indicating that this route is not as favoured for these complexes. For the Cp* compounds, the ions corresponding to successive losses of CO from $[M\text{-}(CH_2)_n]^+$ are quite significant. The peak corresponding to $[Cp^*FeX]^+$, which would be formed by this fragmentation pathway, is the base peak for the Cp* complexes. A peak corresponding to $[Cp^*{}_2Fe]$ (m/z 326) is not observed in many of the spectra of the Cp* complexes, and in cases where such a peak is seen its assignment is ambiguous.

4.4 THE SYNTHESIS AND PROPERTIES OF $[CpRu(CO)_2\{(CH_2)_nX\}]$ (n = 3, 4; X = Br, I)

The complexes $[CpRu(CO)_2\{(CH_2)_nBr\}]$ (n = 3, 4) were prepared by reacting $Na[CpRu(CO)_2]$ with $Br(CH_2)_nBr$ at -78°C - equation 6.

$$Na[CpRu(CO)_2] + Br(CH_2)_nBr \xrightarrow[\text{THF}]{-78^\circ} [CpRu(CO)_2\{(CH_2)_nBr\}] + NaBr \qquad (\underline{6})$$

(n = 3, 4)

This reaction is similar to that used for the preparation of $[CpFe(CO)_2\{(CH_2)_nBr\}]$ (equation 1) exept that a significantly lower temperature is needed to prevent the formation of $[\{CpRu(CO)_2\}_2\{\mu\text{-}(CH_2)_n\}]$. The $[CpRu(CO)_2\{(CH_2)_nBr\}]$ complexes were obtained as colourless oils in good to moderate yields. The complex $[CpRu(CO)_2\{(CH_2)_4Br\}]$ has been reported before, but was only partially characterised [26]. Like their iron analogues, the $[CpRu(CO)_2\{(CH_2)_nBr\}]$ complexes react with NaI to form $[CpRu(CO)_2\{(CH_2)_nI\}]$ - equation 7.

$$[CpRu(CO)_2\{(CH_2)_nBr\}] + NaI \longrightarrow [CpRu(CO)_2\{(CH_2)_nI\}] + NaBr \qquad (\underline{7})$$

(n = 3, 4)

The complex $[CpRu(CO)_2\{(CH_2)_3I\}]$ was isolated as a white, low melting solid, whilst $[CpRu(CO)_2\{(CH_2)_4I\}]$ was obtained as a colourless oil. The $[CpRu(CO)_2\{(CH_2)_nX\}]$ complexes appear to be significantly more stable to air and light than are their iron analogues . Both iodoalkyl complexes have since been prepared, but not in pure form [27]. The data for the ruthenium haloalkyl complexes are reported in Tables 4.9 and 4.10.

IR

As with the iron haloalkyl complexes, the IR ν(CO) bands of the ruthenium complexes where n = 4 are at a slightly lower frequency than those of the complexes where n = 3. No change in band positions is observed on changing X from Br to I.

^{1}H and ^{13}C NMR

Assignments of the ^{1}H and ^{13}C NMR spectra of these complexes were made using COSY and HETCOR experiments.

The ^{1}H NMR data for the ruthenium complexes are shown in Table 4.9. The chemical shift of the Cp peaks is not affected by either n or X. In contrast both n and X affect the shifts of the $C\underline{H}_2X$ peaks. Thus these

TABLE 4.9

Data for $[CpRu(CO)_2\{(CH_2)_nX\}]$

n	X	yield (%)	m.p. (°C)	IR ν(CO)[a] (cm^{-1})	^{1}H NMR[b] (δ) Cp	CH̲$_2$X	α-CH̲$_2$	β-CH̲$_2$	γ-CH̲$_2$
3	Br	67	oil	2022, 1965	5.24s	3.30t, J = 7.2	1.60m	2.06m	
	I	75	37-39	2022, 1962	5.25s	3.10t, J = 7.4	1.58m	2.04m	
4	Br	54	oil	2020, 1961	5.24s	3.43t, J = 6.8	1.64m	1.64m	1.85m
	I	68	oil	2020, 1960	5.24s	3.21t, J = 7.0	1.76m	1.76m	1.82m

a: in hexane, all peaks sharp and very strong
b: in $CDCl_3$ relative to TMS (δ = 0.00 ppm), J values in Hz, α-CH̲$_2$ refers to those protons on the carbon α to ruthenium etc.

TABLE 4.10

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

n	X	$\underline{C}O$	Cp	$\underline{C}H_2X$	α-$\underline{C}H_2$	β-$\underline{C}H_2$	γ-$\underline{C}H_2$
3	Br	201.8	88.4	36.2	-7.4	42.4	
	I	201.8	88.4	10.1	-4.5	43.5	
4	Br	202.1	88.5	33.8	-5.3	37.7	37.4
	I	202.1	88.5	7.4	-5.6	40.1	38.0

a: in CDCl$_3$ relative to TMS (δ = 0.0 ppm), α-CH$_2$ refers to that carbon atom α to ruthenium etc.

peaks are shifted 0.2 ppm up-field as X changes from Br to I, reflecting the electronegativity difference of the halogens. As n changes from 3 to 4 the $C\underline{H}_2X$ triplets move down-field by 0.1 ppm, presumably reflecting a decrease in the influence of Ru.

The ^{13}C NMR data for the ruthenium complexes are shown in Table 4.10. The CO and Cp peaks of the complexes where n = 4 are at a marginally lower field position than are those of the complexes where n = 3. The effect of the halogen on the δ value of the CH_2 carbon α to iron is very apparent. As with their iron analogues (see earlier), the α-$\underline{C}H_2$ peak for the complexes where n = 3 is at a higher field for X = Br than for X = I. This again implies an interaction between the metal and the γ-C-X bond, with this interaction being stronger for the iodoalkyl complex. Also apparent is the large chemical shift difference (*ca.* 26 ppm) between the carbon α to Br and I respectively, reflecting the different electron withdrawing abilities of the halogens.

Mass Spectra

The low resolution mass spectra of these ruthenium complexes have been recorded [27]. Although they are of fairly poor quality and no high resolution or metastable data was available, they indicate that the ruthenium haloalkyl complexes behave identically to their iron analogues under electron impact mass spectral conditions.

4.5 CONCLUSION

The ω-bromoalkyl iron complexes $[CpFe(CO)_2\{(CH_2)_nBr\}]$ and $[Cp^*Fe(CO)_2\{(CH_2)_nBr\}]$ are easily prepared in high yield by the reaction of $Na[CpFe(CO)_2]$ or $Na[Cp^*Fe(CO)_2]$ with $Br(CH_2)_nBr$. Because of the difficulty in separating $[CpFe(CO)_2\{(CH_2)_nI\}]$ or $[Cp^*Fe(CO)_2\{(CH_2)_nI\}]$ from unreacted $I(CH_2)_nI$, the iodoalkyl iron complexes are best prepared by reacting $[CpFe(CO)_2\{(CH_2)_nBr\}]$ and $[Cp^*Fe(CO)_2\{(CH_2)_nBr\}]$ with NaI. This reaction generally goes in high yield.

The Cp* complexes were observed to be more stable than their Cp analogues. Unlike the Cp complexes, all the Cp* complexes obtained were solids. These observations are in accordance with previously reported comparisons between Cp and Cp* complexes.

Both similarities and differences were observed between the IR, ^1H and ^{13}C NMR and mass spectra of the respective Cp and Cp* complexes. Effects in these spectra due to varying alkyl chain length and differing halogens were also observed.

In a similar way to their iron analogues, the ruthenium bromoalkyl complexes are easily prepared by the reaction of $Na[CpRu(CO)_2]$ with $Br(CH_2)_nBr$ ($n = 3, 4$). A lower temperature is however neccessary to prevent competing reactions. Like their iron analogues, $[CpRu(CO)_2\{(CH_2)_nBr\}]$ react with NaI to form $[CpRu(CO)_2\{(CH_2)_nI\}]$. The $[CpRu(CO)_2\{(CH_2)_nX\}]$ complexes appear to be more stable to air and light than their iron analogues, although they have very similar spectral properties.

The ^{13}C NMR and mass spectral data obtained for both the iron and ruthenium haloalkyl complexes, supports previous observations by other workers that there is an interaction between the metal and the γ-C-X bond in halopropyl transition metal complexes.

The reactivity of the iron ω- haloalkyl complexes is discussed in chapter 5.

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CHAPTER 5

THE SYNTHESIS AND PROPERTIES OF HETERODINUCLEAR ALKANEDIYL COMPLEXES OF IRON(II) CONTAINING MOLYBDENUM(II), TUNGSTEN(II), RHENIUM(I) AND RUTHENIUM(II)

5.1 INTRODUCTION

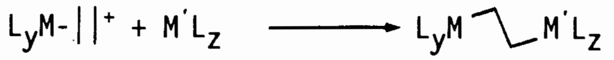
Heterobimetallic catalysts have been found to be superior in activity, selectivity and efficiency to catalysts derived from either of the respective monometallic components. This has resulted in much effort being directed towards the study of heterobimetallic complexes. These complexes could serve as models for catalytic intermediates, as catalyst precursors or as catalysts themselves [1]. It is also of interest to investigate the effect that one metal has on another when the two metals are in close proximity within the same molecule. These complexes also have two different potential metal reactivity sites in the same molecule.

Several strategies have been employed to synthesize heterobimetallic complexes, one of which involves the preparation of compounds with direct metal-metal bonds [2]. Not all metals however will form stable metal-metal bonds, particularly early/late transition metal combinations. Another approach has been to prepare compounds where phosphorus and/or arsenic bridging ligands hold the different metal atoms together [3-7]. The presence of phosphorus or arsenic may however be undesirable if the complex is to be used as a catalyst precursor, since these elements may poison the catalytically active sites. Stone and co-workers have shown the wide applicability of using carbene or carbyne bridging ligands for synthesizing many novel heterobimetallic complexes [8].

Since the metal-carbon sigma bond is ubiquitous in organometallic chemistry, we have developed the strategy of building up the heterobimetallic complexes where the metal centres are bridged by an alkanediyl ligand. This method should be widely applicable to a range of heterobimetallic complexes. It has been previously shown that bridging methylene groups can hold two different metals together, for example Ti/Pt [9] or Ta/Pt [10].

A very large number of homobimetallic alkanediyl (also called methylene bridged) complexes are known and two comprehensive reviews on this type of complex have been published [11, 12]. These complexes are of interest since it is believed that they may be models for intermediates in a number of catalytic reactions, such as the Ziegler-Natta process of alkene polymerisation or the Fischer-Tropsch process.

In contrast to the homobinuclear alkanediyl complexes, very few heterobimetallic alkanediyl complexes have been reported. The methylene bridged complex $[Cl(Me)_2(bipy)PtCH_2AuL]$ was prepared by the reaction of $[AuL(CH_2Cl)]$ $\{L = PPh_3, PEt_3, P(OPh)_3\}$ with $[Pt(bipy)Me_2]$ [13]. Several ethylene bridged complexes of the type $L_yMCH_2CH_2M'L_z$ have been prepared by the reactions of cationic ethylene complexes with metal carbonyl anions [14, 15]. These complexes and their method of synthesis are shown in equation 1.



(1)

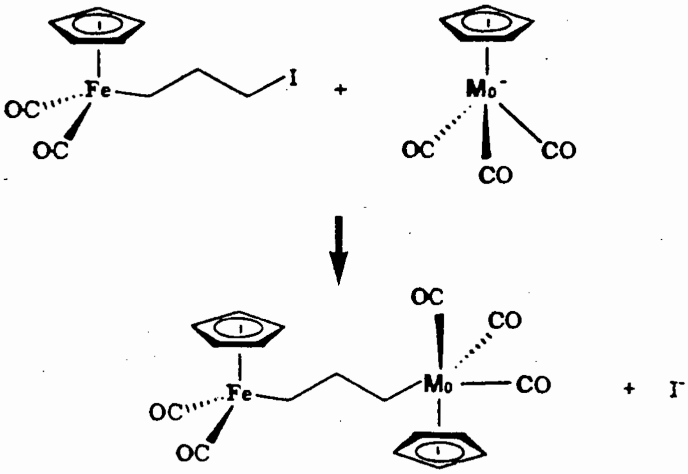
L_yM, L_zM' = $Re(CO)_5$, $Mn(CO)_5$, $Mo(CO)_3Cp$, $W(CO)_3Cp$

Crystal structures of several of these complexes show the ethylene bridge to be in a "zig-zag" conformation. The novel trinuclear complex $[(CO)_5ReCH_2CH_2Os(CO)_4CH_2CH_2Re(CO)_5]$ was prepared by a related route, using the reaction of $[Os(CO)_4]^{2-}$ with 2 mol $[(CO)_5ReCH_2CH_2]^+$ [16]. The route shown in equation 1 is however limited to the preparation of ethylene bridged complexes. This route also does not work for some cases, *e.g.* where $ML_y = M'L_z = Fe(CO)_2Cp$.

Some years ago the propanediyl complex $[Cp(CO)_2Fe(CH_2)_3Mo(CO)_3Cp]$ was prepared by the reaction of $[CpFe(CO)_2\{(CH_2)_3Br\}]$ with $Na[CpMo(CO)_3]$, but the yield was only 18% [17]. Knox and co-workers then demonstrated that the heterobimetallic complex $[Cp(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$ could be obtained in 87% yield by the reaction of the iodoalkyl compound $[CpFe(CO)_2\{(CH_2)_3I\}]$ with $Na[CpRu(CO)_2]$ [18]. This suggested that the use of iodoalkyl complexes may be a more useful and potentially general route for the high yield synthesis of heterobimetallic alkanediyl complexes. This possibility was examined and the results are now presented [19].

5.2 RESULTS AND DISCUSSION

An initial experiment showed that the iodoalkyl compound $[CpFe(CO)_2\{(CH_2)_3I\}]$ [20] reacts with $Na[CpMo(CO)_3]$ to give good yields of the Fe/Mo heterobimetallic propanediyl compound (**SCHEME 5.1**).



SCHEME 5.1

This was subsequently shown to be part of a general route to heterobimetallic alkanediyl complexes as shown in equation 2.

$$[(\eta^5\text{-}C_5R_5)Fe(CO)_2\{(CH_2)_nI\}] \; + \; Na[ML_y] \longrightarrow$$

$$[(\eta^5\text{-}C_5R_5)(CO)_2Fe(CH_2)_nML_y] \; + \; NaI \qquad (\underline{2})$$

{where R = H, ML_y = $Mo(CO)_3Cp$, $W(CO)_3Cp$, $Ru(CO)_2Cp$ or $Re(CO)_5$, n = 3-6;
R = CH_3, ML_y = $Ru(CO)_2Cp$, n = 3-5 or $Re(CO)_5$, n = 4}.

The related mixed ligand complex $[Cp(CO)_2Fe(CH_2)_3Fe(CO)_2Cp^*]$ was prepared by a similar route. Attempts to prepare $[Cp(CO)_2Fe(CH_2)_nCr(CO)_3Cp]$ (n = 3 or 4) by the route shown in equation 2 were not successful, and only a mixture of decomposition products was obtained. This may be due to the instability (kinetic or thermodynamic) of the Cr-CH_2CH_2- group.

All the new alkanediyl complexes were obtained in good yield, except the Fe/Re complex where n = 5, which was obtained in 10% yield. Highest yields of the Fe/Re compounds were obtained with short reaction times, presumably due to the instability of these compounds in the reaction solution. The alkanediyl complexes were all obtained as yellow, crystalline solids which are stable in air for several days but are mildly light sensitive. The Fe/Re and Fe/Mo complexes appear to be the least stable and decompose slowly, even under nitrogen at -15°C. The complexes are generally stable in solution under nitrogen but decompose when the solutions are exposed to air. The Fe/Re and Fe/Ru complexes are very much more soluble in hexane than the Fe/Mo or Fe/W complexes. Also notable is the increased solubility of the Cp* complexes relative to their Cp analogues. This increase in solubility of Cp* complexes relative to their Cp analogues has been observed before [20-22]. The hexane solubility of all the complexes increases with increasing length of the alkyl chain.

Yields, microanalysis, IR and other physical data for the new compounds are given in Tables 5.1 and 5.2.

Table 5.1
Data for $[Cp(CO)_2Fe(CH_2)_nML_y]$

n	ML_y	Rxn time (hours)	Yield (%)	m.p. (°C)	IR ν(CO) (cm^{-1})[a]	Elemental analysis C: found (calcd.)	H: found (calcd.)
3	$Mo(CO)_3Cp$	73	66	97-99	2016s, 2005s, 1951s, 1937s,1925s	*b*	*b*
4	$Mo(CO)_3Cp$	72	80	110-115	2018s, 2008s, 1954s, 1933vs	48.10(47.70)	4.00(3.77)
5	$Mo(CO)_3Cp$	120	41	87-88	2017s, 2008s, 1954s, 1933vs	49.05(48.78)	4.10(4.07)
6	$Mo(CO)_3Cp$	21	45	56-59	2018s, 2008s, 1954s, 1933vs	49.50(49.80)	4.30(4.35)
3	$W(CO)_3Cp$	120	85	113-115(dec)	2014s, 2006s, 1952s, 1928s, 1921s	39.30(39.14)	2.95(2.90)
4	$W(CO)_3Cp$	72	72	143-149(dec)	2016s, 2009s, 1955s, 1925vs	39.35(40.29)	3.20(3.18)
5	$W(CO)_3Cp$	67	10	102-104(dec)	2014s, 2008s, 1954s, 1925vs	41.80(41.41)	3.60(3.48)
6	$W(CO)_3Cp$	45	40	54-63	2015s, 2008s, 1954s, 1925vs	42.40(42.46)	3.60(3.73)
3	$Re(CO)_5$	4	69	110-111	2010vs, 1981m, 1954m	33.30(33.02)	2.20(2.02)
4	$Re(CO)_5$	1.75	89	103-104	2010vs, 1981m, 1955m	34.15(34.34)	2.40(2.32)
5	$Re(CO)_5$	5.25	14	57-59	2010vs, 1982m, 1955m	36.10(35.59)	2.85(2.62)
6	$Re(CO)_5$	19	12	*c*	2009vs, 1981m, 1954s	*d*	*d*
3	$Ru(CO)_2Cp$	48	87	85-86	2017s, 2005s, 1956vs	e	e
4	$Ru(CO)_2Cp$	48	26	131-132	2018s, 2008s, 1959vs	48.00(47.48)	4.10(3.99)
5	$Ru(CO)_2Cp$	48	77	75-77	2018s, 2008s, 1958vs	48.70(48.63)	4.40(4.30)
6	$Ru(CO)_2Cp$	89	50	90-92	2018s, 2008s, 1957vs	49.40(49.68)	4.60(4.55)

a: in hexane, m = medium, s = strong, vs = very strong *b*: data in ref. [17] *c*: waxy solid *d*: not obtained e: data in ref.[18].

Table 5.2

Data for $[Cp^{*}(CO)_2Fe(CH_2)_nML_y]$

n	ML_y	Rxn time	Yield	m.p.	IR ν(CO)	Elemental analysis		Molecular ion
		(hours)	(%)	(°C)	(cm^{-1})[a]	C: found (calcd.)	H: found (calcd.)	(m/z)
3	$Ru(CO)_2Cp$	43	65	99-100	2015s, 1985s, 1957s, 1930s	51.40(51.66)	5.00(5.09)	512
4	$Ru(CO)_2Cp$	84	34	98-101	2018s, 1987s, 1959s, 1933s	52.40(52.57)	5.40(5.33)	526
5	$Ru(CO)_2Cp$	45	75	83-89	2017s, 1987s, 1958s, 1932s	53.40(53.43)	5.70(5.59)	540
4	$Re(CO)_5$	1.75	17	100-102	2008vs, 1986s, 1979s, 1932s	40.10(40.06)	3.80(3.66)	630
3	$Fe(CO)_2Cp$	5	35	88-89	2005vs, 1985vs, 1952vs, 1930vs	56.80(56.68)	5.50(5.58)	466

[a] in hexane, s = strong, vs = very strong

IR

The IR spectra in the ν(CO) region show the expected number of peaks in the expected positions by comparison with data for the related mononuclear alkyl compounds. The ν(CO) peaks assignable to $Cp^*Fe(CO)_2$ are at *ca.* 20 cm^{-1} lower frequency than the bands assignable to $CpFe(CO)_2$. This effect has been described earlier [23, chapter 4].

^1H and ^{13}C NMR

Assignments of the ^1H and ^{13}C NMR data were made by using COSY and HETCOR experiments, as well as by comparison of all the NMR data for the heterodinuclear complexes and comparison of this data with the NMR data of some of their homodinuclear analogues [24, 25] and $[CpFe(CO)_2R]$ (R = alkyl group) complexes [26]. As an example of the results obtained, the ^1H and ^{13}C NMR spectra, as well as the COSY and HETCOR spectra of $[Cp(CO)_2Fe(CH_2)_4Re(CO)_5]$ are shown in **Figures 1 - 4.**

^1H NMR

From the ^1H NMR data (Tables 5.3 and 5.4) it can be seen that the methylene protons on the carbon α to a metal have a chemical shift which is characteristic of that metal. For example, the protons α to Fe all resonate between 1.40 and 1.50 ppm. Similarly, for the compounds where n = 4-6, the β protons have chemical shifts characteristic of the associated metal. The β proton peaks of the complexes where n = 3 show

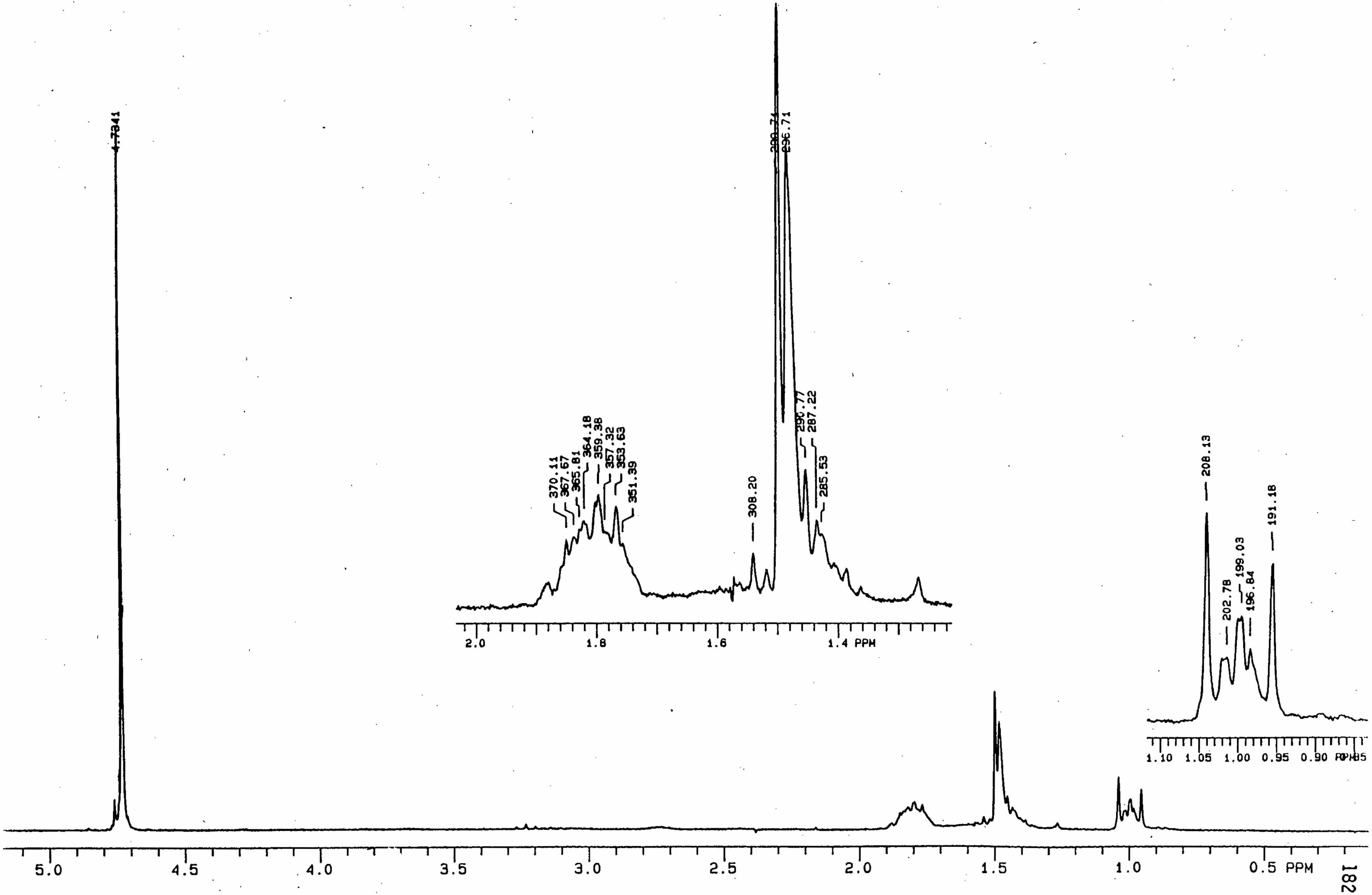


Figure 1: ^{1}H NMR Spectrum of [$Cp(CO)_2Fe(CH_2)_4Re(CO)_5$].

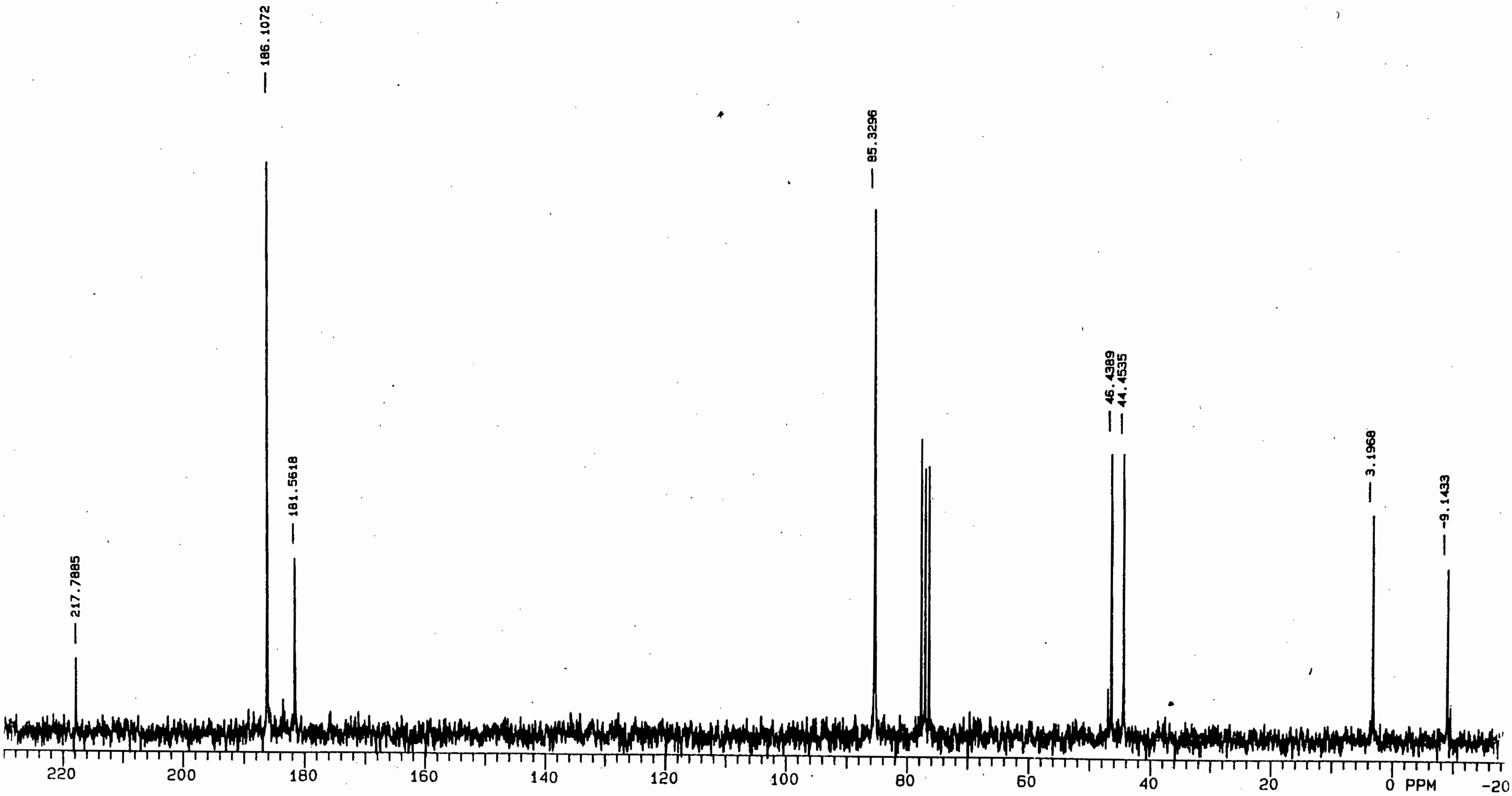


Figure 2: ^{13}C NMR Spectrum of $[Cp(CO)_2Fe(CH_2)_4Re(CO)_5]$.

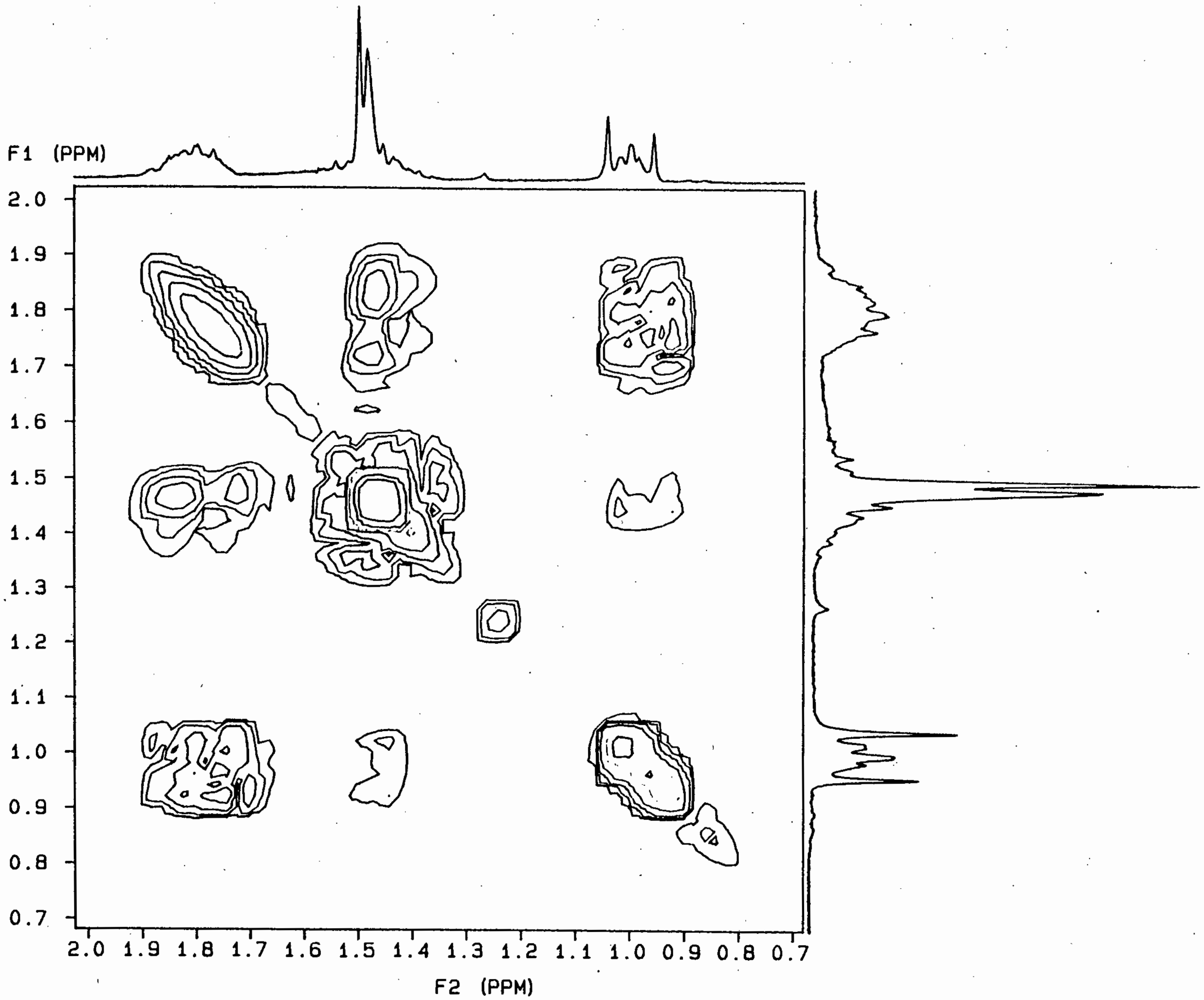


Figure 3: COSY of the Alkyl Region of

[Cp(CO)$_2$Fe(CH$_2$)$_4$Re(CO)$_5$].

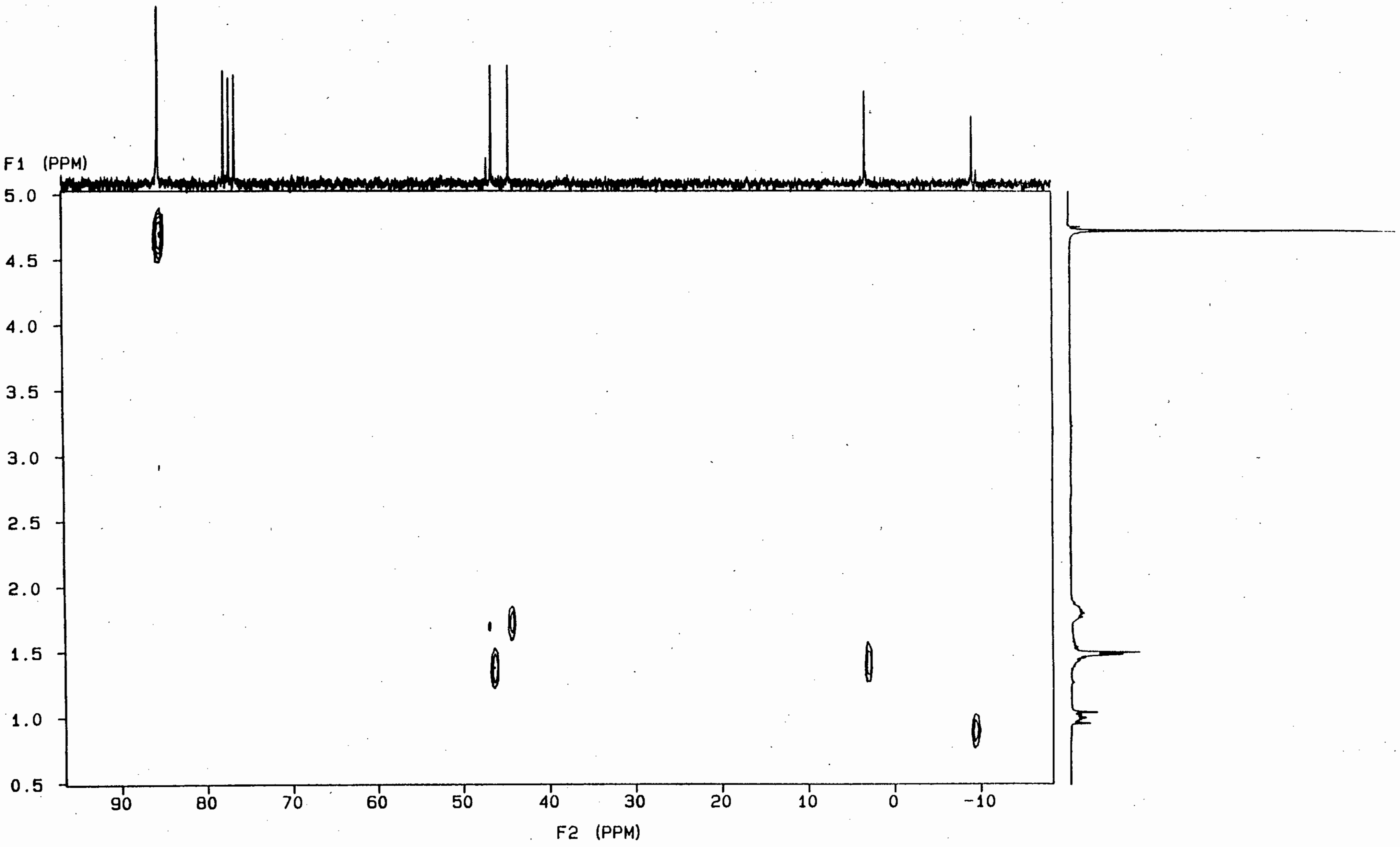


Figure 4: HETCOR of [$Cp(CO)_2Fe(CH_2)_4Re(CO)_5$].

Table 5.3
^{1}H NMR data for $[Cp(CO)_2Fe(CH_2)_nML_y]^a$

n	ML_y	CpM	CpFe	$M\text{-}C\underline{H}_2$	$FeC\underline{H}_2$	$FeCH_2C\underline{H}_2$	$MCH_2C\underline{H}_2$	$FeCH_2CH_2C\underline{H}_2$	$MCH_2CH_2C\underline{H}_2$
3	$Mo(CO)_3Cp$	5.24s	4.74s	1.62m	1.44m	1.71s			
4	$Mo(CO)_3Cp$	5.28s	4.72s	1.68s	1.48s	1.48s	1.68s		
5	$Mo(CO)_3Cp$	5.26s	4.72s	1.60s	1.44s	1.44s	1.60s	1.36s	
6	$Mo(CO)_3Cp$	5.32s	4.73s	1.60s	1.46s	1.46s	1.60s	1.34s	1.34s
3	$W(CO)_3Cp$	5.37s	4.73s	1.58m	1.42m	1.45m			
4	$W(CO)_3Cp$	5.34s	4.69s	1.62s	1.48s	1.48s	1.62s		
5	$W(CO)_3Cp$	5.35s	4.70s	1.52s	1.42s	1.40s	1.51s	1.30m	
6	$W(CO)_3Cp$	5.34s	4.69s	1.51s	1.41s	1.41s	1.51s	1.29s	1.29s
3	$Re(CO)_5$		4.72s	1.00m	1.49m	1.82m			
4	$Re(CO)_5$		4.72s	1.00m	1.50s	1.48s	1.80m		
5	$Re(CO)_5$		4.72s	0.92m	1.44s	1.43s	1.76qn^b	1.30m	
6	$Re(CO)_5$		4.72s	0.92m	1.42s	1.42s	1.74m	1.28s	1.28s
3	$Ru(CO)_2Cp$	5.30s	4.70s	1.64m	1.44m	1.72m			
4	$Ru(CO)_2Cp$	5.22s	4.71s	1.66s	1.50s	1.50s	1.54s		
5	$Ru(CO)_2Cp$	5.23s	4.73s	1.64s	1.44s	1.44s	1.54m	1.30m	
6	$Ru(CO)_2Cp$	5.16s	4.66s	1.67m	1.44s	1.45s	1.54m	1.31s	1.30s

a: in $CDCl_3$ relative to TMS (0.00 ppm), s = singlet, qn = quintet, m = multiplet, *b*: J=7.7 Hz.

Table 5.4

^1H NMR data for $[Cp^*(CO)_2Fe(CH_2)_nML_y]$[a]

n	ML_y	$C_5(C\underline{H}_3)_5$	CpM	$M\text{-}C\underline{H}_2$	$Cp^*FeC\underline{H}_2$	$FeCH_2C\underline{H}_2$	$MCH_2C\underline{H}_2$	$FeCH_2CH_2C\underline{H}_2$
3	$Ru(CO)_2Cp$	1.72s	5.18s	1.64s	0.91m	1.64s		
4	$Ru(CO)_2Cp$	1.72s	5.22s	1.67s	0.96m	1.55s	1.55m	
5	$Ru(CO)_2Cp$	1.72s	5.21s	1.64m	0.90m	1.38m	1.51m	1.30m
4	$Re(CO)_5$	1.72s		0.96m	0.88m	1.48m	1.48m	
3	$Fe(CO)_2Cp$	1.70s	4.68s	1.46m	0.93m	1.46m		

a: In $CDCl_3$ relative to TMS (0.00 ppm) a significant effect due to both metals on each end of the carbon chain. Thus, for the Fe/W complex the chemical shift for the β methylene protons is 1.45 ppm, whilst for the Fe/Mo complex it is 1.71 ppm and for the Fe/Re complex the shift is 1.82 ppm. The δ value of the proton peaks in positions γ to a metal, and beyond, no longer appear to be affected directly by that metal. It therefore seems clear that a metal influences the protons in the α and β positions to it and that the effect is no longer apparent to the protons γ to the metal. Also apparent is the approximately 0.5 ppm upfield shift of the peaks due to the protons α to Fe in the Cp^* complexes relative to the analogous Cp complexes. Neither the Cp peaks nor the methyl protons of the Cp^* ligand show any significant shift with changing either the length of the hydrocarbon chain or the metal on the other end of the chain.

^{13}C NMR

^{13}C NMR data and assignments for compounds $[Cp(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$ and $[Cp(CO)_2Ru(CH_2)_nRu(CO)_2Cp]$ (n = 3 and 4) have been previously reported [18], however, some of these data appear to be incorrect. The ^{13}C NMR data for $[Cp(CO)_2Ru(CH_2)_nRu(CO)_2Cp]$ (n = 5 and 6) have also been reported [27], though some of the assignments appear to be incorrect. For comparitive purposes, the ^{13}C NMR data of the $[Cp(CO)_2Fe(CH_2)_nRu(CO)_2Cp]$ complexes is reported along with those of their homometallic analogues. From the ^{13}C NMR data (Tables 5.5, 5.6 and 5.7) it can be seen that for the methylene chain of the complexes where $n > 3$, the carbon atom peaks α to a metal occur at positions

Table 5.5

^{13}C NMR data for $[Cp(CO)_2Fe(CH_2)_nML_y]^a$

n	ML_y	MCO(trans)^b	MCO(cis)^b	FeCO	CpM	CpFe	MCH_2	$FeCH_2$	βFe^c	βM^d	γFe	γM
3	$Mo(CO)_3Cp$	240.0	227.7	217.7	92.7	85.2	6.4	8.4	45.5			
4	$Mo(CO)_3Cp$	235.0	227.1	217.3	92.6	85.1	2.8	3.3	42.0^e	44.4^e		
5	$Mo(CO)_3Cp$	239.9	227.7	217.7	92.7	85.3	3.0	3.8	38.1	36.4	40.8	
6	$Mo(CO)_3Cp$	239.9	227.7	217.8	92.7	85.3	2.8	3.7	38.3	36.5	34.3	35.1
3	$W(CO)_3Cp$	229.1	217.4^e	217.6^e	91.4	85.2	-5.7	9.1	45.8			
4	$W(CO)_3Cp$	*f*	218.1^e	217.8^e	92.1	85.8	-9.1	3.9	42.4^g	45.3^g		
5	$W(CO)_3Cp$	*f*	217.5^e	217.7^e	91.5	85.3	-9.6	3.8	38.0	36.9	41.2	
6	$W(CO)_3Cp$	*f*	217.5^e	217.8^e	91.5	85.3	-9.8	3.7	38.3	37.0	34.2	35.6
3	$Re(CO)_5$	181.4	186.1	217.2		85.0	-3.9	11.4	48.3			
4	$Re(CO)_5$	181.4	185.9	217.5		85.3	-9.0	3.3	46.4	44.5		
5	$Re(CO)_5$	181.6	186.1	217.8		85.3	-8.9	4.0	37.8	39.0	42.8	
6	$Re(CO)_5$	181.5	186.0	217.7		85.3	-9.1	3.8	38.3	39.2	34.2	37.1

a: in $CDCl_3$ relative to TMS (0.00 ppm) *b*: relative to the alkyl chain

c: βFe refers to the carbon atom of the alkyl chain β to Fe etc.

d: βM refers to the carbon atom of the alkyl chain β to M etc. *e*: assignments could be interchanged

f: not observed *g*: assignments could be interchanged

Table 5.6

^{13}C NMR data for $[Cp^*(CO)_2Fe(CH_2)_nML_y]^a$

n	ML_y	MCO	$Cp^*Fe\underline{C}O$	CpM	$\underline{C}_5(CH_3)_5$	MCH_2	$FeCH_2$	βFe^b	βM^c	γFe	$C_5(\underline{C}H_3)_5$
3	$Ru(CO)_2Cp$	202.7	219.7	88.5	94.7	2.6	18.2	48.3			9.4
4	$Ru(CO)_2Cp$	202.5	219.6	88.5	94.7	-2.9	13.9	43.4	46.4		9.3
5	$Ru(CO)_2Cp$	202.5	219.7	88.6	94.7	-2.8	14.3	37.6	39.9	41.1	9.3
4	$Re(CO)_5$	186.2^d,181.7^e	219.7		94.7	-8.7	13.5	46.0	45.4		9.3
3	$Fe(CO)_2Cp$	217.9	219.6	85.2	94.7	9.4	18.3	46.9			9.4

a: in $CDCl_3$ relative to TMS (0.00 ppm) *b*: βFe refers to the carbon atom of the alkyl chain β to Fe *etc.*
c: βM refers to the carbon atom of the alkyl chain β to M *etc.*
d: CO is in *cis* position, *e*: CO is in *trans* position relative to alkyl chain.

Table 5.7:

^{13}C NMR data for the compounds, [{Cp(CO)$_2$Fe}$_2$(CH$_2$)$_n$], [{Cp(CO)$_2$Ru}$_2$(CH$_2$)$_n$] and [Cp(CO)$_2$Fe(CH$_2$)$_n$Ru(CO)$_2$Cp][a]

[Cp(CO)$_2$Fe(CH$_2$)$_n$Fe(CO)$_2$Cp]

n	Fe-CO	Cp	Fe-$\underline{C}H_2$	Fe-CH_2-$\underline{C}H_2$	Fe-CH_2-CH_2-$\underline{C}H_2$
3[b]	217.9	85.2	7.8	47.4	
4[b]	217.8	85.4	3.8	43.8	
5	217.8	85.3	4.0	38.3	40.2
6	217.7	85.3	3.8	38.3	34.5

[Cp(CO)$_2$Ru(CH$_2$)$_n$Ru(CO)$_2$Cp]

n	Ru-CO	Cp	Ru-$\underline{C}H_2$	Ru-CH_2-$\underline{C}H_2$	Ru-CH_2-CH_2-$\underline{C}H_2$
3	202.6	88.5	0.9	50.1	
4[c]	202.5	88.6	-3.3	45.2	
5[d]	202.5	88.5	-3.0	39.7	40.1
6[e]	202.5	88.5	-3.2	39.9	34.4

[Cp(CO)$_2$Fe(CH$_2$)$_n$Ru(CO)$_2$Cp]

n	Fe-CO	Ru-CO	Ru-Cp	Fe-Cp	Ru-$\underline{C}H_2$	Fe-$\underline{C}H_2$	Fe-CH_2-$\underline{C}H_2$	Ru-CH_2-$\underline{C}H_2$	Ru-CH_2-CH_2-$\underline{C}H_2$	Fe-CH_2-CH_2-$\underline{C}H_2$
3	217.9	202.6	88.5	85.2	1.0	7.7	48.7			
4	217.8	202.5	88.6	85.3	-3.2	3.7	43.8	45.2		
5	217.8	202.5	88.6	85.3	-3.0	4.1	38.2	39.7	40.2	
6	217.8	202.5	88.6	85.3	-3.2	3.9	38.4	39.9	34.4	34.5

a: measured in CDCl$_3$, peaks externally referenced to TMS (0.0 ppm).
b: data from reference [25].
c: data from reference [18] (but new assignments have been made, see text).
d: data from reference [27].
e: data from reference [27] (but new assignments have been made).

characteristic for that metal. Hence carbon atoms α to Fe resonate at between 3 and 4 ppm, whilst carbon atoms α to Re resonate at *ca.* -9 ppm. The α carbon atom peaks are shifted *ca.* 4-5 ppm downfield for the complexes where n = 3. This must be due to the influence of the metal on the other end of the chain. The influence a metal has on the chemical shifts of carbon atoms in the methylene chain diminishes along the chain and is, thus, only really apparent in the α, β and γ positions relative to that metal. As the influence of the second metal decreases and the carbon becomes increasingly influenced by one metal only, the chemical shifts of the carbon atoms move upfield. As has been observed before [20], the peaks of the carbon atoms α to Fe for the Cp^* complexes are shifted *ca.* 10 ppm downfield relative to the positions for the Cp complexes. This deshielding effect is no longer apparent for the β carbon atoms. The alkyl chain length or nature of the metals on the opposite ends of the chain do not appear to affect the positions of the CO, Cp or Cp^* peaks.

The β carbon chemical shift of complex $[Cp(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$ is in an intermediary position to the positions of the β carbon chemical shifts of $[Cp(CO)_2Fe(CH_2)_3Fe(CO)_2Cp]$ and $[Cp(CO)_2Ru(CH_2)_3Ru(CO)_2Cp]$ respectively, suggesting that the two different metals of $[Cp(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$ influence the β carbon equally. For complex $[Cp(CO)_2Fe(CH_2)_4Ru(CO)_2Cp]$ the chemical shifts of the carbons α and β to a particular metal are very similar or identical to their homometallic analogues. The same applies for the cyclopentadienyl Fe/Ru complexes where n = 5 and 6 for the α, β and γ carbon atoms.

Mass Spectra

Mass spectrometry is the simplest readily available method to unambiguously confirm the composition of these heterodinuclear complexes, since all other data obtained does not completely exclude the presence of equimolar quantities of the monodinuclear alkanediyl complexes of the respective transition metals. Thus the heterobimetallic nature of these complexes is confirmed either by the observation of a molecular ion for the proposed structure or fragment ions which are only possible from the heterodinuclear complex. Molecular ions were observed for many of the complexes studied under electron impact conditions and in all cases where chemical ionization was used.

The major ions observed in the electron impact mass spectra of the compounds, $[Cp(CO)_2Fe(CH_2)_nML_y]$ $\{n = 3\text{-}6, ML_y = Mo(CO)_3Cp, W(CO)_3Cp, Ru(CO)_2Cp, Re(CO)_5\}$, are listed in Tables 5.8 and 5.9. Possible fragmentation sequences giving rise to these ions are shown in **SCHEME 5.2**.

Because the species CO and Fe both have masses which are multiples of 14 (the mass of one CH_2 unit) many mass spectral assignments are ambiguous and the exact fragmentation sequence is not certain from the low resolution data obtained. However, often the exact order of fragment loss is not significant and in many cases other data available indicates which of two possible assignments is the more likely.

Table 5.8: Mass spectral data for complexes $[Cp(CO)_2Fe(CH_2)_nML_y]$

ION (singly charged positive)	RELATIVE INTENSITY OF ION[a] [% of base peak]											
	m = $Cp(CO)_2Fe(CH_2)_nMo(CO)_3Cp$				*m* = $Cp(CO)_2Fe(CH_2)_nW(CO)_3Cp$				*m* = $Cp(CO)_2Fe(CH_2)_nRu(CO)_2Cp$			
	3	4	5	6	3	4	5	6	3	4	5	6
m	<1	0	(CI)	(CI)	2	0	(CI)	(CI)	<1	2	1	(CI)
$m - (CH_2)_n$	1	0	0	0	0	0	0	[b]<1	0	[b]2	0	0
$m - CO$	1	1	<1	<1	0	0	0	0	0	2	0	0
$m - 2CO$	<1	0	<1	0	3	0	0	<1	<1	2	<5	1
$m - 3CO$	<1	0	<1	0	2	0	0	<1	0	[b]10	3	0
$m - 4CO$	<1	1	<1	<1	2	0	0	<1	3	[b]10	<2	[b]10
$m - 5CO$	2	3	3	<1	5	5	0	<1	-	-	-	-
$m - 2CO - (CH_2)_x$	Ion intensity ≤ 1% except for ions also representing $[m - (CH_2)_n - (CO)_x]^+$											
$m - (CH_2)_n - CO$	1	0	0	<1	2	0	0	<1	14	12	20	12
$m - (CH_2)_n - 2CO$	2	1	0	<1	5	0	0	<1	9	9	12	2
$m - (CH_2)_n - 3CO$	3	3	0	0	10	5	<1	1	7	9	9	6
$m - (CH_2)_n - 4CO$	2	3	0	1	12	7	1	1	31	22	32	10
$m - (CH_2)_n - 5CO$	10	15	15	2	21	15	5	5	-	-	-	-
$m - 2CO - CpH$	0	0	1	0	0	5	1	2	0	10	23	10
$m - 3CO - CpH$	1	1	1	1	10	5	4	4	5	15	28	13
$m - 4CO - CpH^c$	5	17	10	<1	15	35	6	3	16	40	18	12
$m - 5CO - CpH$	10	0	10	3	8	20	8	5	-	-	-	-
$m - 2CO - CpH - (CH_2)_x$	Ion intensity ≤ 10% except for values corresponding to above ions.											

(continued............)

Table 5.8 (............continued)

ION (singly charged positive)	RELATIVE INTENSITY OF ION[a] [% of base peak]											
	m = $Cp(CO)_2Fe(CH_2)_nMo(CO)_3Cp$				m = $Cp(CO)_2Fe(CH_2)_nW(CO)_3Cp$				m = $Cp(CO)_2Fe(CH_2)_n$**Ru**$(CO)_2Cp$			
	3	4	5	6	3	4	5	6	3	4	5	6
$m - Cp(CO)_2Fe - (14)_2$[d]	10	30	20	3	8	10	5	0	0	85	17	15
$m - Cp(CO)_2Fe - (14)_3$	10	0	1	<1	21	4	2	0	59	0	12	5
$m - Cp(CO)_2Fe - (14)_4$	6	15	0	1	10	50	1	4	17	75	12	15
$m - Cp(CO)_2Fe - (14)_5$	10	0	5	<1	12	0	4	0	30	0	24	0
$m - Cp(CO)_2Fe - (14)_6$	5	25	5	5	8	15	8	8	1	40	0	3
$m - Cp(CO)_2Fe - (14)_7$	10	5	5	2	8	0	6	0	53	0	25	0
$m - Cp(CO)_2Fe - (14)_8$	10	15	0	5	6	15	3	10	–	72	0	35
$m - Cp(CO)_2Fe - (14)_9$	20	10	30	1	12	3	10	0	-	-	45	0
$m - Cp(CO)_2Fe - (14)_{10}$	–	35	1	5	–	40	4	10	-	-	-	85
$m - Cp(CO)_2Fe - (14)_{11}$	–	–	30	4	–	–	10	0	-	-	-	-
$m - Cp(CO)_2Fe - (14)_{12}$	–	–	–	30	–	–	–	12	-	-	-	-
$[MC_3H_3]$	5	6	5	10	3	5	3	3	8	8	8	<1
$Cp(CO)_2Fe(CH_2)_n$	5	0	0	0	5	5	2	2	0	2	20	20
$Cp(CO)_2Fe(CH_2)_n - (14)_2$[e]	0	0	0	3	3	0	0	0	0	28	80	80
$Cp(CO)_2Fe(CH_2)_n - (14)_3$	10	20	20	2	50	25	100	100	15	0	8	3
$Cp(CO)_2Fe(CH_2)_n - (14)_4$	15	2	10	3	32	0	2	0	30	30	20	15
$Cp(CO)_2Fe(CH_2)_n - (14)_5$	5	40	20	1	45	40	20	14	23		23	0
$Cp(CO)_2Fe(CH_2)_n - (14)_6$	15	1	65	0	28	0	40	0	4	30	3	5
$Cp(CO)_2Fe(CH_2)_n - (14)_7$	2	48	1	8	4	30	1	40	100	-	30	-
$Cp(CO)_2Fe(CH_2)_n - (14)_8$	100	12	42	1	100	4	40	2	-	100	0	40

(continued............)

Table 5.8 (.............continued)

ION (singly charged positive)	RELATIVE INTENSITY OF ION[a] [% of base peak]											
	m = $Cp(CO)_2Fe(CH_2)_nMo(CO)_3Cp$				*m* = $Cp(CO)_2Fe(CH_2)_nW(CO)_3Cp$				*m* = $Cp(CO)_2Fe(CH_2)_nRu(CO)_2Cp$			
	3	4	5	6	3	4	5	6	3	4	5	6
$Cp(CO)_2Fe(CH_2)_n - (14)_9$	-	100	6	15	-	100	1	36	-	-	100	-
$Cp(CO)_2Fe(CH_2)_n - (14)_{10}$	-	-	100	0	-	-	69	3	-	-	-	100
$Cp(CO)_2Fe(CH_2)_n - (14)_{11}$	-	-	-	100	-	-	-	68	-	-	-	-
$[FeC_3H_3]$	10	17	16	20	8	8	8	8	4	10	10	10
Fe	50	60	60	70	27	30	67	54	28	36	34	70
M	10	4	5	15	0	0	0	0	21	3	1	3
Cp_2Fe	40	33	30	18	17	25	18	13	15	24	38	15
Cp_2M	20	21	55	6	15	15	16	9	33	32	54	84
FeCpM	Equivalent to $[CpM(CO)_2]^+$				Equivalent to $[CpM(CO)_2]^+$				Equivalent to $[CpM(CO)_2]^+$			

$(CH_2)_x$: $2 \le x \le n$

$(CO)_x$: x = 1-4, M = Ru ; x = 1-5, M = Mo, W

(CI) : molecular ion evident in chemical ionization spectrum only.

– : ion not applicable to this complex.

a : ion intensity listed is that of the most abundant isotope combination.

b ion has more than one possible asignment:-another assignment is more probable.

c : $[m - 4CO - CpH]^+$ is numerically equivalent to $[m - Cp(CO)_2FeH]^+$.

d : ions at these masses could be due to any appropriate combination of losses of CH_2 and CO; the final species after the series of losses is $[CpM]^+$.

e : ions at these masses could be due to any appropriate combination of losses of CH_2 and CO; the final species after the series of losses is $[CpFe]^+$.

Table 5.9: Mass spectral data for [$Cp(CO)_2Fe(CH_2)_nRe(CO)_5$]

ION (singly charged positive)	RELATIVE INTENSITY OF ION^a [% of base peak]			
	m = $Cp(CO)_2Fe(CH_2)_nRe(CO)_5$			
	3	4	5	6
m	8	4	(CI)	(CI)
$m - (CH_2)_n$	2	$^b2$	0	$^b1$
m – CO	1	2	0	< 1
m – 2CO	3	2	< 1	2
m – 3CO	1	$^b44$	< 1	1
m – 4CO	3	$^b10$	< 1	$^b1$
m – 5CO	2	$^b8$	< 1	< 1
m – 6CO	2	$^b17$	< 1	< 1
m – 7CO	4	$^b10$	< 1	1
$m - 2CO - (CH_2)_x$	Ion intensity ≤ 1% except for ions also representing [$m - (CH_2)_n - (CO)_x$]$^+$			
$m - (CH_2)_n - CO$	25	44	3	1
$m - (CH_2)_n - 2CO$	4	10	< 1	< 1
$m - (CH_2)_n - 3CO$	4	8	1	< 1
$m - (CH_2)_n - 4CO$	30	17	4	1
$m - (CH_2)_n - 5CO$	16	10	5	1
$m - (CH_2)_n - 6CO$	8	8	4	< 1
$m - (CH_2)_n - 7CO$	4	4	2	1
m – 2CO – CpH	9	2	< 1	1
m – 3CO – CpH	2	10	2	< 1
m – 4CO – CpH^c	4	20	6	1
m – 5CO – CpH	3	10	3	< 1
m – 6CO – CpH	3	4	1	< 1
m – 7CO – CpH	4	2	1	< 1
$m - 2CO - CpH - (CH_2)_x$	Ion intensity ≤ 10% except for values corresponding to above ions.			
$m - Cp(CO)_2Fe - (14)_2^d$	10	50	< 1	< 1
$m - Cp(CO)_2Fe - (14)_3$	35	0	1	0
$m - Cp(CO)_2Fe - (14)_4$	10	62	< 1	< 1
$m - Cp(CO)_2Fe - (14)_5$	15	0	6	0
$m - Cp(CO)_2Fe - (14)_6$	3	25	< 1	2
$m - Cp(CO)_2Fe - (14)_7$	10	0	6	0
$m - Cp(CO)_2Fe - (14)_8$	3	15	0	2
$m - Cp(CO)_2Fe - (14)_9$	5	0	5	0
$m - Cp(CO)_2Fe - (14)_{10}$	2	5	0	2
$m - Cp(CO)_2Fe - (14)_{11}$	2	0	3	0
$m - Cp(CO)_2Fe - (14)_{12}$	2	2	< 1	< 1

(continued.............)

Table 5.9 (.............continued)

ION (singly charged positive)	RELATIVE INTENSITY OF ION^a [% of base peak]			
	m = $Cp(CO)_2Fe(CH_2)_nRe(CO)_5$			
	3	4	5	6
$m - Cp(CO)_2Fe - (14)_{13}$	4	1	< 1	0
$m - Cp(CO)_2Fe - (14)_{14}$	–	3	1	< 1
$m - Cp(CO)_2Fe - (14)_{15}$	–	–	0	0
$m - Cp(CO)_2Fe - (14)_{16}$	–	–	–	< 1
$Cp(CO)_2Fe(CH_2)_n$	1	0	0	< 1
$Cp(CO)_2Fe(CH_2)_n - (14)_2{}^e$	1	0	0	0
$Cp(CO)_2Fe(CH_2)_n - (14)_3$	5	31	32	7
$Cp(CO)_2Fe(CH_2)_n - (14)_4$	12	0	1	0
$Cp(CO)_2Fe(CH_2)_n - (14)_5$	30	40	16	2
$Cp(CO)_2Fe(CH_2)_n - (14)_6$	20	1	23	0
$Cp(CO)_2Fe(CH_2)_n - (14)_7$	5	36	1	14
$Cp(CO)_2Fe(CH_2)_n - (14)_8$	100	4	38	0
$Cp(CO)_2Fe(CH_2)_n - (14)_9$	–	100	3	28
$Cp(CO)_2Fe(CH_2)_n - (14)_{10}$	–	–	100	6
$Cp(CO)_2Fe(CH_2)_n - (14)_{11}$	–	–	–	100
$[FeC_3H_3]$	8	9	12	13
Fe	27	27	55	73
M	4	3	0	< 1
Cp_2Fe	26	16	34	2
Cp_2M	-	-	-	-
FeCpM	5	5	3	0

$(CH_2)_x$: $2 \leq x \leq n$

$(CO)_x$: x = 7, M = Re

(CI) : molecular ion evident in chemical ionization spectrum only.

– : ion not applicable to this complex.

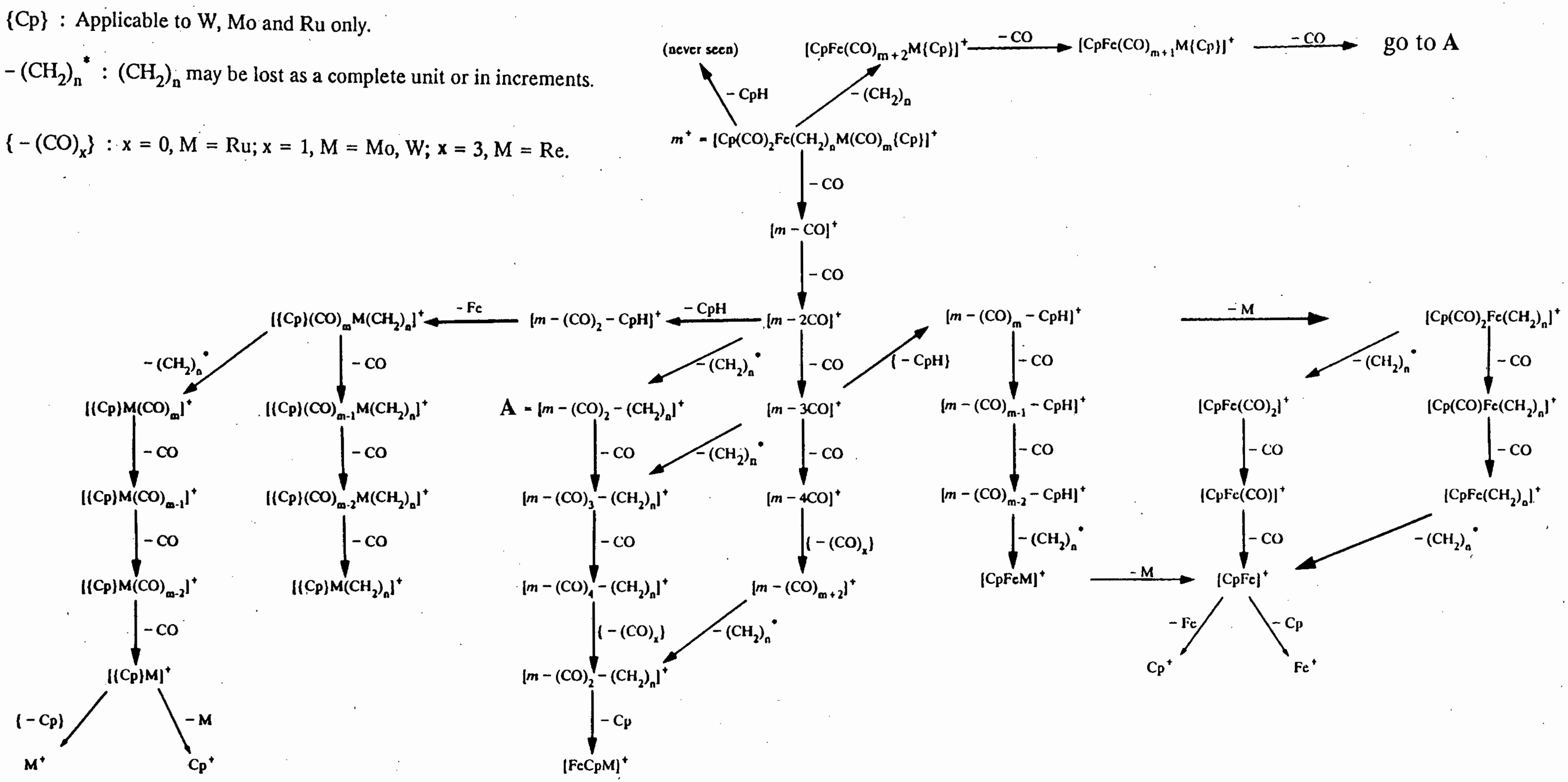
a : ion intensity listed is that of the most abundant isotope combination.

b ion has more than one possible asignment:-another assignment is more probable.

c : $[m - 4CO - CpH]^+$ is nominally equivalent to $[m - Cp(CO)_2FeH]^+$.

d : ions at these masses could be due to any appropriate combination of losses of CH_2 and CO; the final species after the series of losses is $[Re]^+$.

e : ions at these masses could be due to any appropriate combination of losses of CH_2 and CO; the final species after the series of losses is $[CpFe]^+$.



SCHEME 5.2: Illustration of possible mass spectral fragmentations giving rise to ions observed.

Ions corresponding to $[Cp_2Fe]^+$ and $[Cp_2M]^+$ are observed in all the spectra. The formation of ferrocene in complexes containing the $[Cp(CO)_2Fe]$ unit has been observed previously [20, 28] and it is of interest to observe that other metals with Cp ligands in these type of complexes behave similarly. High resolution accurate mass data obtained for the complex, $[Cp(CO)_2Fe(CH_2)_3Mo(CO)_3Cp]$ confirm the formation of $[Cp_2Mo]^+$ with a relative intensity of 20%. The ions, $[CpM(CO)_x]^+$ (M = Mo, W; x = 0-3) are relatively abundant and thus also comparable with their Fe analogs $\{[CpFe(CO)_x]^+$ (x = 0-2)$\}$. $[CpFe]^+$ (m/z 121) is the base peak in all these spectra except for the Fe/W complexes where n = 5 or 6 where it is $[CpFe(CO)_2(CH_2)_n - C_3H_6]^+$.

The ion due to the free metal species is always observed for Fe (25-70%), Mo (4-15%), Re (<5%) and Ru (<4%), but is never seen for W.

Ions involving metal-metal bonding after loss of the methylene bridge are relatively abundant, even though the expected precursor, $[Cp(CO)_2FeML_y]^+$, {M = Mo, W, L_y = $Cp(CO)_3$; M = Ru, L_y = $Cp(CO)_2$; M = Re, L_y = $(CO)_5$} is only observed unambiguously in the cases when n = 3 and M = Mo, Re. This indicates a stronger interaction between Fe and the metal atom at the other end of the carbon chain for shorter chain complexes, as was also observed in the mass spectra of the complexes, $[Cp(CO)_2Fe(CH_2)_nX]$ (n = 3 - 10, X= I, Br) [20].

The ion representing [CpFeMCp] (M = Mo, W and Ru) or [CpFeRe] is most abundant in the cases where n = 3 and progressively decreases in relative intensity as the methylene chain lengthens to n = 6. The presence of both $[CpFeM]^+$ and $[CpM(CO)_2]^+$, which have the same nominal mass, is indicated by the accurate mass data obtained for m/z 219 in the complex $[Cp(CO)_2Fe(CH_2)_3Mo(CO)_3Cp]$. These data show that both the species $[CpFeMo]^+$ and $[CpMo(CO)_2]^+$ are present, with relative intensities of 0.2% and 9% respectively. In the case of Re, the ions observed at m/z 308 must be due to $[CpFeRe]^+$, as it is unlikely that $[CpRe(CO)_2]^+$ would be present. In all the spectra, the ion corresponding to $[FeM]^+$ is not observed except possibly in the case of Re where it may also be assigned to $[Re(CO)_2]^+$.

The loss of C_5H_5 (65 dalton) is not usually observed in the mass spectral fragmentation of the compounds. In contrast, the loss of C_5H_6 (66 dalton) does seem to occur, not from the molecular ion itself, but after the initial loss of 2 or more carbonyls from the molecular ion.

Although a large number of Cp metal derivatives have been investigated by mass spectrometry, very few Cp* metal complexes have been investigated by this technique [29-31].

The mass spectral data for the complexes $[Cp^*(CO)_2Fe(CH_2)_nML_y]$ (ML_y = $Ru(CO)_2Cp$, n = 3-5; ML_y = $Re(CO)_5$, n = 4; ML_y = $Fe(CO)_2Cp$, n = 3) are reported in Table 5.10. All the assignments for the complex $[Cp^*(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$ were confirmed by high resolution mass spectrometry. Molecular ions were observed in the mass spectra of all these Cp* complexes. The relative abundance of these peaks was found to be greatest for the complexes where n = 3.

Table 5.10: Mass spectral data for the complexes $[Cp^*(CO)_2Fe(CH_2)_nML_y]$

ION (singly charged positive)	RELATIVE INTENSITY OF ION[a] [% of base peak]				
	m = $Cp^*(CO)_2Fe(CH_2)_n$**Ru**$(CO)_2Cp$			m = $Cp^*(CO)_2Fe(CH_2)_3$**Fe**$(CO)_2Cp$	m = $Cp^*(CO)_2Fe(CH_2)_4$**Re**$(CO)_5$
	3	4	5		
m	3	<1	<1	6	<1
$m - (CH_2)_n$	3	0	0	2	0
m – CO	2	0	0	0	0
m – 2CO	1	0	0	0	0
m – 3CO	3	<1	0	0	<1
m – 4CO	0	<1	0	1	<1
m – 5CO	-	-	-	-	<1
m – 6CO	-	-	-	-	<1
m – 7CO	-	-	-	-	<1
$m - 2CO - (CH_2)_x$	Ion intensity ≤ 1% except for ions also representing $[m - (CH_2)_n - (CO)_x]^+$				
$m - (CH_2)_n - CO$	7	<1	<1	8	<1
$m - (CH_2)_n - 2CO$	6	<1	1	5	<1
$m - (CH_2)_n - 3CO$	3	0	1	10	<1
$m - (CH_2)_n - 4CO$	13	3	7	17	<1
$m - (CH_2)_n - 5CO$	-	-	-	-	1
$m - (CH_2)_n - 6CO$	-	-	-	-	<1
$m - (CH_2)_n - 7CO$	-	-	-	-	1

(continued.............)

Table 5.10 (.............continued)

ION (singly charged positive)	RELATIVE INTENSITY OF ION[a] [% of base peak]				
	m = Cp*(CO)$_2$Fe(CH$_2$)$_n$**Ru**(CO)$_2$Cp			m = Cp*(CO)$_2$Fe(CH$_2$)$_3$**Fe**(CO)$_2$Cp	m = Cp*(CO)$_2$Fe(CH$_2$)$_4$**Re**(CO)$_5$
	3	4	5		
m – Cp*(CO)$_2$Fe – (CH$_2$)$_n$ - CO	13	17	12	10	4
m – Cp*(CO)$_2$Fe – (CH$_2$)$_n$ - 2CO	35	20	20	62	4
m – Cp*(CO)$_2$Fe – (CH$_2$)$_n$ - 3CO	-	-	-	-	3
m – Cp*(CO)$_2$Fe – (CH$_2$)$_n$ - 4CO	-	-	-	-	3
m – Cp*(CO)$_2$Fe – (CH$_2$)$_n$ - 5CO	-	-	-	-	1
m – Cp*(CO)$_2$Fe – (CH$_2$)$_n$ - Cp	2	1	0	6	-
m – Cp*(CO)$_2$Fe – (CH$_2$)$_n$ - Cp- 2CO	9	<1	<1	0	-
Cp	4	2	2	6	-
CpH	1	0	0	5	-
[MC$_3$H$_3$]	9	3	3	4	-
Cp*(CO)$_2$Fe(CH$_2$)$_n$	0	0	0	0	0
Cp*(CO)$_2$Fe(CH$_2$)$_n$ – (14)$_2$[b]	51	60	70	47	50
Cp*(CO)$_2$Fe(CH$_2$)$_n$ – (14)$_2$ - 2H	8	3	6	6	3
Cp*(CO)$_2$Fe(CH$_2$)$_n$ – (14)$_3$	14	0	0	0	0
Cp*(CO)$_2$Fe(CH$_2$)$_n$ – (14)$_3$ - 2H	0	0	0	6	0
Cp*(CO)$_2$Fe(CH$_2$)$_n$ – (14)$_4$	75	29	3[c]	50	21
Cp*(CO)$_2$Fe(CH$_2$)$_n$ – (14)$_4$ - 2H	20	100	100	10	100
Cp*(CO)$_2$Fe(CH$_2$)$_n$ – (14)$_5$	38	0	10	80	0
Cp*(CO)$_2$Fe(CH$_2$)$_n$ – (14)$_5$ - 2H	4	1	2	8	0
Cp*(CO)$_2$Fe(CH$_2$)$_n$ – (14)$_6$	2	41	5	6	38
Cp*(CO)$_2$Fe(CH$_2$)$_n$ – (14)$_6$ - 2H	2	8	3	2	3
Cp*(CO)$_2$Fe(CH$_2$)$_n$ – (14)$_7$	100	1	35	100	0
Cp*(CO)$_2$Fe(CH$_2$)$_n$ – (14)$_7$ - 2H	-	1	0	-	1
Cp*(CO)$_2$Fe(CH$_2$)$_n$ – (14)$_8$	-	60	0	-	75
Cp*(CO)$_2$Fe(CH$_2$)$_n$ – (14)$_8$ - 2H	-	-	1	-	-

(continued.............)

Table 5.10 (.............continued)

ION (singly charged positive)	RELATIVE INTENSITY OF ION[a] [% of base peak]				
	m = Cp*(CO)$_2$Fe(CH$_2$)$_n$**Ru**(CO)$_2$Cp			m = Cp*(CO)$_2$Fe(CH$_2$)$_3$**Fe**(CO)$_2$Cp	m = Cp*(CO)$_2$Fe(CH$_2$)$_4$**Re**(CO)$_5$
	3	4	5		
Cp*(CO)$_2$Fe(CH$_2$)$_n$ – (14)$_9$	-	-	55	-	-
[FeC$_3$H$_3$]	1	1	1	4	2
Fe	22	10	10		14
M	5	<1	<1	0	0
Cp*$_2$Fe	0	0	0	3	0
Cp$_2$M	5	2	18	15	-
Cp*	20	12	3	18	12
Cp* - 2H	50	35	34	43	40

(CH$_2$)$_x$: $2 \leq x \leq n$

– : ion not applicable to this complex.

a : ion intensity listed is that of the most abundant isotope combination.

b : ions at these masses could be due to any appropriate combination of losses of CH$_2$ and CO; the final species after the series of losses is [CpFe]$^+$.

c : ion has more than one possible asignment:-another assignment is more probable.

The most prominent fragmentation sequence from the molecular ion is the sequential loss of CO following the loss of $(CH_2)_n$, even though the expected precursor, $[Cp^*(CO)_2FeML_y]^+$ {M = Ru, Fe, $L_y = (CO)_2$; M = Re, $L_y = (CO)_5$} is only observed in the cases where n = 3 (as was found for the CpFe analogues of these Cp* complexes).

Ions due to the loss of ML_y are not observed. However, ions representing $[Cp^*Fe(CO)(CH_2)_n]^+$ are relatively abundant in all the spectra (45-70%).

The base peak in the spectra of the complexes where n = 4 or 5 is due to the ion $[Cp^*Fe(CH_2)_n - 2H]^+$. This indicates the occurence of cyclisation comparable with that dicussed by Cloke *et al.* **(figure 5)** [30], although the possibility of a $M^cLafferty$ type rearrangement [32] cannot be completely ruled out. The latter rearrangment is, however, believed to be extremely unlikely, since it is not observed for the CpFe complexes and since the necessary ring sizes of the required intermediates are very large. When n = 3, this proposed cyclisation gives rise to an ion of lower intensity, indicating that it is a less favoured pathway.

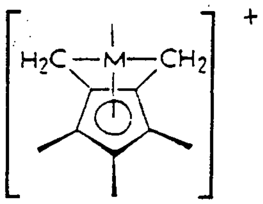


Figure 5: The interaction between the Cp* methyl groups and the metal as proposed by Cloke *et al.* [30].

When n = 3, the base peak corresponds to the ion $[Cp^*Fe]^+$ (m/z 191), which has a relative intensity of between 55 and 75 % when n > 3. In contrast to the above findings, Cloke *et al.* found the base peaks of their Cp* complexes to correspond to the ion $[C_5Me_4CH_2]^+$ (m/z 134) [30]. Peaks at m/z 134 are also observed in the spectra of the $[Cp^*(CO)_2Fe(CH_2)_nML_y]$ complexes at relative abundances of 34-50 %.

Losses of Cp, CpH, Cp* or Cp*H are not observed in any of the spectra of these Cp*Fe complexes, in contrast to the spectra of the CpFe complexes where loss of CpH was observed.

DSC data

μ-Alkanediyl complexes can be used as models for hydrocarbon fragments interacting with two active metal sites on a catalyst surface [33]. Decomposition studies of these complexes are thus relevant to chain termination processes in catalytic reactions. Differential Scanning Calorimetry (DSC) was used to obtain some quantitative information about the decomposition of the heterodinuclear alkanediyl complexes. Previously, results of a DSC study (up to 230°C) of the di-iron complexes $[Fp(CH_2)_nFp]$ {n = 3-12, Fp = $CpFe(CO)_2$} were reported [34] . The DSC data for the compounds $[Fp(CH_2)_nFp]$, $[Rp(CH_2)_nRp]$ and $[Fp(CH_2)_nRp]$ {where n = 3-6, Rp = $CpRu(CO)_2$} are summarized in Table 5.11. All of the compounds show a sharp endotherm at low

Table 5.11: DSC data for alkanediyl complexes (°C)^a.

	$Fp(CH_2)_nFp$			$Rp(CH_2)_nRp$			$Fp(CH_2)_nRp$		
n	3	4	5	3	4	5	3	4	5
m.p.^{b}	104-105	112-115 (125-126)	83-85	84-87	131-132	77-84	85-86	131-132	75-77
T_{max} endo	105	115 (128)	85	91	138	86	94	126	78
T_{max} exo	143	160	158	221	177	156	174	163	174
T_{max} endo	283	271	290						
T_{max} exo				277	248	284	311 386	325 435	320 386

a: Fp = $CpFe(CO)_2$, Rp = $CpRu(CO)_2$

b: m.p. determined on a Kofler hot-stage microscope.

temperature that corresponds to the melting point (m.p.) of the individual compound. For [Fp$(CH_2)_4$Fp], there appear to be two crystalline forms with different m.p.s as noted previously [34]. Notable is that the m.p.s of the mixed metal compounds are very close to those of the di-ruthenium compounds. For all three series, the m.p.s of the compounds where n = 4 are higher than those when n = 3 or 5. This was also observed for the Fe/W and Fe/Mo complexes (Table 5.1). Also, the m.p.s tend to decrease with increasing chain length as found for the more extensive series [Fp$(CH_2)_n$Fp] (where n = 3-12) [34], [Rp$(CH_2)_n$Rp] (where n = 3-10) [18, 28] and other heterobimetallic complexes (Table 5.1).

For the compounds [Fp$(CH_2)_n$Fp], (where n = 3-5) (see Table 5.11) the first T_{max} exotherm (exo) could be assigned to decomposition which results in the loss of the hydrocarbon chain, as has been reported previously and confirmed by identifying the organic decomposition products [34, 18]. The compound [Fp$(CH_2)_n$Fp], where n = 3, decomposes at the lowest temperature compared to the di-iron compounds where n = 4 or 5. The second T_{max} endotherm (endo) for the compounds [Fp$(CH_2)_n$Fp] is probably due to the decomposition of [$Cp_2Fe_2(CO)_4$] which has T_{max} endo at 285°C under these conditions.

For the compounds [Rp$(CH_2)_n$Rp] (n = 3-5), the first T_{max} exo, believed to be due to decomposition, occurs at the highest temperature for [Rp$(CH_2)_3$Rp] (221°C) when compared with the tetra- and penta- methylene bridged di-ruthenium compounds. This shows an opposite trend to that for the di-iron analogues. Thus the mechanism of decomposition of the trimethylene compounds may be metal dependent. That a different decomposition mechanism is operative for [Fp$(CH_2)_3$Fp] and [Rp$(CH_2)_3$Rp] is further borne out by the differing ratios of propene : cyclopropane observed on decomposition. Thus, decomposition of [Fp$(CH_2)_3$Fp] gives mainly cyclopropane, decomposition of [Rp$(CH_2)_3$Rp] gives mainly propene whereas the decomposition behaviour of [Fp$(CH_2)_3$Rp] lies somewhere between the two [34, 18]. The DSC results support this with the first T_{max} exo for [Fp$(CH_2)_3$Rp] (at 174°C) which lies midway between that for [Fp$(CH_2)_3$Fp] (143°C) and [Rp$(CH_2)_3$Rp] (221°C.) For compounds [Rp$(CH_2)_n$Rp] (where n = 3-5) another T_{max} exo is seen in the range 248-284°C which can be ascribed to further decomposition.

For the compounds [Fp$(CH_2)_n$Rp], the first T_{max} exo shows little variation with chain length (174, 163 and 174°C for n = 3-5 respectively). Thus, the apparent easy decomposition pathway for [Fp$(CH_2)_3$Fp] does not appear accessible for [Fp$(CH_2)_3$Rp] or [Rp$(CH_2)_3$Rp]. The final T_{max} exo for the mixed metal dimers are higher than those for either of the homometallic species and a second T_{max} exo is also observed. The DSC data for the mixed metal dimers are different to either of the monometallic dimers but the overall behaviour is closest to that of [Rp$(CH_2)_3$Rp]. This suggests that the mixed metal compounds retain their mixed metal character during decomposition and do not decompose to homometallic species; they may well yield Fe/Ru decomposition products *e.g.* [$Cp_2(CO)_4$FeRu]. This suggests that the decomposition pathways are intramolecular rather than intermolecular.

The consequences of this behaviour for catalysis, that may be implied, are that a catalyst derived from a heterodinuclear compound may well lead to different species on decomposition than would be obtained from a mixture of the homometallic analogues. Thus heterodinuclear compounds may be good precursors for new types of catalysts.

5.3 CRYSTAL STRUCTURE OF [Cp(CO)$_2$Fe(CH$_2$)$_6$Ru(CO)$_2$Cp]

Single crystals of [Cp(CO)$_2$Fe(CH$_2$)$_6$Ru(CO)$_2$Cp] were obtained from slow crystallisation of a dilute hexane solution at -15°C. A suitable single crystal was selected and subjected to a X-ray diffraction study. The positions of the heavy atoms were found from a Patterson map in the space group P2$_1$/C with Z = 2. The structure was found to be disordered, with the assymetric unit being Cp(CO)$_2$(Ru/Fe)(CH$_2$)$_3$. The centre of the molecule lay on a special position. The cyclopentadienyl ring exhibited orientational disorder, with relative populations being 80:20. Other details of the final refinement are given in Table 5.12. Fractional atomic coordinates are available [35]. The extent of the disorder in this structure allows nothing but the gross conformation of the moleculed to be observed (**Figure 6**). Similarly to other structures of alkanediyl complexes, the two metals are connected by a zig-zag alkyl chain [15, 25, 27]. As necessitated by the centre of symmetry within the molecule, the Cp rings and CO groups lie on opposite sides of the molecule (**Figure 7**). This is as observed for the structures of [Cp(CO)$_2$Fe(CH$_2$)$_n$Fe(CO)$_2$Cp] (n = 3, 4) [25], but different to the conformations observed for [Cp(CO)$_2$Ru(CH$_2$)$_5$Ru(CO)$_2$Cp] [27] and

TABLE 5.12: Crystal data and parameters for data collection and refinement for $[Cp(CO)_2Fe(CH_2)_6Ru(CO)_2Cp]$

Crystal data

Molecular formula	$C_{20}H_{22}FeO_4Ru$
Space group	$P2_1/C$
a/Å	7.836(2)
b/Å	10.358(2)
c/Å	12.615(2)
β/°	98.21(2)
V/Å^3	1013
D_c for Z = 2/gcm^{-3}	1.58
F(000)	488

Data collection

μ (MoK_α)/cm^{-1}	13.7
Crystal dimensions/mm	0.35 x 0.52 x 0.48
Crystal decay/%	1.3
Scan mode	$\omega - 2\theta$
Scan width/°ω	$(0.85 + 0.35\tan\theta)$
Aperture width/mm	$(1.12 + 1.05\tan\theta)$
θ Range scanned/°	1-25

Refinement

No. of reflections collected	1784
No. of reflections observed (with $I_{rel} > 2\sigma I_{rel}$)	1579
No. of parameters	167
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.055
$R_w = \Sigma w^{\frac{1}{2}}\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma w^{\frac{1}{2}}\lvert F_o\rvert$	0.049
weighting scheme	$5.81(\sigma^2F)^{-1}$

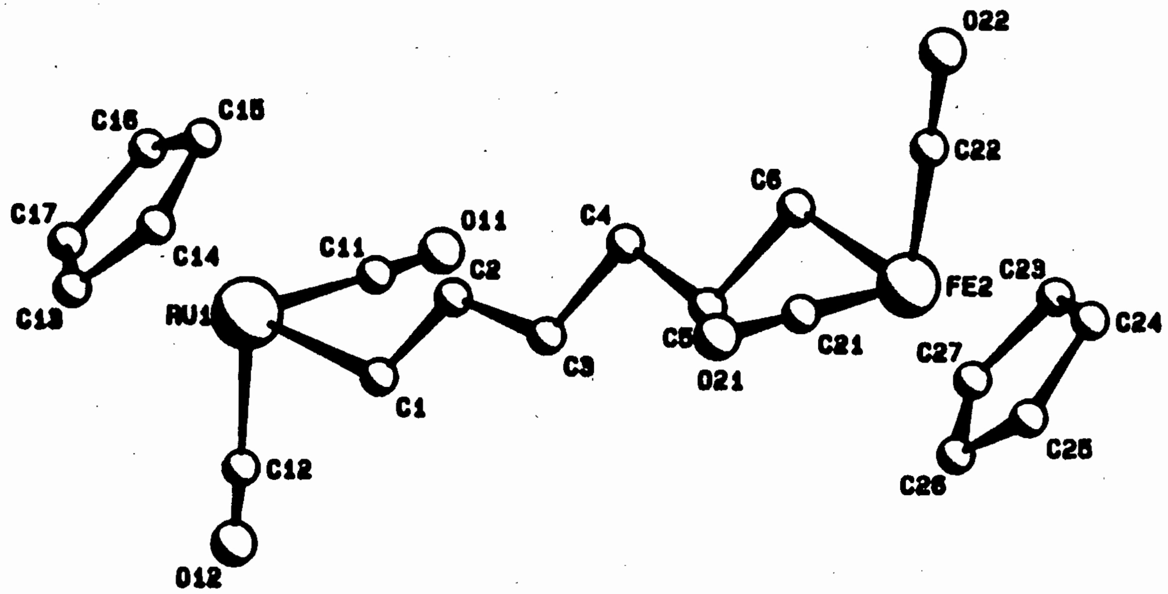


Figure 6: Molecular Structure of $[Cp(CO)_2Fe(CH_2)_6Ru(CO)_2Cp]$

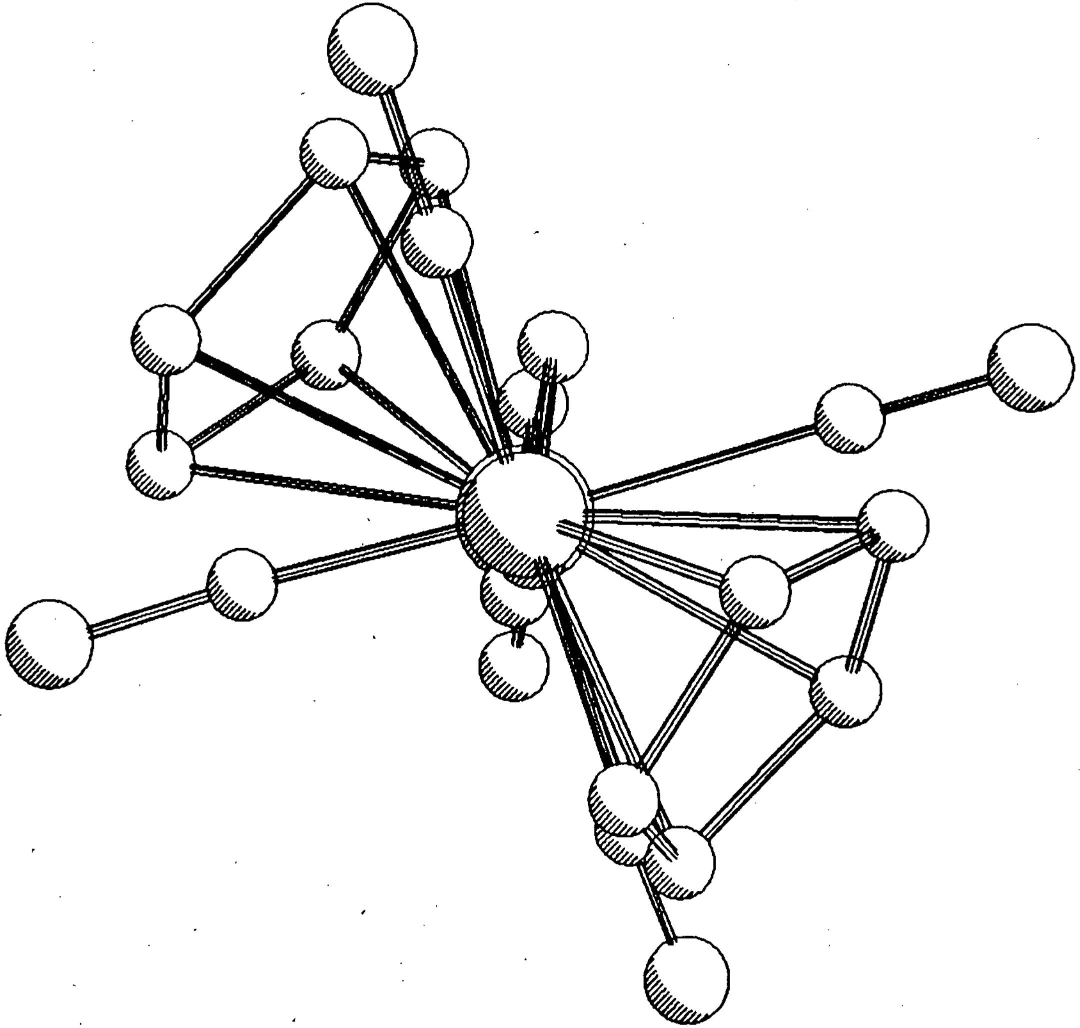


Figure 7: A View Down the Fe-Ru axis of $[Cp(CO)_2Fe(CH_2)_6Ru(CO)_2Cp]$.

$[Cp(CO)_2FeC(O)(CF_2)_3C(O)Fe(CO)_2Cp]$ [36] where the Cp rings are on the same side of the molecule.

It is interesting to note that the same type of disorder has been observed in the complex $[Cp(CO)_2FeCH_2CHCH_2Ru(CO)_2Cp]^+PF_6^-$ (see chapter 6). The cause is clearly that the two ends of the molecules are virtually identical. In each case it may be argued that the lattice energies for the observed disordered structure and the hypothetical structure without disorder must be of the same order of magnitude [37]. Maximisation of entropy is then the driving force behind the occurrence of the mixed Fe/Ru structures, at least at -15°C, under the conditions used for crystal formation. Disorder could presumably be avoided by altering the ligand system on one of the metal atoms.

5.4 CONCLUSIONS

We have shown that good yields of heterobimetallic alkanediyl compounds can be obtained by reactions of the iodoalkyl iron compounds $[CpFe(CO)_2\{(CH_2)_nI\}]$ (n = 3-6) and $[Cp^*Fe(CO)_2\{(CH_2)_nI\}]$ (n = 3-5) with several transition metal carbonyl anions.

In complexes with a shorter alkanediyl chain length the data obtained implies a degree of intermetallic interaction. The study of a wider range of transition metal alkyl bridged complexes has also shown that several previous ^{13}C NMR assignments of the alkyl chain of these complexes were erroneous. The correct assignment of the NMR peaks of these complexes is important to avoid possible misinterpretation of the results of reactivity studies on these complexes.

Mass spectral studies on the complexes $[Cp^{*}(CO)_2Fe(CH_2)_nML_y]$ (ML_y = $Ru(CO)_2Cp$, n = 3-5; ML_y = $Re(CO)_5$, n = 4; ML_y = $Fe(CO)_2Cp$, n = 3) appear to support the findings of other workers that two of the methyl groups of the Cp* ligand bond to the metal atom, under mass spectral conditions, to form a cyclometallated ion.

The results of some reactivity studies on these heterobimetallic alkanediyl complexes are reported in chapter 6.

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CHAPTER 6

SOME REACTIVITY STUDIES ON THE COMPLEXES $[(\eta\text{-}C_5R_5)(CO)_2Fe(CH_2)_nML_y]$

6.1 INTRODUCTION

Although a large number of homometallic $\mu(\alpha,\omega)$ alkanediyl complexes are known [1-3], their reactivity has been little studied. Pettit *et al.* have shown that the thermally induced reaction of CO with the complexes $[\{CpFe(CO)_2\}_2\{\mu\text{-}(CH_2)_n\}]$ (n = 3, 4) lead to the diacyl complexes $[\{CpFe(CO)_2\}_2\{\mu\text{-}C(O)(CH_2)_nC(O)\}]$ [4]. Recently, the complexes $[\{CpFe(CO)_2\}_2\{\mu\text{-}(CH_2)_n\}]$ (n = 3 - 7) were reported to undergo a stepwise reaction with neutral donor ligands, L, to give the monosubstituted acyl complex $[Cp(CO)LFeC(O)(CH_2)_nFe(CO)_2Cp]$ initially, and then the disubstituted diacyl complex $[Cp(CO)LFeC(O)(CH_2)_nC(O)FeL(CO)Cp]$ [5]. Similar reactions of $[\{CpW(CO)_3\}_2\{\mu\text{-}(CH_2)_n\}]$ with L gave the disubstituted acyl complexes $[Cp(CO)_2LWC(O)(CH_2)_nC(O)WL(CO)_2Cp]$ as well as $[Cp(CO)_2LW(CH_2)_nW(CO)_3Cp]$ and $[Cp(CO)_2LW(CH_2)_nWL(CO)_2Cp]$ [5]. The alkanediyl iron complexes react with halogens with cleavage of both iron-carbon bonds to yield $[CpFe(CO)_2X]$ and $X(CH_2)_nX$. The alkanediyl iron complexes where n = 3 - 6 have also been shown to undergo a β-hydride abstraction when treated with Ph_3CPF_6 (trityl salt) to form complexes of the type $[\{CpFe(CO)_2\}_2\{\mu\text{-}(C_nH_{2n-1})\}]$ [6,7]. The complex $[\{Cp(CO)_2Fe\}_2\{\mu\text{-}(CH_2)_3\}]$ was also shown to react with SO_2 to produce the mono- and di-sulphinato species $[Cp(CO)_2FeS(O)_2(CH_2)_3Fe(CO)_2Cp]$ and $[Cp(CO)_2FeS(O)_2(CH_2)_3S(O)_2Fe(CO)_2Cp]$ [8].

The reactivity of the complexes $[(CO)_5M(CH_2)_nM(CO)_5]$ (M = Mn, n = 4 - 6; M = Re, n = 3, 4) with tertiary phosphines, CO, CO/H_2 and halogens has recently been reported [9]. The di-manganese complexes were reported to react with tertiary phosphines to form bis(phosphine)diacyl compounds. In contrast, the rhenium complex $[(CO)_5Re(CH_2)_4Re(CO)_5]$ reacts with tertiary phosphines to form $[(CO)_4(PR_3)Re(CH_2)_4Re(PR_3)(CO)_4]$. These reactions proceed via the diacyl intermediate $[(CO)_4(PR_3)ReC(O)(CH_2)_4C(O)Re(PR_3)(CO)_4]$. The complexes $[(CO)_5Mn(CH_2)_nMn(CO)_5]$ (n = 4,5) react with halogens in CH_2Cl_2 to give the expected cleavage products $[Mn(CO)_5X]$ and $X(CH_2)_nX$. The reactions of $[(CO)_5Mn(CH_2)_4Mn(CO)_5]$ with Br_2 and I_2 <u>in THF</u> do not give the expected cleavage products, and adipic acid and an unidentified inorganic product are obtained instead. Both the di-manganese and di-rhenium alkanediyl complexes react with CO to form the diacyl species. The reaction of $[(CO)_5Mn(CH_2)_4Mn(CO)_5]$ with synthesis gas (CO/H_2 1:1) resulted in the formation of the diol $HOCH_2(CH_2)_4CH_2OH$ and $[Mn_2(CO)_{10}]$. In all comparative reactions, the manganese complexes were observed to react faster than their rhenium analogues.

The electrophilic cleavage of both Zr-C bonds in $[\{Cp_2ZrCl\}_2\{\mu\text{-}(CH_2)_2\}]$ on reaction with excess HCl, to give 2 mol $[Cp_2ZrCl_2]$ and C_2H_6, has been reported [10].

Very few heterobimetallic alkanediyl complexes are known and few reactivity studies have been carried out on them. The μ-methylene bridged complex $[Cl(Me)_2bipyPtCH_2AuPPh_3]$ was reported to react with the electrophiles HCl, Cl_2 and $HgCl_2$ by selective cleavage of the Au-C bond to give $[AuPPh_3Cl]$ and $[Cl(Me)_2bipyPt(CH_2Y)]$, Y = H, Cl and HgCl respectively [11].

The μ-ethylene bridged complexes $[(CO)_5Re(CH_2)_2ML_y]$ $\{ML_y = Mn(CO)_5$, $W(CO)_3Cp$ and $Mo(CO)_3Cp\}$ reacted with $[Re(CO)_5]^-$ with elimination of the ML_y group to form $[(CO)_5Re(CH_2)_2Re(CO)_5]$ [12-15]. The relative nucleophilicity of the anions is $[Re(CO)_5]^- \gg [CpW(CO)_3]^- >$ $[CpMo(CO)_3]^-$ [16]. The stability of the metal-carbon σ-bond decreases in the same order [17]. Thermolysis of the above heterobimetallic ethylene bridged complexes gives ethylene and the metal-metal bonded dimers $[ML_y]_2$ [12,13,15]. Thermolysis of $[(CO)_5Re(CH_2)_2Mn(CO)_5]$ also affords $[(CO)_5ReMn(CO)_5]$ [13].

The only experiment carried out on a heterobimetallic alkanediyl complex where n > 2 appears to be a study of the thermal decomposition of $[Cp(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$ [18]. An almost equimolar quantity of cyclopropane and propene was obtained. This is a result which falls in between those obtained from the thermal decompositions of $[\{CpFe(CO)_2\}_2\{\mu\text{-}(CH_2)_3\}]$, which favours cyclopropane, and $[\{CpRu(CO)_2\}_2\{\mu\text{-}(CH_2)_3\}]$, which favours propene formation. A mixture of $[CpFe(CO)_2]_2$ and $[CpRu(CO)_2]_2$ was obtained as the organometallic products of this experiment. Evidence obtained suggested that a dimetallacycle may be an intermediate in the thermal decomposition process.

The study of binuclear metal alkyl complexes is thus interesting since it is possible that new primary processes, pertaining only to bi- or poly-nuclear systems, will be revealed. Thus an alkanediyl ligand bridging two metals may undergo a transformation that is not possible for mononuclear metal complexes [19,20]. Having different metals present within the same molecule adds the possibilities of metalloselective reactions and of one metal influencing the reactivity of the other.

6.2 REACTIVITY OF $[(\eta\text{-}C_5R_5)(CO)_2Fe(CH_2)_nML_y]$ (R = H, n = 3 - 6, ML_y = $Ru(CO)_2Cp$, $W(CO)_3Cp$, $Mo(CO)_3Cp$, $Re(CO)_5$; R = CH_3, n = 3, ML_y = $Ru(CO)_2Cp$)

(i) with neutral nucleophiles

The reactions of the alkyl compounds $[CpMo(CO)_3R]$ (R = alkyl group) with ligands, L, shown in equation 1, represent classic examples of the migratory CO insertion reactions [21,22].

$$[CpMo(CO)_3R] \; + \; L \longrightarrow [CpMoL(CO)_2C(O)R] \qquad (\underline{1})$$

This type of reaction still receives considerable attention [23,24], in part because it is a fundamental process which is believed to be crucial to many catalytic reactions.

For binuclear metal alkyl complexes, such reactions are not necessarily predictable, since there is no corresponding library of fundamental processes with which to model transformations at complexes with more than one metal centre [9].

All the numbered complexes in this chapter are listed in **SCHEME 6.1**.

As mentioned in the introduction, the di-iron complex $[Cp(CO)_2Fe(CH_2)_3Fe(CO)_2Cp]$ **(1)** was found to react with 1:1 molar ratio of PPh_3 in THF to give the monosubstituted acyl complex $[Cp(CO)_2Fe(CH_2)_3C(O)Fe(PPh_3)(CO)Cp]$ **(2)** [5]. The reaction of complex **(1)** with 2 mol PPh_3 in THF gave the diacyl complex $[Cp(CO)(PPh_3)FeC(O)(CH_2)_3C(O)Fe(PPh_3)(CO)Cp]$ **(3)**. Evidence suggested that the monoacyl complex **(2)** was initially formed rapidly in this reaction, followed by a slow further reaction of the monoacyl species to give the diacyl product **(3)** [5]. The phosphine thus showed a preference to attack the unsubstituted iron site in complex **(1)**, rather than the unsubstituted iron site in the monoacyl complex **(2)**. Reasons for this may be largely steric.

In contrast, the reaction of $[Cp(CO)_3Mo(CH_2)_4Mo(CO)_3Cp]$ **(4)** with 1 mol PPh_3 in CH_3CN gave a mixture of the monoacyl product $[Cp(CO)_3Mo(CH_2)_4C(O)Mo(PPh_3)(CO)_2Cp]$ **(5)** and the diacyl product $[Cp(CO)_2(PPh_3)MoC(O)(CH_2)_4C(O)Mo(PPh_3)(CO)_2Cp]$ **(6)** in a 10:7 ratio (as

(1) $[Cp(CO)_2Fe(CH_2)_3Fe(CO)_2Cp]$

(2) $[Cp(CO)_2Fe(CH_2)_3C(O)Fe(PPh_3)(CO)Cp]$

(3) $[Cp(CO)(PPh_3)FeC(O)(CH_2)_3C(O)Fe(PPh_3)(CO)Cp]$

(4) $[Cp(CO)_3Mo(CH_2)_4Mo(CO)_3Cp]$

(5) $[Cp(CO)_3Mo(CH_2)_4C(O)Mo(PPh_3)(CO)_2Cp]$

(6) $[Cp(CO)_2(PPh_3)MoC(O)(CH_2)_4C(O)Mo(PPh_3)(CO)_2Cp]$

(7) $[Cp(CO)_2Fe(CH_2)_3Mo(CO)_3Cp]$

(8a) $[Cp(CO)_2Fe(CH_2)_3C(O)Mo(PPh_3)(CO)_2Cp]$

(8b) $[Cp(CO)_2Fe(CH_2)_3C(O)Mo(PMe_2Ph)(CO)_2Cp]$

(9) $[Cp(CO)_2Fe(CH_2)_6Mo(CO)_3Cp]$

(10) $[Cp(CO)_2Fe(CH_2)_6C(O)Mo(PPh_3)(CO)_2Cp]$

(11) $[Cp(CO)_2Fe(CH_2)_3C(O)Mo(CO)_3Cp]$

(12) $[Cp(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$

(13) $[Cp(CO)(PPh_3)FeC(O)(CH_2)_3Ru(CO)_2Cp]$

(14) $[\{CpRu(CO)_2\}_2\{\mu\text{-}(CH_2)_5\}]$

(15) $[Cp(CO)_2Fe(CH_2)_3W(CO)_3Cp]$

(16) $[Cp(CO)(PPh_3)FeC(O)(CH_2)_3W(CO)_3Cp]$

(17) $[Cp(CO)_2Fe(CH_2)_3Re(CO)_5]$

(18) $[\{CpFe(CO)_2\}_2\{\mu\text{-}(CH_2)_4\}]$

(19) $[\{Cp(CO)(PPh_3)Fe\}_2\{\mu\text{-}CO(CH_2)_4CO\}]$

(20) $[Cp(CO)_2Fe(CH_2)_3Re(PPh_3)(CO)_4]$

(21) $[Cp(CO)(PPh_3)FeC(O)(CH_2)_3Re(PPh_3)(CO)_4]$

(22) $[\{CpFe(CO)_2\}_2\{\mu\text{-}(CH_2CHCH_2)\}]PF_6$

(23) $[Cp(CO)_2Fe(C_3H_5)Mo(CO)_3Cp]PF_6$

(24) $[Cp(CO)_2Fe(C_3H_5)Ru(CO)_2Cp]PF_6$

(25) $[Cp(CO)_2Fe(C_4H_7)Mo(CO)_3Cp]PF_6$

(26a) $[Cp(CO)_2Fe(CH_2CHCH_2CH_2)Ru(CO)_2Cp]PF_6$

(26b) $[Cp(CO)_2Fe(CH_2CH_2CHCH_2)Ru(CO)_2Cp]PF_6$

(27) $[Cp(CO)_2Fe(C_4H_7)W(CO)_3Cp]PF_6$

(28) $[Cp(CO)_2Fe(C_6H_{11})Ru(CO)_2Cp]PF_6$

SCHEME 6.1

determined by ^1H NMR spectroscopy). In this case, thus, the phosphine showed no selectivity in its attack on the unsubstituted Mo sites of complexes (**5**) and (**6**), presumably because of the rates of the reactions involved. The reactions to yield the mono- and diacyl complexes can be represented as shown in equations (2) and (3).

$$[L_y(CO)M(CH_2)_nM(CO)L_y] + PR_3 \xrightarrow{k_1} [L_y(PR_3)MC(O)(CH_2)_nM(CO)L_y] \qquad (\underline{2})$$

$$[L_y(PR_3)MC(O)(CH_2)_nM(CO)L_y] + PR_3 \xrightarrow{k_2} [L_y(PR_3)MC(O)(CH_2)_nC(O)M(PR_3)L_y] \qquad (\underline{3})$$

{M = Fe, L_y = Cp(CO); M = Mo, L_y = $Cp(CO)_2$; k = rate constant}

Hence for M = Fe $k_1 > k_2$, whilst for M = Mo $k_1 \simeq k_2$.

The reaction of complex (**4**) with 2 mol PPh_3 in CH_3CN gave the diacyl complex (**6**) in high yield (equation 4).

$$[Cp(CO)_3Mo(CH_2)_4Mo(CO)_3Cp] \;+\; 2\;PPh_3 \longrightarrow$$
$$[Cp(CO)_2(PPh_3)MoC(O)(CH_2)_4C(O)Mo(PPh_3)(CO)_2Cp] \qquad (\underline{4})$$

The heterobimetallic Fe/Mo complex $[Cp(CO)_2Fe(CH_2)_3Mo(CO)_3Cp]$ (**7**) reacted with 1 mol PPh_3 in CH_3CN at room temperature to give a yellow precipitate which was identified as the monoacyl complex $[Cp(CO)_2Fe(CH_2)_3C(O)Mo(PPh_3)(CO)_2Cp]$ (**8a**), equation 5. No evidence of a reaction occurring at the Fe side of the molecule was observed.

$$[Cp(CO)_2Fe(CH_2)_nMo(CO)_3Cp] + L \longrightarrow [Cp(CO)_2Fe(CH_2)_nC(O)MoL(CO)_2Cp] \quad (\underline{5})$$

$n = 3$, L = PPh_3 (**8a**), PMe_2Ph (**8b**), CO (**11**)

$n = 6$, L = PPh_3 (**10**)

Similarly, PMe_2Ph reacts at the Mo side of complex (**7**) only, to give the complex $[Cp(CO)_2Fe(CH_2)_3C(O)Mo(PMe_2Ph)(CO)_2Cp]$ (**8b**). The length of the alkyl chain does not appear to affect the type of product obtained in the reactions of the Fe/Mo alkanediyl complexes. Thus $[Cp(CO)_2Fe(CH_2)_6Mo(CO)_3Cp]$ (**9**) reacts with PPh_3 to give the complex $[Cp(CO)_2Fe(CH_2)_6C(O)Mo(PPh_3)(CO)_2Cp]$ (**10**) only, as shown in equation <u>5</u>.

Complex (**7**) was reacted with CO gas in CH_3CN at room temperature and atmospheric pressure. Infrared monitoring of the reaction solution showed the disappearance of a Mo-CO band at 2010 cm^{-1}, the concurrent growth of a band at 1943 cm^{-1} (also assignable to a Mo-CO bond) and the appearance of an acyl band at 1645 cm^{-1}. This implied that reaction of the CO molecule in complex (**7**) occured at the Mo end of the molecule to form $[Cp(CO)_2Fe(CH_2)_3C(O)Mo(CO)_3Cp]$ (**11**). Complex (**11**) was isolated as a yellow solid under nitrogen at room temperature. The complex was however air-sensitive and rapidly decomposed into a dirty yellow oily mixture of products.

Thus, all these reactions of the Fe/Mo alkanediyl complexes occurred at the Mo end of the molecule. This is what would be expected by comparison of the reactivities of the mononuclear alkyl complexes of iron and molybdenum, since molybdenum alkyl complexes undergo the CO insertion/alkyl migration reactions much more readily than their iron analogues do [21,22,25,26].

The reaction of $[Cp(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$ (**12**) with 1 mol PPh_3 in refluxing THF gave exclusively $[Cp(CO)(PPh_3)FeC(O)(CH_2)_3Ru(CO)_2Cp]$ (**13**) in good yield (equation 6).

$$[Cp(CO)_2Fe(CH_2)_3Ru(CO)_2Cp] \quad + \quad PPh_3 \longrightarrow [Cp(CO)(PPh_3)FeC(O)(CH_2)_3Ru(CO)_2Cp] \qquad (\underline{6})$$

Thus the nucleophile, PPh_3, attacked complex (**12**) only at the Fe side of the molecule. Again, this is as expected, since iron alkyl complexes are known to undergo migratory insertion reactions with tertiary phosphines in THF [25,26], whilst ruthenium alkyl complexes undergo migratory insertion reactions reluctantly [27,28]. The homometallic alkanediyl complexes of iron and ruthenium show a similar reactivity pattern to their monometallic alkyl analogues. For example the complexes $[\{CpFe(CO)_2\}_2\{\mu\text{-}(CH_2)_n\}]$ (n = 3 - 7) were found to undergo thermally induced migratory insertions with PPh_3 in THF, as described in section 6.1. In contrast, the complex $[\{CpRu(CO)_2\}_2\{\mu\text{-}(CH_2)_5\}]$ (**14**) showed no reaction with PPh_3 even after 25 hours of reflux in THF [29]. Complex (**14**) did however react with PPh_3 in refluxing xylene to give a mixture of $[Cp(CO)_2Ru(CH_2)_5C(O)Ru(PPh_3)(CO)Cp]$ and $[\{Cp(CO)(PPh_3)Ru\}_2\{\mu\text{-}C(O)(CH_2)_5C(O)\}]$. IR monitoring of the separate concurrent reactions of equal quantities of $[Cp(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$ and $[\{CpFe(CO)_2\}_2\{\mu\text{-}(CH_2)_3\}]$ with 1 mol PPh_3 each in refluxing THF, indicated that the reaction of $[Cp(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$ was complete first. This suggested that the Fe atom was slightly activated towards attack by the phosphine by the Ru atom in the same molecule. This data was, however, qualitative and further measurements are neccessary.

Since iron alkyl complexes [25,26] undergo the migratory insertion reaction much more readily than do tungsten alkyl complexes [30,31], in the light of the above results, the reaction of $[Cp(CO)_2Fe(CH_2)_3W(CO)_3Cp]$ (**15**) with 1 mol PPh_3 was expected to occur at the iron centre in the molecule. This was indeed observed. Thus the complex $[Cp(CO)(PPh_3)FeC(O)(CH_2)_3W(CO)_3Cp]$ (**16**) was obtained as a yellow solid in 68% yield (equation 7). No evidence for any substitution or migratory insertion reaction occurring at the W centre of the molecule was observed.

$$[Cp(CO)_2Fe(CH_2)_3W(CO)_3Cp] + PPh_3 \longrightarrow [Cp(CO)(PPh_3)FeC(O)(CH_2)_3W(CO)_3Cp] \qquad (7)$$

The reaction of 1 mol PPh_3 with $[Cp(CO)_2Fe(CH_2)_3Re(CO)_5]$ (**17**) promised to be rather interesting. Thus the reaction of $[\{CpFe(CO)_2\}_2\{\mu\text{-}(CH_2)_3\}]$ (**1**) with 1 mol PPh_3 to give $[Cp(CO)_2Fe(CH_2)_3C(O)Fe(PPh_3)(CO)Cp]$ (**2**) was reported to be complete after refluxing the mixture for 24 hours in THF [32]. The reaction of $[\{CpFe(CO)_2\}_2\{\mu\text{-}(CH_2)_4\}]$ (**18**) with 2 mol PPh_3 gave $[\{Cp(CO)(PPh_3)Fe\}_2\{\mu\text{-}CO(CH_2)_4CO\}]$ (**19**) after 48 hours in refluxing THF [5]. The reaction of $[\{Re(CO)_5\}_2\{\mu\text{-}(CH_2)_4\}]$ with PPh_3 to give $[\{Re(PPh_3)(CO)_4\}_2\{\mu\text{-}(CH_2)_4\}]$ was reported to be complete after 42 hours of reflux in THF [33]. Thus the rates of the reactions of the di-iron and di-rhenium alkanediyl complexes with PPh_3 in THF appear to be very similar. Also, the insertion of the first PPh_3 ligand occurs much more rapidly than the second [5]. The PPh_3 ligand would therefore be expected to show a preference for Re on reaction with complex (17), but it was not certain whether the reactivity difference between Fe and Re would be sufficient for total metalloselectivity to occur. The reaction of complex (17) with 1 mol PPh_3 in refluxing THF (70 hours) was found to give $[Cp(CO)_2Fe(CH_2)_3Re(PPh_3)(CO)_4]$ (20) as an orange solid in *ca*. 50% (recrystallised) yield (equation 8).

$$[Cp(CO)_2Fe(CH_2)_3Re(CO)_5] + PPh_3 \longrightarrow [Cp(CO)_2Fe(CH_2)_3Re(PPh_3)(CO)_4] + CO \qquad (\underline{8})$$

No further change in the IR (in the ν(CO) region) was observed for the reaction mixture after 24 hours reflux, suggesting that the reaction was complete at that stage. A small quantity of $[Cp(CO)(PPh_3)FeC(O)(CH_2)_3Re(PPh_3)(CO)_4]$ (21) was also obtained, probably by the further reaction of complex (20) with PPh_3. Thus, the reaction of PPh_3 with complex (17) appears to be totally metalloselective, with PPh_3 preferentially attacking at the Re side of the molecule.

Both $[\{Cp^*Fe(CO)_2\}_2\{\mu\text{-}(CH_2)_4\}]$ [33] and $[\{CpRu(CO)_2\}_2\{\mu\text{-}(CH_2)_5\}]$ (14) [29] have been reported to react very sluggishly with tertiary phosphines in both CH_3CN and THF. Complex (14) was however reported to react with PPh_3 in refluxing xylene [29]. The complex $[Cp^*(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$ was therefore reacted with 1 mol PPh_3 in refluxing xylene. IR monitoring of the carbonyl region of the reaction mixture showed the reaction to be complete after 38 hours. At this stage only an IR band at 1922 cm^{-1}(vs) and another at 1752 cm^{-1}(w) were observed in the ν(CO) region in xylene. The ^{1}H NMR spectrum of the product showed two peaks in the Cp region: at δ = 4.96 ppm and δ = 4.89 ppm. Two peaks were also observed in the Cp region in the ^{13}C NMR spectrum, at δ = 88.7 ppm and δ = 88.9 ppm. It therefore appeared that a mixture of two products was present. Since the CO peaks observed are split into doublets in the ^{13}C NMR spectrum (δ = 203.0, J = 21.4 Hz and δ = 206.2, J = 19.3 Hz), it would seem that both products involved a phosphine substituted Ru group. Peaks at δ = 4.94 ppm (^{1}H NMR) and 88.3 ppm (^{13}C NMR) are characteristic of the Cp moiety of the $Cp(CO)(PPh_3)Ru$ group [29]. A doublet for the CO group of this $Cp(CO)(PPh_3)Ru$ group is observed in the ^{13}C NMR at δ = 205.6 ppm. Since no peak in the region characteristic of a Cp* group was observed in either the ^{1}H or ^{13}C NMR spectra, it appears that this group decomposed under the reaction conditions. All attempts to separate or purify the reaction product(s) were unsuccessful.

The predictable metalloselectivity in the above reactions contrasts with observations made on the reaction of $[MnRe(CO)_{10}]$ with Bu^{t}NC. In this case substitution occured at the Re atom, to give $[Mn(CO)_5Re(CO)_4Bu^tNC]$, and not at the Mn atom, as would be expected [34].

Data for all the new complexes prepared above are reported in Tables 6.1, 6.2 and chapter 7.

Notable in the ^{1}H NMR spectra of the heterodinuclear acyl complexes is the presence of a triplet (as would be expected) for the CH_2 protons α

IR and ^{1}H NMR Data for Complexes (6), (8), (10), (13), (16), (20) and (21).

Complex no.	IR ν(CO)^a cm^{-1}	^{1}H NMR Data^b and Assignments (δ)
(6)	1935s, 1853vs, 1611m	7.39s (30H, PPh_3); 4.96d (10H, MoCp, ^3J = 1.1); 2.97t (4H, 2x($-C(O)CH_2-$), ^3J = 6.5); 1.35qn (4H, $-(CH_2)_2-$, J = 3.5))
(8a)	1999s, 1938vs, 1850vs, 1607m	7.43s (15H, PPh_3); 4.99s (5H, MoCp); 4.70s (5H, CpFe); 3.08t (2H, $-C(O)CH_2-$, ^3J = 7.1); 1.58qn (2H, $-CH_2-$, ^3J = 5.6); 1.31m (2H, $FeCH_2$)
(8b)	1999vs, 1938vs, 1839vs, 1608s	7.59, 7.40m (5H, Ph); 4.92d (5H, MoCp, ^3J = 1.4); 4.68s (CpFe); 3.01t (2H, $-C(O)CH_2-$, ^3J = 7.3); 1.86d (6H, Me_2, ^2J = 8.9); 1.48qn (2H, $-CH_2-$, ^3J = 8.6); 1.25m (2H, $FeCH_2$)
(10)	1998vs, 1937vs, 1850vs, 1614m	7.36m (15H, PPh_3); 4.95s (5H, CpMo); 4.66s (5H, CpFe); 3.00t (2H, $-C(O)CH_2-$, ^3J = 11.7); 1.38s, 1.26s (10H, $-(CH_2)_5-$)
(13)	2009vs, 1944vs, 1912s, 1603m	7.38m (15H, PPh_3); 5.18s (5H, CpRu); 4.41d (5H, CpFe, ^3J = 1.1); 2.84, 2.60m (2H, $-C(O)CH_2-$); 1.38m (4H, $-(CH_2)_2-$)
(16)	2007s, 1911vs, 1603w	7.46m (15H, PPh_3); 5.33s (5H, WCp); 4.40s (5H, CpFe); 2.70m, 2.85m (2H, $-C(O)CH_2-$); 1.26m (2H); 0.88m (2H)
(20)	2072m, 2010m, 1996s, 1965vs, 1933s	7.39m (15H, PPh_3); 4.61s (5H, CpFe); 1.72m (2H, $FeCH_2$); 1.21m (2H, $-CH_2-$); 0.58m ($ReCH_2$)
(21)	2074m, 2033m, 1990m, 1964vs, 1922s, 1602m	7.44m (30H, PPh_3); 4.35d (5H, CpFe, ^3J = 1.1); 2.65, 2.33m (2H, $C(O)CH_2-$); 1.28m ($-CH_2-$); 0.62m ($ReCH_2$)

a: measured in CH_2Cl_2 b: measured in $CDCl_3$ relative to TMS (δ = 0.00 ppm), J values in Hz.

Table 6.2:

^{13}C NMR Data for Complexes (6), (8), (13), (16) and (20).

Complex no.	^{13}C NMR Data[a] and Assignments (δ)													
(6)	267.6d (MoC(O)-) (J = 10.5)	238.0d (MoCO) (J = 24.2)		96.4s (MoCp)		65.3s (C(O)$\underline{C}H_2$-)	25.0s	(C(O)$CH_2\underline{C}H_2$-)		135.4d (J = 44.3)	132.9d (J = 10.6)	130.1d (PPh_3) (J = 2.3)		
(8a)	267.0d (MoC(O)-) (J = 10.9)	238.6d (MoCO) (J = 24.1)	217.6s (FeCO)	96.5s (MoCp)	85.3s (CpFe)	70.3s (C(O)$\underline{C}H_2$-)	34.0s	(C(O)$CH_2\underline{C}H_2$-)	3.7s (FeCH_2-)	135.6d (J = 43.7)	133.1d (J = 9.7)	130.3s	128.5d (J = 11.1)	
(8b)	268.0d (MoC(O)-) (J = 11.9)	237.8d (MoCO) (J = 24.0)	217.5s (FeCO)	95.6s (MoCp)	85.2s (FeCp)	70.5s (C(O)$\underline{C}H_2$-)	34.0s	(C(O)$CH_2\underline{C}H_2$-)	3.8s (FeCH_2-)	138.7d	135.9d (J = 2.3)	129.4d (J = 9.7)	128.6d (PPh) (J = 9.7)	19.8d (PMe) (J = 32.8)
(13)	276.9d (FeC(O)-) (J = 22.4)	202.3s (RuCO)	221.0d (FeCO) (J = 31.3)	88.5s (RuCp)	85.2s (FeCp)	71.5d (C(O)$\underline{C}H_2$-) (J = 5.3)	35.3s	(C(O)$CH_2\underline{C}H_2$-)	-3.1s (RuCH_2-)	136.6d (J = 42.5)	133.3d (J = 9.8)	129.6d (J = 2.3)	128.2d (J = 9.7)	
(16)		229.5s (WCO)		91.4s (WCp)	85.2s (FeCp)	72.2s (C(O)$\underline{C}H_2$-)	32.8s	(C(O)$CH_2\underline{C}H_2$-)	9.8s (WCH_2-)	136.6d (J = 42.5)	133.4d (J = 9.8)	129.7d (J = 2.4)	128.0d (J = 9.6)	
(20)	193.0d (ReCO) (J = 9.8)	190.4d (ReCO) (J = 41.2)	188.2d (ReCO) (J = 6.8)	217.9s (FeCO)	85.1s (FeCp)	48.6d (ReCH_2-) (J = 2.8)	29.7s	(-CH_2-)	12.5s (FeCH_2-)	133.3d (J = 10.8)	130.5s	128.5d (PPh_3) (J = 10.0)		

a: measured in $CDCl_3$ relative to TMS (δ = 0.0 ppm), J values in Hz.

to the acyl group in complexes (**6**), (**8a**), (**8b**), (**10**) (Table 6.1) and $[Cp(CO)_2Fe(CH_2)_3C(O)Mo(L)(CO)_2Cp]$, L = PPh_3 and PMe_2Ph (chapter 7). No such triplet is observed, however, for the CH_2 protons α to the acyl group of complexes (**13**), (**16**) and (**21**). Indeed two separate signals (multiplets) are observed for the two protons α to the acyl group. These two protons are non-equivalent due to the chirality of the $Cp(CO)(PPh_3)Fe$ fragment [35]. Reactions of the organic ligands bound to the $Cp(CO)(PPh_3)Fe$ fragment have been found to be highly stereoselective [35-37], and considerable interest has recently been expressed in the stereospecificity of organic transformations at such chiral metal centres.

(ii) with trityl salt (Ph_3CPF_6)

Mononuclear iron alkyl complexes of the type $[CpFe(CO)_2R]$ are known to undergo β-hydride abstraction to give the cationic species $[CpFe(CO)_2(olefin)]^+$ when treated with triphenyl methyl salts [38,39]. Complex (**1**) was also shown to react with Ph_3CPF_6 to give $[\{CpFe(CO)_2\}_2\{\mu\text{-}(CH_2CHCH_2)\}]PF_6$ (**22**) [6]. A crystal structure of complex (**22**) has confirmed King's proposal (from ^1H NMR evidence) that the complex exists as a transition metal stabilised carbonium ion with the positive charge located on the central carbon atom of the three-carbon chain [40]. The iron atoms were shown to be weakly linked to the β-CH group of the allylic system (**figure 1**).

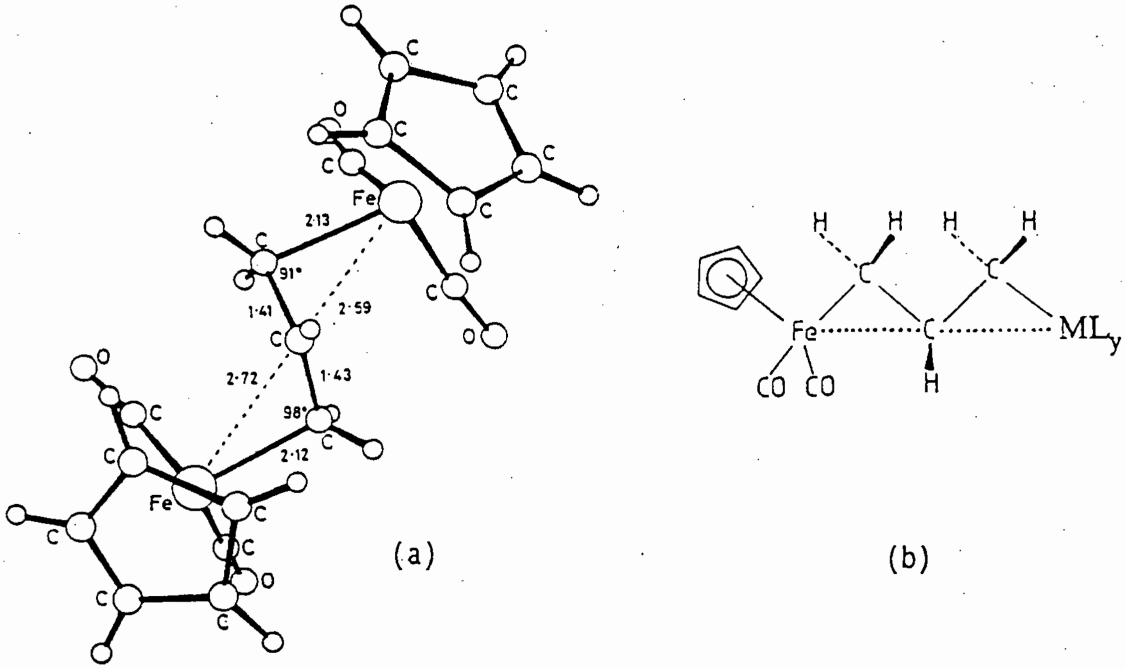
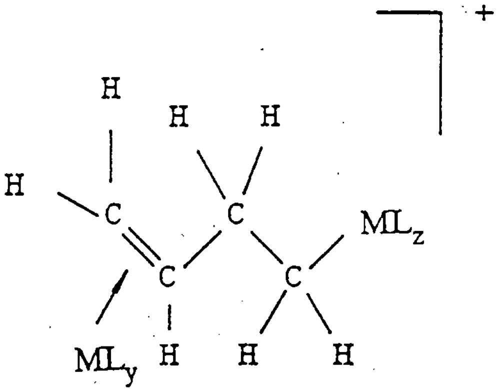


Figure 6.1: (a) Molecular structure of $[\{CpFe(CO)_2\}_2\{\mu\text{-}(CH_2CHCH_2\}]^+$ (22) [40]; (b) Schematic diagram for complex (22), ML_y = $Fe(CO)_2Cp$ and complex (24), ML_y = $Ru(CO)_2Cp$.

Moss and Johnson subsequently investigated the reaction of longer chain alkanediyl complexes with trityl salt [7]. The reactions of $[\{CpFe(CO)_2\}_2\{\mu\text{-}(CH_2)_n\}]$ (n = 4 - 6) with Ph_3CPF_6 were found to give yellow crystalline complexes of formula $[\{CpFe(CO)_2\}_2\{\mu\text{-}(C_nH_{2n-1})\}]PF_6$. On the basis of spectroscopic studies these complexes are believed to have structures where one iron atom is π-bonded and the other σ-bonded to the alkyl chain (figure 2).



compound no.	ML$_y$	ML$_z$
(25)	Fe(CO)$_2$Cp	Mo(CO)$_3$Cp
(26a)	Fe(CO)$_2$Cp	Ru(CO)$_2$Cp
(26b)	Ru(CO)$_2$Cp	Fe(CO)$_2$Cp
(27)	Fe(CO)$_2$Cp	W(CO)$_3$Cp
	Fe(CO)$_2$Cp	Fe(CO)$_2$Cp

Figure 2: Proposed structure of complexes (25) - (27) and $[\{CpFe(CO)_2\}_2\{\mu\text{-}(C_4H_7)\}]PF_6$

Complex (**4**) was also found to react with trityl salt, although this reaction was very much slower than the analogous reaction with $[\{CpFe(CO)_2\}_2\{\mu\text{-}(CH_2)_4\}]$. The product, presumably $[\{CpMo(CO)_3\}_2\{\mu\text{-}(C_4H_7)\}]PF_6$, was very unstable in solution and the product was not isolated in pure form or completely characterised.

The complex $[Cp(CO)_2Fe(CH_2)_3Mo(CO)_3Cp]$ (**7**) was reacted with trityl salt to give $[Cp(CO)_2Fe(C_3H_5)Mo(CO)_3Cp]PF_6$ (**23**) as lustrous golden crystals in 36% yield. Complex (**23**) was found to be insoluble in hexane and ether, very sparingly soluble in CH_2Cl_2 and sparingly soluble in acetone. Two possible limiting structures exist for complex (**23**). Firstly, both the Fe and Mo atoms may be weakly linked to the β-CH group as shown for complex (**22**) in **figure 1**. Alternatively, one of the metals may be π-bonded and the other σ-bonded to the alkyl chain *i.e.* a structure similar to that shown for $[\{CpFe(CO)_2\}_2\{\mu\text{-}(C_4H_7)\}]PF_6$ in figure 2.

The ^{1}H NMR spectrum of complex (23) at room temperature shows a triplet of triplets at $\delta = 6.53$ ppm which can be assigned to tha β-CH proton (figure 3).

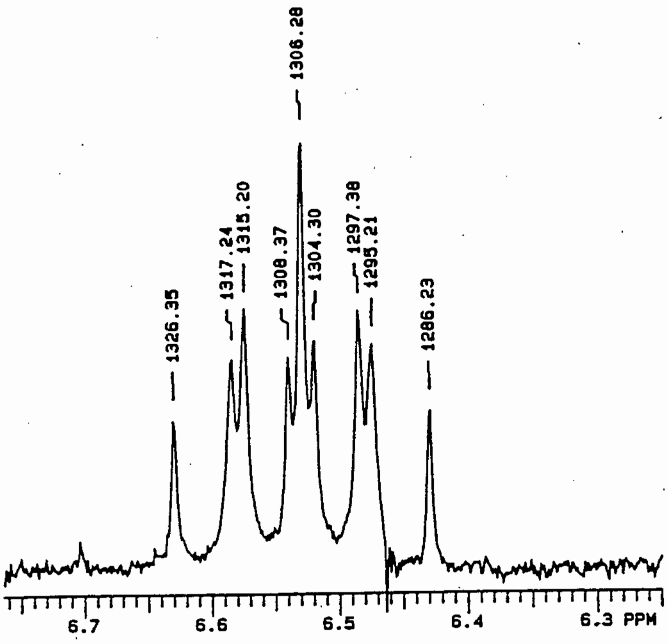


Figure 3: The ^{1}H NMR C<u>H</u> peak of complex (23) at 25°C.

A similar pattern is observed for the β-CH peak of complex (22) [41]. Two singlets at $\delta = 5.70$ and 5.78 ppm can be assigned to the Cp peaks of Fe and Mo. Both Cp peaks are downfield relative to those of complex (7), but the Cp peak of Fe is considerably more shifted than the Cp peak of Mo. A doublet, integrating for 2H, is observed at $\delta = 3.31$ ppm (J = 11.0 Hz). All other peaks are coalesced into the baseline at this temperature. This is similar to the spectrum observed for complex (22) at room temperature.

The ^{1}H NMR spectrum of complex **(23)** obtained at -30°C shows a broad multiplet at $\delta = 6.41$ ppm due to the highly deshielded β-CH group, and singlets at $\delta = 5.78$ and 5.72 ppm due to the Cp protons of Mo and Fe. A multiplet at $\delta = 3.24$ ppm integrates for 2 protons, whilst multiplets at $\delta = 2.83$ and $\delta = 1.91$ ppm integrate for 1 proton each. Since the Cp peak of complex **(23)** is more deshielded than the Cp peak of complex **(22)**, it would seem that a higher positive charge resides on the Fe atom in complex **(23)**.

The ^{13}C NMR spectrum of complex **(22)** shows a peak at $\delta = 127.3$ ppm due to the β-CH group. A singlet due to the two equivalent Cp peaks is observed at $\delta = 87.8$ ppm. These Cp peaks are *ca.* 2.5 ppm more deshielded than those of complex **(1)**. The ^{13}C NMR spectrum of complex **(23)** shows a peak at $\delta = 120.7$ ppm corresponding to the β-CH group. The CpMo peak is observed at $\delta = 95.5$ ppm {3 ppm downfield when compared to the corresponding peak of complex **(7)**}, and the CpFe peak is observed at $\delta = 89.3$ ppm {4 ppm downfield when compared to the corresponding peak of complex **(7)** and 2 ppm downfield relative to the Cp peaks of complex **(22)**}. A peak at $\delta = 40.27$ ppm can be assigned to Fe-$\underline{C}H_2$ and the peak at $\delta = 9.24$ ppm can be assigned to Mo-$\underline{C}H_2$. The Fe-$\underline{C}H_2$ peak is significantly deshielded relative to the corresponding peak in complex **(22)** *i.e.* by *ca.*16 ppm, whilst the Mo-$\underline{C}H_2$ peak is only deshielded by 3 ppm relative to complex **(7)**. All these data thus suggest that the structure of complex **(23)** may be a hybrid of the two limiting structures shown in **figures** 1 and **2**, with the π-bond tending to form on the Fe side of the molecule (**figure 4**).

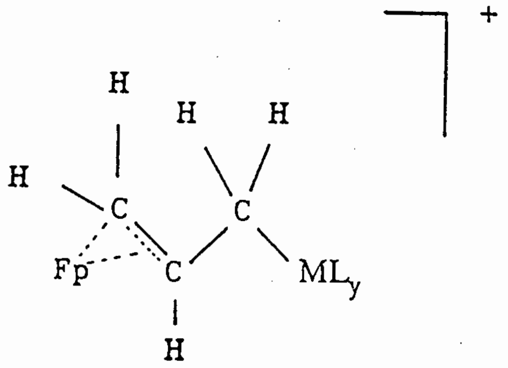


Figure 4: Diagrammatic representation of the proposed structure of complex (23).

The reaction of complex (12) with trityl salt gave a product which was identified as being $[Cp(CO)_2Fe(C_3H_5)Ru(CO)_2Cp]PF_6$ (**24**). This complex was obtained as an orange solid and was insoluble in ether or CH_2Cl_2, but moderately soluble in acetone. The ^1H NMR spectrum of this complex (**24**) obtained at room temperature shows a quintet due to the β-CH proton at $\delta = 6.79$ ppm. Peaks at $\delta = 5.86$ and 5.30 ppm are due to the CpRu and CpFe protons respectively. A doublet is observed at $\delta = 3.28$ ppm, integrating for three protons. The ^1H NMR spectrum of complex (**24**) is in fact very similar to to the one obtained for complex (22) [41]. The ^1H NMR spectrum of complex (**24**) obtained at -30°C shows a complex multiplet at $\delta = 6.75$ ppm (β-CH-) and singlets due to CpRu and CpFe at $\delta = 5.92$ and 5.33 ppm respectively. A multiplet at $\delta = 3.34$ ppm integrates for 2H, whilst a triplet at $\delta = 2.70$ ppm and a doublet of doublets at $\delta = 2.14$ ppm each integrate for 1 H. Assignments for these peaks are shown in Table 6.4 (p. 244).

Variable temperature ^1H NMR spectra were recorded for complex (**24**) (**figure 5**). The multiplet at $\delta = 3.34$ ppm at -30°C was observed to

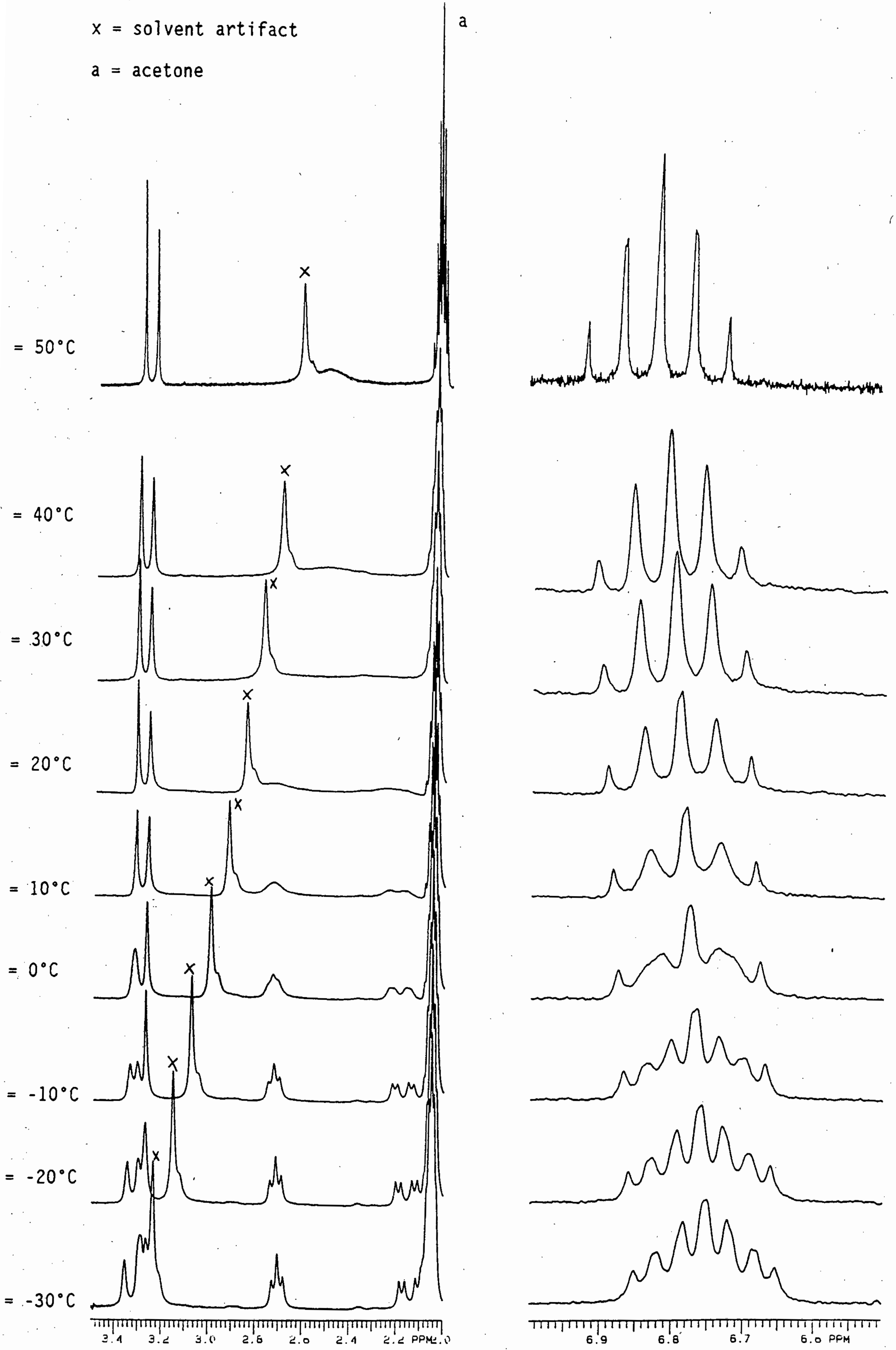


Figure 5: Variable temperature ^{1}H NMR Spectra for Complex (24).

become a doublet at *ca.* 0°C, which becomes sharp at *ca.* 10°C. The triplet at δ = 2.70 ppm and the doublet of doublets at δ = 2.14 ppm (both at -30°C) were observed to coalesce into the base line at 30°C. The α-protons of the alkyl chain thus appear to be fluxional at temperatures greater than -10°C. The protons α to each respective metal thus become equivalent and the signal for the CH group's proton is observed to simplify into a quintet at 30°C. Below -10°C none of the protons of the C_3H_5 group are equivalent. Thus separate signals are seen for each proton and the signal for the CH proton becomes more complex. Similar fluxional behaviour has been observed for complex (**22**) [41]. The ^1H NMR spectrum of complex (**24**) (at -30°C) is however much more complex than that of complex (**22**), since, unlike complex (**22**), it has two different groups at each end of the bridging C_3H_5 group.

The ^{13}C NMR spectrum of complex (**24**) shows a peak at δ = 123.5 ppm for the β-CH carbon atom, and peaks at δ = 90.8 (CpRu), 87.4 (CpFe), 27.4 ($Fe\underline{C}H_2$-) and 18.5 ($Ru\underline{C}H_2$-) ppm. Since the ^{13}C NMR spectrum of complex (**22**) has peaks at δ = 87.7 (CpFe) and 24.0 ($Fe\underline{C}H_2$-) ppm, it can be seen that the data for the Fe side of complex (**24**) are very similar to the data for the di-iron complex (**22**). Both the $Fe\underline{C}H_2$- and $Ru\underline{C}H_2$- peaks of complex (**24**) are deshielded by 20-21 ppm relative to the corresponding peaks of complex (**12**).

The data obtained thus clearly suggests that complex (**24**) has a structure which is very similar to that of complex (**22**) (**figure 1**).

Single crystals suitable for x-ray analysis of complex (**24**) were obtained by slow crystallisation from acetone-d_6 at -15°C. Heavy atoms were found in a Patterson map in space group $p2_1/n$. The structure of complex **(24)** was found to be isomorphous with the di-iron analogue **(22)**. This implied Fe/Ru disorder *i.e.* throughout the structure Fe and Ru atoms occupy the same positions. Therefore accurate bond lengths and angles could not be obtained from the attempted structural determination. This does however imply (as does the NMR evidence) that complex **(24)** has a structure similar to that of complex **(22)** **(figure 1)**. A secondary x-ray analysis carried out in a scanning electron microscope confirmed that Fe and Ru were present in equal atom percentages in the crystal of **(24)** used for the structural determination. Reasons for the observed disorder and possible ways of avoiding this are discussed in section 5.3 in chapter 5.

The complexes $[Cp(CO)_2Fe(CH_2)_4ML_y]$ $\{ML_y = Mo(CO)_3Cp, Ru(CO)_2Cp, W(CO)_3Cp\}$ were reacted with trityl salt to give complexes of the type $[Cp(CO)_2Fe(C_4H_7)ML_y]PF_6$ **(25)**-**(27)**.

Since trityl salt abstracts **one** proton from a β-carbon atom of a transition metal alkanediyl complex, two possible structures are possible for complexes **(25)** - **(27)**. Thus the hydride may be abstracted either from the alkanediyl carbon β to Fe or from the alkanediyl carbon β to M.

Complex **(25)** was found to be unstable in both solution or the solid state and little data could be obtained for it. The IR spectrum of complex **(25)** is however similar to those of complexes **(23)**, **(26)** and

(27), and thus supports its proposed formulation. Since the IR ν(CO) spectrum of $[\{Cp(CO)_2Fe\}_2\{\mu\text{-}(C_4H_7)\}]$ shows bands at 2073, 2036, 2007 and 1950 cm^{-1} [7] and complex **(25)** shows IR ν(CO) bands at 2073, 2038, 2017 and 1922 cm^{-1} *i.e.* no bands at *ca.* 1950 cm^{-1}, it indicates that the Fe atom is π-bonded and the Mo atom is σ-bonded to the alkyl chain.

The ^1H and ^{13}C NMR spectra of complex **(26)** both showed four peaks in the Cp region of roughly equal intensity, and the ^{13}C NMR spectrum also showed 8 peaks assignable to the alkyl carbon atoms. This indicated that the product consisted of a mixture of two complexes, namely $[Cp(CO)_2Fe(CH_2CHCH_2CH_2)Ru(CO)_2Cp]PF_6$ **(26a)** and $[Cp(CO)_2Fe(CH_2CH_2CHCH_2)Ru(CO)_2Cp]PF_6$ **(26b)**. These two structural isomers could not be separated. The NMR data indicated that both isomers were present in equal amounts. The reaction of Ph_3CPF_6 with $[Cp(CO)_2Fe(CH_2)_4Ru(CO)_2Cp]$ is thus not metalloselective. Since the complex $[\{Cp(CO)_2Fe\}_2\{\mu\text{-}(C_4H_7)\}]PF_6$ was shown to have the structure shown in **figure 2**, it is probable that complexes **(26a)** and **(26b)** have similar structures. Hence, complex **(26a)** appears to involve an iron atom which is π-bonded and a ruthenium atom which is σ-bonded to the alkyl chain. Conversely, complex **(26b)** appears to involve a π-bond between ruthenium and a σ-bond between iron and the alkyl chain. Notable is that the peaks assigned to the atoms of the π-bonded section of complex **(26a)** and the σ-bonded section of complex **(26b)** are almost identical to those assigned to the corresponding sections of the complex $[\{Cp(CO)_2Fe\}_2\{\mu\text{-}(C_4H_7)\}]PF_6$ [7].

The complexes **(26)** are significantly more soluble in CH_2Cl_2 and acetone than is complex **(24)**, possibly also reflecting their different structures.

In contrast to the spectra of **(26)**, the spectra of complex **(27)** show it to consist of a single isomer. Comparison of the IR, ^1H NMR and ^{13}C NMR spectral data of complex **(27)** with those of the complexes $[\{Cp(CO)_2Fe\}_2\{\mu\text{-}(C_4H_7)\}]PF_6$ and $[Cp(CO)_2Fe(CH_2)_4W(CO)_3Cp]$ strongly imply that the hydride was abstracted from the alkanediyl carbon β to Fe, resulting in the Fe atom being π-bonded and the W atom still being σ-bonded to the alkyl chain **(figure 2)**.

The complex $[Cp(CO)_2Fe(CH_2)_6Ru(CO)_2Cp]$ also reacted with trityl salt to give $[Cp(CO)_2Fe(C_6H_{11})Ru(CO)_2Cp]PF_6$ **(28)**. The data obtained implied that complex **(28)**, like complex **(26)**, was also obtained as a mixture of two isomers. Hence equal quantities of the Fe π-bonded and Ru-π bonded complexes were obtained. The complexes **(28)** were significantly more soluble than complex **(24)**.

Notable in both the ^1H and ^{13}C NMR spectra of complexes **(22)** - **(28)** is that the peaks due to the CH atoms in complexes with structures as shown in **figure 1** {**(22)**-**(28)**} are significantly more deshielded than are the corresponding =CH atom peaks in complexes with structures as shown in **figure 2** {**(25)**-**(28)**} (^1H NMR: *ca.* 6.5 *vs ca.* 5.3 ppm, ^{13}C NMR: *ca.* 120-127 *vs ca.* 88-92 ppm).

Data for all the complexes synthesized above are reported in Tables 6.3-6.5 and chapter 7.

Table 6.3:

Data for Complexes (23), (24), (26) and (27).

Complex no.	mp. (°C)	IR (ν(CO) cm^{-1}	Elemental Analysis			
			C: found	(calcd.)	H: found	(calcd.)
(23)	>180 dec	2067s, 2021s, 1944(sh), 1909[a]	34.90	(35.53)	2.30	(2.47)
(24)	182-187 dec	2076(sh), 2030(sh) 2002s, br 1948(sh)[a]	34.70	(34.87)	2.60	(2.60)
(26)	102-119	2079s, 2037s, 2010s, 1950s[b]	36.20	(36.06)	3.00	(2.84)
(27)	149-153 dec	2075w, 2036w, 2014w, 1922(sh), 1912w[b]	32.32	(32.13)	2.60	(2.40)

a: Nujol mull b: in CH_2Cl_2 solution

Table 6.4:

^{1}H NMR Data for Complexes (23), (24), (26) and (27).

Complex no.	^{1}H NMR Data^a and assignments (where possible) (δ)
(23)^b	5.78s (5H, MoCp); 5.72s (5H, FeCp); 6.41m (1H, CH); 3.30d (1H, J = 8.5); 3.28d (1H, J = 13.3); 2.83m (1H); 1.91m (1H)
(24)^{b,c}	5.92s (5H, RuCp); 5.33s (5H, RuCp); 6.75m (1H, CH); 3.29m (2H, FeCH$_2$); 2.70t (1H, RuCH$_2$, J = 4.8) 2.17dd (1H, RuCH$_2$, J = 4.7/13.9)
(26a)	5.84s (5H, FeCp); 5.45s (5H, RuCp); 5.35m (1H, =CH); 3.93d (1H, =CH$_2$, J = 8.2); 3.50d (1H, =CH$_2$, J = 14.8); 2.53m (2H, CH$_2$); 1.87m (2H, RuCH$_2$)
(26b)	6.12s (5H, RuCp); 4.97s (5H, FeCp); 3.92d (1H, =CH$_2$, J = 8.5); 3.86d (1H, =CH$_2$, J = 14.4); 1.61m (2H, CH$_2$); 1.25m (2H, FeCH$_2$)
(27)	5.86s (5H, FeCp); 5.69s (5H, WCp); 5.33m (1H, =CH); 3.99d (1H, =CH$_2$, J = 8.2); 3.53d (1H, =CH$_2$, J = 14.7); 2.70tt (1H, CH$_2$, J = 3.7/11.7); 1.87m (1H, CH$_2$);

a: measured in CDCl$_3$ relative to TMS (δ = 0.00 ppm), J values in Hz, dd = doublet of doublets, tt = triplet of triplets.
b: recorded at -30°C. c: assignments aided by COSY and HETCOR experiments. d: =CH peak not observed

Table 6.5:

^{13}C NMR Data for the Complexes (22)-(24), (26) and (27).

Complex no.	^{13}C NMR Data[a,b] and Assignments. (δ)
(22)	127.3 (CH); 87.7 (FeCp); 24.0 ($FeCH_2$)
(23)	120.0 (CH); 95.0 (MoCp); 88.9 (FeCp); 40.1 ($FeCH_2$); 9.2 ($MoCH_2$)
(24)	123.5 (CH); 90.8 (RuCp); 87.4 (FeCp); 27.4 ($FeCH_2$); 18.5 ($RuCH_2$)
(26a)	90.5 (=CH); 89.7 (RuCp); 89.9 (FeCp); 52.8[c] (=CH_2); 46.7[c] (CH_2); -1.0 ($RuCH_2$)[d]
(26b)	87.9 (=CH); 91.9 (RuCp); 86.7 (FeCp); 49.8[c] (=CH_2); 45.9[c] (CH_2); 6.1 ($FeCH_2$)[e]
(27)	92.3 (=CH); 94.4 (WCp); 91.1 (FeCp); 54.2 (=CH_2); 45.8 (CH_2); -7.5 (WCH_2)

a: in $CDCl_3$, relative TMS (δ = 0.0 ppm) b: assignments assisted by APT and HETCOR experiments
c: assignments uncertain d: δ = 211.3, 209.1 (FeCO)[c]; 202.9 (RuCO)
e: δ = 196.7, 195.1 (RuCO)[c]; 218.1, 218.0 (FeCO).

(iii) miscellaneous studies on some heterobimetallic alkanediyl complexes

Since Me_3NO is known to assist in the removal of a coordinated carbonyl group [42-44], complex (7) was reacted with Me_3NO in an attempt to prepare the complex $[Cp(CO)_2Fe(CH_2)_3Mo(CO)_2Cp]$ (*i.e.* a complex which may involve a Fe-Mo bond). No reaction was, however, observed to occur, either when standing the solution for 22 hours at room temperature or refluxing the solution for 48 hours. On work-up, only products of decomposition and starting material were isolated. It thus appears that under these conditions, a carbonyl group of complex (7) is not suseptible to removal by Me_3NO.

In another attempt to induce the formation of a Fe-Mo bond, the complex $[Cp(CO)_2Fe(CH_2)_4Mo(CO)_3Cp]$ was heated in toluene-d_8. The reaction was monitored by ^1H NMR spectroscopy. No change was observed in the chemical shifts of the Cp, alkyl or Fe-$\underline{C}O$ atoms, suggesting that no reaction occurred. The peak assignable to the *trans*-Mo-$\underline{C}O$ group was no longer observed at 40°C, and both the *cis*- and *trans*-Mo-$\underline{C}O$ groups had coalesced into the base-line at 70°C. No change was observed in the spectrum at 100°C. It would thus appear that at temperatures between 70 and 100°C, the carbonyl groups bonded to the Mo atom are fluxional. No evidence of fluxionality between the CO groups of Mo and Fe was observed. Work-up of the NMR solution yielded starting material and small quantities of $[CpFe(CO)_2]_2$ and $[CpMo(CO)_3]_2$.

Electrophilic cleavage of transition metal-carbon σ bonds, using a variety of reagents, has been widely studied for a number of different metal systems [45]. Halogen cleavage has been found to be useful for both synthetic purposes as well as the characterisation of organometallic compounds [46]. Usually, the reaction of halogens with metal alkyl complexes results in the formation of a metal halide and an alkyl halide (equation 9).

$$L_yMR + X_2 \longrightarrow RX + L_yMX \qquad (\underline{9})$$

(L_yM = a transition metal and its associated ligands, R = an alkyl group)

Exceptions are reactions, in coordinating solvents, of systems where "CO insertion" into metal-alkyl bonds proceeds readily. Thus the reaction of $[\{Mn(CO)_5\}_2\{\mu\text{-}(CH_2)_n\}]$ with halogens in THF yields $HOOC(CH_2)_nCOOH$, on work-up [9]. Similarly the complex $[CpMo(CO)_3CH_3]$ produces CH_3OI on reaction with iodine [47].

The complex $[Cp(CO)_2Fe(CH_2)_5Ru(CO)_2Cp]$ was reacted with 1 mol I_2 at 0°C in CH_2Cl_2. Only the expected cleavage products $[CpFe(CO)_2I]$, $[CpRu(CO)_2I]$ and a trace of $I(CH_2)_5I$ were obtained on work-up, as identified by IR and ^1H NMR spectroscopy. Thus no evidence for a metalloselective reaction was obtained. Also, no evidence of a cationic species, $[Cp(CO)_2Fe(CH_2)_5Ru(CO)_2Cp]^+$, was observed, although the cationic species $[\{Cp(CO)_2Fe\}_2\{\mu\text{-}(CH_2)_4\}]^+$ was isolated in the reaction of $[\{Cp(CO)_2Fe\}_2\{\mu\text{-}(CH_2)_4\}]$ with I_2 [5]. No similar cationic product was obtained on the reaction of $[\{Cp(CO)_2Ru\}_2\{\mu\text{-}(CH_2)_5\}]$ with I_2 [29].

The reaction of a suspension of $[Cp(CO)_2Fe(CH_2)_6W(CO)_3Cp]$, in hexane, with HCl gas at -78°C gave approximately equal amounts of $[CpW(CO)_3Cl]$ and $[CpFe(CO)_2\{(CH_2)_5CH_3\}]$ (equation <u>10</u>).

$$[Cp(CO)_2Fe(CH_2)_6W(CO)_3Cp] + HCl \longrightarrow [CpFe(CO)_2\{(CH_2)_5CH_3\}] + [CpW(CO)_3Cl] \qquad (\underline{10})$$

This result is perhaps a little surprising since the W-C bond is believed to be stronger than the Fe-C bond [32,48-50] and cleavage would thus be expected to occur at the W end of the molecule. Since no evidence of $[CpFe(CO)_2Cl]$ or $[CpW(CO)_3\{(CH_2)_5CH_3\}]$ was obtained, the reaction of HCl with $[Cp(CO)_2Fe(CH_2)_6W(CO)_3Cp]$ appears to be totally metalloselective.

6.3 CONCLUSIONS

The reactions of neutral nucleophiles (CO, PR_3) with the heterobimetallic alkanediyl complexes $[Cp(CO)_2Fe(CH_2)_nML_y]$ $\{ML_y$ = $Ru(CO)_2Cp$, $W(CO)_3Cp$, $Mo(CO)_3Cp$, $Re(CO)_5$; n = 3-6$\}$ in THF and CH_3CN have been shown to be metalloselective. The metal site , of a particular heterobimetallic complex, attacked by the nucleophile was found to be predictable. Thus that metal, whose mono- or homo-metallic analogue reacted more readily with neutral nucleophiles, would be attacked first. The reaction rates appeared to differ in some cases.

The reactions of the heterobimetallic alkanediyl complexes with trityl salt were found to be more complex. Thus the complexes $[Cp(CO)_2Fe(CH_2)_3ML_y]$ $\{ML_y$ = $Ru(CO)_2Cp$, $W(CO)_3Cp$, $Mo(CO)_3Cp\}$ reacted with Ph_3CPF_6 to give the transition metal stabilised carbonium ions $[Cp(CO)_2Fe(C_3H_5)ML_y]PF_6$, in which the β carbon atom appears to be weakly bonded to both transition metal atoms. The complex $[Cp(CO)_2Fe(C_4H_7)Mo(CO)_3Cp]PF_6$ was found to be unstable and was not fully characterised. No metalloselectivity could be observed in the reactions of the Fe/Ru alkanediyl complexes $[Cp(CO)_2Fe(CH_2)_nRu(CO)_2Cp]$ (n = 4,6) with Ph_3CPF_6. The hydride appeared to be abstracted with equal ease from the carbon β to either metal. The reaction of $[Cp(CO)_2Fe(CH_2)_4W(CO)_3Cp]$ with Ph_3CPF_6 was however found to be metalloselective and only the hydride β to Fe was abstracted. All the carbonium ion complexes isolated, where $n \geq 4$, appear to involve a π-bond between one metal and the alkyl chain.

Whilst no metalloselectivity was observed in the reaction of $[Cp(CO)_2Fe(CH_2)_5Ru(CO)_2Cp]$ with I_2, the reaction of $[Cp(CO)_2Fe(CH_2)_6W(CO)_3Cp]$ with HCl was found to completely metalloselective, with the reaction occurring only at the W end of the molecule.

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CHAPTER 7
EXPERIMENTAL

7.1 GENERAL

All reactions were carried out under nitrogen using standard Schlenk-tube techniques.

Tetrahydrofuran (THF) and hexane were distilled over $LiAlH_4$ or sodium. Toluene, diglyme, benzene and xylene were distilled over sodium. Methanol was distilled over $CaCl_2$ or Mg/I_2, and acetone and CH_2Cl_2 were distilled over $CaCl_2$. Acetonitrile was distilled over P_2O_5.

Tertiary phosphines (Strem Chemicals Inc., excluding PPh_3 which was obtained from Merck), tertiary amines and dimethylsuphide (Merck) were used without further purification. PMe_3 was synthesized by the method of Mann and Wells [1]. NaI was dried before use, by heating at 150°C at 0.1 mm Hg pressure for 4 hours. The dihaloalkanes (Aldrich) were used without further purification. Alumina (BDH, active neutral, Brockmann grade 1) was deactivated before use. Dry HI gas was prepared by the literature method [2]. $[\{CpFe(CO)_2\}_2\{\mu\text{-}(CH_2)_n\}]$ (n = 3-6) [3,4] and $[\{CpRu(CO)_2\}_2\{\mu\text{-}(CH_2)_n\}]$ (n = 3-6) [5,6], $[CpRu(CO)_2]_2$ [7-9], $[CpW(CO)_3]_2$ [10,11] were prepared by literature methods. All other reagents were obtained commercially, unless otherwise stated.

Melting points were recorded on a Kofler Hot stage microscope (Reichert

Thermovar) and are uncorrected. Microanalyses were performed by the University of Cape Town Microanalytical Laboratory. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer in solution cells with NaCl or KBr windows or as Nujol mulls on NaCl plates. ^{1}H NMR spectra were recorded on a Varian XL100, Varian EM60, Brücker WH90 or a Varian XR200 spectrometer. ^{13}C NMR spectra , as well as COSY, HETCOR and APT experiments, were recorded on a Varian XR200. Chemical shifts are reported relative to TMS (δ = 0.00 ppm) as an internal (XL100, EM60, WH90) or external (VXR200) reference standard.

Low resolution mass spectra and metastable traces were recorded with a VG Micromass 16F spectrometer, operated at 70 eV ionising voltage, unless otherwise stated. The source temperature was initially 50°-60°C and was raised to *ca*.150°C during data collection.

The m/z values quoted are those peaks in a peak cluster which correspond to the ions containing the metal isotope with the highest natural abundance. Calculated mass spectra were obtained using a computer program. (Where the isotope pattern for any particular parent ion is in close agreement with a particular combination of isotopes, this has been stated).

The X-ray analyses were carried out on an Enraf-Nonius diffractometer, using MoK$_\alpha$ (λ = 0.7107 Å) radiation. Cell parameters were obtained from least-squares analysis of the setting angles of 24 reflections in the range 16° < θ < 17°. During data collection, the intensities of three reference reflections were monitored every hour and recentering was checked after every 100 measured reflections. Data were Lp processed and empirical absorption corrections applied [12]. The structure was solved using SHELX76 [13]. Complex neutral atom scattering factors were taken from Cromer and Mann [14] and dispersion correction from Cromer and Liberman [15]. PLUTO produced the drawings [16].

7.2 EXPERIMENTAL DETAILS PERTAINING TO CHAPTER 2

(i) General Details:

[$CpFe(CO)_2CH_2OCH_3$], [$CpFe(CO)_2CH_2Cl$] and [$CpFe(CO)_2CH_2Br$] were prepared by the reported method [17].

(ii) Preparative Details:

Preparation of [$CpFe(CO)_2CH_2I$]

Method (i) A solution of Na[$CpFe(CO)_2$] (14.18 mmol) in THF (20 ml) was added to a stirred solution of $ClCH_2OCH_3$ (1.25 ml, 15.50 mmol) in THF (4 ml) at -78°C. The solution was allowed to attain room temperature. After 2.5 hours the solvent was removed under reduced pressure and the product, [$CpFe(CO)_2CH_2OCH_3$] {^1H NMR ($CDCl_3$): δ = 4.68s (Cp), 4.84s (CH_2), 3.24s (CH_3); ^{13}C NMR ($CDCl_3$): 216.7 (CO), 85.9 (Cp), 65.3 (CH_2), 60.3 (CH_3)}, extracted with hexane. The extract was filtered and dry HI gas was vigorously bubbled through the solution for 70 minutes, after which infrared monitoring of the carbonyl bands of both starting material and products showed the reaction to be complete. The solvent was removed under reduced pressure, the product dissolved in a minimum of hexane and the solution transferred to a silica gel column. Upon elution with 20:1 hexane/ether a yellow band was collected and the solution evaporated *in vacuo*. The dark yellow solid was then recrystallised from hexane at -78°C yielding 1.32g (59%) of [$CpFe(CO)_2CH_2I$] (**1c**) as a yellow crystalline solid. Found: C, 30.40; H, 2.30 $C_8H_7FeIO_2$ calcd: C,30.20; H, 2.20.%

Method (ii) [$CpFe(CO)_2CH_2Br$] (0.196g, 0.720 mmol) was dissolved in acetone (5 ml). Dry NaI (0.154g, 1.027 mmol) was added and the solution stirred for 60 minutes. The solvent was then removed under reduced pressure and the product extracted with hexane. The extract was filtered, concentrated and transferred to a silica gel column. On elution with 20:1 hexane/ether a yellow band was collected and the solution was concentrated under reduced pressure, filtered and cooled to -78°C. A yellow crystalline precipitate of (**1c**) (0.138g, 60%) formed.

Reactions of [CpFe(CO)$_2$CH$_2$Br] (1b) with PMe$_3$, PMe$_2$Ph, PPh$_2$CH$_2$CH$_2$PPh$_2$, NMe$_3$, C$_5$H$_5$N, and SMe$_2$ in tetrahydrofuran; Synthesis of Compounds (**2a**), (**2b**), (**2f**), (**2h**), (**2i**), (**2j**), (**4**) - General Procedure.

Compound (**1b**) (1 mmol) was dissolved in THF (20 ml) and the ligand (1 mmol) was added. An excess of the ligand was added in the cases of NMe$_3$ and SMe$_2$. The reaction mixture was allowed to remain at room temperature in the dark for several days. For reaction times see Table 2.3. The crystalline products were collected by vacuum filtration, washed with tetrahydrofuran or diethylether (2 x 10 ml) and recrystallised from dichloromethane/diethylether or methanol/diethylether to give the products (**2a**), (**2b**), (**2f**), (**2h**), (**2i**), (**2j**) as yellow, air-stable crystalline solids. {Complex (**2f**) was isolated as its BPh$_4^-$ salt.} For yields and characterisation data for the products see Table 2.3.

Reaction of (1b) with PPh$_2$CH$_2$CH$_2$PPh$_2$ in acetonitrile

A mixture of (**1b**) (0.38g, 1.40 mmol) and dppe (0.56g, 1.4 mmol) in acetonitrile (20 ml) was stirred and heated under reflux for 1.5 h. The product (**4**) came out of solution after 10 mins. The reaction mixture was cooled (-15°C) and the product (**4**) then collected by vacuum filtration, washed with diethylether (2x10 ml) and dried in vacuo. Yield 0.07g (7.5%). The solid was shown by spectral data to be identical in all respects to the product (**4**) obtained from the reaction of (**1b**) with dppe in tetrahydrofuran. The acetonitrile filtrate was evaporated *in vacuo* and washed with diethylether (3x50 ml) in order to remove unreacted dppe; drying in vacuo then gave an orange solid IR ν(CO) (CH_2Cl_2): 2021s, 1967s cm^{-1}. The ^1H NMR (CD_3OD) suggested that it was an impure sample of (**4**). This product resisted further attempts at purification.

Reaction of (1b) with pyridine in acetonitrile

A mixture of (**1b**) (0.33g, 1.22 mmol) and dry pyridine (distilled from KOH) (0.15 ml = 0.10g, 1.20 mmol) in acetonitrile (10 ml) was stirred and heated under reflux for 1.25 h. Evaporation of the reaction mixture *in vacuo* gave a yellow solid which was recrystallised from MeOH/Et_2O to give 0.30g (67%) of orange/yellow polyhedra, m.p.: 168-174°C dec. The IR and ^1H NMR spectral data were identical to those of the product (2i) obtained by using tetrahydrofuran as solvent. The product appeared to be the monohydrate.

Reaction of (1b) with PBu^t_3 in CH_3CN

[$CpFe(CO)_2CH_2Br$] (0.62g, 2.28 mmol) was dissolved in CH_3CN (12 ml) and PBu^t_3 (0.46g, 2.28 mmol) added. The solution was allowed to stand at room temperature for 11 days. The solvent was then removed *in vacuo* to leave a red-brown oily solid. This was taken up in methanol and a solution of $NaBPh_4$ (0.78g, 2.28 mmol) in methanol was added. The precipitate was filtered off and recrystallised from CH_2Cl_2/ether, to give the yellow air-stable solid [$CpFe(CO)_2CH_2PBu^t_3$]BPh_4, in 68% yield.

Reaction of (**1b**) with PPh_3, PMe_2Ph, $PMePh_2$, pyridine and SMe_2 in CH_3CN

Complex (**1b**) (0.035g, 0.131 mmol) was dissolved with the ligand (0.262 mmol) in CH_3CN (1.5 ml) in an NMR tube, which was sealed under N_2. The reactions were followed by ^1H NMR (observing the Cp peaks), and the products (**2b**), (**2c**), (**2g**), (**2i**) and (**2j**) isolated as their BPh_4^- salts as described before.

Reaction of (**1b**) with triethylamine

Use of the general procedure with tetrahydrofuran as solvent gave a 40% yield of a colourless solid which was identified by its ^1H NMR spectrum as $[Et_3NH]Br$. No organometallic product was isolated. When the reaction was carried out in refluxing acetonitrile there was extensive decomposition. IR monitoring of the reaction mixture showed bands attributable to $[CpFe(CO)_2]_2$. With methanol as solvent $[Et_3NH]Br$ was isolated in 62% yield and the formation of $[CpFe(CO)_2CH_2OCH_3]$ inferred from ^1H NMR and IR data.

Reaction of $[CpFe(CO)_2CH_2PMe_2Ph]Br$ (**2b**) with excess PMe_2Ph

A mixture of (**2b**) (0.20g, 0.50 mmol) and dimethylphenylphosphine (0.2ml 0.19g, 1.50 mmol) in acetonitrile (10ml) was allowed to stand at room temperature in the dark for 2 days. Colourless cuboid crystals were present in the reaction mixture along with decomposition material. The decomposition material was discarded and the colourless solid dried *in vacuo*. Yield 0.02g (30%), ^1H NMR (CD_3OD): δ = 2.62d [9H, $^2J(PH)$ = 14

Hz], δ = 7.86-8.66m (5H); ^{13}C NMR (CD_3OD): δ = 9.78d [$^1J(PC)$ = 56.5 Hz]; 123.35d [$^1J(PC)$ = 87.6 Hz]; 130.98d [$^2J(PC)$ = 12.5 Hz]; 132.16d [$^3J(PC)$=10.4 Hz]; 135.38d [$^4J(PC)$ = 2.8 Hz]. These data support the structure $[(CH_3)_3PPh]Br$. The clear filtrate was evaporated in vacuo giving a brown oil, which was washed with diethylether (3 x 20 ml) and dried *in vacuo*. To a solution of sodium tetraphenylboron (0.34g, 1.00 mmol) in methanol (1 ml) was added a solution of the oil in the same solvent (2 ml). The precipitate that formed was washed with methanol (2 x 10ml) and dried. It was recrystallised from CH_2Cl_2/Et_2O to give $[CpFe(PMe_2Ph)_2(CO)]BPh_4$, 0.20g (55%). The spectral data were fully consistent with those in the literature [18]. The methanolic filtrate and washings were evaporated in vacuo, and dried to give a colourless solid, 0.06g. ^{1}H NMR ($CDCl_3$/DMSO-d_6) indicated that it was impure $[(CH_3)_3PPh]BPh_4$.

Reaction of $[CpFe(CO)_2CH_2PMe_3]Br$ (**2a**) with excess PMe_3

A mixture of (**2a**) (0.17g, 0.50 mmol) and trimethylphosphine (3.12 mmol) in acetonitrile (10 ml) was left at room temperature in the dark for 2 days. The reaction mixture was filtered to remove products of decomposition and the clear filtrate was evaporated *in vacuo*. The resulting orange oil was dissolved in methanol (5 ml) and the solution added to one of sodium tetraphenylboron (0.17g, 0.50 mmol) in the same solvent (2 ml). The precipitated that formed was washed with methanol (2 x 2 ml) and recrystallised from CH_2Cl_2/Et_2O to give a yellow solid; yield 0.10g (35%). ^{1}H NMR and IR data were fully consistent with its being $[CpFe(PMe_3)_2(CO)]BPh_4$ [18]. The methanolic filtrate and washings were concentrated *in vacuo* and diluted with diethylether to give a colourless solid, 0.12g. The ^{1}H NMR suggested that this product was $[(CH_3)_4P]BPh_4$, although the data were not definitive.

Reaction of $[CpFe(CO)_2CH_2NMe_3]Br$ (2h) with excess PMe_3

The compound (2h) (0.17g, 0.50 mmol) was dissolved in acetonitrile (20 ml) and PMe_3 (6.20 mmol) added. In the first reaction the mixture was left in the dark at room temperature for 8 days. Work-up gave a quantitative recovery of starting material as indicated by spectral data. In a second reaction the mixture was heated under reflux for 6h. Work-up gave a 73% recovery of starting material along with decomposition material.

Attempted reaction of NMe_3 with (2a)

A mixture of (2a) and excess NMe_3 in acetonitrile was allowed to stand at room temperature in the dark for 7 days. Work-up gave a 60% recovery of starting material, the remainder being products of decomposition.

Reaction of (1a) with PMe_3 in THF

$[CpFe(CO)_2CH_2Cl]$ (0.297g, 1.311 mmol) was dissolved in THF (10ml) and PMe_3 (1.311 mmol) was added. The solution was kept at room temperature in the dark for 6 days, after which a large quantity of yellow crystals had precipitated. These crystals were filtered off to give $[CpFe(PMe_3)_2(CO)]Cl$ (0.290g, 39%). IR $\nu(CO)$ (CH_2Cl_2): 1962 cm^{-1}; ^{1}H NMR

($CDCl_3$) : δ = 5.04t (5H, ^3J = 4.1 Hz), δ = 1.67d (18H, ^2J = 10.4 Hz). The product was very hygroscopic, becoming a yellow oil in air . The elemental analysis of C : 40.45, H : 6.65 % suggested that the product was in the monohydrate form once exposed to air. $C_{13}H_{25}ClFeO_2P_2$ requires C, 40.63; H, 7,05 %. Treatment of the product with $NaBPh_4$ in methanol, yielded [$CpFe(PMe_3)_2(CO)$]BPh_4 [18].

Reaction of (1a) with PMe_2Ph in THF

Complex (**1a**) (0.24g, 1.06 mmol) was dissolved in THF (10ml). PMe_2Ph (0.15 ml, 1.06 mmol) was added, and the solution was kept in the dark for 10 days at room temperature. The solvent was removed under reduced pressure and the product extracted with MeOH. To the extract was added a solution of $NaBPh_4$ (0.36g, 1.06 mmol) in methanol. The yellow precipitate of [$CpFe(CO)_2CH_2PMe_2Ph$]BPh_4 was filtered off (0.49g, 72%).

The reaction of (1c) with PPh_3 in CH_3CN

Complex (**1c**) (0.042g, 0.131 mmol) was dissolved along with PPh_3 (0.069g, 0.262 mmol) in CH_3CN (1.5 ml) in an NMR tube which was sealed under N_2. The reaction was monitored by ^1H NMR spectroscopy, and found to be complete in 12 minutes. Work-up as described above, yielded [$CpFe(CO)_2CH_2PPh_3$]I (0.045g, 59%).

Reaction of (1a) with $PMePh_2$ or PPh_3 in CH_3CN

Complex (**1a**) (0.030g, 0.131 mmol) was dissolved along with the required phosphine (0.131 mmol) in CH_3CN (1.5 ml) in an NMR tube and the tube sealed under N_2. The reaction was monitored by ^1H NMR spectroscopy. The products (**2c**) and (**2g**), respectively, were isolated as their BPh_4^- salts, as described previously.

Preparation of $[CpFe(CO)_2CH_2PPh_3]Br$ (2g)

The reaction of (**1b**) with triphenylphosphine in methanol under reflux gave (**2g**) in 71% yield, mp 119-121°C, IR ν(CO) (CH_2Cl_2) 2022s, 1969s cm^{-1}. The spectroscopic properties of this compound are similar to those reported for the corresponding iodide salt [18].

Reaction of $[CpFe(CO)_2I]$ with PMe_2Ph

This method was similar to a reported procedure for the preparation of $[CpFe(PMe_3)_2(CO)]I$ [19]. $CpFe(CO)_2I$ (0.27g, 0.89 mmol) was dissolved in benzene (5.5 ml), and PMe_2Ph (0.14 ml, 0.98 mmol) was added. The mixture was refluxed for 20.5 hours. The yellow precipitate of $[CpFe(PMe_2Ph)(CO)_2]I$ which had formed over this period was filtered off and washed with hot hexane (40 ml). The product was recrystallised from CH_2Cl_2 / hexane; yield: 0.35g (89%). IR ν(CO) (CH_2Cl_2): 2049vs, 2005vs cm^{-1}; ^1H NMR (acetone-d_6): δ = 5.66d (5H, ^3J = 2.1 Hz, Cp), 2.50d (6H, ^2J = 11.0 Hz, Me_2), 7.60, 7.85m (5H, Ph); m.p.: 105-107°C; Found: C, 40.70; H, 3.10; calculated for $C_{15}H_{16}FeIO_2P$: C, 40.72; H, 3.62 %.

Preparation of $[CpFe(PMe_2Ph)(CO)_2]BPh_4$

$[CpFe(PMe_2Ph)(CO)_2]I$ (0.224g, 0.507 mmol) was dissolved in a minimum of MeOH and filtered into a solution of $NaBPh_4$ (0.174g, 0.508 mmol) in MeOH. The yellow precipitate of $[CpFe(PMe_2Ph)(CO)_2]BPh_4$ was filtered off (0.234g, 73%) and recrystallised from CH_2Cl_2 / ether (0.174g, 54%). IR ν(CO) (CH_2Cl_2): 2053vs, 2010vs cm^{-1}; ^{1}H NMR (acetone-d_6): δ = 7.78m (2H), 7.60m (3H), 7.38m (8H); 6.94t (8H), 6.79m (4H) [5xPh]; 5.44d {5H, ^3J(PH) = 1.7 Hz, Cp}, 2.18d {9H, ^2J(PH) = 11.2 Hz, Me_6}; ^{31}P NMR (acetone-d_6): δ = 34.85 (relative to TMP); ^{13}C NMR ($CDCl_3$): 122.2s, 126.0qn, 130.1m, 132.3d, 136.9s (Ph); 88.7s (Cp); 18.76d (^1J = 35.4 Hz, Me); Found: C, 73.70; H, 5.40%; calculated for $C_{39}H_{36}BFeO_2P$: C, 73.78; H, 5.68%.

Reaction of $[CpFe(PMe_2Ph)(CO)_2]I$ with PMe_2Ph

The complex $[CpFe(PMe_2Ph)(CO)_2]I$ (0.139g. 0.310 mmol) was dissolved in CH_3CN (1.5 ml) and PMe_2Ph (0.05 ml, 0.35 mmol) was added. The solution was refluxed for 24 hours. Evaporation of the solvent under reduced pressure gave a dark oil. IR ν(CO) (CH_2Cl_2): 1961 cm^{-1}. This oil was dissolved in MeOH and added to a solution of $NaBPh_4$ (0.097g, 0.280 mmol) in MeOH. The resultant yellow precipitate of $[CpFe(PMe_2Ph)_2(CO)]BPh_4$ (0.60g, 34%) was filtered off. IR ν(CO) (CH_2Cl_2): 1967 cm^{-1}.

Attempted formation of [CpFe(CO)$_2$(CHPR$_3$)]

Use of (**2g**) as the starting material and NaOMe/MeOH as a base in the presence of benzophenone gave no new products as indicated by IR and TLC data. The use of tetrahydrofuran as the solvent and butyllithium as the base also did not give any isolable products. In the absence of any ketonic trapping agents, attempted preformation of the ylide (**2g**) did not lead to any isolable products.

7.3 EXPERIMENTAL DETAILS PERTAINING TO CHAPTER 3

(i) General details

The complexes [CpW(CO)$_3$CH$_2$OCH$_3$], [CpW(CO)$_3$CH$_2$Cl], [CpW(CO)$_3$CH$_2$Br] [17], and [CpW(CO)$_3$H] [20] were prepared according to the published procedures.

(ii) Experimental details

Preparation of [CpW(CO)$_3$CH$_2$I] (2c)

Dry NaI (0.059g, 0.394 mmol) was added to a solution of [CpW(CO)$_3$CH$_2$Br] (0.102g, 0.267 mmol) in acetone (5 ml). The solution was stirred for 90 minutes and the solvent was then removed under reduced pressure. The product was extracted with hexane (1x3, 2x2 and 2x1 ml), filtered and cooled to -78°C. A yellow/orange crystalline precipitate of **(2c)** separated (0.11g, 87%). Found: C, 23.80; H, 1.70 $C_9H_7FeIO_3W$ calc.: C, 22.79; H, 1.48 %.

Reaction of $[CpW(CO)_3CH_2Cl]$ with PPh_3 in THF

Complex **(2a)** (0.148g, 0.387 mmol) was dissolved in THF (7 ml) and PPh_3 (0.203g, 0.778 mmol) was added. The solution was refluxed overnight and the solvent removed under reduced pressure. The residue was dissolved in MeOH and filtered into a solution of $NaBPh_4$ (0.130g, 0.387 mmol) in MeOH. The resultant yellow precipitate of $[CpW(CO)_3CH_2PPh_3]BPh_4$ was filtered off and recrystallised from CH_2Cl_2/hexane (0.025g, 11%).

Reaction of (2a) with PMe_2Ph in THF

Complex **(2a)** (0.099g, 0.259 mmol) was dissolved in THF (3 ml) and PMe_2Ph (0.28g, 2.03 mmol) was added. The solution was refluxed for 26 hours. The solvent was removed under reduced pressure. The product was dissolved in MeOH and filtered into a solution of $Bu^n{}_4NPF_6$ (0.099g, 0.256 mmol) in MeOH (2.5 ml). A yellow precipitate formed gradually. The product, $[CpW(PMe_2Ph)_2(CO)_2]PF_6$, was filtered off and recrystallised from CH_2Cl_2/ether (0.044g, 23%).

Reaction of [CpW(CO)$_3$CH$_2$Br] (**2b**) with PMe$_3$ in THF

Complex (**2b**) (0.154g, 0.361 mmol) was dissolved in THF (3 ml) and the solution cooled to -198°C. PMe$_3$ (0.36 mmol) was condensed onto the reaction mixture. The reaction was allowed to attain room temperature and stood in the dark for 6 days. Yellow needles of [CpW(CO)$_3$CH$_2$PMe$_3$]Br had precipitated. The mother liquor was decanted and the product recrystallised from CH$_2$Cl$_2$ / hexane (0.007g, 4%). IR ν(CO) (CH$_2$Cl$_2$): 2029s, 1940(sh), 1918vs cm^{-1}; ^{1}H NMR (CDCl$_3$): 5.86s (5H), 1.95d (9H), 2.25d (2H, ^2J = 16.2 Hz). The previously decanted mother liquor was found to contain only starting material.

Reaction of (**2b**) with PEtPh$_2$ in THF

Complex (**2b**) (0.185g, 0.433 mmol) was dissolved in THF (1 ml). PEtPh$_2$ (0.092g, 0.430 mmol) was added with THF (2 ml). The solution was kept at room temperature in the dark for 140 days. The solvent was then removed under reduced pressure. The resultant orange oil was dissolved in MeOH and filtered into a solution of NaBPh$_4$ (0.149g, 0.435 mmol) in a minimum of MeOH. The resultant precipitate was filtered off to give yellow crystals of [CpW(CO)$_3$CH$_2$PEtPh$_2$]BPh$_4$ (0.167g, 44%).

Reaction of (**2b**) with dppe in THF

Complex (**2b**) (0.056g, 0.131 mmol) was dissolved with dppe (0.052g, 0.131 mmol) in THF (3ml). The solution was left to stand in the dark for 24 days after which the solvent was removed under reduced pressure. The product was extracted with MeOH and filtered into a solution of $NaBPh_4$ (0.045g, 0.131 mmol) in MeOH. The resultant yellow product was filtered off. The IR and ^1H NMR spectra of this complex suggested that it was $[CpW(CO)_3CH_2PPh_2(CH_2)_2PPh_2CH_2(CO)_3WCp]BPh_4$.

Reactions of (2a) with PPh_3, $PMePh_2$, PMe_2Ph, $PEtPh_2$ and $AsPh_3$ in MeOH Preparation of complexes (**3f**), (**3c**), (**3b**), (**3e**) and (**3h**) - General procedure:

Compound (**2a**) (0.60 mmol) was dissolved in MeOH and the ligand (0.60 mmol) was added. The mixture was refluxed for 3-24 hours (see below) and the solvent then removed *in vacuo* leaving an oily solid. The residue was then dissolved in MeOH and filtered into a solution of $NaBPh_4$ (0.70 mmol) (for L = PPh_3, $PMePh_2$, PMe_2Ph and $PEtPh_2$) or $Bu^n{}_4NPF_6$ (0.70 mmol) (for L = $AsPh_3$) in a minimum of MeOH. The resultant yellow precipitate was recrystallised from CH_2Cl_2/hexane or CH_2Cl_2/ether. Reactions times and yields for the various ligands are in parentheses. (PPh_3: 3.25h, 35%; $PMePh_2$: 3.5h, 47%; PMe_2Ph: 16h, 8%; $PEtPh_2$: 21h, 51%; $AsPh_3$: 23.5h, 36%).

An attempt was made to isolate the chloride salt of $[CpW(CO)_3CH_2AsPh_3]^+$ (**3h**). Thus the crude oily solid was triturated with hexane to give a yellow solid. This was recrystallised from CH_2Cl_2/hexane to give yellow platelets of $[CpW(CO)_3CH_2AsPh_3]Cl$ in 6% yield. IR (CH_2Cl_2): 2028s, 1924vs cm^{-1}; m.p. 103-115°C. The elemental analysis (C, 44.15; H, 3.25%) suggested that the product was in the monohydrate form once exposed to air ($C_{27}H_{24}AsO_4W$ requires C, 45.85; H, 3.40 %).

Reaction of (2b) with $AsPh_3$ in MeOH

Complex (**2b**) (0.134g, 0.314 mmol) was dissolved in MeOH (7 ml) and $AsPh_3$ (0.097g, 0.317 mmol) was added to the solution. The mixture was refluxed for 2.5 hours, after which the solvent was evaporated *in vacuo*. The dark oily product was washed with hexane (2x10, 1x5, 1x4 ml). The washings were concentrated under reduced pressure and cooled to -78^{o}C. A yellow precipitate of $[CpW(CO)_3H]$ (0.060g, 57%) separated from solution, as shown by IR and ^1H NMR spectroscopy. The hexane insoluble residue was taken up in MeOH and filtered into a solution of $Bu^n{}_4NPF_6$ (0.122g, 0.314 mmol) in MeOH. (This recrystallisation was performed using dry, N_2 saturated MeOH under an atmosphere of N_2.) The solution was allowed to stand overnight during which time fine yellow needles of $[CpW(CO)_3CH_2AsPh_3]PF_6$ precipitated (0.034g, 32%).

Reactions of (2a) with $AsPh_3$ in MeOH

(i) Complex (**2a**) (0.235g, 0.614 mmol) was dissolved in MeOH (12 ml) and $AsPh_3$ (0.188g, 0.614 mmol) was added to this solution. The mixture was refluxed for 3 hours. The solvent was then removed under reduced pressure, leaving a yellow/green oil. This oil was washed with hexane (3x10, 1x5 ml). The yellow washings were concentrated *in vacuo* and cooled to -78^{o}C. A yellow precipitate separated. The melting point, IR, ^1H NMR and mass spectra of this product were identical to those of an authentic sample of $[CpW(CO)_3H]$. The hydride was obtained in 49% yield. The hexane insoluble residue was dissolved in MeOH and treated with a solution of $Bu^n{}_4NPF_6$ in MeOH as described earlier, to afford $[CpW(CO)_3CH_2AsPh_3]PF_6$ in 22% yield.

(ii) Complex (**2a**) (0.101g, 0.264 mmol) was dissolved in MeOH (12 ml) and left standing for 3 hours in the dark. IR monitoring of the ν(CO) region showed only bands due to $[CpW(CO)_3CH_2OCH_3]$. $AsPh_3$ (0.081g, 0.264 mmol) was then added to the solution and the mixture stood in the dark for 9 months. The solvent was removed under reduced pressure. The products were worked up as described above, to afford $[CpW(CO)_3H]$ (0.030g, 34%) and complex (**3h**) (0.057g, 22%).

Reaction of (2a) with refluxing MeOH

Complex (**2a**) (0.09g, 0.23 mmol) was dissolved in MeOH (12 ml) and the solution refluxed for 3.25 hours. IR monitoring of the ν(CO) region showed the initial formation of $[CpW(CO)_3CH_2OCH_3]$, followed by the appearance of bands due to $[CpW(CO)_3H]$. The solvent was evaporated *in vacuo* and the product extracted with hexane (1x5, 3x1 ml). The extract was cooled to -78°C to give a pale yellow precipitate of $[CpW(CO)_3H]$ as identified by IR, ^1H NMR and mass spectroscopy.

Attempted reaction of $[CpW(CO)_3CH_2OCH_3]$ (1) with $AsPh_3$ in MeOH

Complex (**1**) (0.109g, 0.290 mmol) was dissolved in MeOH (5 ml) and $AsPh_3$ (0.088g, 0.29 mmol) was added. The mixture was refluxed for 3 hours. The solvent was subsequently removed under reduced pressure. The product was extracted with hexane and cooled to -78°C, affording starting material in almost quantitative yield.

Attempted reaction of(1) with MeOH or CH_3CN

Complex (1) was dissolved in MeOH or CH_3CN respectively. Even after refluxing the solutions for 3 days, only unchanged (1) was present, as shown by IR spectroscopy of the ν(CO) region.

Reaction of (2a) with CH_3OD

Complex **(2a)** (0.087g, 0.227 mmol) was dissolved in CH_3OD (1 ml) and the solution refluxed for 3.5 hours. The solvent was evaporated *in vacuo* and the product extracted with hexane. Cooling the extract to -78°C gave a yellow precipitate. The ^1H NMR of this solid showed a peak at $\delta = 5.50$, assignable to the Cp peak. A peak at $\delta = -7.21$ integrated for a ½H, relative to the Cp peak. It thus appeared that an equimolar mixture of [$CpW(CO)_3H$] and [$CpW(CO)_3D$] was present. This was also indicated by the mass spectrum of the mixture.

Reactions of (2a) with L, L = $PMePh_2$, $PEtPh_2$, PPh_3, $AsPh_3$ and NMe_3 in CH_3CN

Synthesis of complexes **(3c)**, **(3e)**, **(3f)**, **(3h)** and **(3i)**.
General procedure:

Complex **(2a)** (0.50 mmol) was dissolved in CH_3CN (10 ml) and the ligand (0.50 - 1.00 mmol) was added. The mixture was allowed to stand in the dark (for reaction times and percentage yields see values in parentheses). The product was then worked up with $NaBPh_4$ as described before, to give yellow crystals of $[CpW(CO)_3CH_2L]BPh_4$. L = $PMePh_2$ (**3c**) (5.5d, 21%), $PEtPh_2$ (**3e**) (23d, 10%), PPh_3 (**3f**) (8d, 10%), $AsPh_3$ (**3h**) (24d, 18%) and NMe_3 (**3i**) (34d, 20%).

Reaction of (**2a**) with PMe_3 in CH_3CN

The reaction of (**2a**) with both 1 and 2 molar ratios of PMe_3 in CH_3CN afforded a mixture of complexes $[CpW(CO)_3CH_2PMe_3]^+$ (**3a**) and $[CpW(PMe_3)_2(CO)_2]^+$ (**4a**), as determined by IR and ^1H NMR spectroscopy, after standing in the dark for 6 - 7 days.

Reaction of (**2a**) with PMe_2Ph in CH_3CN

Complex (**2a**) (0.133g, 0.348 mmol) was dissolved in CH_3CN (1.5 ml) in an NMR tube and PMe_2Ph (0.049g, 0.355 mmol) was added. The NMR tube was heat sealed under N_2 and kept at 57°C. The reaction was followed by ^1H NMR (observing the Cp peaks) and the products (**3a**) - (**3f**) and (**3h**) - (**3k**) were isolated as their BPh_4^- salts as described before. Reaction times, yields and deviations from the general procedure are noted in parentheses. L = PMe_3 (22h, 68%), PMe_2Ph (4.75h, 68%), $PMePh_2$ (11.5h, 63%), $PEtPh_2$ (27.5h, 74%), PPh_3 (51h, 62%), $AsPh_3$ (123h, 42%), NMe_3 (2.5h, 72%, 0.29 mmol NMe_3), py (48.75h, 51%) and SMe_2 (24h, 49%).

Reaction of (**2b**) with dppe in CH_3CN

Complex (**2b**) (0.093g, 0.218 mmol) and dppe (0.173g, 0.439 mmol) were dissolved in CH_3CN (4.5 ml). The mixture was stirred in the dark at room temperature for 4 days. The solvent was then evaporated *in vacuo*. The product was taken up in MeOH (leaving unchanged dppe). Concentrating this solution and adding ether gave a very low yield of $[\{CpW(CO)_3CH_2\}_2(\mu\text{-dppe})]Br_2$ (IR ν(CO) (CH_2Cl_2) : 2034s, 1955m, 1928s cm^{-1}). The solvent was then evaporated *in vacuo* and the product redissolved in MeOH and filtered into a solution of $NaBPh_4$ (0.075g, 0.218 mmol) in a minimum of MeOH. The resultant yellow precipitate was filtered off to give $[\{CpW(CO)_3CH_2\}_2(\mu\text{-dppe})](BPh_4)_2$ (0.161g, 43%). This product was found to be very unstable in solution.

Reaction of (**2b**) with PCy_3 in CH_3CN

Complex (**2b**) (0.08g, 0.19 mmol) was dissolved in CH_3CN (7 ml). PCy_3 (0.073g, 0.262 mmol) was added and the suspension allowed to stand in the dark. After 4 days all the PCy_3 had dissolved. The solvent was removed under reduced pressure after 7 days. The oily yellow product was worked up with $NaBPh_4$ as described before to give complex (**3g**) (0.030g, 17%).

Reactions of $[CpW(CO)_3CH_2I]$ (**2c**) with PEt_3 and PPh_3

Complex (**2c**) (0.062g, 0.131 mmol) was dissolved in CH_3CN or CD_3CN (1.5 ml) in an NMR tube. The phosphine (0.262 mmol) was added and the tube was sealed under N_2. The reactions were followed by ^1H NMR (observing the Cp peaks). The $t_{\frac{1}{2}}$ for the reaction of (**2c**) with PEt_3 was too short to be observed. The products (**3d**) and (**3f**) were isolated as their BPh_4^- salts as described previously. Reaction times and yields are in parentheses. L = PEt_3 (15 min, 40%) and L = PPh_3 (10h, 70%).

7.4 EXPERIMENTAL DETAILS PERTAINING TO CHAPTER 4

(i) General Details:

High resolution mass spectra and linked scans were recorded on a Kratos MS 80 RFA spectrometer, operating at a source temperature of 200°C and solid probe temperature of *ca.* 140°C.

(ii) Preparative Details:

Preparation of $[CpFe(CO)_2\{(CH_2)_nBr\}]$, n = 3-10

$Na[CpFe(CO)_2]$ (10 mmol) in THF (20 ml) was added over 20 min. to a stirred solution of $Br(CH_2)_nBr$ (n = 3-10) (12 mmol) in THF (20 ml) at -20 to -25°C. The solution was stirred at -20 to -25°C for 15 min, then allowed to attain room temperature (*ca.*75 min.). The solvent was removed under reduced pressure, leaving a yellow/brown oily residue. This was extracted with hexane, and the solution was filtered, concentrated under reduced pressure and transferred to an alumina column. Upon elution with hexane, a broad yellow band was collected, and this was concentrated and cooled to -78°C under N_2. The yellow product precipitated out of this solution. The mother liquor was syringed off and the product dried under reduced pressure. Yields and physical properties are listed in Table 4.1. Elution of the column with ether gave two red bands containing small quantities of $[CpFe(CO)_2Br]$ [21] and $[CpFe(CO)_2]_2$ respectively, as identified by IR and ^1H NMR spectroscopy.

Preparation of $[Cp^*Fe(CO)_2\{(CH_2)_nBr\}]$, n = 3-5

$Na[Cp^*Fe(CO)_2]$ (3.0 mmol) in THF (12 ml) was added over 15 min to a stirred solution of $Br(CH_2)_nBr$ (n = 3-5) (3.3 mmol) in THF (25 ml) at between -60 and -40°C. The temperature of the solution was allowed to rise to -25°C and kept there for 20 min. The solution was then allowed to attain room temperature (*ca*.75 min). The work-up procedure was identical to that for the $[CpFe(CO)_2\{(CH_2)_nBr\}]$ compounds. Yields and physical properties are listed in Table 4.4. Minor quantities of $[Cp^*Fe(CO)_2Br]$ and $[Cp^*Fe(CO)_2]_2$ were isolated as byproducts.

Preparation of $[(\eta\text{-}C_5R_5)Fe(CO)_2\{(CH_2)_nI\}]$ (R = H, n = 3-6, 8-10; R = CH_3, n = 3-5)

NaI (12.0 mmol) was added to a solution of $[(\eta\text{-}C_5R_5)Fe(CO)_2\{(CH_2)_nBr\}]$ (6 mmol) in acetone (8 ml). The solution was stirred at room temperature for 24 hours, after which the ^1H NMR spectrum of a sample isolated from the reaction solution no longer showed the triplet due to the $-C\underline{H}_2Br$. The solvent was removed under reduced pressure and the product extracted with hexane, concentrated and transferred to an alumina column. Elution with hexane gave a yellow band, which was concentrated and cooled to -78°C under N_2. The $[(\eta\text{-}C_5R_5)Fe(CO)_2\{(CH_2)_nI\}]$ complex separated out, the mother liquor was syringed off and the product dried under reduced pressure. Yields and physical properties are listed in Tables 4.1 and 4.4. Elution of the column with ether gave a red band, from which a small quantity of $[(\eta\text{-}C_5R_5)Fe(CO)_2I]$ was isolated.

7.5 EXPERIMENTAL DETAILS PERTAINING TO CHAPTER 5

(i) General Details:

Mass spectral data was obtained on one of four instruments: (A) a VG micromass 16F magnetic sector; (B) a Kratos MS80 RFA double focussing spectrometer, (C) a Kratos MS50 double focussing spectrometer and (D) a Finnigan quadrupole spectrometer. Compounds that were examined on more than one system were always found to yield similar mass spectra on all mass spectrometers, and instrumental bias was found to be negligible. All spectra were obtained with a source temperature of less than 170°C and with a probe temperature of 40°C increased to *ca*. 150°C at approximately 20° per minute. Electron impact spectra were obtained with a beam energy of 70 eV; ion acceleration voltages were 4 KV for instruments (A) and (B) and 8 KV for instrument (C). Chemical ionization was with isobutane as reagent gas on instrument (B), and with methane on instrument (D). CIMS was applied only to those compounds for which no molecular ion was seen under electron impact conditions.

Differential Scanning Calorimetry was performed on a Du Pont 910 DSC instrument and a Du Pont 990 Thermal analyser; samples were heated in hermetically sealed pans in air.

(ii) **Preparative Details:**

Preparation of $[Cp(CO)_2Fe(CH_2)_nML_y]$; $n = 3\text{-}6$, ML_y = $Mo(CO)_3Cp$, $W(CO)_3Cp$, $Re(CO)_5$ and $Ru(CO)_2Cp$

general method:

A solution of the sodium salt of the transition metal anion (1.60 mmol) in THF (9 ml) was added to a solution of $[CpFe(CO)_2\{(CH_2)_nI\}]$ (1.47 mmol) in THF (6 ml) over 5 minutes with stirring at -78°C. The solution was allowed to attain room temperature and stirred until the reaction was complete as judged by monitoring the IR $\nu(CO)$ region. (For yields and reaction times see Table 5.1). The solvent was removed under reduced pressure. The crude product was then extracted with CH_2Cl_2, filtered and dried under reduced pressure. One of the following work-up procedures was used:

For $[Cp(CO)_2Fe(CH_2)_nM(CO)_5]$, M = Re, Ru; n = 3-6:

The crude product was dissolved in a minimum of hexane and transferred to an alumina column. Upon elution with hexane a broad yellow band was collected and this was concentrated and then cooled to -78°C. The yellow product separated from this solution. The mother liquor was syringed off and the product dried under reduced pressure.

For $[Cp(CO)_2Fe(CH_2)_nM(CO)_3Cp]$, M = Mo, n = 3, 5, 6; M = W, n = 5, 6:

The crude product was dissolved in a minimum of CH_2Cl_2 and transferred to an alumina column made up in hexane. Elution with hexane first yielded a pale yellow band which was shown to contain only the $[CpFe(CO)_2\{(CH_2)_nI\}]$ starting material. Further elution with hexane or 5% CH_2Cl_2 in hexane yielded a second broad, intense yellow band. This band was collected and the solution concentrated and cooled to -78°C. The yellow product separated from this solution. The mother liquor was syringed off and the product dried under reduced pressure.

For $[Cp(CO)_2Fe(CH_2)_3W(CO)_3Cp]$ and $[Cp(CO)_2Fe(CH_2)_4Mo(CO)_3Cp]$:

The product was dissolved in hot hexane, filtered and cooled to -78°C. The product separated from the solution. The mother liquor was syringed off and the product dried under reduced pressure.

For $[Cp(CO)_2Fe(CH_2)_4W(CO)_3Cp]$:

The crude product was recrystallised from CH_2Cl_2/hexane.

Crystallisation of $[Cp(CO)_2Fe(CH_2)_6Ru(CO)_2Cp]$

Single crystals suitable for X-ray analysis were prepared by slow recrystallisation of $[Cp(CO)_2Fe(CH_2)_6Ru(CO)_2Cp]$ from a dilute, filtered, N_2 saturated solution of hexane at -15°C. Initially fine crystals precipitated out of solution. The mother liquor was removed, filtered and cooled to -15°C. After *ca.* 2 days a few crystals had formed and a suitable one was selected for x-ray structural determination.

Preparation of $[Cp^*(CO)_2Fe(CH_2)_nML_y]$, n = 3-5, ML_y = $Ru(CO)_2Cp$; n = 4, ML_y = $Re(CO)_5$; n = 3, ML_y = $Fe(CO)_2Cp$:

A solution of the sodium salt of the appropriate transition metal anion (1.06 mmol) in THF (4 ml) was added to a solution of $[Cp^*Fe(CO)_2\{(CH_2)_nI\}]$ (0.77 mmol) in THF (4 ml) at -78°C with stirring over 5 minutes. The solution was allowed to attain room temperature and stirred until the reaction was judged to be complete by IR monitoring in the ν(CO) region. For yields and reaction times see Table 5.2. The solvent was removed under reduced pressure. The product was extracted with hexane and the solution was filtered, concentrated and transferred to an alumina column. Elution with hexane gave a yellow band which was collected, concentrated and cooled to -78°C. The product separated from the solution. The mother liquor was syringed off and the product dried under reduced pressure.

7.6 EXPERIMENTAL DETAILS PERTAINING TO CHAPTER 6

(i) General Details

The complexes $[\{CpMo(CO)_3\}_2\{\eta\text{-}(CH_2)_4\}]$ [22] and $[\{CpFe(CO)_2\}_2\{\eta\text{-}(CH_2CHCH_2)\}]PF_6$ [23] were prepared by reported procedures.

The reaction of $[\{CpFe(CO)_2\}_2\{\eta\text{-}(CH_2)_3\}]$ with 1 mol PPh_3 was carried out according to the published procedure [24].

(ii) Synthetic details

Reaction of $[\{CpMo(CO)_3\}_2\{\eta\text{-}(CH_2)_4\}]$ (4) with 1 mol equivalence PPh_3 in CH_3CN

PPh_3 (0.096g, 0.366 mmol) was added to a suspension of $[\{CpMo(CO)_3\}_2\{\eta\text{-}(CH_2)_4\}]$ (4) (0.199g, 0.366 mmol) in CH_3CN (3.5 ml). The product was filtered off after allowing the mixture to stand for 2.75 hours at room temperature. This gave a yellow solid (0.254g). Both the IR and ^1H NMR spectra imply that this product is a 10:7 mixture of $[Cp(CO)_2(PPh_3)MoC(O)(CH_2)_4Mo(CO)_3Cp]$ (5) and $[\{Cp(CO)_2(PPh_3)Mo\}_2\{\eta\text{-}C(O)(CH_2)_4C(O)\}]$ (6). This ratio of products was supported by the elemental analysis data obtained. Found: C, 59.90; H, 3.70%; Calculated for 10:7 ratio of (5) : (6): C, 59.02; H, 4.24%.

Reaction of (4) with 2 mol equivalence PPh_3 in CH_3CN

Complex (4) (0.174g, 0.320 mmol) and PPh_3 (0.170g, 0.690 mmol) were dissolved in CH_3CN (4.5 ml). The mixture was stirred at room temperature for 15 hours. The resulting precipitate was filtered off to afford (6) as a yellow solid (0.249g, 73%). Analytically pure samples of (6) can be obtained on recrystallisation from CH_2Cl_2 / hexane.

Reaction of $[Cp(CO)_2Fe(CH_2)_3Mo(CO)_3Cp]$ (7) with PPh_3 in CH_3CN

Complex (7) (0.200g, 0.431 mmol) and PPh_3 (0.113g, 0.431 mmol) were dissolved in CH_3CN (3.5 ml). The mixture was stirred at room temperature for 2 hours. A yellow precipitate started forming after 18 minutes. This precipitate was filtered off to yield $[Cp(CO)_2Fe(CH_2)_3C(O)Mo(PPh_3)(CO)_2Cp]$ (8) (0.214g, 68%). Analytically pure samples can be obtained on recrystallisation from CH_2Cl_2 / hexane.

Reaction of (7) with PMe_2Ph in CH_3CN

Complex (7) (0.190g, 0.409 mmol) was dissolved in CH_3CN (2 ml) and a solution of PMe_2Ph (0.058 ml, 0.409 mmol) in CH_3CN (1.5 ml) was added. The mixture was stirred at room temperature for 130 minutes. Evaporation of the solvent under reduced pressure left a dark oil. The product was taken up in CH_2Cl_2 and transferred to an alumina column. Elution with CH_2Cl_2 gave a broad yellow band which was collected and evaporated to dryness, leaving $[Cp(CO)_2Fe(CH_2)_3C(O)Mo(PMe_2Ph)(CO)_2Cp]$ as a yellow oil. All attempts to solidify this product failed.

Reaction of (7) with CO in CH_3CN

Complex (7) (0.200g, 0.431 mmol) was dissolved in CH_3CN and CO gas was bubbled through this solution for 105 minutes with stirring. IR monitoring of the ν(CO) region showed no further change in the spectra of the mixture after 1 hour. The solvent was evaporated *in vacuo* leaving a dark yellow oil. The IR spectrum of the product {IR ν(CO) (CH_2Cl_2): 2078w, 2001s, 1943vs, 1902s, 1645w cm^{-1}} implied that the product was [$Cp(CO)_2Fe(CH_2)_3C(O)Mo(CO)_3Cp$]. The product was recrystallised under N_2 from hot hexane to give a yellow oil (0.100g, 47%). The product was vert air-sensitive for further measurements were not performed on it.

Reaction of [$Cp(CO)_2Fe(CH_2)_4Mo(CO)_3Cp$] with 1 mol equivalence PPh_3 or PMe_2Ph in THF

general method:

[$Cp(CO)_2Fe(CH_2)_4Mo(CO)_3Cp$] (0.21 mmol) was dissolved in THF (8 ml) and the phosphine was added. The solution was stirred at room temperature for 23 hours. Evaporation of the solvent *in vacuo* left a yellow oil, which was recrystallised from hot hexane. Both products were obtained in very low yield (4%). ^{1}H NMR and IR data implied that the complexes formed were [$Cp(CO)_2Fe(CH_2)_3C(O)MoL(CO)_2Cp$], L = PPh_3 (yellow solid) and L = PMe_2Ph (oily yellow solid). L = PPh_3: IR ν(CO) (CH_2Cl_2): 1999s, 1938vs, 1851vs, 1607br, w cm^{-1}; ^{1}H NMR ($CDCl_3$): 7.44m (15H, PPh_3), 5.00d (5H, CpMo), 4.69s (5H, CpFe), 3.05t (2H, -C(O)C$\underline{H}_2$-), 1.55m (6H,

-$(CH_2)_3$-);

L = PMe_2Ph: IR ν(CO) (hexane): 2007s, 1953s, 1929m, 1851vs, 1634w cm^{-1}. ^1H NMR ($CDCl_3$): 7.42m (PPh), 4.95d (5H, CpMo), 4.70s (CpFe), 2.96t (2H, MoC(O)C$\underline{H}_2$-), 2.48m (2H), 2.24m (2H), 1.88d (6H, PMe_2), 1.38m (2H).

Reaction of $[Cp(CO)_2Fe(CH_2)_6Mo(CO)_3Cp]$ (9) with PPh_3 in CH_3CN

Complex (9) (0.240g, 0.470 mmol) was dissolved with PPh_3 (0.125g, 0.470 mmol) in CH_3CN and the mixture stirred at room temperature for 140 minutes, after which time an IR ν(CO) spectrum of the mixture showed only bands due to the reaction product {IR ν(CO) (CH_3CN): 1998vs, 1937vs, 1850vs, 1614m cm^{-1}}. The solvent was removed under reduced pressure leaving a yellow oil, which was washed with hexane to give $[Cp(CO)_2Fe(CH_2)_6C(O)Mo(PPh_3)(CO)_2Cp]$ as an oily yellow solid (0.217g, 60%). Found: C, 60.10; H, 4.70 %. Calculated for $C_{39}H_{37}FeMoO_5P$: C, 60.91; H, 4.82 %.

Reaction of $[CpFe(CO)_2(CH_2)_3Ru(CO)_2Cp]$ (12) with PPh_3 in THF

Complex (12) (0.270g, 0.610 mmol) and PPh_3 (0.161g, 0.610 mmol) were dissolved in THF (9 ml) and the mixture was refluxed for 5 days. Evaporation of the solvent *in vacuo* left an orange oily residue. The product was washed with hexane to remove any unreacted starting material. The product was then dissolved in a minimum of CH_2Cl_2 and transferred to an alumina column made up with hexane. Elution with hexane gave a pale yellow band from which a very small quantity of starting material was recovered (<1%).

Elution with 20% CH_2Cl_2/hexane gave an orange band, which was collected and the solvent was removed under reduced pressure. This gave a dirty orange solid which was recrystallised from either CH_2Cl_2/hexane or ether/hexane to give $[Cp(CO)(PPh_3)FeC(O)(CH_2)_3Ru(CO)_2Cp]$ (13) (0.193g, 45%) as an orange solid. Found: C 59.50; H, 4.70 %; calculated for $C_{35}H_{31}FeO_4PRu$: C, 59.71; H, 4.41 %.

A repeat of this reaction using complex (**12**) (0.202g, 0.460 mmol) and PPh_3 (0.123g, 0.470 mmol) in refluxing THF (7.6 ml) was found to be complete {by IR monitoring of the ν(CO) region} after 2 days 23 hours.

Reaction of $[Cp(CO)_2Fe(CH_2)_3W(CO)_3Cp]$ (15) with PPh_3 in THF

Complex (**15**) (0.176g, 0.319 mmol) and PPh_3 (0.085g, 0.324 mmol) were dissolved in THF (6 ml). The mixture was refluxed for 64 hours. The course of the reaction was followed by IR spectroscopy of the ν(CO) region. Once the reaction was judged complete, the solvent was evaporated in vacuo, leaving a dirty yellow solid. This solid was dissolved in a minimum of CH_2Cl_2 and transferred to an alumina column made up with hexane. Elution with 20% CH_2Cl_2/hexane gave a pale yellow band from which the solvent was evaporated under reduced pressure to leave a yellow oil. This was identified as unchanged starting material (**15**). Elution with 50% CH_2Cl_2/hexane gave an orange band, which, on evaporation under reduced pressure, gave a yellow/orange solid. This was identified as $[Cp(CO)(PPh_3)FeC(O)(CH_2)_3W(CO)_3Cp]$. Found: C, 52.00; H, 4.00%. Calculated for $C_{36}H_{31}FeO_5PW$: C, 53.07; H, 3.81%.

Reaction of $[Cp(CO)_2Fe(CH_2)_3Re(CO)_5]$ (17) with 1 mol equivalence PPh_3 in THF

Complex (17) (0.160g, 0.293 mmol) was dissolved in THF (5 ml) and PPh_3 (0.078g, 0.297 mmol) was added to the solution. The mixture was refluxed for 70.5 hours. IR monitoring of the reaction showed very little change in the spectra of the ν(CO) region after *ca.* 24 hours.

The solvent was evaporated under reduced pressure to leave a yellow / orange oily solid. This oily solid was washed with hexane and the washings were filtered and cooled to -78°C. A fine pale yellow solid separated. This solid was identified as $[Cp(CO)(PPh_3)FeC(O)(CH_2)_3Re(PPh_3)(CO)_4]$ (21) (0.02g, 7%). The residual orange solid was identified as $[Cp(CO)_2Fe(CH_2)_3Re(PPh_3)(CO)_4]$ (0.142g, 63%).

Reaction of $[Cp^*(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$ with 1 mol equivalence PPh_3 in xylene

$[Cp^*(CO)_2Fe(CH_2)_3Ru(CO)_2Cp]$ (0.170g, 0.330 mmol) and PPh_3 (0.088g, 0.330 mmol) were dissolved in xylene (6 ml) and the mixture was refluxed for 39.5 hours. The reaction was followed by IR spectroscopy {in the ν(CO) region}. Evaporation of the solvent gave a red oily product. IR ν(CO) (xylene): 1922vs, 1752w cm^{-1}. The ^1H NMR ($CDCl_3$) showed a multiplet at δ = 7.40 (PPh_3) and two peaks in the Cp region: 4.96d and 4.89s. The product(s) could not be further purified.

Attempted reaction of (4) with Ph_3CPF_6

Complex (4) (0.191g, 0.350 mmol) was dissolved in CH_2Cl_2 (6 ml). A solution of Ph_3CPF_6 (0.146g, 0.380 mmol) in CH_2Cl_2 (4 ml) was added and the mixture was stood at room temperature for 23 hours. A dark blue precipitate formed during this period. The precipitate was filtered off (0.055g) and washed with ether. This precipitate was insoluble in CH_2Cl_2 but dissolved in acetone. Extraction with acetone gave an orange solution (which rapidly turned black) which was evaporated to dryness under reduced pressure to give a yellow solid contaminated with a fine blue impurity. The IR ν(CO) (Nujol): 2011m, 1935s, 1903s, 1670br,w cm^{-1} implied that the product contained $[Cp(CO)_3Mo(C_4H_7)Mo(CO)_3Cp]PF_6$, but that it was contaminated with finely divided metal and/or oxides. All attempts to purify the product were unsucccessful.

Reactions of complexes (7), (12) and (15) with Ph_3CPF_6
general method:

The heterobimetallic complex {(7), (12) or (15)} (0.5 mmol) was dissolved in CH_2Cl_2 (2 ml), and a solution of Ph_3CPF_6 (0.6 mmol) in CH_2Cl_2 (4 ml) was added. The mixture was allowed to stand at room temperature (for reaction times and yields see Table 7.1). The product precipitated out of solution and was filtered off. The product was recrystallised from acetone/hexane and washed with ether. Thus $[Cp(CO)_2Fe(C_3H_5)Mo(CO)_3Cp]PF_6$ **(23)** was obtained as lustrous golden platelets, $[Cp(CO)_2Fe(C_3H_5)Ru(CO)_2Cp]PF_6$ **(24)** as orange needles, and

$[Cp(CO)_2Fe(C_4H_7)W(CO)_3Cp]PF_6$ **(27)** as a yellow solid.

Reactions of $[Cp(CO)_2Fe(CH_2)_4Mo(CO)_3Cp]$ and $[Cp(CO)_2Fe(CH_2)_nRu(CO)_2Cp]$ $(n = 4,6)$ with Ph_3CPF_6

general method:

The heterobimetallic complex (0.33 mmol) was dissolved in CH_2Cl_2 (2 ml) and a solution of Ph_3CPF_6 (0.41 mmol) in CH_2Cl_2 (4 ml) was added. The solution was allowed to stand at room temperature (for reaction times and percentage yields see Table 7.1). The product was precipitated by adding ether to the reaction solution. The product was filtered off and washed with ether and hexane. Thus complex **(25)** was obtained as an orange solid and complexes **(26)** and **(28)** as yellow solids.

Table 7.1:

Reaction times and yields for the complexes **(23)** - **(28)**

Complex no.	Reaction Time (h)	Percentage Yield
(23)	77	30
(24)	4	74
(25)	48	26
(26)	8.5	51
(27)	2.75	57
(28)	77	55

Crystallisation of $[Cp(CO)_2Fe(C_3H_5)Ru(CO)_2Cp]PF_6$

Single crystals suitable for X-ray analysis were obtained by standing a saturated solution of complex (**24**) in acetone-d_6 in an NMR tube at -15°C for *ca.* 6 days. During this time several suitable crystals for X-ray analysis had formed.

Reaction of (7) with Me_3NO

Complex (**7**) (0.11g, 0.24 mmol) was dissolved in CH_2Cl_2 (2 ml). Anhydrous Me_3NO (0.03g, 0.30 mmol) was added and the solution allowed to stand for 22 hours at room temperature. IR monitoring of the ν(CO) region showed only bands due to the starting material. More CH_2Cl_2 (3 ml) was added and the solution was refluxed for 48 hours. Still no change was observed in the IR spectra of the mixture. Evaporation of the solvent *in vacuo* led to recovery of the starting material (**7**) (*ca.* 70%) and small quantities of $[CpFe(CO)_2]_2$ and $[CpMo(CO)_3]_2$.

^{13}C NMR monitoring of $[Cp(CO)_2Fe(CH_2)_4Mo(CO)_3Cp]$ in heated toluene

The complex $[Cp(CO)_2Fe(CH_2)_4Mo(CO)_3Cp]$ was dissolved in toluene-d_8 and ^{13}C NMR spectra were run of the solution at 25, 40, 70 and 100°C. At 25°C peaks at δ = 240.5, 228.3 (MoCO), 218.3 (FeCO), 45.0, 42.6, 3.7 and 3.0 ($4xCH_2$) ppm were observed. The peak at δ = 240.5 was no longer observed at 40°C. At 70 and 100°C no signals for the Mo-CO groups (δ = 240.5, 228.3) were observed. The solution darkened with heating and decomposition material was observed to form.

Reaction of $[Cp(CO)_2Fe(CH_2)_6W(CO)_3Cp]$ with HCl gas

A solution / suspension of $[Cp(CO)_2Fe(CH_2)_6W(CO)_3Cp]$ in hexane was left to stand under an atmosphere of HCl gas at -78°C for *ca.* 2 hours. The solution changed colour from yellow to orange. The solvent was evaporated under reduced pressure and the product dissolved in a minimum of hexane and transferred to an alumina column made up in hexane. Elution with hexane gave a yellow solution which yielded a yellow oil on evaporation under reduced pressure. The IR ν(CO) (hexane) (2008vs, 1954vs cm^{-1}), ^1H NMR ($CDCl_3$) and ^{13}C NMR ($CDCl_3$) spectra of this product (obtained in 25% yield) were exactly identical to those of a freshly prepared sample of $[Cp(CO)_2Fe\{(CH_2)_5CH_3\}]$ [25]. Elution of the column with CH_2Cl_2 gave an orange solution which, on evaporation under reduced pressure, gave $[CpW(CO)_3Cl]$ in 22% yield.

Reaction of $[Cp(CO)_2Fe(CH_2)_5Ru(CO)_2Cp]$ with I_2

The complex $[Cp(CO)_2Fe(CH_2)_5Ru(CO)_2Cp]$ (0.08g, 0.17 mmol) was dissolved in CH_2Cl_2 (2 ml). A solution of I_2 (0.44g, 0.17 mmol) in CH_2Cl_2 (8 ml) was added at 0°C. The solution was stirred at 0°C for 10 minutes. Evaporation of the solvent *in vacuo* left a purple solid. This product was dissolved in CH_2Cl_2 and transferred to an alumina column made up in hexane. Elution with hexane separated two yellow bands, whilst elution with 10% CH_2Cl_2/hexane gave a third yellow solution. Evaporation of the solvents under reduced pressure gave orange oily solids which were identified (by IR and ^1H NMR spectroscopy) to be mixtures of

$[CpFe(CO)_2I]$ [21] and $[CpRu(CO)_2I]$ [26] in differing ratios. A trace of $I(CH_2)_5I$ was also observed. No other products could be isolated.

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APPENDIX CALCULATION OF THE RATE CONSTANT FOR THE REACTION OF $[CpW(CO)_3CH_2Br]$ WITH 2 MOL PMe_2Ph.

If the reaction proceeded via the mechanism shown in **Scheme 3.2** of chapter 3, the rate of the reaction could be written as :

Rate = k[(**Z**)]

where [(**Z**)] = the concentration of the reaction intermediate $CpW(CO)_3CH_2X\cdot\cdot PMe_2Ph$ (**Z**).

Since the second step is too fast for the intermediate to be observed the rate can also be written as:

Rate = $k[CpW(CO)_3CH_2Br][PMe_2Ph]$

{$[CpW(CO)_3CH_2Br]$, $[PMe_2Ph]$ = the concentration of the species $CpW(CO)_3CH_2Br$ and PMe_2Ph respectively.} If $[PMe_2Ph]$ is sufficiently large (in excess), its concentration can be assumed to be constant throughout the reaction and the rate equation can be written as :

Rate = $k_{obs}[CpW(CO)_3CH_2Br]$.

Thus a plot of $\ln[CpW(CO)_3CH_2Br]$ *vs*. t (time) should give a straight line with the slope = k_{obs}. The plots of $\ln[CpW(CO)_3CH_2Br]$ vs t for 2:1, 3:1 and 4:1 ratios of $[PMe_2Ph]$:$[CpW(CO)_3CH_2Br]$ over 70-75% of the reaction range are given in **figures 1-3.**

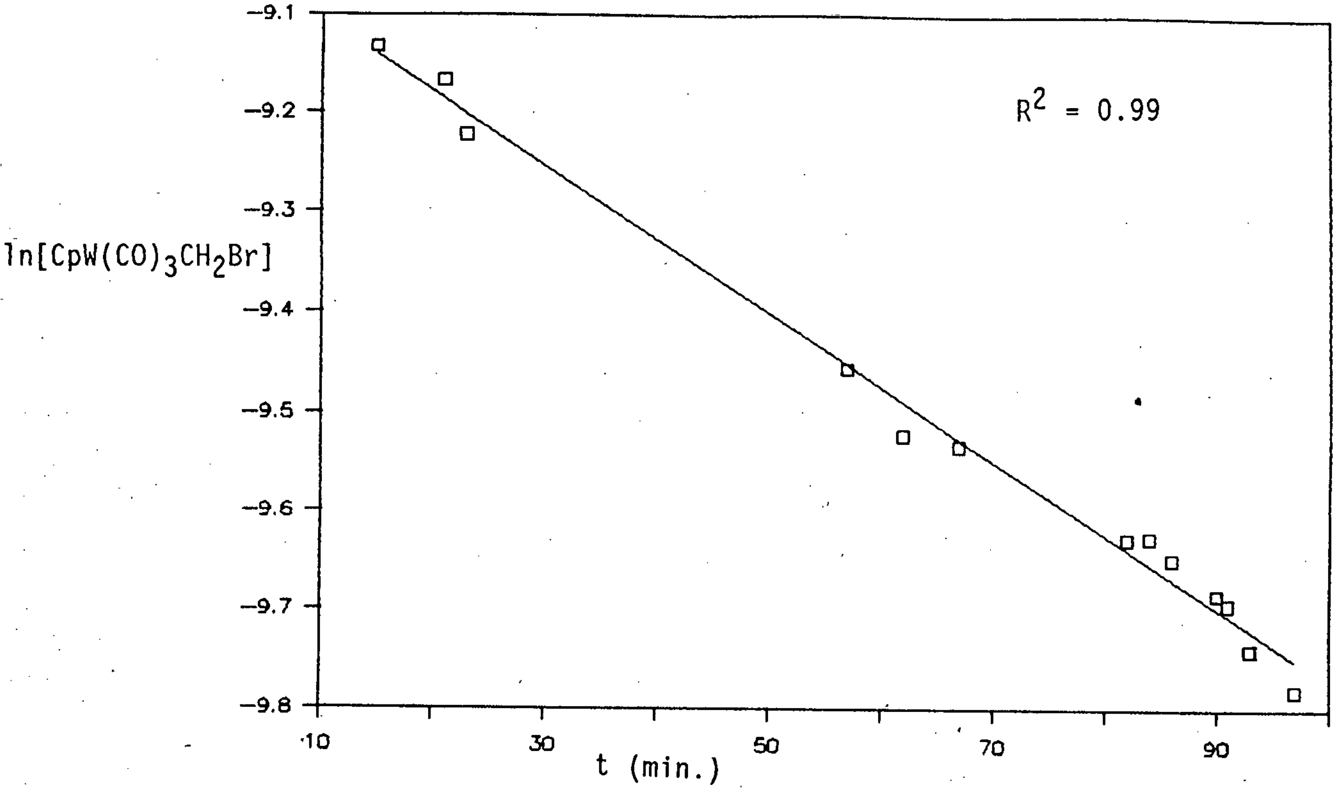

Figure 1: Plot of ln[CpW(CO)$_3$CH$_2$Br] (**2b**) vs time for a 2:1 ratio of L:(**2b**).

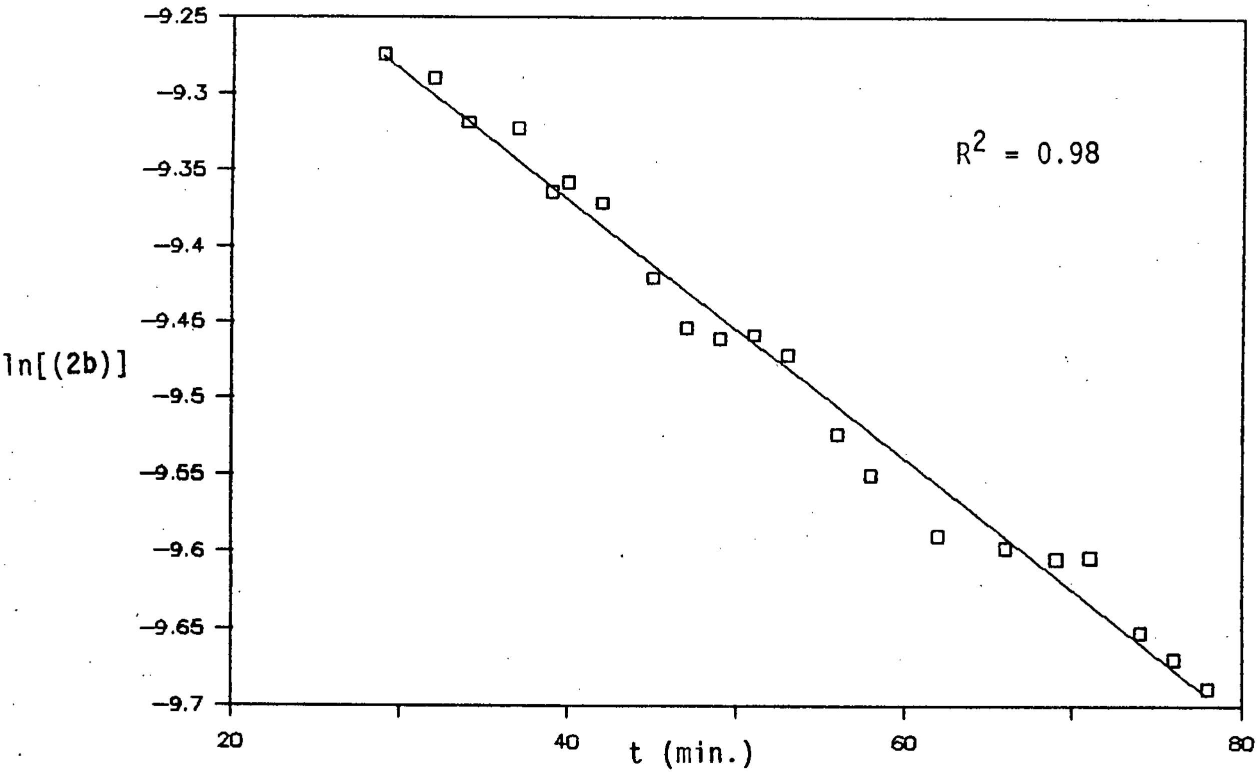

Figure 2: Plot of ln[(**2b**)] vs time for a 3:1 ratio of L:(**2b**).

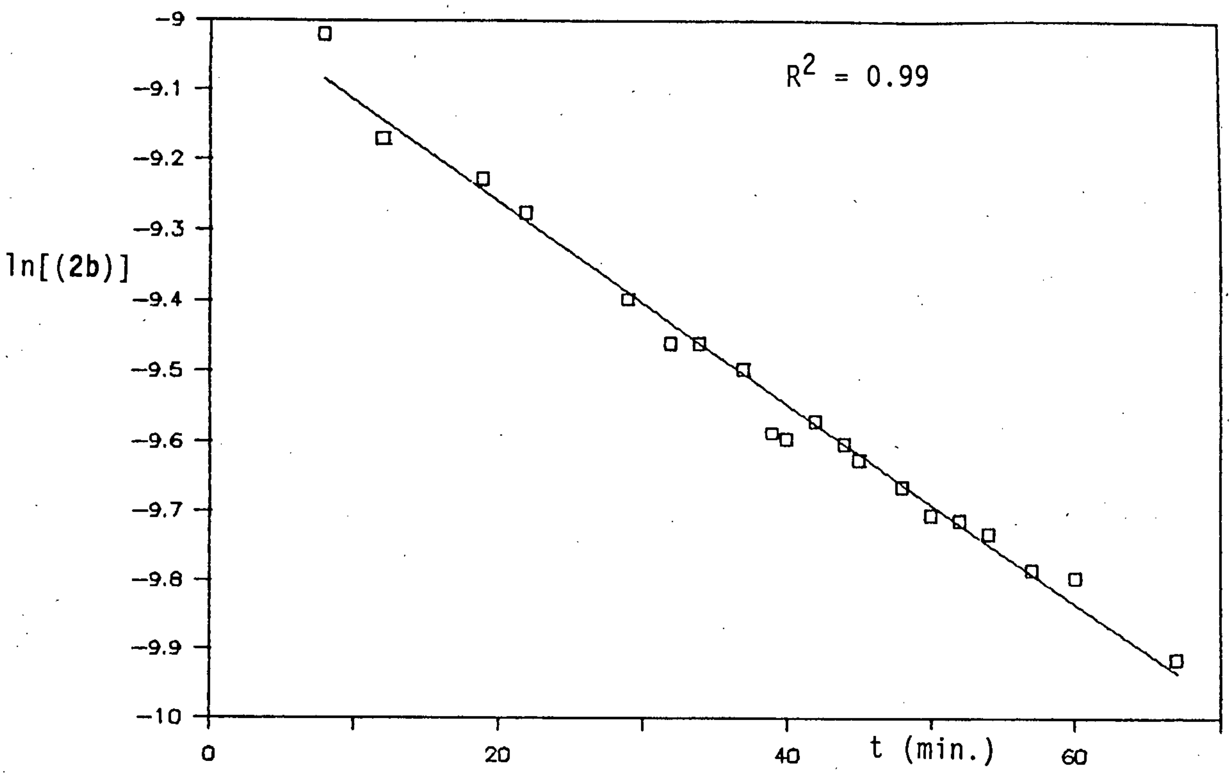

Figure 3: Plot of ln[(**2b**)] vs time for a 4:1 ratio of L:(**2b**).

Now, since $k_{obs} = k[PMe_2Ph]$, a plot of k_{obs} vs various concentrations of PMe_2Ph should give a straight line with its slope = k. This plot is shown in **figure 4**. The value of k obtained = 0.44 (±0.17) s^{-1}. The error coefficient for k is fairly high, since the assumption that $[PMe_2Ph]$ is sufficiently high to be constant throughout the course of the reaction does not strictly apply (especially for the reaction where the ratio of [(**2b**)] : $[PMe_2Ph]$ is 1:2). The value of k obtained does however provide a reasonable estimate of the true value, as is shown below.

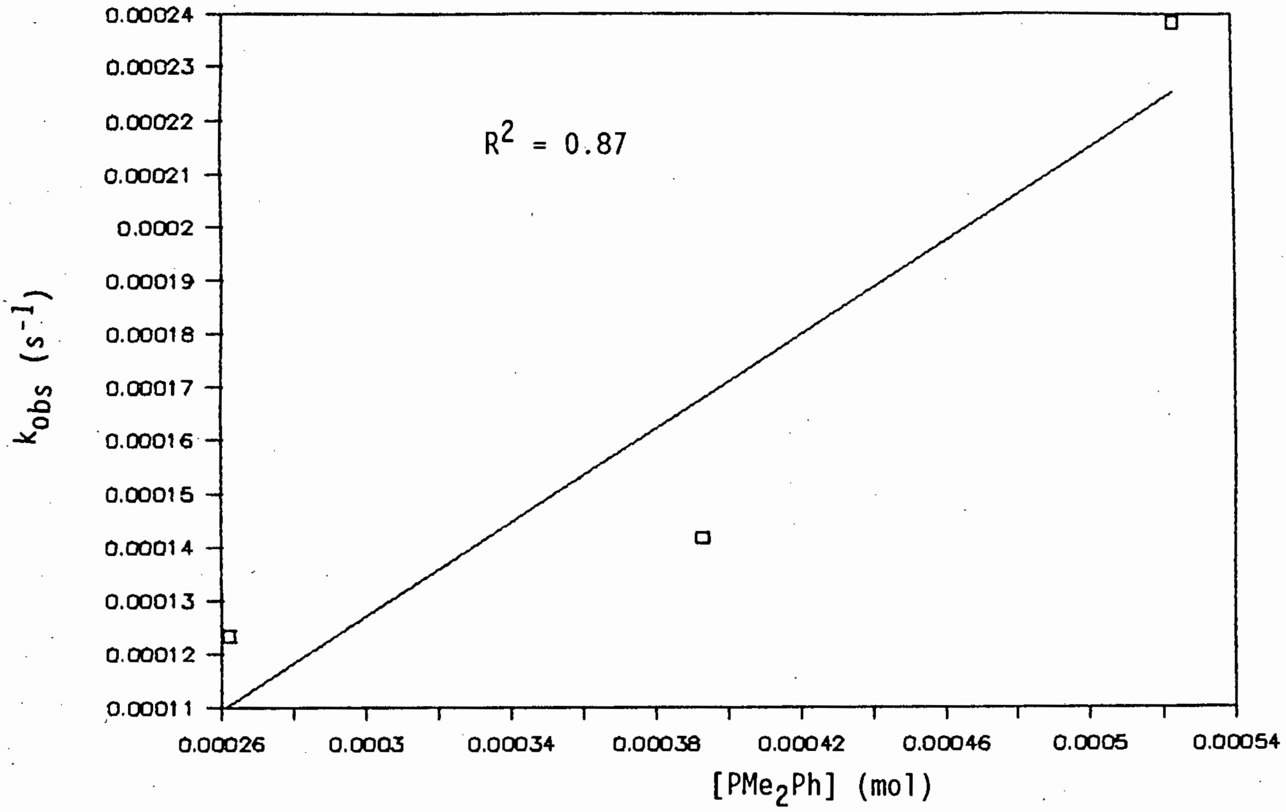

Figure 4: Plot of k_{obs} vs [PMe_2Ph]

An alternative method for calculating k is as follows. If the rate = $k[CpW(CO)_3CH_2Br][PMe_2Ph]$, as proposed, a plot of

$$\left\{\frac{1}{[CpW(CO)_3CH_2Br] - [PMe_2Ph]}\right\} \ln\left\{\frac{[CpW(CO)_3CH_2Br]_t[PMe_2Ph]_0}{[CpW(CO)_3CH_2Br]_0[PMe_2Ph]_t}\right\} \quad \text{vs } t$$

should give a straight line with its slope = the rate coefficient (k) [1]. ($[PMe_2Ph]_0$, $[CpW(CO)_3CH_2Br]_0$ = initial concentration of reactants; $[PMe_2Ph]_t$, $[CpW(CO)_3CH_2Br]_t$ = concentrations of reactants at time = t.) This plot is shown in **figure 5.**

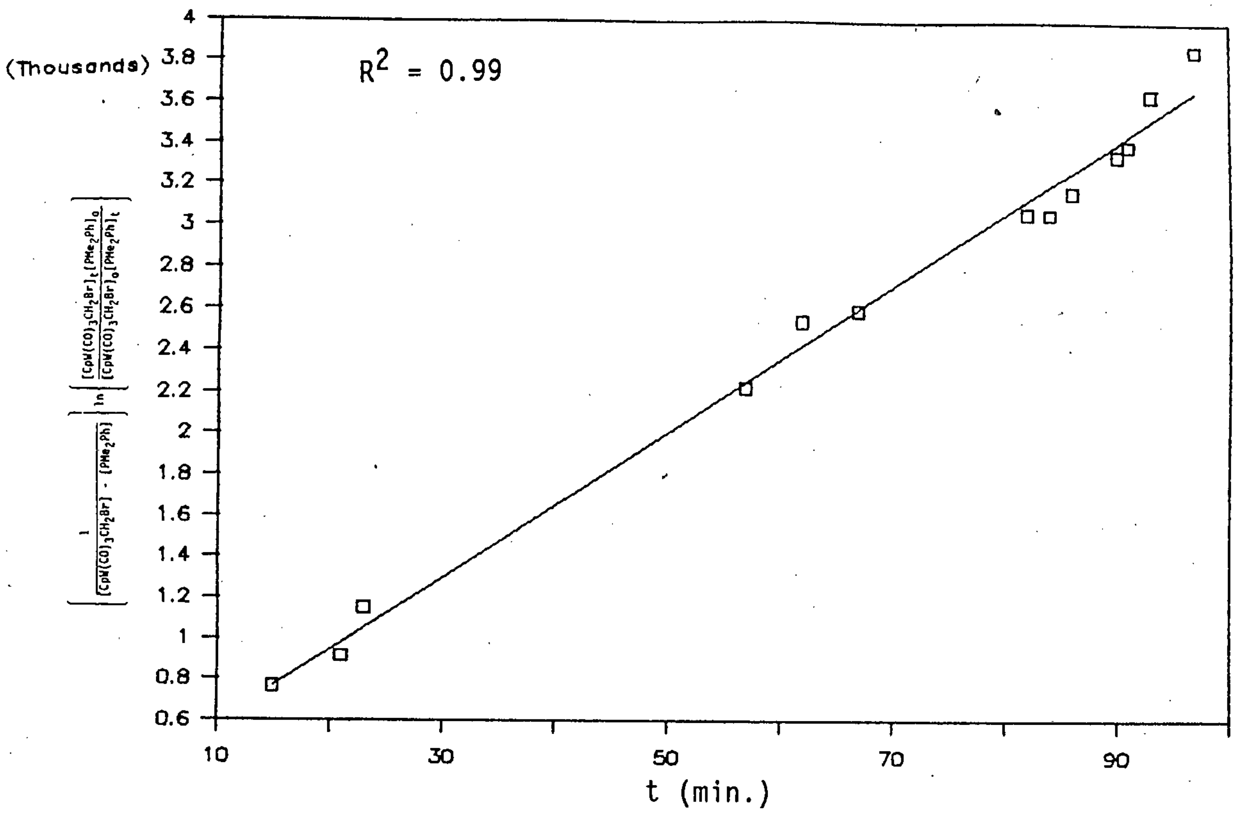

Figure 5

The rate coefficient obtained via this method = 0.59 (±0.02) s^{-1}. This latter method gives a more precise value for k. As can be seen though, this value of k is within the error coefficient of the estimated k value obtained by the earlier method.

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