CHLOROMETHYL AND METHOXYMETHYL TRANSITION METAL COMPLEXES: AN INVESTIGATION INTO THEIR SYNTHESIS AND REACTIVITY

by

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ABSTRACT

Transition metal methoxymethyl and chloromethyl complexes may be versatile starting materials for the synthesis of several types of new complexes, including hydroxymethyl and carbene complexes, respectively $[L_nMCH_2OH]$ and $[L_nMCH_2]^+$ (M = transition metal, L = ligands). Hydroxymethyl and carbene transition metal complexes are models of catalytic intermediates in the Fischer-Tropsch reaction.

We have synthesized the new chloromethyl complexes $[Ru(Cp)(CO)_2CH_2Cl]$, $[Re(CO)_5CH_2Cl]$, and *cis*-$[Mn(CO)_4(PPh_3)CH_2Cl]$, and the new methoxymethyl complexes $[Ru(Cp)(CO)_2CH_2OCH_3]$ and $[Re(CO)_5CH_2OCH_3]$. The existence of rotational isomerism in the complexes $[Ru(Cp)(CO)_2CH_2OCH_3]$ and the previously reported $[Fe(Cp)(CO)_2CH_2OCH_3]$,[48] is proposed on the basis of infrared data. Mass spectra of several methoxymethyl and chloromethyl transition metal complexes have been recorded.

The reactions of some chloromethyl and methoxymethyl transition metal complexes with tertiary phosphine ligands and triphenylarsine, have been investigated. The reactions of $[Fe(Cp)(CO)_2CH_2Cl]$ (VI) with L = PPh_3, $PMePh_2$, $PEtPh_2$, PMe_2Ph, and $AsPh_3$ respectively, in refluxing methanol yield the cations $[Fe(Cp)(CO)_2CH_2L]^+$. The reactions of (VI) with L = PPh_3 and $PMePh_2$ respectively at room temperature in acetonitrile also yield the cations $[Fe(Cp)(CO)_2CH_2L]^+$; however the reactions of (VI) with L = PMe_2Ph, PMe_3, PEt_2Ph respectively yield the cations $[Fe(Cp)(CO)L_2]^+$ at room temperature, in acetonitrile. The reaction of $[W(Cp)(CO)_3CH_2Cl]$ with PPh_3 in acetonitrile at room temperature yields the cation $[W(Cp)(CO)_3CH_2PPh_3]^+$. The reaction of $[Mn(CO)_5CH_2OCH_3]$ (VIII)

with PPh_3 in acetonitrile at room temperature yields *cis*-$[Mn(CO)_4(PPh_3)$-$COCH_2OCH_3]$; however in refluxing methanol (VIII) reacts with PPh_3 to give *cis*-$[Mn(CO)_4(PPh_3)CH_2OCH_3]$ and *trans*-$[Mn(CO)_3(PPh_3)_2CH_2OCH_3]$. $[Mn(CO)_5CH_2Cl]$ reacts with PPh_3 in methanol to give *trans*-$[Mn(CO)_3$-$(PPh_3)_2Cl]$. Neither $[Re(CO)_5CH_2OCH_3]$ nor $[Re(CO)_5CH_2Cl]$ react with PPh_3 in acetonitrile. The only product isolated from the reaction of $[Ru(Cp)(CO)_2CH_2Cl]$ with PPh_3 in refluxing methanol is $[Ru(Cp)(CO)_2CH_2OCH_3]$.

Attempts have also been made to synthesize hydroxymethyl transition metal complexes.

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CONTENTS

ABBREVIATIONS

The following abbreviations are used in this project:

Cp	=	η^5-cyclopentadienyl
THF	=	tetrahydrofuran
Ph	=	phenyl
Me	=	methyl
Et	=	ethyl
Bu	=	butyl
Pr	=	propyl

CHAPTER ONE

1. INTRODUCTION

1.1 The scope of this work

Chloromethyl and methoxymethyl transition metal complexes are possible precursors of a number of important compounds, such as hydroxymethyl complexes and carbene complexes, both of which have been proposed as intermediates in the Fischer-Tropsch reaction. However not many $[L_nMCH_2Cl]$ or $[L_nMCH_2OCH_3]$ (M = transition metal, L = ligands) complexes have been synthesized, and little is known of their chemistry.

In this work we have synthesized and characterised some new chloromethyl and methoxymethyl complexes and have investigated the reactions of a number of such complexes with some tertiary phosphines, $P(OMe)_3$ and $AsPh_3$. We have also attempted to synthesize some hydroxymethyl $[L_nMCH_2OH]$ complexes.

In view of the relevance of this work to the synthesis of Fischer-Tropsch intermediates, an overview of the Fischer-Tropsch reaction is now presented.

1.2 The Fischer-Tropsch reaction

Current and pending shortages of petroleum, and the associated rising costs of it and petroleum based products, have led to an increase in the search for alternative sources of energy. A fairly readily available and plentiful source of energy, that is receiving renewed attention, is coal. The conversion of coal to oil and other industrially important chemicals is becoming a viable economic prospect as oil becomes more

expensive. Coal has an unfavourable ton-of-oil equivalent (TOE) (1.5 tons coal is equivalent in energy to 1 ton oil[1]); this, coupled with the relative ease of using oil in industrial plants, has meant that the dirty and relatively inconvenient coal has generally been overlooked as an industrial energy source. However shortages and rising costs of oil, and political embargoes have caused renewed interest in coal.

The synthesis of hydrocarbons and other chemicals from CO and H_2 dates back to early this century.[1,2] Germany, with no oil reserves but abundant coal, conducted intensive research into the synthesis of oil from coal. In 1922, Franz Fischer and Hans Tropsch obtained their first patent on "Synthol", a mixture of oxygen containing derivatives of hydrocarbons, produced from CO and H_2 at 100-150 atm. and 400-450°C, with alkali-treated iron shavings as the catalyst.[1,2]

As the aim of the research in Germany was the synthesis of motor fuels, it was essential that the reaction developed by Fischer and Tropsch be directed more towards hydrocarbons suitable for use as fuel. In 1925, the process was developed to give predominantly straight-chain hydrocarbons, at atmospheric pressure, 250-300°C and using Fe/ZnO or Co/Cr_2O_3 catalysts. The use of cobalt or iron catalysts at medium pressures (5-30 atm.) was later found to substantially improve yield and catalyst lifetime.[1]

It took some 10 years for suitable plants to be developed,[3] but between 1939 and 1945 there were nine plants using the Fischer-Tropsch process in Germany, producing one fifth of Germany's synthetic fuel.[4] However the low post-war oil prices led to decreasing interest in the expensive and fairly inefficient process.

South Africa had considered the idea of obtaining oil from coal as long ago as in 1927 when a White Paper was published by the Government on such processes and their applicability to the country.[5] In 1950 the South African Coal, Oil and Gas Corporation Ltd. (SASOL) was formed and in 1955, the first of three plants, SASOL ONE, began production of oil from coal. The escalating costs of oil led later to the building of two more plants, SASOL TWO (which began producing oil in 1980), and SASOL THREE (under construction at present).[5] These plants are as yet the only large scale commercial oil-from-coal plants in the world.

SASOL ONE uses two different versions of the Fischer-Tropsch process.[1,6] The first, the Arge-Lurgi process, uses a CO/H_2 ratio of 3:5 by volume and a fixed bed catalyst. It produces relatively large amounts of diesel oil and paraffin waxes. The second, the Synthol-Kellog process, uses a CO/H_2 ratio of 1:3 and fluidised catalyst on a moving bed. The pressures are similar for the two processes (*c.a.* 20 atm.). Table 1 and Table 2 compare the products from the two processes.

Table 1 gives the percentages by weight of different products formed for each catalytic method. Table 2 gives the percentages by volume of different products in the liquid fractions produced by each method. Thus the fixed bed method produces a relatively higher proportion of diesel oil and paraffin waxes. The liquid fraction contains approximately equal amounts of olefins and alkanes. The circulating bed method gives largely C_5-C_{11} hydrocarbons and oxygen-containing products, with the liquid fraction containing a remarkably high proportion of olefins.

Apart from gasoline, diesel oil and waxes the SASOL process also produces other important products, including, amongst others, methane, ethylene,

Table 1. (after ref. 1)

Comparison of the products obtained with fixed bed catalyst and with circulating catalyst (in weight - %).

Fraction	Fixed bed catalyst (220-240°C)	Circulating catalyst (310-340°C)
C_3-C_4	5.6	7.7
C_5-C_{11} (gasoline)	33.4	72.3
Gas oil (diesel)	16.6	3.4
Paraffin m.p. < 60°C	22.1	3.0
Paraffin m.p. 95-97°C	18.0	-
Alcohols + ketones	4.3	12.6
Acids	traces	1.0

Table 2. (after ref. 1)

Comparison of the composition of the liquid fraction for fixed bed and circulating bed catalyst (in volume - %).

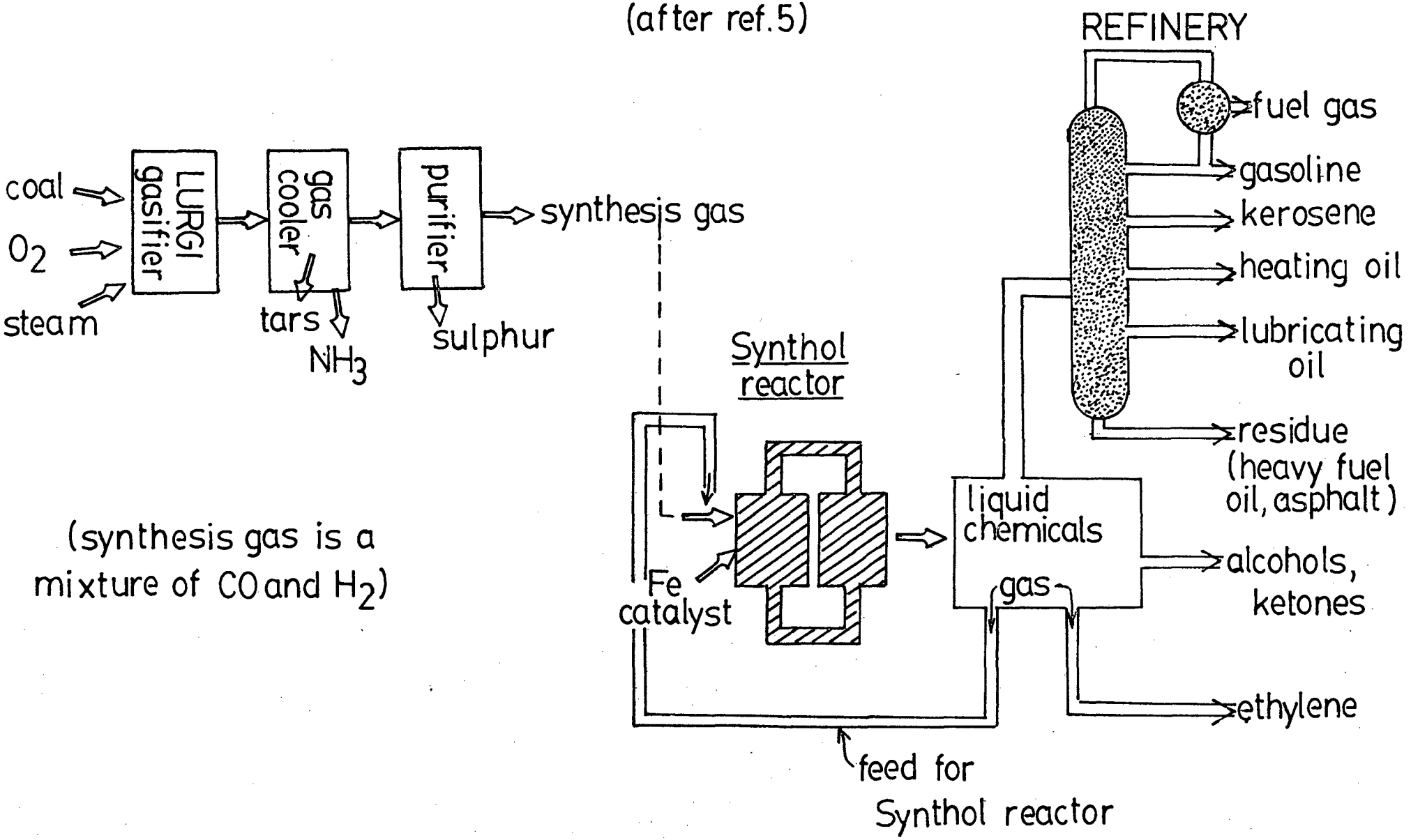
Components	Fixed bed catalyst		Circulating catalyst	
	C_5-C_{10}	C_{11}-C_{18}	C_5-C_{10}	C_{11}-C_{18}
Olefins	50	40	70	60
Paraffins (alkanes)	45	55	13	15
Oxygen containing compounds	5	5	12	10
Aromatics	-	-	5	15

methanol and other alcohols, ketones, aromatics, ammonia (from the gasification process) sulphur, (from the purifying of the synthesis gas) and tars.[5,6]

SASOL TWO and SASOL THREE use the Synthol-Kellog process alone.[6] The catalytic processes have now been developed to a high degree of technical maturity in all three SASOL plants, and the plants are adapted to use low grade coal.[1,5] The key disadvantage of the Fischer-Tropsch process, and hence the SASOL process, is poor product quality and selectivity.[3]

A diagrammatic representation of the SASOL process using a Synthol reactor is given in Figure 1.

Figure 1: The SASOL process (Synthol reactor)
(after ref. 5)



(synthesis gas is a mixture of CO and H_2)

1.3 The products and mechanism of the Fischer-Tropsch reaction

A simplistic representation of the Fischer-Tropsch reaction is given in Equation 1.

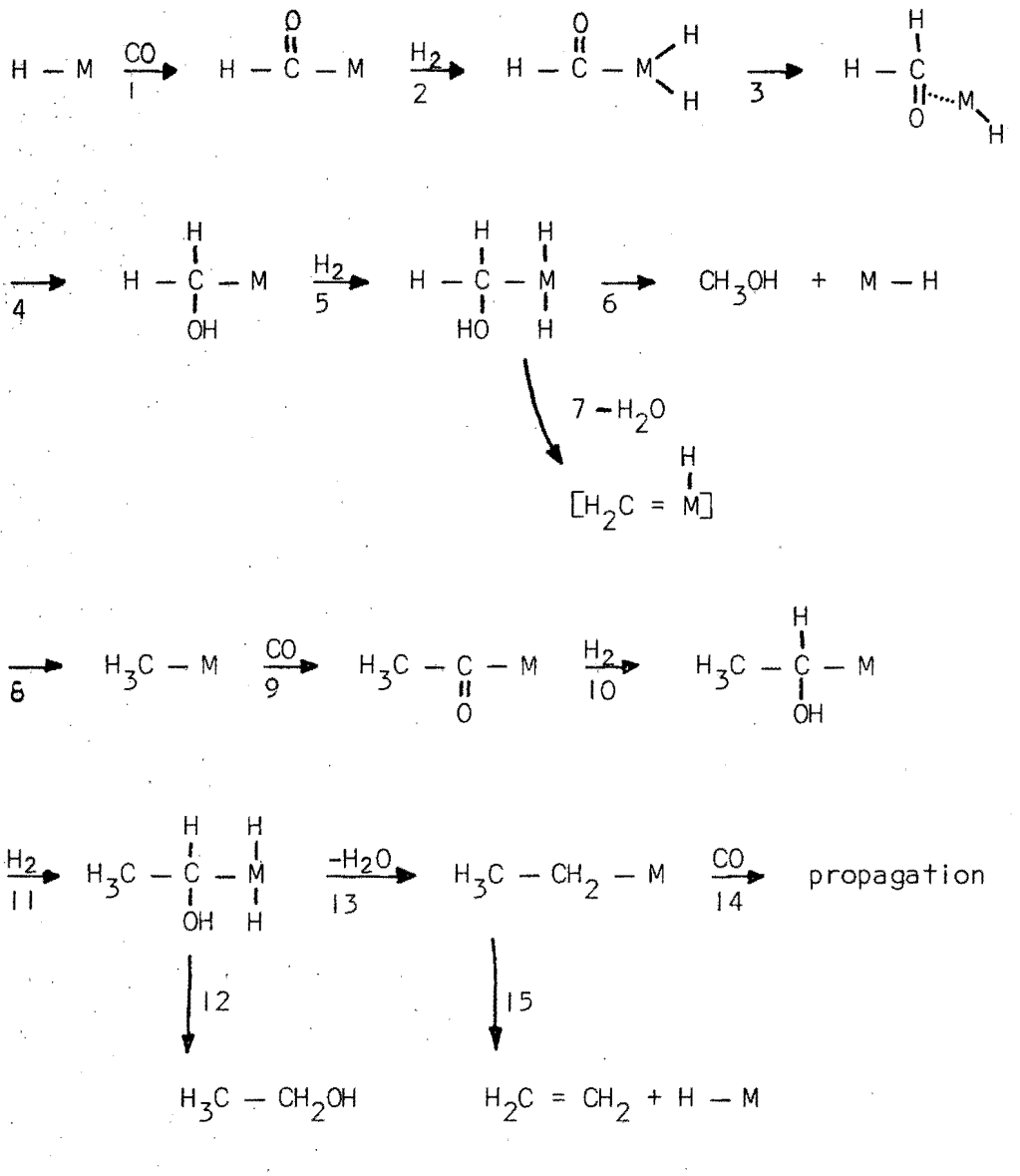
$$\text{coal + steam} \longrightarrow \underset{\text{(synthesis gas)}}{CO + H_2} \xrightarrow{\text{catalyst}} \text{alcohols, hydrocarbons and other products} \qquad (1)$$

The reduction of CO by H_2 takes place on a heterogeneous catalyst to give mainly alkanes, alkenes, and alcohols, but also acids, esters and aromatic compounds in varying amounts.[1] Changing the conditions of the synthesis (the temperature, pressure, the H_2:CO ratio and the catalyst), can direct the reaction more towards alcohols, or towards hydrocarbons. Linear α olefins (1-alkenes) and linear alcohols are considered to be the main primary products of the synthesis; linear and non-linear alkanes result from subsequent reduction of the primary alkenes. The catalysts are generally iron, cobalt, nickel or ruthenium metals or metal oxides, as shavings or powders.[1]

The mechanism of the catalytic procedure is the subject of speculation.[7,8] The first mechanism proposed was the so-called "carbide intermediate" hypothesis[9] (see Section 1.3.3). This has been replaced in more recent times largely by mechanisms involving unstable intermediates containing C, H and O atoms bonded to metals (*i.e.* an active site on the catalyst surface), with initiation, propagation and termination steps.[1,8] However, recently the carbide mechanism has been revised.

1.3.1 A mechanism involving unstable intermediates with C, H and O atoms bonded to metals

In mechanisms involving unstable metal - C, H and O-containing intermediates, the first step has usually been assumed to be the formation of a coordinated formyl species, M-CHO, from M-H and CO, though there is no evidence that this occurs.[7] Henrici-Olivé and Olivé[1] have formulated a scheme involving the initial formation of a formyl species. (Scheme I).



Scheme I. A proposed mechanism for the Fischer-Tropsch reaction (after ref. 1) (M = active site on metal catalyst surface).

The mechanism given in Scheme I is based on steps well established in homogeneous catalysis reactions such as coordination of CO, oxidative addition (oxidative addition of H_2 occurs in steps 2,5, and 11 in Scheme I) and reductive elimination (*e.g.* step 3, Scheme I). Many of the proposed intermediate species had known analogues in organometallic chemistry (*e.g.* formyl species, metal hydrides) and since the publication[1] of scheme I, analogues of other postulated species have been characterised. The scheme is thus a plausible one.

I.3.2. Complexes analogous to intermediates postulated in the Fischer-Tropsch reaction

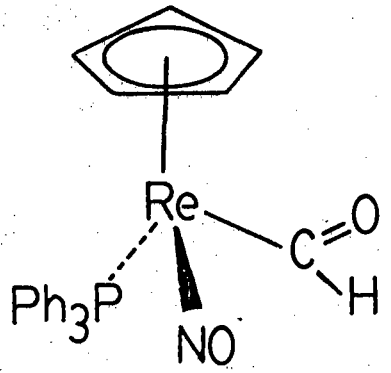
In Scheme I a number of intermediates containing C, H and O atoms bonded to a metal were proposed. Several compounds analogous to these intermediates have been synthesized - complexes containing formyl, coordinated formaldehyde, hydroxymethyl, carbene, alkyl and acyl ligands.

Formyl complexes are in many cases unstable and difficult to characterise. The first to be prepared and characterised was $[(CO)_4Fe(CHO)]N(PPh_3)_2$.[10] Since then, several other formyl complexes have been identified by their proton nmr and infrared spectra, having been synthesized by the reaction of metal trialkyl- or trialkoxyborohydrides on carbonyl compounds (Equation 2)[11-16] or $NaBH_4$ on a carbonyl compound.[17]

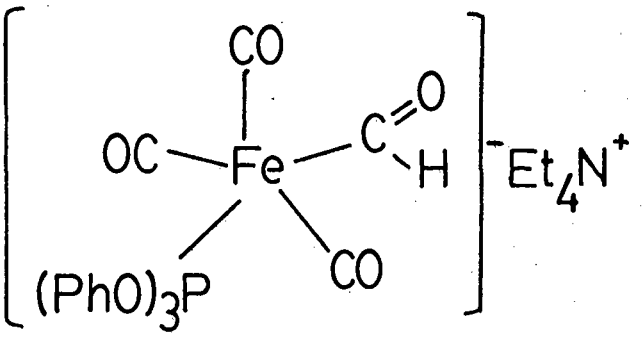
$$[L_nM - CO] + R_3\,BH^-M'^+ \longrightarrow [L_nM - C(=O)H]^- + R_3B \qquad (2)$$

(L = ligands, M = transition metal, R = alkyl or alkoxy group. M' = alkali metal).

The compounds $[Re(Cp)(PPh_3)(NO)CHO]$ (I)[13] and {*trans*-$[(PhO)_3P](CO)_3FeCHO\}$-Et_4N (II)[11] have been fully characterised.



(I)



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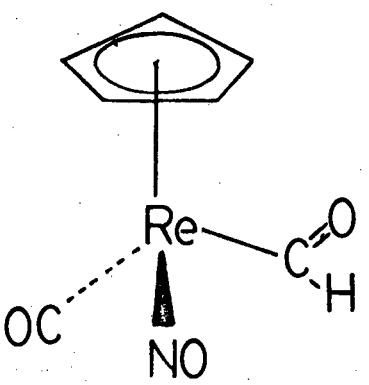
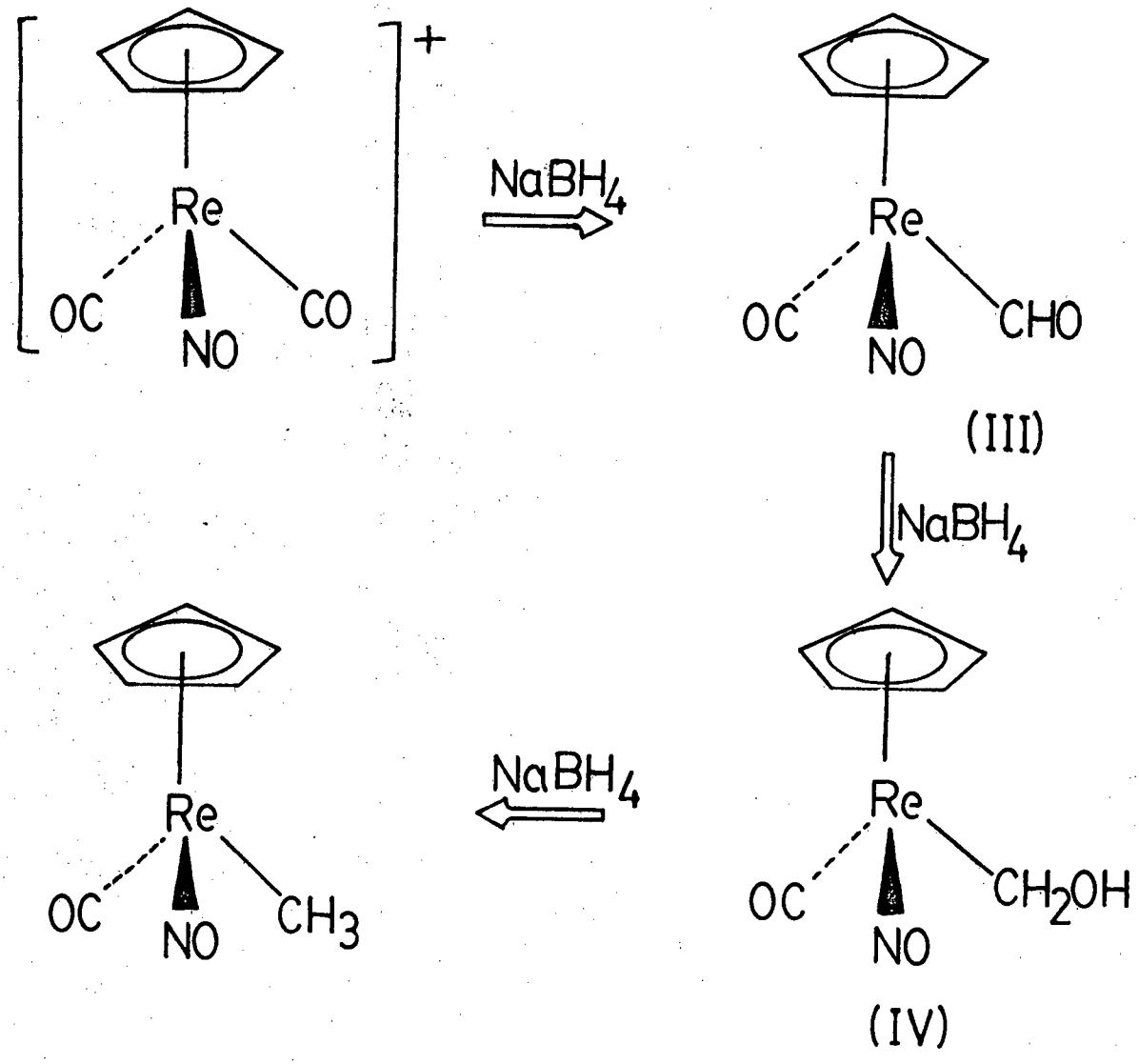


(III)

Graham and Sweet[17] have shown that using a strong reducing agent ($NaBH_4$), a carbonyl ligand can be reduced to a methyl group through a formyl group and a hydroxymethyl group (Scheme 2). This shows that the reduction of coordinated CO to CH_3, as proposed on Scheme I *vide supra*, is a feasible process, and, at least under Graham's[17] conditions, goes through a formyl and a hydroxymethyl species, as proposed.

Casey *et al*[16] found that $[Re(Cp)(CO)(NO)CHO]$ (III) can be reduced by diisobutylaluminium hydride, $HAl(i\text{-}Bu)_2$ to give the hydroxymethyl complex $[Re(Cp)(CO)(NO)CH_2OH]$ (IV), and also $[Re(Cp)(CO)_2NO]^+$ can be reduced by $Na[H_2AlEt_2]$ to give (IV) (Scheme 3). (IV) is the first authentic

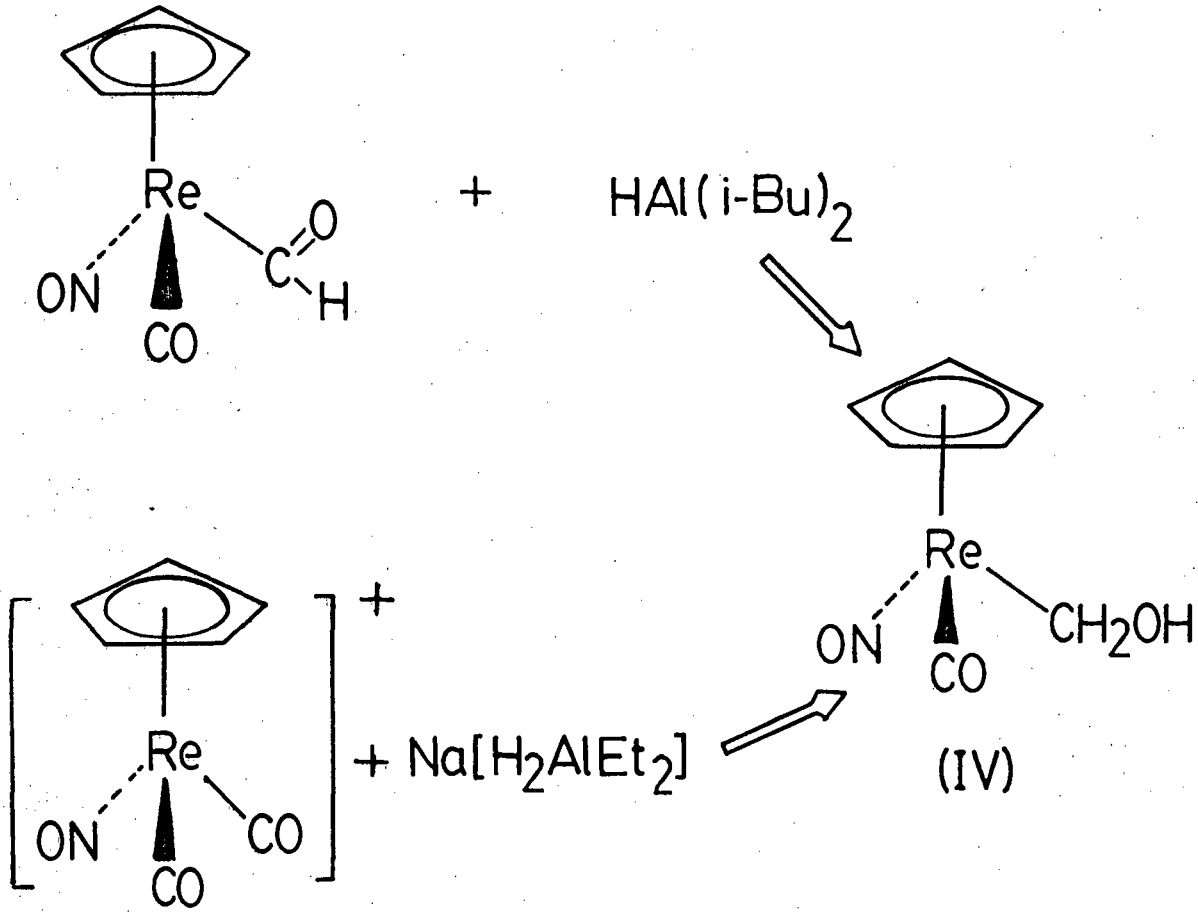


Scheme 2. Reduction of $[Re(Cp)(CO)_2NO]^+$ to $[Re(Cp)(CO)(NO)CH_3]$

hydroxymethyl compound to be isolated and characterised.[16,17]

Transition metal hydroxymethyl complexes are further discussed in Chapter 4. Chloromethyl and methoxymethyl transition metal complexes are possible precursors of hydroxymethyl complexes.

Step 3 of Scheme I postulates the formation of a species with a formaldehyde molecule bonded to the catalyst surface. Roper *et al*[18]



Scheme 3. Synthesis of (IV) from $[Re(Cp)(CO)(NO)CHO]$ and $[Re(Cp)CO)_2NO]^+$

have synthesized $[Os(CO)_2(PPh_3)_2(\eta^2\text{-}CH_2O)]$ from the reaction of aqueous CH_2O with $[Os(CO)_2(PPh_3)_3]$ (Equation 3) (Figure 2). The formaldehyde complex has been converted to a hydroxymethyl complex (see Section 4.1).[91]

$$[Os(CO)_2(PPh_3)_3] + CH_2O \xrightarrow{\text{Benzene}} [Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2] \qquad (3)$$

Step 7 of Scheme I postulates the formation of a carbene species, $[M = CH_2]$. Three $[M = CH_2]$ complexes have been identified: $[Ta(Cp)_2(CH_3)CH_2]$,[19] $[Re(Cp)(NO)(PPh_3)CH_2]PF_6$,[20] and $[Fe(Cp)(Ph_2PCH_2CH_2PPh_2)CH_2]^+$.[21] Stevens and Beauchamp[22,23] have also reported observing $[Fe(Cp)(CO)_nCH_2]^+$

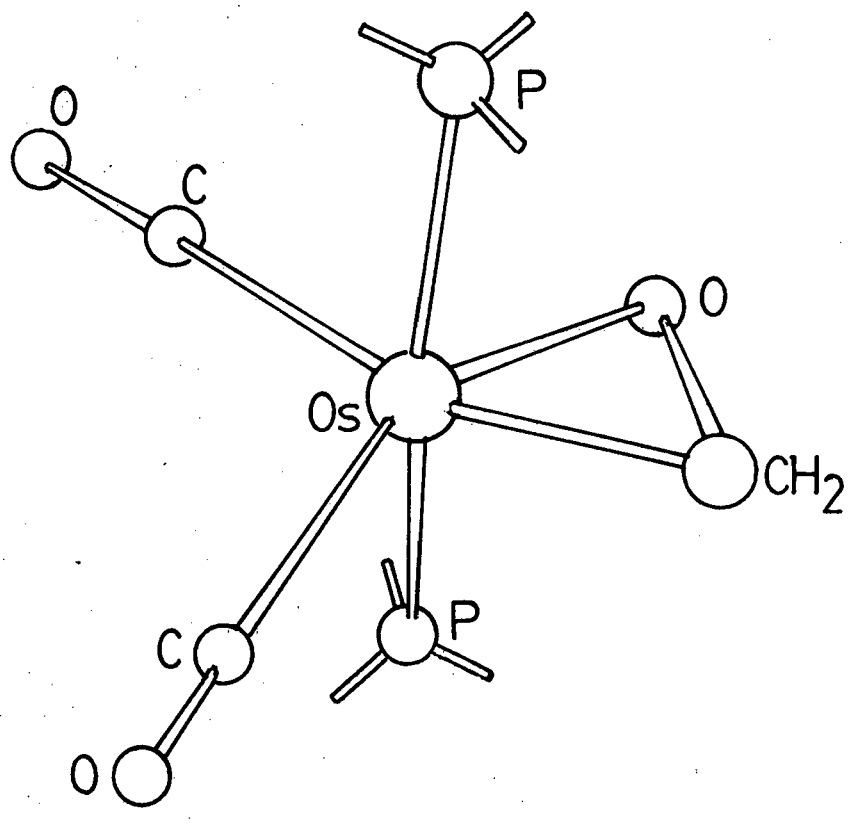


Figure 2. Structure of the inner coordination sphere of $[Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2]$ (from ref. 18).

(n = 1,2) and Mn carbene species in the gas phase, using Ion Cyclotron Resonance Spectroscopy.

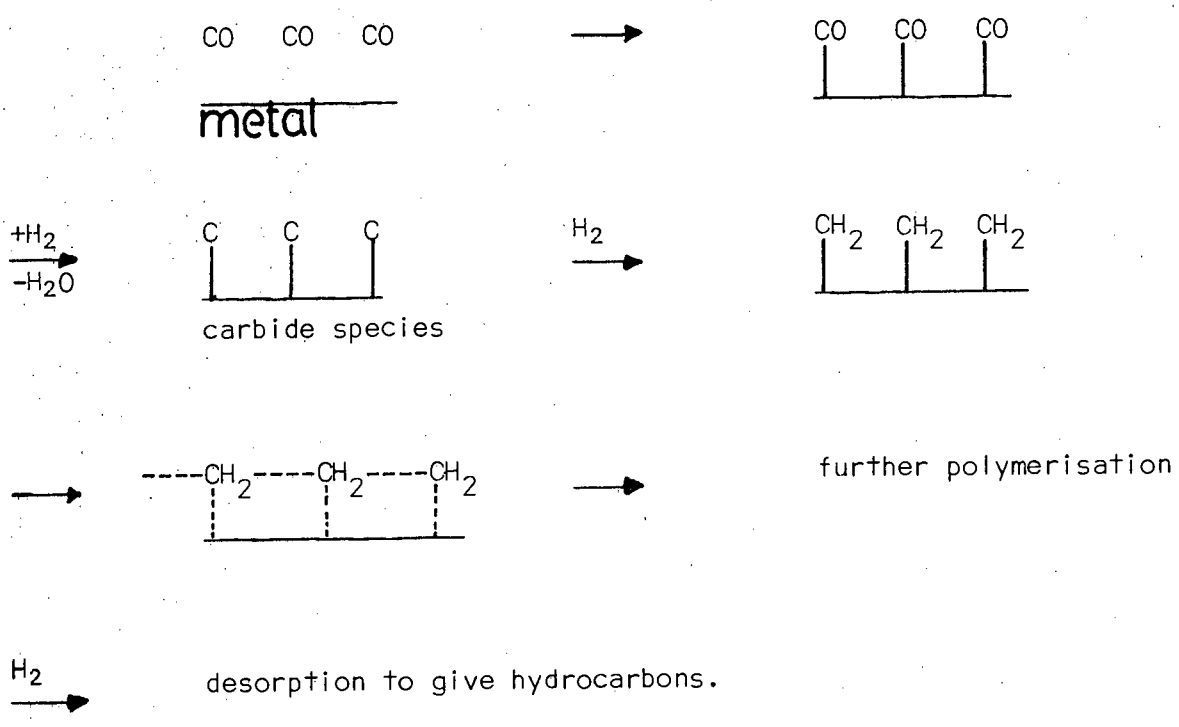
Methoxymethyl and chloromethyl complexes are potential precursors for carbenes, and $[M = CH_2]^+$ species have been postulated as intermediates in the reactions of a number of $[L_nMCH_2OCH_3]$ and $[L_nMCH_2Cl]$ (M = transition metal, L = ligands) complexes. This is further discussed in Section 2.2.

Acyl species[24] (formation postulated in step 9, scheme 1) and alkyl species[24,25] (step 8, scheme 1) are both well known.

A mechanism involving unstable intermediates with C, H and O atoms bonded to the metal catalyst surface, for example that outlined in Scheme I, involves known species. It is hence a plausible scheme for the reduction of CO by H_2 on Fischer-Tropsch catalysts.

1.3.3 The carbide mechanism of the Fischer-Tropsch reaction

The first mechanism for the Fischer-Tropsch reaction, proposed by Fischer and Tropsch, and other workers,[9] was the so called "carbide intermediate" hypothesis. It assumed that CO reacts with the metal surface and is reduced to a carbide species, which is subsequently polymerized by reaction with H_2 (Scheme 4).



Scheme 4. The carbide mechanism as originally proposed (ref. 9).

This mechanism did not give the expected Flory-Schulz distribution of molecular weights.[8] Hence it was replaced by other hypotheses, such as that outlined in Scheme I, which distinguish initiation, propagation and termination steps, with one C atom added in each propagation step, and with oxygen-containing intermediates.[8,26]

In the last five years, however, there has arisen increasing evidence that the Fischer-Tropsch reaction does in fact involve a carbide species. A number of workers[26-29] have shown that CO can dissociate on Co, Ni and Fe catalysts to give a carbonaceous layer, given the right conditions of temperature and pressure. This carbonaceous layer has been studied by Auger Electron spectroscopy.[28,29] The layer is found to be highly reactive towards H_2 reduction, giving mostly methane,[26-29] but also some heavier hydrocarbons.[26,29]

The next step in the Fischer-Tropsch reaction may well be reduction of the carbide to give a carbene species, $[M = CH_2]$.[7] Evidence in support of this includes the fact that $[M = CPh_2]$ complexes have been reacted with H_2, or with CO, or both, to form organic molecules. $[W(CO)_5CPh_2]$ reacts with H_2 to give diphenyl methane (Equation 4).[30]

$$(CO)_5W = C(Ph)(Ph) \xrightarrow[\text{20 hrs}\\ \text{69 atm. } H_2]{100^\circ C} (Ph)_2CH_2 + W(CO)_6 \text{ and other minor products} \qquad (4)$$

Also, a Mn carbene complex has been reacted with H_2 and CO to give aldehydes and alcohols.[31] (Equation 5).

$$(CO)_2(Cp)Mn = C(Ph)(Ph) \xrightarrow[50^\circ C,\ 25 \text{ hrs}]{\simeq 650 \text{ atm CO}} (CO)_2(Cp)Mn{-}CPh_2(C{=}O) \xrightarrow[50^\circ C,\ 20 \text{ hrs}]{\simeq 750 \text{ atm}}$$

$$Ph_2CHO \quad \text{and} \quad Ph_2CH - CH_2OH \qquad (5)$$

Thus a carbide mechanism may well be operative in the Fischer-Tropsch reaction.

1.3.4 Homogeneous Fischer-Tropsch reactions

A selective Fischer-Tropsch synthesis is a desirable technological process. In order to achieve selectivity, the reactions occurring in the catalytic process must be better understood. One of the ways of gaining this better understanding is to synthesize, and study the reactions of, complexes with ligands the same as the C, H and O - containing moieties of intermediates postulated in mechanistic schemes for the homogeneously catalysed Fischer-Tropsch reaction (*e.g.* Scheme I); *i.e.* compounds with, for example, formyl or hydroxymethyl ligands. This kind of approach is discussed in Section 1.3.2.

However, perhaps the best way of achieving a selective Fischer-Tropsch synthesis is to find and use a homogeneous catalyst. Homogeneous catalysts are often more selective than heterogeneous catalysts.[32] On the other hand however, homogeneous catalysts are often unstable to moisture, oxygen and temperature extremes, conditions common in many industrial processes. They are also usually more expensive, and difficult to separate from the products of the reaction.

Attempts to find homogeneous catalysts for Fischer-Tropsch-type reactions have to date been largely unsuccessful.[7] However the reduction of CO by H_2 has been achieved using a few different homogeneous catalysts.

The production of methane, ethane, propane and isobutane has been reported,

from the reaction of H_2/CO mixtures with $Ir_4(CO)_{12}$ as the catalyst.[33] (Figure 3).

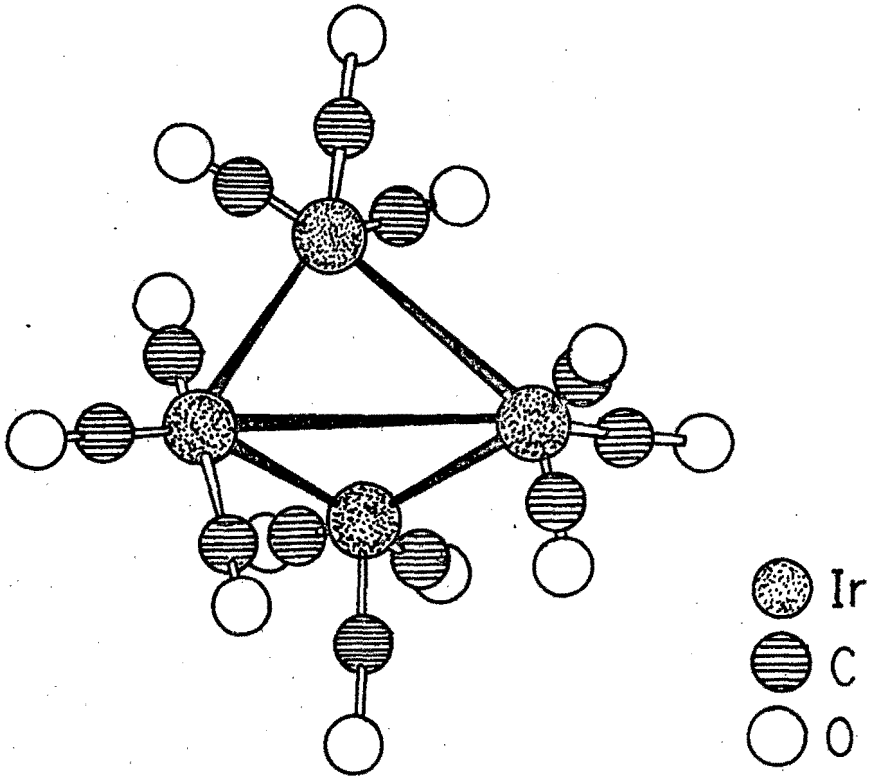


Figure 3. The structure of $Ir_4(CO)_{12}$. (Ref. 34).

Wilkinson *et al*[35,36] have recently reported that CO can be reduced by H_2 to methanol, ethanol and related products using V, Cr, Mn, Fe, Co, Ru, Rh, and Os complexes. Catalytic cycles were proposed.

The reaction of a 3:1 mole ratio of H_2:CO at 150°C to give methane has been achieved homogeneously using $[Ti(Cp)_2(CO)_2]$.[37]

Cobalt carbonyl was found to catalyse homogeneous hydrogenation of CO to methanol, higher primary alcohols and their formate esters.[38]

The actual catalytic species appared to be $[Co(H)(CO)_4]$. Also, a mononuclear Ru species, $[Ru(CO)_5]$, appears to be the catalyst in the homogeneous hydrogenation of CO at 1300 atm. and 225-275°C, resulting in methanol and methyl formate.[39] Addition of PPh_3 increased the selectivity towards methanol (>95% selectivity achieved) in the latter process.

The stoichiometric (as opposed to catalytic) reduction of CO in transition metal complexes by H_2, $LiAlH_4$, acids, or AlH_3, has been investigated by a number of workers.[40-44] For example, treatment of $[Fe(Cp)(CO)_2]_2$ with $LiAlH_4$ produces CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8 and C_4H_{10}.[44] Such reactions may provide useful information about the mechanisms of catalytic reductions of CO by H_2.

CHAPTER TWO

2. THE SYNTHESIS AND CHARACTERISATION OF SOME CHLOROMETHYL AND METHOXYMETHYL TRANSITION METAL COMPLEXES

2.1 Monohalomethyl and methoxymethyl transition metal complexes

Monohalomethyl $[L_nM\text{-}CH_2X]$ (X = Cl, Br, I) and methoxymethyl complexes $[L_nM\text{-}CH_2OCH_3]$ (L = ligands, M = transition metal) are considered together in this section. Although one has an alkyl halide ligand, and the other an ether ligand, they have many similarities, as will emerge from the discussion following.

Methoxymethyl and monohalomethyl transition metal complexes may be versatile starting materials for the synthesis of several types of new complexes, including complexes containing the carbene (CH_2) ligand (Section 2.2), binuclear complexes containing a CH_2 group bridging two metal atoms, and a range of complexes of the type $[L_nMCH_2Nu]$ (Nu = a nucleophile, *e.g.* OH^- [16]) (Section 2.2).

Halomethyl complexes of main group metals are well known and have been extensively studied.[45,46]* They are not discussed further in this section. Also complexes containing CF_3 ligands (see, for example, reference 104) are not discussed in this section.

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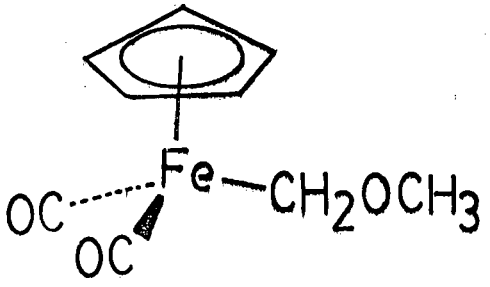
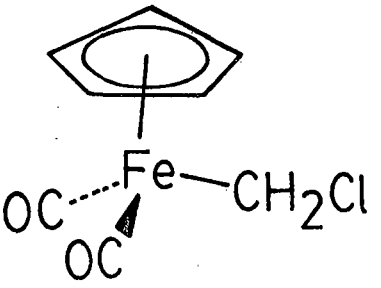
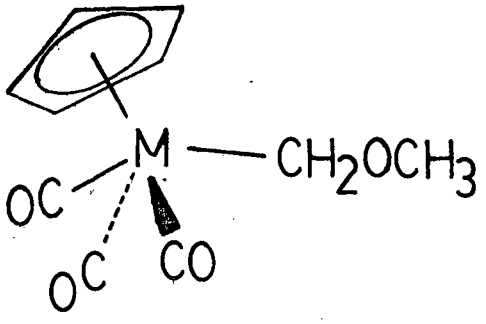
* D. Seyferth and co-workers have studied haloalkyl complexes of main group metals extensively and the results are reported in a series (Part 70, see reference 45, Part I, *J. Organomet. Chem.*, 1965, 4, 127).



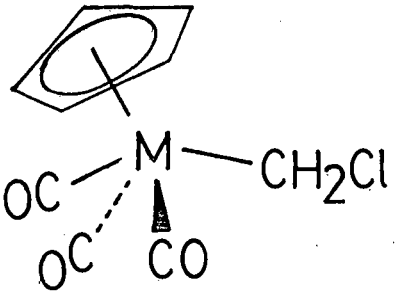
(V)



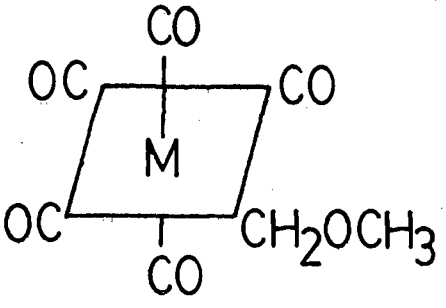
(VI)



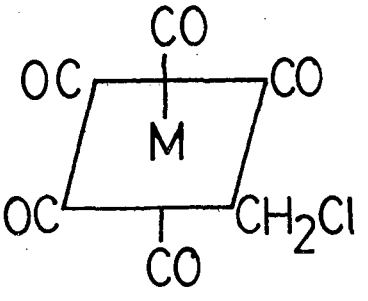
(XI) M= Mo
(XII) M= W



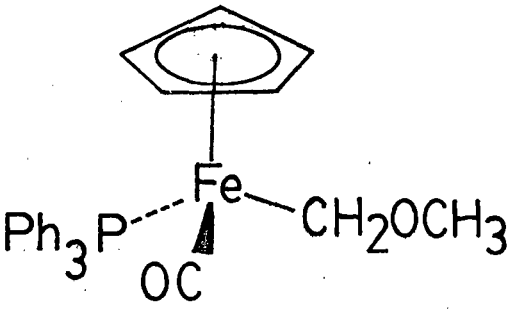
(XIII) M= Mo
(XIV) M= W



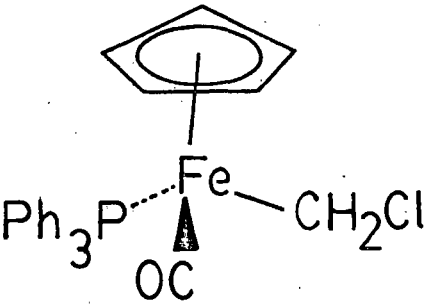
(VII) M= Re
(VIII) M= Mn



(IX) M= Re
(X) M= Mn



(XV)



(XVI)

The syntheses of $[Fe(Cp)(CO)_2CH_2OCH_3]$ (V), $[Fe(Cp)(CO)_2CH_2Cl]$ (VI) and $[Mo(Cp)(CO)_3CH_2OCH_3]$ (XI) were reported by Jolly and Pettit,[47] and Green *et al.*[48] Green further reported the synthesis of $[Mo(Cp)(CO)_3CH_2Cl]$ (XIII), the tungsten complexes $[W(Cp)(CO)_3CH_2X]$ (X = OCH_3, (XII) and X = Cl, (XIV)), and the bromomethyl analogues of (VI), (XIII) and (XIV).[48] Both Jolly and Green used similar synthetic routes: The methoxymethyl complexes (V), (XI), (XII) were synthesized by the reaction of the appropriate metal carbonyl anion with chloromethyl methyl ether (Equation 6).

$$Na^+[M]^- + ClCH_2OCH_3 \longrightarrow [M\text{-}CH_2OCH_3] + HCl \qquad (6)$$

(M = $FeCp(CO)_2$, $W(Cp)(CO)_3$, $Mo(Cp)(CO)_3$)

The chloromethyl and bromomethyl complexes were synthesized by the reaction of the appropriate methoxymethyl complex with HX (Equation 7).

$$[M\text{-}CH_2OCH_3] + HX \longrightarrow [M\text{-}CH_2X] + HOCH_3 \qquad (7)$$

(M as in equation 6, X = Cl, Br).

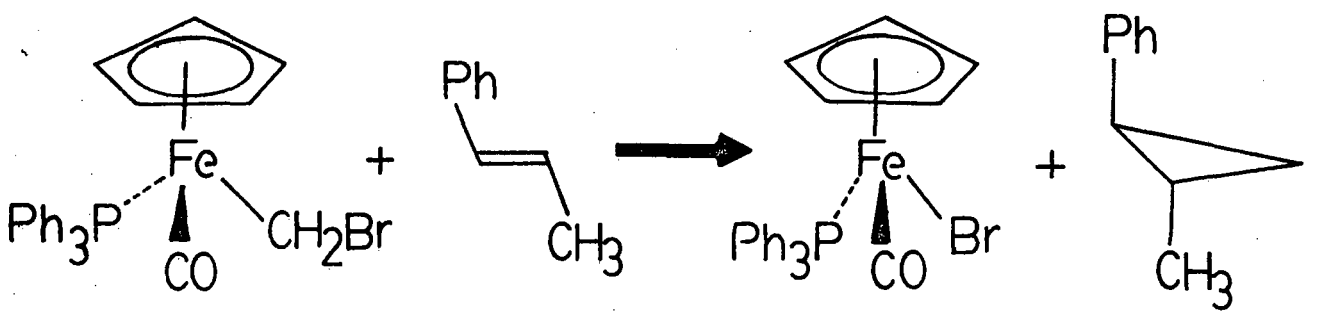
The methoxymethyl complexes were isolated as oils (except (XII) which was a solid) which were easily oxidised by air, and the chloromethyl complexes as light-sensitive unstable solids. The bromomethyl analogues of (VI), (XII), and (XIV) were found to be even less stable than (VI), (XII) and (XIV) in all respects.[48]

Facile conversion of (VI) to the methoxymethyl derivative (V) was achieved by reaction with NaOMe; complexes (XIII) and (XIV) underwent a similar conversion to (XI) and (XII) respectively but yields were low.[48] In fact the Cl in $[Fe(Cp)(CO)_2CH_2Cl]$ (VI) proved to be very susceptible to attack by a number of nucleophiles, and a number of complexes of the type $[Fe(Cp)(CO)_2CH_2Z]$ where Z = OEt, SEt, $OCR_2CH = CH_2$ (R = Me, H), $O(CH_2)_2\ NMe_2H^+$ were synthesized.[48]

The triphenylphosphine-containing complexes, (XV) and (XVI), and the iodomethyl analogue of (XVI), were briefly reported by Davison *et al*;[49] however the full characterisation of (XV) and (XVI) was reported by Flood *et al*.[50] (XV) was obtained by irradiation of a benzene/pentane solution of the corresponding dicarbonyl (V), in the presence of PPh_3. Reaction of (XV) with HCl gas (as in equation 7) gave the chloromethyl (XVI). Optically pure (-) (XVI) was prepared from the reaction of (-)[Fe(Cp)(CO)(PPh_3)CH_2OMen] (men = menthyl) with HCl at 0°C. Flood further reported the preparation of the bromomethyl and iodomethyl analogues of (XVI), prepared from (XV) by using HBr or HI;[50] of the bromomethyl and iodomethyl analogues, only the former was stable enough to be characterised.

Again the Cl of the chloromethyl [Fe(Cp)(CO)(PPh_3)CH_2Cl] (XVI) was found to be susceptible to attack, by such nucleophiles as $[OMe]^-$, and CN^-. (XVI) was also converted to alkyl compounds, [Fe(Cp)(CO)(PPh_3)R] using Grignard reagents, RLi (R = alkyl group).[50]

(XVI) and its bromomethyl and iodomethyl analogues were found to be sources of $[CH_2]$. For example treatment of [Fe(Cp)(CO)(PPh_3)CH_2Br] with [PhCH = $CHCH_3$] resulted in the formation of a cyclopropane (Equation 8).



(8)

The complex $[Fe(Cp)(diphos)CH_2OCH_3]$ (diphos = $Ph_2PCH_2CH_2PPh_2$) was synthesized by irradiation of (V) with bis-(diphenylphosphino)ethane.[62]

King and Braitsch[51] have reported the synthesis of a number of halomethyl complexes of transition metals by the reaction of the appropriate metal carbonyl anion with dihalomethanes. Equation 9 outlines the general method used and Table 3 outlines the results obtained.

$$Na[M] + CH_2XX' \longrightarrow [M\text{-}CH_2X] + NaX' \qquad (9)$$

M = $Mo(Cp)(CO)_3^-$, $W(Cp)(CO)_3^-$, $Fe(Cp)(CO)_2^-$, $Mn(CO)_5^-$.

CH_2XX' is a dihalomethane, *e.g.* $ClCH_2I$ (see Table 3).

Table 3.

Reactions of metal carbonyl anions with dihalomethanes (ref. 51).

Metal carbonyl anion	Dihalomethane	Products (yields)
$Mo(Cp)(CO)_3^-$	$ClCH_2I$	$[Mo(Cp)(CO)_3CH_2Cl]$ (60-70%)
$W(Cp)(CO)_3^-$	$ClCH_2I$	$[W(Cp)(CO)_3CH_2Cl]$ (60%) and $[W(Cp)(CO)_3CH_2I]$ (12%)
$Fe(Cp)(CO)_2^-$	$ClCH_2I$	$[Fe(Cp)(CO)_2CH_2Cl]$ (13%)
$Mn(CO)_5^-$	$ClCH_2I$	$[Mn_2(CO)_{10}]$ (~30%)
$Mo(Cp)(CO)_3^-$	CH_2Br_2	$[Mo(Cp)(CO)_3]_2$ and trace $[Mo(Cp)(CO)_3Br]$
$Mo(Cp)(CO)_3^-$	CH_2I_2	$[Mo(Cp)(CO)_3CH_2I]$ (17%)
$W(Cp)(CO)_3^-$	CH_2I_2	$[W(Cp)(CO)_3CH_2I]$

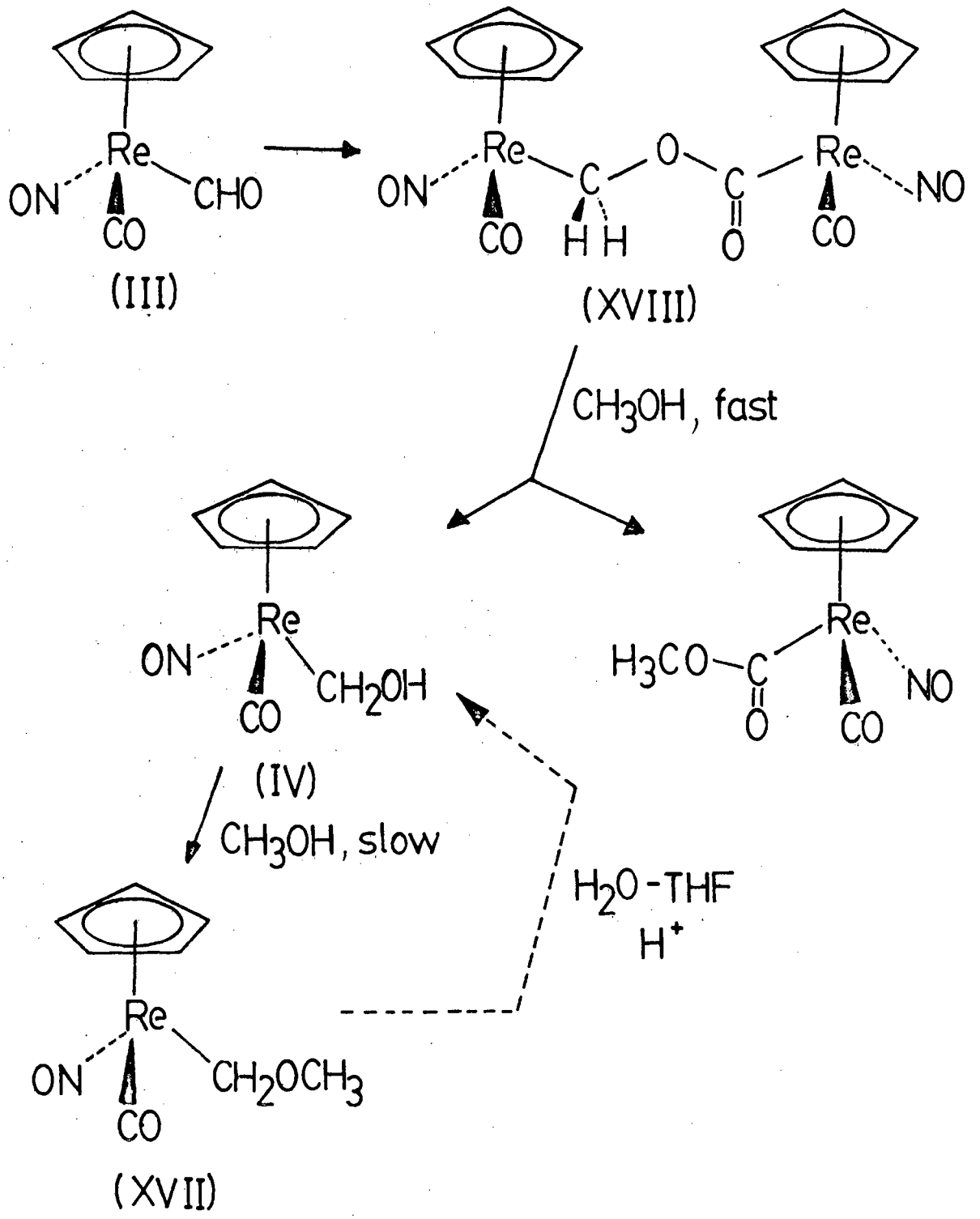
The method , using the reported conditions,[51] is a good synthetic method for the chloromethyls of Mo and W, (XIII) and (XIV), but not for those of Mn or Fe, (X) and (VI). The reaction of the Mo and W carbonyl anions with CH_2I_2 gave the then new iodomethyl compounds $[M(Cp)(CO)_3CH_2I]$ (M = Mo, W) but in poor yields.

King and Braitsch[51] found that $[Mn_2(CO)_{10}]$ was the only product of the reaction of $Na[Mn(CO)_5]$ with $ClCH_2I$ at room temperature. However Moss[52] found that the same reaction, conducted at -20°C instead of at room temperature, gave $[Mn(CO)_5CH_2Cl]$ (X) as pale yellow prisms in 50% yield. (X), and the Re chloromethyl (IX), had been previously briefly mentioned by Jolly and Pettit.[47] (X) has also been proposed as a product of the photochemical decomposition of the chloroacetyl complex, $[Mn(CO)_5COCH_2Cl]$.[53] The major product of this reaction proved to be $[Mn(CO)_5Cl]$, but a new resonance at δ 5.3 ppm was noted in the ^1H nmr of the reaction product, different from the singlet obtained in the spectrum of the starting material, the chloroacetyl complex (δ4.37 ppm). The new resonance was attributed to traces of (X); this in fact would appear not so, on the basis of more recent evidence.[52]

(Methoxymethyl)pentacarbonylmanganese, (VIII) has been reported.[54] It was synthesized by reaction of $Na[Mn(CO)_5]$ with $ClCH_2OCH_3$. (VIII), and the Re methoxymethyl, (VII) had been previously mentioned by Jolly and Pettit.[47]

The methoxymethyl complex $[Re(Cp)(CO)(NO)\ CH_2OCH_3]$ (XVII) has been synthesized by Casey *et al.*[16] The formyl complex [Re(Cp)(CO)(NO)CHO] (III) was found to undergo facile disproportionation to a dimeric metallo-ester (XVIII). Methanolysis of (XVIII) gave a mixture of (XVII) and a

methyl ester (Scheme 5).



Scheme 5. Synthesis of $[Re(Cp)(CO)(NO)CH_2OCH_3]$ (Reference 16).

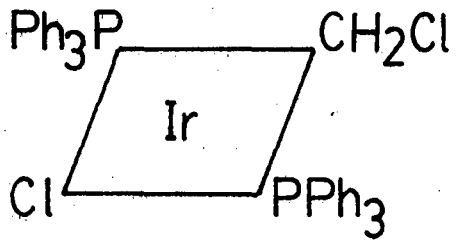
The triphenylphosphine containing counterpart of (XVII), $[Re(Cp)(NO)(PPh_3)CH_2OCH_3]$ has been synthesized by Gladysz *et al.*[20] from the carbene species $[Re(Cp)(NO)(PPh_3)CH_2]PF_6$.

A chromium chloromethyl complex, $[Cr(Cp)(NO)_2CH_2Cl]$, has been prepared by the reaction of $[Cr(Cp)(NO)_2Cl]$ with diazomethane. This reaction is interesting in that it involves an insertion of CH_2 into the Cr-Cl bond. Yields however were low and the product very unstable. It was characterised on the basis of its infrared spectrum.

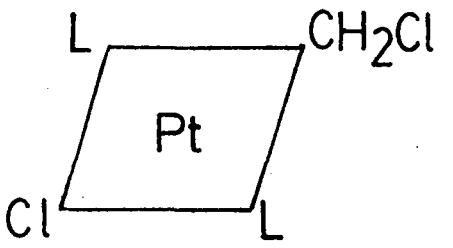
The reaction of $[Ir(CO)(PPh_3)_2Cl]$ with CH_2N_2 gave an orange crystalline product.[56] This was identified as the chloromethyl (XIX), though this identification was made only on the basis of its infrared spectrum, and its reactivity. Again it appears that a methylene group has inserted into the metal-chloride (*i.e.* Ir-Cl) bond.

Young and Whitesides[57] investigated the thermal decomposition of 1,4-tetramethylenebis(tri-n-butylphosphine)platinum(II), in several solvents. In CH_2Cl_2 the complex $[Pt(L_2)(CH_2Cl)Cl]$ (XX) (L = Bu_3P) was postulated as an intermediate; it was identified by a doublet in its ^{31}P nmr spectrum and a 1:2:1 triplet (with satellites) in the ^{1}H nmr spectrum, and also by its chemical behaviour. Other chloromethyl complexes were postulated as possible intermediates in the reaction but there was no evidence of their existence reported.

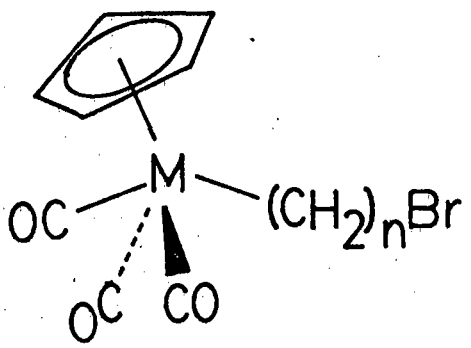
Young and Whitesides[57] also synthesized and characterised the complex (XXI) (Equation 10).



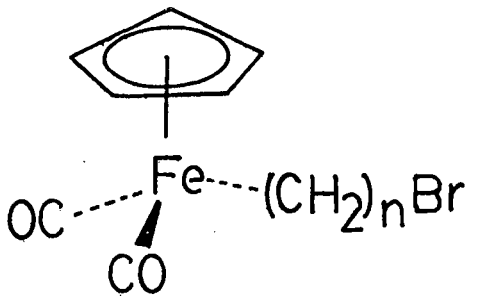
(XIX)



(XX) L = Bu_3P
(XXII) L = PPh_3

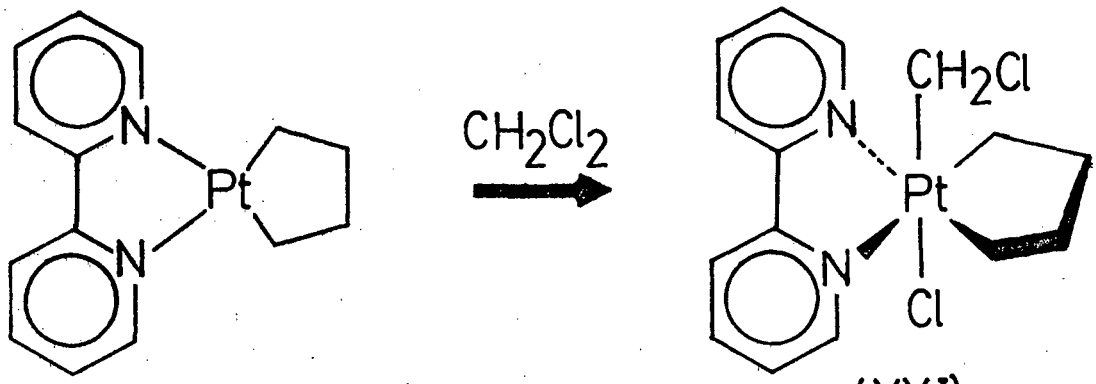


(XXII) M = Mo
(XXIII) M = W
n = 3,4



(XXIV)
n = 3,4

The Pt chloromethyl (XXII) and its *cis* isomer were recently reported,[58] having been synthesized by the photo-induced oxidative addition of CH_2Cl_2 to $[Pt(PPh_3)_2(C_2H_4)]$. The reaction appears to involve free radicals and is inhibited by addition of duroquinone.



(XXI)

(10)

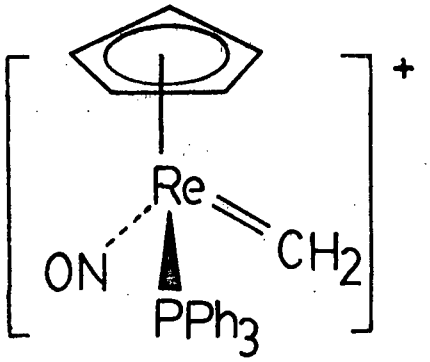
Finally, although they are not actually monohalomethyl complexes, it is worth noting that a few complexes with $[(CH_2)_nBr]$ ligands have been synthesized. Thus King and Bisnette[59] have reported the synthesis of $[M(Cp)(CO)_3(CH_2)_nBr]$ (n = 3,4; M = Mo, (XXII); W, (XXIII)], from the reaction of 1,3-dibromopropane or 1,4-dibromobutane with the appropriate metal carbonyl anion, $[M(Cp)(CO)_3]Na$. Similar iron complexes have been synthesized,[60] *viz.* $[Fe(Cp)(CO)_2(\{CH_2\}_nBr)]$ (n = 3,4) (XXIV), from the reaction of $[Br(CH_2)_nBr]$ with $[Fe(Cp)(CO)_2]Na$.

2.2 The synthesis of Fischer-Tropsch intermediates using chloromethyl and methoxymethyl complexes

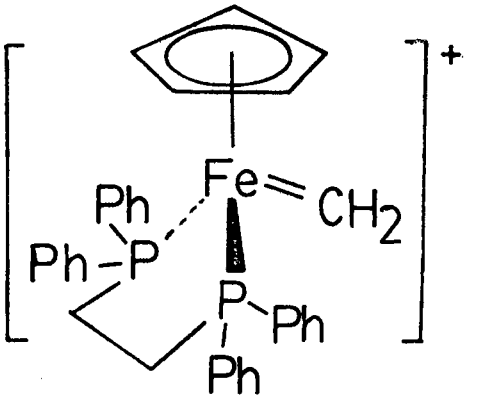
Species containing hydroxymethyl groups [M-CH_2OH] and carbene groups [M = CH_2] have been postulated as intermediates in the Fischer-Tropsch reaction[1] (Scheme 1, Page 8). Chloromethyl and methoxymethyl complexes are possible precursors of complexes containing [M-CH_2OH] groups and [M = CH_2] groups.

The first hydroxymethyl transition metal complex to be isolated and characterised was synthesized from a methoxymethyl complex.[16] Hydroxymethyl complexes are further discussed in Chapter 4.

To date only three transition metal [M = CH_2] carbene complexes have been identified. [$Ta(Cp)_2(CH_3)CH_2$] was isolated as a buff coloured solid,[19] while [$Re(Cp)(NO)(PPh_3)CH_2$]$^+$ (XXV)[20] and [$Fe(Cp)(Ph_2PCH_2CH_2PPh_2)CH_2$]$^+$ (XXVI)[21] were too unstable to be isolated and were identified by their nmr spectra in their particular reaction mixture. (XXV) could, however, be trapped with pyridine, PPh_3 or (n-Bu_3P).[20]

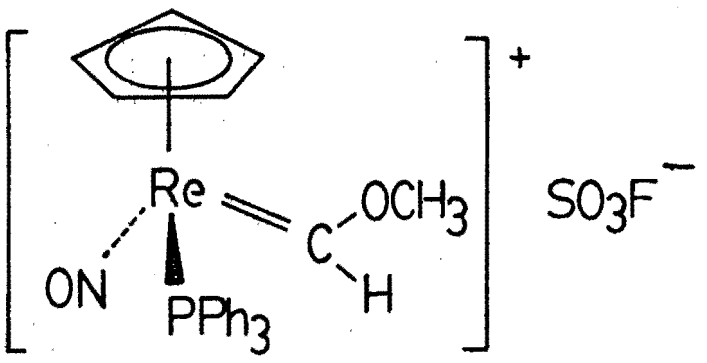


(XXV)



(XXVI)

Both (XXV) and (XXVI) are associated with methoxymethyl complexes. If (XXV) is trapped with pyridine, and then reacted with the base NaOMe, it is easily converted to the methoxymethyl $[Re(Cp)(NO)(PPh_3)CH_2OCH_3]$.[20] This suggests that the reverse reaction may be possible, *i.e.* treatment of the methoxymethyl with acid may give the carbene. In this way Gladysz[20] reacted $[Re(Cp)(NO)(PPh_3)CH_2OCH_3]$ with CH_3SO_3F, and the ^1H nmr of the reaction mixture indicated the formation of $(CH_3)_2O$, the methyl complex $[Re(Cp)(NO)(PPh_3)CH_3]$, and the complex $[Re(Cp)(NO)(PPh_3)CHOCH_3]^+$ (XXVII).

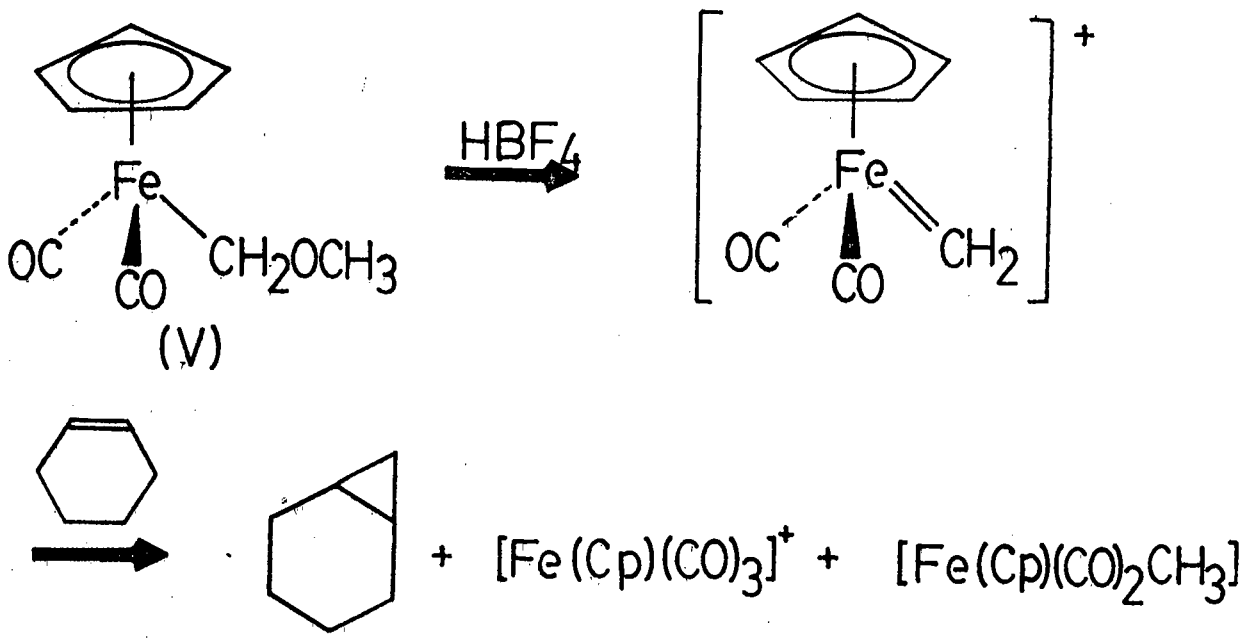


(XXVII)

(XXVI) was synthesized from the reaction of the ethoxymethyl complex $[Fe(Cp)(Ph_2PCH_2CH_2PPh_2)CH_2OCH_2CH_3]$ and trifluoroacetic or triflic acid,[21] thus showing that complexes of the type $[L_nMCH_2OR]$ (L = ligands, M = transition metal, R = alkyl group) are susceptible to attack by acids to give $[L_nM{=}CH_2]^+$.

There is evidence for the existence of carbene species, $[M{=}CH_2]$, as intermediates in reactions of methoxymethyl complexes. Jolly and Pettit[47] reported the production of norcarane from the reaction of $[Fe(Cp)(CO)_2CH_2OCH_3]$ (V) with HBF_4 in the presence of cyclohexene. (Scheme 6). Similarly *cis*- and *trans*-2-butene were converted to

cis- and *trans*-1,2-dimethyl cyclopropane. These reactions suggest the intermediacy of a carbene species.



Scheme 6. Production of norcarane from $[Fe(Cp)(CO)_2CH_2OCH_3]$ and cyclohexene *via* a carbene.

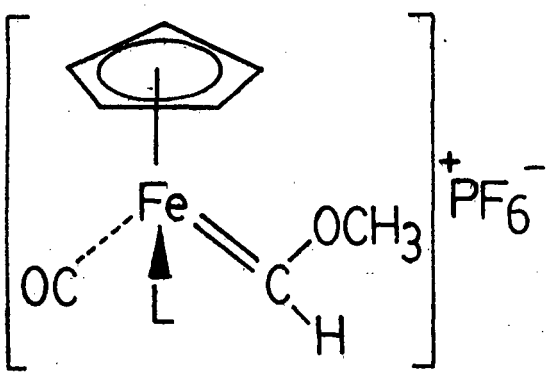
Both Jolly and Pettit[47] and Green *et al*[48] found that reaction of (V) with acids, *e.g.* HBF_4, gave the complex $[Fe(Cp)(CO)_2(C_2H_4)]^+$. This ethylene containing complex was postulated as implying the intermediacy of $[Fe(Cp)(CO)_2CH_2]^+$.[48]

The reaction of $[Fe(Cp)(CO)(PPh_3)CH_2OCH_3]$ (XV) and $[Fe(Cp)(Ph_2PCH_2CH_2PPh_2)CH_2OCH_3]$ with HBF_4 in the presence of cyclohexene was also found to result in the production of norcarane.[62] Again, the intermediacy of $[M{=}CH_2]$ species was postulated.

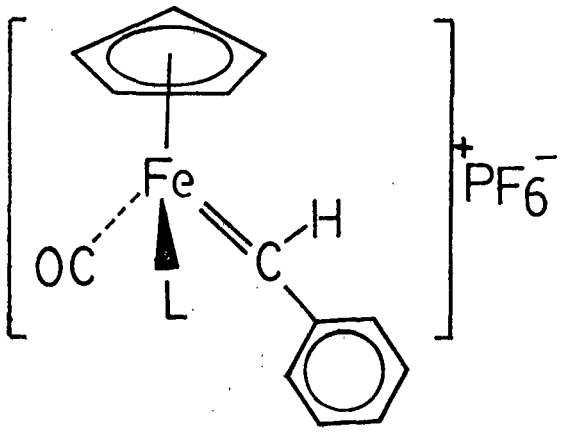
Although there is no direct evidence for their existence, $[M{=}CH_2]$ species have been proposed as intermediates in the conversion of (V) to

$[Fe(Cp)(CO)_2CH_2Cl]$ (VI)[48] and in the conversion of $[Fe(Cp)(CO)(PPh_3)$-$CH_2OMen]$ (Men = menthyl) to $[Fe(Cp)(CO)(PPh_3)CH_2Cl]$ (XVI).[50]

Secondary carbene complexes have been synthesized from a methoxymethyl complex[63] and from α-methoxybenzyl complexes.[61,64] Cutler[63] obtained (XXVIII) by treating $[Fe(Cp)(CO)(L)CH_2OCH_3]$ (L = CO, PPh_3) with Ph_3CPF_6.



(XXVIII)

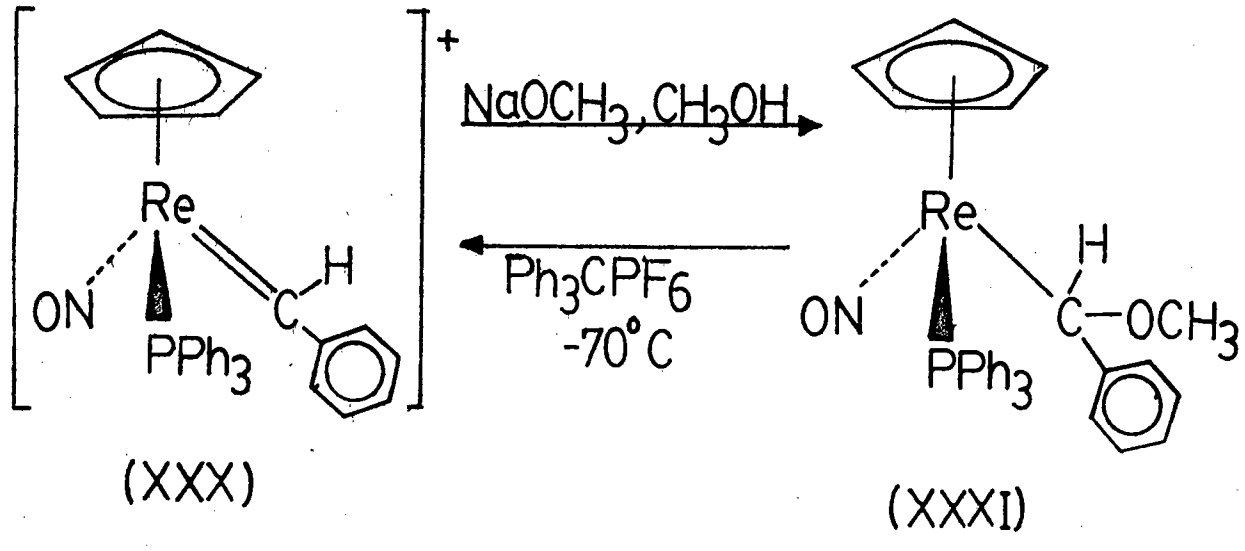


(XXIX)

L = CO, PPh_3

Brookhart and Nelson[61] found that Ph_3CPF_6 abstracts $[OMe]^-$ rather than H^- from $[Fe(Cp)(CO)(L)CH(Ph)OCH_3]$ (L = CO, PPh_3), giving [XXIX]. The same cation as in (XXIX) was also generated from $[Fe(Cp)(CO)(L)CH(Ph)OCH_3]$ (L = CO, PPh_3) with CF_3COOH, and identified by its ^1H nmr spectrum.[61] Gladysz *et al*[64] found that the secondary carbene (XXX) could be easily converted to the α-methoxybenzyl (XXXI) and *vice versa*. (Equation II).

The above discussion has centred around the formation of $[M{=}CH_2]$ complexes from reactions of methoxymethyl (or α-substituted methoxymethyl) complexes. The use of chloromethyl complexes as sources of carbene has not been the subject of much investigation, though it is reasonable to propose that



(XXX) (XXXI)

(11)

chloromethyl complexes are possible precursors of carbenes as the Cl of the $[M\text{-}CH_2Cl]$ group is susceptible to attack by nucleophiles (Section 2.1). Dilgassa and Curtis[53] have proposed the intermediacy of carbene complexes in the thermal decomposition of $[Mn(CO)_5COCH_2Cl]$.

2.3 Rotational isomerism in complexes of the type [Fe(Cp)(CO)(L)(R)] (L = PPh_3, CO, R = ligands).

Rotational isomerism in complexes of the type [Fe(Cp)(CO)(L)R] (L = CO, or a tertiary phosphine, R = ligands) was first reported by Jetz and Graham.[65] The complex $[Fe(Cp)(CO)_2SiCl_2CH_3]$ showed 4 bands in its infrared spectrum instead of the expected two, a fact which was attributed to the existence of two rotamers. (Figure 4).

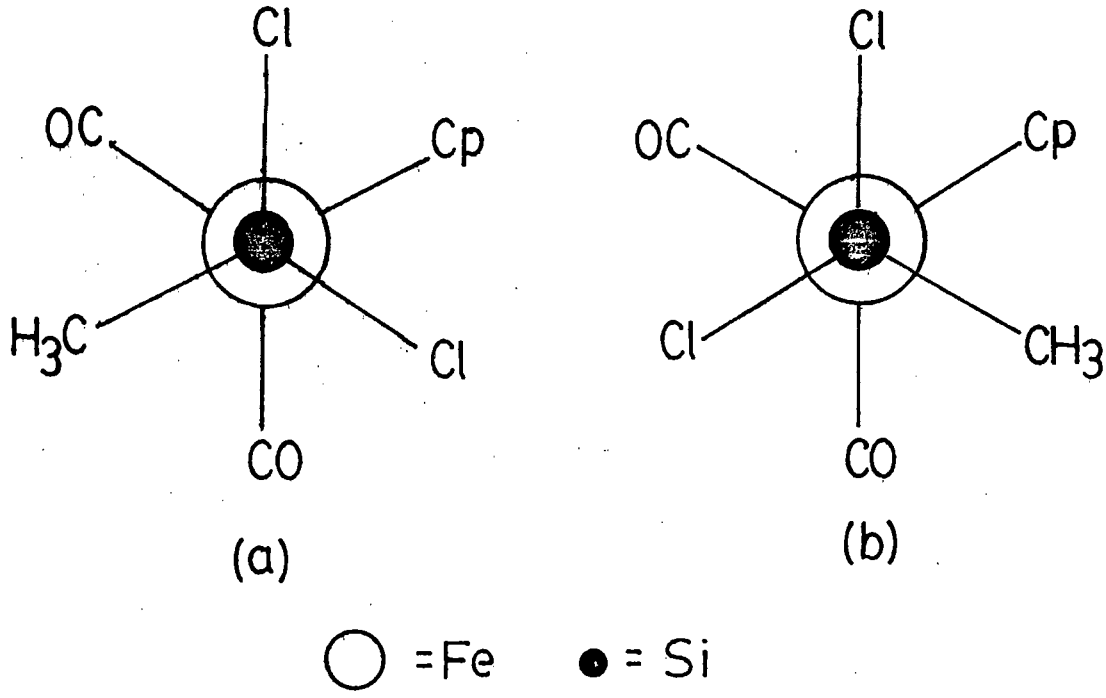
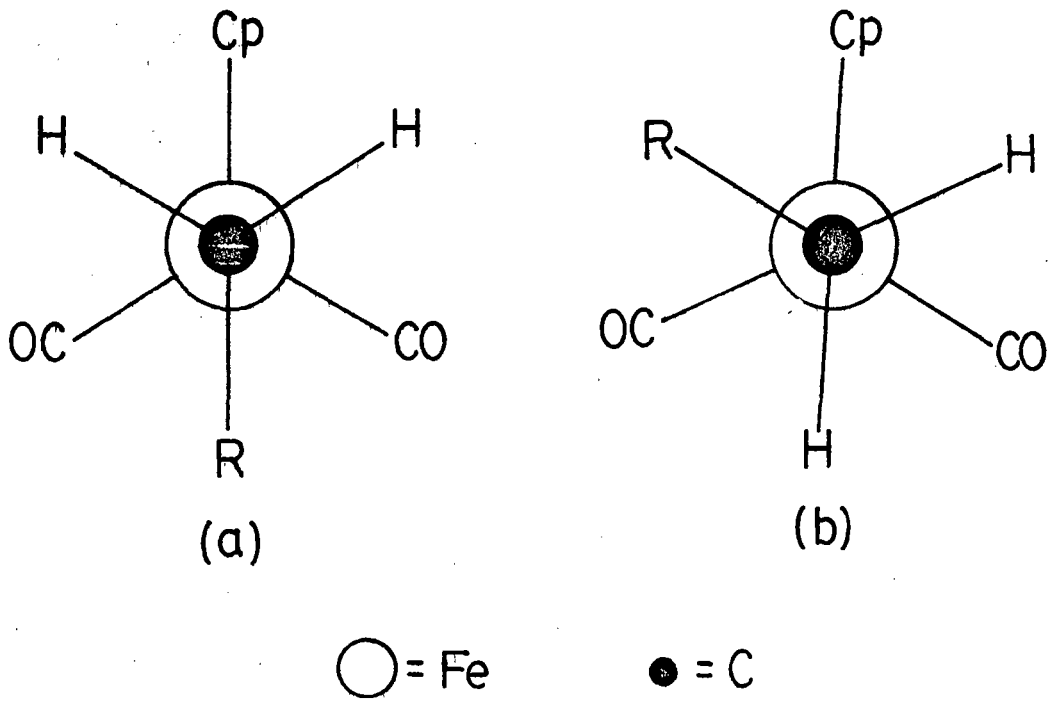


Figure 4. The rotamers of $[Fe(Cp)(CO)_2SiCl_2CH_3]$. (Reference 65).

(a) is expected to be the most stable. The existence of 4 νCO bands in the ir spectrum of $[Fe(Cp)(CO)_2SiCl_2CH_3]$ indicates that both rotamers are occupied. Only one set of ^1H nmr resonanceswas found, however, indicating that rotation was too rapid to be seen on the nmr time scale.[65]

Baird *et al* have investigated the rotational isomerism of several

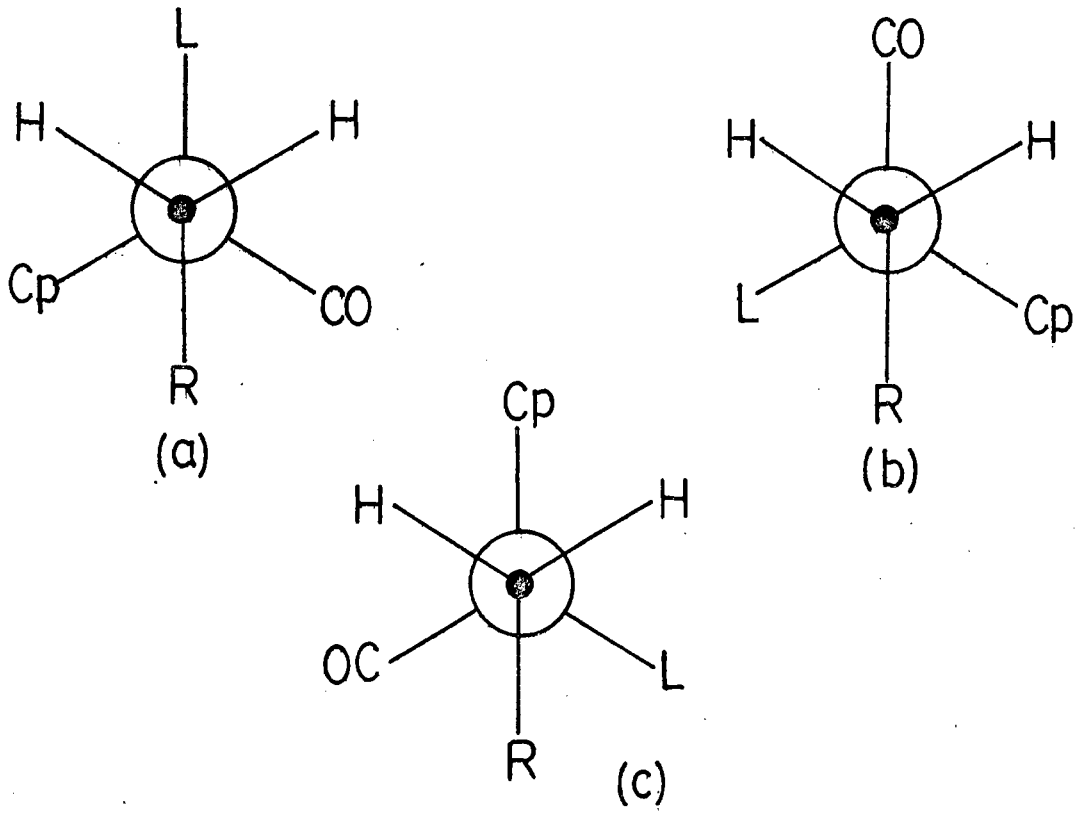
complexes
[Fe(Cp)(CO)(L)(R)] (L = CO, or a tertiary phosphine, R = ligands),[66,67] using infrared, ^{1}H and ^{31}P nmr methods, amongst others. While the infrared spectrum of $[Fe(Cp)(CO)_2R]$ (R = Br, I, CH_3) showed only two νCO bands, the spectra of the complexes R = CH_2Ph, CH_2CH_2Ph, CH_2SiMe_3 and CH_2Naph (Naph = naphthyl)showed 4 νCO bands.[67] The existence of a bulky group in the complexes R = CH_2Ph, CH_2CH_2Ph, CH_2SiMe_3 and CH_2Naph leads to the existence of two rotamers (a) and (b) of slightly different potential energies (Figure 5). Both are occupied, which accounts for the four νCO bands seen instead of two.[67]



R = CH_2X; X = Ph, CH_2Ph, $SiMe_3$, Naph.

Figure 5. Rotamers in complexes $[Fe(Cp)(CO)_2R]$. (Reference 67).

Complexes of the type [Fe(Cp)(CO)(L)R] (L = a tertiary phosphine, R = CH_2Ph, CH_2SiMe_3, CH_2Naph) can exist in three different rotamers, a, b and c. (Figure 6).[67] In these complexes, not only is rotation



R = CH_2X, X = Ph, $SiMe_3$ Naph, L = phosphine

Figure 6. Possible rotamers of [Fe(Cp)(CO)(L)R]. (Reference 67).

about the Fe-CH_2X (X = Ph, $SiMe_3$, Naph) bond possible, giving (a), (b) and (c), but also rotation about the Fe-L bond is possible, giving yet more isomers if L is an unsymmetrical phosphine.[67] The νCO region of the ir spectrum is thus expected to be complex.

Baird studied a number of complexes of the type [Fe(Cp)(CO)(L)R] (L = a tertiary phosphine, R = CH_2Ph, CH_2SiMe_3 and CH_2Naph).[67] The ir spectra (νCO region) were complex showing two and in one case three bands; one would expect one νCO band for a monocarbonyl complex with no different rotamers. The ^1H nmr spectra of the complexes were also studied, and a variation of vicinal phosphorus-hydrogen coupling constants with variation of temperature was taken to be indicative of the relative

rotamer populations changing with temperature.[67]

In Section 2.5 we report the observation of rotational isomers in $[M(Cp)(CO)_2CH_2OCH_3]$ (M = Fe, Ru).

2.4 RESULTS AND DISCUSSION

2.4.1 The synthesis of some new methoxymethyl and chloromethyl transition metal complexes

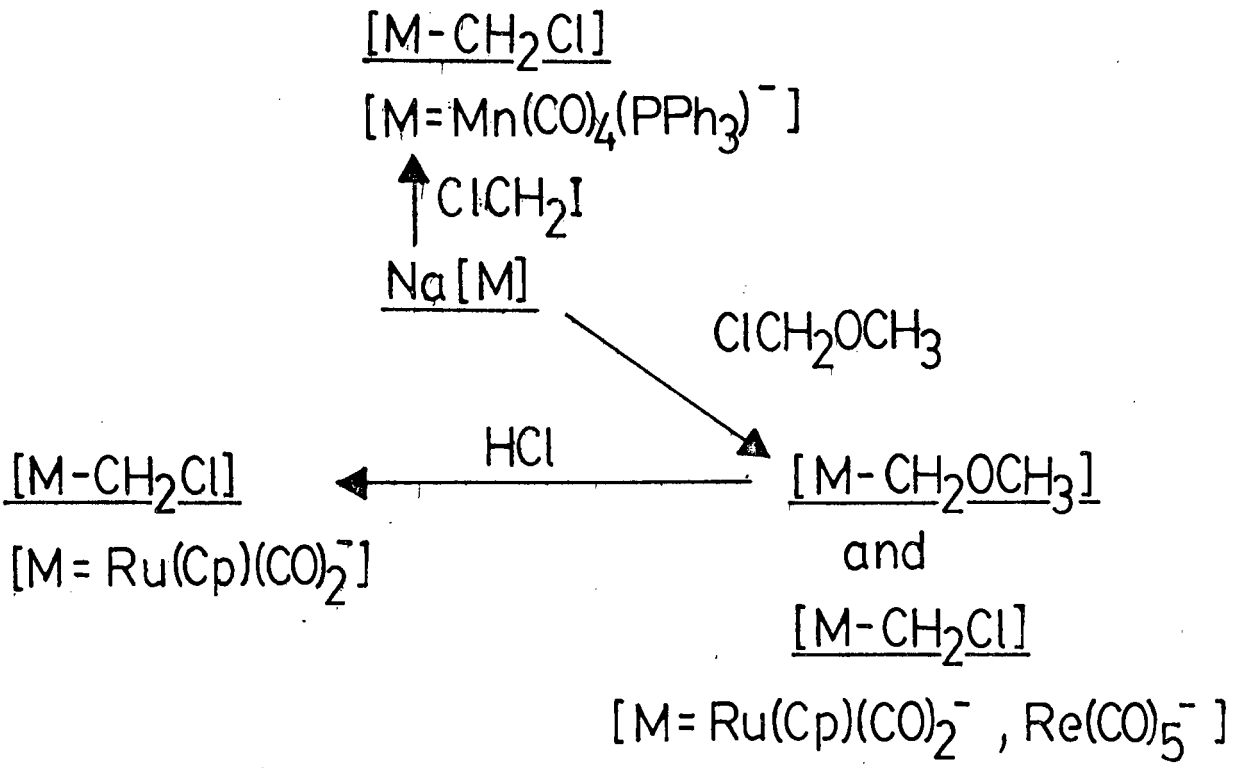
The new complexes $[Ru(Cp)(CO)_2CH_2OCH_3]$ (XXXII), $[Ru(Cp)(CO)_2CH_2Cl]$ (XXXIII), $[Re(CO)_5CH_2OCH_3]$ (VII), $[Re(CO)_5CH_2Cl]$ (IX) and *cis*-$[Mn(CO)_4(PPh_3)CH_2Cl]$ (XXXIV) have been synthesized (Scheme 7).

$[Ru(Cp)(CO)_2CH_2OCH_3]$ (XXXII) was synthesized by the reaction of $Na[Ru(Cp)CO_2]$ with a sixfold excess of chloromethyl methyl ether, in THF, at -78°C (Equation 12). The slightly impure product was isolated as a brown oil and characterised by infrared, ^1H nmr and mass spectroscopy (see Table 6).

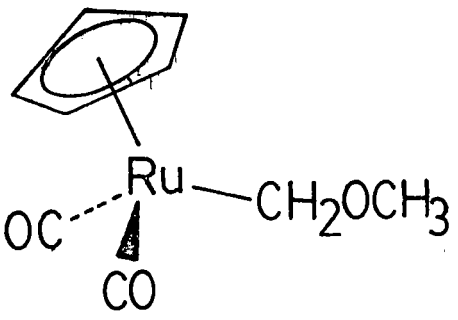
$$Na[Ru(Cp)(CO)_2] + ClCH_2OCH_3 \xrightarrow[-78^{\circ}C]{THF} [Ru(Cp)(CO)_2CH_2OCH_3] + \text{a trace of } [Ru(Cp)(CO)_2CH_2Cl] \quad (12)$$

Good elemental analyses were not obtained, as the product was contaminated by an unidentified colourless oil, which could not be completely separated from (XXXII). The colourless oil is perhaps a product arising from a reaction catalysed by a ruthenium species; for example it is conceivable that a reactive substance such as $ClCH_2OCH_3$ may form a polymer in a reaction catalysed by some Ru species existing in the reaction mixture. It is however surprising that no separation of (XXXII) and the impurity was achieved.

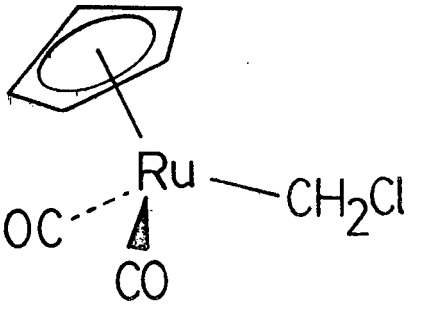
Traces of the chloromethyl compound $[Ru(Cp)(CO)_2CH_2Cl]$ (XXXIII) were also synthesized by the reaction of $Na[Ru(Cp)(CO)_2]$ and $ClCH_2OCH_3$ (Equation 12),



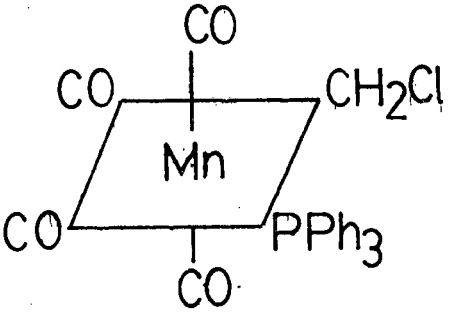
Scheme 7: Synthesis of new [M-CH_2Cl] and [M-CH_2OCH_3] complexes.



(XXXII)



(XXXIII)



(XXXIV)

(see Figure 8, page 47), which indicates that $ClCH_2OCH_3$ is a bifunctional molecule, *vide supra*. (XXXIII) was also synthesized by the reaction of a hexane solution of the methoxymethyl (XXXII) with dry HCl gas at room temperature (Equation 13).

$$[Ru(Cp)(CO)_2CH_2OCH_3] + HCl \longrightarrow [Ru(Cp)(CO)_2CH_2Cl] + HOCH_3 \qquad (13)$$

It was isolated as a sticky yellowish solid, and characterised by infra-red, ^1H nmr and mass spectroscopy (see Table 10), and elemental analysis.

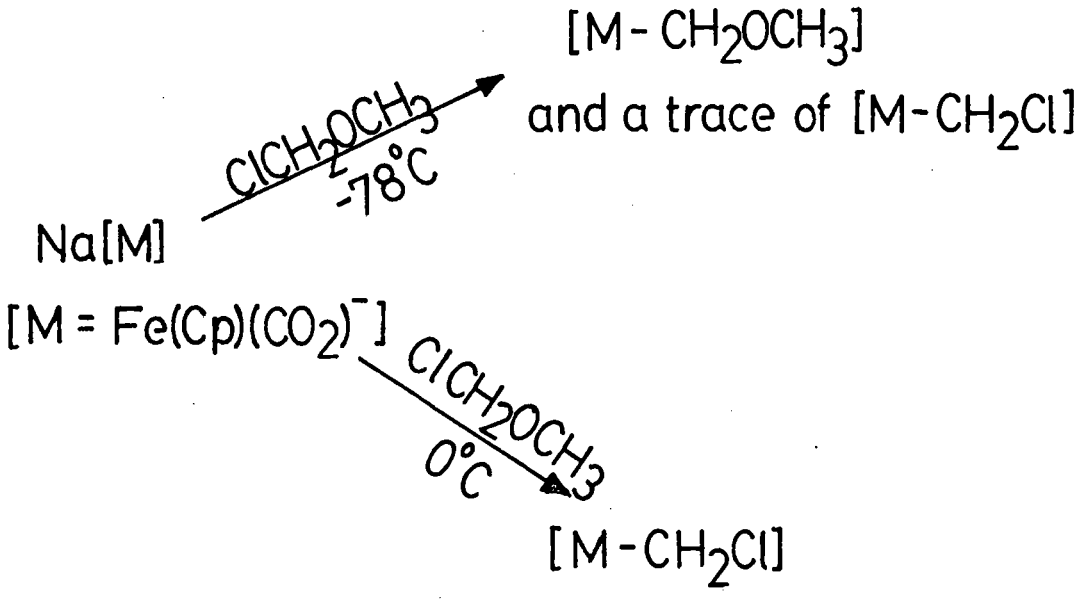
(Methoxymethyl)- and (chloromethyl)pentacarbonylrhenium, (VII) and (IX) respectively, were both synthesized from the reaction of $Na[Re(CO)_5]$ with $ClCH_2OCH_3$ at -78°C. (Equation 14).

$$Na[Re(CO)_5] + ClCH_2OCH_3 \longrightarrow [Re(CO)_5CH_2OCH_3] + [Re(CO)_5CH_2Cl] \qquad (14)$$

A mixture of a white solid and a clear oil were isolated from the reaction mixture and separated by the following method. The total product (oil and solid) was dissolved in a minimum of hexane and cooled to -78°C, at which temperature, (IX) precipitated out as a white solid. Removal of the hexane from the mother liquors gave (VII) as a colourless oil. (VII) was contaminated with small amounts of (IX), as would be expected, but a fairly good separation was achieved, owing to the surprisingly large difference in the solubilities of the two products in hexane; the chloromethyl species is much less soluble than the methoxymethyl species.

The fact that $[Re(CO)_5CH_2Cl]$ (IX) and $[Re(CO)_5CH_2OCH_3]$ (VII) were both synthesized in one reaction using $Na[Re(CO)_5]$ and $ClCH_2OCH_3$, again indicates the bifunctional nature of chloromethyl methyl ether. This was also

noticed in the synthesis of $[Fe(Cp)(CO)_2CH_2OCH_3]$, (V); some chloromethyl complex (VI) was present in the crude hexane extract, as seen in the infrared spectrum. (See Figure 7, page 47). It appears that $ClCH_2OCH_3$ can be a source of either $[ClCH_2]$ or $[CH_3OCH_2]$, the proportions of each of these differing with the metal carbonyl anion used. The conditions of the reaction, particularly temperature also appear to be important. For example, it has been found in our laboratory[68] that with the reactions of $Na[M]^+$ (M = $[W(Cp)(CO)_3]^-$, $[Mo(Cp)(CO)_3]^-$, $[Fe(Cp)(CO)_2]^-$) with $ClCH_2OCH_3$, mixtures of chloromethyl and methoxymethyl compounds, $[M\text{-}CH_2Cl]$ and $[M\text{-}CH_2OCH_3]$ respectively, are obtained, the relative amounts apparently depending on the temperature at which Na[M] is added to $ClCH_2OCH_3$. Thus, addition of a THF solution of Na[M] (M = $[Fe(Cp)(CO)_2]^-$) to $ClCH_2OCH_3$ at -78°C gave mostly $[M\text{-}CH_2OCH_3]$ with a small amount of $[M\text{-}CH_2Cl]$. However when the reaction was conducted at 0°C, only $[M\text{-}CH_2Cl]$ was isolated (Scheme 8).

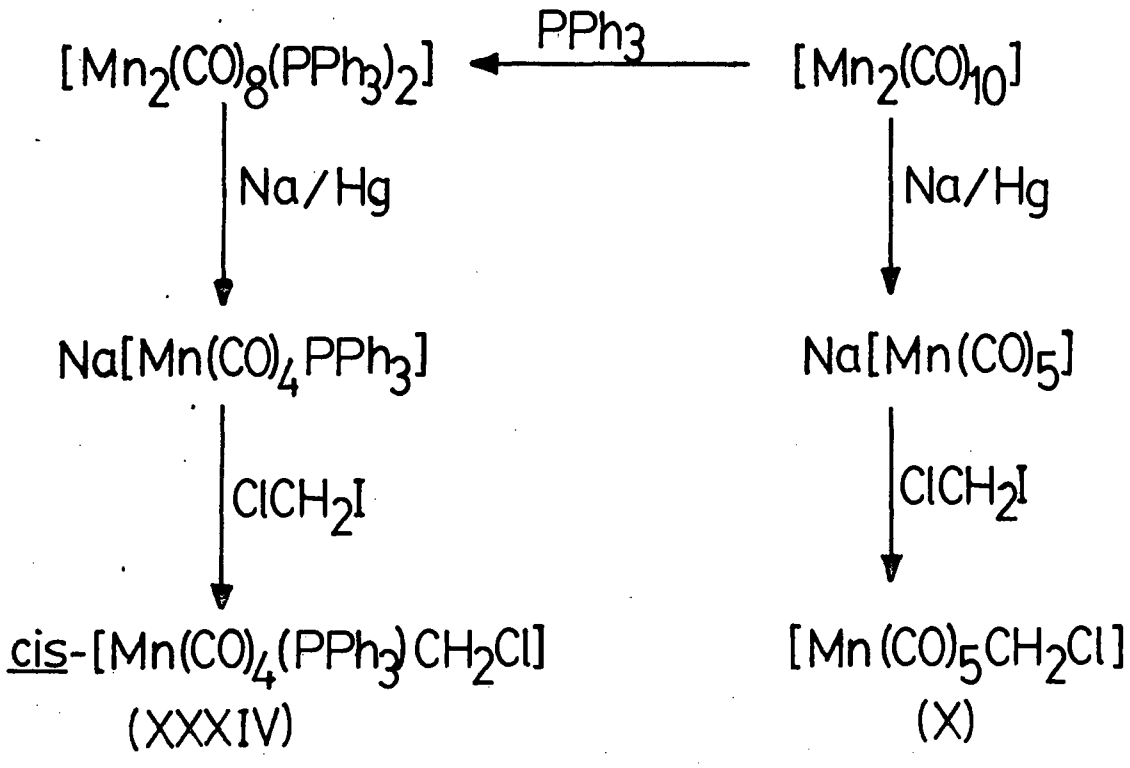


Scheme 8. Reaction of $Na[Fe(Cp)(CO)_2]$ with $ClCH_2OCH_3$ at different temperatures.

Such results are difficult to reproduce and the reactions appear to be complex; they are being further investigated by other workers in our laboratory.[68] It is interesting to note that no other workers have reported similar results when working with $ClCH_2OCH_3$ (see, for example, references 47, 48, 50, 54).

Cis-(chloromethyl)(triphenylphosphine)tetracarbonylmanganese, $[Mn(CO)_4(PPh_3)CH_2Cl]$ (XXXIV) was prepared by the reaction of $Na[Mn(CO)_4PPh_3]$ with $ClCH_2I$ at -78°C. (XXXIV) was isolated as a sticky orange-yellow solid, and characterised by infrared and ^1H nmr spectroscopy, and elemental analysis.

Thus both $[Mn(CO)_5CH_2Cl]$[52] (X) and *cis*-$[Mn(CO)_4(PPh_3)CH_2Cl]$ are prepared by very similar methods in reasonable yields (Scheme 9).



Scheme 9. Synthesis of manganese chloromethyl complexes, (X) and (XXXIV).

The reactivity of two other metal carbonyl anions, $Na[Re(CO)_5]$ and $Na[Fe(Cp)(CO)_2]$, towards chloroiodomethane has been investigated, with the aim of developing one step synthesis of the chloromethyl complexes, (IX) and (VI) respectively. The only method yet reported for the synthesis of $[Fe(Cp)(CO)_2CH_2Cl]$ (VI), is the reaction of $[Fe(Cp)(CO)_2CH_2OCH_3]$ (V) with HCl,[48] essentially a two step reaction. (Equation 15).

$$Na[Fe(Cp)(CO)_2] + ClCH_2OCH_3 \longrightarrow [Fe(Cp)(CO)_2CH_2OCH_3] \xrightarrow{HCl} [Fe(Cp)(CO)_2CH_2Cl] \quad (15)$$

The method we have found for the synthesis of $[Re(CO)_5CH_2Cl]$ (IX) is the reaction of $ClCH_2OCH_3$ with $Na[Re(CO)_5]$, in which (IX) is isolated as one of the products (see Equation 14). Further, Jolly and Pettit[47] reported that the reaction of $[Re(CO)_5CH_2OCH_3]$ with HCl gave (IX) only after several hours, and the product was not characterised.

We find that the reaction of $Na[Re(CO)_5]$ with $ClCH_2I$ at -78^oC gives two products. The major product has νCO values corresponding fairly closely to known values for $[Re(CO)_5Cl]$.[69] The minor product was not identified. No (IX) was seen, an interesting contrast to the reasonable yields of $[Mn(CO)_5CH_2Cl]$ obtained from the reaction of $Na[Mn(CO)_5]$ and $ClCH_2I$.[52]

King and Braitsch[51] reported the synthesis of $[Fe(Cp)(CO)_2CH_2Cl]$ (VI) in 13% yield from the reaction of $Na[Fe(Cp)(CO)_2]$ and $ClCH_2I$ at room temperature. Bearing in mind the success achieved in the synthesis[52] of $[Mn(CO)_5CH_2Cl]$ at a lower temperature than that initially reported,[51] we investigated the reaction of $ClCH_2I$ and $Na[Fe(Cp)(CO)_2]$ at -40^oC.

The crude product of the reaction of $ClCH_2I$ and $Na[Fe(Cp)(CO)_2]$ at -40^oC

was a purple solid, the infrared spectrum (νCO region) of which indicated a mixture of products, including bands corresponding to $[Fe(Cp)(CO)_2I]$[70] and two bands at 2028 and 1978 cm^{-1}, which are similar to the values we have found for (VI) (ν(CO)(cyclohexane) 2028, 1974 cm^{-1}). Further purification was attempted by chromatography; the major product isolated was $[Fe(Cp)(CO)_2I]$, judging from its infrared spectrum. The product with νCO at 2028 and 1978 cm^{-1} appeared to have largely decomposed on the column.

2.4.2 Rotational isomerism in $[M(Cp)(CO)_2CH_2OCH_3]$ (M = Fe, Ru)

Baird[67] postulated that the existence of four νCO bands in the complexes $[Fe(Cp)(CO)_2R]$ (R = CH_2Ph, CH_2SiMe_3, CH_2Naph) was due to the existence of rotational isomers in the complexes (see Section 2.3). We have observed four νCO bands in the infrared spectra of the complexes $[M(Cp)(CO)_2CH_2OCH_3]$ (M = Fe (V), Ru (XXXII)) (See Figures 7 and 8), and on the basis of this we propose that these complexes each exist in two rotamers.

The two possible rotamers of (V) and (XXXII) are given in Figure 9. The positions of the peaks are given in Table 4, along with the νCO bands of $[Fe(Cp)(CO)_2CH_2Cl]$ (VI), $[Ru(Cp)(CO)_2CH_2Cl]$ (XXXIII) and $[Fe(Cp)(CO)(PPh_3)CH_2OCH_3]$ (XV)[50] which are included for comparison.

Of the two rotamers drawn in Figure 9, (a) is expected to have the lowest potential energy and consequently the higher population. Judging from the relative intensities of the νCO bands in Figures 7 and 8, it

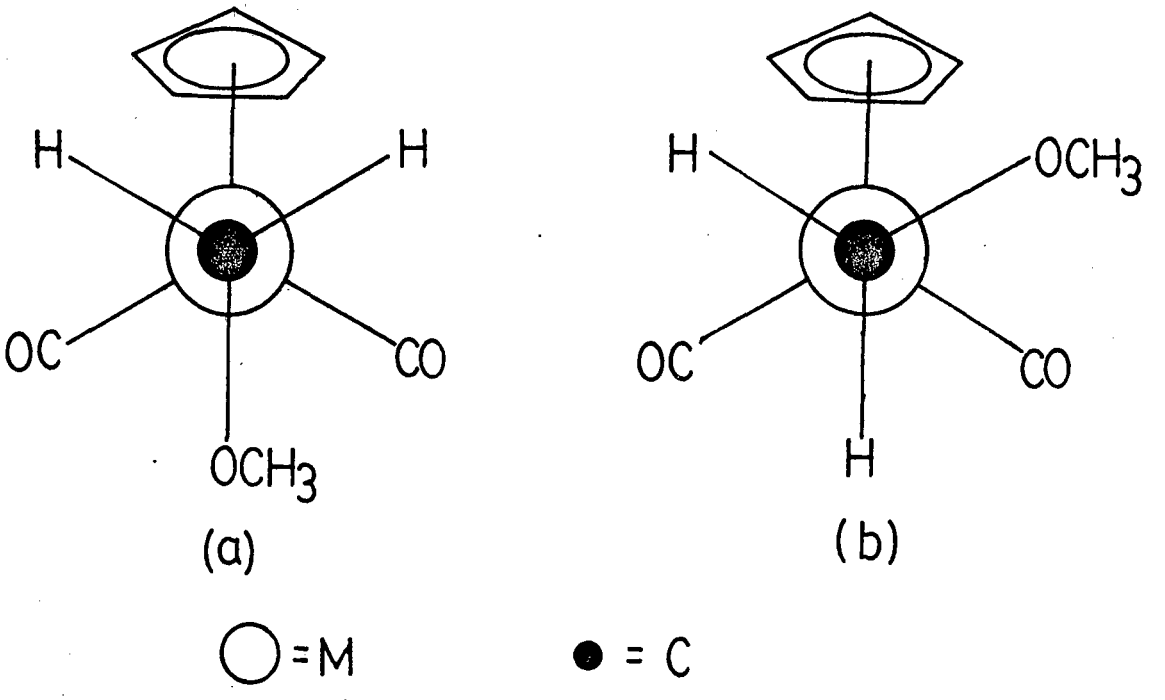


Figure 9. Rotamers of $[M(Cp)(CO)_2CH_2OCH_3]$ (M = Fe, Ru).

Table 4. νCO values for some Fe and Ru complexes

Complex	νCO values (cm^{-1}) [a]
$[Fe(Cp)(CO)_2CH_2OCH_3]$	2016(m) 2006(s) 1961(m) 1949(s)
$[Fe(Cp)(CO)_2CH_2Cl]$[b]	2026(s) 1974(s)
$[Ru(Cp)(CO)_2CH_2OCH_3]$	2026(s) 2017(vs) 1965(s) 1956(vs)
$[Ru(Cp)(CO)_2CH_2Cl]$	2035(s) 1978(s)
$[Fe(Cp)(CO)(PPh_3)CH_2OCH_3]$[c]	1924[d]

a Solvent is cyclohexane except where otherwise stated
b Synthesized by method of Green *et al*[48]
c Synthesized by method of Flood *et al*[50]
d Solvent hexane

would appear that the rotamers have fairly similar populations in the Ru complex (XXXII) but in the Fe complex (V), one rotamer is more populated than the other.

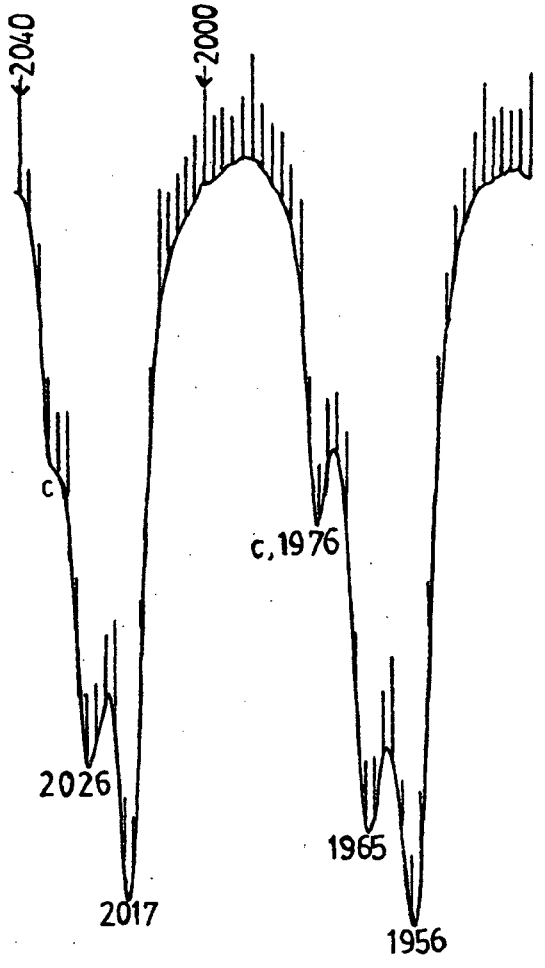
The ^1H nmr of complexes (V) and (XXXII) do not show two sets of resonances, indicating that the two possible rotamers, (a) and (b) (Figure 9) cannot be distinguished by ^1H nmr. It appears that (the rate of exchange between the two isomers, *i.e.*) the rate of rotation about the [Fe-CH_2] bond is too fast to be detected by ^1H nmr and that time-averaged spectra are being observed. Time-averaged ^1H nmr spectra were also observed by Jetz and Graham[65] and Baird [67].

Green[48] reported only two νCO bands in the spectrum of (V), when he reported the original synthesis of the complex. However he recorded the spectrum of (V) as a neat oil which would result in broader bands than in cyclohexane solution with subsequent loss of resolution.

When the spectrum of (V) was run in CH_2Cl_2, we saw only two νCO bands rather than four. This may be due to the broadening of the bands in the more polar solvent; this shows the effect of the conditions of measurement on the resolution of the spectrum. It is possible, however, that the proportions of the two possible rotamers are different in different solutions, and that in CH_2Cl_2 one rotamer predominates to a great extent over the other, due to the solvent stabilizing one rotamer in some way.

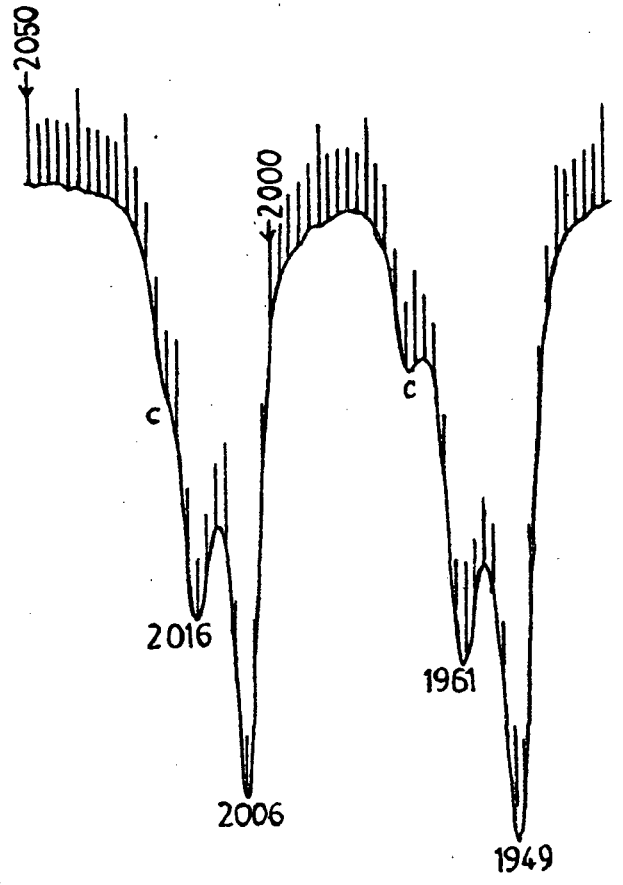
Interestingly, only one νCO band was observed in the infrared spectrum of [Fe(Cp)(CO)(PPh_3)CH_2OCH_3] (XV) in $CHCl_3$ solution,[50] or in cyclohexane solution. This may be due to rotation being sterically hindered by the bulky PPh_3. On the other hand, however, the band width is larger than

Fig. 8. I.r. spectrum (2040-1930 cm^{-1}) of $[Ru(Cp)(CO)_2CH_2OCH_3]$



c = $[Ru(Cp)(CO)_2CH_2Cl]$ bands

Fig. 7. I.r. spectrum (2050-1930 cm^{-1}) of $[Fe(Cp)(CO)_2CH_2OCH_3]$



c = $[Fe(Cp)(CO)_2CH_2Cl]$ bands

the corresponding dicarbonyl complex (V); Baird[67] interpreted the broad bandwidths of the complexes [Fe(Cp)(CO)(L)R] (L = tertiary phosphine, R = CH_2Ph, CH_2SiMe_3, CH_2Naph) as being due to the presence of more than one component in the band.

2.5 The Mass Spectra

The mass spectra of the complexes $[M(Cp)(CO)_2CH_2X]$ (M = Ru, Fe; X = Cl, OCH_3) and $[M(CO)_5CH_2X]$ (M = Re, Mn; X = Cl, OCH_3) have been recorded as part of their characterisation and are reported and discussed in this section. The spectra of $[Fe(Cp)(CO)_2CH_2Cl]$ (VI) and $[Mn(CO)_5CH_2Cl]$ (X) have been previously recorded by Moss[71] but have been recorded again for comparison purposes.

All the compounds are volatile and needed only low source temperatures (Table 13). Their low resolution mass spectra are recorded in Figures 10-21* and Tables 5-12 tabulate some peaks, their intensities and possible assignments. Figures 12,15,18,21 show the calculated mass spectra (*i.e.* the expected isotope combination patterns) for the parent ions of $[Ru(Cp)(CO)_2CH_2OCH_3]$ (XXXII), $[Re(CO)_5CH_2OCH_3]$ (VII), $[Ru(Cp)(CO)_2CH_2Cl]$ (XXXIII) and $[Re(CO)_5CH_2Cl]$ (IX). The expected isotope patterns have also been calculated for other possible fragments; comparison of the expected patterns with the actual mass spectrum of a complex aids identification of fragments of that complex.

Note that in Tables 5-12 only the most intense peak of the expected isotope combination pattern is tabulated.

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* Several spectra of a complex were recorded, but only one is included for reasons of space. Some irregularities can be seen in the included spectra in that occasionally the expected isotope combination pattern is not seen. In most cases the expected pattern was seen in another spectrum of that complex. These irregularities are mentioned in the footnotes to the Tables (5-12); they are believed to be due to a computer fault.

2.5.1 General remarks

A characteristic feature of complexes containing carbonyl ligands, is the successive loss of CO groups from the parent ion.[72,73] The successive loss of CO groups from the parent ion is seen in the spectra of the complexes studied.* Further, it can be seen that in all the complexes studied the loss of CO competes with the loss of the $[CH_2X]$ ligand; thus for example all the spectra of the complexes $[M(CO)_5CH_2X]$ (M = Mn, Re, X = Cl, OCH_3) show peaks corresponding to the ions $[M(CO)_n]^+$ $(n = 5\text{-}0)^+$ with the exception of (VIII) which shows only peaks for the ions n = 2,1,0. Of interest is that the spectrum of $[Re(CO)_5CH_2OCH_3]$ shows no peaks corresponding to $[Re(CO)_nCH_2OCH_3]^+$, but shows all the ions $[Re(CO)_n]^+$ (n = 5-0) (Figure 14). The loss of $[CH_2OCH_3]$ from the parent ion precedes any loss of CO groups.

In all the complexes $[M(Cp)(CO)_2CH_2X]$ (M = Fe, Ru, X = Cl, OCH_3), the loss of $[CH_2X]$ only competes with loss of the second CO group, the loss of the first CO group from the parent apparently preceding any loss of $[CH_2X]$. All the spectra (Figures 10, 11, 16, 17) of these complexes show peaks corresponding to $[M(Cp)CO]^+$, but not to $[M(Cp)(CO)_2]^+$.

This competition between loss of CO and $[CH_2X]$ is seen in such complexes as $[Mn(CO)_5CH_3]$[74]. In this particular case all the ions $[Mn(CO)_nCH_3]^+$ and $[Mn(CO)_n]^+$ (n = 5-0) were seen.

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* Note that the complexes $[Mn(CO)_5CH_2OCH_3]$ (VIII), and $[Re(CO)_5CH_2X]$ (X = Cl (IX), OCH_3 (VII)) do not show the full sequence of $[M(CO)_nCH_2X]^+$ (n = 5-0)

† The fragments $[Re(CO)_n]^+$ (n = 5-0) are also fragments of the dimer $[Re_2(CO)_{10}]$.

A characteristic feature of the mass spectra of virtually all (η^5-cyclopentadienyl) transition metal complexes so far investigated by mass spectroscopy[75] is the appearance of a peak corresponding to the stable fragment $[M\text{-}Cp]^+$. Our spectra of the complexes $[M(Cp)(CO)_2CH_2X]$ all show peaks corresponding to such a fragment.

2.5.2 Further discussion of the mass spectra of the chloromethyl complexes $[M(Cp)(CO)_2CH_2Cl]$ (M = Fe, Ru) and $[M(CO)_5CH_2Cl]$ (M = Re, Mn). (Figures 16-21, Tables 9-12)

The complexes $[Fe(Cp)(CO)_2CH_2Cl]$ (VI), $[Ru(Cp)(CO)_2CH_2Cl]$ (XXXIII)* and $[Re(CO)_5CH_2Cl]$ (IX) all show parent molecular ions in their spectra. $[Mn(CO)_5CH_2Cl]$ (X) did not show a parent ion in the spectrum shown in Figure 19, but when this spectrum was amplified (with respect to intensity) a parent ion was seen. In the spectrum of (X) recorded by Moss,[71] a parent ion was seen.

The spectra of both (VI) and (XXXIII) have peaks identified as the fragments $[M(Cp)CH]^+$. These interesting fragments indicate that the $[M\text{-}CH_2Cl]$ part of the complexes can fragment by loss of HCl. In constrast, the spectra of (X) and (IX) show peaks identified as the fragments $[Re(CO)_3CH_2]^+$ and $[MnCH_2]^+$; in these complexes the $[M\text{-}CH_2Cl]$ part appears to fragment by loss of Cl.

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* The spectrum of (XXXIII) only shows two peaks for the parent ion instead of the expected isotope combination pattern (see Figure 18). The assignment is thus questionable.

It is of interest to compare the fragmentation of the $[M-CH_2Cl]$ part of the complexes with fragmentation patterns of some organic molecules. Chloroethane $[C_2H_5Cl]$, 1-chloropropane $[C_3H_7Cl]$, and 1-chlorobutane $[C_4H_9Cl]$ all show intense peaks corresponding to loss of HCl from the parent ion. However, benzyl chloride $[C_6H_5CH_2Cl]$ loses Cl to give the characteristic resonance stabilised $[C_7H_7]^+$ ion (m/e 91) and 2-chloroethyl benzene $[C_6H_5CH_2CH_2Cl]$ shows only a very weak peak corresponding to loss of HCl, with, again, the $[C_7H_7]^+$ ion prominent.[76]*

The Fe and Mn chloromethyl complexes (VI) and (X), show peaks corresponding to $[M-Cl]^+$ fragments. Such fragments imply a rearrangement process, with loss of $[CH_2]$ from $[M-CH_2Cl]$.

2.5.3 Further discussion of the mass spectra of the methoxymethyl complexes $[M(Cp)(CO)_2CH_2OCH_3]$ (M = Fe, Ru) and $[M(CO)_5CH_2OCH_3]$ (M = Mn, Re). (Figures 10-15, Tables 5-8).

A parent ion is seen in the spectrum of the complex $[Ru(Cp)(CO)_2CH_2OCH_3]$ (XXXII) (Figure 11); the Fe and Mn methoxymethyl complexes, (V) and (VIII), do not show parent ions. The spectrum of $[Re(CO)_5CH_2OCH_3]$ (VII) (Figure 14) is complicated by the presence of $[Re_2(CO)_{10}]$ in the sample of (VII). This is a decomposition product of (VII), not being present

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* The spectra given in reference 76 are not discussed therein; the spectra show peaks at 36 m/e units less than the m/e value of the parent ion, which could be due to loss of HCl. However accurate masses of the fragments are not given.

in a freshly purified sample but accumulating with time (in the sample itself, not in the mass spectrometer). The peaks at m/e 372 are the correct weight and pattern for the fragment Re_2^+, originating from $[Re_2(CO)_{10}]$; this species probably obscures the parent ion which would also give a peak at m/e 272 with the isotopic pattern given in Figure 15. The peaks at m/e 400 are also due to $[Re_2(CO)_{10}]$ and characteristic features[77] of the dimer mass spectrum were also seen at m/e >400.

All the methoxymethyl complexes investigated show loss of the $[CH_2OCH_3]$ group; all the spectra show peaks at m/e 45, which is probably due to a $[C_2H_5O]$ species. A peak at m/e 45 is a characteristic feature of many organic ethers,[76,78] and is usually assigned to the fragment $[H_2C = OCH_3]^+$[78]; a similar species may well be formed from the methoxymethyl group of the complexes studied in this work.

In Figure 13, a peak at m/e 85 is assigned to $[Mn(CH_2O)]^+$; the $[M-CH_2OCH_3]$ group may lose a CH_3 fragment to give $[M-CH_2O]^+$. A peak at m/e 134 in Figure 10 is assigned to $[Fe(Cp)CH]^+$. This may arise from an $[M-CH_2OCH_3]$ species by rearrangement followed by loss of CH_3OH. In the fragment $[Fe(Cp)(CO)CH_3]$ (m/e 164) the $[CH_3]$ group may also arise from a rearrangement reaction, followed by loss of CH_2O from $[M-CH_2OCH_3]$.

In Figure 13, a peak at m/e 222 is assigned to "parent - minus H_2O". A known rearrangement reaction in organic ethers is as in Equation 16.[79]

$$R\text{-}\overset{+}{O}CH_2\text{-}R' \xrightarrow{\text{rearrange}} R\text{-}\overset{+}{O}H_2 \longrightarrow R^+ + H_2O \qquad (16)$$

A similar process may well be occurring in the case of (VIII).

The Ru methoxymethyl (XXXII) (Figure 11) shows a peak at m/e 141, which

is assigned to $[Ru(C_3H_3)]^+$. Fragmentation of the Cp group is often seen in complexes with Cp as a ligand,[75] and the groups C_3H_3, C_2H_2 and C_2H_4 are often split off. $[Ru(C_3H_3)]^+$ thus may arise from $[Ru(Cp)]^+$ by loss of C_2H_2.

Table 5.

The mass spectrum of $[Fe(Cp)(CO)_2CH_2OCH_3]$. Intensities and assignments

m/e	intensity, I, %	Possible assignment[a,b]
194	41.9	$[Fe(Cp)(CO)CH_2OCH_3]$
166	40.9	$[Fe(Cp)CH_2OCH_3]$
164	12.4	$[Fe(Cp)(CO)CH_3]$
149	37.5	$[Fe(Cp)(CO)]$
134	11.6	$[Fe(Cp)CH]$
121	100.0	$[FeCp]$
56	28.8	$[Fe]$
45	5.8	$[C_2H_5O]$

[a] All ions have a single positive charge

[b] A parent ion not seen (m/e 222); spectrum only recorded up to m/e 200 as no peaks above this value.

Table 6.

The mass spectrum of $[Ru(Cp)(CO)_2CH_2OCH_3]$
Intensities and assignments

m/e	intensity, %,	Possible assignment[a]
268	8.6	$[Ru(Cp)(CO)_2CH_2OCH_3]$[b]
240	32.3	$[Ru(Cp)(CO)CH_2OCH_3]$
212	14.8	$[Ru(Cp)CH_2OCH_3]$[c]
195	45.7	$[Ru(Cp)(CO)]$
167	81.9	[Ru Cp]
141	16.7	$[Ru(C_3H_3)]$
114	7.8	[RuC]
101	9.0	Ru [c]
71	47.9	not known
45	100.0	C_2H_5O

[a] All ions have a single positive charge

[b] Peak at m/e 262 expected but not found

[c] Expected isotopic combination pattern not seen, but is seen in other spectrum.

Table 7.

The mass spectrum of $[Mn(CO)_5CH_2OCH_3]$. Intensities and assignments

m/e	intensity, %	Possible assignment[a,b]
222	14.3	parent minus H_2O
212	43.9	$[Mn(CO)_4CH_2OCH_3]$
156	10.7	$[Mn(CO)_2CH_2OCH_3]$
128	9.9	$[Mn(CO)CH_2OCH_3]$
111	18.7	$[Mn(CO)_2]$
110	10.0	not known
100	56.9	$[MnCH_2OCH_3]$
85	9.9	$[Mn(CH_2O)]$
83	19.8	[Mn(CO)]
71	10.4	[MnO]
69	7.1	$[MnCH_2]$
55	88.0	[Mn]
45	100.0	$[C_2H_5O]$

[a] All ions have a single positive charge

[b] No parent ion seen in spectrum.

Table 8.

The mass spectrum of $[Re(CO)_5CH_2OCH_3]$, Intensities and assignments

m/e	intensity, %	Possible assignment[a]
372	26.5	Re_2[b,c]
327	10.0	$[Re(CO)_5]$
299	11.3	$[Re(CO)_4]$
271	8.5	$[Re(CO)_3]$
243	10.8	$[Re(CO)_2]$[d]
242	10.4	not known
239	10.0	not known
238	10.1	not known
237	4.5	not known
215	16.4	[Re(CO)][d]
214	13.3	not known
187	19.1	[Re]
91	27.4	not known
71	47.3	not known
55	31.6	not known
45	100.0	C_2H_5O

[a] All ions have a single positive charge

[b] Re_2^+ from $[Re_2(CO)_{10}]$, a possible decomposition product of $[Re(CO)_5CH_2OCH_3]$. Peak at m/e 400 also from $[Re_2(CO)_{10}]$.

[c] Parent ion expected at m/e 372 (see Fig. 14). Masked by Re_2^+ peaks.

[d] Expected isotopic combination pattern not seen but is seen in another spectrum.

Table 9.

The mass spectrum of $[Fe(Cp)(CO)_2CH_2Cl]$. Intensities and assignments

m/e	intensity, %	Possible assignments[a]
226	3.7	Parent[b]
198	32.6	$[Fe(Cp)(CO)CH_2Cl]$
186	17.0	not known
170	38.9	$[Fe(Cp)CH_2Cl]$[b]
149	12.2	[Fe(Cp)(CO)]
134	72.9	[Fe(Cp)CH]
121	52.1	[Fe(Cp)]
91	16.8	[FeCl]
77	10.4	not known
66	13.1	not known
56	100.0	[Fe]

[a] All ions have a single positive charge

[b] Expected isotope combination pattern not seen, but seen in another spectrum.

Table 10.

The mass spectrum of $[Ru(Cp(CO)_2CH_2Cl]$. Intensities and assignments

m/e	intensities, %	Possible assignments[a]
272	11.1	parent[b]
244	64.9	$[Ru(Cp)(CO)CH_2Cl]$
216	30.2	$[Ru(Cp)CH_2Cl]$
195	33.5	$[Ru(Cp)(CO)]$
180	66.6	$[Ru(Cp)CH]$
167	100.0	$[RuCp]$
139	20.9	not known
102	17.3	$[Ru]$[c]

[a] All ions have a single positive charge
[b] Expected isotopic combination pattern not seen and not seen in other spectra of the complex
[c] Expected isotopic combination pattern not seen but seen in other spectra.

Table 11.

The mass spectrum of $[Mn(CO)_5CH_2Cl]$. Intensities and assignments

m/e	intensity, %	Possible assignment[a,b]
216	63.9	$[Mn(CO)_4CH_2Cl]$
195	16.4	$[Mn(CO)_5]$
188	12.8	$[Mn(CO)_3CH_2Cl]$[c]
167	20.7	$[Mn(CO)_4]$
160	44.0	$[Mn(CO)_2CH_2Cl]$
139	24.3	$[Mn(CO)_3]$
132	24.9	$[Mn(CO)CH_2Cl]$
125	12.4	$[Mn(CO)_2CH_2]$
111	18.4	$[Mn(CO)_2]$
104	69.8	$[Mn(CH_2Cl)]$
90	26.3	$[MnCl]$
83	25.1	$[MnCO]$
69	17.5	$[MnCH_2]$
68	12.6	$[MnCH]$
67	10.0	$[MnC]$
55	100.0	$[Mn]$

[a] All ions have a single positive charge
[b] Parent ion at m/e 244 seen in an amplified (with respect to intensity) spectrum, with expected isotope combination pattern
[c] Expected isotope combination pattern not seen, but was seen in another spectrum.

Table 12.

The mass spectrum of $[Re(CO)_5CH_2Cl]$. Intensities and assignments

m/e	intensity, %	Possible Assignments[a]
377	32.2	Parent [b]
348	39.5	$[Re(CO)_4CH_2Cl]$[b]
327	61.5	$[Re(CO)_5]$
299	54.4	$[Re(CO)_4]$
285	34.2	$[Re(CO)_3CH_2]$
271	44.0	$[Re(CO)_3]$[b]
264	100.0	$[Re(CO)CH_2Cl]$[c]
243	29.7	$[Re(CO)_2]$
236	32.2	not known
225	19.0	not known
215	18.3	$[Re(CO)]$[b]
200	36.5	not known
187	37.1	[Re]

[a] All ions have a single positive charge

[b] Expected isotope combination pattern not seen but is seen in another spectrum

[c] Expected isotope combination pattern not seen, and not seen in another spectrum.

Table 13.

Source temperatures for mass spectra

Compound	Source temperature (°C)
$[Mn(CO)_5CH_2Cl]$	45
$[Mn(CO)_5CH_2OCH_3]$	130
$[Re(CO)_5CH_2Cl]$	65
$[Re(CO)_5CH_2OCH_3]$	85
$[Ru(Cp)(CO)_2CH_2Cl]$	60
$[Ru(Cp)(CO)_2CH_2OCH_3]$	60
$[Fe(Cp)(CO)_2CH_2Cl]$	65
$[Fe(Cp)(CO)_2CH_2OCH_3]$	62

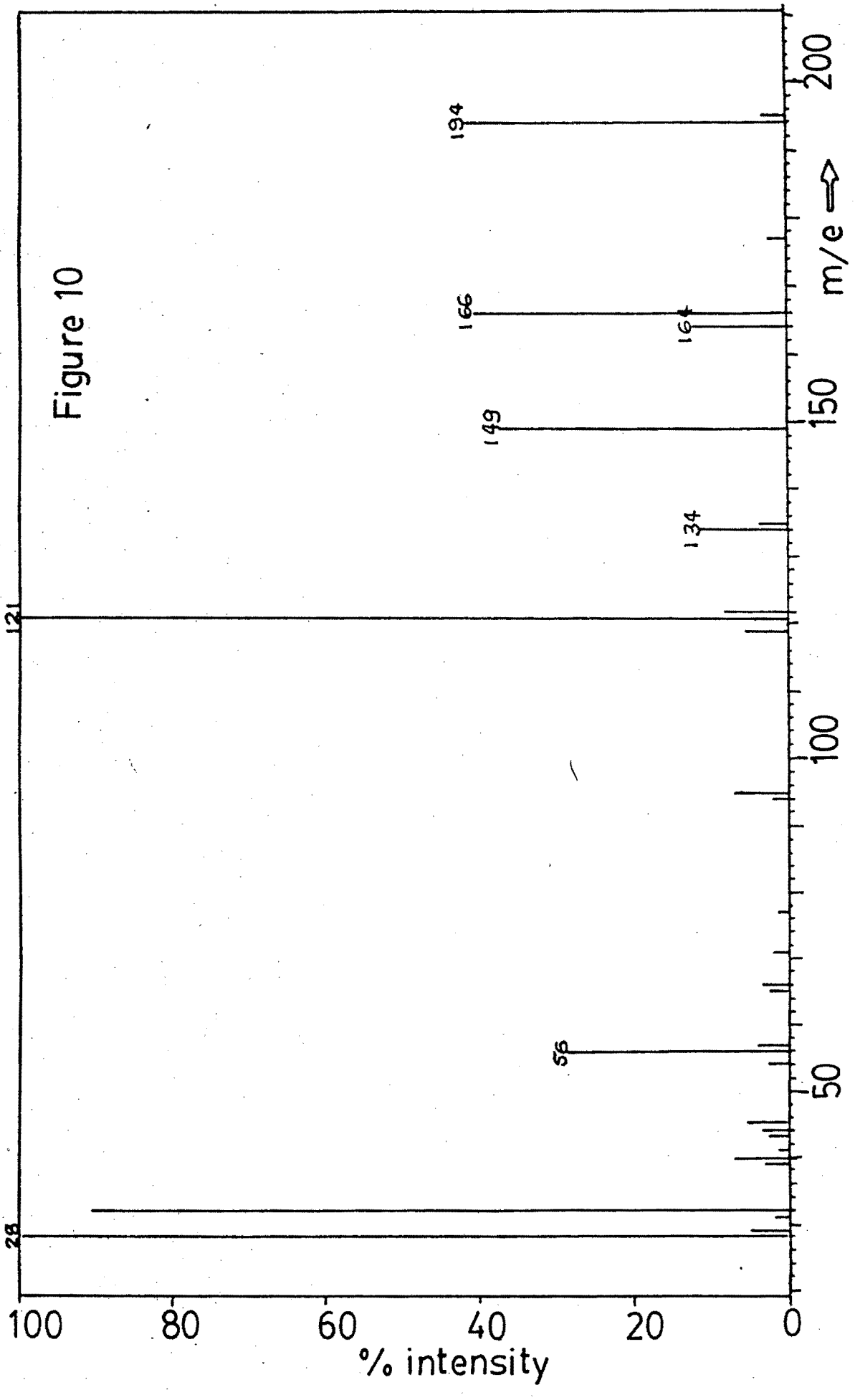
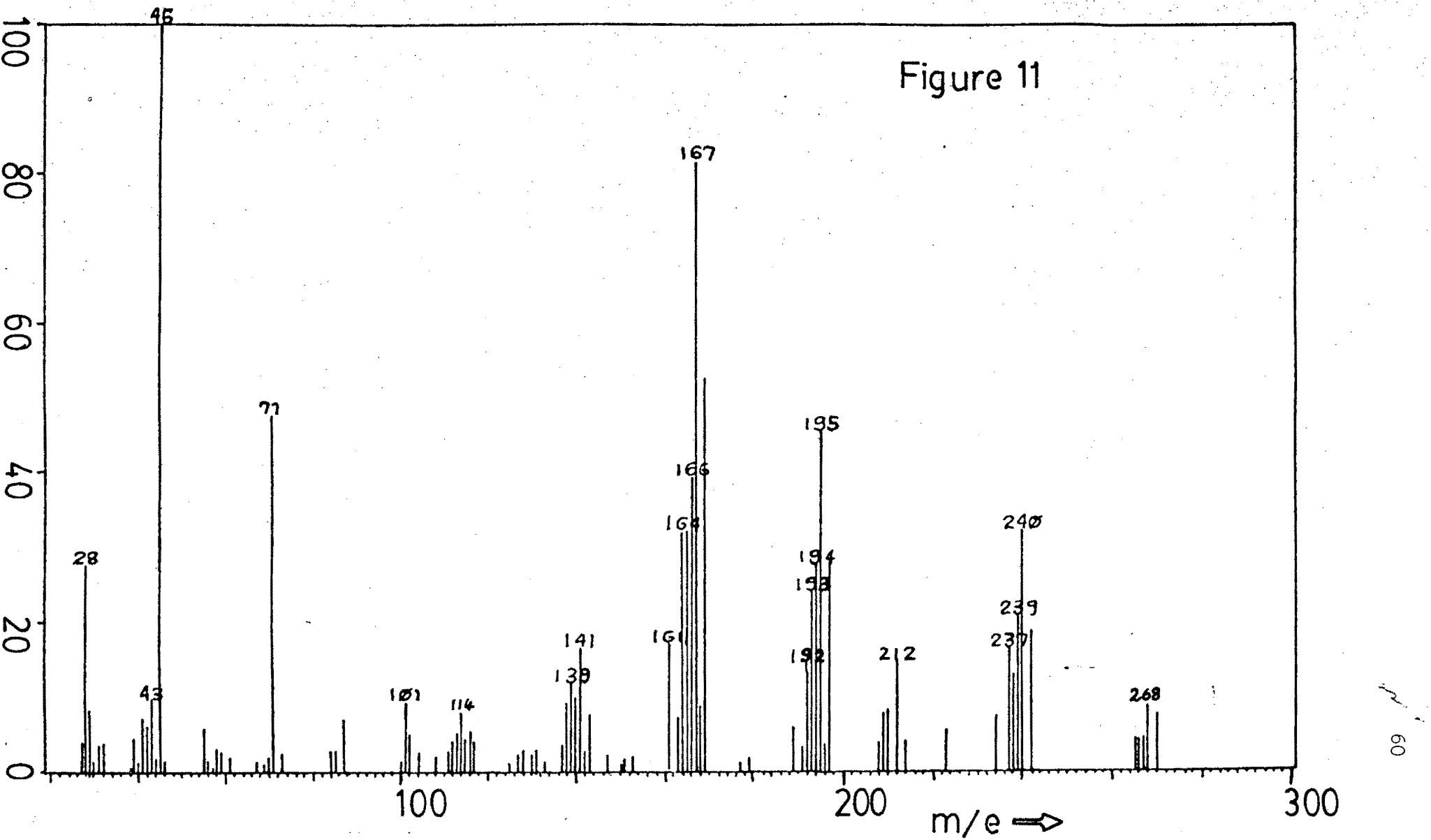


Figure 10. Mass spectrum of $[Fe(Cp)(CO)_2CH_2OCH_3]$ (V).

Figure 11. Mass spectrum of $[Ru(Cp)(CO)_2CH_2OCH_3]$ (XXXII).



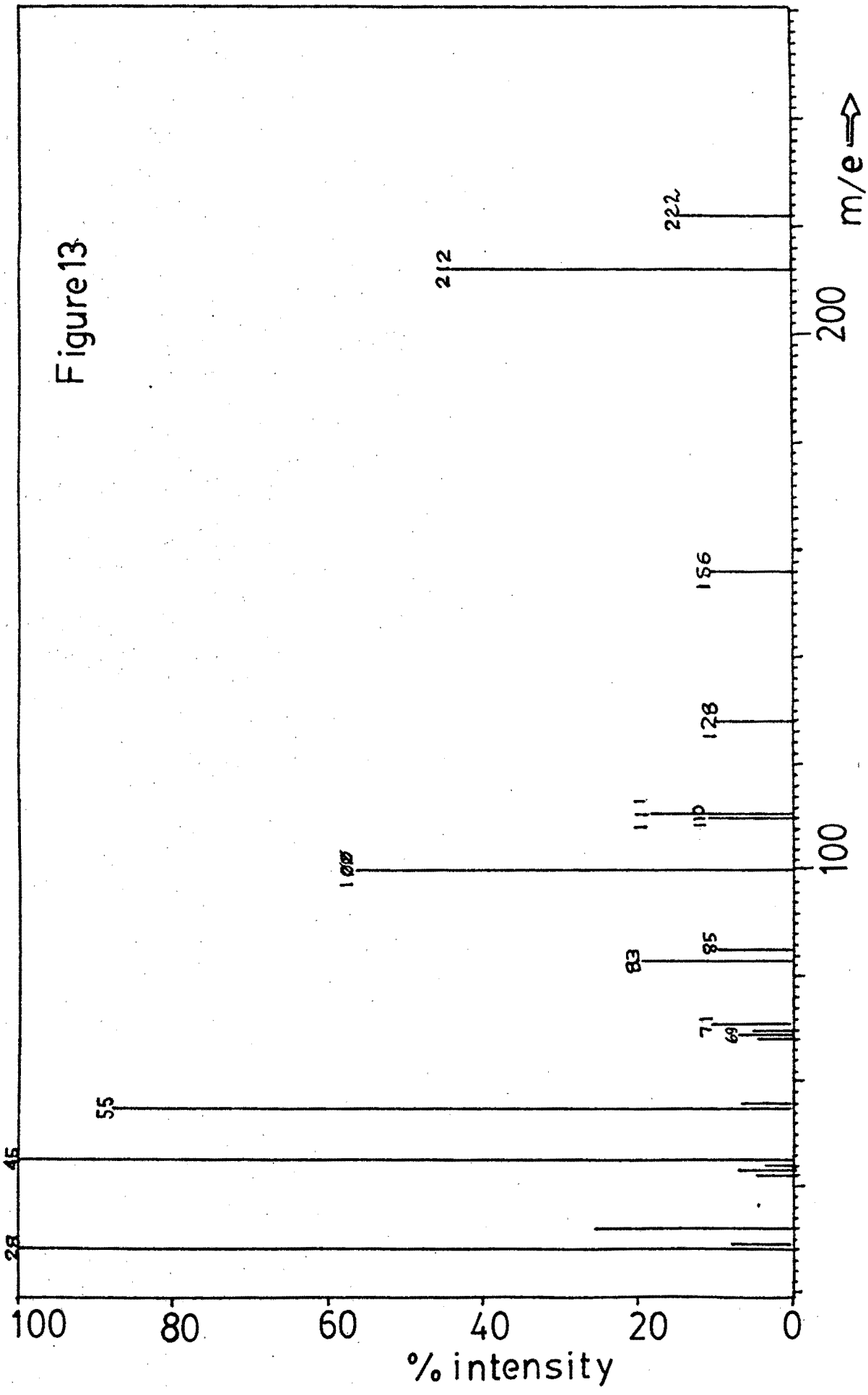


Figure 13. Mass spectrum of $[Mn(CO)_5CH_2OCH_3]$ (VIII).

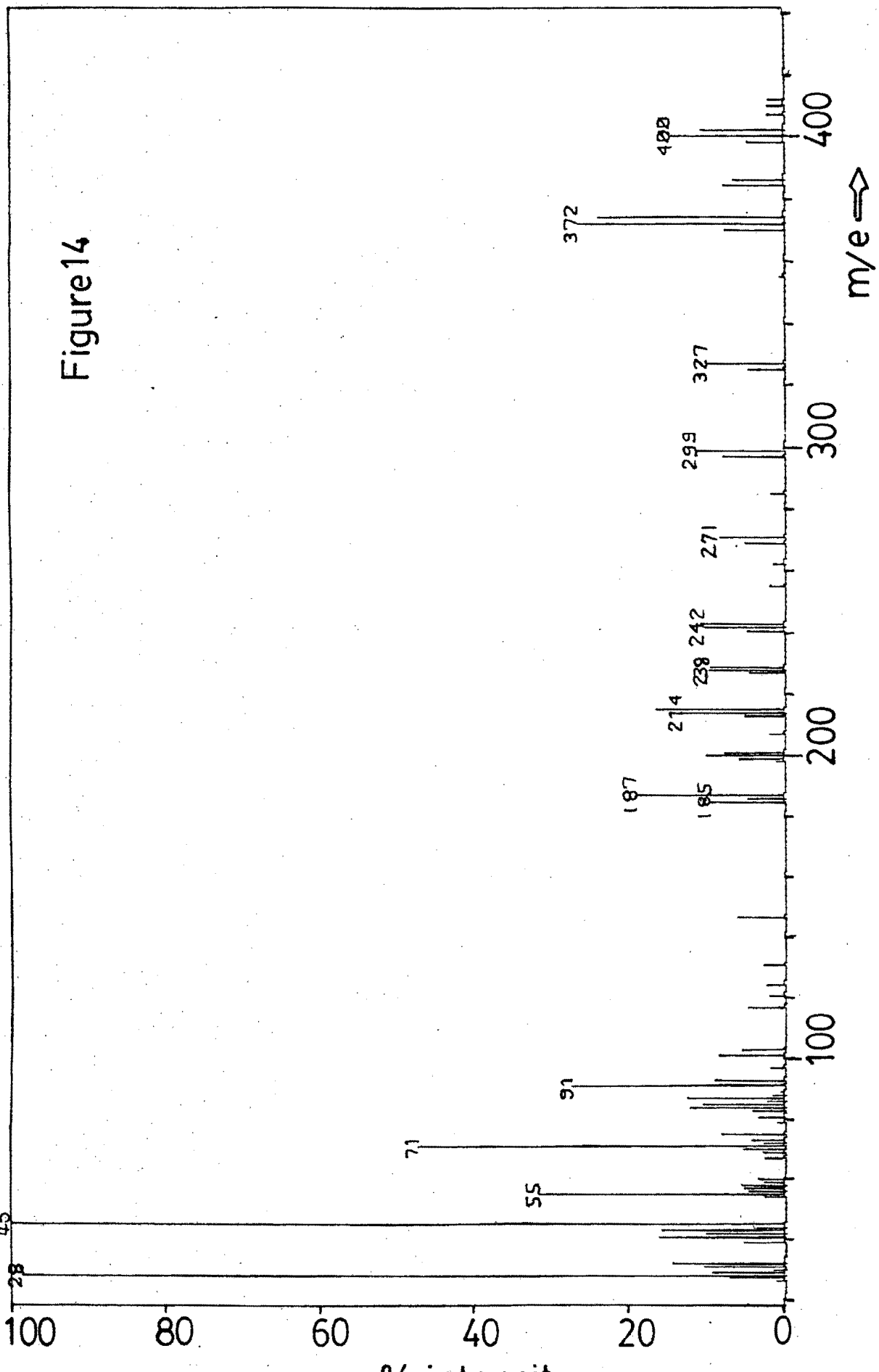


Figure 14. Mass spectrum of $[Re(CO)_5CH_2OCH_3]$ (VII).

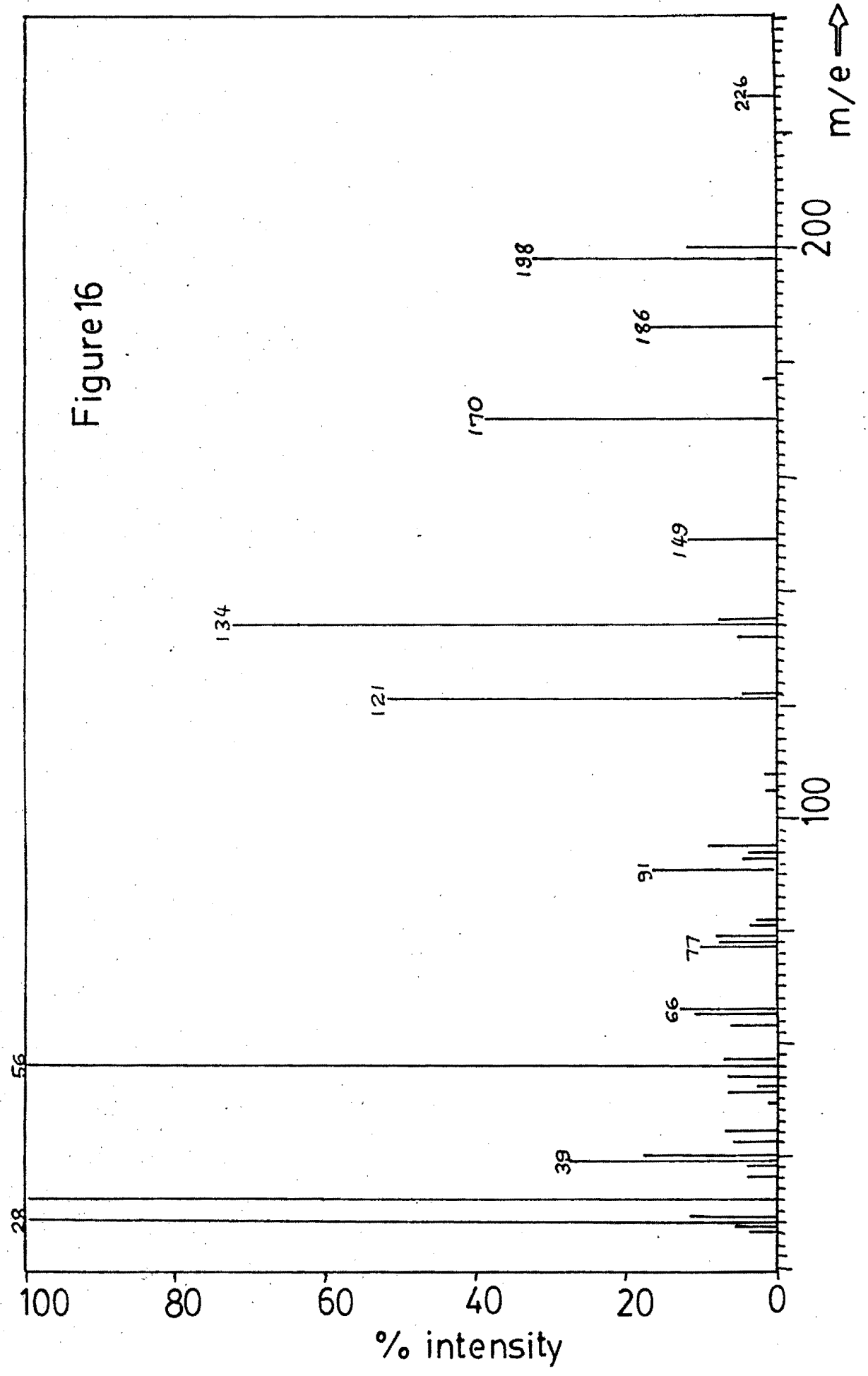


Figure 16. Mass spectrum of $[Fe(Cp)(CO)_2CH_2Cl]$ (VI).

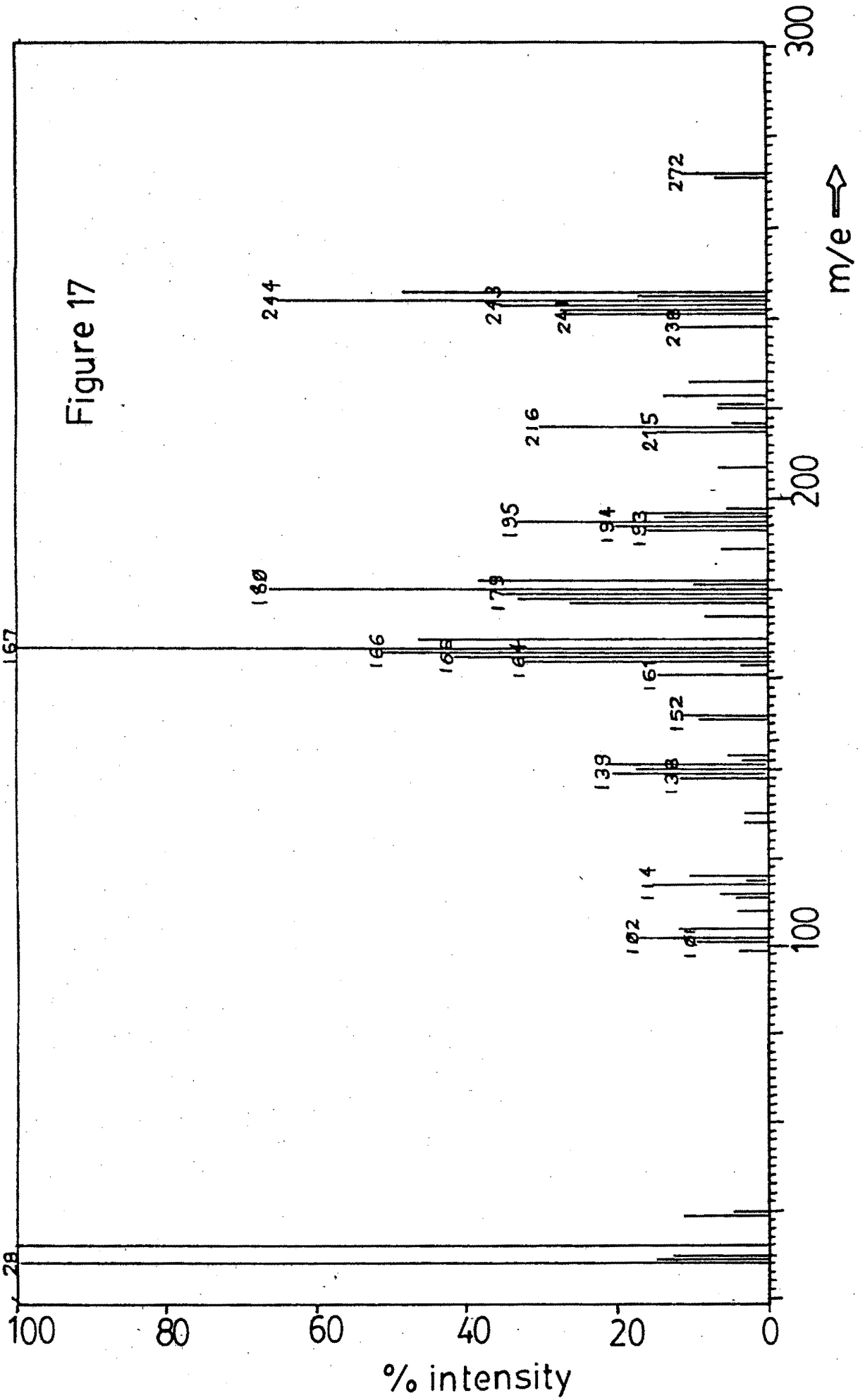


Figure 17. Mass spectrum of $[Ru(Cp)(CO)_2CH_2Cl]$ (XXXIII).

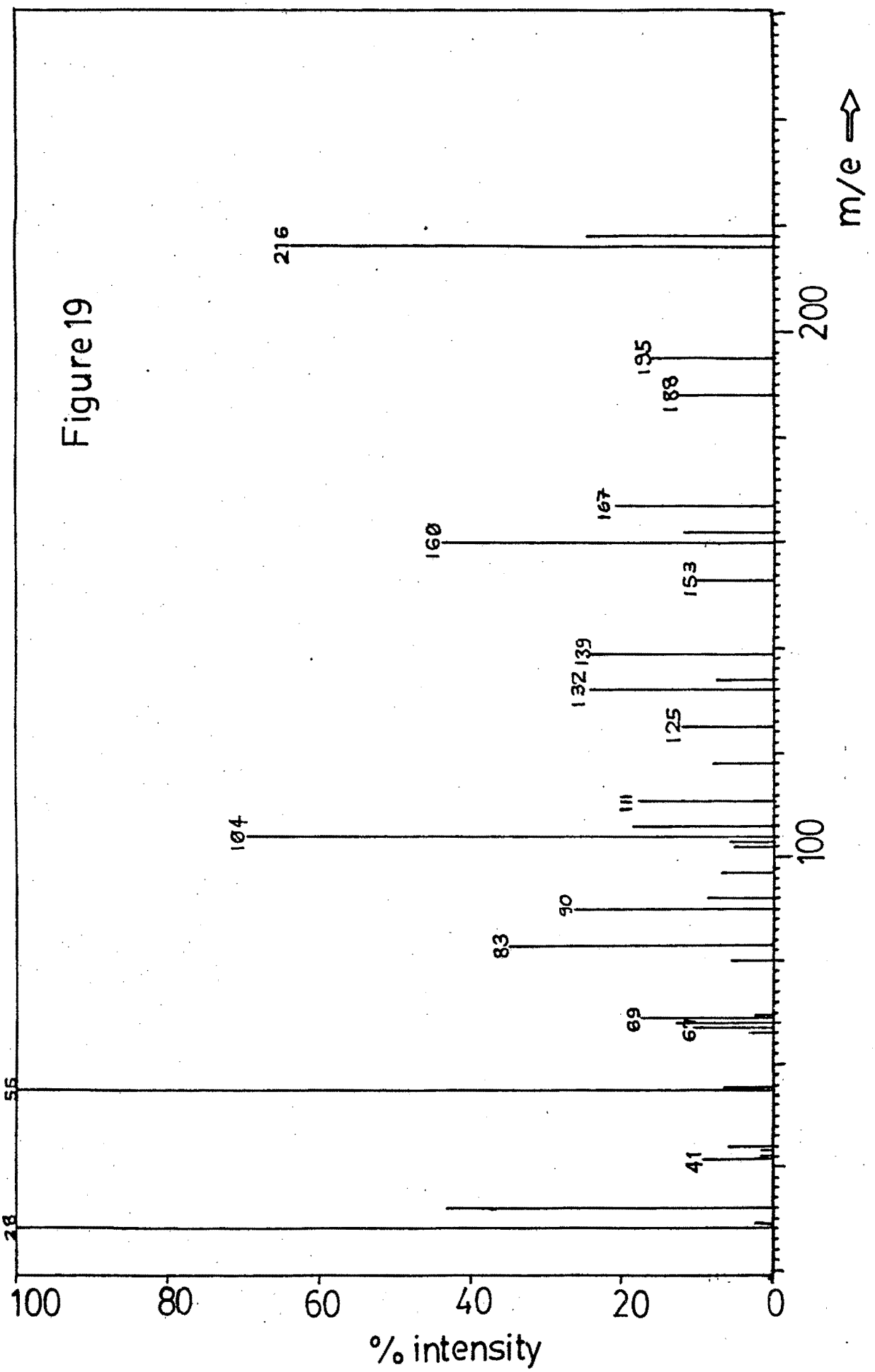
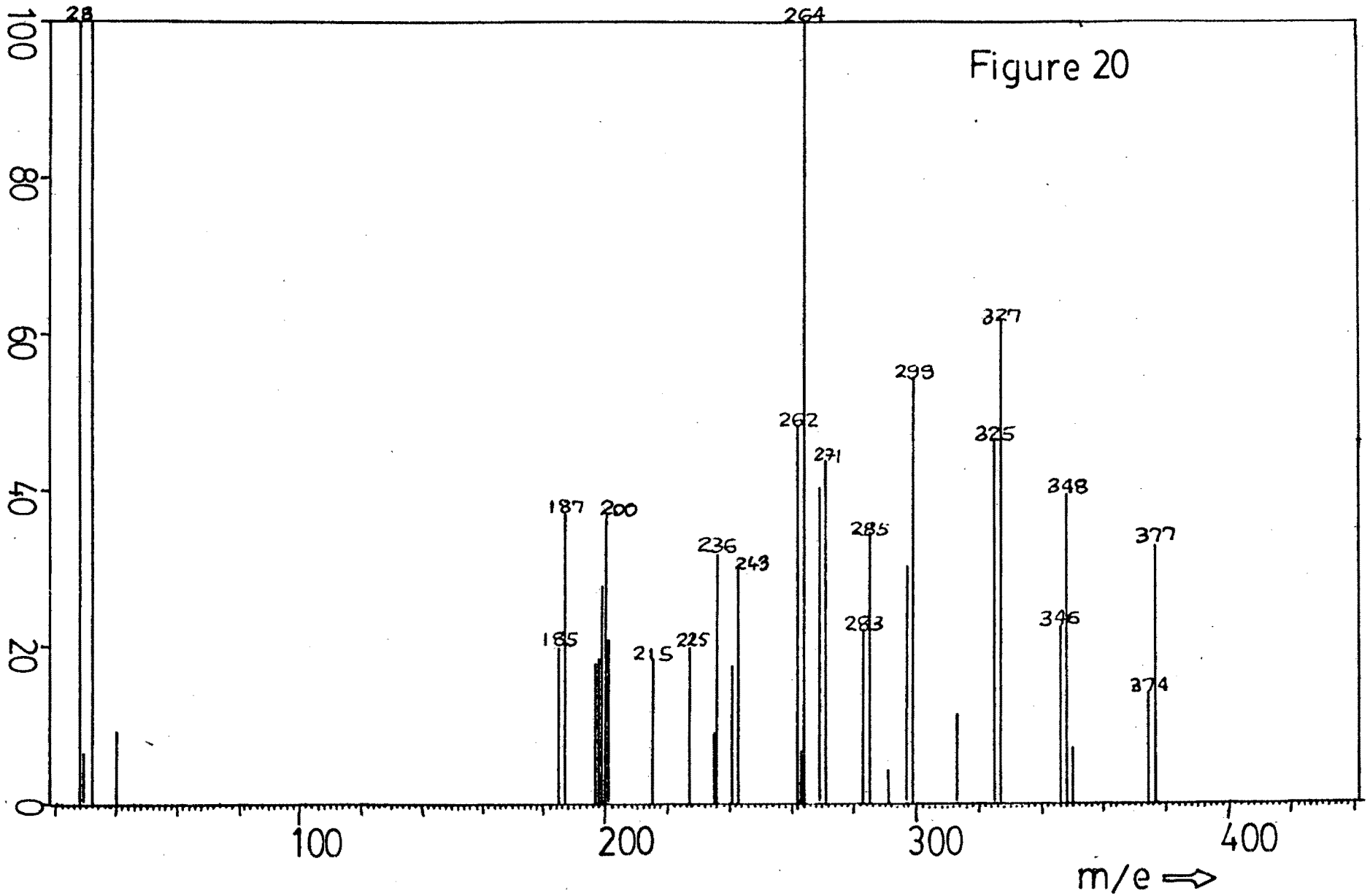


Figure 19. Mass spectrum of $[Mn(CO)_5CH_2Cl]$ (X).

Figure 20. Mass spectrum of $[Re(CO)_5CH_2Cl]$ (IX).



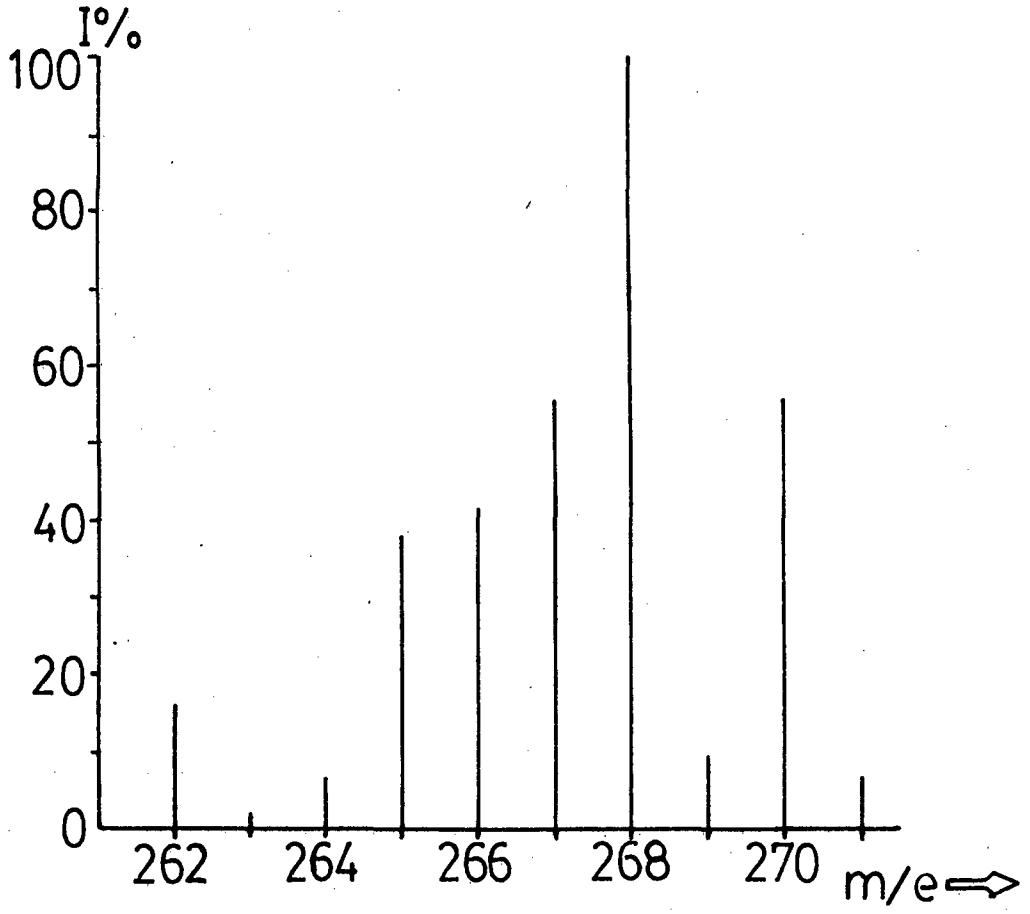


Fig.12 Calculated mass spectrum for $[Ru(Cp)(CO)_2CH_2OCH_3]^+$

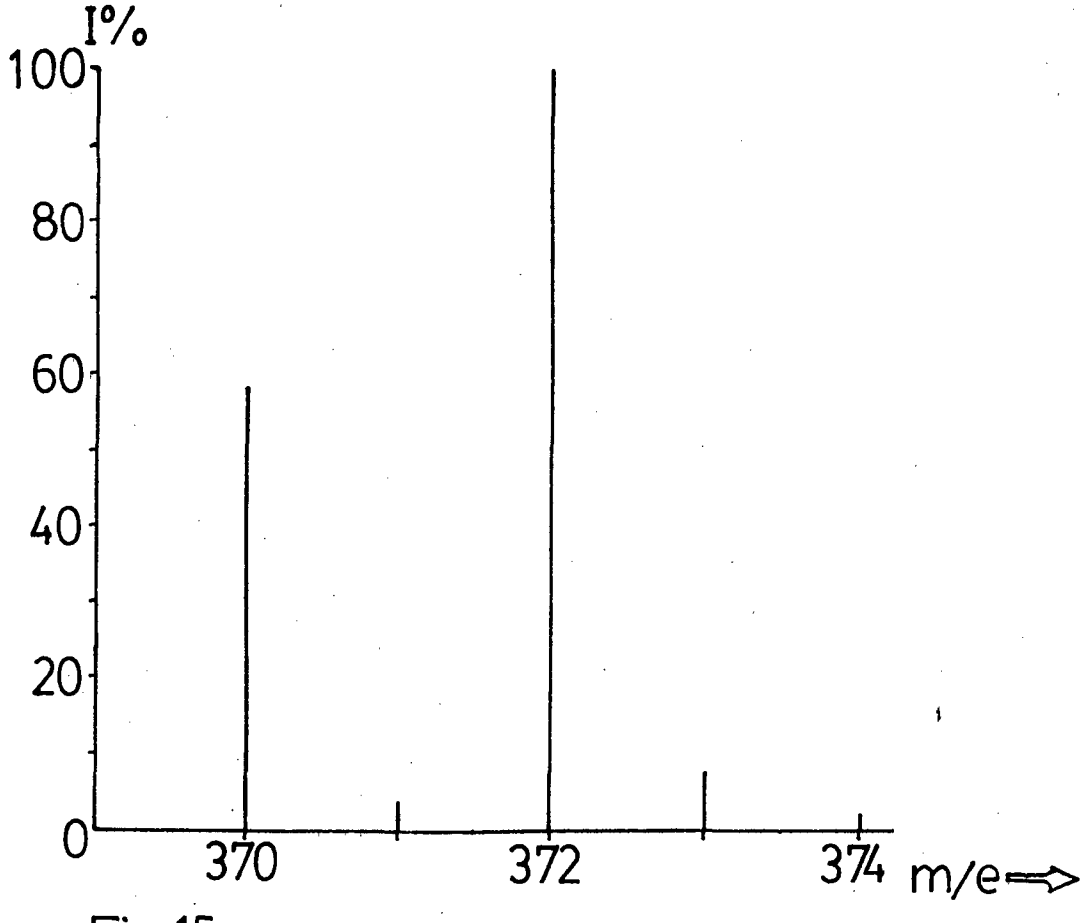


Fig.15 Calculated mass spectrum for $[Re(CO)_5CH_2OCH_3]^+$

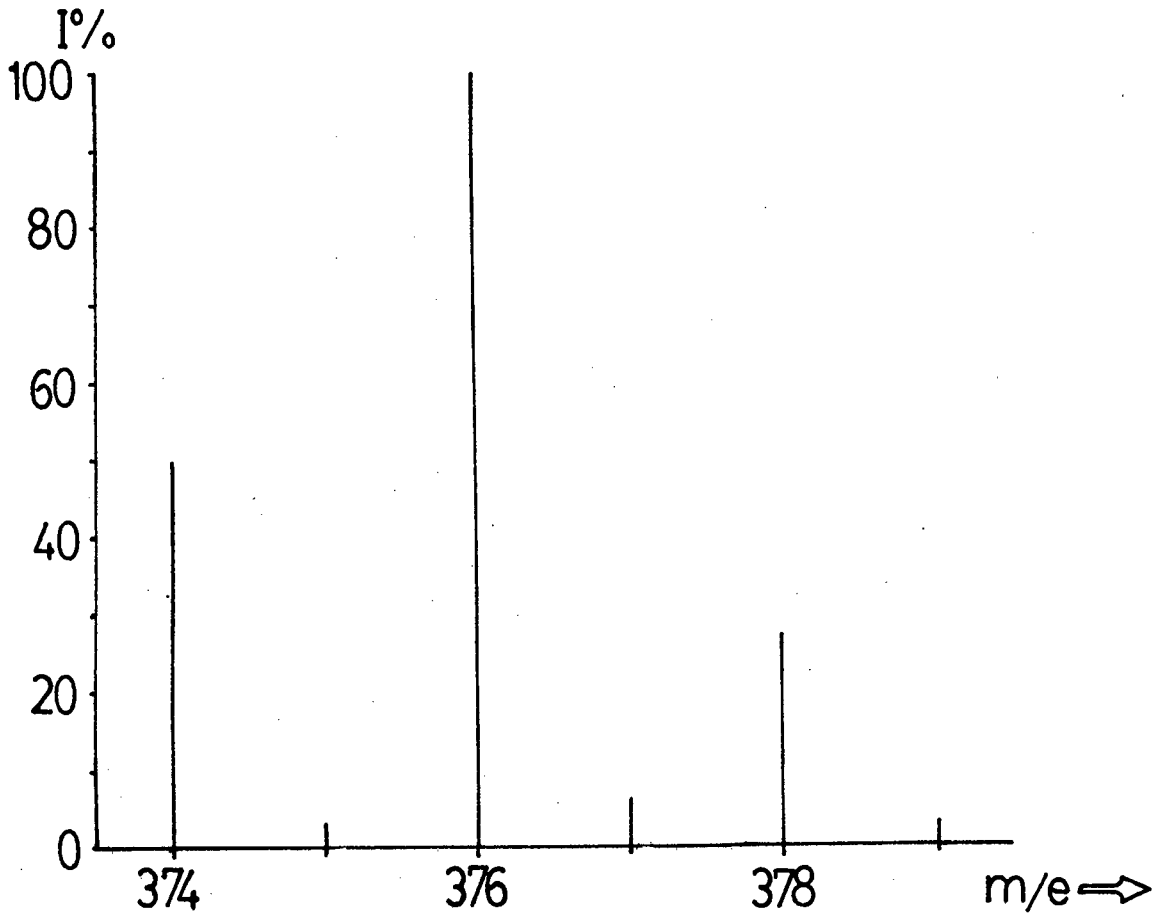


fig. 21 Calculated mass spectrum for $[Re(CO)_5CH_2Cl]^+$

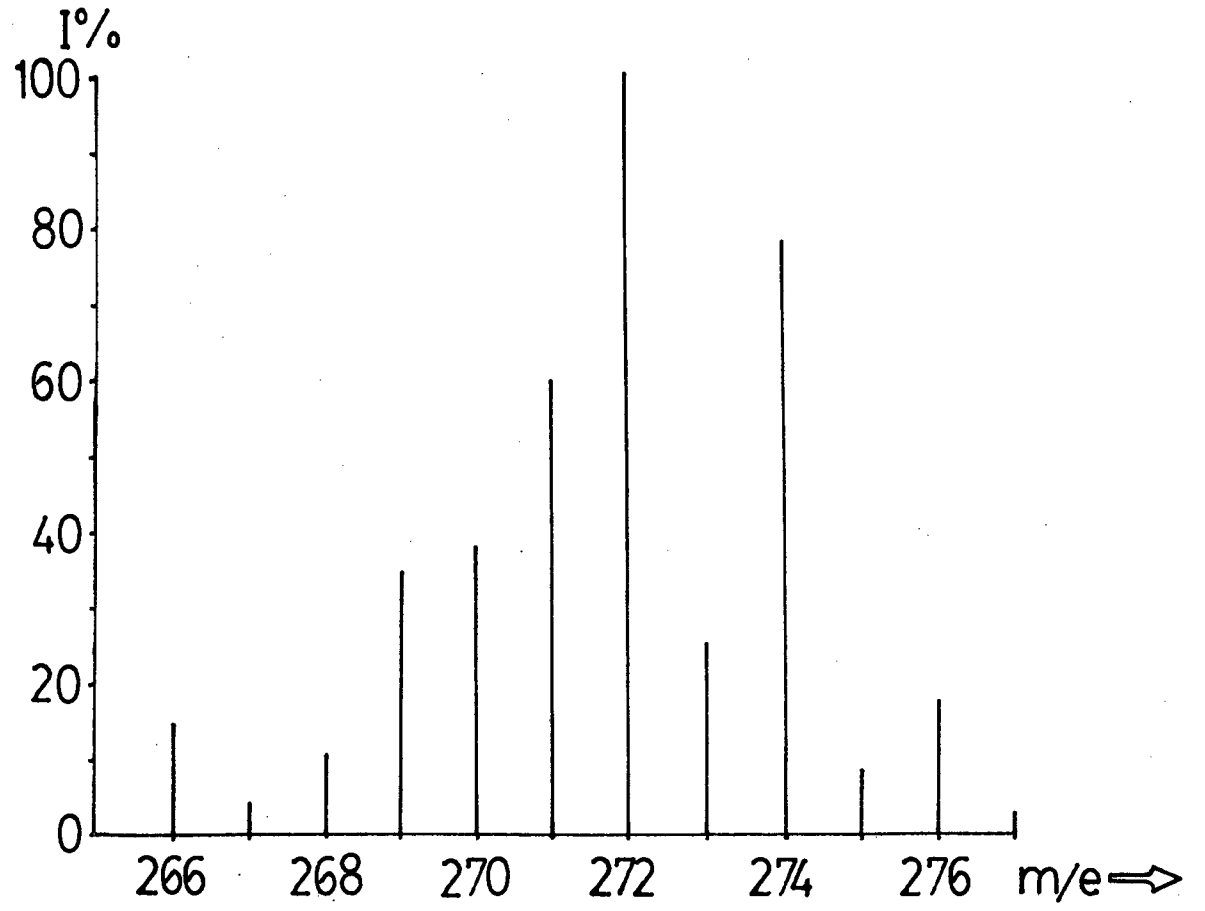


fig.18 Calculated mass spectrum for $[Ru(Cp)(CO)_2CH_2Cl]^+$

CHAPTER THREE

3. SOME REACTIONS OF CHLOROMETHYL AND METHOXYMETHYL TRANSITION METAL COMPLEXES WITH SOME TERTIARY PHOSPHINES, TRIMETHYLPHOSPHITE AND TRIPHENYLARSINE

3.1 Introduction

Methyl transition metal carbonyl complexes often react with tertiary phosphines to yield acyl complexes by carbonyl insertion.[24] However little work has been reported on the reactions of tertiary phosphines with methoxymethyl or chloromethyl transition metal complexes. Flood *et al*[50] have synthesized $[Fe(Cp)(CO)(PPh_3)CH_2OCH_3]$ (XV) by irradiating the corresponding dicarbonyl (V) in the presence of PPh_3, in benzene-pentane solution. (XV) was readily converted to $[Fe(Cp)(CO)(PPh_3)CH_2Cl]$ (XVI) by reaction with HCl.[50] (See section 2.1 for further discussion of this work). Similarly the complex $[Fe(Cp)(Ph_2PCH_2CH_2PPh_2)CH_2OCH_3]$ has been prepared by irradiating (V) in the presence of $[Ph_2PCH_2CH_2PPh_2]$.[62]

In our laboratory we are interested in investigating the reactions of phosphorus ligands* with methoxymethyl and chloromethyl transition metal complexes (see Scheme 10). Moss[52] has found that reaction of $[Fe(Cp)(CO)_2CH_2Cl]$ (VI) with PPh_3 in acetonitrile, in the dark at room temperature for five days, yields the cation $[Fe(Cp)(CO)_2CH_2PPh_3]^+$, isolated and characterized as the PF_6^- salt $[Fe(Cp)(CO)_2CH_2PPh_3]PF_6$. The BF_4^- salt of this cation, $[Fe(Cp)(CO)_2CH_2PPh_3]BF_4$ was reported by Reger and Culbertson,[80] who synthesized it from the reaction of $[Fe(Cp)(CO)_2(THF)]^+$ with CH_2PPh_3 (Equation 17). The analogous tungsten

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* In the following discussion the term "phosphorus ligands" applies to tertiary phosphines and tertiary phosphites.

$$[Fe(Cp)(CO)_2(THF)]^+ + CH_2PPh_3 \xrightarrow{THF} [Fe(Cp)(CO)_2CH_2PPh_3]^+ + THF \qquad (17)$$

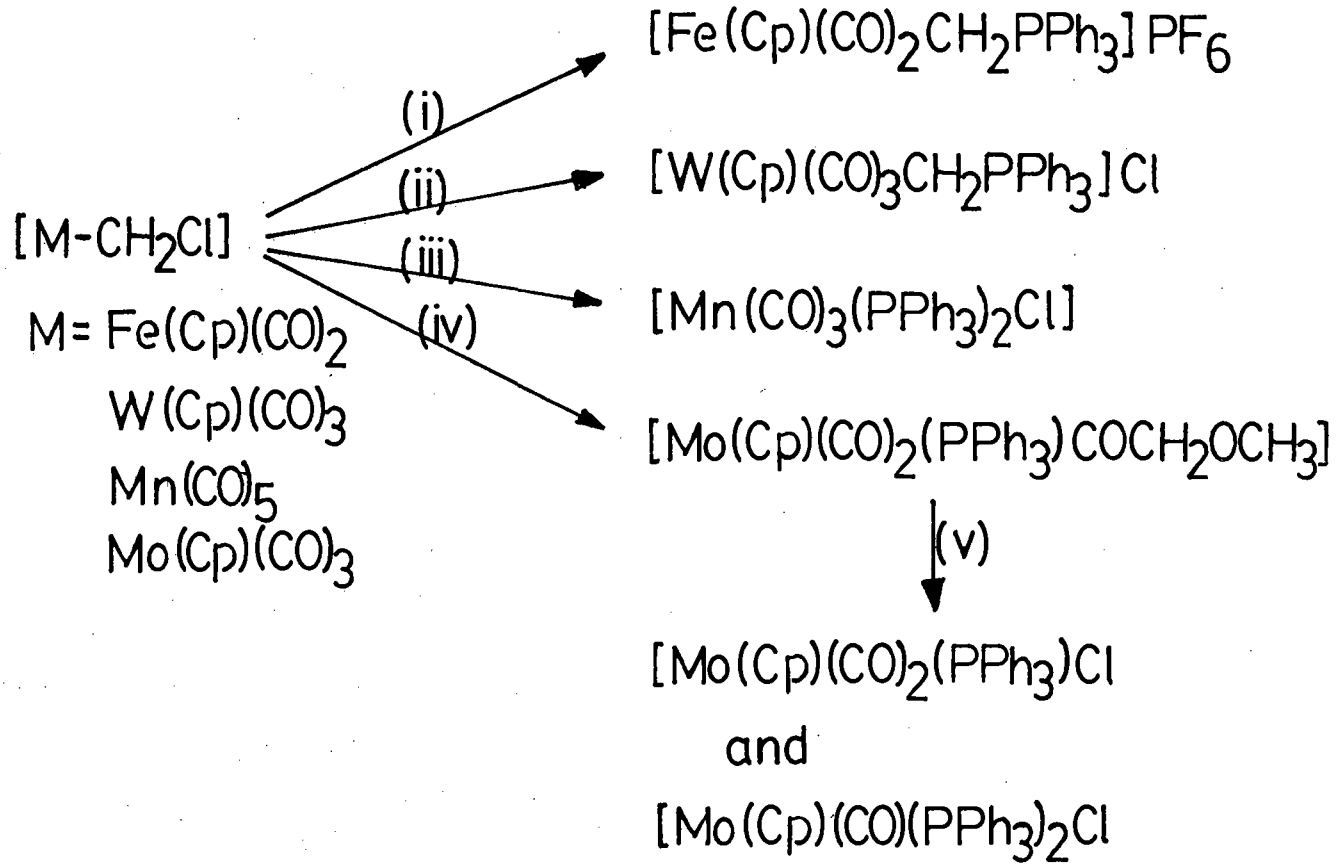
cation, $[W(Cp)(CO)_3CH_2PPh_3]^+$, was isolated as the chloride salt $[W(Cp)(CO)_3CH_2PPh_3]Cl$, from the reaction of $[W(Cp)(CO)_3CH_2Cl]$ (XIV) with PPh_3 in refluxing methanol for 4 hours.[52]

In contrast to the reaction with (XIV), it has been found that the corresponding Mo chloromethyl compound (XIII), when reacted with PPh_3 in refluxing methanol for 30 min., gave a complex identified as $[Mo(Cp)(CO)_2(PPh_3)COCH_2OCH_3]$[52] on the basis of its infrared and ^1H nmr spectra. Longer reaction times however gave $[Mo(Cp)(CO)_2(PPh_3)Cl]$ and $[Mo(Cp)(CO)(PPh_3)_2Cl]$.[52] Moss[52] found that $[Mo(Cp)(CO)_2(PPh_3)Cl]$ was also isolated in 71% yield from the reaction of (XIII) with PPh_3 in acetonitrile at room temperature in the dark for 28 days. These reactions are somewhat different to the reaction of the methyl complex $[Mo(Cp)(CO)_3CH_3]$ which on refluxing with PPh_3 in donor or hydrocarbon solvents (*e.g.* THF, hexane) gave mixtures of $[Mo(Cp)(CO)_2(PPh_3)CH_3]$ and $[Mo(Cp)(CO)_2(PPh_3)COCH_3]$.[81]

$[Mn(CO)_5CH_2Cl]$ (X), when reacted with PPh_3 in acetonitrile, at room temperature in the dark for 2 days, gave $[Mn(CO)_3(PPh_3)_2Cl]$.[52]

The work reported and discussed in this chapter continues the study of the reactions of chloromethyl and methoxymethyl transition metal complexes with phosphorus ligands.

Scheme 10



(i) PPh_3, acetonitrile, room temp., 5 days.

(ii) PPh_3, reflux methanol 4 hrs.

(iii) PPh_3, acetonitrile, room temp., 2 days.

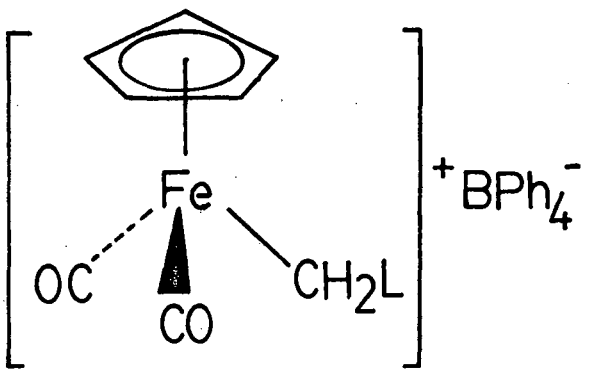
(iv) PPh_3, reflux methanol 30 mins.

(v) PPh_3, reflux methanol.

3.2 Results and discussion; Reactions with $[Fe(Cp)(CO)_2CH_2Cl]$

3.2.1a The reactions of $[Fe(Cp)(CO)_2CH_2Cl]$ with phosphorus ligands and triphenylarsine in methanol

The reactions of $[Fe(Cp)(CO)_2CH_2Cl]$ (VI) with PPh_3, $PMePh_2$, $PEtPh_2$ and $AsPh_3$, in refluxing methanol, gave the tetraphenylborate salts (XXXV), (XXXVI), (XXXVIII) and (XXXIX) respectively, in yields ranging from 54-74%, and in relatively short refluxing times (3½-5 hours, except in the case of $PMePh_2$ which was refluxed with (VI) for 20 hours). (XXXV) was also obtained as the iodide salt, from the reaction of $[Fe(Cp)(CO)_2CH_2OCH_3]$ (V), in refluxing methanol with $[Ph_3PH]I$.



(XXXV), L = PPh_3 (XXXVI), L = $PMePh_2$

(XXXVII), L = PMe_2Ph (XXXVIII), L = $PEtPh_2$

(XXXIX), L = $AsPh_3$ (XL), L = PEt_2Ph

The reaction with PMe_2Ph in refluxing methanol gave only 8% yield of (XXXVII) after 3 days. (XXXV) - (XXXIX) were isolated as air-stable yellowish solids.

The reaction of PEt_2Ph with (VI) in refluxing methanol gave a low yield of a brown powder. This product could not be purified; however the infrared spectrum in CH_2Cl_2 (νCO region) of it shows two strong bands at 2028, 1974 cm^{-1}, similar in position and appearance to those of (XXXV) - (XXXIX). This suggests that the product is (XL), $[Fe(Cp)(CO)_2CH_2PEt_2Ph]$ - (BPh_4) .

The reaction of bis(diphenylphosphino)ethane with (VI) in refluxing methanol gave, on removal of the solvent from the reaction mixture, an orange oil which could not be purified. However its infrared spectrum in CH_2Cl_2 gave two strong bands at 2023(s), 1968(s) cm^{-1} which is indicative of a dicarbonyl complex, possibly $[Fe(Cp)(CO)_2CH_2PPh_2CH_2CH_2PPh_2]^+$. Such a complex however may be reactive, due to the free end of the $[Ph_2PCH_2CH_2PPh_2]$ ligand, and di-iron complexes with a bridging phosphorus ligand may have been formed.

The reaction of $P(OMe)_3$ in refluxing methanol with (VI) was attempted. However after a period of 4 days, infrared spectra of the reaction mixture showed only the methoxymethyl complex, $[Fe(Cp)(CO)_2CH_2OCH_3]$ (V).

The reactions of (VI) with PPh_3, $PMePh_2$ and PMe_2Ph respectively in methanol were also conducted in the dark, at room temperature for several days. The reactions with PPh_3 and $PMePh_2$ gave (XXXV) and (XXXVI) but in slightly lower yield than the reactions conducted in refluxing methanol. No reaction took place between PMe_2Ph and (VI) even after 3 days of standing at room temperature, as shown by the infrared spectrum of the reaction mixture.

3.2.1b The mechanism for the reaction of phosphorus ligands and triphenylarsine with (VI) in methanol

In order to elucidate the prevailing mechanism, the reaction of (VI) with PPh_3 in methanol was investigated more thoroughly.

A small quantity of (VI) was dissolved in methanol, the solution left for 4 hours and the solvent removed. An infrared spectrum of the residue in cyclohexane showed the presence of (VI) and $[Fe(Cp)(CO)_2CH_2OCH_3]$ (V) in approximately equal quantities. This indicates the formation in methanol of an equilibrium mixture of (VI) and (V) (Equation 18); this fact was confirmed by the ^1H nmr spectrum of a solution of (VI) in CD_3OD.

$$[Fe(Cp)(CO)_2CH_2Cl] + CH_3OH \rightleftharpoons [Fe(Cp)(CO)_2CH_2OCH_3] + HCl \qquad (18)$$

When (VI) was dissolved in methanol and a phosphorus ligand added, *e.g.* PPh_3, infrared spectra in CH_2Cl_2 of the reaction mixture a short time after the addition showed only bands due to (V), indicating the equilibrium to be shifted considerably to the right (see Equation 18). It appears that addition of a weak base (*i.e.* the phosphorus ligand) removes HCl from the reaction mixture and hence shifts the equilibrium position to such an extent that (VI) is no longer seen in the infrared spectrum of the reaction mixture; Green[48] found that (VI) could be easily converted to (V) using a strong base, for example $NaOCH_3$. It is interesting to note that when PPh_3 was added to a solution of (VI) in methanol, and a methanolic solution of $NaBPh_4$ added immediately to the reaction mixture, a cream precipitate was formed. This was identified as the phosphonium salt $[Ph_3PH]BPh_4$ by comparison of its infrared spectrum with that of an authentic sample. This further indicates that PPh_3 reacts with HCl; it is suggested that

an equilibrium is formed (Equation 19).

$$PPh_3 + HCl \rightleftharpoons [HPPh_3]^+Cl^- \xrightarrow{NaBPh_4} [HPPh_3]BPh_4 \text{ precipitate} \qquad (19)$$

Thus there are at least four possible reactants in solution; (VI), (V), PPh_3 and $[Ph_3PH]^+$.

The reaction of (V) with PPh_3 was attempted, but no reaction occurred; however addition of an excess of aqueous HCl to the reaction mixture caused conversion of (V) to (VI) followed by the formation of (XXXV). (Equation 20).

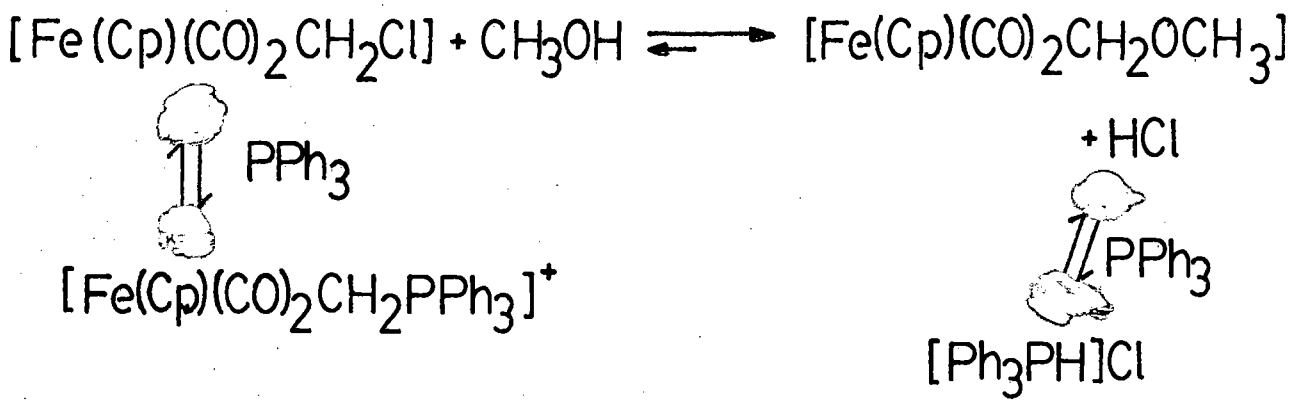
$$[Fe(Cp)(CO)_2CH_2OCH_3] \xrightleftharpoons{HCl} [Fe(Cp)(CO)_2CH_2Cl] \xrightarrow{PPh_3} [Fe(Cp)(CO)_2CH_2PPh_3]^+ \qquad (20)$$

In another reaction (V) was stood in methanol with $[Ph_3PH]I$. (V) was converted to an intermediate product [$\nu CO(CH_2Cl_2)$ 2025, 1972 cm^{-1}], possibly $[Fe(Cp)(CO)_2CH_2I]$. This was followed by the formation of (XXXV) (Equation 21).

$$[Fe(Cp)(CO)_2CH_2OCH_3] + [Ph_3PH]\,I \longrightarrow [Fe(Cp)(CO)_2CH_2I] \text{ (?)}$$
$$+ \; PPh_3 \longrightarrow [Fe(Cp)(CO)_2CH_2PPh_3]I \qquad (21)$$

On the basis of the above information it would appear that the reactive iron species, in the reaction with PPh_3 is (VI) as opposed to (V). (VI) then reacts with PPh_3 to give (XXXV) (Scheme II). It is reasonable to suggest that the other phosphines, which react with (VI) in methanol react in a similar way.

The reaction of (VI) with phosphorus ligands is probably a nucleophilic reaction (either S_N1 or S_N2). (Figures 22, 23). The S_N2 reaction would



Scheme 11: Reaction of (VI) with PPh_3 in methanol.

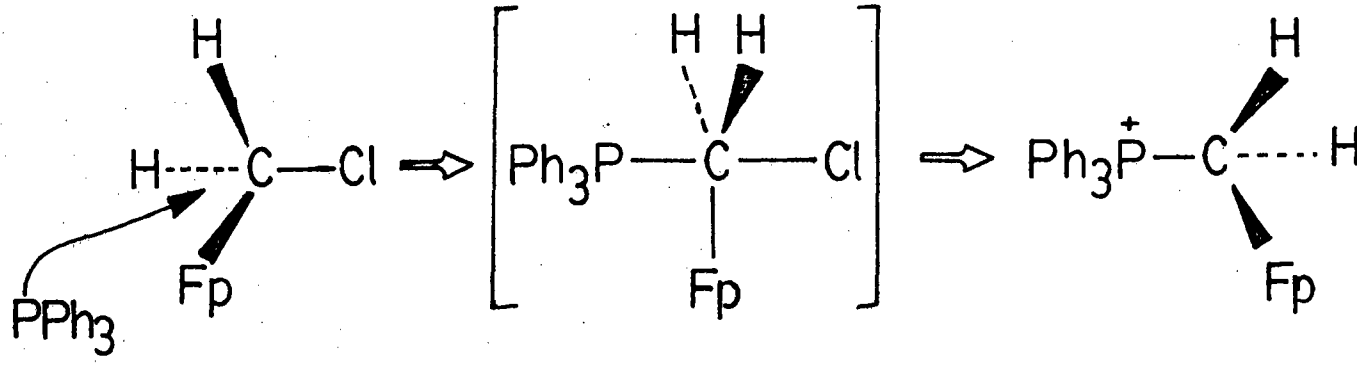


Figure 22: S_N2 reaction of (VI) with PPh_3
[Fp = $Fe(Cp)(CO)_2$]

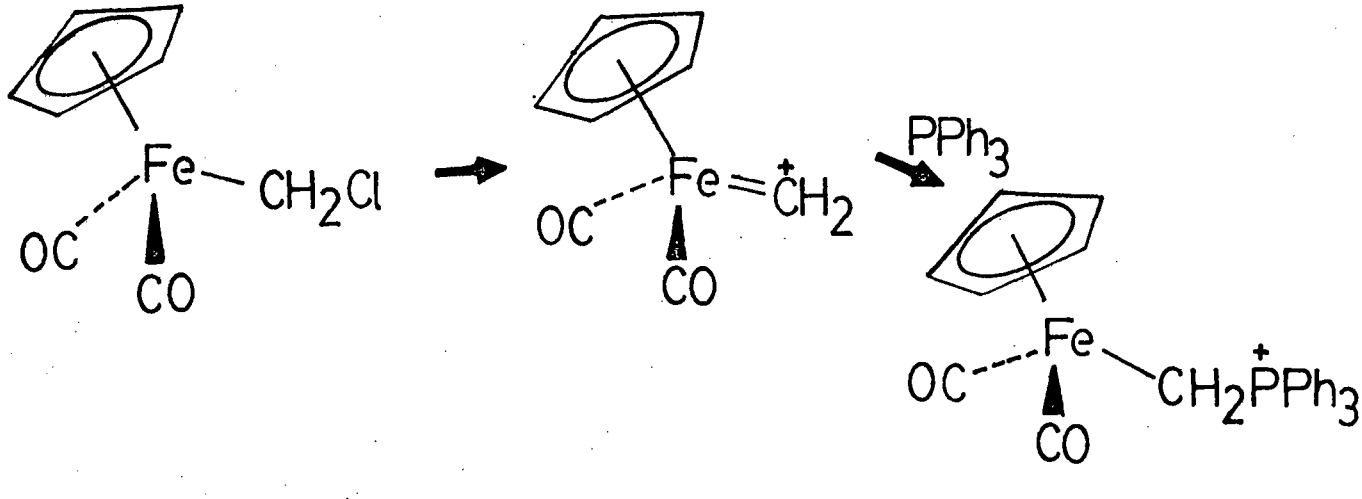


Fig. 23: S_N1 reaction of (VI) with PPh_3

be more influenced by the steric bulk of the phosphorus ligand than the S_N1 reaction, as a phosphorus ligand approaching from behind the molecule (as indicated in Figure 22) would interact sterically with the large $[Fe(Cp)(CO)_2]$ part of the molecule. Thus the more bulky the phosphorus (or arsenic) ligand, the less likely it will be to react with (VI) *via* the S_N2 mechanism.

Tolman[82,83] has defined the cone angle, θ, of a phosphorus ligand, as a semi quantitative model for estimating the steric effect thereof (Figure 24).

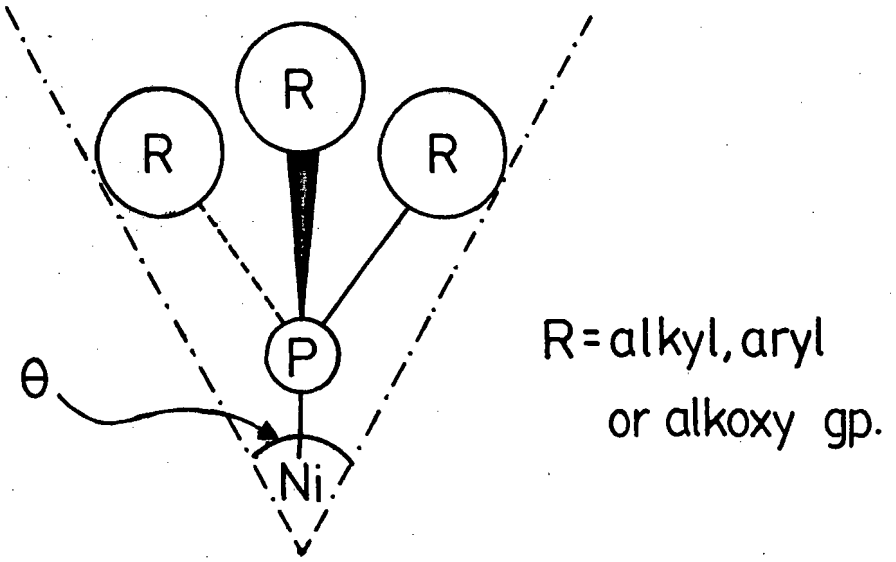


Figure 24. The cone angle, θ, of a phosphorus ligand (Reference 83).

Values of cone angles for the phosphorus ligands used in our work have been presented in Table 14.

It appears that the ease of formation of (XXXV)-(XL) is largely independant of the cone angle. The phosphines PPh_3, $PMePh_2$ and $PEtPh_2$ form (XXXV), (XXXVI) and (XXXVIII) respectively in yields >50% and in reaction times of 3½-20 hours. However PMe_2Ph and PEt_2Ph form (XXXVII) and (XL) much

more reluctantly, in poor yield even after 3-5 days refluxing. PMe_2Ph and PEt_2Ph thus display similar reactivity towards (VI); however their cone angles are different (Table 14). On the other hand, $PMePh_2$ and PEt_2Ph both have cone angles of 136° but the former is considerably more reactive towards (VI) than the latter.

This suggests that the reaction of (VI) with phosphorus ligands is S_N1; if this is so, it implies the intermediacy of a positively-charged intermediate, possibly the carbene species $[Fe(Cp)(CO)_2CH_2]^+$ (Figure 23).

Complexes (XXXV)-(XL) can be regarded essentially as quaternary phosphonium salts. A general synthesis of phosphonium salts is in fact the reaction of a tertiary phosphine with an alkyl halide (Equation 22).[84]

$$Ph_3P + RBr \longrightarrow [Ph_3PR]^+Br^- \qquad (22)$$

R = alkyl groups

However, with primary and secondary alkyl halides [(VI) can be considered a primary alkyl halide] the reaction is usually S_N2.[85] However, preparations of phosphonium salts involving S_N1 mechanisms are known (for example, reference 86).

Table 14.

Phosphine	pKa[a]	Cone angle, θ° [b]
PPh_3	2.73	145
$PEtPh_2$		140
$PMePh_2$		136
PEt_2Ph	6.25	136
PEt_3[c]	8.69	132
PMe_2Ph	6.49	122
PMe_3	8.65	118
$P(OMe)_3$		107

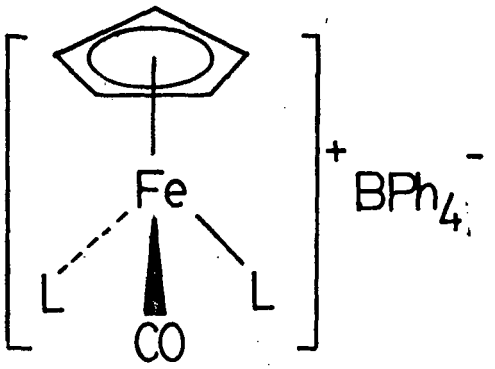
a Reference 87
b Reference 82, appendix B
c Values for PEt_3 are included for comparison but the ligand was not used in our work.

pKa values for the tertiary phosphines are also listed in Table 14.[87] It is interesting to note that the more basic the phosphine the less reactive it has been found to be towards (VI). PEt_2Ph and PMe_2Ph are more basic than PPh_3 but less reactive towards (VI). One would expect the more basic ligands to be more reactive if the reaction is nucleophilic. A possible explanation for this is that a more basic ligand also shows a greater tendency to react with HCl (see Scheme II) to produce the phosphonium salt. This reaction would have the effect of reducing the availability of the reactants (VI) and the phosphorus ligand.

3.2.2 The reactions of $[Fe(Cp)(CO)_2CH_2Cl]$ with some phosphorus ligands in acetonitrile

The reaction of $PMePh_2$ with (VI) in acetonitrile at room temperature gave $[Fe(Cp)(CO)_2CH_2PMePh_2]^+$, as the BPh_4^- salt (XXXVI), in 33% yield. The analogous PPh_3 product (XXXV) was obtained from the reaction of (VI) with PPh_3 in acetonitrile[52] (Scheme IO).

The only products isolated from the reactions of (VI) with PMe_2Ph and PMe_3 were (XLI) and (XLII), isolated as air-stable yellow needles in 81% and 32% yield respectively. (XLII) has recently been reported by Treichel *et al.*[88] Treichel obtained the BF_4^- salt of (XLII) $[Fe(Cp)(CO)(PMe_3)_2]BF_4$, from the reaction of $[Fe(Cp)(CO)_2(THF)]BF_4$ with PMe_3 in refluxing acetone, and the PF_6^- salt of (XLII) by refluxing $[Fe(Cp)(CO)(PMe_3)Br]$ with PMe_3 in toluene. He also obtained the iodide salt of (XLII), $[Fe(Cp)(CO)(PMe_3)_2]I$ by refluxing $[Fe(Cp)(CO)_2PMe_3]I$ with PMe_3 in acetonitrile.[88]



(XLI) L = PMe (XLIII) L = $PEtPh_2$

(XLII) L = PMe_3 (XLIV) L = PEt_2Ph

Two products were isolated from the reaction of (VI) with PEt_2Ph; $[P(CH_3)(C_2H_5)_2Ph]BPh_4$ was isolated as white air-stable needles, and (XLIV) as yellow platelets.

The reaction of (VI) with $PEtPh_2$ gave a yellow solid. This product could not be purified, but its infrared spectrum in CH_2Cl_2 shows one νCO band at 1962 cm^{-1}, which suggests that it is (XLIII). $P(OMe)_3$ did not react with (VI) over 6 days.

Complexes (XLI), (XLII) and (XLIV) all show intermediate phosphorus-phosphorus coupling in their ^1H nmr spectra.[89] Thus $[Fe(Cp)(CO)(PMe_2Ph)_2]BPh_4$ showed two pseudotriplet patterns each integrating for 6 protons and $[Fe(Cp)(CO)(PMe_3)_2]BPh_4$ showed one pseudotriplet pattern, integrating for 18 protons (Figure 25). The complex $[Fe(Cp)(CO)(PEt_2Ph)_2]BPh_4$ shows a complex series of multiplets in the region of δ1-δ2 p.p.m. in its ^1H nmr spectrum which were not resolved.

The way in which, and the extent to which, the basicity of the ligand or

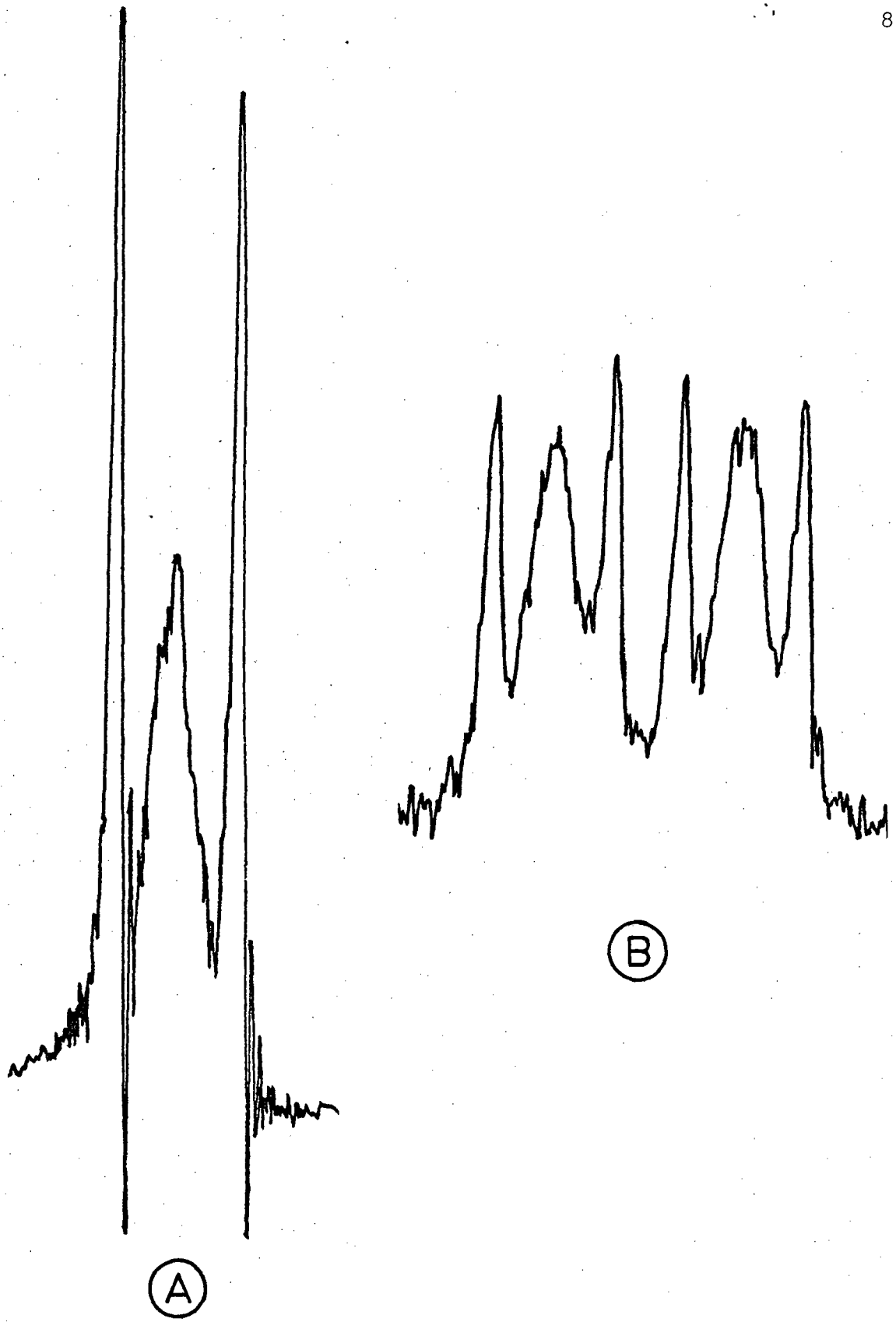


Fig 25. Intermediate P–P coupling.

A. Peaks for (Me) protons, (XLII)

B. Peaks for (Me) protons, (XLI)

the size of the ligand (*i.e.* the cone angle) (Table 14) influence the reaction of (VI) with phosphorus ligands in acetonitrile is not clear from the results obtained. The formation of $[Fe(Cp)(CO)_2CH_2L]^+$ or $[Fe(Cp)(CO)(L)_2]^+$ (L = phosphorus ligand) appears to be influenced by the basicity of the phosphorus ligand in that the more basic ligands tend to form cations of the form $[Fe(Cp)(CO)(L)_2]^+$. The ligands with the largest cone angles would be expected to form cations of the form $[Fe(Cp)(CO)_2CH_2L]^+$; the formation of $[Fe(Cp)(CO)(L)_2]^+$ would result in greater steric crowding due to the two L ligands attached to the Fe atom. However, note that $PEtPh_2$ appears to form $[Fe(Cp)(CO)(PEtPh_2)_2]^+$ whereas $PMePh_2$, having a slightly smaller cone angle, forms $[Fe(Cp)(CO)_2CH_2PMePh_2]^+$. Further, PEt_2Ph forms $[Fe(Cp)(CO)(PEt_2Ph)_2]^+$ although it has the same cone angle as $PMePh_2$.

The mechanisms of the reactions of (VI) with phosphorus ligands, in acetonitrile, under the conditions used, are not known. Noteworthy, however, is the product $[P(CH_3)(C_2H_5)_2(Ph)]BPh_4$, isolated from the reaction of PEt_2Ph with (VI). This phosphonium salt could possibly arise from the abstraction of a CH_2 group by the phosphine from the $[CH_2Cl]$ ligand of (VI).

3.3 Results and discussion; reactions of $[Ru(Cp)(CO)_2CH_2OCH_3]$, $[Mn(CO)_5CH_2Cl]$, $[Mn(CO)_5CH_2OCH_3]$, $[Re(CO)_5CH_2Cl]$, $[W(Cp)(CO)_3CH_2Cl]$ and $[Re(CO)_5CH_2OCH_3]$ with PPh_3.

It is interesting to compare the reactions of some other chloromethyl and methoxymethyl transition metal complexes with PPh_3, with the reactions of (VI) with PPh_3 as discussed in section 3.2. The reactions discussed in this section were conducted either in acetonitrile, or methanol, or both; the only ligand used was PPh_3.

3.3.1 The reaction of $[Ru(Cp)(CO)_2CH_2Cl]$ (XXXIII) with PPh_3 in methanol

We found that when (XXXIII) was refluxed with PPh_3 in methanol for 5 days, the major product isolated was $[Ru(Cp)(CO)_2CH_2OCH_3]$ (XXXII). A small amount of a yellow oil was also obtained, but the quantity was too small to enable its identification.

We suggest then an equilibrium is set up between (XXXII) and (XXXIII) (Equation 23) similar to that described for (VI) and (V) in Equation 18.

$$[Ru(Cp)(CO)_2CH_2Cl] + CH_3OH \rightleftharpoons [Ru(Cp)(CO)_2CH_2OCH_3] + HCl \qquad (23)$$

This equilibrium suggests that (XXXIII) might easily be converted to (XXXII) by the reaction of NaOMe, as shown by Green[48] for the corresponding Fe complexes (VI) and (V). Neither (XXXII) or (XXXIII) however, appeared to react with PPh_3.

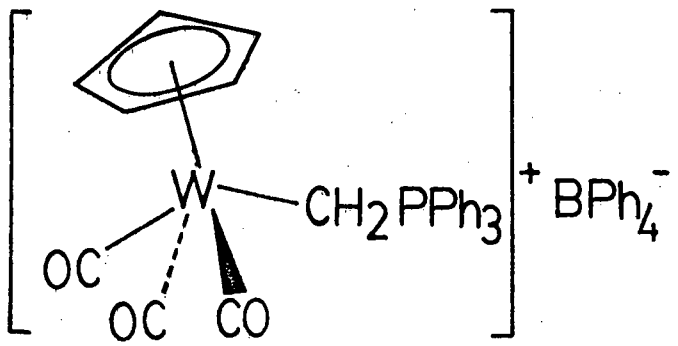
3.3.2 Reaction of $[W(Cp)(CO)_3CH_2Cl]$ (XIV) with PPh_3 in acetonitrile

Other workers in our laboratory[52] found that (XIV) reacted with PPh_3 in refluxing methanol to give the complex $[W(Cp)(CO)_3CH_2PPh_3]Cl$ in 35% yield.

(Scheme 8). We found that the reaction of (XIV) with PPh_3 in acetonitrile gave the same cation (precipitated as the BPh_4^- salt (XLV)) in 20% yield after 34 days (Equation 24). The reaction thus proceeded very

$$[W(Cp)(CO)_3CH_2Cl] + PPh_3 \longrightarrow [W(Cp)(CO)_3CH_2PPh_3]BPh_4 + Cl^- \quad (24)$$

slowly. Similar reaction times were needed for the reaction of $[Mo(Cp)(CO)_3CH_2Cl]$ (XIII) with PPh_3 in acetonitrile;[52] this reaction however gave the complex $[Mo(Cp)(CO)_2(PPh_3)Cl]$ in 71% yield.



(XLV)

3.3.3 The reaction of $[Mn(CO)_5CH_2OCH_3]$ (VIII) with PPh_3

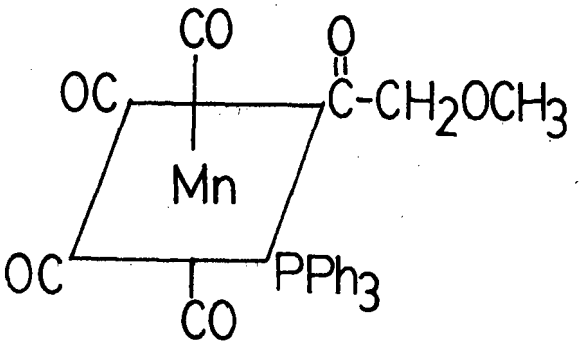
The reaction of (VIII) with PPh_3 in acetonitrile at room temperature gave *cis*-$[Mn(CO)_4(PPh_3)COCH_2OCH_3]$ (XLVI). The *cis* configuration was assigned on the basis of the four terminal νCO bands which appeared in the infrared spectrum. The acyl carbonyl group was indicated by a band at 1640 cm^{-1} in the infrared spectrum in CH_2Cl_2 solution (occurred at 1603 cm^{-1} in the spectrum of a nujol mull of (XLVI)).

When (VIII) was reacted with PPh_3, refluxing in methanol, two products were formed, depending on the reaction time and the quantity of phosphine used. Reaction of (VIII) with a 1:1 mole ratio of PPh_3 (or less PPh_3) gave *cis*-$[Mn(CO)_4(PPh_3)CH_2OCH_3]$ (XLVII) in 74% yield. Reaction (VIII) with an excess of PPh_3 gave (XLVII) initially, but with longer refluxing times (XLVII) was partially converted to *trans*-$[Mn(CO)_3(PPh_3)_2CH_2OCH_3]$ (XLVIII). Yields of (XLVIII) were low; even with a double excess of phosphine (XLVIII) was isolated in only 26% yield, and (XLVII) was still the major product of the reaction.

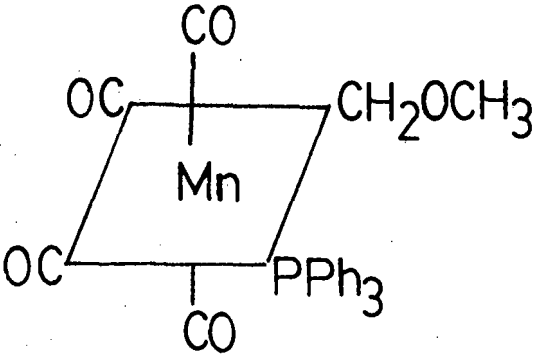
(XLVII) is assigned the *cis* configuration on the basis of the 4 νCO bands which appeared in its infrared spectrum.

It is possible for $[Mn(CO)_3(PPh_3)_2CH_2OCH_3]$ to have three possible configurations, (i), (ii) and (iii) (Figure 26). These three configurations can be distinguished by their infrared and ^1H nmr spectra. Three strong bands are expected to appear in the infrared spectrum of isomer (iii) while the infrared spectrum of (i) is expected to show a weak and two strong νCO bands. Configuration (ii) can be distinguished from (i) by its ^1H nmr spectrum. The $\underline{CH}_2$ protons of the $[CH_2OCH_3]$ ligand are expected to show a triplet in (i) as the symmetry of the molecule makes the PPh_3 ligands equivalent. However in (ii) a doublet of doublets is expected, due to the non-equivalence of the two PPh_3 ligands.

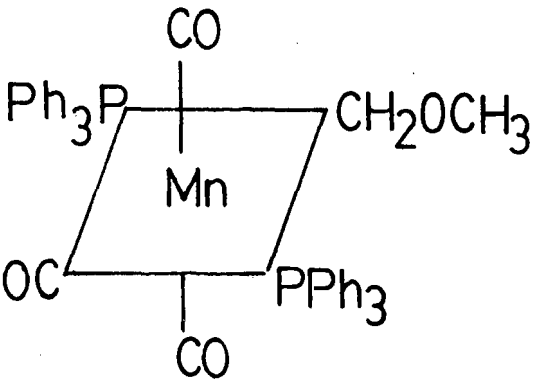
A weak, a strong and a medium band are seen in the infrared spectrum of (XLVIII) in CH_2Cl_2 solution. A triplet appears in the ^1H nmr spectrum of (XLVIII) for the $\underline{CH}_2$ protons of the $[CH_2OCH_3]$ ligand. Thus configuration (i) has been assigned to it, and, on account of the *trans* phosphine ligands, a *trans* nomination.



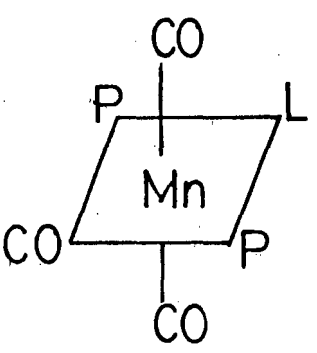
(XLVI)



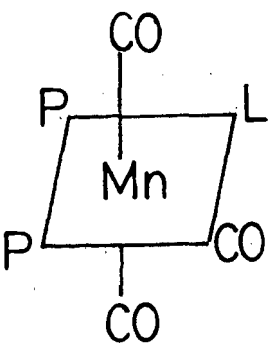
(XLVII)



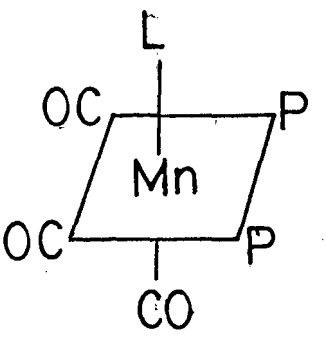
(XLVIII)



(i)



(ii)



(iii)

Fig. 26: possible configurations of $[Mn(CO)_3(P)_2L]$
$P = PPh_3$, $L = CH_2OCH_3$

3.3.4 Reaction of $[Mn(CO)_5CH_2Cl]$ (X) with PPh_3 in methanol

Workers in our laboratory[52] have previously found that the reaction of (X) with PPh_3 in acetonitrile at room temperature gave $[Mn(CO)_3(PPh_3)_2Cl]$. We found that the same complex was obtained from the reaction of (X) with PPh_3 in methanol. The complex $[Mn(CO)_3(PPh_3)_2Cl]$ would appear to be *trans* on the basis of the peaks obtained in infrared spectrum, which shows a weak, a strong and a medium band. ($\nu CO(CH_2Cl_2)$ 2038(w), 1950(s), 1920(m) cm^{-1}).

3.3.5 The reactions of $[Re(CO)_5CH_2Cl]$ (IX) and $[Re(CO)_5CH_2OCH_3]$ (VII) with PPh_3

It is interesting to compare the reactions of (IX) and (VII) with PPh_3 in acetonitrile, with the reactions of the analogous Mn complexes (X) and (VIII) (Sections 3.3.3 and 3.3.4). (IX) showed no reaction with PPh_3 after 5 days at room temperature. (VII) also showed no reaction with PPh_3, neither after 4 days at room temperature, nor after 2 hours in refluxing acetonitrile.

CHAPTER FOUR

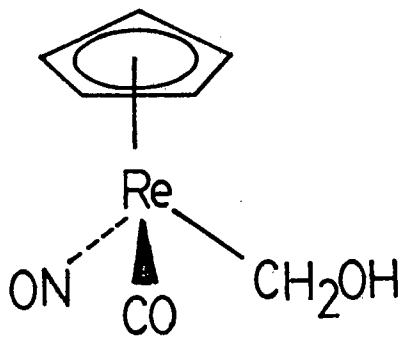
4. SOME ATTEMPTS TO SYNTHESIZE HYDROXYMETHYL COMPLEXES

Hydroxymethyl species, containing a $[CH_2OH]$ ligand, have been postulated as intermediates in the Fischer-Tropsch reaction[1] (see Section 1.3.1). Chloromethyl and methoxymethyl complexes, $[L_nMCH_2X]$ (X = Cl,OCH_3, L = ligands, M = transition metal) are possible precursors of hydroxymethyl complexes, as the $[CH_2X]$ ligand is fairly easily attacked by nucleophiles, Nu^- (Equation 25) (see Section 2.1).

$$[L_nMCH_2X] + Nu^- \longrightarrow [L_nMCH_2Nu] + X^- \qquad (25)$$

4.1 Hydroxymethyl complexes

The first hydroxymethyl complex to be isolated and characterised, complex (IV), was reported virtually simultaneously by Casey *et al*[16] and by Graham and Sweet.[17]



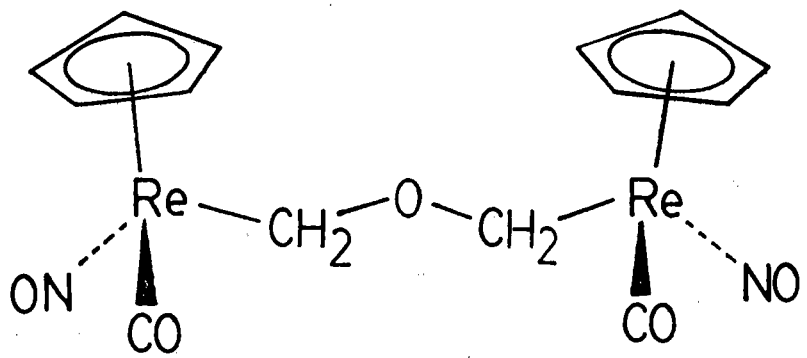
(IV)

It was synthesized by the following methods:

i Hydrolysis of the methoxymethyl complex $[Re(Cp)(CO)(NO)CH_2OCH_3]$ (Equation 26).[16]

$$[Re(Cp)(CO)(NO)CH_2OCH_3] \xrightarrow[CF_3COOH]{THF/H_2O} [Re(Cp)(CO)(NO)CH_2OH] \qquad (26)$$

The reaction outlined in Equation 26 involves acid-catalysed nucleophilic attack of H_2O on the $[CH_2OCH_3]$ ligand, with replacement of the $[OCH_3]$moiety with OH, and probably with elimination of methanol. It was necessary to quench the reaction with triethylamine after 2½ hours reaction time, in order to prevent the formation of the dimer $[Re(Cp)(CO)(NO)CH_2]_2O$ (XLIX).[16]

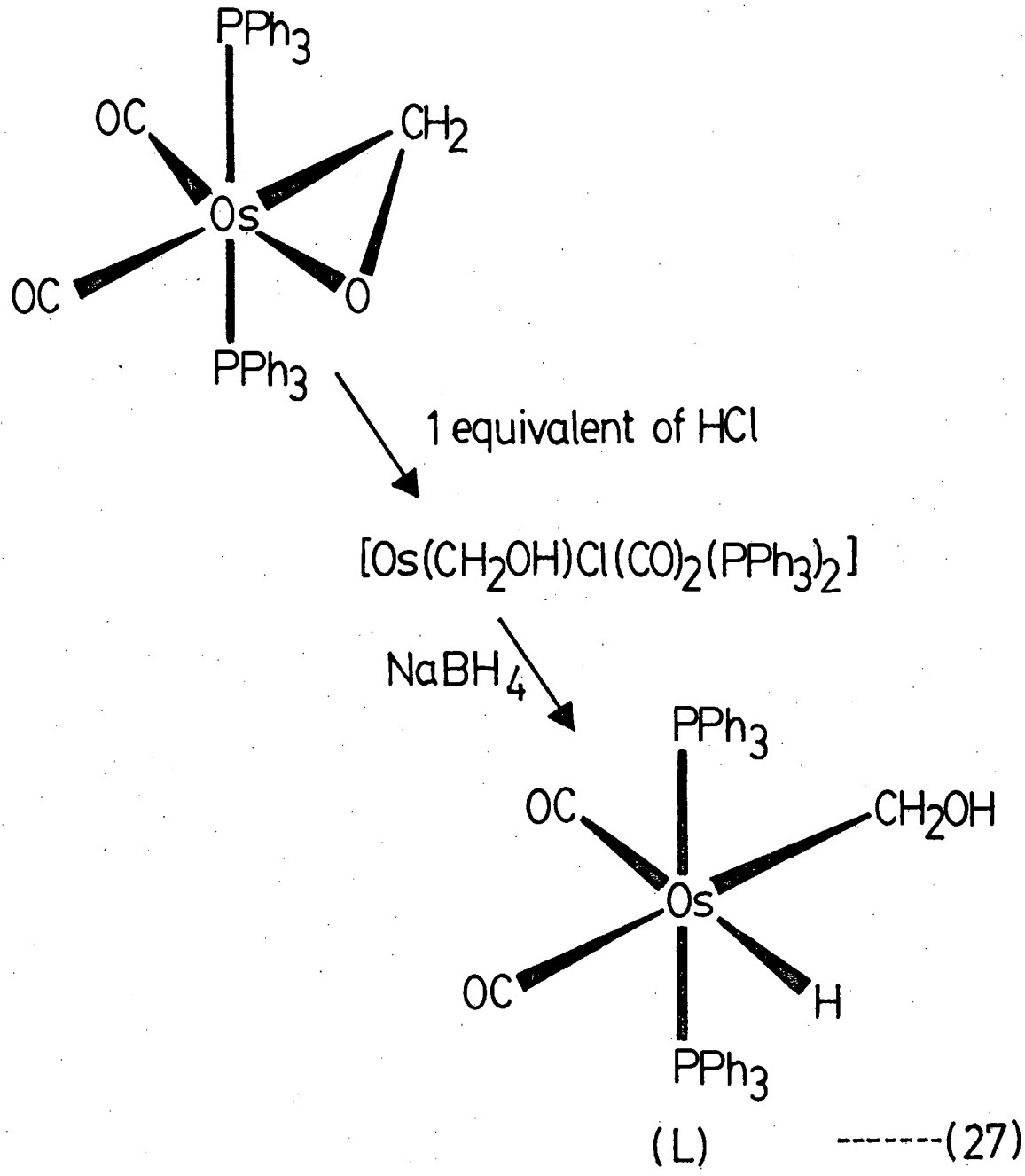


(XLIX)

ii Reductions: Both Casey[16] and Graham[17] synthesized (IV) by reduction reactions. Thus (IV) was a product of the reduction of $[Re(Cp)(CO)(NO)CHO]$ (I) by diisobutylaluminium hydride[16] or by 1 equivalent of $NaBH_4$ in a THF/water mixture.[17] (IV) was also a product of the reduction of $[Re(Cp)(CO)_2NO]^+$ by sodium diethylaluminium hydride,[16] or by 2 equivalents of $NaBH_4$ in a THF/water mixture.[17] (See Scheme 2 and Scheme 3, pages 11 and 12).

^1H nmr studies showed that complex (IV) was an intermediate in the methanolysis of the metallo ester dimer, (XVIII) (Scheme 5, page 25). However (IV) reacted further with methanol to give $[Re(Cp)(CO)(NO)CH_2OCH_3]$.[16]

Since the isolation of (IV), the hydroxymethyl complex $[OsH(CH_2OH)(CO)_2(PPh_3)_2]$ (L) has been isolated and characterized.[91]



(L) -------(27)

(L) was synthesized *via* an intermediate hydroxymethyl complex, $[Os(CH_2OH)Cl(CO)_2(PPh_3)_2]$ from the coordinated-formaldehyde complex $[Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2]$. (Equation 27).[91] Complex L is significant in that it has an hydride ligand adjacent to the $[CH_2OH]$ ligand, and thus models intermediates proposed in the Fischer-Tropsch reaction[1] (Step 5, Scheme I, page 8).

Other than (IV) and (L), transition metal hydroxymethyl complexes have not been isolated. Several, however have been proposed as intermediates in reactions. Casey *et al*[16] have reviewed much of the literature concerning transition metal hydroxymethyl complexes, and it is thus not reviewed again here.

4.2 Results and discussion

We attempted the synthesis of hydroxymethyl complexes in the following three ways:

i Basic hydrolysis of chloromethyl complexes (Equation 28).

$$[L_nMCH_2Cl] + OH^- \xrightarrow{H_2O} [L_nMCH_2OH] + Cl^- \quad (28)$$

(L = ligands, M = transition metal).

ii Acid-catalysed hydrolysis of methoxymethyl complexes (Equation 29).

$$[L_nMCH_2OCH_3] + H_2O \xrightarrow{H^+} [L_nMCH_2OH] + CH_3OH \quad (29)$$

(L = ligands, M = transition metal).

iii Reaction of metal carbonyl anions with formaldehyde (Equation 30).

$$Na[L_nM] + CH_2O \xrightarrow{H^+} [L_nMCH_2OH] \quad (30)$$

(L = ligands, M = transition metal).

4.2.1 Attempted base hydrolysis of $[Mn(CO)_5CH_2Cl]$ (X) and $[Fe(Cp)(CO)_2CH_2Cl]$ (VI)

It is a well known fact that organic alkyl halides can be converted to alcohols by nucleophilic attack of OH^- (Equation 31),[92]

$$R\text{-}X + OH^- \longrightarrow R\text{-}OH + X^- \quad (31)$$

(X = halogen, R = alkyl group).

We thus decided to investigate the reactions of some chloromethyl complexes with OH^-.

No reaction occurred when $[Mn(CO)_5CH_2Cl]$ (X) was stirred in a THF/water mixture, or in a THF/water mixture to which had been added an equimolar quantity of NaOH. However addition of an excess of an aqueous solution of NaOH to a THF solution of (X) gave a brown water soluble product, which was not isolated; we suggest that (X) had decomposed under these conditions.

The reaction of $[Fe(Cp)(CO)_2CH_2Cl]$ (VI) with aqueous NaOH was attempted but the only product isolated was the dimer, $[Fe(Cp)(CO)_2]_2$. In view of the success achieved by several other workers[93,94] in using phase transfer of OH^-, we attempted the reaction of (VI) with aqueous NaOH in the presence of $[N(Et)_3Ph]Cl$. However, again the only product isolated was the dimer, $[Fe(Cp)(CO)_2]_2$.

It is interesting to note the ease with which (VI) is converted to the methoxymethyl complex, $[Fe(Cp)(CO)_2CH_2OCH_3]$, by reaction with the strong base NaOMe[48] (see Section 2.1). One would thus expect that the reaction of (VI) with OH^- would yield $[Fe(Cp)(CO)_2CH_2OH]$. It is possible that $[Fe(Cp)(CO)_2CH_2OH]$ was formed in our reactions, but that it was too reactive to be isolated, and rapidly decomposed to give $[Fe(Cp)(CO)_2]_2$. If this is so, it may be possible to see the formation of $[Fe(Cp)(CO)_2CH_2OH]$ using, for example, low temperature ^1H nmr; further investigations need to be conducted in this direction.

4.2.2 Attempted acid-catalysed hydrolysis of $[Mn(CO)_5CH_2OCH_3]$ (VIII), $[Fe(Cp)(CO)_2CH_2OCH_3]$ (V) and $[Re(CO)_5CH_2OCH_3]$ (VII)

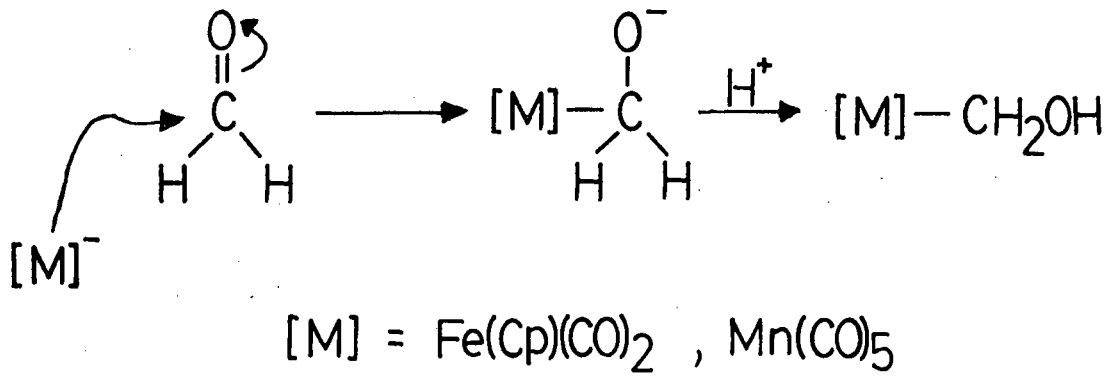
In view of the success achieved by Casey[16] in hydrolysing the methoxymethyl $[Re(Cp)(CO)(NO)CH_2OCH_3]$ to give $[Re(Cp)(CO)(NO)CH_2OH]$, we decided to attempt the hydrolysis of other methoxymethyl transition metal complexes.

(VIII) and (VII) did not react with H_2O and CF_3COOH under the conditions we used. However (V), when reacted with CF_3COOH and H_2O for 2½ hours at room temperature gave a yellow brown oil. This product could not be purified; however the νCO bands shown in its infrared spectrum indicate a dicarbonyl complex, with possibly an acyl CO group (νCO 1777 cm^{-1}) (this band (1777 cm^{-1}) may be due to unreacted CF_3COOH). The bands at 2031 and 1979 cm^{-1} are at somewhat higher frequencies than would be expected for the desired hydroxymethyl $[Fe(Cp)(CO)_2CH_2OH]$. (*c.f.* the positions of the νCO bands for $[Fe(Cp)(CO)_2CH_2Cl]$[48] and $[Fe(Cp)(CO)_2CH_2OCH_3]$ (see Section 5.2.1)). We propose, on the basis of the spectral evidence found, that the product is the ester $[Fe(Cp)(CO)_2CH_2OC(O)CF_3]$, formed by reaction of (V) with CF_3COOH.

When (V) was reacted with CF_3COOH and H_2O for 17 hours at room temperature a brown oily product was formed, the infrared spectrum (νCO region) of which indicated a mixture of products, including possibly the proposed ester $[Fe(Cp)(CO)_2CH_2OC(O)CF_3]$. However none of the products could be isolated.

4.2.3 Reaction of Na[M] with formaldehyde (M = $Fe(Cp)(CO)_2^-$, $MnCO_5^-$)

Synthesis of hydroxymethyl complexes was also attempted using the method outlined in Scheme 12.



Scheme 12

In this way, the only product from the reaction of $Na[Fe(Cp)(CO)_2]$ with formaldehyde gas (when the gas was bubbled directly through the solution of the anion), at 0^oC, was the dimer $[Fe(Cp)(CO)_2]_2$. However addition of a solution of formaldehyde to a solution of $Na[Fe(Cp)(CO)_2]$ at 0^oC, followed by addition of H_3PO_4, gave the hydride $[Fe(Cp)(CO)_2H]$.

Both $[Fe(Cp)(CO)_2]_2$ and $[Fe(Cp)(CO)_2H]$ may arise from an intermediate, reactive hydroxymethyl complex, the latter by β elimination, a pathway which has been proposed for the decomposition of hydroxymethyl transition metal complexes[95] (Equation 32).

$$[L_nMCH_2OH] \longrightarrow [L_nM\text{-}H] + CH_2O \qquad (32)$$

(L = ligands, M = transition metal)

However it is much more likely that the dimer arises simply from recombination of two molecules of $[Fe(Cp)(CO)_2]^-$, and that $[Fe(Cp)(CO)_2H]$ arises from protonation of $[Fe(Cp)(CO)_2]^-$.

The only product isolated from the reaction of $Na[Mn(CO)_5]$ with CH_2O was the dimer $[Mn_2(CO)_{10}]$.

CHAPTER FIVE

5. EXPERIMENTAL SECTION

5.1 General remarks

All experiments were routinely performed under high purity N_2 and in nitrogen-saturated solvents.

$[Mn_2(CO)_{10}]$, $[Re_2(CO)_{10}]$ and $[Fe(Cp)(CO)_2]_2$ were obtained from Strem Chemicals Inc., and used without further purification. $[Ru(Cp)(CO)_2]_2$ was synthesized using the method of Humphries and Knox,[96] $[Mn_2(CO)_8(PPh_3)_2]$ by the method of Osborne and Stiddard,[97] $[Fe(Cp)(CO)_2CH_2Cl]$ by the method of Green *et al*,[48] $[Mn(CO)_5CH_2OCH_3]$ by the method of Cawse *et al*,[54] and $[Mn(CO)_5CH_2Cl]$ by the method of Moss.[52] $[W(Cp)(CO)_3CH_2Cl]$ was synthesized by first synthesizing $Na[W(Cp)(CO)_3]$ from $[W(CO)_6]$ and NaCp,[98] followed by reaction of $Na[W(Cp)(CO)_3]$ with $ClCH_2OCH_3$ and HCl gas.[48] $ClCH_2OCH_3$ was obtained from Merck, tertiary phosphines and $P(OMe)_3$ from Strem Chemicals Inc., and B.D.H. Chemicals Ltd ., and $AsPh_3$ was obtained from Merck. All were used without further purification. PMe_3 was synthesized by the method of Mann and Wells,[99] and $ClCH_2I$ by the method of Miyano and Hashimoto.[100] All other reagents were obtained commercially and used without further purification.

$ClCH_2OCH_3$ is toxic and carcinogenic and thus was handled under a fume hood using rubber gloves. When solvents were evaporated from a reaction mixture containing $ClCH_2OCH_3$, they were condensed into a cold trap and the excess $ClCH_2OCH_3$ decomposed with HI.

Solvents were generally of analytical reagent grade, and were further dried where necessary under N_2 by standard methods.[101] In particular, tetrahydrofuran was dried by standing over KOH, followed by refluxing

over $LiAlH_4$ under N_2. n-Hexane (generally referred to as "hexane" in this project) was dried by refluxing over $LiAlH_4$ under N_2. "Petroleum ether" refers to the fraction boiling at 60-80°C. "Ether" refers to diethyl ether.

Molecular distillations were performed on a modified Hickmann still. Chromatography was performed using Merck Kieselgel 60 (30-70 mesh ASTM).

Microanalyses were performed by the microanalyst of the School of Chemistry, University of Cape Town, Mr W.T. Hemsted, and by Drs F. and E. Pascher, Microanalytisches Laboratorium, Buschstrasse 54, 5300 Bonn 1, Germany. Melting points were determined on a Gallenkamp, and a Reichert, Kofler hotstage apparatus, and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 180 Grating Spectrophotometer and a Beckmann Acculab 10, using solution cells with NaCl windows and 0.1 mm spacers, or KBr discs. The following abbreviations are used in connection with the infrared spectra: (w) = weak, (m) = medium, (s) = strong, (vs) = very strong, (sh) = shoulder.

^1H nmr spectra were recorded on a Varian XL100 (100 M Hz), or on a Bruker WH90 (90 M Hz) operating in Fourier transform mode. Chemical shifts are given downfield of T.M.S., in δ p.p.m.

Mass spectra were recorded using a VG Micromass 16F, operating at 70 e V ionising voltage (1eV = 1.60×10^{-19} J), and coupled to a VG system 2000 data system. The samples were introduced into the instrument as solids or oils, using a direct probe. Calculated mass spectra were obtained using a computer program prepared at the University of Alberta, Alberta, Canada.[102,71] This program calculates exact masses and isotope combination

patterns for any particular parent ion or fragment required.

Pressures are recorded in mm Hg or atmospheres (atm) throughout this project.

1 mm Hg = 101.325 / 760 Pa.

1 atm = 1.01 bar = 101.325 Pa.

5.2 Experimental section pertaining to Chapter 2

5.2.1 (Methoxymethyl)dicarbonyl(pentahaptocyclopentadienyl)iron, $[Fe(Cp)(CO)_2CH_2OCH_3]$, (V)

(V) was first synthesized some years ago by Green *et al*,[48] but as yet no-one has reported observing its rotational isomerism. We have shown that rotational isomerism is present on the basis of the double νCO bands (see discussion) and thus present the analytical and spectral data we obtained for (V). Further, as our synthesis is slightly different from Green's it is reported here.

A brown solution of $Na[Fe(Cp)(CO)_2]$ {synthesized by stirring $[Fe(Cp)(CO)_2]_2$ (2.03 g, 5.7 mmol) with excess Na amalgam (0.75 g Na in 7 mls Hg) in THF (35 mls) for 2 hours} was added dropwise over 15 mins. with stirring to a solution of $ClCH_2OCH_3$ (1.29g, 16 mmol) in THF (5 mls) at -78°C. The reaction mixture was stirred at -78°C for a further 15 minutes and then allowed to warm up to room temperature, and stirred for another 2 hours. The solvent was removed under reduced pressure from the reddish solution and the residue extracted with -hexane (3 x 20 mls). The red hexane extract was filtered, evaporated to an oil on a rotary evaporator, and the product purified by molecular distillation (0.5 mm Hg, with periodic slight warming of the distillation vessel) giving (V) as a brown, unstable oil (1.13 g, 45 %). νCO (cyclohexane) 2016(m), 2006(s), 1961(m), 1949(s) cm^{-1}, (CH_2Cl_2) 2004(s) 1944(s) cm^{-1}; ^1H nmr ($CDCl_3$), δ 3.26 (singlet, 2H), δ 4.81 (singlet, 5H), δ 4.87 (singlet, 2H); found C 48.9 %, H 4.7 %, $C_9H_{10}FeO_3$ requires C 48.69 %, H 4.54 %.

The infrared spectrum in CH_2Cl_2 shows only two νCO bands; the relative broadness of the bands in CH_2Cl_2 (as opposed to cyclohexane) is such that

two bands appear as one.

Some $[Fe(Cp)(CO)_2CH_2Cl]$ was identified, by its infrared spectrum, in the crude red hexane extract (νCO (cyclohexane): 2026(s), 1973(s) cm^{-1}).

5.2.2 (Methoxymethyl)dicarbonyl(pentahaptocyclopentadienyl)ruthenium, $[Ru(Cp)(CO)_2CH_2OCH_3]$ (XXXII)

A dark brown solution of $Na[Ru(Cp)(CO)_2]$ was prepared by stirring $[Ru(Cp)(CO)_2]_2$ (0.60 g, 1.4 mmol) with Na amalgam (0.6 g Na in 7 mls Hg) in THF (15 mls) for 2 hours. The anion solution was then added dropwise over 10 minutes with stirring to a solution of $ClCH_2OCH_3$ (0.65 g, 8.1 mmol) in THF (5 mls) at -78°C, and the reaction mixture stirred at this temperature for 15 minutes. It was then allowed to warm to room temperature, at which temperature it was stirred for 3 hours. The solvent was evaporated under reduced pressure and the residue extracted with hexane (4 x 20 mls). The extract was filtered, and the solvent evaporated under reduced pressure to give a reddish brown oil. (Crude yield >90 %). Further purification was achieved by molecular distillation (0.1 mm Hg, with periodic gentle warming of the distillation vessel) to give slightly impure (XXXII) as a brown oil. νCO (cyclohexane), 2026(s), 2017(vs), 1965(s), 1956(vs) cm^{-1}; ^1H nmr ($CDCl_3$) δ 3.23 (singlet, 3H), δ 4.97 (singlet, 2H) δ 5.31 (singlet, 5H); Found, C 43.8 %, H 4.65 %, $C_9H_{10}O_3Ru$ requires C 40.45 %, H 3.77 %; mass spectrum shows a parent ion with the expected isotope pattern at m/e 268.

The ^1H nmr also showed fairly weak impurity peaks at δ 3.41 (doublet) and δ 4.58 (doublet) as well as other very weak peaks. The infrared spectrum of the crude hexane extract, before molecular distillation, showed small

amounts of $[Ru(Cp)(CO)_2CH_2Cl]$ (XXXIII) [νCO (hexane) 2035(s), 1978(s)].

We were not able to obtain (XXXII) pure, due to traces of an unidentified colourless oil, which distilled over with (XXXII) in the purification process.

5.2.3 (Chloromethyl)dicarbonyl(pentahaptocyclopentadienyl)ruthenium, $[Ru(Cp)(CO)_2CH_2Cl]$ (XXXIII)

$[Ru(Cp)(CO)_2CH_2OCH_3]$ was prepared as described above (Section 5.2.2) from $[Ru(Cp)(CO)_2]_2$ (0.63 g, 1.4 mmol). The methoxymethyl compound was then dissolved in hexane (15 mls) and dry HCl was bubbled through for 7 mins. giving a yellowish cloudy solution. The solution was filtered and cooled to -78°C, at which temperature (XXXIII) crystallized. This product was recrystallized from hexane at -78°C to give pure (XXXIII) as sticky yellowish needles (0.12 g = 15 % based on dimer). νCO (hexane) 2035(s), 1978(s) cm^{-1}, ^1H nmr ($CDCl_3$), δ 4.39 (singlet, 2H), δ 5.37 (singlet, 5H). Found, C 35.7 %, H 2.65 %, Cl 12.54 %, $C_8H_7ClO_2Ru$ requires C 35.37 %, H 2.60 %, Cl 13.05 %.

5.2.4 (Methoxymethyl)pentacarbonylrhenium, $[Re(CO)_5CH_2OCH_3]$ (VII), and (chloromethyl)pentacarbonylrhenium, $[Re(CO)_5CH_2Cl]$ (IX)

$Na[Re(CO)_5]$ was prepared by stirring $[Re_2(CO)_{10}]$ (1.53 g, 2.35 mmol) with excess Na amalgam (0.75 g Na in 7 mls Hg) in THF (20 mls) for 6 hours. The red solution of the anion was then added dropwise with stirring to a solution of $ClCH_2OCH_3$ (0.08 g, 13.4 mmol) in THF (5 mls) at -78°C.

The reaction mixture was stirred for a further 15 mins at -78°C, and then allowed to warm to room temperature, and stirred for another 2 hours to give a cloudy yellow solution. The solvent was removed from this and the residue extracted with hexane (50 mls) giving a yellow cloudy solution, which on evaporation of the hexane yielded a yellowish oily solid. This was further purified by sublimation (0.5 mm Hg, with periodic gentle warming of the sublimation vessel) onto a 0°C probe, giving a white crystalline sublimate. This sublimate, on warming to room temperature gave a mixture of a clear colourless oil and a white solid (total yield 740 mg). Separation of the oil and the solid was achieved by dissolving the mixture in a minimum of hexane and cooling the resulting solution to -78°C, at which temperature (IX) precipitated as a white crystalline solid. (330 mg, 20 %), mpt. 62-65°C, νCO (cyclohexane) 2063(vw), 2044(vw), 2023(s), 1994(m) cm^{-1}; ^1H nmr ($CDCl_3$), δ 3.59 (singlet); found C 19.18 %, H 0.58 %, Cl 9.51 %; $C_6H_2ClO_5Re$ requires C 19.18 %, H 0.56 %, Cl 9.44 %.

After the precipitation of (X), the mother liquors were evaporated to dryness, to yield (VII) as a clear, colourless, volatile oil (410 mg, 24 %). νCO (cyclohexane) 2014(s), 1986(m); ^1H nmr ($CDCl_3$) δ 3.28 (singlet, 3H), δ 4.05 (singlet, 2H); found C 22.95 %, H 1.4 %, $C_7H_5O_6Re$ requires C 22.65%, H 1.35 %.

The infrared spectrum of (VII) showed small amounts of (IX) present, as would be expected; nevertheless the solubilities of (VII) and (IX) are such that the separation achieved by the method described is fairly good.

5.2.5 *Cis*-(chloromethyl)(triphenylphosphine)tetracarbonylmanganese $[Mn(CO)_4(PPh_3)CH_2Cl]$ (XXXIV)

A yellow brown solution of $[Mn(CO)_4PPh_3]Na$ was prepared by stirring $[Mn(CO)_4PPh_3]_2$ (0.44 g, 0.51 mmoles) with Na amalgam (0.5 g Na in 6 mls Hg) in THF (20 mls) for 1.5 hours. It was added dropwise with stirring over 10 mins to a solution of $ClICH_2$ (0.66 g, 3.75 mmol) in THF (5 mls) at -78°C. The resulting reaction mixture was stirred at -78°C for a further 10 mins., allowed to warm to room temperature and stirred for 1.5 hours, giving a greenish suspension. The solvent was removed under reduced pressure, the residue extracted with CH_2Cl_2 (2 x 20 mls, 1 x 10 mls), and the reddish extract dried on a rotary evaporator to give a viscous orange oil (0.64 g).

The oil was chromatographed on a silica-gel column made up in a 5 % ether/petroleum ether mixture. Elution with 5 % ether/petroleum ether separated a broad orange band and a yellow band. The orange band was collected first and the solvent removed under reduced pressure to give (XXXIV) as an orange oily solid (0.29 g, 60 %). The yellow band was eluted using 50 % ether/petroleum ether, and on removal of the solvent gave a yellow orange solid. This had only very weak νCO bands in the infrared spectrum, and was discarded.

(XXXIV) was further purified by two recrystallisations from hexane at -78°C, and finally isolated as a sticky orange-yellow solid. νCO (CH_2Cl_2) 2069(m), 1999(s), 1979(vs), 1950(s) cm^{-1}, ^1H nmr ($CDCl_3$), δ 3.25 (doublet, 2H, $^3J(P-H)$ = 5.25 Hz), δ 7.45 (multiplet, 15H); found C 58.1 %, H 4.2 %, $C_{23}H_{17}ClMnO_4P$ requires C 57.70 %, H 3.58 %.

5.2.6 Reaction of $Na[Re(CO)_5]$ with $ClCH_2I$

$Na[Re(CO)_5]$ was prepared by stirring $[Re_2(CO)_{10}]$ (0.56 g, 0.86 mmol) with Na amalgam (0.6 g Na in 6 mls Hg) in THF (20 mls) for 1.5 hours. The solution of the anion was added slowly over 10 minutes, with stirring, to a solution of $ClCH_2I$ (0.58 g, 3.3 mmol) in THF (4 mls) at $-78^{o}C$. Stirring was continued at $-78^{o}C$ for 15 mins. The reaction vessel was then transferred to an icebath and stirring continued at $0^{o}C$ for 1.5 hours, resulting in a brownish solution. The solvent was evaporated at reduced pressure, and the residue extracted into hexane (3 x 15 mls) giving a cloudy yellow solution. Evaporation of the hexane yielded a yellow solid, with νCO (cyclohexane) 2043(s), 1989(m), 2014(m), 1977(w) cm^{-1}.

Further purification was attempted by sublimation for 3.5 hours (0.5 mm Hg, with periodic gentle warming of the sublimation vessel) and a small quantity of white crystalline material sublimed; it was washed off the probe with CH_2Cl_2. However an infrared spectrum of the sublimate showed that in fact further purification had not been achieved; both products had sublimed. An ^{1}H nmr of the sublimate showed no peaks in the region $\delta 0 \rightarrow \delta 20$ ppm (apart from expected solvent impurity peaks). The νCO bands of the major product (2043, and 1989 cm^{-1}) correspond fairly closely to known values for the compound $[Re(CO)_5Cl]$.[69]

5.2.7 Reaction of $Na[Fe(Cp)(CO)_2]$ with $ClCH_2I$

$Na[Fe(Cp)(CO)_2]$ was prepared by stirring $[Fe(Cp)(CO)_2]$ (1.7 g, 4.8 mmol) with Na amalgam (0.75 g Na in 6 mls Hg) in THF (30 mls) for 5.5 hours. The anion solution was then added slowly over 15 mins., with stirring, to $ClCH_2I$ (2.18 g, 12.0 mmol) at $-40^{o}C$. The resulting mixture was stirred

at this temperature for a further 5 mins., and then allowed to warm to room temperature and stirred for a further ½ hour. The solvent was then removed from the purple-brown solution at reduced pressure, and the residue extracted with hexane (4 x 20 mls). Removal of the hexane from the extract gave a purple solid (0.65 g), νCO (cyclohexane), 2042(s), 2028(vs), 2002(s), 1978(vs), 1961(s), 1794(m) cm^{-1}. The bands at 2028 and 1978 cm^{-1} agree fairly well with values for $[Fe(Cp)(CO)_2CH_2Cl]$ (νCO cyclohexane), 2028, 1974 cm^{-1}). The purple solid was chromatographed on a silica-gel column made up in 5 % ether/hexane. Elution with 5 % ether/hexane separated a yellow band from an orange band and a purple band. The yellow band was collected first, and the solvent removed under reduced pressure giving a yellow sticky solid (64 mg) (νCO (cyclohexane), 2014(s), 1960(s) cm^{-1}). The orange band was then collected and removal of the solvent gave a brown solid (56 mg) (νCO (cyclohexane) 2027(s), 1977(s), 2014(s), 1960(s) cm^{-1}). Finally the purple band was eluted using ether, and evaporation of the solvent yielded a brown-black solid (225 mg), νCO (cylohexane) 2042(s), 2002(s)). The latter values correspond well with known values for $[Fe(Cp)(CO)_2I]$,[70] indicating that this is the major product isolated from this reaction.

5.3 Experimental details pertaining to Chapter 3

5.3.1 The reactions of $[Fe(Cp)(CO)_2CH_2Cl]$ (VI) with some tertiary phosphines, $[Ph_2PCH_2CH_2PPh_2]$, $P(OMe)_3$ and $AsPh_3$

General procedures

The reactions of $[Fe(Cp)(CO)_2CH_2Cl]$ (VI) with some tertiary phosphines, $[Ph_2PCH_2CH_2PPh_2]$, $P(OMe)_3$ and $AsPh_3$ (generally referred to as ligands in the descriptions following) were conducted in methanol and acetonitrile, following the general procedure as follows: (details given afterwards in i → ix).

In methanol

(VI) was dissolved in methanol and the ligand was added in a 1:1 molar ratio or in excess. The reaction mixture was then refluxed for several hours. Monitoring the course of the reaction by infrared spectroscopy (2200-1600 cm^{-1}) showed that, irrespective of the ligand, (VI) rapidly equilibrated with $[Fe(Cp)(CO)_2CH_2OCH_3]$ (V) [$\nu CO(CH_2Cl_2)$ 2006(s), 1946(s) cm^{-1}] (see Chapter 3 for discussion of this). This was followed by the appearance in the infrared spectrum of bands due to the product. When the reaction was complete, as judged by the infrared spectrum of the reaction mixture, the mixture was allowed to cool, and then a solution of an excess of $NaBPh_4$ in methanol was added slowly with stirring. This caused precipitation of the product, which was filtered and recrystallised.*

The reactions of PPh_3, $PMePh_2$ and PMe_2Ph with (VI) were also attempted at room temperature in the absence of light, for several days, followed by workup with $NaBPh_4$, as above. The reaction with PMe_2Ph did not result in

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* Removal of the solvent, addition of $NaBPh_4$ and filtration of the product are further referred to as "workup" unless otherwise stated.

the formation of (XXXVII) under these conditions; the other two phosphines gave (XXXV) and (XXXVI), as in the reaction in refluxing methanol.

In acetonitrile:

(VI) was dissolved in acetonitrile and an excess of the ligand was added in each case. The reaction mixture was left in the absence of light, at room temperature, for several days. The course of the reaction was monitored by infrared spectroscopy (2200-1600 cm^{-1}). The solvent was removed under reduced pressure, the residue dissolved in methanol, and by slowly adding an excess of a methanolic solution of $NaBPh_4$ with stirring, the product was afforded. It was filtered and recrystallized.

Details of the reactions between the ligands and (VI) (such as quantities, times) and the characterisation of the products have been described below (i → ix); any deviations from the general procedure are also mentioned. The reactions of (VI) with $AsPh_3$ and $[Ph_2PCH_2CH_2PPh_2]$ respectively in acetonitrile were not attempted; neither was the reaction of (VI) with PMe_3 in methanol.

i Reaction of (VI) with PPh_3 in methanol; preparation of $[Fe(Cp)(CO)_2CH_2PPh_3]BPh_4$ (XXXV)

(VI) (180 mg, 0.79 mmol) was reacted with PPh_3 (215 mg, 0.82 mmol) in methanol (10 mls) in the dark, at room temperature, for 5 days. Workup with $NaBPh_4$ gave (XXXV) as yellow needles (400 mg, 66 %). (XXXV) was purified by recrystallisation from CH_2Cl_2 with ether followed by recrystallisation from acetone with ether. Mpt: 198-200°C (decomp); νCO (CH_2Cl_2) 2032(s), 1981(s) cm^{-1}; ^1H nmr (CD_2Cl_2), δ 1.50 (doublet, 2H, $^2J(P-H)$ = 12.5 Hz), δ 4.62 (singlet, 5H), δ 6.93, δ 7.33, δ 7.63 (multiplets, 35H);

found, C 77.5 %, H 5.45 %, $C_{50}H_{42}BFeO_2P$ requires C 77.74%, H 5.48 %.

In another reaction (VI) (1.59 mmol) was refluxed with PPh_3 (2.0 mmol) in methanol (20 ml) for 4 hours. Workup with $NaBPh_4$ gave 910 mg (74 %) (XXXVI) as yellow needles.

In a third experiment, conducted on a small scale (VI) was dissolved in methanol and an equimolar quantity of PPh_3 was added. This was immediately followed by the addition of an excess of $NaBPh_4$, dissolved in methanol. A cream coloured precipitate formed. It had no νCO bands in its infrared spectrum; the full-range spectrum (4000-500 cm^{-1}) corresponded exactly with that of an authentic sample of $[Ph_3PH]BPh_4$.

ii Reaction of (VI) with $PMePh_2$; preparation of $[Fe(Cp)(CO)_2CH_2PMePh_2]BPh_4$ (XXXVI)

In acetonitrile:

(VI) (230 mg, 1.0 mmol) was reacted with $PMePh_2$ (210 mg, 1.1 mmol) in acetonitrile (6 mls) for 5 days. The orange reaction mixture turned red. Workup with $NaBPh_4$ followed by recrystallisation from CH_2Cl_2 with ether gave slightly impure (XXXVI) as a yellow-brown powder (235 mg, 33 %).

In methanol:

(VI) (310 mg, 1.36 mmol) was reacted with $PMePh_2$ (274 mg, 1.36 mmol) in methanol (11 mls) for 7 days, in the dark, at room temperature. The orange reaction mixture gradually darkened. Workup with $NaBPh_4$ gave (XXXVI) as yellow needles (500 mg, 52 %); pure (XXXVI) was obtained by three recrystallisations, from CH_2Cl_2 with ether. Mpt: 162-164°C; νCO (CH_2Cl_2) 2031(s), 1978(s) cm^{-1}; ^1H nmr (CD_2Cl_2), δ 1.15 (doublet, 2H, $^2J(P-H)$ = 12.6 Hz), δ 1.97 (doublet, 3H, $^2J(P-H)$ = 12.5 Hz), δ 4.72

(singlet, 5H), δ 6.98, δ 7.35, δ 7.59 (multiplets, 30H); found, C 75.7 %, H 5.7 %, $C_{45}H_{40}BFeO_2P$ requires C 76.07 %, H 5.68 %.

In another reaction (XXXVI) was obtained in *c.a.* 70 % yield by refluxing (IV) (2.13 mmol) with $PMePh_2$ (2.9 mmol) in methanol (20 ml) for 20 hours, followed by workup with $NaBPh_4$.

iii Reaction of (VI) with PMe_2Ph

In acetonitrile: preparation of $[Fe(Cp)(CO)(PMe_2Ph)_2]BPh_4$ (XLI)

(VI) (153 mg, 0.68 mmol) was reacted with PMe_2Ph (310 mg, 2.25 mmol) in acetonitrile (10 mls) for 5 days. The solution gradually turned a deep red; peaks due to small amounts of $[Fe(Cp)(CO)_2]_2$ were seen in the infrared spectra of the reaction solution. Workup with $NaBPh_4$ gave (XLI) as yellow needles (412 mg, 81 %); pure (XLI) was obtained by two recrystallisations, from CH_2Cl_2 with ether. Mpt. 193-196° (decomp.); νCO (CH_2Cl_2), 1967 cm^{-1}; ^1H nmr (acetone d^6) δ 1.65 {multiplet(pseudo-triplet), 6H, $|J(P-H) + J(P'-H)| = 10.0$ Hz}, δ 1.83 {multiplet(pseudotriplet), 6H, $|J(P-H) + J(P'-H)| = 10.0$ Hz}, δ 4.96 (triplet, 5H, $^3J(P-H) = 1.4$ Hz), δ 6.87, δ 7.36, δ 7.53 (multiplets, 30H); found, C 73.8 %, H 6.35 %, $C_{46}H_{47}BFeOP_2$ requires C, 74.21 %, H 6.36 %.

In methanol: preparation of $[Fe(Cp)(CO)_2CH_2PMe_2Ph]BPh_4$ (XXXVII)

(VI) showed no reaction with PMe_2Ph in methanol when the reaction was conducted at room temperature, in the dark, for 3 days.

In another experiment, (VI) (207 mg, 0.91 mmol) was refluxed in methanol (15 mls) with PMe_2Ph (383 mg, 2.77 mmol) for 2 days. The initial yellow solution gradually turned orange. Workup with $NaBPh_4$ gave (XXXVII) as

a yellow powder (45 mg, 8 %). Mpt: 150-153°C, νCO(CH_2Cl_2) 2029(s), 1975(s) cm^{-1}; ^1H nmr (CD_2Cl_2), δ 1.26 (doublet, 2H, ^2J(P-H) = 14.0 Hz), δ 1.58 (doublet, 6H, ^2J(P-H) = 12.5 Hz), δ 4.70 (singlet, 5H), δ 6.95, δ 7.50 (multiplets, 25 H).

iv Reaction of (VI) with PMe_3 in acetonitrile; preparation of $[Fe(Cp)(CO)(PMe_3)_2]BPh_4$ (XLII)

(VI) (284 mg, 1.25 mmol) was reacted with PMe_3 (2.47 mmol) in acetonitrile (10 mls) for 2 days; the initial orange solution became reddish in colour. Workup with $NaBPh_4$ gave (XLII) as yellow needles; (XLII) was purified by recrystallisation from acetone with ether followed by recrystallisation from CH_2Cl_2 with ether. (Recrystallised yield 251 mg, 32 %). Product decomposed without melting >250°C. νCO (CH_2Cl_2) 1971 cm^{-1}; ^1H nmr (CD_2Cl_2), δ1.39 {multiplet (pseudotriplet) 18H, |J(P-H) + J(P'-H)| = 10.0 Hz}, δ 4.56 (triplet, 5H, ^3J(P-H) = 1.9 Hz), δ 6.96, δ 7.30 (multiplets, 20H); found C 69.7 %, H 7.1 %, $C_{36}H_{43}BFeOP_2$ requires C 69.70 %, H 6.98 %.

v Reaction of (VI) with $PEtPh_2$

In acetonitrile:

(VI) (201 mg, 0.89 mmol) was reacted with $PEtPh_2$ (363 mg, 1.69 mmol) for 5 days. The initial orange-yellow reaction mixture turned a deep red, and monitoring the reaction by infrared spectroscopy showed the formation of $[Fe(Cp)(CO)_2]_2$ as one of the products. The work up procedure was slightly different from that described at the beginning of this section (page 105). The solvent was removed under reduced pressure, and the red oily residue extracted with petroleum ether to remove excess phosphine. The remaining petroleum ether insoluble residue was dissolved in methanol, and addition

of an excess of a methanolic solution of $NaBPh_4$ gave an orange precipitate (369 mg), νCO (CH_2Cl_2) 1962 cm^{-1}. This product could not be purified and thus could not be characterized further.

In methanol: preparation of $[Fe(Cp)(CO)_2CH_2PEtPh_2]BPh_4$ (XXXVIII)

(VI) (198 mg, 0.87 mmol) was refluxed for 5 hours in methanol, with $PEtPh_2$ (209 mg, 0.97 mmol). Workup with $NaBPh_4$ gave (XXXVIII) as a yellow crystalline product (340 mg, 54 %); (XXXVIII) was purified by two recrystallisations from acetone with ether followed by recrystallisation from CH_2Cl_2 with ether. Mpt: 178-180°C; νCO (CH_2Cl_2) 2030(s), 1977(s); ^1H nmr (CD_2Cl_2) δ 0.99 (doublet of triplets, 3H, $^3J(P-H)$ = 18.5 Hz, $^3J(H-H)$ = 7.7 Hz), δ 1.09 (doublet, 2H, $^2J(P-H)$ = 12.6 Hz), δ 2.38 (doublet of quartets, 2H, $^2J(P-H)$ = 11.9 Hz, $^3J(H-H)$ = 7.7 Hz), δ 4.63 (singlet, 5H), δ 6.93, δ 7.33, δ 7.60 (multiplets, 30H); found, C 76.05 %, H 5.85 %, $C_{46}H_{42}BFeO_2P$ requires C 76.26 %, H 5.80 %.

vi Reaction of (VI) with PEt_2Ph

In acetonitrile: preparation of $[Fe(Cp)(CO)(PEt_2Ph)_2]BPh_4$ (XLIV) and $[CH_3PEt_2Ph]BPh_4$

(VI) (341 mg, 1.51 mmol) was reacted with PEt_2Ph (583 mg, 3.51 mmol) in acetonitrile (8 mls) for 3 days. The yellow reaction mixture turned a deep red, and monitoring the reaction by infrared spectroscopy showed the formation of a considerable amount of $[Fe(Cp)(CO)_2]_2$. The workup procedure deviated from the general procedure (see page 106) slightly. Removal of the solvent from the reaction mixture under reduced pressure gave a red residue. Extraction with ether removed some of the $[Fe(Cp)(CO)_2]_2$; the remaining residue was dissolved in methanol, and addition of an excess of a methanolic solution of $NaBPh_4$ gave a mixture of yellow platelets and

white needles (850 mg). This product was dissolved in acetone, and petroleum ether added until the solution became cloudy; cooling yielded a crop of white needles (300 mg) (Product A). Addition of further petroleum ether gave Product B, which consisted very largely of yellow platelets, but which still included small quantities of white needles (170 mg).

Product A was further purified by recrystallisation from acetone with ether, followed by recrystallisation from CH_2Cl_2 with hexane. It was identified as the salt $[P(CH_3)(C_2H_5)_2Ph]BPh_4$. Mpt 200-201°C, ^1H nmr (CD_3NO_2), δ 1.29 (doublet of triplets, 6H, $^3J(H-H)$ = 7.5 Hz, $^3J(P-H)$ = 19.5 Hz), δ 2.05 (doublet, 3H, $^2J(P-H)$ = 13.0 Hz), δ 2.42 (doublet of quartets, 4H, $^2J(P-H)$ = 13.0 Hz, $^3J(H-H)$ = 7.5 Hz), δ 6.92, δ 7.37, δ 7.78 (multiplets, 25H); found C 84.2 %, H 7.6 %, $C_{35}H_{38}BP$ requires C 84.00 %, H 7.6%.

Further purification of Product B was not achieved. However the yellow platelets were identified as (XLIV) (*c.a.* 15 %) on the basis of the following: Mpt: 140-142°C, νCO (CH_2Cl_2), 1962 cm^{-1}; ^1H nmr (CD_2Cl_2) δ 0.93, δ 1.65 (both multiplets, integration poor). δ 4.52 (triplet, 5H, $^3J(P-H)$ = 2.0 Hz), δ 6.97, δ 7.35 (multiplets, 30H). Best analysis: found, C 75.8 %, H 7.05 %, $C_{50}H_{55}BFeOP_2$ requires C 75.01 %, H 6.92 %.

In methanol:

(VI) (220 mg, 0.97 mmol) was refluxed in methanol (12 mls) with PEt_2Ph (222 mg, 1.34 mmol) for 5 days. The initial orange colour of the reaction mixture darkened slightly. Workup with $NaBPh_4$ gave a brown powder (81.4 mg); Mpt: 123-126°C, νCO (CH_2Cl_2), 2028(s), 1974(s). This product could not be further purified and thus could not be characterized further.

vii Reaction of (VI) with $[Ph_2PCH_2CH_2PPh_2]$ (= diphos)

In methanol:

(VI) (240 mg, 1.06 mmol) was refluxed with diphos (458 mg, 1.15 mmol) in methanol (25 ml) for 5 hours. The orange reaction mixture darkened in colour. Workup with $NaBPh_4$ gave an orange solid (608 mg); νCO (CH_2Cl_2) 2030(s), 1976(s) cm^{-1}. This could not be further purified, and thus could not be characterized further.

In another experiment (VI) (320 mg, 1.4 mmol) was refluxed with diphos (646 mg, 1.6 mmol) in methanol (25 ml) for 5 hours. The workup was slightly different from the general procedure (page 105). The solvent was removed from the reaction mixture, and the orange residue dissolved in CH_2Cl_2 and reprecipitated with hexane as an orange oil. The oil dried under vacuum to yield a sticky orange powder (680 mg); νCO (CH_2Cl_2) 2023(s), 1968(s) cm^{-1}. This product could not be further purified and could not be characterized further.

viii Reaction of (VI) with $AsPh_3$ in methanol; preparation of $[Fe(Cp)(CO)_2CH_2AsPh_3]BPh_4$ (XXXIX)

(VI) (235 mg, 1.04 mmol) was refluxed with $AsPh_3$ (653 mg, 2.13 mmol) in methanol (20 ml) for 3.5 hours. Workup with $NaBPh_4$ gave (XXXIX) as yellow needles (560 mg, 66 %). (XXXIX) was purified by recrystallisation from CH_2Cl_2 with ether followed by recrystallisation from acetone with ether. Mpt: 194-196°C (decomp); νCO (CH_2Cl_2) 2031(s), 1980(s) cm^{-1}; ^1H nmr (acetone d_6), δ 2.50 (singlet, 2H), δ 5.09 (singlet, 5H), δ 6.88, δ 7.35, δ 7.80 (multiplets, 35H); found C 73.35 %, H 5.15 %, $C_{50}H_{42}AsBFeO_2$ requires C 73.55 %, H 5.19 %.

ix Reaction of (VI) with $P(OMe)_3$

In acetonitrile:

(VI) (326 mg, 1.44 mmol) was reacted with $P(OMe)_3$ (407 mg, 3.28 mmol) in acetonitrile for 6 days. An infrared spectrum of the reaction mixture showed that no reaction had taken place. The reaction mixture was thus discarded.

In methanol:

(VI) (200 mg, 0.88 mmol) was refluxed with $P(OMe)_3$ (228 mg, 1.84 mmol) in methanol (15 ml) for 4 days. Infrared spectra (νCO region) indicated only the formation of the methoxymethyl (V).

5.3.2a Attempted reaction of $[Fe(Cp)(CO)_2CH_2OCH_3]$ (V) with PPh_3 in methanol

(V) (90 mg, 0.4 mmol) was dissolved in methanol (10 ml) with PPh_3 (120 mg, 0.46 mmol). The brown reaction mixture was left in the dark at room temperature for 6 days. No reaction took place, as judged from infrared spectra of the reaction mixture. An excess of aqueous HCl was then added, and the reaction mixture immediately turned an orange colour. Monitoring the reaction mixture by infrared spectroscopy showed that after 4 hours, (V) had been converted almost completely to $[Fe(Cp)(CO)_2CH_2Cl]$ (VI) [νCO (CH_2Cl_2) 2023, 1969 cm^{-1}]; this was followed by a slow, partial conversion to $[Fe(Cp)(CO)_2CH_2PPh_3]^+$. Seven days after the addition of HCl an excess of $NaBPh_4$, dissolved in methanol, was added to the reaction mixture giving a yellow precipitate, which was identified as the tetraphenyl borate salt (XXXV) by its infrared spectrum. (Crude yield 160 mg, 45 %).

5.3.2b The reaction of (V) with $[Ph_3PH]I$

$[Ph_3PH]I$ (263 mg, 0.67 mmol) (synthesized from PPh_3 and HI in hexane) was added to a solution of (V) (126 mg, 0.56 mmol) in methanol (8 ml). The reaction mixture was stood in the dark at room temperature for 7 days. Monitoring the course of the reaction by infrared spectroscopy indicated the formation of a new species with νCO (CH_2Cl_2), 2025(s), 1972(s) cm^{-1} (possibly $[Fe(Cp)(CO)_2CH_2I]$); this was then converted partially to a new product, appearing as high wavenumber shoulders on the bands at 2025 and 1972 cm^{-1}. Small quantities of orange crystals formed in the reaction solution. After 7 days the mother liquors were syringed off the orange crystals which were identified as $[Fe(Cp)(CO)_2CH_2PPh_3]I$, (yield 65 mg, 17 %). Mpt 194-200°C (decomp); νCO (CH_2Cl_2) 2025(s), 1972(s) cm^{-1}, ^1H nmr (CD_2Cl_2) δ 2.21 (doublet, 2H, $^2J(P-H)$ = 12.5 Hz), δ 5.17 (singlet, 5H), δ 7.70 (multiplet, 15H), found: C 53.7 %, H 3.75 %, $C_{26}H_{22}O_2FeIP$ requires C 53.82 %, H 3.82 %.

Addition of a methanolic solution of $NaBPh_4$ to the mother liquors (left after isolation of $[Fe(Cp)(CO)_2CH_2PPh_3]I$, above) gave a precipitate of $[Fe(Cp)(CO)_2CH_2PPh_3]^+$ as the tetraphenylborate salt (XXXV) (82 mg, 16 %) (identified on the basis of its infrared spectrum).

In another reaction, (V) (233 mg, 1.05 mmol) was refluxed with $[Ph_3PH]I$ (491 mg, 1.26 mmol) in methanol (15 ml) for 1 hour. The yellow reaction mixture turned orange. The reaction mixture was then cooled, and an excess of $NaBPh_4$ in methanol added. The resultant yellow precipitate was identified as (XXXV) by its infrared spectrum (yield, after recrystallisation from CH_2Cl_2 with ether, 610 mg, 75 %).

5.3.3 Reaction of $[Ru(Cp)(CO)_2CH_2Cl]$ (XXXIII) with PPh_3 in methanol

(XXXIII) (42 mg, 0.15 mmol) was dissolved in methanol (8 ml) and PPh_3 (60 mg, 0.23 mmol) was added. The resulting yellowish solution was refluxed for 5 days; the colour went darker. Monitoring the reaction by infrared spectroscopy showed the conversion of (XXXIII) to the methoxymethyl (XXXII), but no further reaction occurred. After 5 days the solvent was removed from the reaction mixture. The residue was extracted with hexane, (2 x 10 ml) giving a yellow extract and leaving traces of a hexane-insoluble yellow oil. An infrared spectrum of the hexane extract (in hexane) showed it to contain (XXXII). There was too little hexane-insoluble yellow oil for identification purposes.

5.3.4 Reaction of $[W(Cp)(CO)_3CH_2Cl]$ (XIV) with PPh_3 in acetonitrile; preparation of $[W(Cp)(CO)_3CH_2PPh_3]BPh_4$ (XLV)

PPh_3 (276 mg, 1.05 mmol) was added to a solution of (XIV) (346 mg, 0.90 mmol) in acetonitrile (10 ml). The resultant yellow reaction solution was stood in the dark at room temperature for 34 days; it turned a red-orange colour. The solvent was removed under reduced pressure and the orange oily residue taken up in methanol (10 ml), filtered, and a solution of $NaBPh_4$ in methanol (10 ml) was slowly added with stirring. (XLV) precipitated as yellow needles (170 mg, 20 %); it was purified by repeated recrystallisation from CH_2Cl_2 with ether and from acetone with petroleum ether. Mpt 192-198°C; νCO (CH_2Cl_2), 2036(s), 1952(s), 1933(s) cm^{-1}. ^1H nmr (CD_2Cl_2) δ1.81 (doublet, 2H, $^2J(P-H)$ = 15.5 Hz), δ 5.25 (singlet, 5H), δ 6.93, δ 7.53 (multiplets, 35H); found, C 65.3 %, H 4.85 %, $C_{51}H_{42}O_3BPW$ requires C 65.97 %, H 4.56 %.

5.3.5 Reaction of $[Mn(CO)_5CH_2Cl]$ (X) with PPh_3 in methanol; preparation of *trans*-$[Mn(CO)_3(PPh_3)_2Cl]$

(X) (186 mg, 0.76 mmol) was dissolved in methanol (10 mls), and PPh_3 (207 mg, 0.79 mmol) added. The reaction mixture was stirred magnetically, at room temperature, in the dark, for 6 days, and a yellow precipitate formed. The precipitate was filtered and washed with methanol; it was identified by its infrared spectrum (νCO region) as *trans*-$[Mn(CO)_3(PPh_3)_2Cl]$[52] (yield 90 mg, 33 % based on phosphine).

5.3.6 Reaction of $[Mn(CO)_5CH_2OCH_3]$ (VIII) with PPh_3

a In acetonitrile; preparation of *cis*-$[Mn(CO)_4(PPh_3)COCH_2OCH_3]$ (XLVI)

(VIII) (140 mg, 0.58 mmol) was dissolved in acetonitrile (4 ml) with PPh_3 (147 mg, 0.56 mmol). The pale yellow reaction mixture was stood in the dark at room temperature for 5 days; the colour turned darker yellow. The solvent was evaporated under reduced pressure, giving a yellow oily residue, which crystallized when washed with hexane. Recrystallisation from benzene with hexane gave (XLVI) as a yellow powder (90 mg, 31 %). Mpt 104-106°C; νCO (CH_2Cl_2), 2070(m), 2040(w), 1933(m), 1965(s), 1640(m) cm^{-1}; ^1H nmr ($CDCl_3$), δ 3.26 (singlet, 3H), δ 3.70 (singlet, 2H), δ 7.46 (multiplet, 15H); found, C 60.15 %, H 4.05 %, $C_{25}H_{20}O_6$ MnP requires C 59.78 %, H 4.01 %.

b In methanol; preparation of *cis*-$[Mn(CO)_4(PPh_3)CH_2OCH_3]$ (XLVII) and *trans*-$[Mn(CO)_3(PPh_3)_2CH_2OCH_3]$ (XLVIII)

(VIII) (320 mg, 1.33 mmol) was dissolved in methanol (15 ml) with PPh_3 (356 mg, 1.36 mmol). The pale yellow solution was refluxed for 50 mins.; it rapidly turned a dark yellow colour. Evaporation of the solvent under reduced pressure gave a yellow oily solid. This was dissolved in warm

hexane (60 mls) filtered and cooled to -10°C, at which temperature (XLVII) crystallised out as clusters of yellow needles (468 mg, 74 %). (XLVII) was further purified by recrystallisation from hexane at -10°C. Mpt: 90-92°C; νCO (CH_2Cl_2), 2062(m), 1982(sh), 1967(vs), 1936(s) cm^{-1}, ^1H nmr (CD_2Cl_2) δ 3.07 (singlet, 3H), δ 3.63 (doublet, 2H, $^3J(P-H)$ = 6.8 Hz), δ 7.45 (multiplet, 15H); found C, 60.8 %, H 4.3 %, $C_{24}H_{20}MnO_5P$ requires C 60.77 %, H 4.25 %.

In another experiment (VIII) (550 mg, 2.28 mmol) was refluxed with PPh_3 (1.38 g, 5.27 mmol) in methanol, for 5 hours. The reaction solution was initially a pale yellow; it rapidly turned a dark yellow and after *c.a.* 1.5 hours refluxing, yellow (XLVIII) started precipitating. After 5 hours the reaction mixture was cooled, and the yellow solid was filtered (421 mg, 26 %). It was recrystallised twice from benzene with hexane to give pure (XLVIII).

The mother liquors from this reaction (*i.e.* the filtrate from when (XLVIII) was filtered, above) were evaporated to dryness on a rotary evaporator. The yellow oily residue was dissolved in hexane (50 ml), filtered, and cooled to -10°C, at which temperature pale yellow crystals formed (825 mg). This product was identified as (XLVII) on the basis of peaks in the infrared spectrum.

Characterisation of (XLVIII): Mpt 160-163°C, νCO (CH_2Cl_2), 2010(w), 1921(s), 1885(m) cm^{-1}; ^1H nmr ($CDCl_3$) δ 2.52 (singlet, 3H), δ 3.13 (triplet 2H, $^3J(P-H)$ = 7.5 Hz), δ 7.39 and δ 7.65 (multiplets, 30H); found, C 70.8 %, H 5.25 %, calculated for $C_{41}H_{35}O_4MnP_2[\frac{1}{2}(C_6H_6)]$, C 70.68 %, H 5.12 %.

5.3.7 Attempted reaction of $[Re(CO)_5CH_2Cl]$ (IX) with PPh_3 in acetonitrile

(IX) (320 mg, 0.85 mmol) was dissolved in acetonitrile (10 ml), with PPh_3 (463 mg, 1.77 mmol), and the clear solution left in the dark at room temperature for 6 days. Monitoring the reaction solution by infrared spectroscopy (νCO region) during this period showed that (IX) remained unreacted. The starting materials were recovered unchanged after removal of the solvent from the reaction mixture under reduced pressure.

5.3.8 Attempted reaction of $[Re(CO)_5CH_2OCH_3]$ (VII) with PPh_3 in acetonitrile

(IX) (110 mg, 0.30 mmol) was dissolved in acetonitrile with PPh_3 (99 mg, 1.38 mmol) and the very slightly cloudy solution left in the dark at room temperature for 4 days. No reaction took place, as judged by infrared spectroscopy (νCO region) on the reaction mixture.

The reaction mixture was then refluxed for 2 hours, but an infrared spectrum of the reaction mixture still showed that no reaction had occurred.

5.4 Experimental section pertaining to Chapter 4

5.4.1 Attempted reaction of $[Mn(CO)_5CH_2Cl]$ (X) with H_2O, and with aqueous NaOH

(X) (54 mg, 0.22 mmol) was dissolved in THF (4 ml) and H_2O (0.1 ml) was added to the solution. The resulting clear yellow reaction mixture was stood for 17 hours at room temperature, and then the solvent removed under reduced pressure, giving an orange/red oily residue. An infrared spectrum of the residue, in cyclohexane, showed νCO 2119(w), 2058(w), 2022(vs), 2000(s), which is identical to the starting material (X); the product was thus not purified further.

A number of reactions were then conducted by adding varying concentrations of aqueous NaOH to a solution of (X) in THF. The general procedure used was as follows: (X) (0.2 - 0.25 mmol) was dissolved in THF (4-6 ml). An aqueous solution of NaOH was added (10 ml) and the mixture stirred for approximately 1 hour at room temperature. The THF was then removed under reduced pressure, the residual aqueous suspension extracted with petroleum ether or hexane (2 x 25 ml) and the extract dried over anhydrous Na_2SO_4. The extract was then evaporated to dryness.

In this way, when the reaction was conducted using 0.08 mmol NaOH in 10 ml H_2O, or an equimolar quantity of NaOH in 10 ml H_2O, (X) was recovered unchanged, as judged by its infrared spectrum (νCO region) in cyclohexane. Reaction with an excess of NaOH (1.5 mmol) in H_2O (15 ml) gave rapid decomposition of (X) to form a brown water-soluble product, which was not isolated; it could not be extracted into petroleum ether or CH_2Cl_2.

5.4.2 Reaction of $[Fe(Cp)(CO)_2CH_2Cl]$ (VI) with aqueous NaOH

$[Fe(Cp)(CO)_2CH_2Cl]$ (130 mg, 0.6 mmol) was dissolved in THF (8 ml) giving

a reddish solution. To this solution was added 0.1 M NaOH (5 ml, 0.5 mmol) and the reaction mixture stirred for 40 minutes at room temperature, giving a deep purple solution. Removal of the solvent from the reaction mixture (under reduced pressure) and extraction of the residue into hexane (3 x 20 ml) gave a brownish solution. This was dried over anhydrous Na_2SO_4 and the hexane removed on a rotary evaporator to give a brownish solid. The solid was identified as the dimer $[Fe(Cp)(CO)_2]_2$ by comparison of its infrared spectrum with that of an authentic sample.

5.4.3 Reaction of $[Fe(Cp)(CO)_2CH_2Cl]$ (VI) with aqueous NaOH using a phase transfer catalyst

A benzene (10 ml) solution of (VI) (170 mg, 0.75 mmol) was stirred vigorously with an aqueous solution of NaOH (1 mmol NaOH in 2ml H_2O) for 2 hours at room temperature in the presence of the phase transfer catalyst, phenyltriethylammonium chloride (16 mg, 0.07 mmol). The benzene layer gradually turned purple. An infrared spectrum (νCO region) of the benzene layer showed that (VI) was largely unreacted, though traces of $[Fe(Cp)(CO)_2]_2$ were present.

As no significant reaction had taken place using an equimolar amount of base, a further 1.5 mmol NaOH was added to the reaction mixture, and the stirring continued. The reaction was monitored at intervals by running the infrared spectra (νCO region) of samples of the benzene layer; a gradual conversion of (VI) to the dimer $[Fe(Cp)(CO)_2]_2$ was observed. After 26 hours total reaction time, the benzene layer was removed from the reaction vessel, dried over anhydrous Na_2SO_4 and the solvent evaporated yielding a dark brown solid (96 mg) which consisted of a mixture

of (VI) and $[Fe(Cp)(CO)_2]_2$, as indicated by the νCO bands in the infrared spectrum.

5.4.4 Attempted acid hydrolysis of $[Mn(CO)_5CH_2OCH_3]$ (VIII) using H_2O/THF and CF_3COOH

A solution of (VIII) (105 mg, 0.43 mmol) in a THF/H_2O mixture (6 ml and 7 ml respectively) was cooled to 0°C in an ice bath, and CF_3COOH (2 µl) was added. The cloudy yellow reaction mixture was stirred for 2.5 hours at 0°C, after which time the THF was evaporated under reduced pressure, and the aqueous residue extracted with hexane (2 x 25 mls) giving a pale yellow extract. The extract was dried over anhydrous Na_2SO_4, and evaporated to dryness on a rotary evaporator to give a yellow oil (30 mg). The oil was identified as (VIII) by its infrared spectrum (νCO region).

In other experiments the reaction conditions were varied slightly by changing the quantities of CF_3COOH and H_2O. However in all experiments (VIII) did not react.

5.4.5 Attempted acid hydrolysis of $[Re(CO)_5CH_2OCH_3]$ (VII) using H_2O/THF and CF_3COOH

(VII) (145 mg, 0.39 mmol) was dissolved in a THF/H_2O mixture (5 mls and 2 mls respectively) and the solution cooled to 0°C. CF_3COOH (0.02 ml, 0.26 mmol) was added and the reaction mixture stirred for 4 hours. (VII) did not react, as shown by infrared spectra of the reaction mixture; it was recovered by evaporating the THF from the reaction mixture, extraction of the residue into hexane, and evaporation of the hexane.

5.4.6 Attempted acid hydrolysis of $[Fe(Cp)(CO)_2CH_2OCH_3]$ (V) using THF/H_2O and CF_3COOH

(V) (130 mg, 0.59 mmol) was dissolved in THF/H_2O (5 ml and 6 ml respectively) and CF_3COOH (0.2 ml) was added. The yellow reaction mixture was stirred for 2.5 hours at room temperature; the mixture turned orange. The THF was evaporated under reduced pressure and the aqueous residue extracted with hexane (3 x 20 ml). The extract was dried over anhydrous Na_2SO_4 and the solvent removed on a rotary evaporator to yield a yellow/brown oil (119 mg). The oil showed the following spectral features: νCO (cyclohexane) 2031(s), 1979(s), 1777(w) cm^{-1}; ^1H nmr ($CDCl_3$) δ 4.89 (singlet, 5H(?)), δ 5.51 (singlet, 2H(?)). This product could not be further purified and thus could not be further characterised.

In another experiment, (V) (160 mg, 0.7 mmol) was reacted with CF_3COOH (0.2 ml) in THF/H_2O (5 ml and 6 ml respectively) for 17 hours at room temperature. The THF was removed under reduced pressure, the aqueous residue extracted into hexane (3 x 20 ml) and the solvent removed from the extract on a rotary evaporator, yielding a brown oil (132 mg). The oil showed the following features in its infrared and ^1H nmr spectra: νCO (cyclohexane) 2031(s), 2014(m), 1979(s), 1959(m), 1777(w) cm^{-1}. ^1H nmr (benzene-d_6), δ 3.91 (singlet, 5H(?)), δ 5.28 (singlet, 2H(?)). This product could not be further purified and thus could not be further characterised.

The infrared spectrum of CF_3COOH was run in cyclohexane, and shows a C=O stretch at 1779 cm^{-1}.

5.4.7 Reaction of $Na[Fe(Cp)(CO)_2]$ with formaldehyde

$Na[Fe(Cp)(CO)_2]$ was prepared by vigorously stirring $[Fe(Cp)(CO)_2]_2$ (1.14 g, 3.2 mmol) with Na amalgam (450 mg Na in 6 ml Hg) in THF for 1¾ hours. The THF solution of the anion was then syringed off, placed in another reaction vessel and cooled to 0°C. Formaldehyde was formed by gently heating paraformaldehyde.[103] A steady stream of formaldehyde was bubbled through the THF solution of $Na[Fe(Cp)(CO)_2]$ (at 0°C) for 10 mins. Considerable repolymerisation of the CH_2O occurred. The reaction mixture was then allowed to warm to room temperature and stirred at that temperature for 15 minutes, giving a brown solution. H_3PO_4 (0.6 ml of an 85 % solution) was then added. The solvent was then removed under reduced pressure, and the brownish residue extracted first with hexane (3 x 20 ml) and then with CH_2Cl_2 (4 x 20 ml). The infrared spectra (νCO region) of both the extracts were recorded, but showed only peaks due to the dimer $[Fe(Cp)(CO)_2]_2$.

In another reaction, a solution of formaldehyde was prepared by bubbling CH_2O gas (produced by heating paraformaldehyde) through THF for 10 mins. The amount of CH_2O in the solution could not be measured by weight, (due to loss of solvent when the CH_2O gas was bubbled through the THF) or by titimetry (as the formadehyde slowly repolymerized to give paraformaldehyde). However a quantity was added to a THF solution of $Na[Fe(Cp)(CO)_2]$ (prepared from 1.0 g $[Fe(Cp(CO)_2]_2$) at 0°C, and the mixture stirred at this temperature for 30 mins. H_3PO_4 (1 ml 85 %, dissolved in 5 ml THF) was then added, giving a dark red solution and some solid. The solvent was removed from the reaction mixture giving a brownish oily residue, which was extracted with CH_2Cl_2 (50 ml). Removal of the solvent from the extract gave a mixture of a reddish oil and some purple crystals. This residue had the following spectral features: νCO (CH_2Cl_2), 2015(s), 2000(sh),

1953(s) cm^{-1}; ^1H nmr spectrum (THF solution) showed a peak at *c.a.* δ = -12 ppm. These infrared and ^1H nmr results agree fairly well with known values of the hydride $[Fe(Cp)(CO)_2H]$.[25] The peak at 2000 cm^{-1} is probably due to $[Fe(Cp)(CO)_2]_2$, the presence of which is further indicated by the traces of purple solid in the residue.

5.4.8 Reaction of $Na[Mn(CO)_5]$ with formaldehyde

$Na[Mn(CO)_5]$ was prepared by stirring $[Mn_2(CO)_{10}]$ (0.6 g, 1.5 mmol) with Na amalgam (0.6 g Na in 7 mls Hg) in THF for 2 hours. The solution of the anion was transferred to another reaction vessel and cooled to 0°C.

A solution of CH_2O was prepared by bubbling CH_2O (prepared by heating paraformaldehyde) into THF. The concentration of the solution could not be estimated accurately (see section 5.4.7); however 3 mls were added to the solution of $Na[Mn(CO)_5]$ at 0°C and the reaction mixture stirred for 45 minutes, giving a yellow brown solution. The solution was allowed to warm to room temperature and a solution of H_3PO_4 (0.6 ml) in THF (3 ml) was added, causing a white precipitate to form (probably repolymerised paraformaldehyde). The supernatent liquid was syringed off and evaporated to dryness under reduced pressure, yielding a yellow oily solid. This was shown by infrared spectroscopy to be very largely $[Mn_2(CO)_{10}]$ by comparison of the νCO region of its spectrum with that of an authentic sample of the dimer.

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